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Book of Abstracts

Edited by:

Katalin Nagy-Póra, Vasile Chiş, Simion Aştilean, Onuc Cozar

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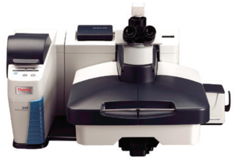

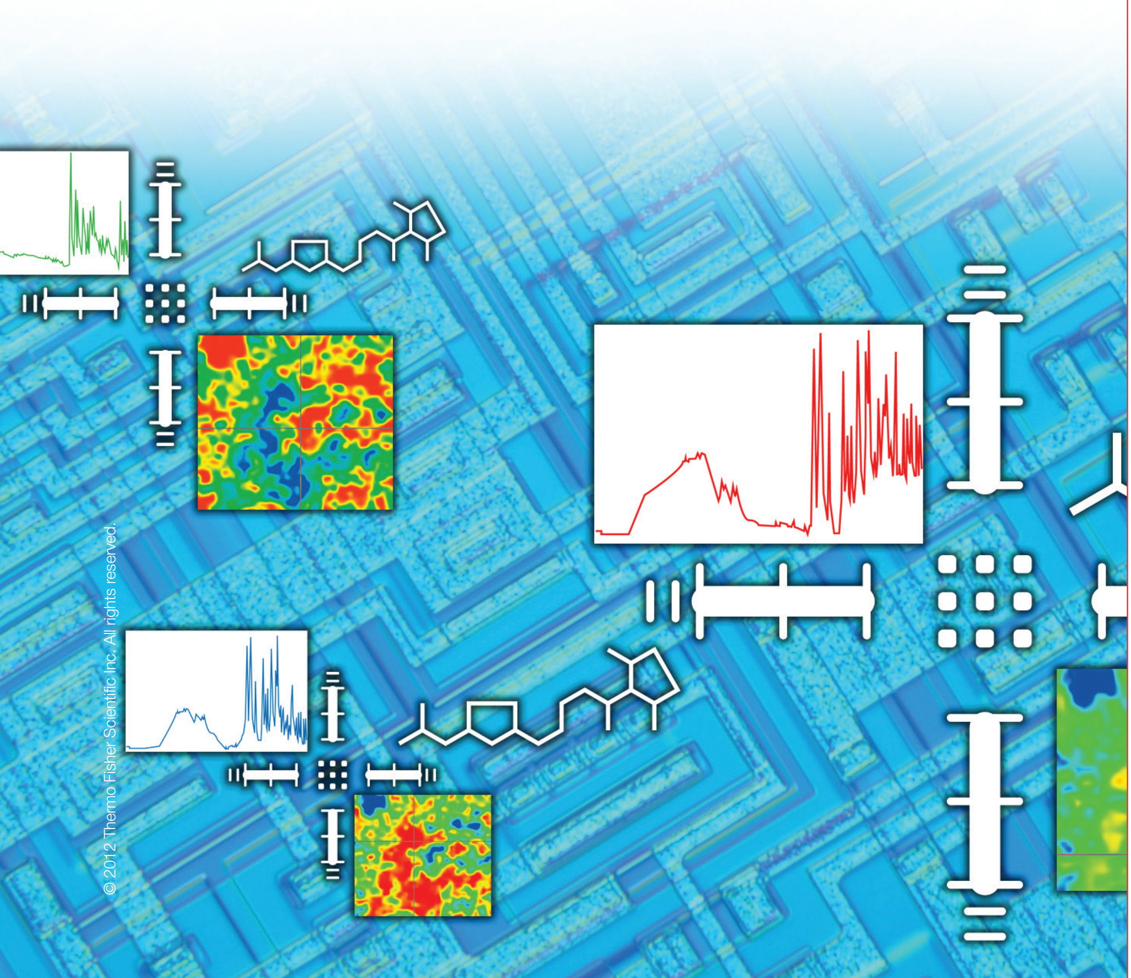


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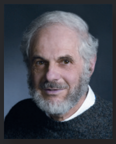

FOREWORD

The European Congress on Molecular Spectroscopy (EUCMOS) is held every other year.
It is our honor to organize in 2012 the 31st EUCMOS at the Babeş-Bolyai University in Cluj-Napoca, Romania, from the 26th to the 31st August. The scope of 31st EUCMOS is to provide an international forum for all scientists interested to share their research, exchange ideas, strengthen collaboration and identify new interdisciplinary trends in the broad field of molecular spectroscopy.

Topics in this congress cover the following areas:

1. Vibrational, electronic and magnetic resonance spectroscopies
2. Spectroscopy of surfaces and interfaces
3. Spectroscopy of biological molecules
4. Computational methods for spectroscopy
5. Applied spectroscopies (archaeology, geology, mineralogy, arts, environmental analysis, food analysis and processing)
6. New materials (nanostructured and supramolecular systems, materials for molecular electronics and optoelectronics, magnetic materials)
7. Analytical methods and new instrumentation

The scientific program of 31st EUCOMS includes 8 plenary lectures, 12 invited lectures as well as a number of 93 contributed oral and 197 poster presentations.

We have made our best to ensure an agreeable and profitable scientific meeting together with a hint of cultural and touristic flavor from Cluj-Napoca.

We sincerely hope that your participation in 31st EUCOMS will remain one of your unforgettable scientific and cultural events.

On behalf of Local Organizing Committee:

Prof Simion Aştilean,	*co-chairman*
Prof Onuc Cozar,	*co-chairman*
Prof Vasile Chiş,	*secretary*

Cluj-Napoca, August, 2012

TIMETABLE

Sunday August 26	
15.00-19.00	**Registration**
20.00-22.30	Welcome party *Chios Restaurant*

Monday, August 27	
9.15 - 9.45	Chair: Austin Barnes *Opening ceremony*
9.45 - 10.30	*Plenary lecture* Mischa Bonn
10.30-11.00	Coffee break
11.00 - 11.30	Chair: Ionel Haiduc *Invited lecture* James Durig
11.30 - 12.00	*Invited lecture* John Maier
12.00 - 12.30	*Invited lecture* Peter Trommsdorff
12.30 - 13.00	*Invited lecture* Dwayne Miller
13.00 - 14.50	Lunch
14.50 - 16.30	Oral presentations Hall AM O1-O5 Hall A1 O11-O15 Hall A2 O21-O25 Hall O36 Workshop PCCE 312/2008
16.30-17.00	Coffee break
17.00 - 18.40	Oral presentations Hall AM O6-O10 Hall A1 O16-O20 Hall A2 O25-O30 Hall O36 Workshop Witec

Tuesday, August 28	
9.00 - 9.45	Chair: Sylvia Turrell *Plenary lecture* Juergen Popp
9.45 - 10.30	*Plenary lecture* Carlo Adamo
10.30-11.00	Coffee break
11.00 - 11.30	Chair: Sevim Akyuz *Invited lecture* Jose Luis Alonso
11.30 - 12.00	*Invited lecture* Bernhard Lendl
12.00 - 12.30	*Invited lecture* Aharon Loewenschuss
12.30 - 13.00	*Invited lecture* Ioan Notingher
13.00 - 15.00	Lunch **Meeting of the editorial board for the Journal of Molecular Structure**
14.50 - 16.30	Oral presentations Hall AM O31-O35 Hall A1 O36-O40 Hall A2 O40-O45 Hall O36 Workshop Thermo Scientific
16.30-17.00	Coffee break
17.00 - 19.00	Poster Session 1
20.00 - 21.00	Organ Concert Erich Türk *St. Michael's Church*

Wednesday, August 29	
9.00 - 9.45	Chair: Juana Bellanato *Plenary lecture* Henry Mantsch
9.45 - 10.30	*Plenary lecture* Hiro-o Hamaguchi
10.30-11.00	Coffee break
11.00 - 12.40	Oral presentations Hall AM O46-O50 Hall A1 O51-O55 Hall A2 O56-O60
12.40 - 14.50	Lunch
15.00 - 19.00	Conference excursion
20.00 - 22.30	Dinner *Aroma Restaurant*

Thursday, August 30	
9.00 - 9.45	Chair: Tony Ford *Plenary lecture* Dietrich Zahn
9.45 - 10.30	*Plenary lecture* Simion Simon
10.30-11.00	Coffee break
11.00 - 13.00	Oral presentations Hall AM O61-O66 Hall A1 O72-O77 Hall A2 O83-O88
13.00 - 14.50	Lunch **International Committee meeting**
14.50 - 16.30	Oral presentations Hall AM O67-O71 Hall A1 O78-O82 Hall A2 O89-O93 Hall O36 Seminar Rui Fausto
16.30-17.00	Coffee break
17.00 - 19.00	Poster Session 2
20.00 - 23.00	Conference dinner *Grand Hotel Italia*

Friday, August 31	
9.00 - 9.45	Chair: Henry Mantsch *Plenary lecture* Masahiro Ehara
9.45 - 10.15	*Invited lecture* Demetrios Anglos
10.15 - 10.45	*Invited lecture* Michael Oshtrakh
10.45-11.15	Coffee break
11.15 - 11.45	Chair: Henryk Ratajczak *Invited lecture* Radu Silaghi-Dumitrescu
11.45 - 12.15	*Invited lecture* Michael Schmitt
12.15 - 12.20	Introducing XXXII EUCMOS Michael Schmitt
12.20 - 12.45	Final remarks Closing ceremony
12.45 - 13.30	Lunch

PLENARY LECTURES – HALL AULA MAGNA

MONDAY	*Chairman: Austin Barnes*	
9.45–10.30	**M. Bonn, L. Piatkowski, H.J. Bakker, C.S. Hsieh, Z. Zhang** STRUCTURE AND ULTRAFAST DYNAMICS OF WATER INTERFACES	PL-1
TUESDAY	*Chairman: Sylvia Turrell*	
9.00–9.45	**J. Popp** RAMAN SPECTROSCOPY: FUTURE TRENDS AND CHALLENGES IN BIOPHOTONICS	PL-2
9.45–10.30	**C. Adamo** THEORETICAL PREDICTION OF OPTICAL PROPERTIES: A PRAGMATIC APPROACH BASED ON DFT	PL-3
WEDNESDAY	*Chairman: Juana Bellanato*	
9.00–9.45	**H.H. Mantsch** APPLICATIONS OF SPECTROSCOPY IN SECURITY	PL-4
9.45–10.30	**H. Hamaguchi** NEW POSSIBILITIES OF VIBRATIONAL SPECTROSCOPY WITH HYPER-RAMAN SCATTERING	PL-5
THURSDAY	*Chairman: Tony Ford*	
9.00–9.45	**D.R.T. Zahn** SPECTROSCOPY OF MOLECULAR THIN FILMS FOR SPINTRONIC APPLICATIONS	PL-6
9.45–10.30	**S. Simon** NANOSTRUCTURATED BIOMATERIALS / BIOFLUIDS INTERFACE PROCESSES STUDIED BY MULTI-MICROSCOPIES AND -SPECTROSCOPIES	PL-7
FRIDAY	*Chairman: Henry Mantsch*	
9.00–9.45	**M. Ehara** RECENT DEVELOPMENTS AND APPLICATIONS OF SAC-CI AND MOLECULAR DOUBLE CORE-HOLE SPECTROSCOPY	PL-8

INVITED LECTURES – HALL AULA MAGNA

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11.30–12.00	**J.P. Maier** ELECTRONIC SPECTRA OF CARBON CHAINS AND RINGS OF ASTROPHYSICAL RELEVANCE	I-02
12.00–12.30	**H.P. Trommsdorff, M.R. Johnson, S.J. Ford, I.R. Evans, I. Frantsurov, A.J. Horsewill, S. Gavinkowski, J. Waluk** SPECTROSCOPIC AND STRUCTURAL CHARACTERIZATION OF PROTON SHIFTS IN STRONG HYDROGEN BONDS	I-03
12.30–13.00	**R.J. Dwayne Miller** MAKING THE MOLECULAR MOVIE: FIRST FRAMES ... NOW WITH REGAE MUSIK	I-04
TUESDAY	*Chairman: Sevim Akyuz*	
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11.30–12.00	**B. Lendl, C. Koch, M. Brandstetter** NEW APPROACHES FOR CHEMICAL SENSING BASED ON VIBRATIONAL SPECTROSCOPY	I-06
12.00–12.30	**A. Loewenschuss** MATRIX FTIR STUDIES OF H-BONDED SYSTEMS - STRONG, WEAK AND SURPRISING	I-07
12.30–13.00	**F.C. Pascut, A. Ghita, H.T. Goh, V. Sottile, C. Denning, I. Notingher** LABEL-FREE MOLECULAR CHARACTERISATION OF LIVE CELLS AND BIOLOGICAL NANOMATERIALS BY RAMAN-MICRO-SPECTROSCOPY	I-08
FRIDAY	*Chairman: Henry Mantsch*	
9.45–10.15	**D. Anglos** LASER TOOLS IN ARCHAEOLOGICAL AND CONSERVATION SCIENCE	I-09
10.15–10.45	**M.I. Oshtrakh, M.V. Ushakov, V.A. Semionkin, V. Šepelák, A.F.R. Rodriguez, P.C. Morais** STUDY OF MAGNETITE AND MAGHEMITE NANOPARTICLES USING MÖSSBAUER SPECTROSCOPY WITH A HIGH VELOCITY RESOLUTION	I-10
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11.15–11.45	**R. Silaghi-Dumitrescu** SHEDDING BLOOD OVER MAGNETS: SOME APPLICATIONS ON UNUSUAL VALENCE STATES IN BIOLOGICAL METAL CENTERS	I-11
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ORAL PRESENTATIONS

MONDAY, AUGUST 27

Spectroscopy of surfaces and interfaces – Hall AULA MAGNA		
	Chairman: James Durig	
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15.30–15.50	**V. Bugris, H. Haspel, Á. Kukovecz, Z. Kónya, M. Sipiczki, P. Sipos, I. Pálinkó** REHYDRATION OF DEHYDRATED CaFe-LAYERED DOUBLE HYDROXIDE FOLLOWED BY THERMOGRAVIMETRY, X-RAY DIFFRACTOMETRY AND DIELECTRIC RELAXATION SPECTROSCOPY	O-03
15.50–16.10	**A. Kokaislová, M. Kalhousová, P. Matějka** SURFACE-ENHANCED VIBRATIONAL SPECTROSCOPY OF B-VITAMINS: WHAT IS THE INFLUENCE OF SUBSTRATE SURFACE TEMPERATURE?	O-04
16.10–16.30	**K. Csankó, G. Kozma, L. Valkai, Á. Kukovecz, Z. Kónya, P. Sipos, I. Pálinkó** SELF-ASSEMBLING OF 2,3-PHENYL/THIENYL-SUBSTITUTED ACRYLIC ACIDS OVER POLYCRYSTALLINE GOLD	O-05
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	Chairman: John Maier	
17.00–17.20	**V. Prokopec, J. Čejková, M. Singh, P. Matějka and F. Štěpánek** USE OF VIBRATIONAL SPECTROSCOPIC TECHNIQUES FOR THE CHARACTERISATION OF CHEMICAL ROBOTS	O-06
17.20–17.40	**M. Kozanecki, M. Olejniczak** INTERMOLECULAR INTERACTIONS IN POLY(2-(2-METHOXYETHOXY)ETHYL METHACRYLATE HYDROGELS – RAMAN SPECTROSCOPY STUDIES	O-07
17.40–18.00	**M. Larraona-Puy, C.S. Sweetenham and I. Notingher** CHARACTERISATION OF THIN SUPPORTED LIPID FILMS BY SIMULTANEOUS SURFACE ENHANCED RAMAN SPECTROSCOPY AND ATOMIC FORCE MICROSCOPY	O-08
18.00–18.20	**A. Milani, M. Tommasini, D. Fazzi, A. Lucotti, L. Brambilla and C. Castiglioni** CUMULENIC SP CARBON CHAINS: AN INVESTIGATION BASED ON VIBRATIONAL SPECTROSCOPY	O-09
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TUESDAY, AUGUST 28

Spectroscopy of biological molecules – Hall AULA MAGNA

Chairman: Juergen Popp

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New materials – Hall A1

Chairman: Carlo Adamo

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Analytical methods and new instrumentation – Hall A2

Chairman: Bernhard Lendl

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AB INITIO DFT AND RAMAN STUDY OF MEDIUM RANGE ORDERING IN g-GeSe$_2$

PS1-02 **A. Akbay, K. Balci**
AN INVESTIGATION ON THE CONFORMATIONAL STRUCTURE AND VIBRATIONAL MOTIONS OF SULINDAC MOLECULE BY IR AND RAMAN SPECTROSCOPIC MEASUREMENTS AND DFT-BASED QUANTUM MECHANICAL CALCULATIONS

PS1-03 **L.M. Andronie, O. Cozar, N. Peica, I. Domsa, S. Cîntă Pînzaru**
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PS1-04 **B. Atak, E. Akalin, S. Akyuz and S. Celik**
STRUCTURAL AND VIBRATIONAL STUDY ON AMRINONE DIMERS AND AMRINONE-H_2O COMPLEXES

PS1-05 **K. Balci, Y. Akkaya, S. Akyuz**
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PS1-06 **C. Bayrak**
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PS1-07 **L. Bistričić, V. Borjanović, L. Mikac and O. Shenderova**
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PS1-08 **A. Brambilla, A. Filippidis, A. Nevin, G.Valentini and D. Anglos**
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WORKSHOPS

MONDAY	ROOM 036
15.00–16.30	**Octavian Popescu** ASSEMBLING MOLECULES ON NANOPARTICLES AND NANOSTRUCTURED SURFACES
	COFFEE BREAK
17.00–18.00	**Ute Schmidt and Lena Welter** CONFOCAL 3D AND TOPOGRAPHIC RAMAN IMAGING
TUESDAY	**ROOM 036**
	HIGH PERFORMANCE SPECTROMETRY SOLUTIONS FROM THERMO FISHER SCIENTIFIC
14.30–14.35	WELCOME AND INTRODUCTION
14:35–15.00	**Steve Reynolds** THERMO SCIENTIFIC SPECTROSCOPY SOLUTIONS FOR UV-VIS, FT-IR AND RAMAN
15.00–15.30	**Bruno Beccard** A NEW CONCEPT FOR MOLECULAR SPECTROSCOPY: THERMO SCIENTIFIC NICOLET iS50 FT-IR SPECTROMETER
15.30–16.00	**Bruno Beccard** EXPANDING CAPABILITIES: MULTIPLE CHANNELS ACQUISITION AND STEP SCAN
16.00–17.00	**Bruno Beccard** MICROSCOPY OR MICROSPECTROSCOPY
17.00–17.45	**Erich Heiden** MEASURING OF SOLID SAMPLES IN REFLEXION AND TRANSMISSION WITH A HIGH END UV/VIS SYSTEM.
17.45–18.15	**Janusz M. Kossakowski, Cole-Parmer** COLE-PARMER PICOSPIN™-45 BENCHTOP NMR SPECTROMETER – REVOLUTION IN LOW FIELD NMR SPECTROSCOPY
18.15–19.00	Q&A SESSION
19.00	CLOSE
THURSDAY	**ROOM 036**
15.00–16.00	**Rui Fausto** Seminar: LIGHT INDUCED REACTIONS IN CRYOGENIC MATRICES

STRUCTURE AND ULTRAFAST DYNAMICS OF WATER INTERFACES

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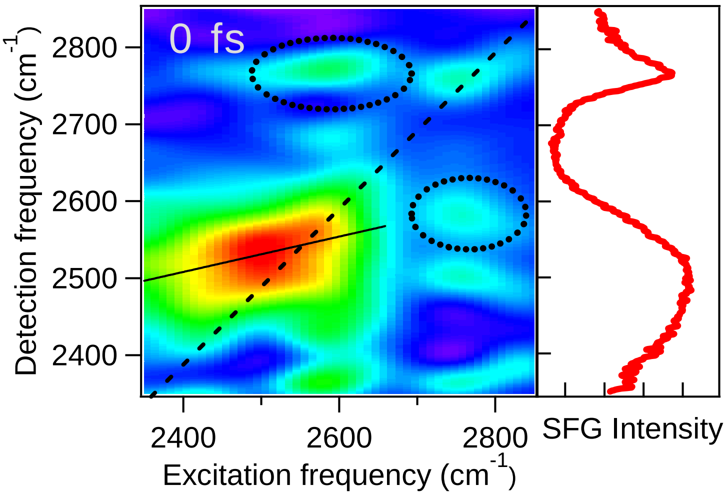
At the surface or interface of water, the water hydrogen-bonded network is abruptly interrupted, conferring properties on interfacial water different from bulk water. Despite its importance for disciplines such as electrochemistry, atmospheric chemistry and membrane biophysics, the structure of interfacial water has remained highly debated.

We elucidate the structure and structural dynamics of interfacial water using ultrafast two-dimensional surface-specific vibrational spectroscopy[1,2]. We present data for the water-air and water-lipid interfaces, which reveal interfaces that are structurally heterogeneous, yet highly dynamical. We determine the timescale on which the heterogeneity decays, reveal the presence of surprisingly rapid inter- and intramolecular energy transfer processes and quantify the reorientational dynamics of interfacial water[3].



Time-resolved 2D-SFG data for interfacial water at the water/air interface at zero delay time between pump and probe. The right panel shows the static SFG spectrum. The 2D spectrum reveals an on-diagonal response with a slope smaller than one (dashed line indicates slope of 1), expected for a heterogeneous surface. Off-diagonal peaks are highlighted by dotted circles.

Keywords: Ultrafast Surface Dynamics, Interfacial Water, Vibrational Spectroscopy, Femtosecond Sum-Frequency Generation

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RAMAN SPECTROSCOPY: FUTURE TRENDS AND CHALLENGES IN BIOPHOTONICS

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During the last years Raman based microspectroscopy has been recognized as an extremely powerful tool for bioanalytical and biomedical applications because the method provides molecular fingerprint information of the molecular structure and biochemical composition of cells and tissues without external markers [1],[2]. Diseases and other pathological anomalies are accompanied by changes in these properties. To overcome the disadvantage of low signal intensities for most biomedical samples, special Raman signal enhancing techniques can be utilized. The two most prominent approaches are the resonance Raman effect and surface enhanced Raman scattering (SERS).[3] Besides these two linear Raman signal enhancing techniques a nonlinear variant of Raman spectroscopy called coherent anti Stokes Raman spectroscopy (CARS) belongs to the most promising Raman techniques because it combines signal enhancement due to the coherent nature of the process with further advantages such as directional emission, narrow spectral bandwidth and no disturbing interference with autofluorescence.[1],[2]

Here, we review our recent results on Raman approaches to address important biomedical questions. We will start with demonstrating that micro-Raman spectroscopy in combination with powerful chemometrics is an appropriate tool for the rapid identification of microorganisms like e.g. pathogens on a single cell level without the need of pure cultures or any cultivation step. The implementation of Raman spectroscopy in a microfluidic chip allows for an automated classification of cells like e.g. circulating tumor cells. The presented SERS examples convincingly demonstrate that SERS is an extremely potent tool in bioanalytical science like e.g. drug monitoring because the technique comprises high sensitivity with molecular specificity. Furthermore we shall discuss our experimental multimodal imaging approach towards a fast, sensitive and selective diagnostic tool for the investigation of cancerous tissue potentially even in vivo. In doing so the joint use of linear Raman microspectroscopy and CARS microscopy allows for complementary characterization of the type and chemical composition of the tissue samples. While linear Raman microspectroscopy is used to obtain the information on critical Raman marker bands at selected spatial position within the sample, CARS microscopy focusing on fast image generation using the previously defined Raman marker bands. The simultaneous application of other nonlinear imaging techniques like second harmonic generation (SHG) and two photon excited fluorescence (TPEF) enables a rapid and label free visualization of the tissue morphology. Finally we will present first *in-vivo* Raman experiments with fiber optic probes to study the chemical constitution of plaque depositions in the aorta of a rabbit. The Raman fibre probe geometry allowed for a comfortable insertion into the blood vessels of rabbits through a flexible catheter, introducing no more stress than other catheter based techniques.

Keywords: Raman; CARS; SERS, pathogen identification, multimodal tissue imaging, Raman fiber probes

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THEORETICAL PREDICTION OF OPTICAL PROPERTIES: A PRAGMATIC APPROACH BASED ON DFT

Carlo Adamo

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Resorting to theoretical tools to predict or interpret the excited state properties of organic and inorganic dyes is of increasing interest due to their efficiency at screening photo-centres for applications in many technological fields. In the present communications we report recent developments [1] defining a quantitative *ab-initio* protocol (based on Time-Dependent Density Functional Theory), for modelling molecular electronic spectra. In particular, the effect of several parameters, such as the models used for exchange-correlation functionals or enviromental (solvent, cage, surface) effects, are discussed and exemplified by some case studies [2-3], including absorption and emission spectra of both organic and inorganic systems. Comments concerning current weak points of these methods, as well as their possible improvements are also discussed.

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APPLICATIONS OF SPECTROSCOPY IN SECURITY

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I am pleased to talk here about a subject that traditionally is not given a lot of room at spectroscopic meetings, namely the use of spectroscopy as an analytical tool to address security issues. To tackle many of today's most pressing problems like the environment, energy, disease or security, we need new thinking and new tools. Whereas forensic evidence based on spectroscopy is already part of the standard repertoire in crime-solving, new applications of spectroscopy in security are only now emerging, in response to the increased threat stemming from terror attacks. As a fingerprinting technique, spectroscopy is eminently suited to deal with security-related issues. Interestingly, the fastest growing new area of demand for Raman spectroscopic instrumentation is in the security market. Furthermore, since September 11, airport security has entered the public spotlight and the research into developing new microwave- and terahertz-based scanners is a real shot in the arm for the neglected area of far-infrared spectroscopy. The growing role of spectroscopy for applications in security is illustrated through a number of representative examples.

NEW POSSIBILITIES OF VIBRATIONAL SPECTROSCOPY WITH HYPER-RAMAN SCATTERING

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Hyper-Raman (HR, Fig. 1) bears unique vibrational information that is distinct either from infrared absorption or from Raman scattering. Though this uniqueness has long been known, HR has not been fully explored because of its experimental difficulties. In the past several years, we have been seeking for new possibilities of HR scattering by using picosecond pulsed laser systems specifically optimized for HR experiments. In the present talk, I discuss the following three new possibilities vibrational spectroscopy with HR scattering.

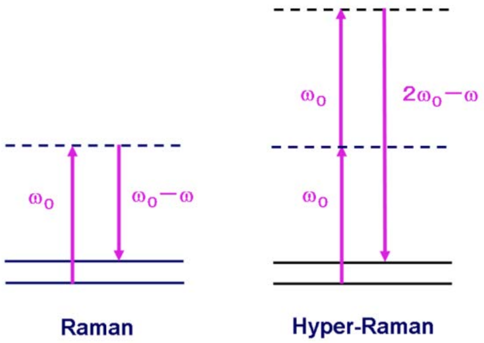

Figure 1. Raman scattering and Hyper-Raman scattering.

Molecular near field effect in resonance HR scattering. Specific solvent bands were observed unexpectedly in resonance HR spectra of all-*trans*-β-carotene in solutions. This effect has been attributed to the intermolecular vibronic coupling, in which a two-photon allowed A_g state and a one-photon allowed A_u state of β-carotene are coupled via a_u vibrations of the solvent. It will lead to new nano-scale vibrational spectroscopy that selectively detects molecules existing in the close vicinity of a HR probe [1].

Super-resolution simultaneous Raman/HR imaging.

Raman scattering intensity is proportional to the incident laser intensity I and HR intensity to I^2. If we make Raman and HR images simultaneously from the same laser spot, we have two independent image data derived from a common laser intensity distribution and the true sample distribution. We can solve this 2x2 problem and obtain the true sample distribution by iterative simulation of the two images. This method has been applied to TiO_2 nano-particles to achieve super spatial resolution of ~100 nm [2].

Fano resonce in HR scattering of TiO_2

Solvents adsorbed on TiO_2 nano-particles show HR bands with characteristic dispersive band shapes. They are attributed intermolecular Fano resonance between solvent vibrations and TiO_2 phonon/electronic excitations.

Keywords: Hyper-Raman scattering; Molecular near-field effect; Nan-scale spectroscopy

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SPECTROSCOPY OF MOLECULAR THIN FILMS FOR SPINTRONIC APPLICATIONS

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Semiconducting organic molecules are studied as candidates for spintronic applications in the frame of the Saxon research unit “Towards Molecular Spintronics”. In particular, phthalocyanines are of interest because their spin state can be tuned by changing the central metal atom. Therefore these molecules are used as model systems in our studies.

Thin films are prepared by organic molecular beam deposition under ultra-high vacuum conditions on silicon and metal substrates. Here the focus is on *in situ* Raman spectroscopy and spectroscopic ellipsometry studies during growth and doping ultra-thin films with alkali atoms.

In order to detect the Raman spectra of ultra-thin (≅ 10 nm) films resonance and interference enhancement is employed. The spectra then show numerous vibrational modes in the spectral range of 0-1700cm^{-1}. Upon doping *e.g.* with potassium strong changes in the Raman spectra are observed and several stages of doping can be identified (see figure 1). These are discussed taking photoemission spectroscopy and electron energy loss spectroscopy [1] results into account.

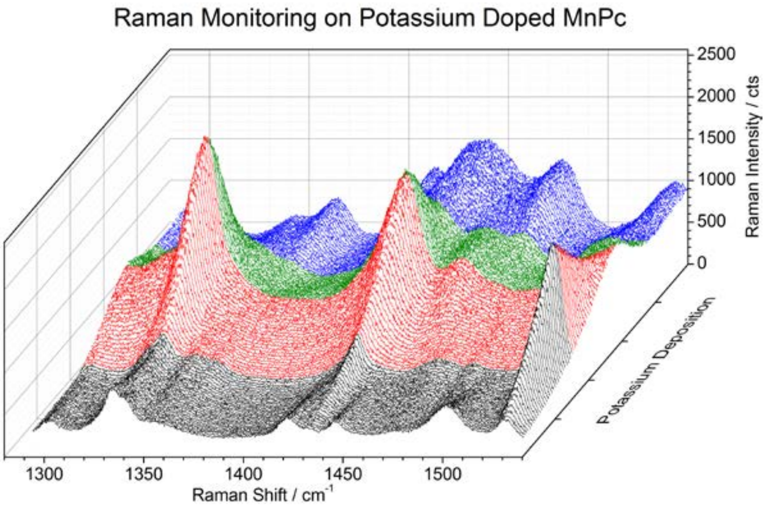

Fig.1 Raman spectra taken in situ during doping of a 10 nm thick MnPc thin film

The strong changes upon doping are also supported by *in situ* performed spectroscopic ellipsometry. The effective dielectric function which provides information about the transitions between occupied and unoccupied electronic states in the ultra-thin molecular phthalocyanine films also shows strong changes upon doping and thus in the electronic properties. The results confirm those obtained by electron energy loss spectroscopy and explain the intensity variation of the substrate related features in the Raman spectra.

Keywords: phthalocyanine thin films; Raman spectroscopy; spectroscopic ellipsometry, alkali doping

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NANOSTRUCTURATED BIOMATERIALS / BIOFLUIDS INTERFACE PROCESSES STUDIED BY MULTI-MICROSCOPIES AND -SPECTROSCOPIES

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The processes that take place at the interface between biomaterials and simulated body fluids, both protein-free and protein enriched simulated body fluids, are very dependent on the surface structure of the biomaterials. The way in which the type and morphology of the nanostructures developed on the biomaterials surface are influencing the processes at the interface with biofluids is characterized by various microscopic (SEM, TEM, AFM) and spectroscopic (NMR, EPR, IR, Raman, XPS) methods. Beside inorganic layered reconstruction on nanostructured surface the adherence and dynamics of the attached biomolecules are well evidenced.

The *in vivo* behaviour of the implant biomaterials is also studied by magnetic resonance imaging on small animals with bone implants.

Keywords: interface processes; biomaterials; biofluids; microscopy; spectroscopy.

RECENT DEVELOPMENTS AND APPLICATIONS OF SAC-CI AND MOLECULAR DOUBLE CORE-HOLE SPECTROSCOPY

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The symmetry-adapted cluster-configuration interaction (SAC-CI) theory [1] has been established as a useful method to investigate molecular excited states via numerous applications to molecular spectroscopy and photochemistry [2]. Recently, we have developed the methods to investigate the solvent effect in the excited states [3] and to calculate the resonance states [4]. In this presentation, we would like to introduce our recent developments based on the SAC-CI method [3,4] and its applications to theoretical spectroscopy [5-7].

The polarizable continuum model (PCM) SAC-CI method and its analytical energy gradients for investigating the solvent effect of molecular excited states have been developed. This method is based on the state-specific and iterative approach with including electron correlations [3]. The method for investigating resonance states (metastable anion states) has also been developed with the complex absorbing potential (CAP) [4]: the CAP/SAC-CI method has been implemented within the projected scheme. We will briefly explain these methodologies and their basic applications and characters.

We also have applied the SAC-CI method to photo-functional molecules such as fused phthalocyanine dimer [5], organic light emitting diodes (OLEDs) [6] and organic dyes for dye-sensitized solar cells (DSSCs) [7]. We will also introduce some of these applications in the talk.

Molecular double core-hole (DCH) states probes the chemical environment more sensitively than the single core-hole (SCH) states. We recently proposed that the relaxation energy and inter-atomic relaxation energy can be extracted from the observation of these ssDCH and tsDCH states, respectively [8]. We also investigated the sequential Auger decay from the DCH states to CVV (triply charged) and VVVV (quadruply charged) states. We introduce our recent works on the DCH spectroscopy [9].

Keywords: SAC-CI; solvent effect; resonance state; photofunctional molecules; double core-hole spectroscopy

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CONFORMATIONAL STABILITY DETERMINATIONS FROM VARIABLE TEMPERATURE INFRARED SPECTRA OF XENON SOLUTIONS

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There were a large number of conformational stability studies carried out in the 1960’s and 70’s which were determined from variable temperature solutions with non-polar solvents or in some cases the pure liquids. Many different techniques were used but infrared and Raman spectroscopy were the most popular. At this time period there were many reasons for obtaining the most stable conformer such as the structure, steric effect, chemical association, to name a few. However the reasons for determining conformational stabilities have drastically increased from the field of biochemistry and nano-chemistry. These areas have caused a great deal of interest in conformational stability due to its effects on binding sites of proteins in biochemistry and the use of conformer interchange to drive molecular motions and shapes in nano-chemistry. Specifically the conformation of five membered rings is currently at work in every human alive, with this being the substituted five-membered rings that are the backbone sugar groups of DNA and RNA. The importance of conformational stability is further demonstrated in biological systems by enzyme binding where the conformational changes of the protein can change the binding site either enhancing or deactivating the enzyme. My research group has been determining the conformational stabilities by utilizing variable temperature infrared spectra of xenon solutions. There are many advantages as well as disadvantages for the utilization of liquid rare gases as solvents for enthalpy determinations. The ten advantages are: (1) The infrared bands are very narrow. (2) Very accurate measurement of the temperature is possible. (3) The temperature range is fairly large. (4) There is normally little interaction of solvent with solute molecules. (5) Small enthalpy changes can be measured. (6) Band areas are easily measured. (7) Paths lengths for the liquids are long so very dilute solutions can be used. (8) The xenon solvent has no absorption bands. (9) Several conformer pairs can usually be measured. (10) The statistical uncertainty of the determined values is very low. The most common disadvantages are: (1) Limited solubility of many polar molecules. (2) It is difficult to have very dry xenon so water can interfere. (3) At low temperatures the sample may deposit on the window. One group of molecules which my research group began to study was the substituted cyclobutane molecules. Initially it was shown that bromocyclobutane had two conformers present at ambient temperature but from later microwave studies the second conformer was not found. Then it was generally concluded that only one conformer was present for the monohalocyclobutane molecules. More recently my group observed a second stable conformer in the variable temperature infrared spectra of the xenon solutions and the enthalpy difference determined between the two conformers. The first of these studies were the chloro-, bromo-, cyano- and fluoro- cyclobutane molecules which were followed by the silylcyclobutane molecule and the monosubstituted five-membered rings of which examples are ethynylcyclopentane and isocyanocyclopentane. Recently my group has also been exploring the structural changes of the enzyme substrates due to allosteric regulation of the protein by utilizing difference spectra in the mid-infrared region.

Keywords: conformational stability; Fourier-transform infrared; vibrational assignment; xenon solutions

ELECTRONIC SPECTRA OF CARBON CHAINS AND RINGS OF ASTROPHYSICAL RELEVANCE

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The electronic spectra of astrophysically relevant ions and radicals are measured in the laboratory. The species focused on are carbon chains and ions which show strong electronic transitions in the visible part of the spectrum, the region where astronomers observe the diffuse interstellar absorptions. The goal is to identify some of the carries causing these. The research involves the use and development of a number of spectroscopic methods. The transient species are produced in discharge and laser vaporization sources coupled with supersonic expansions. The electronic transitions are excited by lasers and detected by resonance multi-photon ionization for the neutral species, by cavity ring-down and degenerate four wave-mixing techniques in absorption for both radicals and ions. The spectra of ions, relaxed by collisions to 10 K, and held in radiofrequency trap can be observed using excitation-fragmentation schemes. Direct absorption measurements on mass-selected neutrals and ions are conducted in 6 K neon matrices and provide a guide for the gas-phase measurements.

Examples from recent research will be given, discussing both the spectroscopy and the dynamics of the excited electronic states. The latter are crucial in deciding which systems are relevant for consideration with astronomical data. In order to predict the rotational profiles in the electronic spectra under astrophysical conditions, processes rare on earth, such as magnetic dipole transitions have to be considered.

SPECTROSCOPIC AND STRUCTURAL CHARACTERIZATION OF PROTON SHIFTS IN STRONG HYDROGEN BONDS

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Hydrogen bonds and proton displacements along these bonds remain a topic of active research. Some of the issues concern the covalent vs. electrostatic contributions to the bond energy, the electronic rearrangements accompanying proton displacements and the coupling of skeleton modes with the proton motion. As the bond energy increases, the covalent character increases, the bond length (i.e. the distance between the two heavy atoms) decreases, the distances of the proton from the two heavy atoms become more equal and frequency of the hydrogen vibration along the bond decreases.

This flexibility of properties has made hydrogen bonds attractive as components in the design of functional molecular materials: photochromic materials, molecular switches and memory, UV radiation protection,… Some new ideas regarding isotopic selectivity of hydrogen bonds will be discussed.

The majority of hydrogen bond lengths lie above ca. 0.255 nm and the proton displacement along these bonds is governed by a double well potential relating two tautomer structures. Carboxylic acid dimers with symmetric double well potentials are examples that have been extensively studied and are well characterized, regarding in particular the multidimensionality of the potential energy surface and the tunneling dynamics therein [1].

Short strong hydrogen bonds are less abundant, one particularly interesting example, crystalline 3,5-pyridinedicarboxylic acid, will be discussed here [2]. In this material a temperature dependent proton displacement from the nitrogen atom at low temperatures to the oxygen atom at high temperature is observed and was characterized by structural studies (X-ray and neutron diffraction), vibrational spectroscopy (IR, Raman, inelastic neutron scattering), NMR T_1 relaxometry, as well as computational studies and modeling. Even though the proton displacements are strongly coupled no sharp phase transition is observed, but a rather broad transition region in which the spectra exhibit intriguing features related to the simultaneous presence of both tautomers and the resulting disorder in the crystal.

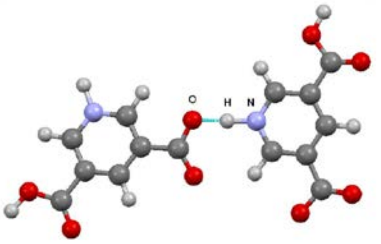

Fig. 1 3,5-Pyridinedicarboxylic Acid

Keywords: short strong hydrogen bonds, 3,5-pyridinedicarboxylic acid, proton migration

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“MAKING THE MOLECULAR MOVIE”: FIRST FRAMES……NOW WITH REGAE MUSIK

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One of the great dream experiments in Science is to watch atomic motions as they occur during structural changes. In the fields of chemistry and biology, this prospect provides a direct observation of the very essence of chemistry and the central unifying concept of transition states in structural transitions. From a physics perspective, this capability would enable observation of rarefied states of matter at an atomic level of inspection, with similar important consequences for understanding nonequilibrium dynamics and collective phenomena. This experiment has been referred to as "making the molecular movie". Due to the extraordinary requirements for simultaneous spatial and temporal resolution, it was thought to be an impossible quest and has been previously discussed in the context of the purest form of a gedanken experiment. With the recent development of femtosecond electron pulses with sufficient number density to execute single shot structure determinations, this experiment has been finally realized (Siwick et al. Science 2003). Previously thought intractable problems in attaining sufficient brightness and spatial resolution, with respect to the inherent electron-electron repulsion or space charge broadening, has been solved. With this new level of acuity in observing structural dynamics, there have been many surprises and this will be an underlying theme. Several movies depicting atomic motions during passage through structural transitions relevant to condensed phase dynamics will be shown (Sciaini et al. Nature, 2009, Ernstorfer et al. Science 2009, Eichberger et al Nature 2010). The primitive origin of molecular cooperativity has also been discovered in recent studies of molecular crystals. These new developments will be discussed in the context of developing the necessary technology to directly observe the structure-function correlation in biomolecules — the fundamental molecular basis of biological systems. The future is even brighter with the advent of a new concept in relativistic electron guns that will open up direct observation of atomic motions in solution phase to gas phase systems with 10 femtosecond time resolution to watch even the fastest atomic motions. Some of the important scientific problems to be addressed with ultrabright electron sources will be discussed to give an impression of the potential impact of this emerging field.

Watching Conformations of Biomolecules: Insigths from Rotational Spectroscopy

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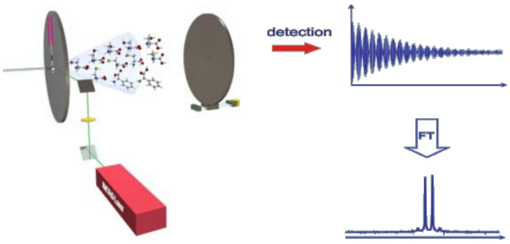
Spectroscopic studies of biomolecules in gas phase are directed to the conformational and structural analysis of the building blocks of life, providing a picture of their intrinsic molecular properties free of intermolecular interactions imposed by the biological environment. The obvious difficulties for the experimental studies in gas phase are due to the high melting points and associated low vapour pressures of these species. The emergence of laser ablation molecular beam Fourier transform microwave (LA-MB-FTMW)[1] spectroscopy has rendered accessible the gas-phase rotational study of solid biomolecules. It combines laser ablation with Fourier transform microwave spectroscopy in supersonic jets overcoming the problems of thermal decomposition associated with conventional heating methods. To date different α- and β-amino acids[1] have been studied using this technique, making possible the characterization of their preferred conformations. Even in conformationally challenging systems these can be identified by rotational spectroscopy, as has been illustrated with the assignment of seven low-energy conformers in serine[2] and threonine[1], six in cysteine[3] aspartic acid[4], five in glutamic[5] and nine in γ-amino butyric (gaba)[6]. The nucleic acid bases have also been studied and their preferred tautomeric forms determined[7]. Among the molecules to benefit from this technique there are common important neurotransmitters and peptides never observed in the gas phase through rotational spectroscopy. This technique has been recently applied to unveiling the shape of aspirin[8]. Last results in methionine, tryptophan, asparagin, dopamine and adrenaline will be presented.



Recently, a new approach of high resolution rotational spectroscopy which provides a sensitive method for broadband detection (CP-FTMW)[9] has been built at the University of Valladolid. First results on monosaccarides show that this new experimental setup is a precious tool to the conformational and structural analysis of solid biomolecules.

Keywords: Biomolecules; Fourier transform Microwave Spectroscopy; Laser Ablationy; Conformation and Structure.

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NEW APPROACHES FOR CHEMICAL SENSING BASED ON VIBRATIONAL SPECTROSCOPY

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Advances in technology for infrared spectrometry are of key importance in the development of innovative analysis systems for use in applied environmental and process monitoring as well as in basic (bio)chemical research. These advances can include novel optical components such as light sources, detectors and fiber optics, but also supporting technologies for enabling new measurement concepts. This presentation reports on recent developments which make use of such technological advances.

This presentation will introduce Quantum Cascade Lasers (QCLs) as a new light source for use in chemical sensors. Step-scan FTIR spectroscopy has been used to characterize pulsed operation of these lasers with a time resolution of 2 ns and a spectral resolution of 0.1 cm^{-1}. Based on these data optimum conditions were found which enabled the implementation of QCLs in a new generation of chemical analyzers. This presentation will report on a recent commercial realization of a QCL based instrument for the determination of oil in water [1]. In the area of biochemical analysis a portable QCL based sensor system for the determination of various parameters in human serum will be shown as well.

A new technology for measuring microorganism inside an industrial bioreactor based on a combination of ultrasonic particle manipulation and fiber optic mid-IR spectroscopy will be presented in continuation. A standing MHz ultrasound field established between the planar attenuated total reflection (ATR) surface of a fiber optic probe and a piezo-ceramic element placed at a distance of a few millimeters can be used to manipulate particles in a suspension. Particles such as beads or microorganisms are captured in the nodes of the standing pressure waves. By controlling the frequency of the standing waves the particles can either be kept away from the ATR surface or pressed against it. In such a way a fiber optic in-line sensor system can be envisioned which is capable to discriminate between particles (micro-organism) and solutes (substrates and products) in a given suspension (fermentation). Data obtained from yeast fermentations will be highlight the achieved state of the art.

Keywords: Quantum Cascade Laser; Ultrasound, Chemical Sensor,

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MATRIX FTIR STUDIES OF H-BONDED SYSTEMS - STRONG, WEAK AND SURPRISING

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The environment of frozen rare gas matrices is most suitable for the studies of hydrogen bonded systems and interactions. The most informative spectroscopic features are related to the H-bonded ν(d-H$\cdots$a) stretching frequencies (d- donor, a- acceptor).

Our first example concerns the $H_2SO_4{*}H_2O$ monohydrate where the bonded ν(OH) was elusive for a while due to the complexity of the spectrum, in general and the large shift and great width of the bonded hydroxyl stretch band.

A second example is the formation of both an H-bonded complex and a ionic charge transfer complex in the same matrix layer containing trapped ammonia and water vapors.

A third example will show that the most abundant complex formed by trapped trimethylamine and water molecules is actually an H-bonded molecular cluster.

Finally we shall show that rare gas matrices are not necessarily inert, where H-bonding is concerned. The polarizable Xe matrix can interact with the trapped species in a manner similar to a proton acceptor.

LABEL-FREE MOLECULAR CHARACTERISATION OF LIVE CELLS AND BIOLOGICAL NANOMATERIALS BY RAMAN-MICRO-SPECTROSCOPY

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Stem cell therapy is widely acknowledged as a key medical technology of the 21st century. These cells have enormous potential for cell replacement therapies in curing age-related illnesses such as Alzheimer's and Parkinson’s disease, as well as diabetes and cardiovascular disorders. One of the main challenges in stem cells research is developing conditions to derive specific cell types with high yield: current methods generally produce only low yields of the desired differentiated lineages within highly heterogeneous populations. Such cell populations are not suitable for clinical use due to the presence of mainly unwanted cell types. Label-free non-invasive techniques capable of phenotypic identification of live cells within highly heterogeneous populations are valuable for improving the differentiations conditions as well as developing methods for enrichment of cell populations.

Raman micro-spectroscopy (RMS) is a label-free technique which can be used for imaging of live cells. This technique combines the high chemical specificity of Raman spectroscopy with the high spatial resolution of optical microscopy to provide detailed molecular information of complex biological samples. Since RMS has only a minimal background signal from water, it allows repeated observations of viable cells maintained under physiological conditions, which is difficult by other molecular vibrational techniques.

In the first part we will focus on using RMS for detection of molecular markers for individual live cardimyocytes (CMs) derived from human embryonic stem cells (hESCs) [1]. The ability to monitor and quantify these spectral markers during differentiation periods as long as 5 days is also demonstrated. The analysis of Raman spectra of hESC-derived CMs were characterised by increased signals associated to myofibrils and glycogen compared to the other differentiated cells present in the cultures. The prospects of label-free Raman activated cell sorting are also discussed.

The second part will present results on using RMS for imaging and quantifying spectral markers in neuronal stem cells (NSCs) [2]. Raman spectra of undifferentiated NSCs are compared to those of glial cells derived from NSCs, aimed at identifying molecular markers which can be used for assessing the differentiation status of the NSCs. High resolution spectral maps corresponding to nucleic acids show that NSCs are characterized by increased concentrations of cytoplasmic RNA.

These studies demonstrate that RMS represents a feasible approach for label-free non-invasive characterization of individual live cells and can be used to assess the differentiation status and the phenotypes of individual cells.

Keywords: Raman micro-spectroscopy; Stem cells; live cells.

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LASER TOOLS IN ARCHAEOLOGICAL AND CONSERVATION SCIENCE. APPLICATIONS AND PROSPECTS

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The study, conservation and protection of works of art and antiquities are essential for knowing, understanding and preserving our cultural heritage. But the meaningful study and successful conservation of cultural heritage objects represent important scientific and technological challenges because of the inherently complex, multi-component nature of materials in such objects, which quite often suffer additionally from different causes of natural or anthropogenic degradation or deterioration. As a result, to identify materials on or in cultural heritage objects and to implement optimal conservation methodologies relies on the existence of effective tools for non-invasive diagnosis and safe intervention. Optical and analytical technologies play a key role in this respect. In particular, modern laser science and technology has enabled the development of adaptable and complementary analytical and structural diagnostic techniques and novel conservation tools based on laser ablation. [1]

As an example of a versatile laser-based technique, representing a fast and straightforward analytical tool, LIBS (laser-induced breakdown spectroscopy) will be presented, with emphasis on mobile and hybrid instrumentation. Mobile or portable instruments are of great use facilitating access to highly valued artworks and objects in museums or excavation sites. Further enhancement of the analytical information can be achieved by using complementary methods, particularly if those can be combined on a common instrumental platform. In this respect the combined use of LIBS with Raman spectroscopy and laser ablation mass spectrometry will be discussed. [2]

Concerning conservation, a number of pulsed laser systems have been successfully implemented for the cleaning of artifacts and monuments, including sculpture at the Athens Parthenon. The unavoidable intrusive character of laser cleaning imposes the need for case-specific optimization and control of the laser parameters employed and a good knowledge of the fundamental processes involved. Advances in this area have greatly improved the quality and potential of laser cleaning, extending its applicability into new demanding conservation problems.

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STUDY OF MAGNETITE AND MAGHEMITE NANOPARTICLES USING MÖSSBAUER SPECTROSCOPY WITH A HIGH VELOCITY RESOLUTION

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Magnetite (Fe_3O_4) and maghemite (γ–Fe_2O_3) nanoparticles are currently used in development of magnetic fluids for various biomedical applications. The presence of iron in such systems permits us to use ^{57}Fe Mössbauer spectroscopy for investigation of these systems and analyze hyperfine interactions, magnetic features, variations in the structure and size of nanoparticles, effect of fluid molecules and nanoparticle coating, etc. Further development of Mössbauer spectroscopy and increase in velocity resolution demonstrated new possibilities of this technique in the study of various iron containing materials [1, 2]. Mössbauer spectroscopy with a high velocity resolution permits to measure spectra with a less step of Doppler modulation of γ-rays using 2^{12} bits (4096 velocity steps) to form saw-tooth shape velocity reference signal and register spectra in 4096 channels of multichannel analyzer [2]. In contrast, other spectrometers permit to use 2^8 bits to measure spectra in 512 or 256 channels. Therefore, Mössbauer spectra measured with a high velocity resolution contain more spectral points; have better quality and less instrumental (systematic) error for each spectral point.

In this work we discuss the results of the study of magnetite, maghemite and maghemite/magnetite nanoparticles as prepared and in some fluids or with coating using Mössbauer spectrometer with a high velocity resolution at 295 and 90 K and in some cases using spectrometer with a low velocity resolution at 295 and 21 K (see Fig. 1). The results obtained demonstrated complicated magnetic patterns which cannot be fitted using well known physical models accounting octahedral and tetrahedral iron sites in magnetite and maghemite. In contrast, Mössbauer spectra were better fitted using superposition of large numbers of magnetic sextets which have not clear physical meaning yet (these sextets may reflect complicated nanoparticle's structure from the surface to internal layers, etc.). Nevertheless, the results obtained demonstrated different hyperfine parameters for studied samples and effect of nanoparticle's coating.

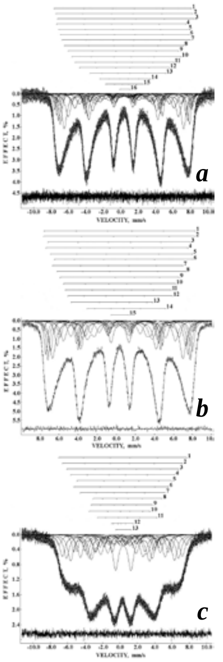

Fig.1 Mössbauer spectra of magnetite (***a***, ***b***) and maghemite (***c***) nanoparticles measured using spectrometers with a high (***a***, ***c***) and low (***b***) velocity resolution. T=295 K.

Keywords: Mössbauer spectroscopy; Magnetite and maghemite nanoparticles; Magnetic fluids

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SHEDDING BLOOD OVER MAGNETS: SOME APPLICATIONS ON UNUSUAL VALENCE STATES IN BIOLOGICAL METAL CENTERS

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A series of recent applications of EPR and NMR spectroscopy on biomolecular systems are discussed, with emphasis on detection, characterization and implications of high-valent metal centers and on the interplay between spectroscopy and theory (ab initio, DFT) in solving problems in this area. Most of these systems involved blood and hemoglobin, or proteins/compounds related to it.

High-valent states important in biological centers are discussed, with focus on the ferryl unit, $[FeO]^{2+}$ as seen in dioxygen-activating enzymes and model compounds, with a comparison towards Fe(IV)-nitrido as seen in methane-activating catalysts as well as with antioxidant enzymes such as the nitric oxide scavenger flavohemoglobin [1-5]. The manners in which these centers can then further engage in formation of free radicals are also discussed, pointing out applications in studying oxidative and nitrosative stress associated with processes such as transfusion experiments with potential blood substitutes[6], side-effects of platinum-based anticancer drugs, or biological effects of plant-based natural extracts [7].

Low-valent metal states, such as Fe(I), Fe(0), or Co(I), are rarely cited as biologically relevant. However, with cobalamin and hydrogenases as examples, such low-valent states are far easier to achieve than previously thought, as illustrated by our recent contributions using a combination of EPR spectroscopy and DFT calculations for solving electronic structures in low-valent biological metal centers and for pointing out electromerism phenomena in these cases [8-10].

Keywords: NMR; EPR; DFT; oxidative stress; nitrosative stress, metalloproteins, free radicals

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EXPLORING AND SHAPING THE CHARACTER OF ELECTRONICALLY EXCITED STATES

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Electronically excited states are subject to shifts in energy upon solvation. In some cases even the energy order of some excited states is changed. We focus to well-defined interactions between the chromophoric system and the solvent molecules which manipulate the energetics of the excited states.

A very prominent example of close-lying electronically excited states which change their energy order is the L_a/L_b system of indole. It has long been known, that polar solvents stabilize the more polar L_a state with respect to the L_b state. For the isolated molecule, the L_b state is generally the more stable one. Even complexation with one water molecule is in some cases (depending on the size of energy gap and the relative polarity of the states) enough to draw the L_a state below the L_b. Examples for this behaviour are the 7-azaindole$(H_2O)_n$ clusters. The lowest escited singlet state in the monomer ist the L_b, while even for the cluster with one water molecule, the L_a state absorbs below the L_b.

The range of energy gaps ($\Delta E = E(L_a) - E(L_b)$) for monomer moieties with the indole chromophore is enourmous. They range from more the +4000 cm^{-1} for methoxyindole over a few hundred cm^{-1} for tryptamine and indole to about -1000 cm^{-1} for tetrahydrocarbazole .

A special case is 2,3-dimethylindole. Here, the energetic ordering of the L_a and L_b states is subject of a long-lasting debate. It is now commonly accepted, that in the gas phase, the L_a origin lies 342 cm^{-1} above the L_b origin. However, the extreme dependence of the relative positions of La and L_b states in 2,3-dimethylindole on the local surrounding is illustrated by the fact, that even in a very non-polar media, the energetic order of L_a and L_b states is interchanged, as determined via fluorescence anisotropy of 2,3-dimethylindole in an argon matrix, and in cyclohexane solution, where the L_a state is found to be shifted below the L_b state.

The relative position of these states influences considerably the photophysics and dynamics of the chromophores, since potentially repulsive states, like the $\pi\sigma^*$ states are differently influenced by microsolvation or the local surrounding. The different couplings of excited states and energetic positions of conical intersections between them and also between excited states and the ground state lead to strongly varying magnitudes and orientations of transition dipoles and of the excited state life times.

The determination of the electronic nature of various indole derivatives, using rotationally resolverd spectroscopy will be discussed.

CHARACTERISATION OF POLYMER DEGRADATION BY VIBRATIONAL SPECTROSCOPIC AND CHEMILUMINESCENCE MEASUREMENTS

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The polymeric surfaces of formwork sheets were aged artificially by environmental simulation experiments such as UV- and Xenon-weathering and by concrete exposure. In order to be able to describe the degradation of the polymeric surfaces as a function of the environmental influence factors several analytical methods were applied on the original and aged samples.

Among others, surface sensitive infrared spectroscopy (attenuated total reflection = ATR and ATR-imaging) in combination with chemiluminescence (CL) measurements turned out to give the most promising results. By comparing the spectra of the original sample with those taken from the environmental simulation after increasing exposure time, a correlation of the spectral changes with the impact of radiation / temperature / chemical media could be derived. Thus, the stability of the polymer respectively the gradually increasing degradation of the surfaces in dependence of the environmental influence factors could be monitored spectroscopically.

This study was primarily focused on PP-surfaces. On increasing exposure of the samples to e.g. Xenon light (= artificial sunlight), the formation of a carbonyl species as well as the insertion of oxygen into the polymer chain could be identified by ATR-infrared spectroscopy. The spatial distribution of the oxidized species on the aged surfaces could be visualized by ATR-imaging experiments.

Parallel measurements of the CL behavior of the aged samples gave valuable information on the pre-damage of the surface induced by the weathering procedure. We found out that weathered samples might exhibit no detectable changes in their surface infrared spectra, but exhibit clear differences in their CL behavior (see Fig.1). By measuring the surface ATR-spectra before and after the CL experiment, direct deduction of the chemical nature of the surface species formed during the CL reaction, is possible. These results indicate the very high sensitivity of the CL measurements to detect activated polymer surface species which can only be visualized and identified by combining this method with IR-spectroscopic measurements. With this analytical tool we aim to optimize the properties of the polymer used as top layer of formwork sheets.

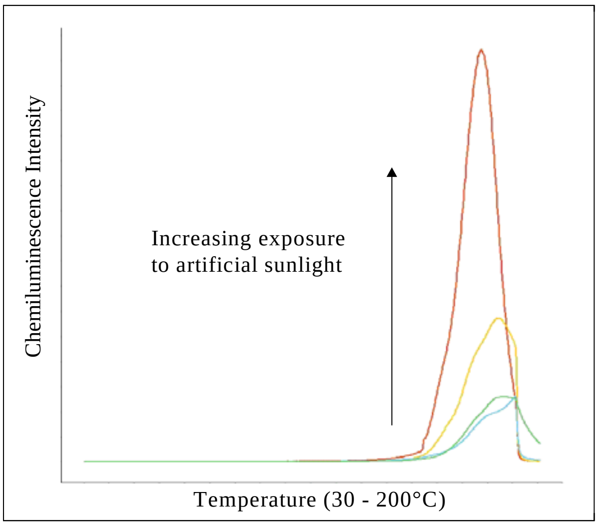

Fig.1 CL-activity of Xenon weathered PP-surfaces

Keywords: ATR Infrared spectroscopy ; Chemiluminescence ; degradation

STUDY OF RIBOFLAVIN ORIENTATION ON AG, AU AND CU SURFACES USING *IN-SITU* SERS SPECTROELECTROCHEMISTRY

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Surface-enhanced Raman scattering (SERS) spectroscopy is a powerful tool to study compounds adsorbed on Ag, Au or Cu [1] surfaces. *In-situ* SERS spectroelectrochemistry allows investigation of surface intermediates in dependence on applied potential. Riboflavin represents vitamin B_2 and its molecule contains several nitrogen and oxygen atoms via those it can adsorb onto metal surface. Aqueous solution (0.1 M KCl) of riboflavin (10^{-5} mol.L^{-1}) was used as electrolyte and deposition bath simultaneously. The investigation of riboflavin molecules orientation was carried out in special spectroelectrochemical cell using dispersive Raman spectrometer with laser excitation at 785 nm. *In-situ* SERS spectra of riboflavin adsorbed on the surfaces were recorded at each applied electrode potential value. The potential was varied usually from 200 mV to -1200 mV with step 100 mV. We observed that bands intensities and their ratios were changing significantly with respect to potential values. From selection rules of SERS it is known that vibration modes perpendicular to the surface and located close to the surface are the most enhanced. We have been able to conclude the way of adsorption on the surface from intensities of some characteristic bands. Orientation of adsorbed riboflavin molecules depends on varying applied electrode potential. The molecules were flipped with alternating potential, molecules were adsorbed via oxygen atoms from hydroxy- and keto- functional groups or via nitrogen atoms from heterocycles. The orientations of molecules were confirmed using theoretical quantum chemical calculations.

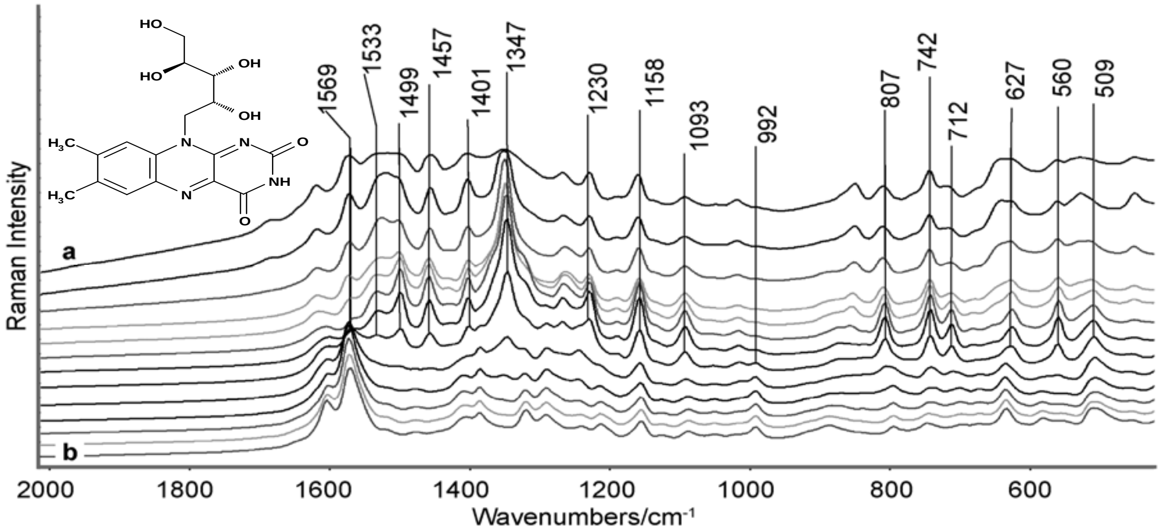

Fig. 1 Structure and in-situ SERS spectra of riboflavin adsorbed on copper surface at changing electrode potential from 100 mV (a) to -1100 mV (b) (step 100 mV)

Keywords: riboflavin; in-situ SERS; spectroelectrochemistry

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REHYDRATION OF DEHYDRATED CaFe-LAYERED DOUBLE HYDROXIDE FOLLOWED BY THERMOGRAVIMETRY, X-RAY DIFFRACTOMETRY AND DIELECTRIC RELAXATION SPECTROSCOPY

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It is well-known that layered double hydroxides (LDHs) lose their layered structure on heat treatment. The procedure may be followed by thermogravimetry and the dehydrated structure is often found to be X-ray amorphous. It is also known that in an environment saturated with water vapour, rehydration occurs and the layered structure is more or less regained [1,2]. This is the so-called memory effect. While the steps of the dehydration are generally known in detail, those of the rehydration are not. It is probably due to tedious experimental work that should consist of keeping the fully dehydrated material under an atmosphere of precisely controlled humidity until equilibrium is reached, then applying a measurement techniques sensitive enough to subtle structural changes. The first part requires much time, and methods capable of directly monitoring variations in structural water content without much complication are not too frequent either.

In this contribution we describe in detail the rehydration procedure of a dehydrated CaFe-layered double hydroxide (LDH) followed by the combination of thermogravimetry (TG–DTG), X-ray diffractometry (XRD), and most importantly dielectric relaxation spectroscopy (DRS). LDH was prepared with the co-precipitation method and was characterised with a range of instrumental methods (scanning electron microscopy, FT-IR spectroscopy, *etc.*) Heat treatment was followed by thermogravimetry. The layered structure was found to collapse above 750 K and X-ray amorphous product was obtained. For studying the rehydration procedure, dehydrated samples were placed in environments in the 6–97% relative humidity range with 12 preset vapour contents at 323 K. For equilibration, 48 hours were allowed. Then, X-ray diffractograms were taken, the DRS spectra were registered (Novocontrol Alpha-A FRA instrument) in the 5×10^{-3}–10^{7} Hz range and after that the partially rehydrated structures were heat-treated and TG–DTG curves were measured. The various methods provided with water uptake data, and the various positions of water molecules in the rehydrated LDH structure could be located and analysed. Thus, mechanistic details concerning the rehydration procedure could be collected.

Keywords: layered double hydroxide; rehydration procedure; dielectric relaxation spectroscopy; thermogravimetry; X-ray diffractometry

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SURFACE-ENHANCED VIBRATIONAL SPECTROSCOPY OF B-VITAMINS: WHAT IS THE INFLUENCE OF SUBSTRATE SURFACE TEMPERATURE?

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Surface-enhanced Raman scattering (SERS) [1] and surface-enhanced infrared absorption (SEIRA) [1] spectroscopies are analytical tools suitable to detect small amounts of analytes adsorbed on metal (predominantly Au, Ag and Cu) surfaces. Both organic and inorganic substances can be identified. During recent years, these spectroscopic methods became important in the investigation of biomolecules [2] and pharmaceuticals [2,3] adsorbed at nanostructured metal surfaces. Several studies [4,5,6] have shown that the temperature of SERS-active substrates can exhibit significant influences on enhancement factors of Raman bands. Moreover, when the temperature of the substrate is elevated above certain value, temperature-induced changes of adsorbed molecules can occur. Temperature dependence of the SERS signal intensity differs regarding the type of SERS-active metal.

In this work, the temperature dependence of surface-enhanced vibrational spectra of B vitamins (riboflavin, nicotinamide and folic acid) has been investigated at electrochemically prepared massive gold, silver and copper substrates using SERS at excitation wavelength 1064 nm (eliminating molecular resonance and photochemical effects) and SEIRA spectroscopy. Newly designed sample holders which allow an adjustment of temperature from 5°C to 55°C were used. In the case of SERS spectroscopy, the spectral mapping device was used to monitor large surface area of the substrates.

The aim of this study was to investigate (i) stability of adsorbed B vitamins at different temperatures, (ii) temperature-induced changes in SERS and SEIRA spectra and (iii) reversibility of temperature-induced changes. Stability of adsorbed analytes at certain temperature was investigated by repeated recording of spectral maps while temperature of the substrate was maintained at a fixed value. To elucidate the temperature-induced changes of spectral features, substrate temperature was risen or decreased stepwise and spectral maps were recorded once at each temperature. The reversibility of changes caused by either rapid increase or decrease of temperature was investigated on spectra recorded at certain temperature, then at significantly changed temperature and finally again at the initial value.

The spectral maps obtained at different temperatures were compared using principal component analysis (PCA) to elucidate the effect of temperature variation. The score-graphs demonstrated the contribution of temperature variation to overall data variability, while the x-loadings graphs enable to distinguish between the “local effects” on individual bands and the “global effects” on the whole spectra (e.g. overall enhancement or changes of background).

Financial support from the specific university research (MSMT No. 21/2012-A2_FCHI_2012_037) is gratefully acknowledged.

Keywords: B-group vitamins; surface-enhanced Raman scattering; surface-enhanced infrared adsorption

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SELF-ASSEMBLING OF 2,3-PHENYL/THIENYL-SUBSTITUTED ACRYLIC ACIDS OVER POLYCRYSTALLINE GOLD

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Cinnamic acid derivative crystals consist of 2D layers [1]. The fundamental units are the acid dimers kept together with strong C=O…HO hydrogen bonds (short-range ordering), while the dimers form the 2D sheets through (aromatic)CH…O short contacts (long-range ordering) [2]. In the crystals, the layers probably interact *via* CH…π and π…π secondary bonds. If the acrylic acid skeleton holds *e.g.,* phenyl and thienyl groups or two thienyl groups in the 2,3 positions (aromatic)CH…S hydrogen bonds become the long-range ordering force in the 2D sheets [3]. The sulfur in the thienyl group can also be used to turn the 2D structure to 3D one by using *e.g.,* gold surface and letting the organic molecules self-assemble on it. Since the sulfur has a strong tendency to covalently interact with Au atoms, the CH…S hydrogen-bonded network existing in the pure crystal is perturbed and new supramolecular structures may form. Results obtained on studying these structures are communicated here.

In the experiments, variously substituted thienyl cinnamic acid analogues were used (most of the molecules were synthesised in our laboratory). Self-assembling was studied over polycrystalline gold surfaces prepared by the pulsed laser deposition (PLD) technique. The supramolecular structures were made by the layer-by-layer (LbL) deposition method. The clean gold surface was studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM).Organic layers deposited were investigated by mid IR microscopy (IRM), SEM and AFM. Energy dispersed X-ray fluorescence spectroscopy (EDX) was used for preparing elemental map on the SEM micrographs of the samples.

SEM and AFM micrographs revealed that the PLD technique produced atomically smooth surface with occasional droplets with diameters of 1-2 μm. IRM and SEM−EDX measurements verified that organic layers were formed on the gold surface and the molecules did not undergo any chemical transformations. The gold surface was fully covered by the organic molecules as was attested by AFM measurements. A 15-20 nm thick organic "carpet" covered the metal surface and out of this layer many peaks with a height of 40-50 nm grew out nearly perpendicularly to the surface with close to even distribution. Molecular modelling indicated that the "carpet" consisted of 4-5 layers of substituted acrylic acids, while the peaks contain more than 10 dimer units. The dimers are kept together with (aromatic)CH…S hydrogen bonds, while the peaks contained bundles of such "oligomers" using CH…π close contacts.

Keywords: self-assembling; thienyl/phenyl-substituted acrylic acid stereo isomers; polycrystalline gold surfaces; atomic force microscopy; FT-IR microscopy; scanning electron microscopy

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USE OF VIBRATIONAL SPECTROSCOPIC TECHNIQUES FOR THE CHARACTERISATION OF CHEMICAL ROBOTS

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Chemical robots can be defined like simple artificial equivalents of single-celled organisms (e.g. amoeba); they are made of carefully designed chemical shells-within-shells, with receptors on their surfaces. Instead of software and processors to guide them, their instructions are written into the chemistry of their constituent parts. A chemical robot should be able to modify the chemical composition of its immediate environment either according to a pre-defined external or internal trigger or in response to local conditions (pH, temperature, concentration of a particular molecule or ion).

Present work is focused on synthesis and mainly on various techniques of characterization of different types of particles that should serve as the outer bodies or internal compartments in chemical robots such as (i) giant lipozomes – spherical enclosures consisting of one or more phospholipid bilayers surrounding an aqueous center; (ii) hollow silica microparticles, alginate microbeads and thermo-responsive PNIPAM (poly-N-isopropylacrylamide) /silica microcapsules, (iii) thermosensitive microgels and hydrogels and (iv) surface-functionalized magnetic nanoparticles [1-2].

Surface properties of chemical robots, which should be affected somehow, are the crucial parameter in their construction and implementation. They should be controlled very precisely in order to detect and clarify all the changes in chemical robots body behavior in consequence of various chemical reactions on the receptors or any type of interaction with the surroundings. From this point of view, methods of vibrational spectroscopy can be suitably used for the purpose of surface characterization, being usually able to provide quick, non-destructive analysis with minimal requirements for the pretreatment of the sample.

However, taking into account the complexity of chemical robots body, their small size and low concentrations of the substances on the surface, the characterization process should imply the development of measurement technique including the adaptation of measurement device, adjustment and optimization of pretreatment procedure and measurement conditions. In the light of these facts especially techniques of surface-enhanced Raman scattering (SERS) and surface-enhanced infrared absorption (SEIRA) appear to be very challenging in characterisation of chemical robots body surface properties [3-5].

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Keywords: Chemical robot; vibrational spectroscopy; silica microparticles; magnetic nanoparticles

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INTERMOLECULAR INTERACTIONS IN POLY(2-(2-METHOXYETHOXY)ETHYL METHACRYLATE HYDROGELS – RAMAN SPECTROSCOPY STUDIES

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Polymers exhibiting lower critical solution temperature (LCST), such as poly(2-(2-methoxyethoxy)ethyl methacrylate (pMEO$_2$MA), are commonly used for synthesis of thermo-sensitive hydrogels. These thermo-responsive materials reveal relatively large and abrupt change in their physical properties at the LCST as a result of redistribution of intermolecular interactions. Such properties as well as good biocompatibility allow to perceive them as a perfect materials in various biomedical and pharmaceutical applications such us wound dressings, contact lenses, carriers for targeted drug delivery and many others [1,2].

Intermolecular interactions play a crucial role in hydrogels. They stabilise expanded conformation of polymer network in fully swollen state leading to high swelling degrees (weight ratio of water and polymer content) characteristic for many hydrogels. Fragile balance between hydrophobic and hydrophilic water-polymer and polymer-polymer interactions determines also other physical properties of hydrogels: diffusivity, mechanical modulus, fragility, etc.. Due to that, the special attention should be focused on the changes in interactions occurring during volume phase transition (VPT). The consequence of induced by temperature breakdown of water-polymer interactions is dehydration of polymer chains resulting in collapse of polymer network.

Raman spectroscopy seems to be the most powerful technique useful to monitor intermolecular interactions in water systems. In this work an influence of water content and temperature on intermolecular interactions in pMEO$_2$MA hydrogels obtained by atom transfer radical polymerisation as well as by free radical polymerisation will be presented. The role of polymer architecture will be additionally discussed. Spectroscopic data will be supported by the results of dynamical mechanical analysis and differential scanning calorimetry.

Acknowledgments
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Keywords: poly(2-(2-methoxyethoxy)ethyl methacrylate; stimuli-responsive hydrogels, intermolecular interactions

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CHARACTERISATION OF THIN SUPPORTED LIPID FILMS BY SIMULTANEOUS SURFACE ENHANCED RAMAN SPECTROSCOPY AND ATOMIC FORCE MICROSCOPY

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Thin supported lipid films have a wide range of applications in nano-biotechnology including their use as selective biosensors and models of the cell membrane. The study of these supported lipid films with a combined instrument integrating surface enhanced Raman spectroscopy (SERS) and a high resolution topographic technique such as atomic force microscopy (AFM) has the advantage of allowing simultaneous spectroscopic and morphological measurements, resulting in a better control of such biological interfaces. Previous SERS investigations on lipid films of nanometer thickness have been performed incorporating molecules of high Raman cross-sections (known as Raman labels) to the thin films [1] or by applying high external fields to the lipid films [2]. To our knowledge, studies without the addition of these external factors have not been reported. As well as spectroscopic information, morphololological characterisation of the lipid films is possible using AFM. The novel aspect of the current work is the simultaneity of the AFM and SERS measurements in the absence of invasive probes (such as external voltages) across the lipid films. Supported thin lipid films with thickness of up to 25nm composed of phospholipids and fatty acids were deposited on substrates of sapphire/silver and mica/silver prepared by nanosphere lithography. The combined AFM-SERS technique successfully enabled the "dual" simultaneous characterisation of thin supported lipid films.

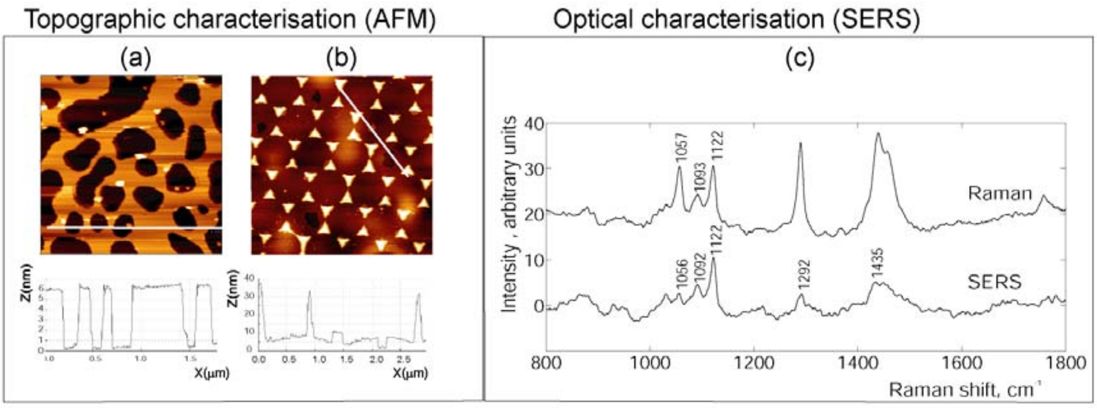

Fig.1 (a) AFM image of a hydrated bilayer of DPPC (b) Height and line profile of a thin film of arachidic acid on a sapphire/Ag SERS-active substrate fabricated by nanosphere lithography.(c) Raman spectra of DPPC powder versus the SERS spectra of the thin film of DPPC. (b) and (c) are reprinted with permission from the Society of Applied Spectroscopy (SAS) © 2011, [3].

Keywords: SERS; AFM; thin supported lipids

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CUMULENIC SP CARBON CHAINS: AN INVESTIGATION BASED ON VIBRATIONAL SPECTROSCOPY

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sp carbon chains have appealing electronic structures which affects their optical and transport properties. Indeed, they are intriguing systems with structure-, length- and termination-dependent properties. The model carbyne (infinite chain) can display two geometries: equalized (e.g. cumulene) or dimerized (e.g. polyyne). The metallic character of cumulene can change into the semiconducting behavior of polyyne due to Peierls' distortion and a longitudinal optical phonon branch appears lead by the folding of the first Brillouin zone [1]. In finite length chains, the end groups play a major role in affecting the chain structure. In this context, Raman spectroscopy is a powerful technique to reveal the connection between structural, vibrational and electronic properties of sp-carbon chains as a function of bond length alternation (BLA) [2]. While different polyynes have been synthesized and characterized, cumulenes are more elusive both for their preparation (due to their lower stability) and their characterization (very low Raman intensity of the LO modes). Only in a few works the observation of cumulenes is reported [3-5]. We present here a study of cumulene species based on Raman and IR spectroscopy and Density Functional Theory (DFT) calculations. First, we find that for finite length chains the equilibrium geometry is fully determined by end effects and the LO mode consisting of the BLA oscillation (responsible for the strongest Raman lines of polyynes) becomes weak for cumulenes. However, other LO modes of cumulenic chains can be observed, demonstrating that these systems can be investigated by means of Raman spectroscopy [6]. As a second case, the IR spectrum of an adamantyl-capped polyyne is investigated: a new band is observed upon UV photoexcitation revealing the existence of new photogenerated molecular species. DFT calculations assign these photoinduced IR spectral features to the presence of metastable states as forbidden singlet or triplet excited states, both characterized by cumulenic structures [4]. Finally we report an investigation of the Raman and SERS spectra of phenyl-capped polyynes: the interaction with metal nanoparticles induces a charge transfer from the metal to the chain that modifies the electronic structure and the vibrational properties. With the help of DFT calculations we evidence the key role of charge-transfer processes in inducing a cumulenic structure in these systems [5]. In conclusion, we have shown how vibrational spectroscopy can be crucial to unveil the connections between structural, vibrational and electronic properties of unusual cumulenic carbon chains.

Keywords: Linear carbon chains; First principles calculations; Raman intensity; Bond length alternation

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SUPEROXIDE DISMUTASE INSPIRED Fe−AMINO ACID COMPLEXES COVALENTLY GRAFTED ONTO CHLOROPROPYLATED SILICA GEL – SYNTHESES, STRUCTURAL CHARACTERIZATION AND CATALYTIC ACTIVITY

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Homogeneous catalysts are most often complex compounds containing a metal(ion) and various organic compounds. They can be highly active and extremely selective. However, their recovery from the reaction mixture and therefore their reuse are usually difficult. Metal ions are cofactors in many enzymes, most frequently in oxidoreductases. The ions there are able to alter their redox state as well as their coordination number. The ligands are bound to the metals through the donor atoms of various amino acids. The cofactor together with the proteomic skeleton forms the most selective of all catalysts, the enzymes. Enzymes are working under relatively mild conditions. However, if we prepare metal ion−amino acid complexes inspired by the metal ion containing enzymes, and immobilise them on various supports, then we may be able to produce catalysts with activities and selectivities resembling to those of the enzymes [1]. These substances are capable of working under more rigorous conditions and they can easily be recovered and recycled.

In this work the syntheses, structure and SOD-activity of covalently grafted Fe(III)−complexes formed with various N- or C-protected amino acid ligands (L-histidine and L-tyrosine) inspired by the active site of the Fe-SOD enzyme is presented. Chloropropylated silica gel was used as support to mimic the proteomic skeleton of the enzyme. The amino acids were covalently grafted onto the support, then, the complexes were built with soaking the amino acid grafted support in an isopropanolic solution of the metal salt (the complexes prepared under ligand-poor conditions). The complexes prepared were allowed to rearrange in the presence of excess added amino acid (complexes constructed under ligand-excess conditions). The products were characterised by mid and far FT-IR and Raman spectroscopies, the Kjeldahl method and ICP spectroscopy.SOD activities of the substances were determined via the Beauchamp-Fridovich test reaction. Anchored complexes having uniform amino acids as well as their two-component mixtures have been prepared.

It was found that the preparation of covalently anchored Fe(III)−amino acid complexes was successful in all cases. The coordinating groups were identified through comparing the mid IR and the Raman spectra of the pristine protected amino acids and the difference spectra (the spectrum of the support subtracted from the spectrum of the immobilised complex), observing the Fe(III)−coordinating atom interactions directly in the far IR spectra, quantitatively determining the amino acid and the Fe(III) ion contents, inspecting the colour of the substances and chemical evidences. It was found that the structure of the complexes made under ligand-poor conditions often differed from that of complexes made under ligand-excess conditions, however, occasionally added amino acids did not cause rearrangement. All the covalently immobilised complexes displayed SOD activity, in some instances it was appreciable.

Keywords: Fe(III)−amino acid complexes; immobilisation by covalent anchoring; structural characterisation by FT-IR spectroscopy; superoxide dismutase activity

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SPECTRA, STRUCTURES, AND POTENTIAL ENERGY SURFACES OF 1,3-BUTADIENE, PYRIDINES, AND CYCLIC ALCOHOLS

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Spectroscopic methods and theoretical computations have been used to determine the structures, conformations, and potential energy surfaces of selected molecules. The gas-phase Raman spectra of 1,3-butadiene and three isotopologues averaged over hundreds of hours of collection showed bands from the minor (2%) *gauche* conformer as well as those from the predominant *trans* rotamer. The torsional potential energy function for the internal rotation was determined from the data and agreed well with that predicted by *ab initio* calculations. Numerous combination bands involving the torsion were observed throughout the spectra. The ground state vibrations of pyridine and several halo-pyridines were investigated using infrared and Raman spectra and the excited state vibrations using ultraviolet absorption spectroscopy. *Ab initio* and DFT computations complemented the work. Pyridine is very floppy and quasi-planar in its $S_1(n,\pi^*)$ excited state. The fluoropyridines also become floppier in their excited states but are more rigid than pyridine. Several molecules possessing weak π-type intramolecular hydrogen bonding were investigated using high temperature vapor-phase infrared and Raman spectroscopy, jet-cooled fluorescence excitation spectroscopy, and *ab initio* calculations. Each molecule possesses several conformational energy minima in both ground and excited electronic states, and in each case the conformer with weak hydrogen bonding is of lowest energy and most abundant. The lowest energy hydrogen-bonded form of 3-cyclopenten-1-ol, for example, is about 400 cm^{-1} lower in energy than any of the other three conformers, which can interconvert into one another through the ring-puckering or –OH torsional vibrations.

Keywords: Raman; infrared; potential energy surface

MÖSSBAUER SPECTROSCOPY AS A PROBE OF THE ELECTRIC FIELD IN DEOXYHEME PROTEINS: THEORETICAL APPROACH

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Heme proteins are intensively used to study relationship between the structure, dynamics and function of proteins. It was shown that the protein electric field affects spectroscopy and functions of these proteins, see for example [1, 2]. Earlier we studied the effect of the protein electric field on the C-O vibrational frequency of carbonmonoxyheme proteins [1, 3] and showed that both position of the C-O vibrational band and its shape are controlled by the protein structure and dynamics, respectively.

In this study we used quantum chemical calculations (DFT) to find out to what extent the protein electric field in the heme pocket affects Mössbauer spectra of deoxyheme proteins. We studied both models (effect of different charges and water molecules located close to the heme) and deoxymyoglobin (Mb). In the latter the heme pockets can contain water molecule [4, 5]. We computed effect of the heme distortions, the whole protein electric field and pocket water on the Mössbauer spectra of different Mb. We obtained that presence of the water molecule in the heme pocket critically affects the spectra, this fact allowed us to interpret experimentally observed broadening of the hemoglobin Mössbauer spectra [6]. It is also shown that the Mössbauer spectra are very strongly affected by lengths of the iron-nitrogen covalent bonds and, consequently, can be used to verify results of X-ray crystallographic studies

It follows from our study that in the case of deoxyheme proteins Mössbauer spectra can be used to study the protein electric field in their heme pockets. In particular, this conclusion provides basis for using molecular dynamics for interpretation of Mössbauer spectra of cytochrome c oxidase [7].

Keywords: DFT, deoxyheme proteins, protein structure, protein dynamics, myoglobin

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IR SPECTROSCOPY OF POLYMERS CRYSTALS FROM FIRST PRINCIPLE CALCULATIONS: POLYMORPHISM IN POLYAMIDES

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The development of structure-property correlations in macromolecular materials is very important in polymer science and technology. Vibrational spectroscopy has been widely used to this aim, both as basic and advanced characterization tool. However, the variety of phenomena taking place at the nano-, meso- and macroscale usually causes difficulties in the interpretation of the spectra, generating the ambiguities, contradictions and discrepancies which can be often found in the literature. Computational tools suitable for an accurate prediction of solid state effects (e.g crystal structure) in periodic systems are now available but their application for the prediction of the spectroscopic response of polymeric materials is so far limited to very few cases. In this contribution, we show how Density Functional Theory calculations including an empirical correction for dispersion interactions (DFT-D) [1a] and explicit use of space group symmetry as implemented in the CRYSTAL09 code [1b], can be applied successfully to solve many discrepancies in the interpretation of the IR spectra of nylon6 polymorphs. Polyamides show a peculiar and complex polymorphism, which often requires a careful and detailed study for the interpretation of the related structural and vibrational features; nylon 6 in particular is one of the most intriguing cases. Indeed, the complexity of the phenomena related to the existence of several polymorphs determines non negligible problems in the intepretation of the experimental data, often preventing a reliable structural characterization of new systems, such as nanocomposites or electrospun nanofibers. DFT-D calculations carried out on the isolated chain of nylon 6 (*i.e.* infinite 1-D model) and on its α and γ crystalline polymorphs allowed us to give a sound insight on the interactions ruling polymorphism at the molecular scale. Moreover, the simulation of the IR spectra gave very important results for the correct interpretation of the experimental data. The structural parameters of both crystalline polymorphs are accurately predicted and new insights on the interplay of conformational effects, hydrogen bonding and van der Waals interactions which affect the properties of the crystal structures of polyamides are found. A set of marker bands of the IR spectra is proposed for the identification of the two polymorphs and is compared to previous assignment: several "old" markers are confirmed, others are criticized and new ones are proposed. Parallel to nylon 6, we analyzed successfully also the vibrational properties of nylon 6,6. Our results demonstrate that DFT-D methods and modern ab-initio periodic codes, as the CRYSTAL09 program [1b], provide valuable and powerful tools for the interpretation of spectroscopic data of semicrystalline polymers, even if they have been seldom applied to polymeric systems [2,3]. The results obtained strongly encourage its applications to other classes of polymeric materials or molecular crystals, still lacking a reliable vibrational assignment and thorough interpretation of the experimental spectra.

Keywords: polymer spectroscopy; polymorphism; nylon 6; periodic DFT calculations.

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PERFORMANCE OF NEW DFT METHODS IN CALCULATIONS OF THE MOLECULAR STRUCTURES AND VIBRATIONAL SPECTRA OF CISPLATIN AND PICOPLATIN

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Picoplatin, *cis*-[$PtCl_2(NH_3)$(2-picoline)] is a new generation platinum anticancer agent which shows remarkable activity against a wide range of cisplatin-resistant tumors, in particular, in the treatment of SCLC, a very aggressive form of lung cancer. Theoretical calculations on platinum complexes can greatly facilitate the design of novel platinum agents. Accurate theoretical prediction of the geometric parameters, vibrational frequencies and IR(Raman) intensities complemented with the experimental studies of vibrational spectra may confirm the structure of the novel compound.

At first, we have made an assessment of eight density functional theory (DFT) methods on their performance on cisplatin. The examined functionals included those recently introduced into the Gaussian program (M06, M06-2x, M06-L, B2-PLYP) and earlier (mPW1PW, PBE0, LSDA, B3LYP) combined with different effective core potentials (ECP) and basis sets. The results show that PBE0 and mPW1PW are the best performing functionals for the molecular geometry and vibrational spectra of cisplatin. The M06-type methods reproduce very well the Pt-Cl stretching frequencies, but they overestimate the Pt-Cl bond lengths. In calculations by the M06-L and M06-2x functionals, the frequencies of the ν(Pt-N) stretching vibrations are too low, by about 70 cm^{-1}, in comparison to experiment. The SDD effective core potential and valence basis set (for Pt and Cl) performs better than LanL2DZ for the molecular geometry of cisplatin.

Next, the molecular structure and theoretical vibrational spectra of picoplatin were calculated by using the mPW1PW and PBE0 methods with the SDD/D95V(d,p) combined basis sets. Picoplatin was synthesized in our laboratory. The experimental IR and Raman spectra of this drug are reported, for the first time. The clear-cut assignments of the spectra have been made on the basis of the calculated potential energy distribution (PED), as in our earlier works on Pt(II) compounds [1-3]. In the experimental Raman spectrum of picoplatin, the strong band at 542 cm^{-1} is assigned to the $\nu(Pt\text{-}N_{amm})$ stretching mode. The $\nu(Pt\text{-}N_{pic})$ ring stretching vibration contributes mainly to the Raman band at 262 cm^{-1}. The two distinct bands with the maxima at 328 and 316 cm^{-1} are assigned to the ν(Pt-Cl) stretching vibrations. The two latter bands should disappear from the spectra upon hydrolysis of picoplatin.

The presented results will be helpful in the studies on hydrolytic reactions and interactions of picoplatin with other biomolecules (DNA) in aqueous solution, using Raman spectroscopy.

Keywords: Density functional theory; vibrational spectra; cisplatin; picoplatin

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COMPUTATIONAL STUDIES ON WATER-POLY(VINYLMETYLETHER) INTERACTIONS

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Polymer gels become increasingly important in everyday life. Many sophisticated ideas for hydrogel applications have been already realized, such as contact lenses, semi-permeable membranes, drug delivery systems, artificial muscles and many others. The stimuli sensitive gels are a particularly interesting group of so called smart materials. The special attention attract thermo-responsive hydrogels undergoing volume phase transition (VPT) as a result of. limited miscibility of the polymer at the temperatures higher than lower critical solution temperature (LCST). The VPT commonly leads to a sudden change of physical properties, and it results from changes in water-polymer interactions.

Recently observed flowering of quantum chemistry and computational studies is a consequence of the development of computer cluster technology and of common accessibility to such clusters. Currently very precise calculation may be realized even with very high precision on the large systems containing hundreds of atoms. The size scale is a crucial point in a case of the modeling of polymer systems.

Poly(vinylmetylether) PVME hydrogels are representative of thermo-responsive materials. Small size of mer unit as well as broad experimental database devoted to PVME makes it an ideal candidate to be a model object for computation. The most interesting problem to be solved concerns the changes in molecular interactions occurring during VPT. Moreover that it has been postulated that in fully swollen hydrogels PVME form a relatively stable complex with water. This hypothesis has been still insufficiently documented, and computations seem to be a good tool to support or to reject it.

The aim of presented studies is to verify the hypothesis about the PVME:H_2O complex formation and to compare the intermolecular interaction in PVME hydrogels differ on swelling degree. The PVME:H_2O 1:1, 1:2, etc. systems, with various chain lengths (from dimer to pentameter) were tested. Intermolecular interactions water-PVME were examined using MP2 and DFT methods and the basis set 6-31G (d, p). The MP2 method was chosen because it is commonly regarded as a good method to model hydrogen bonds and vibrational frequencies in water systems. All results will be discussed in the light of experimental data - IR and Raman spectra as well as DSC thermograms.

AN AB INITIO STUDY OF THE PROPERTIES OF SOME LITHIUM-BONDED COMPLEXES – COMPARISON WITH ANALOGOUS HYDROGEN-BONDED COMPLEXES

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Ab initio calculations have been carried out on a series of complexes formed between lithium fluoride, chloride and bromide on the one hand, and ammonia, water, phosphine and hydrogen sulphide on the other. The calculations were performed using the Gaussian-09 program, at the second order level of Moller-Plesset perturbation theory and with Dunning’s augmented correlation-consistent polarized valence triple-zeta basis set. The properties studied were the molecular structures, interaction energies, vibrational spectra, molecular orbital properties and charge density topologies. The results have been compared with those for an analogous set of complexes formed between the Lewis acids hydrogen fluoride, chloride and bromide, and the same set of four Lewis bases. Common features between the properties of both sets of complexes have been highlighted, and the differences rationalized.

Keywords: ab initio complexes; lithium-bonded complexes; vibrational spectra.

CONFORMATONAL AND VIBRATIONAL ANALYSIS OF 12-THIACROWN-4 AND 18-THIACROWN-6

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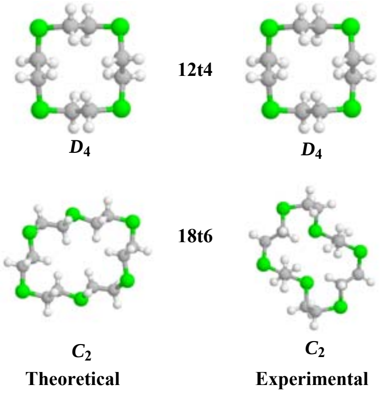
Conformational analysis was performed using the efficient CONFLEX conformational search method of cyclic molecules for free 12-thiacrown-4 (12t4) and 18-thiacrown-6 (18t6) and some of their metal complexes. The ab initio computations were done at the HF, B3LYP, CAM-B3LYP, M06, M062x and MP2 levels using the 6-311G** basis set. Conformational analysis of free 12t4 predicted that 12t4 exists in the D_4 conformation. Conformational analysis of free 18t6 predicted a new C_2 conformation to be the ground state conformation. At the MP2/6-311G** level this new C_2 conformation is more stable by 4.67 kcal/mol than the experimentally known C_2 conformation of 18t6 [1].

Comparison between the dihedral angles of some of the low and high energy conformations concluded that for the stability of 12t4 and 18t6, a SCCS dihedral angle of 180° requirement is more important than a gauche CSCC dihedral angle requirement. It is known that thiacrown ethers adopt exodentate structure and that in 18t6 two of the sulfur atoms violate this rule [1]. A problem with this definition is that it is based on crystal structure where crystal packing forces may affect the molecular structure while the structure of molecules has to be judged by that of the gas phase. Since computations correspond to gas phase isolated molecule, the new predicted C_2 ground state conformation of free 18t6 has all of the SCCS dihedral angles, without any exception, adopt exodentate structure.

Conformational analysis of the 12t4–Ag^+, Bi^{3+}, Cd^{2+}, Cu^+ and Sb^{3+} complexes predicted a C_4, C_4, C_4, C_{2v} and C_4 structures, respectively, to be the ground state structures of these complexes. Conformational analysis of the 18t6–Ag^+, Co^{2+}, Cu^+ and Ni^{2+} complexes predicted C_2, C_i, C_1 and C_2 structures, respectively, to be the ground state structures.

Comparison between the experimental and calculated vibrational spectra confirmed the X-ray solid state structure of both 12t4 and 18t6. The vibrational study is being extended now in our Lab to include that of the 12t4 and 18t6 metal complexes.



Keywords: Conformational analysis, vibrational analysis, thiacrown ethers.

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MODEL DIELECTRIC FUNCTIONS EXPLAINING EVANS HOLES AND PHONON INTERACTIONS IN THE REFLECTANCE SPECTRA OF MONOCLINIC SINGLE CRYSTALS

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The coupled-optical-phonon-mode theory of Barker and Hopfield [1] of two mode interaction in optically isotropic crystals has been extended to monoclinic crystals. The analytical expressions for the calculation of the dielectric tensor elements in the *ac* crystal plane have been derived. It has been shown that the interaction dielectric model is a generalized expression of the dielectric tensor for monoclinic case when no interaction between modes is present [2, 3]. Also, the results in ref. [1] are obtained from this more general theory, when an isotropic case is considered. Employing the fitting procedure on a model taking into account interactions between all pares of modes is very difficult. To make this possible, a model dielectric function taking into account the interaction between modes with closest frequencies has been derived. The validity of the model obtained has been tested on a Tutton salt single crystal of $K_2Co(SO_4)_2{\cdot}6H_2O$ [4]. The recorded spectra from the *ac* crystal plane were fitted in order to obtain best fit parameters. The comparison between the experimentally recorded spectra and the model reflectance function give good results and verify this model to be applicable.

Reflectance spectra may show very different and interesting shapes. The most interesting may be connected to Evans holes. Model calculations to reproduce this effect were done applying model dielectric functions. When a weak oscillator appears within the frequency region of a strong one (i.e. between its TO and LO frequencies), its LO-mode frequency shifts towards higher wavenumbers. As a consequence, the oscillator strength of the corresponding weak mode becomes negative which produces a dip (Evans hole) in the reflectance spectrum. This model was successfully applied to analyze polarized reflectance spectra of potassium hydrogen succinate single crystal in the ac crystal plane. The crystal symmetry was described by phenomenological model and by full symmetry consideration. Both approaches describe all basic spectral features, the wide reflectance of ν_{as}(OH) and the two Evans holes appearing on its shoulder [5].

Keywords: Dielectric model function; Evans holes;Tutton salts, potassium hydrogen succinate single crystal

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ASSESSMENT OF DRUG CARRIERS' POTENTIAL FOR IONIC LIQUIDS BASED MESOPOROUS MATERIALS THROUGH OBSERVED FT-IR SPECTROSCOPIC QUANTUM FLUCTUATION

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There is already a fact that the mesoporous sizes can be controlled by varying the chain length of the ionic surfactants or by adding organic molecules, "cosolvent" which act as spacers inside the micelles [1]. The porous biomaterials with large surface areas and large pore volumes make themselves good candidates for drug delivery systems [2-4]. However, the important issue addresses to which extent such materials can be classified for their structural potency to covalently or ionic binding with farmaceuticals in order their carrier features be activated. The present work advances a structurally related criterion for ordering such nano-binding potential, based on the recently introduced ratio of the particle-wave nature of quantum objects within extended Heisenberg uncertainty formulation [5]

$$\left(\frac{Particle}{Wave}\right)_{\substack{Observed\\Evolution}} = \frac{1}{\sqrt{3+2n^2}}\exp\left(\frac{3+n^2}{6+4n^2}\right) = \begin{cases} 0.952 \ldots n = 0 \\ 0.667 \ldots n = 1 \\ 0 \quad\;\; \ldots n \to \infty \end{cases}$$

Here, the working variable stays the quantum fluctuation magnitude [5]

$$n = \sqrt{\frac{\left\langle x_0^2 \right\rangle_{Exp}}{\left| \left\langle x^2 \right\rangle_{Exp} - \left\langle x_0^2 \right\rangle_{Exp} \right|}}$$

with x_0 and x appropriately considered for each type of experiment. Currently, they are respectively considered as the statistical mean for classical records and the instantaneous values for quantum measurement of FT-IR (bonding) bands' assignment for samples with different base concentration and different thermal treatment [6], here sampled with same ionic liquid chain length - cetyltrimethylammonium bromide (CTAB), with n-dodecyl trimethyl ammonium bromide (DTAB) and with their combination CTAB+DTAB, in a basic environment. This way the spectroscopic assignments of the IR vibrations on ionic liquid based mesoporous materials (even under thermal treatment) may be computationally employed to produce particle-to-wave or ionic-to-covalent hierarchy of binding as a sign of decreasing drug carrier potency aided by structural quantum information.

Keywords: FT-IR spectra; sol-gel synthesis; ionic liquids; particle-wave quantum ratio

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INTERPRETATION OF THE RAMAN SPECTRUM OF A STRONGLY ZWITTERIONIC PUSH-PULL DYE BASED ON QUINOIDAL THIAZOLE

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The inclusion of quinoidal rings between electron donor and acceptor groups helps to their charge transfer connection due to the intrinsic pro-aromatic character of the quinoidal moiety [1,2]. This allows the control of the transference of the charge from the donor to the acceptor in the ground electronic state and, in the ultimate case, to the generation of totally zwitterionic dyes. We have recently published a series of these push-pull compounds in which a 1,3-dithiol-2-ylidene electron donor is combined with a dicyanomethylene electron acceptor through a conjugated bridge which is composed of derivatives of the thiazole group bearing quinoidal form within the five-member ring [3]. The extension of the conjugational quinoidal structure in the bridge has been proved to be an important factor controlling the extent of the movement of the charge between both electro-active groups. This zwitterionic property of dipolar push-pull compounds has been intensively exploited in non-linear optics indicating that the incorporation of pro-aromatic quinoidal segments seems to represent a promising approach towards the optimization of zwitterionic non-linear optical response of the chromophore.

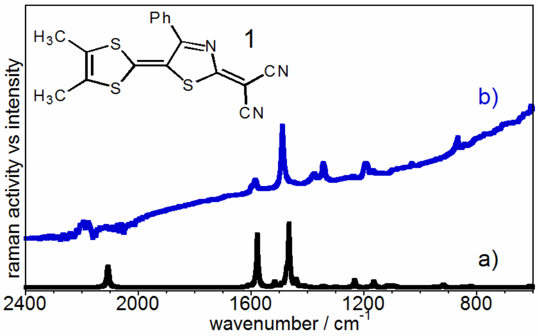

Fig.1 a) MP2/6-31G** theoretical and b) 1064 nm experimental FT-Raman spectra of **1**.

In this communication, we will study the vibrational Raman spectrum of the shortest element of the 1,3-dithiol-2-ylidene dicyanomethylene thiazole series, compound **1** in Fig. 1. We will interpret the vibrational Raman spectrum of **1** as the fingerprint of the zwitterionic character of the molecule in the ground electronic state. To this end, we will carry out a detailed quantum mechanical study aimed to reproduce the complete set of molecular, electronic and spectroscopic properties. In this regard, we have scanned several theoretical methods, in particular DFT and MP2 methods, with the objective to obtain the best description of the molecular parameters able to provide the best adjustment between experimental and theoretical spectra. The theoretical data will be used to: i) Guide the assignment of the Raman vibrational features in terms of vibrational normal modes; ii) propose a realistic distribution of the charge in the molecule; iii) and to conclude about is partial or total zwitterionic character.

Dipolar push-pull dyes, quinoidal rings, pro-aromaticity, theoretical calculations, Raman spectroscopy

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CONTRIBUTION OF FTIR AND RAMAN MICROSPECTRSOCOPY TO DEFAULT ANALYSIS

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The manufacturing processes are becoming more and more controlled as products themselves become more and more identification sophisticated. FTIR and Raman are complementary techniques , allowing identification of particles. Depending on size of particles or defaults on chemical nature of these, Raman or FTIR may be the best choice. A single technique may be sufficient, but in many cases the residues are complex mixtures, requiring more than one technique. Examples in the car and electronic industry will be presented.

SPECTROSCOPIC ANALYSIS OF YELLOW LAKES

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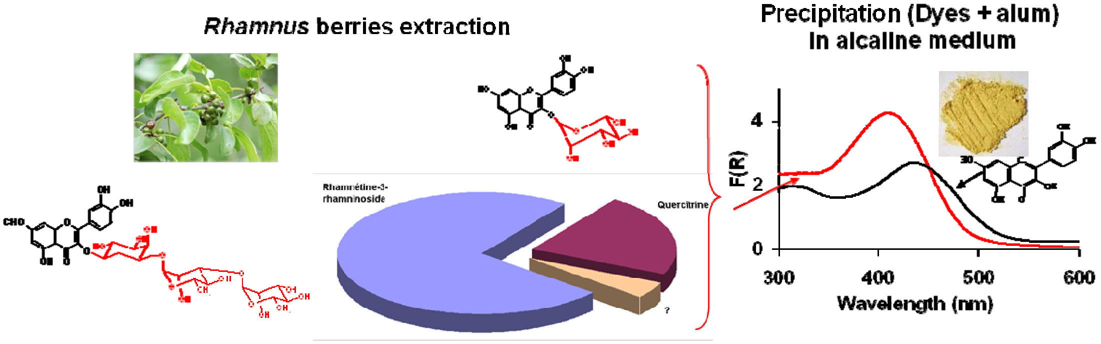
The first objective of this study was to acquire an understanding of lake synthesis and thus obtain information on interactions between the organic (natural flavonol) and inorganic constituents (alum, carbonate). *Rhamnus* berry and yellow lake model compounds based on quercetin as a chromophore were prepared and compared in terms of color and stability with those of historical, reconstituted samples. The extraction process of the natural dyes was optimized by varying the quantity of *Rhamnus* berries, the solvent, the temperature, the time and the extraction method in order to evaluate the role of the natural dye composition on the lake properties. The samples in solution or under solid state were characterized by various technics: high performance liquid chromatography-photodiode array (HPLC-PDA), UV–Visible absorption fluorescence, IR and Raman spectroscopy. The conditions of preparation were correlated to physico-chemical features.



Preparation and DRUV characterization reflectance of yellow lakes

We finally report the extraction of the dyes from a lake or a textile while preserving the glycosidic linkage This procedure will enable an improved analysis to be made of current historical materials.

Keyword : flavonoids, aluminium, molecular spectroscopy, complexation

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SEAWATER ANIONS, SALINITY AND ORGANIC CONTENT SIMULTANEOUSLY ASSESSED BY SURFACE ENHANCED RAMAN SCATTERING

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Environmental seawater of Dubrovnik-Neretva County (Croatia) has been investigated for the first time using vibrational spectroscopy techniques in order to assess the possibility to monitor the salinity, anions concentration and possible contaminants resulted from intensive agriculture, aquaculture, navigation transport and mining in the Neretva basin river [1]. Complex economic activity in the area leads to very different properties of land and water like salinity, temperature, heavy metals content of pesticides and herbicides, oil derivatives and PAH-s, etc. These pollutant materials could potentially harm local population and tourists. Raman spectroscopy was unable to evidence such species, therefor, we employed surface enhanced Raman scattering (SERS) using highly reproducible noble metal naopoarticles and different water samples both from aquaculture and wild environment. SERS signal of the seawater provided complex and rich information within a simultaneous manner concerning the inorganic phosphates, nitrates, nitrites, ammonia, carbonates, sulphates content as well as organic species and micro-organisms. The preliminary results revealed accurate, narrow, very well resolved SERS bands, for different seawater samples, using three different prepared Ag colloidal nanoparticles and without any chemical preparation of the raw seawater (samples collected from four distinct regions of the Croatian coast). The signal has been obtained within 3 seconds integration time using a compact, mini-Raman spectrometer. Seawater anions monitoring could be achieved by recording and calibrating the SERS intensity and half-width of the SERS fingerprint bands of individual components. Calibrations curves were used to track the SERS signal intensity as a function of concentration in domain compatible with the aquaculture conditions. The presence of the chloride in the SERS system is proved by the ubiquitously observed huge band at 242 cm^{-1}, that has been assigned to the Ag-Cl bond. Its intensity is sensitive to the halide concentration, as previously shown by Liang et al. [2] for a large range of halide concentrations and aggregation status of nanoparticles. Monitoring the three parameters of this SERS band, position, intensity and half-width, respectively, would provide the water salinity range concentration for fast tracking, simultaneously with the anions tracking. Moreover, in situ prepared Ag nanoparticles could provide fast and efficient SERS sensing approach, suitable for long run marine monitoring programs.

Keywords: SERS, seawater.

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STUDY OF SE COMPLEXATION WITH ORGANIC MATTER BY MOLECULAR SPECTROSCOPY FOR ITS ENVIROMMENTAL IMPACT COMPREHENSION

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Selenium (Se) is a natural trace element in the environment that has chemical and physical properties that are intermediate between those of metals and non-metals. It is distributed throughout the environment as a result of human activities (industrial and agricultural uses) and natural processes (weathering of minerals, erosion of soils and volcanic activity). Selenium is known to play an essential role in the development of many organisms such as plants, animals and humans, but it can also be toxic at levels rather above the ones considered as necessary. Studies of Se biogeochemical cycle in aquatic ecosystems indicate inorganic Se uptake and assimilation by planktonic organisms, but the knowledge of biotransformation mechanisms is very limited actually. Selenium speciation appears thus as a key component to understand Se biogeochemistry.

There is a general agreement on the fact that selenium is associated with organic matter (OM) inaquatic environments. However, mechanistic processes of the interactions governing selenium/organic associations are still poorly understood. As a matter of fact, natural organic matter in surface waters is composed of a vast array of molecules (proteins,polysaccharides, lipids, low molecular mass organic acids, humic substances...) most of which have not been identified [1,2]. The organic compounds are highly heterogeneous which makes more complicated the study of the properties, like ion complexation ability, or the biogenic processes underlying their formation [40]. The characterization of complexes of Se with dissolved organic matter (DOM) will be of prime importance to better understand the influence of DOM on Se speciation and bioavailability.

The objective of the study is to determine the bonding mechanisms of selenate and selenite, the major Se species in natural waters, with organic matter using strategically a panel of various analytical techniques: absorption, emission and vibrational spectroscopy. Selenium complexes will be prepared in batch or by dynamic methods with varying Se concentration and:

- different organic material : organic (citric acid as one of most abundant low weight organic acids) models, then commercially available natural organic matter (NOM) from Suwannee River and Nordic Lake, International Humic Substances Society)
- varying physico-chemical conditions: pH (range 6-8), ionic strength (range 0.1-1 mol.L^{-1}), presence of Al^{3+} or Fe^{3+}

The UV/visible, fluorescence, FT-IR and Raman spectra of organic material alone and after Se oxyanions addition permit us to estimate structural modifications of complexes in solution and solide and determine their stability constants, stoechiometry, kinetics.

Keywords: Selenium, organic matter, complexation, molecular spectroscopy

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SPECTROSCOPIC CHARACTERISATION AND BIOCOMPATIBILITY OF GOLD NANOPARTICLES OBTAINED BY BIOSYNTHESIS USING *ALLIUM SATIVUM* EXTRACT

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Gold nanoparticles exhibit unique, size-dependent chemical, optical and electronic properties, which are different from the bulk gold. Their properties are closely related to the shape, size, degree of aggregation and surface functionalizing agents. Gold nanoparticles are especially attractive for the presence of surface plasmon bands and for their large area to volume ratio which allows loading large amounts of biofunctionalising agents onto their surface especially important in catalysis and biomedicine applications.

Biosynthesis of gold nanoparticles using plants, plant extracts, and plant biomass [1],[2], bacteria and fungi [3],[4], yeasts [5] is receiving increasing attention due to the continuous need to develop inexpensive, environmental friendly, nontoxic particles.

In this study we report the synthesis of stable, biocompatible gold nanoparticles with diameters below 16 nm, by using *Allium sativum* aqueous extract as a reducing agent for the gold tetracloroaurate ($HAuCl_4$) solution. The obtained nanoparticles were characterised by UV-VIS spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), Surface Enhanced Raman Spectroscopy (SERS), and Transmission Electron Microscopy (TEM). *In vitro* experiments were also carried out for testing the nanoparticles biocompatibility with fibroblast cell cultures.

The reduction process was studied by varying the amounts of *Allium sativum* extract. It was observed that the size and concentration of the synthesised nanoparticles is strongly dependent on the amount and addition rate of the reducing agent. The Au^{+3} ions reduction occurs almost instantaneoulsy at boiling conditions, giving stable coloidal suspensions, containing particles of spherical shape. The *Allium sativum* extract acts both as reducing and capping agent. FTIR measurements show that the obtained nanoparticles are capped by biomolecules in the extract. Also, the nanoparticles were found to be non toxic for the fibroblast cells.

Keywords: surface enhanced Raman spectroscopy, Fourier transform infrared spectroscopy, transmission electron microscopy, gold nanoparticles, biosynthesis

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MICRO-RAMAN AND MICROINFRARED SPECTROSCOPY STUDIES OF Pb-BEARING ATACAMITE GROUP MINERALS FROM THE POLKOWICE-SIEROSZOWICE COPPER ORE DISTRICT, LOWER SILESIA, SW POLAND

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Raman spectroscopy, infrared spectroscopy and electron microprobe studies of botallackite and paratacamite (atacamite group minerals) from the Polkowice-Sieroszowice copper ore district (Lubin area, Kupferschiefer, Lower Silesia, SW Poland) are presented.

The copper hydroxide chloride $Cu_2(OH)_3Cl$ comprise several polymorphs: botallackite (monoclinic), paratacamite (triclinic – rhomboedrical), clinoatacamite (monoclinic), anatacamite (triclinic) and atacamite (orthorhombic). It is hard to discern these members using standard mineralogical techniques (microprobe analysis). These minerals form thin layers and colomorph aggregates. The best method to investigate them is Micro-Raman spectroscopy. Some of these minerals are methastable and sensitive to temperature and chemical environment (water, humidity) as it will be shown in presented work.

The samples were collected in the Sieroszowice copper mine, in the shaft SG-1 (St.Jakob shaft), 800 m below the sea level, directly from the small waterfall from the warm water (on average 30°C). Botallackite and paratacamite, both enriched in Pb (up to 8.92 wt %), were noticed for the first time all over the World.

The ore deposit was formed in the Permian sedimentary rocks consist of dolomites, black shales enriched in cooper, limestones, anhydrites and halitite. The most common primary mineralization includes sulphides such as: bornite, chalcocite, digenite, chalcopyrite, covellite, sphalerite, pyrite, marcasite and galena. In the oxidation zone of the deposit occurs secondary mineralization (sulphates, carbonates and chlorides of copper) e.g. gypsum, azurite, malachite, tenorite, chalcantite, atacamite group minerals, chrysocolla, cuprite and also native copper.

Polarized micro-Raman and MIR experiments was used to determine an orientation of “additional” water molecules able to penetrate copper hydroxide chloride network. Influence of water content and temperature on –OH stretching mode will be discussed.

Analysis of the MIR and Raman spectra confirms the existence of isomorphic substitutions lead in place of copper. Evidenced by the significant shift of bands in the spectra compared to spectra of "pure" and Pb-bearing bottallackite and Pb-bearing paratacamite.

Keywords: Atacamite; Paratacamite; Bottallackite ; Isomorphic substitutions

Acknowledgement

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AIR MONITORING IN IASI AREA BY SPECTROSCOPIC TECHNIQUES

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Today, environmental issues are of great worldwide concern. The hot topics to be studied range from global warming to the stratospheric ozone hole. All these issues are related to atmospheric trace constituents: CO_2, NO_x, SO_2, O_3, VOC_s (volatile organic compounds), etc. In the last decades, the key role of trace gases has been outlined for the hot topics of global warming, stratospheric ozone depletion and photochemical smog formation [1]. Due to their great impact on the environment and on the global climate, complex monitoring techniques are required for understanding and modeling of the complex atmospheric chemistry driven by those atmospheric constituents, of the transport and exchange processes between the atmosphere and the hydrosphere and lithosphere[1].

This paper will present different air monitoring techniques available on the measurement site located on the Science and Technology Park TehnopolIS (Iasi city - 47° 7'17.16"N, 27°34'15.35"E, ASL 60m). Air sampling is performed by in situ monitoring devices (HORIBA) and by remote sensing systems (^{ESYRO}LIDAR) [2]. In the first case, the method is often less sensitive and selective than an extractive method, but offers the great advantage of real-time measurements. In remote sensing, the analyzer is located far away from the air sample under study and measurements offer three-dimensional concentration profiles of the air pollution, which are essential for the validation of distribution models for exhaust plumes or ozone distribution in the trophosphere [3].

Using the ^{ESYRO}LIDAR with a depolarization module, real-time measurements for understanding the processes involved in cloud seeding, relevant for hail prevention and increase of rainfall are shown.

Finally the simulation of trace gases concentration results at regional scale performed with the meteorological model MM5 included in the INOE2000 (National Institute for Research and Development for Opto-Electronics Magurele, Romania) Air Quality Forecast system will be compared with lidar data in daytime [4].

This work was supported by the European Social Fund in Romania, under the responsibility of the Managing Authority for the Sectorial Operational Programme for Human Resources Development 2007-2013 [grant POSDRU/CPP 107/DMI 1.5/S/78342].

Keywords: air monitoring, spectroscopy, Lidar.

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CHARACTERISATION OF BLUE CAR PAINTS BY THE USE OF RAMAN SPECTROSCOPY FOR CRIMINALISCTIC PURPOSES

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Small particles of unknown paint are often object of forensic examinations. Fast, non-destructive, selective and sensitive examination methods are needed. Micro-Raman spectroscopy proved to be a promising technique in the area of forensic examination, where optical microscopy, micro-infrared spectroscopy and microspectrophotometry in the visible and UV range used to be applied for identification and differentiation between traces [1,2]. Often no dyes are detected using these methods because their concentration in a trace is usually too low. Modern industry fabricates a great number of dyes, their mixtures and pigments being suitable for colouring of paints, and by that reason dye composition is a very characteristic feature of forensic traces. The aim of this paper was to evaluate, if micro-Raman spectroscopy can supply information about the dyes present in a micro paint chip.

Raman spectra were measured by the use of an InVia spectrometer (Renishaw, USA) using three excitation lasers: 514, 633 and 785 nm. Spectra were recorded in the 200-2500 cm^{-1} region with an acquisition time of 10 s and 5 accumulations. About 70 samples of blue car paint chips solid and metallic were examined. Each paint sample was measured three times. Identification of pigments was based on the peaks wavelengths values using spectral reference database.

Generally, it was observed that the best excitation laser source providing information on pigment content is 785 nm laser for blue paints, while the laser 514 nm induced fluorescence for the majority of the samples. In some cases fluorescence of the samples made the dye identification impossible. So, an attempt was made to reduce fluorescence of a paint sample by application of the photobleaching method. The samples were irradiated with the appropriate laser for several minutes before analysis. The laser power and duration of irradiation was specified for each sample individually. In some cases there were obtained spectra allowing for identification of the main pigment present in the sample.

It was found that the majority of the obtained Raman spectra provides information about the main dyes present in the sample (about 95% of paint spectra). It was observed that some pigments were more common for metallic paints and some for solid ones. However, it seems that the same set of pigments was used in both the examined types of paints, but the concentration ratio of pigments was various.

Acknowledgments
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Keywords: Car paints; Raman spectroscopy; Identification

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USING RAMAN SPECTROSCOPY FOR THE UNDERSTANDING OF THE COLOURS OF NATURE: ELECTRONIC AND MECHANICAL CONFINMENT IN POLYCONJUGATED PIGMENTS FROM BIRD'S FEATHERS TO MOLLUSCAN SHELLS

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The relevance of polyconjugated molecules in the biochemistry of human, animal and vegetable world is commonly known and the role of the ubiquitous carotenoids in determining specific biosynthetic processes has been and is still matter of extensive studies in various fields of natural science. The early studies by Rimai (1987) on Raman spectroscopy of β carotene offered a unique tool for the study of polyconjugation. Let us briefly consider the two very strong Raman lines observed for polyenes near 1500 cm^{-1} (ν_1) and near 1150 cm^{-1} (ν_2) whose frequencies (and intensities) are known to be conjugation length dependent [1]. Their selective strength is necessarily associated to resonance conditions, but also to the fact that, because of π delocalization, the HOMO-LUMO energy gap is relatively narrow, thus allowing electron-vibration interactions (electron/phonon coupling, e/ph) that extend at large distances along the π conjugated chain [1]. While group frequency correlations associate ν_1 and ν_2 qualitatively and simply to C=C stretch and C-C stretch respectively , studies of molecular dynamics have shown that the observed frequencies originate from normal modes consisting of a *collective C=C+C-C stretching* which involves the whole chain, even if very long. This mode has been traditionally labeled as "Я mode"[1]. When the chain becomes shorter and/or conformational distortions modulate π conjugation along the polyenic chain π delocalization necessarily becomes "confined", e/ph coupling changes and ν_1 and ν_2 shift. The theoretical rationalization of these shifts has provided a very useful probe for the chemical identification and the structural analysis of many polyconjugated systems. The interest and the use of the Raman active Я mode started many years ago when polyacetylene opened a new field in material science [1].More recently the Я mode has been the center of interest in the study of the spectra of bio-relevant molecules that, fully or partly, consist of segments of polyconjugated linear chains variously methylated (carotenoids), or fully demethylated (psyttacofulvines) [2] that have been found in bird feathers, crustaceous, pearls, corals etc. Strangely enough the chemical nature of the polyenic chain in the pigment of *corallium rubrum* turned out to be a puzzle not fully clarified. In this paper we will present the results of our recent experimental and DFT studies of the Raman spectrum of *corallium rubrum* [3]; we have shown that, for seemingly unusual biochemical processes, the polyenic chain of *corallum rubrum* is neither a carotenoid nor a psyttacofulvin, but consists of partially methylated polyenic chain.These studies of bio-relevant polyenic chains have introduced a new important concept, namely in addition to the well known *electronic confinement* we must also account for a *mechanical confinement* generated by chemical substitution along the chain.

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MATRIX ISOLATION STUDIES OF *TRANS*- AND *CIS*-STILBENE

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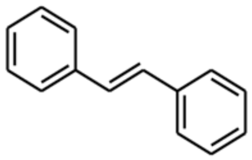
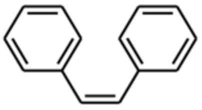
Monomers of *trans* and *cis*-stilbene were isolated in solid argon and xenon and their infrared spectra in these environments fully assigned. The interpretation of the vibrational spectra received support from theoretical calculations undertaken at the DFT level of theory with the 6-311++G** basis set. Annealing of the matrices allowed identification of characteristic spectral features due to dimers of the compounds.

The UV-induced isomerization of the compounds was also investigated. *Cis*-stilbene was found to convert to the *trans* isomer, which is produced primarily in a distorted (non-planar) configuration and,upon subsequent annealing, relaxes to the most stable planar form. On the other hand, *trans*-stilbene was found to be photostable under the used experimental conditions.



Trans-stilbene



Cis-stilbene

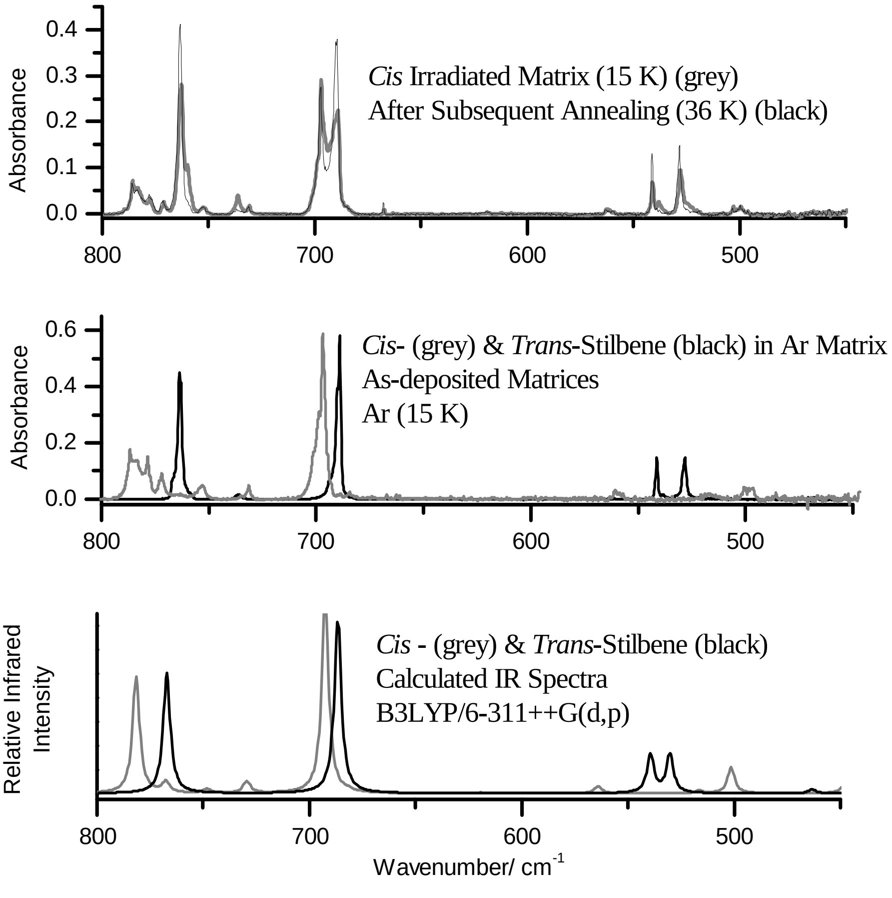


Figure 1. Calculated (bottom) and observed (argon matrix, 15 K; middle) infrared spectra of *trans*- and *cis*-stilbene, and spectra of the *cis*-stilbene UV-irradiated matrix before (top; grey line) and after (top; black line) annealing to 36 K. Note the initial formation of the non-planar form of the *trans*-isomer after irradiation of the *cis*-stilbene matrix and its conversion to the stable planar *trans* form after annealing of the irradiated matrix.

Keywords:Matrix isolation FTIR spectroscopy; Stilbene; UV-induced cis-trans isomerization.

RAMAN MICROSPECTROSCOPY OF THE YEAST VACUOLES

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Extensive effort was undertaken recently to understand pathogenicity and virulence of some *Candida* species [1]. Their ability to escape immune defense of the host and survive even under the severe nutrition limitations and in the presence of various stress factors or antimycotics seems to be related, among others, to preservation of their vacuolar functions. Non-invasive methods providing information about chemical composition of the vacuoles within living cells exposed to various external factors are thus of great importance for development of novel antifungal strategies.

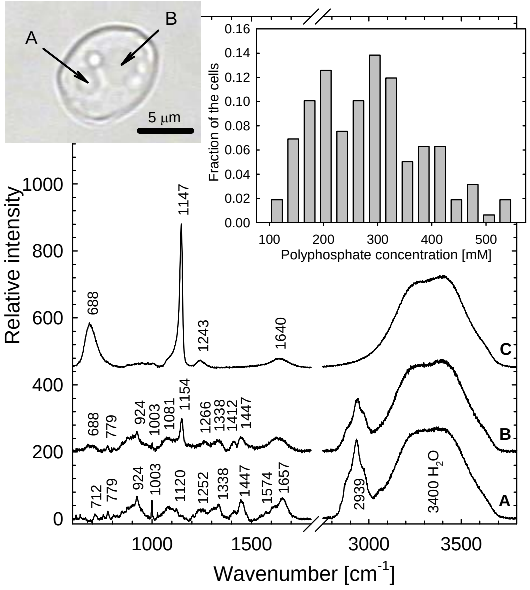

Fig.1. Representative Raman spectra of protein-containing cell compartment (A), vacuole (B) and 2 M aqueous solution of hexamethaphosphate (C). Inserts: image of the cell and distribution of abundance of yeasts (in the same population) with different polyphosphate concentration.

Especially, concentration and structural properties of polyphosphates accumulated in the yeast vacuoles are of particular interest, since they are sensitive to nutritional limitations and environmental stresses, and can thus reflect physiological state of the cell [2]. Recently, Raman microspectroscopy was suggested as practical alternative to laborious and time-consuming chemical analysis of intracellular polyphosphate inclusions in polyphosphate-accumulating bacteria [3]. In the present work, the method was used to monitor polyphosphates and other chemical compounds dissolved in the vacuoles of living *Candida* yeasts of different physiological state and/or under various stress conditions. It was shown that using proper immobilization protocols, the spatially-resolved Raman spectra from individual yeasts throughout statistically sound sets of living cells can be collected routinely. Abundance distributions of actual concentration and polymerization degree of polyphosphates can be assessed employing advanced multivariate methods for spectral analysis of structurally sensitive polyphosphate bands (~688 and ~1154 cm^{-1}) properly normalized with respect to the water OH stretches at 3400 cm^{-1} [4].

Ministry of Education of the Czech Republic (MSM0021620835) and the Grant Agency of the Czech Republic (P208/10/0376) are acknowledged for financial support.

Keywords: Raman microspectroscopy, yeast vacuole, polyphosphate

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IMPACT OF BACTERIAL ADHESION IN COMPETITION WITH PROTEIN ADSORPTION ON GRAFTED CHAINS REVEALED BY SUM FREQUENCY GENERATION (SFG) SPECTROSCOPY AND FLUORESCENCE CONFOCAL MICROSCOPY

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In food industry or biomedical field, surface colonization by bacteria is hazardous because it leads to biofilm formation, a microbial consortia more resistant to antiobiotics than planktonic bacteria. Bacterial adhesion is an extremely complicated process that is affected by many environmental factors, in particular the presence of proteins. In order to design materials resistant to biofilm formation, the effect of bacteria on materials in natural conditions has to be well-characterized.

In this work, we are interested to study *in situ* the effect of bacterial adhesion onto a well-ordered surface composed of a Self-Assembled Monolayer (SAM) of OctaDecaneThiol (ODT) onto a gold surface, in the absence [1] and in the presence of the Bovin Serum Albumin (BSA) protein [2] (Fig. 1.A). The bacteria are hydrophilic *Lactococcus lactis*, non pathogen models for *Streptococcus agalactie* bacteria, and its hydrophobic mutants. Changes of the SAM conformation induced by bacteria, BSA, or both are probed using the Sum Frequency Generation (SFG) spectroscopy, a sensitive, non destructive, second order non linear optical technique well-adapted to probe interfaces at the molecular level. It consists in overlapping in time and in space a visible beam (800 nm) and an infrared beam (3 µm, the wavelength of molecular vibrational transitions of C-H bonds) onto the sample. Different behaviors of the ODT were observed depending on the hydrophilic/hydrophobic character of the bacterial cell wall and on the absence or the presence of BSA proteins before or during bacterial adhesion (Fig. 1.B).

These results show that there is a competition between bacterial adhesion and protein adsorption that change the bacterial adhesion impact onto the surface and thus the biofilm development. This should be taken into account for the design of new materials.

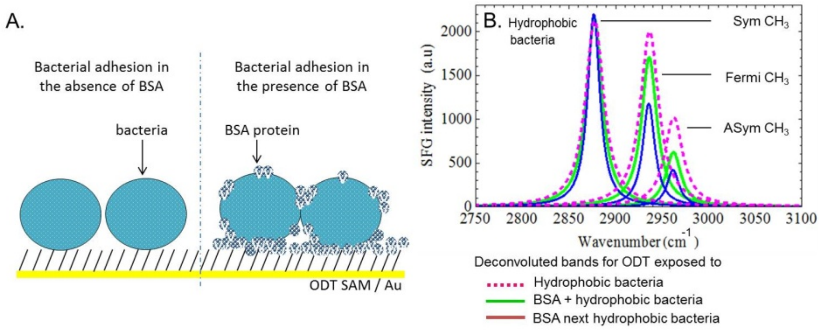

Fig. 1. A. Schematic bacterial adhesion in the absence and in the presence of BSA onto the ODT SAM.
B. SFG deconvoluted vibrational bands of the SAM CH_3 groups in contact with different biological environments.

Keywords: Bacterial adhesion, protein adsorption, SFG spectroscopy, surface

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INTRA-OPERATIVE APPLICATIONS OF VIBRATIONAL SPECTROSCOPY

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During the past years many groups have demonstrate that vibrational spectroscopy has the potential for clinical applications, because the methods provide a biochemically based profile of tissue in real time and without requiring additional contrast agents. Although various techniques are established for pre- and even intra-operative characterization of tissue, several other methods based on new technology are under development [1]. However, there is still a clear need for a quick and objective intra-operative diagnostics especially in brain surgery. Currently, Raman and infrared (IR) spectroscopy complement the standard methods for tissue diagnostics. In this contribution we report the current status of applicability of infrared spectroscopy and coherent antistokes Raman spectroscopy (CARS) microscopy in neuro surgery.

IR spectra of freshly resected human brain tissue were recorded in the operation room by using a portable small FT-IR ATR spectrometer. In a larger study, tissue samples from more than 80 patients were investigated and the spectroscopic results evaluated while the surgery is going on. Reasonably distinct and reliable alterations of several bands were seen between non tumor and tumor tissue. These bands are weak, but distinct and arise from phosphate vibrations of RNA and DNA molecules. Furthermore, CARS micro imaging was used to study spinal cord lesions. In addition to the CARS images fluorescence and second harmonic images were recorded. The obtained multimodal image allows the identification of necrotic and living tissue. The main potential in this case is the identification of the borderline between normal / damaged and destroyed tissue.

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CYTOPLASMIC RNA IN UNDIFFERENTIATED NEURAL STEM CELLS: A POTENTIAL LABEL-FREE RAMAN SPECTRAL MARKER FOR ASSESSING THE UNDIFFERENTIATED STATUS

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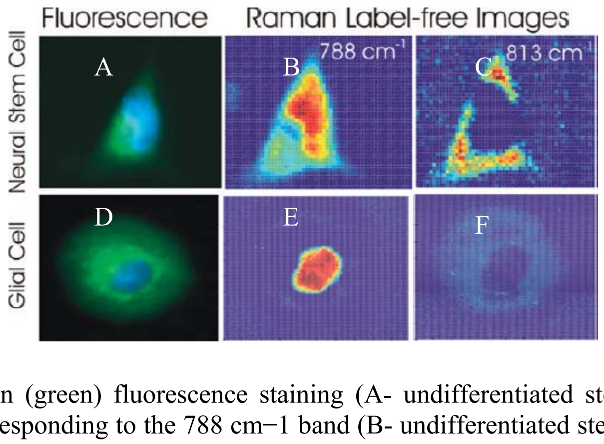
Raman microspectroscopy (RMS) was used to identify, image, and quantify potential molecular markers for label-free monitoring the differentiation status of live neural stem cells (NSCs) in vitro. Label-free noninvasive techniques for characterization of NCSs in vitro are needed as they can be developed for real-time monitoring of live cells. Principal component analysis (PCA) and linear discriminant analysis (LDA) models based on Raman spectra of undifferentiated NSCs and NSC derived glial cells enabled discrimination of NSCs with 89.4% sensitivity and 96.4% specificity. The differences between Raman spectra of NSCs and glial cells indicated that the discrimination of the NSCs was based on higher concentration of nucleic acids in NSCs. Spectral images corresponding to Raman bands assigned to nucleic acids for individual NSCs and glial cells were compared with fluorescence staining of cell nuclei and cytoplasm to show that the origin of the spectral differences were related to cytoplasmic RNA. On the basis of calibration models, the concentration of the RNA was quantified and mapped in individual cells at a resolution of ~700 nm. The spectral maps revealed cytoplasmic regions with concentrations of RNA as high as 4 mg/ mL for NSCs while the RNA concentration in the cytoplasm of the glial cells was below the detection limit of our instrument (~1 mg/mL). In the light of recent reports describing the importance of the RNAs in stem cell populations, we propose that the observed high concentration of cytoplasmic RNAs in NSCs compared to glial cells is related to the repressed translation of mRNAs, higher concentrations of large noncoding RNAs in the cytoplasm as well as their lower cytoplasm volume. While this study demonstrates the potential of using rms for label-free assessment of live NSCs in vitro, further studies are required to establish the exact origin of the increased contribution of the cytoplasmic RNA.



Nuclei (blue)/nestin (green) fluorescence staining (A- undifferentiated stem cell and D –glial cell), Raman spectral images corresponding to the 788 cm−1 band (B- undifferentiated stem cell and E–glial cell) and 813 cm−1 band (C- undifferentiated stem cell and F–glial cell)

Keywords: Raman spectroscopy; neural stem cells; RNA

ANALYSIS OF THE MOLECULAR MECHANISMS OF THE ACTIVATION OF THE BETAINE TRANSPORTER BETP FROM *CORYNEBACTERIUM GLUTAMICUM* BY FT-IR SPECTROSCOPY

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The secondary transporter BetP is an integral membrane protein found in the gram-positive soil bacterium *Corynebacterium glutamicum* and is a member of Betaine/Choline/Carnitine transporter family. An increase in the external solute concentration of a cell due to drought results in water efflux followed by the dehydration and shrinkage of the cell. In order to ensure the normal turgor pressure, very important for the vitality of a cell, *C. glutamicum* counteracts hyperosmotic stress by an instant increase in the cytoplasmic K^+ concentration which is a trigger stimulus to activate BetP [1,2]. The Na^+-coupled betaine symporter BetP senses hyperosmotic stress via its osmosensor associated with the C-terminal domain and regulates transport activity solely in its trimeric state depending on the level of cytoplasmic K^+ concentration. BetP has a four-transmembrane-helix bundle in its core structure which harbors the key part for transport of substrate/co-substrate. However, molecular mechanisms of activation/regulation of BetP and the contribution of lipids to activate the transport cycle are still under debate. In the present study, the two-dimensional crystals of BetP were titrated stepwise with increasing K^+ concentration using an attenuated total reflection (ATR) cell equipped with a home-built microdialysis cell [3] in order to investigate molecular mechanisms of the activation of BetP. The infrared (IR) difference spectra were recorded by changing the concentration of K^+ *in situ* within the measurement cell in order to characterize the structural differences between the inactive and active state of the protein. On the basis of the IR spectra, protonated aspartic and glutamic acid COOH modes were observed that shift and intensify upon activation, suggesting pronounced alterations in the H-bonding pattern of these residues together with an increase in their population. Additionally, IR data also prove that arginine and deprotonated Asp/Glu residues shift upon activation with observation of minute conformational changes in the α-helices and turns/loops. These altogether indicates that the activation of BetP is initiated by a H-bonded network with Asp/Glu and arginine residues in response to a perturbation by an increase in cytoplasmic K^+ concentration. It is proposed that activation of BetP occurs in two steps: an upregulation step with increasing of K^+ (0-200 mM) and a relaxation step with relatively stable BetP for K^+ above ~250 mM.

Keywords: IR spectroscopy, BetP, osmoregulation, signal transduction, membrane transporter, in situ activation, difference spectrum.

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ONE-STEP MICROWAVE SYNTHESIS OF FLUORESCENT CARBON DOTS USING ARGININE AS A SINGLE PRECURSOR

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Carbon dots, or C-dots, represent a new class of nanocarbon materials, approximately spherical in shape, with size in the range of 5–20 nm, that exhibit attractive optical properties, in particular intense fluorescence emission that can be tuned by varying the excitation wavelength. It is primarily for this versatile fluorescence behaviour, promising for sensing applications in biology, medicine and the environment, that these new nanoparticles have been the subject of intensive research over the past five years.

Various methods for fabricating C-dots have been reported, based, for example, on laser ablation of graphite or pyrolytic carbonization of simple precursors [1,2,3]. Rich in surface carboxylic groups, C-dots can be easily prepared with side chains of different physical and chemical nature that may facilitate solubility in various solvents, including water, or even association with biological substrates. In search of faster, straightforward and economical methods the use of microwave heating of aqueous solutions of appropriate precursors has been explored with encouraging results.

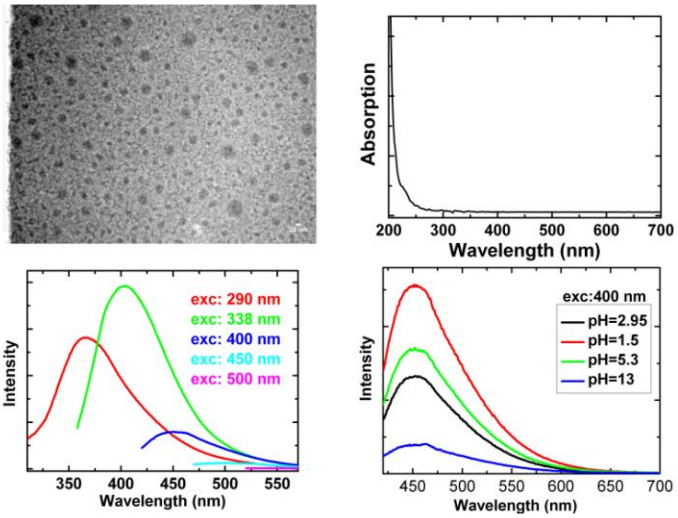

Fig.1 TEM image, absorption, fluorescence spectra and fluorescence vs pH

In the context of the present work, a new type of C-dots has been synthesized solely from arginine, by microwave heating of an aqueous solution of the amino acid. The highly fluorescent synthesis product, isolated through a straightforward gel chromatography procedure, exhibits the main characteristics of C-dots. As shown by TEM studies the arginine C-dots are discrete, quasi-spherical nanoparticles with size in the range of 10-20 nm, with the dominant ones around 15 nm. In aqueous solutions they emit intense fluorescence in the visible, 400-650 nm, following excitation in the 300-550 nm range, with a fluorescence quantum yield, measured against a quinine sulphate solution, in the range of 30%. Fluorescence anisotropy studies are underway as a means of measuring nanoparticle size distribution in solution environment. More importantly, the fluorescence emission of these arginine-based C-dots shows a clear dependence on pH and this may be promising in the context of pH sensing applications.

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APPLICATION OF INFRARED SPECTROMETRY FOR QUANTITATIVE ANALYSIS OF FUNCTIONAL GROUPS ON MULTIWALL CARBON NANOTUBE

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Carbon nanotubes (CNTs) have been considered a lot in recent years due to their unique mechanical and physical characteristic. The increase in efficiency in contrast to the potential decrease in consumption of carbonic materials results in a comprehensive growth of using this kind of nano-materials. Although the research in this field is mostly limited to labs, the biggest challenge of CNTs is their hydrophobic and lack of good dispersity. Functionalizing is a method to overcome this problem, during which it is struggled to avoid any agglomeration by replacing different functional groups on neutral surface of the tube. Different methods have been used in functionalization of CNT. It this research microwave radiation was used as an energy source for acid treatment to functionalize carbon nano tube by nitric acid. The process of functionalization was optimized based on the amount of success in formation of COOH functional groups in the structure of CNT. Quantitative amount of functional group, as a process output, was monitored by infrared spectrometry, being compared with results obtained from Boehm titration. The IR spectrometric data was processed by chemometrics, making a multivariate approach for this aim as a green analytical method. The partial least square has been confirmed to be a robust data processing technique with reliable output. Infrared spectroscopy in capable of being considered as a non-destructive, rapid, helpful analytical technique also for nanotechnology

Keywords: CNT, functionalization, microwave, experimental design, Bohem titration

SINGLE CRYSTALS OF CONJUGATED POLYMERS AS MODEL SYSTEMS FOR CHARGE TRANSPORT STUDIES

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In order to improve optoelectronic properties of conjugated polymers, a profound understanding of the excitonic and electronic transport with respect to structure is crucial. By gaining a precise control over both molecular conformations and morphology we aim to obtain a correlation between orders at a macromolecular level to charge transport properties. The best controlled system for such a study is a single crystal which is free of grain boundaries and molecular disorder/defects.

Here, we report the preparation and structural properties of Poly(3-hexylthiophene) single-crystal grown by crystallization in dilute solutions. By employing a self-seeding approach, we were able to circumvent the nucleation process. To this end, we first dissolved all but a few small thermodynamically stable crystals, which then act as nuclei (seed crystals) for the subsequent crystallization step at higher polymer concentrations or at lower temperatures. This approach extends the accessible range for crystallization to lower degrees of supersaturation or supercooling. Using such conditions, we could control crystal size in all three dimensions as well as aspect ratio.

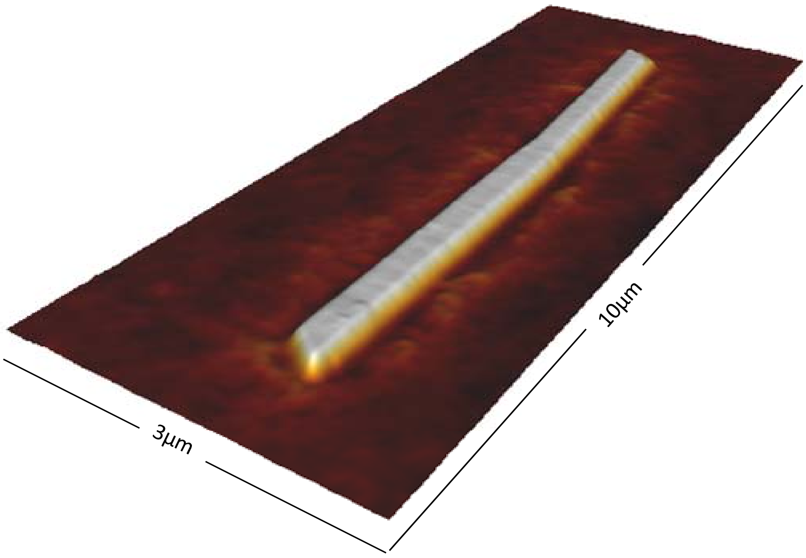

Figure 1. Atomic force micrograph depicting a single P3HT crystal grown in 1,2,4-Trichlorobenzene solution (34 g/L) at 55°C for 10 hours. The height and width of the grown crystal are respectively 80 nm and 500 nm.

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CHEMICAL IMAGING BEYOND THE DIFFRACTION LIMIT: EXPERIMENTAL VALIDATION OF THE PTIR TECHNIQUE

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Photo Thermal Induced Resonance (PTIR), is a new technique that attracted great interest for enabling chemical identification and imaging with nanoscale resolution.[1-3] PTIR uses a tunable pulsed laser for sample illumination in ATR configuration and an AFM tip in contact mode to measure the sample instantaneous thermal expansion induced by light absorption. Infrared spectra are obtained by plotting the amplitude of the tip deflection with respect to the laser frequency. Our set up requires placing the sample over an optically transparent prism. PTIR was previously used for nanoscale chemical characterization under the assumption that the PTIR signal is proportional to the energy absorbed. However, this assumption was not previously verified experimentally, nor was proved that PTIR can be used for quantitative chemical analysis at the nanoscale.

In this work, electron beam nano-patterned polymer samples were fabricated directly on ZnSe prisms using customized adaptor pieces to evaluate the PTIR lateral resolution, sensitivity and linearity. The samples analyzed here can be grouped into 2 categories: samples with constant thickness patterned with features of various size and samples with variable height patterned with lines.

Results shows that PTIR lateral resolution for chemical imaging is comparable to the lateral resolution obtained in the AFM height images, up to the smallest feature measured (100 nm). Spectra and chemical maps were produced from the thinnest sample analyzed (40 nm). Additionally, we demonstrate, for the first time, that the intensity of the PTIR spectra of thin films (< 1 µm) depends linearly on the sample thickness. This is arguably the most important contribution of this work since it proves that PTIR spectra and imaging can be effectively used for quantitative analysis at the nanoscale. Finally, by analyzing samples with an extended range of thicknesses we demonstrate that the PTIR signal is proportional to the local energy absorbed, to the thermal expansion and to persistence time of the thermal excitation in the sample, as previously predicted theoretically.[4] We believe that our findings provide experimental evidence of PTIR usefulness, allowing its use for quantitative characterization in a variety of nanotechnology applications.

Keywords: nanoscale chemical imaging, IR spectroscopy, nanofabrication

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SPECTROSCOPIC INVESTIGATION OF SOME NEW TELLURATE GLASSES DOPED WITH RARE EARTH OR TRANSITION METAL IONS OBTAINED BY SOL-GEL PROCESS

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New tellurate glasses doped with rare earth or transition metal ions were obtained by using the sol-gel method. Several spectroscopic methods, namely IR, UV-Vis and EPR spectroscopies, were used to investigate their structure and spectroscopic properties.

The spectroscopic investigation of tellurate glasses provide interesting information concerning the basic structural units of the host glass matrix. Thus, spectroscopic data prove the presence of [TeO_3], [TeO_4] and ([TeO_6] in the host tellurate vitreous matrix. The compositional evolution of these units was followed. The role of the nature and amount of the dopant ions on the interconversion of tellurate structural units was evidentiated [1, 2].

The spectroscopic study of tellurate glasses offers also information concerning the dopant ions. Thus, the earth and transition metal ions appear in the host matrix in multiple valence states. The obtained data provide information concerning the location of the dopant ions in the host glass matrix as well as the compositional evolution of the redox equilibrium of their valence states [1, 2].

Keywords: Spectroscopic methods, Tellurate glasses, Sol-gel;

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CHARACTERIZATION AND QUANTITATIVE ANALYSIS OF HEAVY METALS IN WINE USING "STATE OF THE ART" SPECTROSCOPY

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Wine is one of the oldest cultural products in human history. Wines have been cultivated for over 8000 years. The oldest known archaeological evidence of winemaking is an 8000-year old wine- and fruit press found near Damascus.

Winemaking is a rather simple process: freshly harvested grapes are crushed and the resulting juice (must) is collected. The must contains fermentable sugars and natural yeasts which, either by themselves or with the help of additional yeast cultures, start the fermentation process in which mainly ethyl alcohol and carbon dioxide are formed. The latter is a gas and escapes from the must. The fermentation process comes to a halt when all of the sugars are fermented or the alcohol concentration becomes too high and kills off the yeasts. At this point the must has turned into wine.

In order to guarantee a certain level of quality, standards are fixed in the national wine regulations such as the German "Weinverordnung" [1] from 21st April 2009, which includes the classification of wines from different locations but also the production process, alcohol concentrations and the maximum allowable concentrations of elements.

A meticulous quality control procedure is essential, and during each stage of the production process spectroscopic methods such as AAS-, ICP-, FTIR-, and UV-VIS spectroscopy are applied for quality assurance or for product characterisation. The colour of the red wine is an important factor to understand the quality of the raw material but also the treatment and the storage. Typical measurements have to be performed at 520 nm for example using a UV-VIS spectrophotometer.

For the quantitative determination of essential elements such as potassium, sodium, calcium and magnesium, as well as heavy metals such as lead, arsenic, and cadmium, the ICP spectrometry is the method of choice, since a simultaneous instrument, such as the ICPE-9000 allows a fast and precise analytical procedure.

Keywords: UV-VIS spectrophotometer; wine color; heavy metals; ICP-OES spectrometer

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INFRARED ATR SPECTROSCOPY FOR PROCESS ANALYTICAL CHEMISTRY AND QUALITY CONTROL OF FATTY ACID ESTERS

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When meeting the demands for analytical instrumentation for process analytical chemistry, vibrational spectroscopy [1-4] can comply with the requirements for many applications involved in quality control and industrial process monitoring. IR-spectroscopy has many favourable options with routine transmission measurements, but especially the attenuated total reflection technique (ATR), using fibre-optic probes based on silver halide fibres and a diamond micro-prism, can advantageously be used for demanding in-situ measurements, which require remote sensing capabilities. Examples will be presented for the application of infrared spectroscopy for monitoring accelerated ageing processes in lipids and alternative fuels derived from natural, renewable materials such as vegetable oils. Monitoring of oxidation stability and conformational cis-trans isomerisation under thermal stress and UV-radiation exposure has been achieved for biodiesel and several vegetable oils, also with the addition of natural anti-oxidants. The Rancimat-method published by CEN [5], which is an established oxidation stability test for the industry, can be replaced by an on-line infrared spectroscopic method with in-situ monitoring, providing a wealth of chemical information on the degradation and isomerisation processes involved. Limitations of the spectroscopic measurement technique will be discussed.

Keywords: infrared ATR spectroscopy; fiber-optics; fatty acid esters; oxidation stability

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THE EFFECT OF TEMPERATURE ON SURFACE-ENHANCED VIBRATIONAL SPECTRA: IS IT IMPORTANT FOR ANALYTICAL APPLICATIONS?

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Surface-enhanced Raman scattering (SERS) and surface-enhanced infrared absorption (SEIRA) are optical phenomena forming a branch of vibrational spectroscopy called surface-enhanced vibrational spectroscopy (SEVS) [1]. Both SERS and SEIRA spectra are measured usually under ambient laboratory conditions (at room temperature and under standard atmospheric pressure). An early study of temperature effect on SERS spectra of pyridine demonstrated no significant change in the band intensities during warming of vapor-deposited copper and gold substrates, while in the case of the Ag substrate a growth of the 1006 cm^{-1} feature on warming and improvement in the optical quality of the pyridine overlayer with a final dramatic decrease of SERS intensities at laboratory temperature was described [2]. Experimental results of several temperature-dependent studies are still controversial. Some studies shows a significant increase of enhancement at increased temperatures (50°C [3]) while other authors (e.g. [4]) describe a dramatic increase of spectral signal caused by the decrease of temperature below room value. Thus, we decide to develop temperature-controlled sample holders both for SERS and SEIRA spectroscopy and to perform systematic chemometric studies of the effect of substrate temperature on the SEVS spectra obtained on three different metals, i.e. silver, gold and copper.

In this study we describe (i) the design of tailored temperature-controlled holders of SEVS-active samples and (ii) a comparison of results obtained for large spectral sets evaluated by chemometric procedures. Electrochemically prepared Ag, Au and Cu nanostructured surfaces on Pt targets were used to deposit (bio)-organic analytes. The SEVS spectral datasets recorded for various pharmaceuticals, B-vitamins and carotenoids in the range 5 – 50 °C exhibit evident common behavior important from the point of view of data repeatability and reliability. A comparison of the results obtained at various temperatures with spectral data measured at room temperature (e.g. [5]) demonstrates several advantages of a temperature decrease below laboratory conditions which can be related to low data variability both from the spatial and time resolution.

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Keywords: Temperature-dependent SERS; SEIRA; Pharmaceuticals; Carotenoids; B-vitamins

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ACCURATE CALIBRATION OF THE LASER RAMAN SYSTEM FOR THE KARLSRUHE TRITIUM NEUTRINO EXPERIMENT

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The **KA**rlsruhe **TRI**tium **N**eutrino experiment (KATRIN) will measure the neutrino mass with a sensitivity of m_ν = 200 meV/c^2 (90% C.L.). The methodology is based on high-precision β-electron spectroscopy of tritium near its kinematic endpoint at about 18.6 keV [1]. The systematic uncertainty of this measurement is influenced by several parameters; specifically important is the precise knowledge of the composition of the tritium gas which is used in the gaseous β-electron source.

While one strives for the highest possible tritium molecule purity, due to technical reasons the gas is composed of a mixture of T_2 (>90%), DT (<10%) and traces of HT, D_2, HD and H_2. The tritium-containing isotopologues (T_2, DT, HT) exhibit different final state distributions of the corresponding daughter nuclei (^{3}HeT, ^{3}HeD, ^{3}HeH), influencing the energy of the β-electrons in the region of interest. Analytical data from the purity monitoring have to be sent to the KATRIN control continuously in time intervals of less than 250 s and with a measurement precision of at least 10^{-3}. That this is feasible we have demonstrated using laser Raman spectroscopy (LARA) for the task [2]. To gauge the actual trueness of the LARA measurement thorough calibration is required, which is problematic since the production of high-purity tritium samples is not trivial, considering (i) its radioactivity and (ii) the similarity in chemical properties of all hydrogen isotopologues (such as e.g. permeability in metals).

Here we present two complementary calibration methods aiding to achieve truly quantitative Raman spectroscopy. The first method utilizes a (purpose-built) gas mixing loop for the accurate mixing of pure gases and a catalyst bed for the production of the hetero-nuclear isotopologues (e.g. HD). This method has been successfully applied to LARA calibration with the inactive isotopologues (H_2, HD, D_2). The second method relies on the calculation of molecular polarizability tensors, which give access to theoretical Raman line intensities and allow one to link these to absolute measurement-system response (using a NIST-traceable LED-based calibration system). The polarizabilities for all six hydrogen isotopologues have been calculated [3,4]; recently we validated these in Raman depolarization measurements, mostly with excellent agreement. Results for both calibration methods are presented and compared; the implications of these findings for the Raman monitoring of the hydrogen isotopologues in the KATRIN experiment are discussed.

Keywords: quantitative Raman spectroscopy; absolute calibration; hydrogen isotopologues

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LO-RAY-LIGH® DIFFRACTION GRATINGS FOR ULTRA LOW STRAY LIGHT APPLICATIONS IN UV-VIS SPECTROSCOPY

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It has been more than half a century since the release of the first Shimadzu UV-VIS spectrophotometer QB-50 in 1952 and during this time more than 160.000 UV-VIS spectrometers have been produced and installed in a wide variety of different applications. A lot of technical innovations have been implemented to improve the performance and significantly reduce the stray light levels. The latest innovation during development of sophisticated spectrophotometers is based on a new holographic exposure method and optimized etching process which has made it possible to produce both high-efficient and exceptionally low stray light gratings.

These LO-RAY-LIGH® gratings have guaranteed values of stray light at the intermediate position between zero-order and + first-order lights. The values are measured by Shimadzu's laser stray-light-measuring system.

The latest development in the series of UV-VIS spectrophotometers is the UV-2700 which is a true double beam double monochromator system in a compact design for high-precision spectral analysis of a wide range of samples including organic and inorganic compounds, biological samples, optical materials and photovoltaics. The high performance optical system is designed with "LO-RAY-LIGH®" diffraction gratings, featuring highest efficiency and exceptionally low stray light. The spectrophotometer operates in the wavelength range of 185 to 900 nm and allows highly sophisticated applications such as direct measurement of high density samples up to 8 absorbance units without dilution.

A typical example for high density measurements of $KMnO_4$ solutions is shown in Figure 1 with an excellent linearity of up to 8 absorbance units. A variety of possible system configurations will be discussed on recent application examples and advantages of the new spectrophotometer series will be explained.

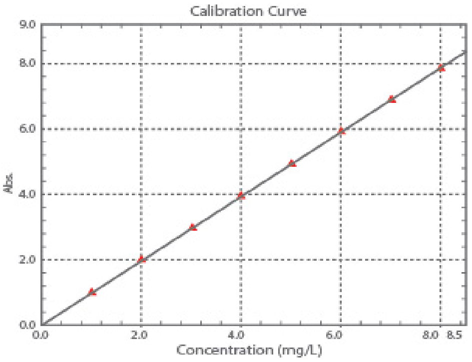

Fig.1 Calibration Curve of $KMnO_4$

Keywords: UV-VIS spectrophotometer; Stray light; Diffraction gratings

REPRODUCIBLE IDENTIFICATION OF BACTERIAL SPECIES AND STRAINS USING MICRO-RAMAN SPECTROSCOPY

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Rapid and effective diagnosis remains the key factor to successfully combat infectious diseases. Unfortunately, the complete diagnosis process can take up to several days thus delaying appropriate antibiotic treatment. Therefore, there is a need for a method combining reproducibility, precision and speed; increasingly Raman spectroscopy is gaining acceptance as a potential new tool in clinical microbiology.

The aim of current efforts is to gauge the potential of Micro-Raman spectroscopy for identifying bacteria at both the species and strain level, and further to discriminate between strains that may reveal different profiles of antibiotic resistance. Here we present some results from systematic studies on a selection of bacteria, namely *Staphylococcus epidermidis* (strains 1457 and 9142), *Escherichia coli* including wild-types (strains B, K12 and Top10) and specimen expressing ampicillin and kanamycin resistance (Top 10^{Amp} and Top 10^{Kan}).

In general, Micro-Raman spectra were recorded from at least 30 individual bacterial colonies of a single cultivation. In order to gauge the reproducibility and reliability of the approach, spectral recordings were normally taken on four consecutive days, but also over longer periods of time up to and beyond a few weeks. Care was taken, to replicate all conditions (both for bacteria cultivation and Micro-Raman analysis) as closely as possible; however, systematic variations of individual parameters were introduced as well in order to explore the diagnostic potential of our approach even under slightly adverse conditions. For a summary of the experimental and methodological aspects see e.g. [1].

Spectra were processed automatically to correct for offsets and fluorescence background, using a novel approach based on rolling-circle filter procedure coupled with Savitzky-Golay smoothing; this allows for isolating of important Raman features but simultaneously interpreting fluorescence contributions (for details of the methodology see e.g. [2]). The spectral data were analyzed using principal component and cluster analysis techniques. The bio-informatics processing and analysis reveal that the replicate spectra for each individual strain exhibited very high reproducibility, and showed that bacterial species, strain and isogenic mutant strains with defined resistance could be separated into discrete clusters. As expected, the degree of separation decreased in the order 'species' → 'strain' → 'isogenic strain'.

Overall we have demonstrated that the combination of Micro-Raman spectroscopy, microbiology and bioinformatics has the potential for the successful discrimination of bacteria species and strains, and for the determination of antibiotic resistance profiles.

***Keywords**: micro-Raman spectroscopy; bacteria; antibiotic resistance*

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FTIR AND EDXRF INVESTIGATIONS OF THE SECOND GENERATIONS OF SALT TOLERANT SOYBEAN MUTANTS

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Soybean (*Glycine max* L. Merr.) is one of the most important industrial oilseed crops in the world. Soybean plant has ability to grow in widely diverse climates and on different soil types. It is well known that gamma irradiation causes physicochemical and biological alterations in living organisms. The aim of this study is to investigate the elemental and structural alterations of the gamma induced mutants of salt tolerant soybean seeds in comparison with those of unirradiated control groups.

In this study soybean (*Glycine max* L. Merr.) seeds of Ustun-1 variety divided into two groups. Firstly, a group of the seeds were gamma irradiated with 150 Gy dose, using Cs-137 gamma source in IBL 437C irradiation property at dose rate of 6.248 Gy/min while the other group of the seeds (control group) were unirradiated. The irradiation doses have been selected according to cause minimum physiological damages [1]. The control and γ-irradiated group of soybean seeds were planted into experimental fields. Three months later from the planting on to the experimental field, single plants were harvested (M_1 generation). The seeds were planted into plastic pots to obtain M_2 generation. The salt tolerant mutants were selected in M_2 generation of Ustun variety under in vivo and in vitro conditions for their growth performances and callus formation at 90 Mm NaCl respectively.

In this study the protein and lipid structures of the second (M_2) generations of the salt tolerant soybean seeds and control group were investigated by FTIR spectrometry. The alterations of the elemental compositions of the γ-irradiated mutations of salt tolerant Ustun-1 soybean seeds in comparison with the control group were determined by EDXRF spectrometry. The IR spectra of the samples were recorded on a Bruker Tensor FTIR spectrometer by using a diamond ATR attachment, in the 4000-400 cm^{-1} range. 16 background and 70 sample spectra were accumulated (2 cm^{-1} resolution). Amide I, II and III bands provide a probe for conformational variability within the protein secondary structure.Therefore, curve fitting technique was applied for the conformational investigation of the proteins of the soybeans. Examination of the secondary structure of proteins revealed the presence of some alterations in M_2 mutants comparison to those of control groups.

Keywords: Soybean seeds; FTIR spectroscopy; protein secondary structure.

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THERMAL TRANSITIONS OF BACTERIAL BIOLUMINESCENCE ENZYMES IN VISCOUS MEDIA STUDIED FROM THEIR INTRINSIC FLUORESCENCE

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Viscous and gelatinous media can be considered as the simplest models of intracellular environment for the enzymes. To reveal the peculiarity of enzymes functioning *in vivo* the mechanism of bacterial bioluminescent reaction in viscous media has being investigated [1]. Earlier it was found that in the presence of glycerol and sucrose the intensity of bacterial bioluminescence reaction and thermostability of enzymes changed. One of the possible mechanisms is the influence of the cosolvents on the conformation transitions of the enzymes. The aim of our study was to describe the thermally induced conformational transitions of bioluminescent enzymes in viscous media using fluorescence spectroscopy techniques.

The following chemicals were used: bacterial luciferase from *Photobacterium leiognati* and NAD(P)H:FMN-oxidoreductase from *Vibrio fischeri* (IBP SB RAS), glycerol (Gerbu), sucrose (Gerbu). Emission spectra were recorded with spectrofluorimeter Fluorolog 3-22 (Horiba Jobin Yvon, France). Measurements were performed at 15-70°C.

Blue shifted emission spectra of both enzymes were obtained in concentrated solutions of glycerol and sucrose at low temperatures (~5 nm). The thermally induced monotonic decrease in fluorescence intensity of enzymes was detected in all three environments with small break near 40°C. The red shift of the maximum (from 330 to 335 nm) and pronounced broadening of the spectrum of enzymes were found to start at the same temperature. The addition of sucrose or glycerol (20 wt%) doesn’t influence the temperature dependences but slightly changes the overall intensity of the intrinsic fluorescence of the proteins studied. The results obtained indicate that up to 40°C the conformation of luciferase molecule stayed the same. Than the conformational transition started in all three media and didn’t complete up to 70°C.

The patterns obtained for enzymes were compared with temperature effects on the fluorescence of free tryptophan in viscous and buffer solutions. The final conclusions gave explanation for the mechanisms underlying the thermal inactivation of bioluminescence reaction observed in modified media [1].

Keywords: Luciferase; Thermal Transition; Intrinsic Fluorescence

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FTIR SPECTROSCOPY DISCRIMINATES VERY EARLY DIFFERENTIATION STAGES IN LIVING HUMAN STEM CELLS

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Human cells derived from stem cells destined for use in the clinic for regenerative medicine therapies will first need to be differentiated to specific differentiation or lineage commitment states for these treatments to be effective. Conversely, the transplantation of undifferentiated stem cells into the human body presents a danger as it may lead to the formation of cancerous tumours. In this context, we have been investigating using FTIR spectroscopy to define lineage commitment in human stem cells, and envisage spectroscopic approaches may be useful for quality control and selection of differentiated stem cells for use in the clinic. Recently, we have been successful in using FTIR spectroscopy to discriminate living, undifferentiated human embryonic stem cells from those differentiated to commitment stages equivalent to the earliest phases of embryonic development. These measurements used a specialised IR wet chamber and were acquired using the IR microspectroscopy beamline at the Australian Synchrotron [1]. Apart for the obvious practical need to analyse live cells in line with the aim to develop a new modality for cell selection for clinical practice, measurements using living cells had advantages compared to those from dried, fixed cells. Significantly, in terms of detecting changes in differentiation state, bands from DNA and RNA were observed in the FTIR spectra of live cells that were not detected at all or were much less prominent in the FTIR spectra from the dried cells [2]. Indeed, changes in bands assigned to nucleic acids, including the carbonyl stretching band from DNA at ~1720 cm^{-1}, the anti-symmetric phosphodiester stretching band from DNA and RNA at ~1220 cm^{-1}, and stretching bands from C-O groups in DNA and RNA sugars at ~1120 and 1050 cm^{-1}, associated with the differentiation of cells from the stem cell progenitors, were observed in average spectra and loaded prominently in Partial Least Squares Regression (PLS-R) models used to classify the spectra. Prominent changes in lipid absorbance were also observed as the live stem cells underwent differentiation, matching changes previously observed in the spectra of dried cells [3]. We will discuss these findings and the potential for FTIR spectroscopy as a quality control tool for cell selection in regenerative medicine practice.

Keywords: Stem Cells; FTIR Microspectroscopy; Synchrotron.

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SPECTROSCOPY INVESTIGATION OF COLLAGEN BASED GOLD NANOPARTICLES SUBSTRATE FOR STEM CELL DIFFERENTIATION

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3D scaffolds have been shown to be promissing for regenerative medicine and tissue engineering based on their ability to direct the fate of the stem cultured cells. In this study, we developed a new smart bio-nano-material, a 3D collagen-based gold nanoparticles (GNPs) substrate that has the capacity to promote mesenchimal stem cell adesion, proliferation and differentiation into neuronal and cardiac stem cells.

The substarte was synthesised by using a layer by layer method, where each layer was composed of gold metalized collagen nanofibers. Prior to its application in cell differentiation, high performance spectroscopic techniques such as- XPS, FTIR, UV-VIS and imaging techniques such as TEM, SEM were used for its characterization. FTIR and XPS results revealed the precise location of the binding sites and the nature of chemical interaction between GNPs and thee collagen. The utilization of these atomic/molecular level spectroscopy techniques were extremely useful in investigating the mechanism of intereaction between collagen and GNPs. The imaging techniques confirmed the formation and croslincking of GNPs over the surface of the collagen protein in a uniform and monodispersed film.

Further, we demonstrated using MTT proliferetion assays and iminohistochemistry, that the substrate possesses excellent biocompatibility and improve the neuronal and cardiac differentiation process of placental MSCs. There are several potential advantages in using collagen-based GNPs as a substrate such as *in vitro* pre-differentiated MSCs on metalized collagen substrate with internalized GNPs can be tracked and used to deliver biologically active molecules, drugs, or genes for the *in vivo* transplantation of stem cells in regenerative medicine.

SUBSTRATES FOR PLASMON-ENHANCED OPTICAL SPECTROSCOPIES *VIA* CONVECTIVE ASSEMBLY OF NANO- AND MICRO-PARTICLES

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Optical spectroscopy techniques, like Raman scattering, fluorescence and infrared absorption take great benefits from the development of the field of Plasmonics. Their plasmon-enhanced correspondents, Surface Enhanced Raman Scattering, Surface Enhanced Fluorescence and Surface Enhanced Infra-Red Absorption are reaching nowadays unprecedented levels of sensitivity. This achievement stems in the design and control of electromagnetic fields at the metal surface, greatly enhanced by the excitation of surface plasmons (SPs) [1]. In turn the manipulation of SPs is made possible by the advancement of nano-fabrication techniques, which allow controlling the size and shape of metal nanostructures. Chemical synthesis, a bottom-up approach, appears more versatile than top-down lithographic techniques due to its capability to produce nanoparticles (NPs) of different sizes and shapes (spheres, rods, cubes, pyramids, prisms), from many types of metals, single or bi-component (alloys or core-shell) [2]. Another advantage is the NPs surface quality (smooth, less defects, compared to physical, top-down techniques). A current challenge remains to arrange these colloids into superstructures onto solid substrates.

Here we present our recent efforts in fabricating substrates for plasmon-enhanced spectroscopies by Convective Assembly of nano- and micro-colloids. We show how by controlling several parameters of this evaporation-induced assembly process [3] one can direct the arrangement of colloids into well defined arrays (see examples in Fig.1). Finally, we give some relevant examples of the use of these colloidal arrays in plasmon-enhanced Raman scattering or fluorescence, both on practical and fundamental level [4].

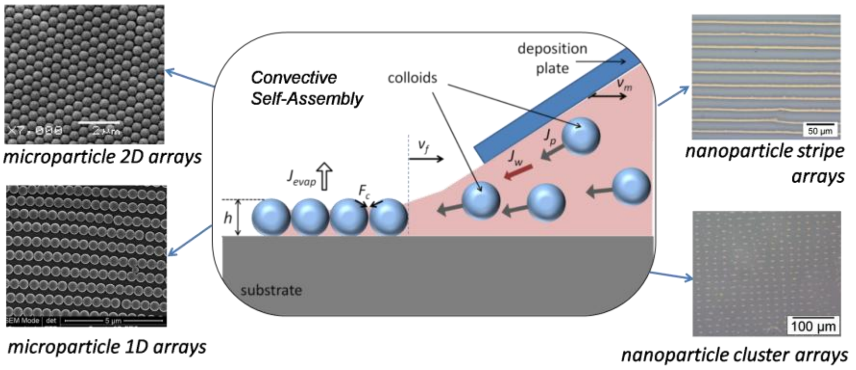

Fig.1 Scheme of convective assembly (center). Examples of plasmonic structures obtained by convective assembly of micro-colloids (left) and nano-colloids (right).

Keywords: plasmon-enhanced spectroscopy; colloids; convective assembly

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OPTICAL PROPERTIES OF GOLD NANOSTRUCTURES: APPLICATION TO THE SURFACE ENHANCED RAMAN SCATTERING AND TO THE DEVELOPMENT OF A NANOBIOSENSOR

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Huge enhancement factors in SERS process can be obtained using substrates such as metallic colloids[1,2] or metallic island films[3]. These samples are good candidates for single molecule detection[1,4] but, due to their intrinsic complexity, they are suitable to reach a precise control of their optical porpeties. Considering only the electromagnetic contribution of SERS and then have a better understanding of the underlying processes, it is important to be able to investigate more “controllable” samples, namely arrays of gold nanoparticles, which can be designed through electron beam lithography and lift off techniques. [5,6,7]

Thus, we have studied the effect of the size and geometry of nanostructures on their optical properties (localised surface plasmon resonance, LSPR) and their SERS efficiency. For such studies, we have used shape controlled metallic nanocylinders and nanowires which can act as nano-antenna at the nanometer scale. The observation of the dependence of the Raman enhancement versus the nanoparticle size and shape is clearly demonstrated and remarkably the enhancement is observed to be maximum for a specific diameter or length. Our results support the fact that the optimization of SERS efficiency, relative to the LSPR, strongly depends on the size and the shape of the metallic nanoparticles. The enhancement strongly depends on the nanoparticle parameters, which is a crucial point to determine the optical efficiencies of such structure and to optimise the SERS processes.

The SERS technique can be used to observe and detect specific molecules such as hydrocarbon or proteins. Thus, the nanoantenna can be used to develop a novel optical nanobiosensor based on extraordinary vibrational signal enhancement of the molecules to be detected. Our sensor will then reach high sensitivity and our aim is to detect only a few proteins with concentration much lower than 1pM and finally to reach detection threshold such as femtomole or lower. High molecular selectivity will be reached with the functionalisation of the nanoantenna. Such functionalisation will selectively favour the immobilisation of the protein to be detected at the vicinity of the nanoparticle surface, providing the best enhancement and then the detection of the targeted protein. Our nanobiosensor will be validated on the detection of proteins on body fluids. Thus, the detection of molecules with SERS substrate could be used to the design of a new type of nanosensor.[8]

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Keywords: SERS, Biosensor, Plasmon

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CORRELATION OF MORPHOLOGICAL AND RAMAN SPECTROSCOPIC PROPERTIES IN INORGANIC NANOCOMPOSITES

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Nowadays, several material science studies are focused on nano-scaled materials due to the unique properties (electronic, thermal, mechanical, magnetic etc.) related to their tiny size which makes these materials different from their bulk counterparts.

Titanate nanotubes are one of the recently discovered and widely researched nanomaterials. They represent a beneficial mixture of the positive chemical features of titanium-dioxide and the morphological advantages related to their one dimensional nanostructure. They have 6-10 nm in diameter and up to 200 nm in length. They are open-ended and resemble miniscule rolled-up carpets consisting of layers no more than a few atoms thick.

High specific surface area due to the tiny size, high aspect ratio and special crystal structure are clothing these materials with high mechanical strength and ability for the usage as a filler material for polymers, ceramics, glasses to enhance tensile strength, wear resistance, hardness and other mechanical properties. In our work, such positive properties of the titanate nanotubes are exploited for low-temperature ceramic-type nanocomposite synthesis.

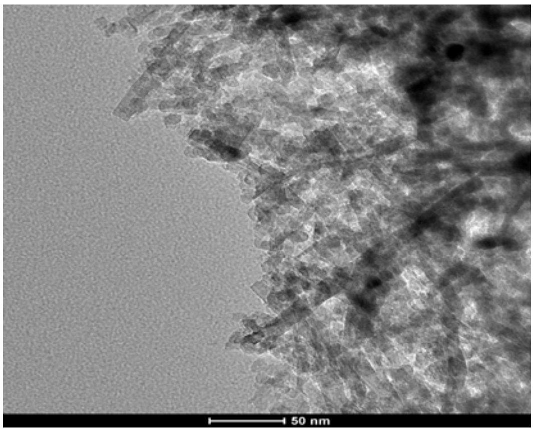

Fig. 1. TEM image of titanate ceramics

Several composites based on titanate nanotubes, vanadium-dioxide, borone-trioxide, aluminium-oxide, magnesium-oxide and silica are synthesized by systematically varied composition. The resulted materials were thermally treated at different temperatures with different duration. [1]

The resulted materials were characterized by Transmission electron microscopy (TEM), Scanning electronmicroscopy (SEM), Energy dispersive spectroscopy (EDS) and X-ray as well as electron diffractometry (XRD, ED), Raman spectroscopy, and UV-VIS spectrometry. In this contribution we will focus on the correlation between the Raman spectroscopic properties and the morphology of products.

Keywords: titanate nanotubes, low temperature co-fired ceramics (LTCC), nanocomposite

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THERMO RAMAN SPECTROSCOPY STUDY OF BARIUM TITANATE NANORODS SYNTHESIZED BY TEMPLATE ASSISTED SOL GEL PROCEDURE

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The room temperature ferroelectric properties of $BaTiO_3$ (BTO) make it one of the most widely used ferroelectric material. The requirement for miniaturization of the electronic devices increases importance of the synthesis of BTO in the form of one-dimensional nanostructres. The study of phase transition from ferroelectric, tetragonal, phase to paraelectric, cubic, phase state is essential for the use of such novel nanostructures.

In present work multiphase polycrystalline BTO nanorods were synthesized by template assisted sol-gel deposition and studied by thermo Raman spectroscopy (RS) using Horiba, Jobin-Yvon T64000 with an argon ion laser Coherent, Innova 400 operating at 514.5 nm for excitation. Thermo Raman measurements were performed in air using micro-Raman configuration with cryo/thermo micro chamber “Lincam”. The heating process was performed from room temperature (RT) to 200 °C while cooling process was performed from RT to -95 °C.

In BTO nanorods the tetragonal phase was the dominant phase, while the band at 640 cm^{-1} indicated the coexistence of the high-temperature hexagonal phase which was also confirmed by HRTEM. Hexagonal structure was stable in the whole investigated temperature range (from -95 °C to 200 °C). The tetragonal to cubic phase transition of nanorods undergo a phase transition diffuse with respect to temperature, while the T_C was shifted to higher values than in the nanocrystalline BTO or even in the bulk BTO. The low-temperature orthorhombic to rhombohedral phase transition was also shifted to the higher temperatures. The higher temperatures of observed phase transitions could be explained by the presence of the nanolamellas of hexagonal phase intergrown within tetragonal nanocrystals. This result indicates that the temperature of the ferroelectric phase transition in the polycrystalline BTO nanorods consisting predominantly of tetragonal nanocrystallites can be shifted to higher values by introducing stable hexagonal phase in their structure.

Keywords: $BaTiO_3$ nanorods, thermo-Raman spectroscopy, phase transition, hexagonal phase

RAMAN SELECTION RULES IN CUPROUS OXIDE

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Cuprous oxide (Cu_2O) is one of the principal copper oxides which crystalizes in a primitive cubic structure. Cu_2O is a red pigment due to its band gap and usually a *p*-type semiconductor extensively studied in the past for photovoltaic applications. More recently the Voigt constant was reported using magneto-optical Kerr effect in polar geometry [1] reigniting the interest in the potential of this material for spintronic applications.

In spite of the extensive studies, the origin of the features in Raman spectra is still under debate, as most of the vibrations should be Raman silent according to group theory, except an elusive mode at 515 cm^{-1} assigned by Compann and Cummins [4] by measuring a (101) face in (y,y) and (y, -x+z) geometry.

In this work the Raman selection rules are revisited using parallel and cross micro- configurations for measuring natural, one side polished (100), (110), and (111) oriented Cu_2O oxide crystals purchased from SurfaceNet GmbH.

The depolarization ratio for the most intense Raman peak at 220 cm^{-1} is plotted in figure 1 for the (100) orientation of the Cu_2O crystal.

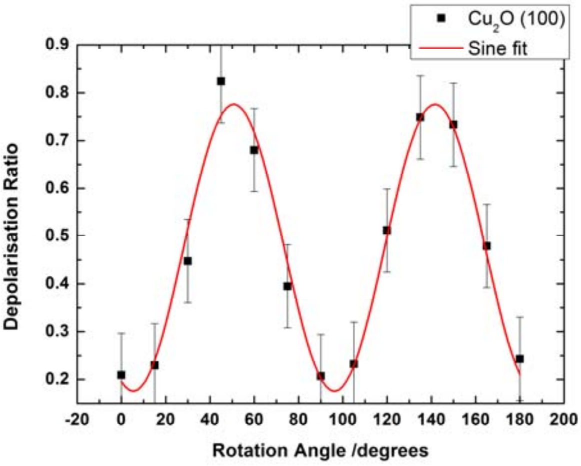

Fig.1 Depolarization ratio calculated for the 220 cm^{-1} Raman peak of the (100) oriented Cu_2O crystal.

Early assignment [1] attributes the 220 cm^{-1} to a first order Γ_{25} mode. Later the 220 cm^{-1} was assigned as an overtone of the 110 cm^{-1} phonon with symmetry $\Gamma_{15}(E_u)$ [3] or Γ^-_3 [4]. The presence of other Raman peaks is attributed to non-stoichiometry and other crystal defects. The high-resolution X-ray diffraction measurements performed in this study revealed inhomogeneous changes in the interplanar spacings that are related to the local strain fields and/or to the local fluctuations of the chemical composition, and a large mosaicity of the Cu_2O crystals. Earlier ion bombardment experiments [5] indicate that lattice defects can induce several Raman modes, which could explain the differences reported in literature.

Keywords: cuprous oxide; Raman spectroscopy; X-ray diffraction

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REVEALING STRUCTURAL MOTIFS IN FLEXIBLE MOLECULES

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The approach of studying structural and dynamical properties of biomolecules is of substantial interest, as it allows decoding the shapes and intrinsic properties of isolated molecular constituents, which have an influence on the selectivity and functionality in biological processes. Recently great strides have been made in understanding their structures and effects on basic properties. This progress follows from the combination of quantum computations together with novel experiments on biomolecules in their gas phase *isolated* environment. The available methods employ double resonance or hole burning techniques, monitoring the vibrational frequencies using infrared (IR) sources. Nevertheless, the IR sources have so far restricted most of these data to the near IR range, covering hydride stretch vibrations, which are diagnostic for parts of the global structure. By contrast the *low-frequency modes*, which have not been measured yet, are indicative of intra- and inter-molecular vibrations and can provide key information on dynamics of conformational changes, hydrogen bonding and structural details. For this reason, we have developed the method of ionization-loss stimulated Raman spectroscopy (ILSRS) [1-3] and applied it to prototype molecules (2-phenylethylamine, 2-phenylethylalcohol and tryptamine) for measuring the spectral features, including low frequency modes. The bands observed in the ILSR spectra, uniquely identify the conformers and structure of these molecules and are in accord with anharmonic results obtained by density functional theory calculations. These findings point to future opportunities for ILSRS as a powerful conformational probe and set new standards for detailed interrogation of structure and intra- and inter-molecular interactions.

Keywords: Double-resonance, laser spectroscopies, conformational probes, biomolecules

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EFFECT OF THE "HOST-GUEST" INTERACTIONS ON THE LOW FREQUENCY VIBRATIONAL DYNAMICS OF (R, S)-IBP/ME-β-CD INCLUSION COMPLEX: AN INS STUDY

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Complexation is of interest in pharmaceutical field, since it increases solubility and bioavailability of drugs [1, 2]. In this work we report the results of a study of low-frequency vibrational dynamics, by an inelastic neutron scattering investigation, of the inclusion complexes of methyl-β-cyclodextrin (Me-β-CD, host) with the non-steroidal anti-inflammatory drug ibuprofen (IBP, guest) in its racemic (R, S)- form.

The INS spectrum of the complex will be compared with that of the single components and physical mixtures with the aim at obtaining a detailed understanding of the "host-guest" interactions, by monitoring how the low frequency ($E < 200$ meV) vibrational modes, very sensitive to the conformational properties, are affected by the complexation process. The analysis, performed as a function of temperature, allowed us to probe the correlation between the dynamics on the ns-ps timescale and the thermal stability of these systems.

This information can be helpful to optimize the drug design of cyclodextrin-based pharmaceutics.

Keywords: Ibuprofen; Inclusion Complex; Inelastic Neutron Scattering

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^{1}H NMR SPECTROSCOPIC CHARACTERIZATION OF INCLUSION COMPLEXES OF TOLFENAMIC AND FLUFENAMIC ACID WITH β-CD

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Tolfenamic (TA) and flufenamic acid (FF) are nonsteroidal anti – inflammatory drugs (NSAID), which along with other derivatives of anthranilic acid are widely used as analgesic, anti – inflammatory and antipyretic drugs. Like many NSAID drugs, TA and FF are very sparingly soluble in water. Therefore aqueous solubility and wettability of these fenamates gives rise to difficulties in pharmaceutical formulations for oral or parenteral delivery, which may lead to variable bioavailability.

To overcome these drawbacks, increasing the aqueous solubility of TA and FF is an important goal. The complexation of TA and FF with cyclodextrins (CDs) may resolve this problem and may also reduce the irritation or local damage of the gastrointestinal mucosa. ^{1}H NMR spectroscopy is one of the most common useful techniques for investigating the stability and stoichiometry of the CDs complexes, particularly in the solution. Its main advantage is the possibility to use several independent signals for the determination of the association constants. The observed chemical shift changes together with 2D NMR spectra can provide insight into the structure of the complexes allowing estimating the orientation of the guest molecules within the CD cavity.

In this paper 1D and 2D NMR experiments were carried out on a Bruker AVANCE 500 spectrometer equiped with a multinuclear 2 – gradient inverse probehead. In all experiments the probe temperature was maintained at 298 K. 2D – ROESY spectra were recorded with a mixing time of 200ms during the spin lock. Firstly the stoichiometry of the inclusion complexes was investigated using the current Job plot method. The obtained results indicate that for TA and FF molecules, the simultaneous inclusion of both rings occur, giving rise to two isomeric 1:1 complexes. The view of a bimodal binding of TA and FF with β – CD was also supported by ROESY experiments. The association constants were calculated by non – linear least squares regression analysis, applying an iterative procedure. Furthermore, the spatial configuration of the complexes has been proposed based on the obtained NMR data and molecular modeling.

Keywords: NMR spectroscopy; inclusion compounds; stoichiometry

SPECIFIC INTERACTIONS IN N-YLID SOLUTIONS, STUDIED BY NMR AND ELECTRON SPECTROSCOPY

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The aim of this paper is to study the intermolecular interactions in liquid solutions of some N-ylids by means of NMR and electronic spectra. Universal and specific forces act simultaneously in the protic solutions of N-ylids. The contributions of the universal and specific interactions to the total spectral shift measured in the absorption electronic spectra were separated on the basis of solvatochromic effects.

The strength of the specific interactions is directly dependent on the electronic charges localized on the partner-atoms in hydrogen bonds. Consequently, a direct proportionality between the chemical shift of the -OH NMR-signal measured in protic solutions and the energy of hydrogen bonds was emphasized in this paper. A linear dependence between the spectral shifts measured in the electronic spectra of some N-ylids and the chemical shifts of the –OH signal from the NMR spectra of the corresponding protic solvents was evidenced.

Important information about the strength of the specific interactions was obtained from the spectral study of N-ylids ternary solutions in binary solvents achieved with protic and non-protic molecules. The model of ternary solutions was used to estimate the potential energy in the pairs of the type N-ylid-protic solvent molecules. This kind of determination is very important for the simple liquid theories in which the hypothesis that the total potential energy can be written as a sum of the interaction energies of molecular pairs is applicable.

Keywords: N-ylids, specific and universal interactions, NMR and electronic spectra.

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Keywords: Analytik Jena; Atomic Absorption Spectroscopy

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RAMAN SPECTRAL HISTOPATHOLOGY OF TISSUE BLOCKS: TOWARDS UNSUPERVISED EVALUATION OF TUMOUR RESECTION MARGINS

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Intra-operative evaluation of tumour resection margins remains a challenge in the surgery of many cancer types. In this study we investigated the potential of Raman micro-spectroscopy (RMS) combined with multivariate analysis methods to diagnose and locate basal cell carcinoma (BCC) tumours at the surface of tissue blocks without sectioning or other tissue preparation procedures. The study was based on tissue specimens from 69 patients, which included nodular, superficial and infiltrative BCC. First, a supervised classification model based on 667 Raman spectra obtained from 60 patients was built to discriminate BCC from the other tissue structures found in healthy skin (epidermis, hair follicles, dermis, inflamed dermis, fat, sebaceous gland, and muscle). The overall sensitivity and specificity of the model for the discrimination of BCC was 90 % and 97 %, respectively. This classification model was then applied to new tissue samples to provide automatic unsupervised imaging and diagnosis of the BCC and the tissue structures. In a comparison with the gold-standard histopathology images, the spectral images containing the quantitative diagnosis of BCC showed an excellent correlation. In the case of clear tissue samples, the correct diagnosis was achieved in all cases. Although the RMS technique employed in this study requires long acquisition times, the use of a recently developed selective sampling technique allowed the evaluation of larger tissue samples in ~30 minutes for cases of nodular BCC. This study establishes the most sensitive spectral regions which enable accurate diagnosis of BCC, which in combination with alternative faster Raman microscopy techniques may be potentially used for fast intra-operative evaluation of the tumour resection margins.

THEORETICAL AND SPECTRAL CHARACTERIZATION OF BIOLOGICALLY ACTIVE LIGANDS AND THEIR METAL COMPLEXES

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Density functional theory (DFT) and modern FT-IR and FT-Raman spectroscopy have proven to be efficient tools in the prediction of molecular structures, conjugations, hydrogen bonding harmonic force field, vibrational frequencies and IR and Raman activities of the bioactive molecules and their metal complexes. The results have been extensively employed in the unambiguous identification of vibrational modes and provide deeper insight into the bonding and structural features of complex coordination. The present work deals with the theoretical, analytical, FT-IR and FT-Raman spectral investigations, supported by density functional theory calculations, to understand the structural and bonding features, the intramolecular interactions of biologically active coumarin derivatives and their metal complexes.

As a part of our continuing work on the synthesis, characterization and pharmacological applications of newly synthesised metal complexes, it was observed that changes in the structure of the ligands, using different metals as well as the reaction conditions had profound effects on selectivity and activity of the products obtained [1-3]. In the present work different metal complexes with coumarin ligands were synthesized and their structures were determined by means of analytical and spectral analyses.

The group of coumarins is a source of lead compounds, which are considered as promising drugs in the therapy of many diseases [4-5]. Coumarins have a lot of different structures, due to the various types of substitutions of their core, which could in turn influence their biological activity. This class of compounds has attracted significant attention as appropriate ligands for the synthesis of new coordination compounds. Our recently published data on the new coumarins and their lanthanide complexes indicate that the number of these compounds has demonstrated anti-proliferative activity on various cancer cell lines. Promising results prompted us to synthesize and investigate the new metal complexes. These structures have been further investigated by means of high-level DFT theoretical calculations, allowing the determination and comparison of the energies, geometrical parameters, as well as the identification of the most important structural features. The DFT calculated geometries and harmonic vibrational wavenumbers were in good agreement with the experimental data and the complete assignment being proposed. The recorded spectra and the marker bands of characteristic functional groups of the ligands and their complexes were identified, in order to use them as data bank for further application in trace analysis of other complexes of coumarins. The overall results from the preliminary screening program revealed, that the ligands and their novel metal complexes are potent cytotoxic agents.

Keywords: metal complexes; coumarins; IR; Raman; DFT

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TERAHERTZ SPECTROSCOPY AND COMPUTATIONS OF PROTEINS IN AQUEOUS ENVIRONMENTS

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Proteins are dynamic molecules that exhibit individual motions of atoms or residues side chains and collective, large-scale motions that involve their domains or even the entire structure. The latter represent high amplitude, low frequency vibration modes relevant for protein function.

Terahertz (THz) spectroscopy is a powerful tool for the investigation of protein vibrational modes and conformational transitions [1]. THz radiation involves the spectral region between 0.06 THz (2 cm^{-1}) and 10 THz (333 cm^{-1}), is non-ionizing and uses low average powers (<1 mW), allowing measurements both *in vivo* and *in vitro* without damaging the biological samples. THz spectroscopy inherently monitors motions on a sub-picosecond to picoseconds timescale, which is difficult to address using other techniques. Time-domain THz spectroscopy (THz-TDS) was successfully used to identify different molecular species, different mutations within a single species and different conformations of a given molecule [2, 3]. One of the challenges of THz spectroscopy is the difficult interpretation of THz spectra. A better understanding of the absorption features observed on experimental spectra can be achieved by theoretical studies trough simulated THz spectra. Mainly, there are two methods of simulating the vibration spectra of proteins: normal modes analysis [3] and molecular dynamics [4].

Given the extreme sensitivity of THz spectroscopy to molecular properties, we first addressed the question of which CHARMM [5] force field is suited for THz spectra simulation. We answered this question by comparing the experimentally recorded THz spectrum of lyophilized hen egg white lysozyme (HEWL) [2] with spectra simulated using different CHARMM parameter sets based on the known crystal structure of HEWL [6]. We than used THz spectroscopy to investigate the structure and flexibility of bovine serum albumin (BSA), a protein with unknown crystal structure, in conditions ranging from lyophilized to dilute 10% w/w solution and highly concentrated 50% w/w solutions. Computations were performed using a structural model of BSA. Based on the agreement between simulated THz spectra of dry and hydrated BSA with the experimental data, we validated the structural model of BSA and the solution models.

Keywords: THz spectroscopy; Molecular modeling; THz spectra simulation

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MODIFIED OLIGONUCLEOTIDES CELLULAR UPTAKE MONITORED BY USING TIME-RESOLVED MICROSPECTROFLUORIMETRY AND FLORESCENCE IMAGING

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Modified oligonucleotides (ON) as sequences of synthesized deoxyribo- or ribonucleotides are able to inhibit primarily transcription of a specific gene (antigene strategy), translation from mRNA into protein (antisense strategy) or the function of a key targeted protein (aptamer strategy) [1]. Potential successful healing properties are conditioned by effective ON uptake through the cellular membrane. Synthetic derivatives of porphyrins seem to be one of the promising candidates for this purpose. Their cationic forms have been already studied and successfully employed in the ON uptake [2]. Cationic porphyrins (5,10,15,20-tetrakis (1-methyl-4-pyridyl)-porphine and zinc 5,10,15,20-tetrakis (1-methyl-4-pyridyl)-porphine) assisted delivery system is used to facilitate ON intracellular transport.

Our confocal microspectrofluorimeter adapted for time-resolved intracellular fluorescence measurements by using a phase-modulation principle and homodyne data acquisition method was employed to acquire intracellular spectra for lifetime determination from selected sites inside the cell [3]. Time-resolved fluorescence spectra will demonstrate the possibility in monitoring ON interactions with biological molecules inside the cell. Fluorescence confocal microimaging is utilized as suitable complementary technique to observe the oligonucleotide uptake into the living cells and its intracellular distribution. It clearly visualizes penetration of the ONs through cellular membrane and their progress inside the cell.

Keywords: time-resolved fluorescence spectroscopy, modified oligonucleotide, cationic porphyrin

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SCATTERING STUDY OF VIROID DYNAMICS

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It is now broadly accepted that the biomolecular structure alone is not sufficient to account for the biological function, but that molecular dynamics also plays an essential role. The necessity of RNA dynamics investigation is underlined by a rich diversity of properties RNA displays. RNA extraordinary capabilities led to the formulation of the RNA World hypothesis in origin of Life studies. It states that in the early stage of evolution RNA molecules combined storage and transmission of genetic information (now assured mainly by DNA) and enzymatic activity (now assured mainly by proteins). In this context, the recently discovered RNA molecules called **viroids** are particularly interesting. Viroids are small naked, circular, single stranded RNA molecules containing from about 250 to 400 nucleotides that are pathogenic to plants. They infect plants causing pathologies similar to those observed for viruses. In contrast to viruses, however, viroids do not contain a protein capsid and do not code for proteins; their pathogenic effects are induced through direct interactions with host proteins. These naked RNA molecules have adapted to be strikingly stable, resistant and flexible. The *Avsunviroidae* viroid class is of particular interest for us characterised by a hammerhead ribozyme structure, which permits self-cleavage during replication in chloroplasts. It has been proposed that proto-tRNA was most plausibly a viroid-like self-cleavable replicable ribozyme possessing a possible hammerhead-like structure [1] and recently it was shown viroids can replicate in yeast cells, providing the first evidence that viroids can replicate in organisms other than plants [2].

In this context it is interesting to investigate viroid dynamic properties. For this purpose we have used neutron scattering, Raman spectroscopy and molecular dynamics simulation methods. In neutron scattering studies we have used the protocol originally developed for investigation of molecular dynamics of proteins in solution and its relation to biological function [3,4,5]. We have used the elastic incoherent neutron scattering method, where the changes in momentum of a neutron beam caused by its interaction with a sample provide molecular dynamics parameters in terms of a mean square displacement and molecular resilience [6]. The method is sensitive to a large range of molecular dynamics in the same time scale that is currently accessible in molecular dynamics simulations (MD), thus allowing a powerful combination of experiment and simulation to address biological functional molecular dynamics. The overall dynamics information obtained from neutron scattering and MD simulation was completed by Raman studies of the ribozyme part of the viroid molecule. Altogether it gives us a solid base for establishing the dynamics-function relations.

Keywords: viroid; molecular dynamics; neutron spectroscopy

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CIRCURAL DICHROISM STUDY OF THE GUANOSINE/BILE PIGMETS INTERACTIONS

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Bile pigments – bilirubin (BR) and its metabolic precursor biliverdin (BV) are heme degradation products. It has been proposed as physiological antioxidants and antimutagens. It is known [1] that bilirubin forms a complex with the metal ions, where the complex of BR and BV with Cu(II) was shown to cause DNA damage [2]. Guanosine (G), one of the four bases in DNA, is a biologically important unit in supramolecular chemistry as well as in nanotechnology. Depending on the physico-chemical condition guanosine derivatives form various self-assembled structures: ribbons, tetramers, and the columnar stacked monomers or tetramers. Guanosine is abundantly present in telomeric DNA, where its presence leads to a spontaneous formation of guanosine quartets (G4). Therefore, the most important role of G4 is connected with their potential influence in *in vivo* processes. Furthermore they are the fundamental building block of supramolecular reversible gels, which may arise in certain pH, temperature and presence of added ion [3].

Most of natural processes, that are essential for life, are controlled by the chiral interactions. It is therefore necessary to study non-covalent interactions also with regard to the chirality of the components in the system. Conventional spectroscopic techniques (NMR, UV-Vis, IR absorption and Raman spectroscopy) do not distinguish the individual enantiomers. Therefore, for the study of interactions of guanosines with bile pigments, which have strong chiral character, we used chiroptical methods that are very well established for structural studies of chiral systems in a solution. In the visible and ultraviolet regions we used electronic circular dichroism (ECD), which monitors the electronic transitions and rather reflects the molecule as a whole composed of chromophores. In the IR region we used vibrational circular dichroism (VCD), that through the vibrational transitions has more local character and provides in most cases detailed and well-localized information on the structure of molecules.

Keywords: Circular Dichroism; Guanosine; Bile Pigments

Acknowledgement
Financial Support from Specific University Research (MSMT No. 21/2012) and by The Grant Agency of the Czech Republic (P206/11/0836) is gratefully acknowledged.

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LABEL-FREE TIME-COURSE STUDY OF CARDIOMYOCYTES DIFFERENTIATION FROM HUMAN EMBRYONIC STEM CELLS BY RAMAN MICRO-SPECTROSCOPY

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Raman micro-spectroscopy (RMS) was used to detect and image molecular markers specific to cardiomyocytes (CMs) derived from human embryonic stem cells (hESCs). This technique is non-invasive therefore can be used for discrimination of individual live CMs within highly heterogeneous cell populations as obtained following diffeentiation of hESCs. Principal component analysis (PCA) of the Raman spectra was used to build a classification model for the cells as CMs. Retrospective immuno-staining imaging was used as gold-standard for phenotypic identification of each cells. The discrimination accuracy of CMs from other phenotypes was >97% specificity and >96% sensitivity, calculated using cross-validation algorithms (target 100% specificity)[1]. Following a comparison between Raman spectral images of selected Raman bands identified by the PCA model and immuno-staining of the same cells, it was concluded that glycogen and myofibril proteins are responsible for the discrimination of CMs, glycogen being the main contributor. In addition, the combination between high-laser power and sampling cells with a laser beam focused to a line eliminates the need of raster scanning and ensure high prediction accuracies > 95%, at 5 seconds per cell while the use of higher power lasers currently available would enable sorting speed of ~8 cells per second[2]. The use of RMS in the study of Embryoid Bodies differentiation process will be presented. In particular the evolution of various biochemical inside live beating clusters derived following a cardiac differentiation protocol will be shown. This study demonstrates the potential of RMS for non-invasive phenotypic identification of hESCs progeny making Raman activated cell sorting a potentially viable alternative for the enrichment and purification of hESC-derived cardiomyocytes.

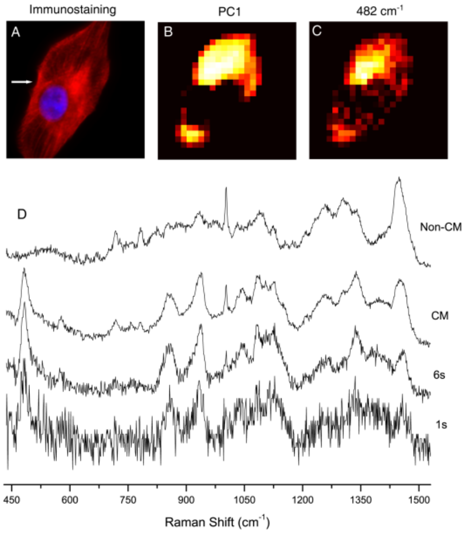

Fig. 1 (A) Immuno-fluorescence for α-actinin, (B) Raman map of the Cardiac Phenotype, (C)Raman map of the 482 cm^{-1} band attributed to glycogen for a typical CM (D) Average Raman spectrum for the same CM compared to a typical average spectrum for a non-CM. The line scans over the CM for acquisition times from 1 to 6 second at the position indicated by the arrow in (a)

Keywords: Raman spectroscopy; human embryonic stem cells; cardiomyocytes; Embryoid bodies

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SPECTRAL SIMILARITY ALGORITHM OF PHYTO-PATHOGENES ISOLATES USING FTIR-ATR SPECTROSCOPY AND PCA CALCULATION

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It is highly desirable to understand the extent of similarity between the different fungal strains and isolates of phyto-pathogens. Tracing the similarity may be helpful for tracking the origin and propagation of these isolates and may eventually prevent the spread of the disease. It may be noted that DNA sequencing can determine the extent of similarity between fungal isolates based on their genoms; however the process is complicated and expensive. Soil-borne fungi are considered as major pathogens to many plants and can cause severe economic damage. It is very helpful to detect and identify these pathogens at early stages, as it allows the best chances to control their spread. FTIR-ATR spectroscopy is considered to be a comprehensive and sensitive method for the detection of minute molecular changes in intact cells.

In earlier studies, we have successfully differentiated in the level of genus and strain [1-3] among different fungi genera of Rhizoctonia, Colletotrichum, Verticillium and Fusarium using FTIR-ATR spectroscopy and multivariate analysis tools such as PCA and LDA. The primary innovation in the present study is the success in determining the relative spectral similarity of different examined fungal isolates based on their spectral data. We applied advanced statistical techniques PCA and LDA on the FTIR-ATR spectra of Colletotrichum, Verticillium and Fusarium isolates. We were thus able to examine the feasibility of distinction between these fungi strains and develop relative spectral similarity algorithm between the different investigated strains. This method may have an important potential diagnostic tool in agricultural research, since it outlines the extent of the biological similarity between fungal isolates and simultaneously differentiate between the examined isolates. Spectral similarity may indicate the extent of biological similarity, as well as the relationship between certain isolates. We plan to more deeply examine the correlation between the spectral and structural biological similarity of various fungal strains. We believe that there is a great potential in using FTIR-ATR for the diagnosis and identification of fungal pathogens and estimating their relative similarity. In the future, this method can be developed for in-situ or in-vivo measurements of fungi using infrared fiberoptic sensors.

Keywords: FTIR-ATR, PCA, LDA, Spectral similarity.

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QUANTIFICATION AND CONFORMATIONAL ANALYSIS OF DNA IN SIMPLE EUKARYOTIC CELLS AND BACTERIA USING FOURIER TRANSFORM INFRARED SPECTROSCOPY

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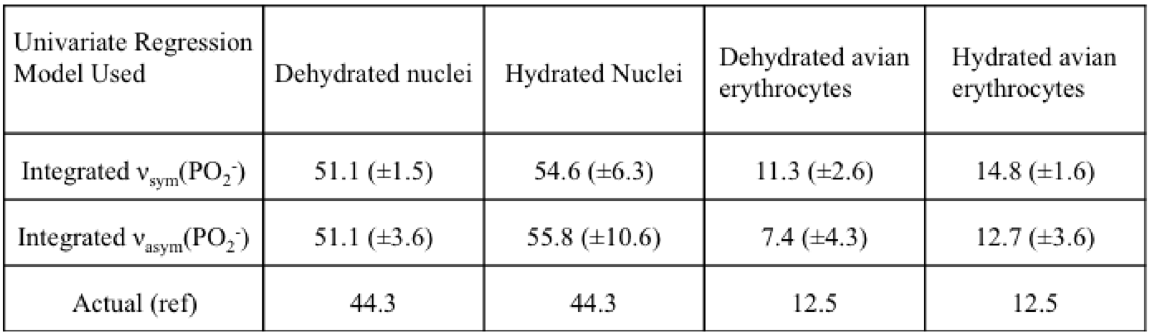
A technique capable of detecting and monitoring nucleic acid concentration offers potential in diagnosing cancer and further developing an understanding of the biochemistry of cancer progression. Fourier transform infrared (FTIR) spectroscopy has previously been combined with multivariate methods to successfully detect cancer. However, the spectral differences used to differentiate cancerous from non-cancerous cells have not been fully elucidated. This is partly because of a perceived inability of FTIR to fully detect the contribution of DNA in dehydrated and fixed cells. Here we demonstrate that the concentration of DNA in avian erythrocytes can be calculated accurately from the FTIR spectrum using both Beer-Lambert univariate regression curves and multivariate partial least squares (PLS) regression models. Table 1 shows the average predicted DNA content of avian erythrocyte nuclei and cells compared to literature references [1,2] using univariate methods. The approach offers a new way to quantify nucleic acids in cells and demonstrates that the Beer-Lambert law is obeyed even when the DNA is compacted in cell nuclei.

By systematically monitoring the dehydration and rehydration of single and double stranded DNA, RNA, extracted nuclei and three types of eukaryotic cells including chicken erythrocytes, mammalian lymphocytes and cancerous rodent fibroblasts using Fourier transform infrared (FTIR) spectroscopy we unequivocally assign the important DNA conformation marker bands within these cells.[3]

We further report that a B-like to A-like DNA conformational change can occur in bacteria in response to dehydration. This transition is reversible upon rehydration in air-dried bacteria. Moreover, the bacteria can still function and reproduce after this extreme desiccation. The result infers that the A-like DNA conformation plays an important role in protecting bacteria against extreme dehydration.



Univariate Regression Model Used	Dehydrated nuclei	Hydrated Nuclei	Dehydrated avian erythrocytes	Hydrated avian erythrocytes
Integrated $\nu_{sym}(PO_2^-)$	51.1 (±1.5)	54.6 (±6.3)	11.3 (±2.6)	14.8 (±1.6)
Integrated $\nu_{asym}(PO_2^-)$	51.1 (±3.6)	55.8 (±10.6)	7.4 (±4.3)	12.7 (±3.6)
Actual (ref)	44.3	44.3	12.5	12.5

Keywords: FTIR, DNA conformation, cells, bacteria

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VIBRATIONAL AND ELECTRONIC CIRCULAR DICHROISM FOR ANALYZING MODELS OF PROTEIN-MEMBRANE SYSTEMS WITH BILIRUBIN

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Bilirubin, the final product of the hem catabolism, has been in focus for a long time owing to both the positive and negative functions that it fulfills in the human organism. As it is considered [1-3], that the neurotoxic properties of bilirubin are caused by its enantiodiscimination on the membrane surface, we analyzed the interaction of bilirubin with model membranes using chiroptical techniques: vibrational and electronic circular dichroism (VCD, ECD). We also studied ternary systems with polypeptides bounded to the membranes as models for the interaction of bilirubin with membrane proteins. Because the electrostatic interactions at the lipid membrane surface play an important role in the binding of proteins to membranes, we also examined the systems composed only of the model membrane and charged polypeptide.

As a monolayer membrane model, we used micelles composed of negatively-charged sodium dodecyl sulfate (SDS), positively-charged trimethyl(tetradecyl)ammonium bromide or non-charged N-Decanoyl-N-methylglucamine. Large unilamellar vesicles composed of phospholipids (DPPG, DSPG, DOPC and DMPC) and sphingolipids (sphingosine, sphingomyelin) were used as a bilayer membrane model. Positively-charged poly-L-lysine (PLL) and poly-L-arginine (PLAG) were used as appropriate model systems for peripheral membrane proteins.

We described the conformational changes of the polypeptides caused by the interaction with the model membranes [4]. Among others, the presence of the liposomes in the solution generated special conditions for the formation of the α-helical structure of PLAG; the presence of SDS induced the formation of the β-structure of PLL. We documented the enantioselectivity of bilirubin on the model membranes and its unexpected preference for the P-form upon binding to the membranes. The specific interaction of bilirubin with the polypeptides bounded to the membranes was also proven.

The obtained results suggested that the cell membrane disruption induced by bilirubin is caused by its enantiodicrimination. The mutual interaction of bilirubin with membranes is probably governed by the molecular structure of the lipids.

Acknowledgement: Financial support from specific university research (MSMT No 21/2012) and by the Grant Agency of the Czech Republic (P206/11/0836) is gratefully acknowledged.

Keywords: circular dichroism; model membranes; bile pigments; polypeptides

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EXPERIMENTAL AND THEORETICAL RAMAN SPECTRA OF TRIPEPTIDES AND PROTEINS

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Raman spectroscopy is a major analytical technique used for studying proteins. Its efficiency is strictly dependent on the correct attribution of the protein Raman bands. The Raman spectrum of a protein is complex due to their large number of bands. Among these bands, those bands belonging to the side chains of the amino acid residues are particularly important in monitoring chemical reactions involving proteins. The assignment of these bands is often difficult because their exact positions and intensities are dependent on the molecular environment. In the present work we have detected, attributed and compared the side chain Raman bands of three model proteins: Bovine Serum Albumin, β-lactoglobulin and Lysozyme. The attribution of the bands was based on the measurement and *ab initio* calculation of Raman spectra of several tripeptides of the form: Gly-AA-Gly, where the central amino acid AA was tryptophan, tyrosine, phenylalanine, methionine, histidine, lysine and leucine. The central amino acids were chosen as a reason of their significant reactivity.

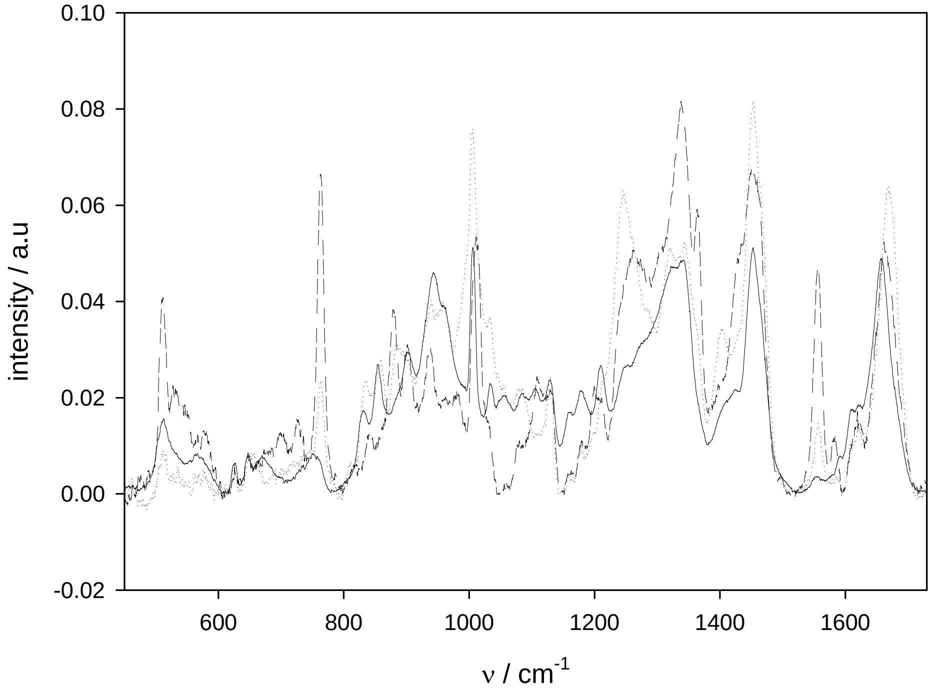

Figure 1 : Raman spectra for Bovine Serum Albumin (——), β-lactoglobulin (·····) and Lysozyme (----).

THE INFLUENCE OF SYNTHESIS METHODS, DIFFERENT DOPANT IONS AND RATIOS ON THE LUMINESCENCE OF $SrAl_2O_4$ NANOPARTICLES

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Inorganic phosphors have been extensively investigated for various applications in the optical and electronical fields. Within the different type phosphors the alkali earth aluminates have attracted great attention due to the very long persistent phosphorescence and high chemical stability. These alkali earth aluminates are mainly activated with divalent europium ions and co-doped with trivalent co-dopant ions, such as dysprosium. These $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphors have good luminescent properties with long afterglow time which made them ideal material for many practical applications.

Traditionally the $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors are prepared at high temperatures with solid-state reaction method. In this case, the host material and the activators which replace some of the host ions are incorporated simultaneously during the calcination. In the preparation $Sr(CO_3)_2$, Al_2O_3, Eu_2O_3 and Dy_2O_3 along with some flux is mixed together and blended to get homogeneous mixture and fired at a suitable temperature.

Besides the solid-state synthesis, phosphors are also prepared by combustion method. The combustion method is a facile and very efficient method, which takes only few minutes. In this method, all precursors are used as salts such as in their nitrate forms in our case. During the synthesis a proper amount of organic fuel is added to the aqueous solution of the nitrates and as a result of this exothermic redox reaction the doped strontium-aluminates formed in several minutes at relatively low temperature.

The $SrAl_2O_4:Eu^{2+}$ phosphors were prepared by solid-state reaction and also with combustion method at 500 ºC. We used different rare-earths metals as co-dopants beside of the europium activator, namely dysprosium, holmium, gadolinium, samarium and terbium were used.

In the solid-state synthesis the Al_2O_3, $SrCO_2$, Eu_2O_3 and the co-dopand compound were mixed in ball mill with various amount of H_3BO_3. The effects of the co-dopant ions, the optimal amount of the flux were investigated beside the optimal parameters of ball milling. In the much faster combustion synthesis the precursors were used in their nitrate forms along with urea as the organic fuel. The samples after the two kind of synthesis were calcinated at 1200 ºC for 3 hours in 5% H_2 and 95% N_2 atmosphere.

The samples were characterized using XRD, TEM, SEM, EDX and PL measurements to compare the effect of varying the different parameters and co-dopant ions. In order to complement the XRD data we used Raman spectroscopy measurements. The interpretation of the spectra was complicated because of the large number of modes, nevertheless this technique was used for phase identifications. We also investigate the decay behavior of the synthesized and doped phosphor samples. The decay rates varied upon the synthesis methods and dopant ions which was attributed to the presence of various types of traps with different depths in the samples.

Keywords: Phosphorescence, strontium-aluminate, combustion synthesis, solid-state synthesis

A CONFOCAL RAMAN AFM STUDY OF GRAPHENE

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The discovery by Novoselov and Geim of a simple method to transfer a single atomic layer of carbon from the c-face of graphite to a substrate suitable for measurements of its electrical and optical properties has led to an increased interest in studying and employing two-dimensional model systems. An important goal however, is the detection of such angstrom-thick two dimensional sheets, and precisely determine their physical and optical properties. In the past two decades, AFM (atomic force microscopy) was one of the main techniques used to characterize the morphology of nano-materials spread on nanometer-flat substrates. From such images it is possible to gain information about the physical dimensions of the material on the nanometer scale, without additional information about their chemical composition, crystallinity or stress state. On the other hand, Raman spectroscopy is known to be used to unequivocally determine the chemical composition of a material. By combining the chemical sensitive Raman spectroscopy with high resolution confocal microscopy, the analyzed material volume can be reduced below 0.02 μm^3, thus leading to the ability to acquire Raman images with diffraction limited resolution from very flat surfaces. The combination of confocal Raman microscopy with Atomic Force Microscopy (AFM) is a breakthrough in microscopy. Using such a combination, the high spatial and topographical resolution obtained with an AFM can be directly linked to the chemical information provided by confocal Raman spectroscopy.

An example of a confocal Raman-AFM measurement is illustrated in the figure of this abstract. Fig. 1a shows the AFM topography image of a graphene flake consisting of mono-, bi- and multilayers deposited on a Si substrate. A Raman image was recorded from the same sample area by acquiring a spectral array of 85x50 complete Raman spectra. The thousands of Raman spectra were evaluated using peak fitting algorithms, which are very sensitive to small variations of Raman band position and width. The Raman image presented in Fig. 2b highlights the variations of the G-band within the analyzed graphene. The mono-layer of graphene (brown color) can be clearly discriminated from a graphene bi-layer (pink color). In yellow color a flipped over graphene sheet is presented.

The various data acquisition and evaluation methods will be discussed in this contribution. Furthermore, the correlation of spectral features with other physical properties of the graphene layers will be shown.

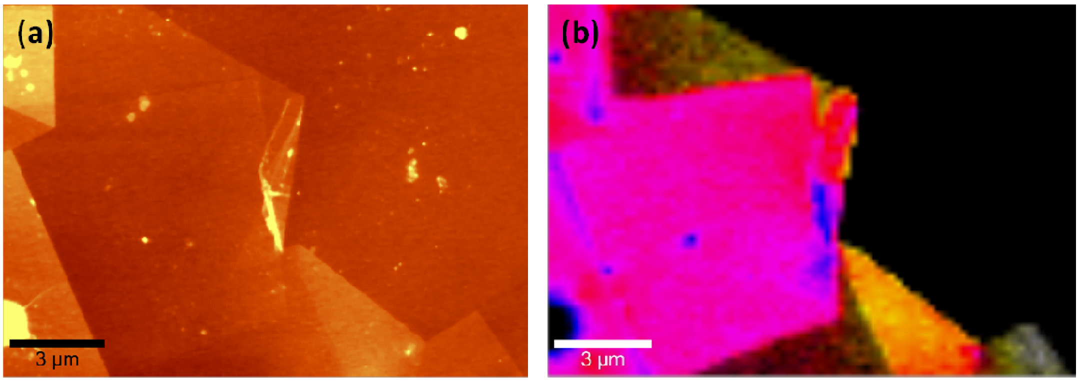

Fig.1. AFM topography of a graphene flake (a) and Raman image of the same graphene flake (b) revealing the optoelectronic properties of the graphene.

Keywords: physical and optical properties of graphene

FT-IR STUDY OF THERMAL DEGRADATION MECHANISM OF POLYETHYLENE/MONTMORILLONITE NANOCOMPOSITES

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The effects of pristine (MMT), organic-modified montmorillonite (OMMT), magnesium hydroxide (MDH) and combination of montmorillonites and magnesium hydroxide on the fire retardancy of high density polyethylene were investigated.

Thermogravimetric analysis coupled with infrared spectrometry (TGA-IR) was used to study thermal degradation characteristics and gas products of PE composites. Real time FT-IR was used to monitor the thermal oxidative stability and the high temperature performance of the flame retardant PE composites. The results of TGA and TGA-IR show that for OMMT/MDH/PE composite, quaternary alkyl ammonium modifier stimulates the dehydration of OMMT, and produces gas bubbles which are helpful for the formation of an intumescent char. In order to explain the relationship between microstructure of carbonaceous silicate char and flame retardancy performance, the morphologies of char residues after cone calorimeter test were studied by FTIR-ATR spectroscopy. To explain the role of MMT and OMMT in the thermal and oxy-degradation of polymer the observation of the changes in integral absorbencies and frequencies of ν Si-O were done with the increase of the temperature For all samples that contain the OMMT (Fig.1), the dramatic increase of the intensity of the stretching vibration νSi–O group is observed compared to the bands of C–H bending and C–H stretching. It indicates that the silicate char forms in the surface of the composite, as soon as the composites are fired. It is an inorganic-rich surface that has better barrier property.

The rise in absorbance of Si-O band, which was observed in the spectra of the OMMT composites with the rise of the temperature, indicates a new order in the silicate framework such that the dipoles are more strongly coupled.

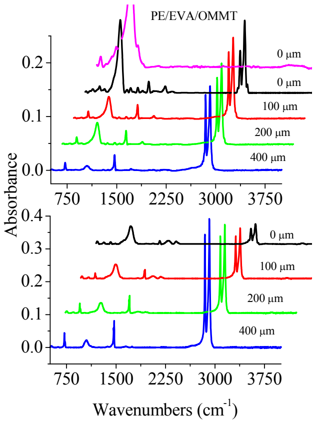

Fig1. Depths profile of FT-IR spectra of PE/EVA5/OMMT5 during combustion in the direction of propagation of the combustion from the flame front (0 μm) to the bulk of the polymer. *Bottom layer* – prior to ignition step, *top layer* – 200 s after ignition step, *magenta line* – after burning.

INVESTIGATION ON CHEMICAL STABILITY, INTERFACIAL PROPERTIES AND SOLID STATE CRYSTALLIZATION OF HIGH-K METAL OXIDE THIN FILMS FORMED BY E-BEAM EVAPORATION

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As the semiconductor industry drives towards smaller device sizes while striving to maintain power consumption at acceptable levels, in particular for portable applications, the incorporation of new materials becomes inevitable. High dielectric constant (high-*k*) metal oxides materials are leading candidate to replace, or be combined with, silicon dioxide in many applications. Lanthanum oxide (La_2O_3) is considered to be a potential candidate for gate oxide applications in the future high-/metal gate MOSFET devices beyond the 35nm node while hafnium oxide (HfO_2) is being already used in the 35nm CMOS technologies. One of the challenges associated with La_2O_3 and HfO_2 based high- thin films is the moisture and CO_2 absorption when exposed to air resulting formation of carbonates and hydroxyls. In this work we explore the solid phase crystallization of amorphous HfO_2 and La_2O_3 based thin films and their time dependence reaction with moisture and CO_2. Uncapped and SiO_2-capped (in-situ without breaking the vacuum) HfO_2 and La_2O_3 thin films were deposited on HF last terminated double side polished silicon (100) substrates by electron beam evaporation from solid La_2O_3 and HfO_2 pellets (99.9% purity, Cerac) at 150^{o}C. After deposition the samples were exposed to forming gas (5%H_2/95%N_2) Rapid Thermal Annealing and nitrogen gas annealing at several temperatures ranging from 450^{o}C to 1050^{o}C. High Resolution TEM, XRD, Time resolved FTIR and Raman measurements were performed to investigate the chemical stability and crystallisation of the HfO_2 and La_2O_3 based thin films. The films thickness and optical properties have been inferred from the spectroscopic ellipsometry. Carbonates and hydroxyls species have been detected by FTIR on HfO_2 thin films after two weeks of air exposure. Time-resolved FTIR and Raman measurements performed over a period of three weeks on uncapped La_2O_3 thin films, indicate that the formation of $La(OH)_3$ is thickness dependent but is not as fast as was considered in the literature. For HfO_2 thin films a transition to a crystalline phase occurs at a temperature greater than 450^{o}C depending to the layer thickness. The crystalline grains consist of cubic and monoclinic phases already classified in the literature but this work provides the first evidence of amorphous-cubic phase transition at a temperature as low as 500^{o}C. According to SE, XRR and FTIR results, an increase in the interfacial layer thickness can be observed only for high temperature annealing. We report on a different behaviour of crystallisation into pure La_2O_3 hexagonal phase for uncapped and SiO_2-capped La_2O_3 films. The SiO_2-capped La_2O_3 films require a much lower temperature (700^{o}C) while for uncapped films temperatures higher than 900^{o}C are needed. Following the forming gas annealing the La_2O_3 films exhibit a significantly enhanced resistance to $La(OH)_3$ formation. We report here the infrared and Raman active modes of both amorphous and crystalline HfO_2 and La_2O_3 thin films.

Acknowledgments: This work was supported by Science foundation Ireland (05/IN/1751)

LASER PERFORMANCE AND SPECTROSCOPIC PROPERTIES OF Yb-DOPED Lu_2O_3 AND YAG CERAMICS

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Since the first laser oscillation achieved in 2003 [1], several efforts have been focused on Yb-doped transparent polycrystalline ceramics, which are nowadays considered a strategic material for the development of innovative diode-pumped solid-state-laser able to reach high average powers and pulse with a short time duration [2].

The excellent results achieved can be explained considering both the intrinsic characteristic of Ytterbium ions (Yb) and ceramic matrices. As a matter of fact, Yb^{3+} has only two manifolds, $^2F_{5/2}$ and $^2F_{7/2}$, which reduce the quantum defects determining a relatively low thermal load, a long lifetime of the upper state of the laser transition and a wide range of tunability. The ceramic matrices, if compared with the corresponding crystalline materials, show comparable optical qualities, higher uniformity in the distribution of dopants, better thermo-mechanical properties. Moreover, ceramics have a shorter processing time and lower processing temperature, which result particularly advantageous for two cubic sesquioxides as Lu_2O_3 and Sc_2O_3. Due to their high melting point (above 2400 °C) only recently they have been grown in small-size crystals with good optical quality. Sesquioxides are has been considered very promising host matrices because of their high undoped thermal conductivity (up to 12 W/mK).

We present an in-deep spectroscopic investigation and the laser performance achieved by two different A/R coated Yb-doped ceramics as Lu_2O_3 and YAG. The pumping wavelength as well as the concentration of dopants have been opportunely chosen in order to have an almost comparable absorption coefficient and thermal conductivity [3]. In particular, Yb:Lu_2O_3 [4,5] is pumped at 968 nm while Yb:YAG [6] at 933 nm. Both are longitudinally pumped in *quasi*-CW (Duty Factor of 20%) at room temperature. The doping levels are 1% *at.* (Lu_2O_3) and 0.7% *at.* (YAG), respectively.

To focus on the laser performance, with both samples we measured the output power as a function of the absorption pump power and we estimated the corresponding slope efficiency. An almost comparable values of the output power is measured while the slope efficiency is found to be higher in Yb:YAG.

Keywords: Solid-state lasers; Ytterbium laser materials; Rare earth solid-state lasers

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STRUCTURAL STABILITY TEST OF CERIUM-PHOSPHATE NANOWIRES FOR A POTENTIAL APPLICATION IN SOLID OXIDE FUEL CELLS

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Nowadays global warming and air pollution such as smog have become one of the most urgent problem mostly caused by our inadequate industrial and transport technology. Currently fuel cells are the most promising candidates which could provide a quite elegant solution for these problems.

Solid oxide fuel cells are a class of fuel cell in which a solid oxide or ceramic material is used as the electrolyte. This type of fuel cells has the advantages of high efficiency, fuel flexibility, long-term stability, low emissions, and relatively low cost. Nevertheless their typical operating temperature can reach the 500-1000°C which raises some mechanical and chemical compatibility issues.

In the recent years much attention has been focused on the preparation of rare-earth phosphate nanomaterials. Their unique electronic configuration makes them promising candidates for the application in optoelectronics, catalysis, biological fluorescent labeling and fuel cells [1]. However only few studies have been published on the structural stability of $CePO_4$ nanowires and sea urchin-like nanostructures against elevated temperatures [2] and pressures.

$CePO_4$ one-dimensional nanostructures can be prepared by various synthetic procedures such as template based, microemulsion, sonochemical, microwave assisted or hydrothermal methods [3],[4],[5].

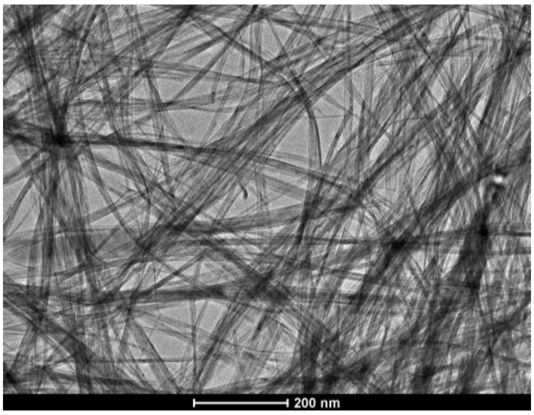

Fig.1 TEM image of $CePO_4$ nanowires

Recently a simple, template-free, room temperature synthesis has been developed by our research group for the preparation of ultra-long cerium-phosphate nanowires and sea urchin-like nanostructures in hexagonal phase.

In this study thin membranes have been prepared from $CePO_4$ nanostructures applying different temperatures and pressures. The structural stability and crystallinity of the nanostructures have been examined by transmission electron microscopy, x-ray diffraction and Raman spectroscopy. The microstructure and the porosity of the membranes have been examined by scanning electron microscopy and nitrogen adsorption surface area analyzer.

Keywords: $CePO_4$ nanowires; fuel cell; structural stability

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EFFECT OF ELABORATION PARAMETERS ON THE LOCALIZATION OF RARE-EARTH EMITTER SITES IN TIN SILICATE SOL-GEL DERIVED GLASS-CERAMICS

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The use of rare earth (RE) ions as luminescence centers incorporated into different hosts are of great interest because of their promising applications in many fields, such as solid lasers, planar waveguides, flat panel displays, high-density optical data storage and even biological multicolor imaging [1-3]. The production of active (RE) nanoparticles in a glass matrix can give rise to high luminescence efficiency.

However, the solubility of RE ions being quite low in silicate glasses, an alternative is to employ glass ceramics. As a result, silica-based nanostructured glass ceramics now attract great attention because of their applications towards various photonic devices. In fact, these materials present a double interest, because they combine the mechanical and optical properties of the glass with a crystal-like environment for the RE ions [4].

In this work, SiO_2 glass is combined with the semiconductor SnO_2 as the crystalline host matrix for the optically active RE ions. In addition, this semiconductor presents the advantage of having a bandgap of 3.6 eV, which overlaps some of the energy levels of Er^{3+} and Eu^{3+}ions. Hence, if the RE ions can be doped into semiconductor nanoclusters, there can be an energy transfer between the clusters and the ions, thus compensating for the small cross section of rare-earth ion transitions.

The present studies of sol-gel-derived silica-based vitroceramics containing tin oxide precursors and Eu^{3+} and Er^{3+}-ions benefitted from a broad line of investigative techniques. FTIR, FT Raman and conventional Raman spectroscopies and x-ray diffraction were used to demonstrate the effect of sample morphology (thin film or bulk) on the densification kinetics of the matrix and on the crystallization of the SnO_2 nanoparticles. AFM studies showed the effects of RE ions on the surfaces of SiO_2- SnO_2 thin films. Emission spectra showed the presence of two sites for the RE ions. The ensemble of techniques indicate that the concentration of SnO_2 can be used to control the sites occupied by the RE ions and hence the luminescence efficiency.

Keywords: Tin-silicate vitro-ceramics; erbium doping; energy transfer; vibrational spectra; rare-earth site

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INFRARED SPECTROMETRIC ANALYSIS OF HUMAN BLOOD SERUM SAMPLES FOR ESTIMATING THE GLOMERULAR FILTRATION RATE

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Clinical assessment of kidney function is part of routine medical practice for adults and is essential for assessing overall health. The glomerular filtration rate (GFR) is considered the best overall index of kidney function in health and disease. The GFR cannot be measured easily in clinical practice; instead, it is estimated from equations by using serum creatinine level, age, sex, and body size. Current approaches are based on some equations which have limited precision and systematically underestimate measured GFR at higher values. During the last 2 decades, it has been proved that IR spectroscopy of human body fluids is helpful for clinical diagnosis and even environmental monitoring. Lipid based characteristics, protein amide related signals in mid-IR region in addition with hydrocarbon side-chains could be utilized for clinical supportive decision making [1,2]. Kidney disfunction (glomerulonefritis) has also been monitored via IR spectroscopy of patients' sweat. In order to develop a new estimating approach for GFR, blood serum samples were analyzed by infrared spectrometry and the spectral data was processed by chemometric techniques. Totally, 50 human samples within different stages were obtained being modeled by partial least squares and orthogonal signal correction. R^2 and standard deviation for the calibration and prediction set were 0.987, 5.915% and 0.972, 8.166% respectively.

Keywords: GFR, Kidney Function, FTIR, Chemometrics

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MAGNETO-OPTICAL STUDY OF DIFFERENT METAL-PHTHALOCYANINES BY COMBINING SPECTROSCOPIC MOKE AND ELLIPSOMETRY

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Organic materials experience much attention because of their potential applications in spintronic devices predominantly due to their long spin life-times. Magneto-optical Kerr effect (MOKE) is commonly used to study the magnetic properties of inorganic ferromagnetic layers or magnetic nanostructures. This work focusses on the systematic magneto-optical characterisation of metal free and transition metal phthalocyanines (H_2Pc, VOPc, CuPc, MnPc, FePc, NiPc, and CoPc). The films in the typical thickness range between 30 nm and 100 nm were prepared by organic molecular beam deposition in high vacuum.

A numerical analysis of the energy dispersion of the real and imaginary part of the complex magneto-optical Kerr rotation angle and of the optical constants allows the determination of the magneto-optical material constant, the so-called Voigt constant [1]. This procedure additionally requires the optical constants of the films as input. These data were obtained by spectroscopic ellipsometry. A fit of the Voigt data using an oscillator model was performed in order to gain more insight in the electronic origin of the features in the Voigt constant and subsequently in the MOKE spectra. For instance, the hybridisation of Co3d states with the HOMO π-orbital of CoPc leads to additional features in the magneto-optical spectra compared to *e.g.* CuPc. This effect is much more pronounced in the magneto-optical spectra than in the dielectric function which is commonly assessed by spectroscopic ellipsometry alone.

Furthermore, the magnitude of the Voigt constant is found to be highly sensitive to the orientation of the molecules with respect to the substrate plane [2]. This opens new possibilities to accurately determine the molecular orientation in organic thin films.

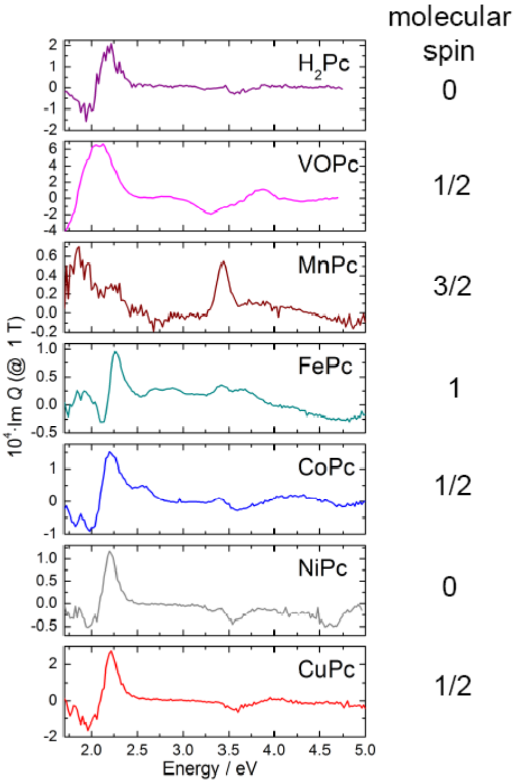

Fig.1 Imaginary part of the Voigt constant of metal phthalocyanines.

Keywords: metal phthalocyanines, magneto-optical Kerr effect

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SYNTHESIS AND CHARACTERIZATION OF WO_3 NANOWIRES AND METAL NANOPARTICLE-WO_3 NANOWIRE COMPOSITES

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Nanostructured materials have been in the center of the attention because of their fascinating new properties. These properties, which differ from the ones in bulk phase, can open the door to brand new forms of applications.

Recently, much effort has been devoted to the synthesis of nanosized semiconductors. Among metal oxides, tungsten oxide (WO3) has many interesting optical, electrical and structural properties. It is a wide band gap semiconductor and can be used in many applications like semiconductor gas devices, electrochromic devices or photocatalysis.

WO_3 nanowires can be synthetized using different techniques for example by heating a tungsten foil in argon gas [1] or by electrochemically etching a tungsten tip [2].

In this work the hydrothermal method was used for preparing WO_3 nanowires. We used sodium-tungstate as precursor, sodium-sulphate as structure directing agent and hydrochloric acid to set the pH of the solution. The mixture was transferred into a Teflon lined stainless steel autoclave and it was kept at 180 °C for 48 h. The white precipitate was collected by centrifugation, washed with water and ethanol several times and dried at 80 °C.

Using metal-salts as precursors the as prepared nanowires were decorated with metal nanoparticles by using the wet impregnation method.

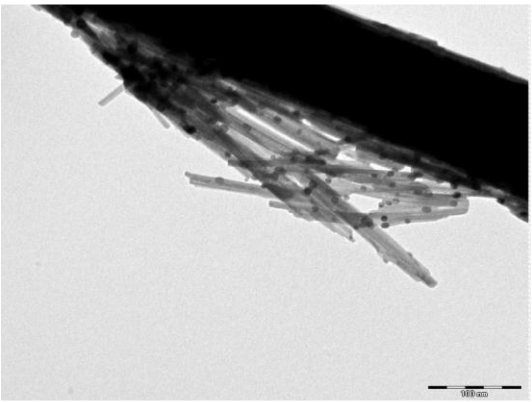

Fig.1 TEM image of the Pd decorated WO_3 nanowires

The WO_3 nanowires and the metal decorated nanowires were investigated by XRD, TEM, SEM and IR spectroscopy. Band gaps have been also calculated from UV-Vis reflectance spectra.

Keywords: tungsten-trioxide, nanowires, hydrothermal, wet impregnation

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SYNTHESIS, CHARACTERIZATION AND SPECTROSCOPIC PROPERTIES OF Bi AND Bi-Sb-COATED MULTIWALL CARBON

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In the past few years several studies have been published about nanoscaled materials because of their unique chemical and physical properties, and potential applications due to their size. After the discovery of carbon nanotubes one-dimensional (1D) nanostructures (nanotubes, nanowires, nanorods) have gotten great attention in nanotechnology.

The properties and the applicability of these structures could be improved by different metal or metal alloy coatings such as bismuth or antimony. Bismuth has high thermal conductivity and electric resistance. Although it is a heavy metal it has low toxicity. The advantageous physical properties suggested the use of Bi-coated CNTs in biosensors. Bi-alloys, such as Bi-Sb alloy could also be used for this purpose. Bismuth–antimony is a semi-metal thermoelectric material which crystallizes in a rhombohedral structure with low effective mass and highly anisotropic fermi surface [1].

In this work the synthesis and the characterization of bismuth-based monometallic and bimetallic MWCNT nanocomposites were demonstrated and their comparison was investigated by spectroscopy. The MWCNTs were coated with bismuth nanoparticles and with bismuth–antimony alloy nanoparticles. Bismuth and bismuth–antimony alloy nanoparticles have been synthesized by a modified solvothermal method [1] using ethylene glycol as solvent/reducing agent, $BiCl_3$ and $SbCl_3$ as precursors, and citric acid as a surface modifier/stabilizing agent. The nanocomposites were characterized by transmission electron microscopy (TEM), scanning electronmicroscopy (SEM), X-ray and electron diffractometry (XRD, ED), Energy dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), Infrared Spectroscopy (IR) and Raman spectroscopy.

In this contribution we will focus on applicability of spectroscopic methods to the monitoring of the coating process.

Keywords: Bi-Sb alloy nanoparticles; nanocomposites; MWCNTs; Raman spectroscopy

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TEMPERATURE VARIABLE MÖSSBAUER SPECTROSCOPIC AND ELECTRON PARAMAGNETIC RESONANCE STUDIES OF HUMAN FERRITIN, FERRUM LEK AND MALTOFER®

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Ferrum Lek and Maltofer® are commercial pharmaceutical models of iron storage protein ferritin used for a treatment of the iron deficiency anemia. Ferrum Lek and Maltofer® are iron polymaltose complexes with an iron core in the form of the ferric hydrous oxide, probably β–FeOOH, surrounded with a polymaltose shell. In contrast, the ferritin consists of 24 protein subunits shell surrounding the iron core in a form of the ferrihydrite. In spite of numerous studies of the ferritin and its pharmaceutical models performed so far, there is no exact information about the iron core structure in these macromolecules. Therefore, we continue the investigation of the ferritin, Ferrum Lek and Maltofer® using the Mössbauer spectroscopy and the electron paramagnetic resonance (EPR) at various temperatures.

A human liver ferritin and commercial samples of Ferrum Lek and Maltofer® were studied using a Mössbauer spectrometric system with a high velocity resolution (registration in 4096 channels) at 295 and 90 K, and using a Mössbauer spectrometer with a lower velocity resolution (registration in 256 channels on both direct and reverse motion with a following channels folding) at 40 and 20 K. Additionally, the EPR spectra were recorded on the samples using a Bruker ElexSys E500 X-band EPR spectrometer.

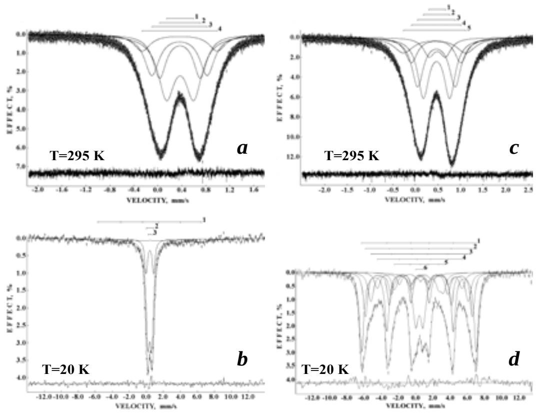

Fig.1 Mössbauer spectra of human ferritin (***a***, ***b***) and Ferrum Lek (***c***, ***d***) measured with the high velocity resolution spectrometer in 4096 channels (***a***, ***c***) and with the low velocity resolution one in 256 channels (***b***, ***d***).

Mössbauer spectra of the ferritin and Ferrum Lek samples are shown in Fig. 1. It was revealed that the studied samples had different superparamagnetic behavior at chosen temperatures. Such behaviour could be a result of a different iron core size and/or its structure. The present data confirmed our previous results on a complex iron core structure in the ferritin and its models [1]. The EPR spectra of the ferritin, Ferrum Lek and Maltofer® could be decomposed into multiple spectral components that demonstrated the presence of ferro- or ferrimagnetic phases along with revealing marked differences among the substances.

Keywords: Mössbauer spectroscopy; Electron paramagnetic resonance; Ferritin and its pharmaceutical models

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ASSESSMENT OF MOLECULAR SELF-ASSOCIATION BY ^{1}H NMR SPECTROSCOPY AND ISOTHERMAL TITRATION CALORIMETRY

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The molecular self-assembly relies on noncovalent interactions the key elements being the chemical complementarity and structural compatibility. Even if the individual interactions are weak, due to their large numbers they will dominate the conformation of the built supramolecular structures. The materials built by self-assembly allow for a higher structural tunability their bulk properties being imposed by the specific characteristics of individual monomeric building blocks.

A self-association process in solution seems to be extremely often encountered in the case of organic molecules that have aromatic rings. The tendency is to aggregate into stacking structures which reduce the potential energy related to π-π interaction and also the hydrophobic energy which depends mainly on solvent accessible surface area.

The equilibrium size distribution of *n*-mers depends on the association constants K_n which govern the step-wise self-association processes where a monomer is captured by an aggregate with *n*-1 monomeric units. Depending on their particular field of interest different research teams use a variety of models which they consider appropriate for describing such processes.

The main goal of our contribution is to provide a comparative study of several models used to describe the molecular self-association processes. The models will be tested on experimental data provided by two frequently employed techniques: ^{1}H NMR spectroscopy and Isothermal Titration Calorimetry (ITC).

The appearance of stacked aggregates is reflected by the strong concentration dependence of proton chemical shift. NMR spectroscopy has some advantages over optical investigations of molecular self-association in solution because it can be used to determine both the equilibrium and structural details of aggregates formation in solution.

Alongside NMR experiments we will assess the envisaged models by testing their capability to fit calorimetric data. ITC is one of the most relevant calorimetric techniques designed to investigate the physical basis of molecular interactions. A single well-designed experiment can provide complete thermodynamic characterization of a binding reaction, including the equilibrium constant K, the Gibbs free energy ΔG, the reaction enthalpy ΔH, the entropic effect ΔS and the reaction stoichiometry (n).

Keywords: molecular self-association; stacking molecular aggregates; size distribution.

A RAMAN SPECTROSCOPY STUDY OF THE BETA-LACTOGLOBULIN OXIDATION BY HYDROGEN PEROXIDE

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Beta-lactoglobulin is a major protein of whey. It has been widely studied thanks to its easy purification and stability [1]. Proteins like beta-lactoglobulin are used in the food industry for lipid emulsion and protect lipids from oxidation. It has been shown that some of the residues of the protein were first oxidized before lipid oxidation starts [2]. In order to investigate this activity, for which the mechanism remains unknown, we have studied the beta-lactoglobulin oxidation by the hydrogen peroxide using Raman spectroscopy. Among the reactive oxygen species (ROS) present in the living cell, hydrogen peroxide has a rather weak reactivity. Its importance comes from the fact that it is a byproduct of the normal aerobic cell metabolism, hence its concentration in the biological environment is significant.

A preliminary study has been carried out on the oxidation of tripeptides containing reactive residues in the presence of hydrogen peroxide. The following tripeptides have been studied: Gly-Trp-Gly, Gly-Tyr-Gly, Gly-His-Gly, Gly-Phe-Gly and Gly-Met-Gly. Among all the oxidized tripeptides, only the Gly-Met-Gly showed relevant Raman spectrum modifications. Those modifications arose from the formation of a sulfoxide group with a characteristic Raman band at 700 cm^{-1}. The appearance of this Raman band has been monitored with respect to time and allowed us to determine the corresponding reaction rate constant (Fig.1).

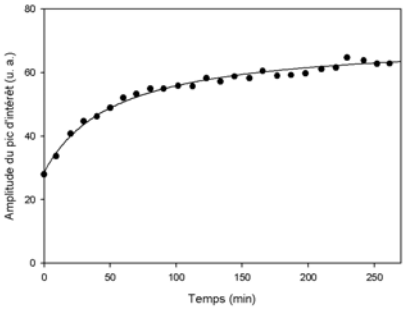

Fig.1 Reaction kinetics studied for the Gly-Met-Gly oxidation by hydrogen peroxide.

The Raman band at 700 cm^{-1} has then been used as a marker to study the beta-lactoglobulin oxidation by hydrogen peroxide. The evolution of the amplitude of this band was used to determine the reaction rate constant. The comparison of the reaction rate constant for the tripeptide and respectively for protein oxidation gives information about the role of the protein environment in the oxidation process.

Keywords: Raman spectroscopy; beta-lactoglobulin; methionine; hydrogen peroxide; oxidation

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FOURIER TRANSFORM MICROWAVE SPECTRUM OF *N*-PENTANOL

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In order to obtain information on stable conformations and internal motions of saturated C_4 alcohols and thiols, we have analyzed their rotational spectra observed by Fourier transform microwave (FTMW) spectroscopy combined with quantum chemical calculations, and have found that the most stable conformers of the *n*-butanol and the *iso*-butanol were *Gt* forms, namely *gauche* with respect to the C-CO bond axis and *trans* with respect to the C-OH bond axis. We have extended the microwave study to the *n*-pentanol, and will report the results in the present paper, in comparison with those on the *n*-butanol.

The *n*-pentanol has four internal rotation axes: three C-C bond axes, which generate either *gauche* or *trans* conformers: *G*, *G'* or *T* and the fourth around a C-O bond axis, yielding again *gauche* or *trans* conformers *g*, *g'* or *t*. We thus expect 41 rotational conformers to be stable. The vapor pressusre of the *n*-pentanol is low at room temperature, requiring the nozzle to be heated up to around 50ºC. We scanned the frequency region from 6 to 23 GHz using a sample of *n*-pentanol diluted with Ar or Ne. With Ar as a buffer gas, we readily detected the spectra of three conformers: *TTGt*, *TGTg*, and *TTTt* and assigned them with the aid of quantum chemical calculations. Among them the *TTGt* is likely to be most stable because its spectra were strongest. When Ar carrier gas was replaced by Ne, we found three new conformers, *TTTg*, *TTGg'* and *TTGg*. The spectrum of the *TTTg* was found to be split by a few MHz, presumably because of the internal rotation of the OH group. The assignment of the observed spectra to the *TTGg* form was based upon the fact that the *b*-type transitions were stronger than the *a*-type ones. It is interesting to note that all the six conformers of the *n*-pentanol make good correspondence with those of the *n*-butanol: *TGt*, *GG't*, *TTt*, *GTg*, *TGg*, *TTg*, and *TGg'*, if *T* is added as the conformation for the first C–C bond, except for *GG't*.

Quantum chemical calculations at the MP2, B3LYP, and *cam*-B3LYP levels with basis sets 6-311++G(*d*, *p*) all showed that the most stable conformer was *TTGt*. The *cam*-B3LY among others yielded results in best agreement with the experimental results. The MP2 calculation tends to overestimate the strength of the hydrogen bond, and is thus not suitable for estimating the conformational stabilities of alcohols, and DFT calculations are preferred in this respect.

The relative intensities of the doublets of the *TTTg* form were significantly different, the $I_{\text{antisymmetric state}}$ to $I_{\text{symmetric state}}$ ratios of the *a*-type transitions being around 0.6. We derived the eigenvalues and eigenfunctions of the internal rotation of the OH group by using a *cam*-B3LYP/6-311++G(*d*, *p*) calculated potential energy surface around the C-O bond axis. The energy difference between the *symmetric* and *antisymmetric* states was calculated to be 1.5 cm^{-1}, leading to the intensity ratio of 0.67, in good agreement with the experiment, provided that the beam temperature was assumed to be 5 K.

Keywords: Fourier transform microwave spectroscopy, alcohol, rotational isomer, quantum chemical calculation

A NEON-MATRIX ISOLATION STUDY OF THE REACTION OF NON-ENERGETIC H-ATOMS WITH CO MOLECULES AT 3 K

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The efficiency of HCO formation stemming from non-energetic H-atoms and CO molecules is highlighted both in the condensed phase and within a neon matrix environment which is half-way from the condensed-phase and the gas-phase. Our experiments demonstrated that HCO production within the neon-matrix needed very little activation energy, if any, and that the efficiency of HCO formation depended only on the capacity for H-atoms to diffuse in the solid to subsequently encounter CO molecules. The novelty of the present matrix experiment sheds light to some point on the debated question of the requirement or not of activation energy in order to produce HCO, because of the use of non-energetic ground state H-atoms within the neon-matrix.

WATER ACCESSIBILITY TO MEMBRANE-BOUND LIPOPEPTIDE BY PULSED EPR

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Trichogin GA IV is a membrane-active lipopeptide antibiotic of fungal origin, which is known to be able to modify the membrane permeability. The electron spin echo envelope modulation (ESEEM) technique allows examining different water accessibilities for peptide-attached spin labels at different levels of membrane insertion.[1-3] Application of this technique originates from the interaction of the anisotropic hyperfine (hfi) interactions as well as nuclear quadrupole interactions between the unpaired electron of a spin label with the nearby located magnetic deuterium nuclei of D_2O hydrated membranes. Since water molecules are less abundant in the hydrophobic core of the membrane, the amplitude of the ESEEM spectrum depends on the depth of the peptide label position relative to the membrane surface. Thus, the water-induced modulation amplitudes observed for spin labels attached to different positions of the peptide chain provide an indicator for the orientation as well as the penetration depth of the membrane bound peptide.

In the presentation, the usefulness of a double calibration ESEEM method will be demonstrated to determine the immersion depth of the peptide attached spin labels as a function of the lipid acyl chain carbon numbers. The new method is based on the ESEEM modulation that occurs by interaction between the peptide attached spin label and deeply membrane inserted deuterated alkyl chains of CHOL-d_7 molecules. In this manner both the orientation and immersion depth of the lipopeptide molecules are determined independently and compared with the data obtained from the D_2O method. The mismatch between the immersion depths found by these two different methods might be attributed to peptide associated water on top of the presence of natural abundance water in the membrane.

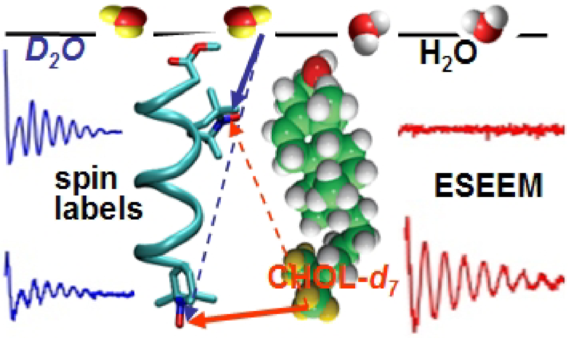

Fig. 1. Double calibration used to determine the position of the spin label in the lipid membrane

Keywords: ESEEM, TOAC spin label, cholesterol

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FLUORINATED MOLECULES/OLIGOMERS AND HYDROGEN BONDING A SPECTROSCOPIC AND DFT INVESTIGATION

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A wide set of fluorinated and emifluorinated molecules and oligomers containing functional groups have been studied. The chemical groups considered are: Rf-CH_2–OH (alcoholic groups) [1] Rf-COOH (carboxylic acid) [2] Rf-$CONH_2$ (amidic groups) [3,4] and Rf-COO-X^+ (carboxylic acid salts). They have been studied by means of vibrational spectroscopy (IR-Raman) and the experimental data have been supported by a wide computational investigation based on Density Functional Theory (DFT) calculations: this combined approach gave very fruitful results.

We observed that these structures may give rise to strong inter and intramolecular interaction; some experimental data showed indeed complex spectral patterns (e.g. Fig.1). The spectroscopic features observed are clear signs of aggregation phenomena which prevent the simple and easy use of intensity data for analytical purposes. In some cases we studied also the effect of the presence of water (hydration) and temperature on the overall spectroscopic behaviour.

Kinetic experiments [3] from RT till 150^{o}C allowed to follow the evolution of the aggregation phenomena from the spectroscopic behaviour and where possible, also melting phenomenon and crystallization. DFT modeling guided us to the correct assignments of main band variations in the spectral data collected.

Another approach to study the spectroscopic evolution is Two Dimensional Correlation Spectroscopy (2D-COS) [4]; this has been expecially useful to reveal minor spectroscopic variations and their relations with bands due to the same chemical species, but involving different normal modes.

These studies actually demonstrate the importance and the effectiveness of a synergic experimental/computational approach in the investigation of complex fluorinated materials. The results obtained allowed to propose definite assignments to main features observed and to find out absolute intensities; these information are now used in a classical analytical framework.

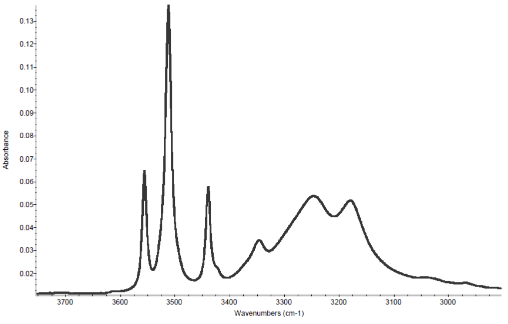

Fig. 1 IR Spectrum fluorinated amide: NH stretching region

Keywords :vibrational spectroscopy; fluorinated molecules; quantum mechanical modeling; two dimensional correlation spectroscopy

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STRUCTURE AND EQUILIBRIA OF THE Ca–HEPTAGLUCONATE COMPLEX IN AQUEOUS SOLUTION STUDIED BY MULTINUCLEAR NMR SPECTROSCOPY, POTENTIOMETRY AND COMPUTATIONS

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Sugar derivatives are known to form weak complexes with Ca^{2+} ion. Their structures in solution have only been studied sporadically. Recently, we have been involved in a comprehensive study concerning the structure and equilibria of Ca^{2+}–gluconate complexes in aqueous solutions, using a broad range of Ca^{2+} and gluconate concentrations and ionic strengths [1] at room temperature. Structural information was derived from multinuclear NMR measurements and stability constants were quantitatively estimated with the help of the PSEQUAD program [2].

As the continuation of the work the ligand was changed to the heptagluconate ($HGlu^{-}$) ion, the pH of the solution was extended from neutral to basic and the temperature range was also widened to the 5°C–55°C region. ^{43}Ca and ^{1}H NMR spectroscopies were the major experimental tools and measurements were complemented with potentiometric titrations using Ca-ISE and also with quantum chemical calculations. The aim of this combined experimental and computational work was finding the complexation sites on the ligand(s) and to elucidate the structure and also to characterize equilibria of the complex(es) formed.

The ^{1}H NMR spectra recorded for alkaline $Ca^{2+}/Hglu^{-}$ system at 5 °C the chemical exchange between the various forms of $Hglu^{-}$ (uncomplexed and complexed) became slow enough on the NMR time scale. The signal of the OH proton belonging C2 of $Hglu^{-}$ and that of the Ca^{2+} complex appeared separately reflecting the deprotonation of that group. At 55 °C the chemical exchange between the two types of heptagluconate ions were fast on the NMR time scale, thus they appear together on the spectrum. This was the case for somewhat less basic solutions at each temperature, however, 2 D ^{1}H–^{43}Ca NMR measurements could be used for identifying complexation sites.

Structural model for the Ca-heptagluconate complex could be given combining the results of multinuclear NMR measurements and quantum chemical calculations. For molecular modeling the initial geometries of the naked cation was taken from *ab initio* (HF 6−31 G** basis set) calculations previously performed on the isolated cations, then in the presence of explicit water molecules reoptimisation was performed. The combination of experimental and computational efforts lead to a scorpionate type of model in which beside the coordination of the carboxylate oxygens and the oxygen of the deprotonated OH at C2, the oxygen atom of the OH group at the terminal carbon was also a coordinating site.

Keywords: Ca-heptagluconate complex; basic solutions; multinuclear NMR spectroscopy; molecular modeling; scorpionate-type complex

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THE STABILITIES OF CaFe LAYERED DOUBLE HYDROXIDES WITH VARIOUS Ca:Fe RATIOS STUDIED BY MÖSSBAUER SPECTROSCOPY, X-RAY DIFFRACTOMETRY AND THERMAL ANALYSIS

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Layered double hydroxides (LDHs) are inorganic lamellar compounds with the general chemical formula: $[M_{1-x}{}^{2+}M_x{}^{3+}(OH)_2]_x+(A_{x/n}{}^{n-})\times mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal ions, and x is the ratio $M^{3+}/(M^{2+} + M^{3+})$. Through partial isomorphous substitution of M^{2+} for M^{3+} , their structure can be varied leading to interesting properties that are important in industrial applications as catalysts (after calcination), catalyst supports, anion exchangers, polymer stabilizers, adsorbents, fillers, *etc.* [1,2].

The aim of the present work was to investigate the effect of the Fe content on the structure of the LDH and the microenvironment of Fe in $[Ca_{1-x}{}^{2+}Fe_x{}^{3+}(OH)_2]_x+(Cl_{x/n}{}^{n-})\times mH_2O$ LDH on one hand, and studying the stabilities of the various samples with changing Ca:Fe ratios, on the other. The CaFe LDHs were prepared by the co-precipitation method applying aqueous NaOH with Ca:Fe ratios from 2 to 6. For the characterization of the obtained substances, ^{57}Fe Mössbauer spectroscopy in the 20 K – 295 K temperature range, powder X-ray diffractometry and thermal methods (TG, DTG, and DTA) were applied.

XRD measurements confirmed the formation of LDH structures.. All reflections could be indexed as LDH for the Ca_2Fe LDH sample, while for the others reflections of $Ca(OH)_2$ also appeared, in increasing intensities with the increase in the Ca:Fe ratios. Although d(003) basal distances also increased with the increase in the Ca:Fe ratio, the proportion of $Ca(OH)_2$ went up reaching ~60 weight% for the Ca_6Fe LDH sample.

Thermogravimetric measurements also revealed that there was significant difference in the thermal behavior of Ca_2Fe and the Ca_6Fe LDH samples.

^{57}Fe Mössbauer patterns for all the samples at all temperatures were asymmetric doublets. The Mössbauer parameters reflected high spin Fe(III) microenvironments. At all temperatures, the quadrupole splittings (QS) were the same for all samples except for the Ca_2Fe LDH, for which QS was significantly higher. Interestingly, upon standing, the quadrupole splitting of the Ca_2Fe LDH sample was changed, while those of the others did not. This an indication of the deterioration of the sample on ageing verified by XRD measurement as well. It has been found that the clean Ca_2Fe LDH reacted with the CO_2 content of the air, turning the substance predominantly to $CaCO_3$. At the same time the presence of $Ca(OH)_2$ seemed to stabilize the LDH samples with higher Ca:Fe ratios.

Keywords: CaFe layered double hydroxide; varying Ca:Fe ratios; ^{57}Fe Mössbauer spectroscopy; X-ray diffractometry; thermal methods; stabilities of the LDHs

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N, N'-DIALKYLIMIDAZOLIUM TETRACHLOROAURATE IONIC LIQUID SALTS

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Geometrical optimization, spectroscopic analysis, electronic structure and nuclear magnetic resonance of N,N'-dialkylimidazolium tetrachloroaurate were investigated by utilizing a*b-initio* (MP2) and DFT(B3LYP) computational methods. Geometrical parameters (bond lengths, bond angles and torsion angles) were computed and compared with the experimental values obtained using X-ray single crystal measurements of the title compound. The computed data showed good agreement with the experimental results.

The theoretical infrared spectra have been simulated at B3LYP/Lanl2Dz and MP2/ Lanl2Dz level of theories. All the data obtained in this investigation was considered to be reliable. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) chemical shifts of N,N'-dialkylimidazolium tetrachloroaurate were calculated using GIAO methods in $CDCl_3$ solution using IEF-PCM model and compared with the experimental data. Intramolecular hydrogen bonding interaction in this compound was investigated by means of NBO analysis. The calculated HOMO and LUMO energies show that charge transfer occurs within the molecule.

From this study it can be concluded that the computational investigation on the geometrical structure, molecular spectroscopy and electronic properties of the title compound matched well and the compound could be of potential use as a candidate in non-linear optics (NLO) applications.

Keywords: ionic liquid; gold; Spectroscopy

OPTICAL SPECTROSCOPIC STUDIES ON S-DERIVATIVE BIOMOLECULES INTERACTION WITH GOLD NANOSTRUCTURES

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Noble metal, particularly Au-functionalized molecule nanostructures are of considerable interest due to their potential applications to chemical, electronic devices, catalysts, material science and others fields [1].

Gold nanostructures may be passive structural elements, so that their superstructures can offer high surface area for molecules deposition, where the local interaction can be controlled by optical spectroscopic techniques such as UV-Vis, IR and Raman. Anchoring of the S-redox-active compounds on gold nanoparticles has been achieved by Au-S bonding [2,3] and electrostatic interactions [4], especially for the conductive supports [2,5].

In this contribution we present an optical spectroscopic study concerning the interaction of gold nanostructures with S-derivative biomolecules, cysteine and its dimmer cystine as zwitterion-type molecular cross-linkers, in order to elucidate its nature: covalent bonding or electrostatic one. Infrared spectra highlighted the Au-S bonding, whereas the kinetics study gave a scale-time dimension of the process relating to the molecules dimension. Also, transmission electron microscopy (TEM) images for these systems evidenced their evolution towards developing of supermolecular structures.

Keywords: S-derivative biomolecules, optical spectroscopic techniques; gold nanostructures

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AB INITIO DFT AND RAMAN STUDY OF MEDIUM RANGE ORDERING IN g-GeSe$_2$

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Amorphous (*a*) and/or glassy (*g*) chalcogenides are attractive class of non-crystalline semiconductor materials. Due to the unique physico-chemical properties of Ge-based chalcogenides they have a wide range of applications in infrared and non-linear optics, photonics, ultrafast signal processing and optical regeneration, information recording, biosensing etc. It is well known that crystalline GeSe$_2$ exist in two different low-temperature (LT or α) and high-temperature (HT or β) modifications. The common structural motif of these modifications is 6-member ring consisting three shared GeS$_4$ tetrahedra. The 3D network of LT GeSe$_2$ phase represents mutually connected 6-member rings. In contrast with LT, the HT-GeSe$_2$ contains 4-member rings or so called edge-shared GeSe$_4$ tetrahedra. The layer-like 2D network of HT-GeSe$_2$ can be viewed as infinite parallel chains of 6-member rings connected by edge-shared (4-member ring) blocks. The structure (especially at medium range order (MRO) scale) of a glassy state of GeSe$_2$ is more complex, contains homopolar Ge-Ge and Se-Se bonds and has been the subject of extensive studies during last decade.

Recently *ab initio* DFT calculations (B3LYP/LANL2DZ ECP polarized (p,d)) were performed on Ge$_n$Se$_m$ nanoclusters (n=2, 3, 5, 6, 12; m=6-9, 14, 16, 30) that represent the local structure of GeSe$_2$ glass and on some “defect” Ge$_n$Se$_m$ clusters that are thought to be related to the inhomogeneity of the structure at the nanoscale [1]. In this work we present the results of *ab initio* calculations together with Raman studies of binary GeSe$_2$ glass. The detail analysis of total cluster energies and their derivatives show the preference in formation of four-, six-member rings and bigger clusters that are topologically similar to the β-GeSe$_2$. We have found that the formations of so called “wrong” Ge-Ge and Se-Se bonds are energetically favourable when they are incorporated in five-member rings rather than in form of ethane-like cluster with Ge-Ge bond and cluster with Se-Se bridge. Also, some peculiarities in electronic properties of clusters with Se-Se bonds and their correlations with dihedral and bond angles were established [1]. We report here the results of extended spectroscopical studies of Ge$_n$Se$_m$ nanoclusters in order to elucidate the medium range structures of *g*-GeSe$_2$. The calculated frequencies (212 cm^{-1} (i=4), 194 cm^{-1} (i=6) and 184-185 cm^{-1} (i=8, 10) of main Raman active modes of Ge-Se stretching vibrations of i-member rings demonstrate red-shifting with increasing ring size (i). Also, the Raman mode at 168 cm^{-1} was calculated for 5-member ring with “wrong” Ge-Ge bond. The contribution of calculated Raman active modes of 4-, 5-, 6-, 8-, 10-member rings and bigger Ge$_n$Se$_m$ nanoclusters in the curve fitted micro Raman and FT-Raman spectra of GeSe$_2$ glass is analysed and discussed.

Keywords: Ab initio; Raman spectra; GeSe$_2$ glass

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AN INVESTIGATION ON THE CONFORMATIONAL STRUCTURE AND VIBRATIONAL MOTIONS OF SULINDAC MOLECULE BY IR AND RAMAN SPECTROSCOPIC MEASUREMENTS AND DFT-BASED QUANTUM MECHANICAL CALCULATIONS

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Stable conformers of *Sulindac* molecule (*Fig.1*) in electronic ground state were searched by molecular dynamics simulations carried out using *MM2* force field. The obtained results have indicated that the monomer molecule should have at least eighteen stable conformers. For each of the found conformers, the corresponding total energy, equilibrium geometrical parameters and vibrational spectral data were determined by means of successive geometry optimization and harmonic frequency calculations carried out at *B3LYP/6-31G(d)*, *B3LYP/6-31++G(d,p)* and *B3LYP/6-311++G(d,p)* levels of theory. Furthermore, for the most stable conformers which are expected to dominate the room-temperature experimental spectra of the molecule, the corresponding natural charges, *HOMO-LUMO* energy gaps, electronegativity and chemical hardness parameters were calculated at *B3LYP/6-311++G(d,p)* level of theory. In order to reveal the effects of dimerization on the structure and vibrational spectral data of *Sulindac*, the same calculations were repeated also for the energetically most favorable dimer forms of the stable conformers determined for the free molecule case. The overestimations at the calculated harmonic wavenumbers were corrected using two different scaling procedures called “Scaled Quantum Mechanical Force Field (*SQM FF*) methodology” and “Dual scaling approach”. In the light of these improved theoretical data, a correct assignment of the fundamental bands observed in the experimental IR and Raman spectra of the molecule, which was determined to be in dimer form at room temperature, was achieved.

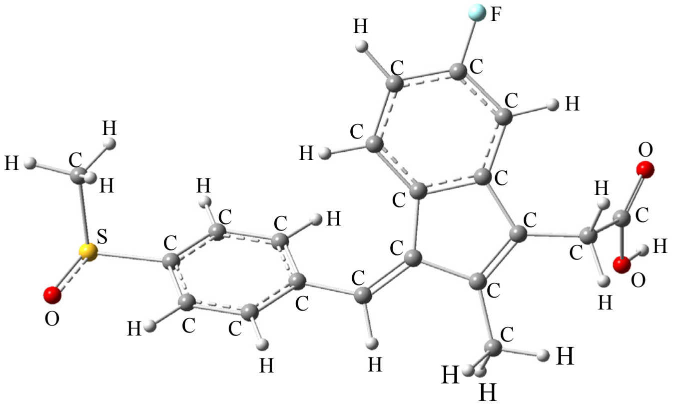

Fig.1. *The chemical structure of Sulindac molecule*

RAMAN SPECTROSCOPY OF THE HEMATOXYLIN-EOSIN STAINED TISSUE FROM PATIENTS WITH ADENOCARCINOMA

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Micro-Raman spectroscopy in conjunction with the classical histopathology has been employed for the diagnostic assessment of colon adenocarcinoma in human using hematoxylin-eosin (H&E) stained tissue. Ex vivo tissue samples from 9 patiens undergoing surgical intervention at the CFR Clinical Hospital of Cluj-Napoca have been analyzed. Raman spectra have been collected using different sampling protocol. Both malignant and histopathology normal tissue from the same patient have been analyzed, revealing good Raman reproducibility. The spectral response of the stained tissue has been analyzed taking into account H&E staining agents contribution [1].

The bands attributable to the tissues have been analyzed in comparison to those from the FT-micro-Raman measurement of the formalin fixed tissue samples. It was concluded that hematoxylin and eosin does not interfere in the tissue Raman signal, but the xylene and *Biomount* resins used in the staining protocol could hamper the Raman signal, particularly the high wavenumbers range (3000-2800 cm^{-1}) as well as in the fingerprint region. However, several significant bands in tissue Raman diagnostic are clearly resolved. Results from these H&E stained tissue samples point out the capability of the Raman techniques to evaluate the enormous archival tissue material available in clinical diagnostic laboratories and could further better assist the histopathology conclusions with high specificity and sensitivity.

Keywords: Micro-Raman, colon carcinoma, adenocarcinoma, hematoxylin, eosin, stained tissue

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STRUCTURAL AND VIBRATIONAL STUDY ON AMRINONE DIMERS AND AMRINONE-H_2O COMPLEXES

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Amrinone (3-amino-5-(pyridin-4-yl)-1,2-dihydropyridin-2-one), is a bipyridine cardiotonics and is used as a drug (trade name Inocor) in heart failure. It increases strength of contraction of myocardium. It is a phosphodiesterase inhibitor that has both positive inotropic and vasodilator actions. The combined actions of amrinone produce an increase in cardiac stoke output without an increase in cardiac stroke work. Amrinone is effective as single-agent therapy in the management of low output states caused by systolic heart failure.

The equilibrium structures, binding energies and vibrational harmonic frequencies for low energy conformations of amrinone dimers and amrinone-H_2O complexes have been studied using density functional theory at B3LYP/6-31G++(d,p) theory level. The widely used counterpoise correction scheme for basis set superposition error (BSSE) has been included in the calculations to take into account the BSSE effects during geometry optimization (on structure), on binding energies and on the vibrational frequencies of the dimers. The BSSE influence is found to be important, therefore removing this effect is necessary. The assignment of the vibrational modes was based on the Potential Energy Distribution data using GAR2PED program. The experimental vibrational wavenumbers of solid amrinone are found to be more close to the calculated wavenumbers of dimeric form amrinone of than its monomeric form.

Keywords: Amrinone, vibrational spectra, DFT calculations.

Acknowledgement:
This study was supported by the Research fund of Istanbul Kultur University.

A VIBRATIONAL SPECTROSCOPIC STUDY ON DANSYL FLUORIDE MOLECULE BY IR AND RAMAN SPECTROSCOPIC MEASUREMENTS AND DFT CALCULATIONS

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Possible stable conformers of Dansyl fluoride molecule (*Fig.1*) in electronic ground state were searched by molecular dynamics simulations carried out with MM2 force field. The obtained results have indicated that the molecule should have at least five stable conformers. For each of these conformers, the corresponding total energy, equilibrium geometrical parameters and vibrational spectral data were obtained by means of geometry optimization and harmonic frequency calculations carried out at B3LYP/6-31G(d), B3LYP/6-31++G(d,p), B3LYP/6-311++G(d,p) and B3LYP/aug-cc-pvTZ levels of theory. The corresponding effective atomic charges, HOMO-LUMO energy gaps, electronegativity, chemical hardness parameters of the conformers were determined by Mulliken Population Analysis and Natural Bonding Orbital (NBO) calculations performed at the same levels of theory and then these data were used in the interpretation of charge transfers between the sulfonyl-fluoride group and the naphthalene ring within the molecule. In order to reveal the anharmonicity characters of the vibrational normal modes, the cubic and quadratic anharmonicity correction terms to the harmonic wavenumbers calculated for the most stable two conformers, which are expected to dominate the experimental spectra of the molecule, were obtained at B3LYP/6-31++G(d,p) level of theory. The harmonic IR and Raman spectral data calculated for these two conformers were successfully fitted to those observed in the experimental IR and Raman spectra recorded at room temperature by using two different scaling procedures called “Scaled Quantum Mechanical Force Field (SQM FF) methodology” and “Dual scaling approach”.

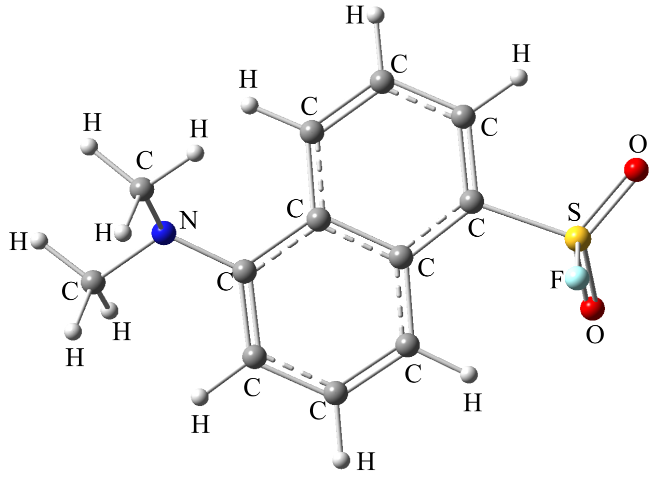

Fig.1. *The chemical structure of Dansyl Fluoride molecule*

VIBRATIONAL SPECTROSCOPIC INVESTIGATION OF 2-AMINO-4-METHYLPYRIMIDINE TETRACYANONICKELATE COMPLEXES

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In this study, the $M(AMPM)_2Ni(CN)_4$ (M= Mn, Co, Ni or Cd) complexes of 2-Amino-4-methylpyrimidine (AMPM) were prepared for the first time and their FT-IR (4000-400), FT-Raman (4000-50 cm^{-1}), far-IR (400-50 cm^{-1}) spectroscopy, X-ray diffraction, thermal and elemental analyses were investigated. All the vibrational modes of coordinated AMPM have upward shifts in frequencies compared to those in the free molecule, these shifts being metal dependent. Far-IR spectroscopic study allowed us to make correction in the bonding mode of AMPM. 2-Amino-4-methylpyrimidine molecules are found to involve coordination through one of the pyrimidine ring nitrogen atoms. The spectral features suggest that the compounds are similar in structure to the Hofmann type two dimensional coordination polymer compounds, formed with $Ni(CN)_4^{2-}$ ions bridged by $M(AMPM)_2^{2+}$ cations. Vibrational bands originated from both AMPM and $Ni(CN)_4$ group were assigned. Thermal behaviours of these compounds are followed using TG and DTA techniques.

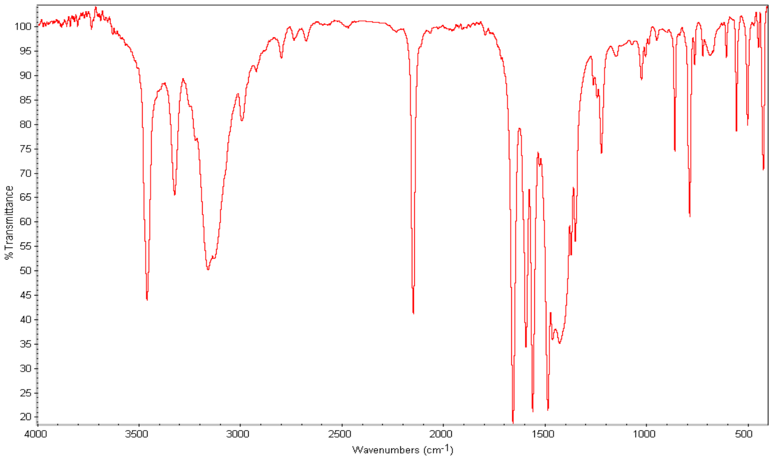

Fig. The FT-IR spectrum of the Cd-AMPM-Ni complex in KBr

Keywords: 2-Amino-4-methylpyrimidine; Infrared;Far infrared and Raman spectra

RAMAN SPECTRA OF POLY(DIMETHYLSILOXANE) NANOCOMPOSITES

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Polymer nanocomposites have attracted a great attention because the addition of inorganic nanoparticles to polymer matrix improves or generates new physical properties such as thermal, mechanical, electrical, magnetic or optoelectronic properties. It has now become clear that optimized properties can be achieved by a tailored manipulation of the interface between polymer and nanofiller.

Poly(dimethylsiloxane) (PDMS; repeating unit -O-Si(CH_3)$_2$-) is the most commonly used silicone polymer. Due to the good thermal stability, good biocompatibility, low toxicity and high chemical resistance pure PDMS as well as its nanocomposites have great potential for applications in biomaterial science (implants, contact lenses, tissue engineering), in aerospace as well as in the electronics and semiconductor industry. Recently we reported that PDMS nanodiamond composite exhibit enhanced stability against high energy proton irradiation as compared to pure PDMS [1].

In this research PDMS network was prepared by cross-linking based on hydrosilylation [2]. Cross-linked PDMS nanocomposites were prepared with different fractions of detonated nanodiamond (DND) and onion-like carbon (OLC) nanoparticles (0, 1, 2 and 5 wt %) [3]. The structure and vibrational dynamics of cross-linked PDMS nanocomposites was investigated by micro-Raman spectroscopy. The knowledge of the vibrational properties of prepared nanomaterials is of fundamental importance to the understanding of the influence of embedded nanoparticles on the process of polymerization and cross-linking. The analysis of Raman spectra of PDMS nanocomposites is based on the assignment of vibrational spectra of cross-linked PDMS nanocomposites and comparison with spectra of pure PDMS as well as with spectrum of DND or OLC nanoparticles. Changes in vibrational spectra of PDMS due to the inclusion of different fraction of nanoparticles were also used to explain the interaction in the interface and the effect of presence of nanoparticles on the polymer network structure.

Keywords: poly(dimethylsiloxane); nanocomposites; cross-linking

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SURFACE ENHANCEMENT RAMAN SPECTRA OF AMINO ACIDS

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Surface Enhanced Raman Spectroscopy (SERS) has successfully provided a way to detect and identify many organic compounds without the need for extensive sampling or the adoption of a destructive technique. The possibility to apply this diagnostic tool to investigate living beings or valuable objects, like artworks or archaeological finds, therefore, has been thoroughly evaluated [1]. In this study, the Surface Enhanced Raman effect has been exploited to reveal amino acids in aqueous solutions at different concentrations (10^{-1} to 10^{-5} M): the choice of relatively simple analytes aims for a more complete understanding of the chemical dynamics of the interaction between the molecule and the SERS substrate.

The measurements involved in this research work have been mainly carried on with the help of a commercially available portable Raman spectrometer (Horiba – Jobin Yvon); silver colloid, synthesized according to Lee and Meisel's recipe [2], have been tested as metal substrate for the Raman effect enhancement. A set of five amino acids, namely Lysine, Arginine, Methionine, Cysteine and Phenylalanine, has been chosen for the analysis under different experimental conditions.

Raman spectra of the amino acids in crystallized form (powder) has been compared to the ones of the water solutions of the same molecules. The same solutions, without changing the experimental parameters, have been analyzed 15 minutes after mixing (1:1 v/v) with the Silver colloid. Raman spectra of dried droplets of these samples have been taken as well.

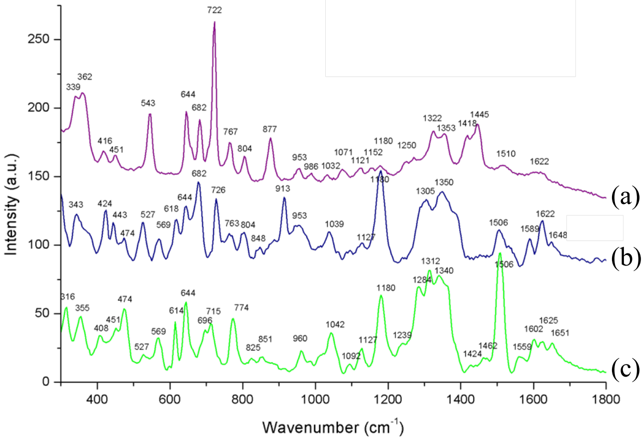

Fig. 1 Raman spectra (a) of L-Methionine in powder and in a solution 10^{-4} M, after mixing with Ag nanoparticles: liquid (b) and dried samples (c)

Notable enhancement has been recorded for different vibrational bands in the whole series of spectra, but detection of Methionine (Fig. 1) and Phenylalanine was made particularly easy by the interaction with the Ag colloid. Spectra of the dried samples of these two mixtures were collected with a significantly short acquisition time (30 s *circa*).

The successful detection and identification of two amino acids in water solution by the adoption of Silver nanoparticles paves the way for the analysis of more complex molecules (peptides, proteins) which can be present in traces over historical artifacts. The need for limited exposure times and the effectiveness of a compact Raman spectrometer are promising factors for a possible *in situ* application of this method.

Keywords: Amino acid; Surface Enhanced Raman Scattering; Methionine; Phenylalanine;

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NORMAL COORDINATES ANALYSIS AND COMPLETE ASSIGNMENTS OF THE VIBRATIONAL SPECTRA OF SUCROSE IN SOLID PHASE

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The crystal and molecular structure of sucrose ((2-[3,4-dihydroxy-2,5-bis(hydroxymethyl) oxolan-2-yl] oxy-6-(hydroxymethyl) oxane-3,4,5-triol) were experimentally determined by means of X-ray reflections [1,2] and neutron diffraction analysis [3]. The molecular structure is observed in the Figure 1. So far, only the main characteristics of the vibrational spectra in solid phase were reported in the literature, for this reason, in this study we perform a more detailed study of the IR and Raman spectra of sucrose combining an approximate normal coordinate analysis with the Pulay´s Scaled Quantum Mechanics Force Field (SQMFF) methodology [4] in order to carry out a complete and reliable vibrational analysis for sucrose. Here, the initial geometries for the compound were calculated with the Gaussian 03 [5] program at B3LYP theory level by using the 6-31G* and 6-311++G** basis sets. The optimized geometries of sucrose show that the glucopyran ring exists in the chair conformation while the glucofuran ring adopts an envelope conformation.

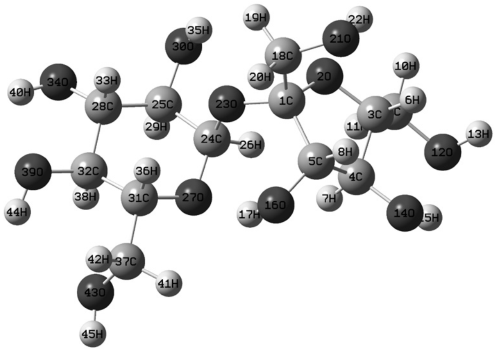

Fig.1 Theoretical structure of sucrose

In this study, we presented the assignments of the 129 vibration normal modes of sucrose and a set of scaled force constants fitting the theoretical wavenumbers values to the experimental ones. Moreover, the bond orders of both glucopyran and glucofuran rings and its second order perturbation energies were studied by using the NBO calculations [6] while, the possible charge-transfers and topological properties of those rings were analyzed by means of a AIM investigation [7].

Keywords: sucrose, Infrared spectrum, molecular structure, force field.

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NEW EVIDENCES FOR THE PRODUCTION OF *p,p'*-DIMERCAPTOAZOBENZENE THROUGH THE COUPLING REACTION OF *p*-AMINOTHIOPHENOL ON METALLIC NANOSTRUCTURES

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Since its discovery, Surface Enhanced Raman Scattering (SERS) has become an important tool for the spectroscopic analysis of molecular species, providing highly sensitive detection of analytes down to single-molecule level [1, 2]. The extensive application of SERS lies in its ability to give a high-quality vibrational spectrum of the molecular probe, adsorbed on the surface of a plasmonic nanostructure. Thus, SERS provides the means of elucidating the interaction of molecules with metallic nanoparticles, which is of critical importance for the foreseen biomedical applications of nanotechnology, ranging from targeted drug delivery vectors to sensing and imaging in living bio-environments.

In a previous work, through mapping the spatial distribution of the SERS signal of *p-aminothiophenol* (*p*-ATP), we demonstrated the presence of two molecular species onto the same plasmonic nanostructures, namely *p*-ATP and *p,p'*-dimercaptoazobenzene (DMAB) [3]. The results suggested a plasmon–assisted catalyst mechanism which takes advantage of the local temperature increase occurring at specific 'hot-spots' under laser irradiation Here we present further experimental results concerning the generation of DMAB through the coupling reaction of *p*-ATP adsorbed onto gold nanoparticles-decorated polystyrene nanospheres. Specifically, we investigate the direct effect of substrate temperature on the SERS response of *p*-ATP molecules by conducting controlled heating of the substrate (between 25 and 90 °C) with simultaneous recording of the SERS spectra. We found an intricate thermal-induced behavior of the charge transfer bands (1138, 1388 and 1432 cm^{-1}) which is consistent again with the presence of a new molecular species. In addition, the shape analysis of the vibrational band at 1078 cm^{-1}, enhanced through the electromagnetic mechanism, reveals a balanced contribution, depending on temperature, of two distinct bands which are assignable to *p*-ATP and DMAB, respectively. These results demonstrate that *p*-ATP adsorbed onto the surface of metallic nanostructures is subject to a thermal-assisted chemical conversion leading to the generation of DMAB.

Keywords: SERS, temperature, p-aminothiophenol, p,p'-dimercaptoazobenzene.

Acknowledgement

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CONFORMATIONAL PREFERENCES AND VIBRATIONAL SPECTRA OF GLYCYL-TYROSINE DIPEPTIDE

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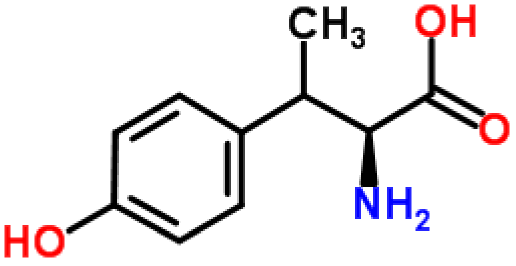
In this study conformational behavior of anti-tumor active Glycyl-Tyrosine (Gly-Tyr) dipeptide and its dimers have been investigated by molecular mechanics and DFT calculations. The calculations on Gly-Tyr dipeptide as a function of side chain torsion angles, enable us to determine their energetically preferred conformations. The relative positions of the side chain residues of the stable conformations of dipeptide were obtained, depending on the obtained conformational analysis results. The lowest energy conformation of the dipeptide has been determined by using the Ramachandran maps and the geometrical parameters of obtained stable conformations were used as starting parameters for DFT calculations. The geometry optimization, vibrational wavenumbers calculations of Gly-Tyr dipeptide were carried out with the Gaussian03 program by using density functional theory method with B3LYP functional and using 6-31++G(d,p) basis set. The dimeric forms of the dipeptide were also formed and energetically preferred conformations of dimers were investigated using the same method and the same level of theory. The fundamental vibrational wavenumbers, IR intensities and Raman activities of the global conformation of monomeric and dimeric forms of the dipeptide were calculated and compared with the experimental vibrational spectra of solid Gly-Tyr dipeptide. The assignments of the vibrational spectra were performed on the basis of the Potential Energy Distribution (PED) of the vibrational modes, calculated with Gar2ped program



Glycyl-Tyrosine dipeptide

GOLD NANORODS FOR IN VIVO CANCER SERS DETECTION AND PHOTOTHERMAL THERAPY

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In this work we show that the near-infrared plasmon resonance of gold nanorods (NRs) may be exploited to provide an integrated platform for in vivo multiplexed SERS detection and cancer photothermal heating. Particular emphasis will be given on in vivo SERS imaging and it will be shown how this technology can be integrated with photothermal cancer therapy and in situ drug delivery.

By screening mixed-monolayer NRs, coated with polyethyleneglycol polymers alongside SERS active molecules, we identified three NR formulations that can be uniquely distinguished in vivo over a spectral bandwidth of only 6 nm, a spectral multiplexing density over an order of magnitude greater than semiconductor quantum dots and fluorescence. Such dense multiplexing is fundamental for in vivo applications and allows Raman scattering to be efficiently excited and detected within the near-infrared optical window, where endogenous tissue absorption coefficients are minimal.

Unluckily, traditional means for delivering external energy into tumors lack selectivity over surrounding normal tissues. Plasmonic nanoantennas offer an opportunity to alter this paradigm by imparting their optical properties to tumor tissue and enabling deposition of otherwise harmless near-infrared energy into tumors. We utilized gold nanorods with peak plasmon resonance at 790nm, designed to match our SERS excitation source (785 nm) and still provide strong optical absorption at 810nm for photo-thermal heating. Our SERS-coded NRs are found to be highly stable, to be detectable down to attomolar particle concentrations, and to have low baseline cytoxicity in vitro. In vivo, they were efficiently detected and enabled remote photothermal tumor heating to ablative temperatures. Moreover, the NRs or a saline solution was injected intravenously into mice bearing two tumors on opposite flanks. Once the NRs had cleared from circulation, the right flank of each mouse was irradiated for 5 min and all tumors were measured at regular intervals. Within 10 days all the irradiated, NR-targeted tumors completely disappeared, while all other tumors continued to grow.

We also combined SERS imaging and photo-thermal therapy with in situ cancer drug delivery, using SERS- coded NRs and thermo-responsive liposomes loaded with anticancer drugs. Both nanomaterials passively accumulate into the tumor tissues. The heat generated via the NRs's surface plasmon was exploited for direct cancer destruction but also for triggering the selective release of drugs from the liposomes and increasing the therapy efficacy.

Keywords: Nanomaterials; Cancer Therapy; In vivo

NMR INVESTIGATION OF THE STRUCTURE OF CORN STARCH WITH PLASTICIZERS USED TO OBTAIN LOOSE FILL PACKING

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Native starches are non-plastic due to the intra- and intermolecular hydrogen bonds between the hydroxyl groups. Thermo-mechanical processing is used to disrupt and transform the semi-crystalline structure of starch granules to form a homogeneous and amorphous material. This transformation is usually accomplished by small amounts of plasticizers. The ratio between starch, glycerol and water, influences the structure and dynamics of polymer chains of this mixture and final product, too. The NMR relaxation method is successfully used in the last years to investigate these aspects for biodegradable polymers [1,2].

The normal corn starch with water content on wet basis (wt. b) of 10,76 % was mixed with glycerol with a concentration of 99.5% and a density of 1.262 g/cm^3 and water in different ratios. For homogenization, the components were thoroughly mixed and stored in sealed containers for 24 hours before performing the tests.

The ^{1}H NMR data were recorded using the Bruker Minispec spectrometer with the 10 mm probe-head working at 19.688 MHz Larmor frequency. The pulse length was 8.5 μs and 64 scans were recorded for the 1000 CPMG echoes with a recycle delay of 0.5 sec. In all measurements the temperature was set to 35 0C. Finally, in order to find the traverse T2 times distributions, the CPMG decays were analysed using the UPIN algorithm, which perform a Laplace inversion of the measured data [3].

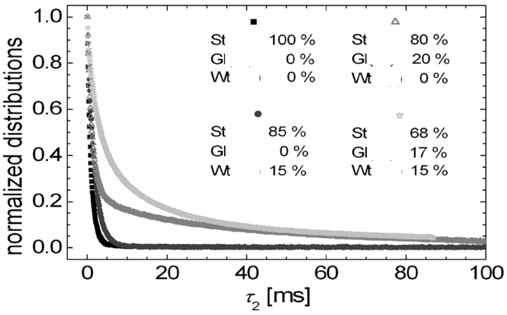

Fig.1. The CPMG echoes decays for the pure starch and starch (St) with plasticizers glycerol (Gl) and water (Wt)

Significant differences between the CPMG curve were observed for pure starch and the formulas in which water is added, whether these have or not glycerol in composition. For the formula that contains both plasticizers, the CPMG curve (light grey stars) decay slowest. The spin-spin relaxation time distribution has three peaks for pure starch and also for starch-water mixture. A distribution with four peaks appears in the case of starch-glycerol mixture, while remaining a significant part rigid enough (peak centered at 0.6 ms), the other peaks being in the area with dynamic soft-solid behavior (~2ms) and similar to liquid (~20ms and 70 ms). By combining the starch with glycerol and water the four peaks in spin-spin relaxation time distribution are kept. We mention however, that the maintaining of a rigid dynamic component of the starch polymer chain segments (~ 20 μs) corresponds to amylopectin component.

Keywords: NMR, starch, plasticizers, structure and dynamics

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OPTIMIZATION OF SERS SPECTROSCOPIC RESULTS: EFFECT OF METAL SELECTION AND EXCITATION WAVELENGTH USED

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Surface-enhanced Raman scattering (SERS) is an optical phenomenon used for spectroscopic detection and identification of trace amounts of analytes situated in the vicinity of a nanostructured surface of proper substrate. Suitable SERS-active substrates possess enhancements of several order of magnitude of acquired Raman signal. The band intensities of analytes can be affected by a number of more or less controllable factors. The most important effect is the quality of nanoscale structural motives of the surface morphology and repeatability of their preparation. The deposition conditions of a selected analyte as well as instability of experimental settings can also affect the spectral intensity. Electrochemical preparation of the substrate is a good and cheap alternative to commercially produced substrates and various colloidal systems. Recently, we have developed repeatable procedures for preparation of gold, silver and copper substrates, based on optimized sequence of current densities in the cathodic reduction of metal from electrochemical baths with/without additional post-modification of the surface morphology (e.g. oxidation-reduction cycles) [1-3]. The crucial question that has to be solved is: Is there any relationship among used metal materials, used electrochemical baths, excitation wavelengths and obtained spectra?

This study has been focused on various electrochemically prepared large-scale SERS-active substrates from coin metals (Ag, Au and Cu) with deposited monolayer of model aromatic analyte (4-aminobenzenethiol). Selected model analyte ensure a stable, regular organic monolayer and thus provide repeatable properties of organic layer. Each deposited substrate was measured repeatedly with series of excitation wavelength (i.e. 1064, 785, 633 and 488 nm). All measured spectra were accumulated under the same experimental conditions at ambient laboratory temperature. Obtained spectra were evaluated by chemometric analysis, usually after preprocessing (filtration of interferences [4], and removal of outliers [5]). We used chemometric multivariate methods to evaluate mainly the relation of measured spectral intensity to the metal material used. Furthermore, the parameters of preparation procedures were taken into account. Therefore, the possibility to harmonize the substrate for individual excitation wavelength by selection of appropriate material was tested.

The results show a rather complicated chemometric model with combined influence of many parameters. In addition to the selected metal, especially the composition of the electrochemical bath should be considered as a key parameter of optimization.

Financial support from the Czech Science Foundation (project No. P206/11/0951) is gratefully acknowledged.

Keywords: SERS spectroscopy; metal selection; wavelength selection, intensity dependence

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SPECTROSCOPIC INVESTIGATION OF A NEW THIAZOLIDINE COMPOUND WITH ANTIMICROBIAL POTENTIAL

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The treatment of infectious diseases is an important and challenging problem due to a combination of factors, including emerging infectious diseases and the increasing number of multi-drug resistant microbial pathogens. Bacterial resistance has become a serious public health problem, demanding new classes of antibacterial agents. Thiazoles and their derivatives have attracted the interest over the last decades because of their varied biological activities: antibacterial, antiviral, antifungal, inflammation or in the treatment of allergies.

A new synthesized compound 3-[2-(4-Methyl-2-phenyl-thiazol-5-yl)-2-oxo-ethyl]-thazolidine-2,4-dione was investigated by 1H NMR and vibrational spectroscopy [1].

The ^{1}H and ^{13}C NMR spectra of this new compound were recorded at room temperature on a Bruker Avance III NMR spectrometer operating at 500 MHz for ^{1}H and 125.76 MHz for ^{13}C, internal standard TMS. The sample was prepared by dissolution in DMSO-d_6 (signal for ^{1}H at 2.512 ppm and at 39.476 ppm for^{13}C). The spectra were recorded using a single excitation pulse of 10.1 μs for ^{1}H and 8 μs for ^{13}C. The FID signal was acquired 32 times for ^{1}H and 1024 times for ^{13}C [2].

In addition, vibrational techniques (IR and Raman) were used to evidence the structure of the new synthesized compound and the spectra obtained present the bands corresponding to the structural units of this compound. Vibrational spectroscopy offers functional group analysis through direct observation of the chemical bond itself [3]. It can also determine the formation of the reaction products through the obtained spectra.

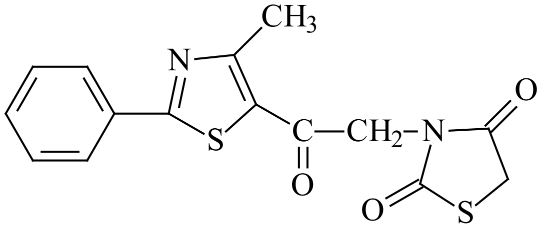

Fig. 1. 3-[2-(4-Methyl-2-phenyl-thiazol-5-yl)-2-oxo-ethyl]-thiazolidine-2,4-dione

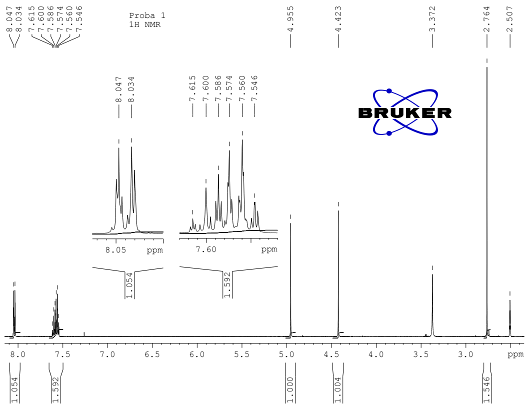

Fig. 2. ^{1}H-NMR spectrum of 3-[2-(4-Methyl-2-phenyl-thiazol-5-yl)-2-oxo-ethyl]-thiazolidine-2,4-dione

Keywords: thiazolidine, NMR, vibrational spectroscopy

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IR, RAMAN AND NMR INVESTIGATION OF A NEW BENZALDEHYDE ISONICOTINO-HYDRAZIDE COMPOUND

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A new aroyl-hydrazone compound was synthesized by condensing the 4-[2-(4-methyl-2-phenyl-thiazole-5-yl)-2-oxo-ethoxy]-benzaldehyde with isonicotinoyl hydrazide, in refluxing acetic acid 50%. The purity of this compound was determined by thin layer chromatography (TLC) and its antibacterial activity was also demonstrated [1].

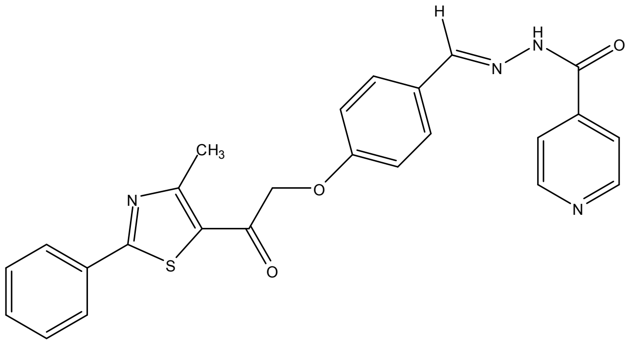

Fig.1. N'-{4-[2-(4-methyl-2-phenyl-thiazole-5-yl)-2-oxo-ethoxy]-benzylidene}izonicotinohydrazide

The following spectroscopic methods IR, Raman and ^{1}H, ^{13}C-NMR, and also DFT calculations were used to elucidate some structural aspects of the investigated compound.

The IR spectrum shows the absorption band at 1654 cm^{-1} characteristic for the carbonyl group in hydrazide moiety and ν (N-H) band from CONH group appears at 3397 cm^{-1}. The band at 1552 cm^{-1} assigned to ν(C=N) of azomethine group is an evidence for the condensation reaction between the aldehyde group and the hydrazide. The band at 1669 cm^{-1} is assigned to ν(C=O) group from the 5 position of the thiazole ring [2].

The chemical shift of the singlet NH proton peak appear at 11.99 ppm. The N=CH proton signal appears at 8.44 ppm. The chemical shift of the protons from methyl group appears at 2.78 ppm in the form of a singlet peak and the protons from methylene appears at 5.43 ppm in the form of a singlet peak. The chemical shift of the aromatic protons appears at 7 – 9 ppm.

Geometrical isomerism has an important role in the bioactivity of the aroyl-hydrazones and in their capability of bonding with the target. Thus, the ^{1}H NMR spectra indicated that the chemical shift of the NH proton at 11.99 ppm in the form of a singlet peak of an intense signal is assigned to the NH proton of E isomer. The presence of single downfield resonating (8.44 ppm) CH=N signal accounts for formation of E-isomers exclusively [3].

Keywords: isonicotinoyl hydrazide, IR, Raman, NMR

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EPR STUDY OF QUERCETIN RADICALS PRODUCED BY LACCASE

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Laccases are copper-containing oxidase enzymes, that couple the four-electron reduction of oxygen with the oxidation of a broad range of organic substrates including phenols, polyphenols and even some inorganic compounds [1, 2]. The various aromatic substrates (particularly phenolic hydroxyl groups) typically generate free radicals:

$$4\ \mathrm{Phe-OH} + \mathrm{O_2} \xrightarrow{\text{laccase}} 2\ \mathrm{H_2O} + 4\ \mathrm{Phe-O^{\bullet}}$$

Such free radicals are expected to be detectable by Electron Paramagnetic Resonance (EPR) spectroscopy. A commonly applied technique in this respect is the spin trapping method.

In our contribution we employ EPR on a newly-isolated laccase from *Sclerotinia sclerotiorum* [3] in order to produce, detect and characterize the free radicals generated by this enzyme, using quercetin as organic substrate. The spin trapping agent, 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), was employed to this end, due to its known efficiency in determination of carbon-, oxygen-, sulfur-, and nitrogen-centered radical species.

Simulations of the experimental EPR spectrum (Fig. 1) based on estimated coupling constants of the spin-trapped quercetin radical using the Winsim program [4] show that the lowest configuration for the best fitting, consists of mixture of three radicals. A first species with A_N=15.11 G and A_H=23.67 G is specific to the DMPO/-carbon radical, and may be taken to represent a quercetin radical; density functional theory (DFT) results on such a species are presented. A second species with A_N=14.21 G and A_H=9.67 G corresponds to the DMPO/OH spin adduct, suggesting that under turnover our enzyme does allow for generation of hydroxyl radicals; a possible explanation may be the direct reaction between quercetin free radicals and molecular oxygen. A third spin-trapped species, with A_N=14.72 G, can be considered as a ditert-butyl-nitroxide derivative, that may occur upon oxidation of DMPO.

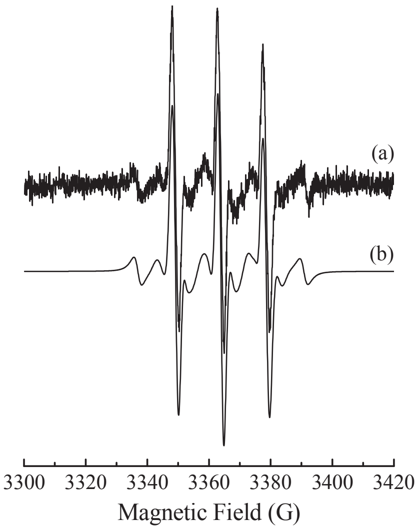

Fig.1. Experimental (a) and simulated (b) EPR spectrum of DMPO/quercitin derived radicals

Keywords:Laccase, Quercitin, DMPO, EPR

Acknowledgement. Funding from the Romanian Ministry of Education and Research, grant PCCE 140/2008 is gratefully acknowledged.

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THERMAL DECOMPOSITION OF 3-AZIDOPROPIONITRILE STUDIED BY UV PHOTOELECTRON SPECTROSCOPY AND MATRIX-ISOLATION IR SPECTROSCOPY

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Compounds containing the azido group (-N_3) have drawn considerable attention [1, 2] mainly because of their role as primary agents in explosive reactions. They may react violently upon increase of temperature or a strong mechanical stimulus, releasing a large amount of energy through elimination of N_2 from the azide chain. The way the decomposition onsets usually leads to two different outcomes. If a nearby hydrogen or alkyl group is captured, via 1, 2-H or CH_3 shift, an imine is formed (Type 1 mechanism) [1]. A Type 2 process, involves nucleophilic attack of the electron deficient nitrogen in the N_3 group on a remote site of the molecule; in this case, fragmentation of the molecule from formation of a cyclic intermediate or transition state is possible with formation of nitrogen during this process.

Nitrenes and imines are known intermediates in the thermal decomposition and photochemistry of organic azides, sometimes giving rise to byproducts that can be detected if appropriate techniques are employed. Being used together, UV photoelectron spectroscopy (UVPES) and IR spectroscopy of matrix-isolated species (matrix-isolation IR) share a common history of success regarding the pyrolysis of azides and real-time monitoring of their decomposition processes [2].

A recent example concerns the pyrolysis of methyl 2-azidopropionate ($N_3CHCH_3COOCH_3$), where the corresponding iminopropionate is found to be formed from the most favourable decomposition pathway, albeit the existence of a competing channel that leads to the formation of 5-oxazolidone [2].

The 3-azidopropionitrile (3APN), $N_3CH_2CH_3CN$, is studied in terms of its electronic structure and vibrational behaviour, using UVPES and matrix isolation IR spectroscopy. The pyrolysis of 3APN is also monitored using these techniques, up to full thermal decomposition. This study is supported by several quantum chemical methods, in order to provide a mechanistic explanation of the overall pyrolysis process [3].

Keywords: 3-azidopropionitrile, ketenimine, photoelectron spectroscopy, matrix-isolation IR

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STUDY OF INTERACTIONS BETWEEN DNA/RNA NUCLEOTIDES AND PHENPOD BY SURFACE ENHANCED RAMAN SPECTROSCOPY

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PHENPOD is a multifunctional molecule consisted of 1,10-phenanthroline as linkage for two aza-crowns containing pyridine.

Surface-enhanced Raman scattering (SERS) was used to study interactions between PHENPOD and DNA/RNA mononucleotides (AMP, GMP, CMP, UMP), single-stranded RNA polynucleotides (poly A, poly G, poly C, poly U) and double-stranded DNA/RNA polynucleotides (poly dAdT-poly dAdT, poly dGdC-poly dGdC, poly rA-poly rU).

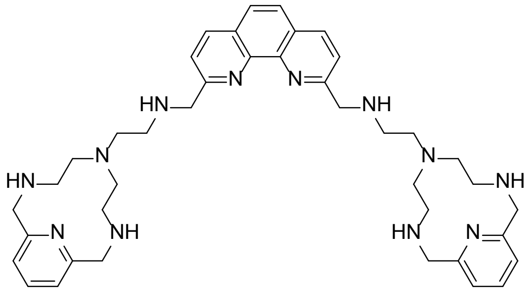

Fig.1 Molecular structure of PHENPOD

New bands observed in the SERS spectra of PHENPOD with mononucleotides and single-stranded polynucleotides originated mainly from nucleic bases, indicating interactions between the PHENPOD molecules and the nucleotides. However, mixtures of PHENPOD and nucleotides containing guanine produced very weak bands arising from vibrational modes of the purine base, if compared to the spectra of the polyamine molecules with other nucleobases.

SERS measurements with double-stranded polynucleotides indicated selective binding of the PHENPOD molecules with the DNA polynucleotides. Adding poly dAdT-poly dAdT into the PHENPOD solution, an intensity of the polyamine bands decreased and new bands appeared, belonging to adenine stretching modes. It can be assumed that the PHENPOD molecules interacted with the minor and major groove of the adenine-thymine polynucleotide, while the phenanthroline moiety intercalated between the base pairs. On the other hand, in the spectra of mixtures of PHENPOD with poly dGdC-poly dGdC new bands were not obtained, and the intensity of the polyamine bands slightly increased, implying the lack of interactions between the polyamine molecules and the guanine-cytosine polynucleotide. In the spectrum of the PHENPOD molecules with the double-stranded RNA polynucleotide no significant changes were observed, as well.

Keywords: surface-enhanced Raman spectroscopy; nucleotides; intercalation; groove binding

EXCITED STATE DYNAMICS OF AMINOARYL-TRIAZINE COMPOUNDS

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Recently, a set of compounds containing one, two or three identical chromophores linked to *sym*-triazine ring was synthesized in order to study electronic excitation energy migration [1],[2]. As the chromophores, 1-aminopyrene or 1- or 2- or 9-aminoanthracene were used. The structure of the prepared compounds was confirmed by MS and NMR. Fluorescence anisotropy measurements indicate that the lowest excited state is localized on a single chromophore, while excitation to higher excited states leads to electronic excitation energy migration or delocalization [3].

Though a certain progress in understanding the photophysics of this particular type of compounds has been achieved, the picture of their excited state dynamics remains still incomplete. Particularly, the origin of two-exponential fluorescence decay kinetics in monoarylamino-triazine compounds, which indicates that additional states are involved in their deexcitation cascade, has to be clarified.

In this contribution, we present the solvent polarity and temperature dependence of fluorescence decay kinetics of relevant aminoanthracene derivatives measured by the TCSPC method. Plausible kinetic model and deactivation pathways responsible for two-exponential decay behavior are discussed.

Acknowledgement:
The research is supported by the grant no. GAP208/10/0941.

Keywords: Excitation energy migration; Excited state dynamics; Fluorescence anisotropy

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INFRARED SPECTROSCOPIC STUDIES OF A PROTON PATHWAY IN THE Ca^{2+} ATPASE

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Muscle relaxation is mediated by the sarcoplasmic reticulum (SR) Ca^{2+} ATPase, an ion pump, which transports Ca^{2+} from the cytoplasm into the SR against the concentration gradient. ATP is the energy source for this transport process. During the Ca^{2+}ATPase reaction cycle 2-3 protons are counter transported. It has been proposed that the protons bind to the carboxyl groups in Ca^{2+} binding sites, which provides charge neutralization of negatively charged amino acids in the sites and allows for the transmembrane helixes to stay together. However the details of proton counter transport mechanism are not completely understood. It is not clear for example if all Ca^{2+} ions need to be released for protons to bind and vice versa. It has also been under question whether the protons are transported through the same channels as Ca^{2+} or if there is a separate pathway for protons.[1]

Our group has previously proposed a model in which the proton path is different from the Ca^{2+} path. Possible proton pathways were investigated by inspection of E2/E2P and E1/E1P structures, which revealed two chains of water molecules with water O-O distances up to 5.6 Å between transmembrane helices M1, M2 and M4-M8, which constitute possible proton or Ca^{2+} paths.[2]

The aim of this work is to test this model, by examining whether the proton path is accessible when the Ca^{2+} path is closed.

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EXPERIMENTAL AND THEORETICAL STUDIES OF DACARBAZINE ANTI-CANCER CHEMOTHERAPY DRUG

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Dacarbazine (DTIC), a chemotherapeutic drug indicated for the treatment of patients with metastatic malignant melanoma was studied using Raman and SERS spectroscopies coupled with quantum chemical (DFT) calculations.

The lowest energy conformers of DTIC have been identified by DFT calculations in vacuo as well as in an aqueous environment using continuum solvation models. Subsequently, the corresponding optimized geometry was used for electronic structure calculations, including the UV-Vis and vibrational spectra.

Experimental and theoretical studies were employed for the detection and identification of different species of DTIC. The protonated and the unprotonated forms were found below pH 4 and above pH 12, respectively, both being in good agreement with the pKa values.

SERS spectroscopy was used to estimate the detection limit of DTIC neutral form and additionally its adsorption on silver surface was proposed. The molecule was detected in aqueous solution up to a concentration of 10^{-7} M. The enhanced band in the SERS spectrum (Fig. 1a) at 1588 cm^{-1} corresponds to the 1547 cm^{-1} band in the calculated Raman spectrum which was assigned to NH_2 bending vibrations. A blue shifting of this band is expected when the NH_2 group is involved in hydrogen or van der Waals bonds [1]. The major enhancement of the 1353 cm^{-1} band assigned to N-N stretching coupled to C-N-H bending vibrations indicates the orientation of this bonds perpendicular to the Ag surface. Additionally, the appearance of the CH_3 stretching vibration in the high wavenumber range (2928 cm^{-1}) suggest a distortion of the molecule in the vicinity of the Ag nanoparticles in such a way that it is oriented with both the NH_2 and CH_3 groups close to the metal surface.

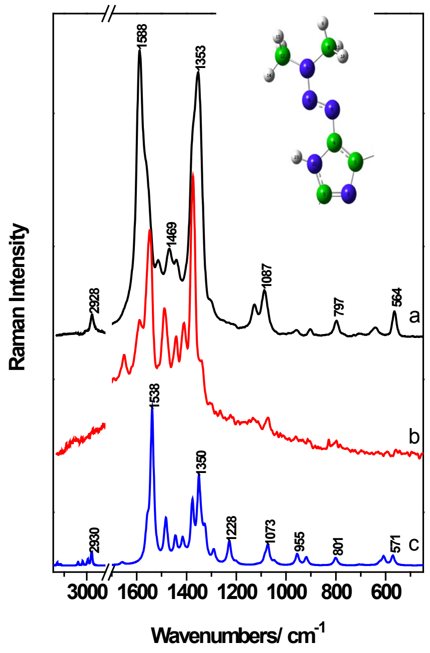

Fig.1 (a) SERS spectrum of DTIC 10^{-3} M on Ag nanoparticles, (b) Raman spectrum in aqueous solution and (c) calculated Raman spectrum of DTIC in water. Excitation 633 nm

Interaction of DTIC with adenine and guanine has also been investigated by using Raman, SERS and DFT approaches.

Keywords: dacarbazine, Raman, SERS, pH, DFT

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SPECTROSCOPIC METHOD IN THE STUDY OF TALLUS OF TOLERANT LICHEN SPECIES

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Objects of investigations are tallus of synanthropic epiphytic macrolichens and physical processes of mechanisms of response which occur in the cells of investigated species to changes of air quality under influence of pollutants. Mechanisms of response of lichen tallus to external influence are investigating by method of spectroscopy, determining the contain of amount of chlorophylls and carotenoids. Prior results proved that carotenoids weight per unit of chlorophyll weight in lichens determines the value of environment pollution [1].

In the present work the task is to use analytical and experimental methods of absorption spectroscopy for quantitative analysis of pigments, which are contained in the tallus of Xanthoria parietina. This method establishes not just common quantity of carotenoids, but also part of each of them (zeaxanthin, violoxanthin, astaxanthin and other). Dependence between weight of carotenoids, photoprotecting pigment parietin in the tallus of lichen Xanthoria parietina and distance to the source of pollution have been found. Also this method showed, that pigment content of Xanthoria parietina is confined to the certain sorts of trees.

Thus, conducted experiments show that pigments content depend on conditions of growth (lever of antropogenious influence, climate, substrate).

Keywords: Lichen; Absorption spectra; Pigments;

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RAMAN RESONANCE EFFECT IN WATER SOLUTIONS OF SILVER NANOPARTICLES

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Resonance effect is a phenomenon that strongly enhance Raman signal from the sample and strictly depends on excitation wavelength. It occurs when an incident electromagnetic wave interact not only with vibrational, but additionally with electronic states. This phenomenon was observed for various organic as well as in inorganic compounds.

Raman resonance effect in liquid water was demonstrated by Pastorczak *et al.* [1]. Polarized Raman spectroscopy showed that the intensity ratio of two main components with maxima around 3200 and 3400 cm^{-1} (assigned to strongly and loosely hydrogen-bonded water molecules respectively) depends on the excitation wavelength in the visible range. It was also shown, that the Raman resonance effect in water directly corresponds to the supramolecular structure of liquid water.

Noble metal (gold, silver) nanoparticles have been successfully applied for Surface Enhanced Raman Spectroscopy (SERS). Significant increase in Raman signal found for many organic molecules adsorbed on expanded metal surface put attention on SERS as a very sensitive analytical technique allowing to study single molecules. Because of this fact, currently, SERS technique is more willingly used in interesting studies on the field of medicine, biology, biochemistry or crystallography [2].

In this work studies on Raman resonance effect in water solutions of silver nanoparticles (AgNPs) synthesized according to the formula proposed by Frank *et al.* [3] will be presented. Investigations concern the impact of AgNPs for water vibrational spectra. Additionally influence of AgNPs size will be discussed.

Keywords: Raman resonance effect; water; silver nanoparticles;

References

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INVESTIGATION OF FLUOROPHORE-METAL INTERACTION AT SINGLE NANOPARTICLE LEVEL USING OPTICAL MICROSCOPY AND SPECTROSCOPY

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The complex interaction of metallic nano-objects with fluorescent molecules has been intensively addressed over the last few decades as an extremely challenging issue. Despite the already reported applicability of such nanohybrids in bioscience [1,2], there is still a growing need to develop more stable and reproducible fluorescent labels for biomedical applications. In this context, optical microspectroscopy represents an ideal platform for the accurate analyze and characterization of single fluorescent nanoprobes.

The aim of our contribution is to provide reliable optical characterization and evaluation of the fluorescent properties of gold nanoparticles (AuNPs) grafted with fluorescent entities. We investigated the direct interaction of the LY fluorophore with gold nanopyramides and nanostars, a unique class of AuNP endowing intense electromagnetic fields at their rather sharp tips when interacting with excitation light. In this particular case, the fluorophore molecules are spaced at less than 5 nm from the metallic surface, case in which the fluorescence emission is generally reported to be quenched at experimental level. On the contrary, we successfully managed to image individual fluorophore-decorated AuNPs exhibiting strong fluorescence signal, in agreement with the predictions available at theoretical level.

Our experimental findings may significantly contribute to optimizing the design of efficient and reliable fluorescent probes for biomedical applications.

Keywords: plasmonic nanoparticles, fluorescence, optical microspectroscopy

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Acknowledgements

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CONFORMATIONAL AND VIBRATIONAL SPECTROSCOPIC ANALYSIS OF AMILORIDE MOLECULE

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In this study, the stable conformers of amiloride (Fig.1), a compound showing antihypertensive effect and is used as diuretic drug effective material, has been investigated via molecular dynamics simulations and Density Functional Theory (DFT) based on electronic structure calculations. The obtained calculation results confirmed that the molecule has many stable conformers at room temperature. The total energies, equilibrium geometrical parameters and vibrational spectral data of the determined conformers were calculated using DFT-B3LYP method, 6-31G(d) and 6-311++G(d,p) Pople style basis sets. In addition to these, corresponding anharmonic wavenumbers for the vibrational normal modes of the conformers which are expected to dominate the room-temperature experimental spectra of the molecule has also been calculated at B3LYP/6-311++G(d,p) level of theory. In order to correct the overestimations at the calculated harmonic wavenumbers, two different empirical scaling approaches, referred to as “Scaled Quantum Mechanical Force Field (SQM FF) methodology” and “Dual scaling approach”, were applied, independently. The improved theoretical spectral data obtained within these two approaches are in good agreement with each other and with our assignments for the fundamental bands observed in the experimental IR and Raman spectra of amiloride.

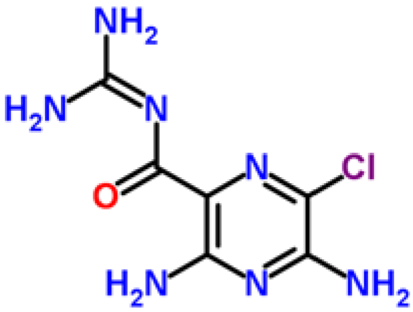

Fig.1. *The chemical structure of Amiloride molecule*

DETERMINATION OF HYDROCARBONS USING INFRARED FIBER-OPTIC SPECTROSCOPY FOR ENVIRONMENTAL POLLUTION ANALYTICS

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Environmental pollution is still an important issue in industrial production or transport accidents. The compartments usually involved are water and soil, although recently also oilfield waters have been especially in the focus, because pollution from petroleum production using offshore drilling platforms and larger spills from accidents have been reported. For the determination of a hydrocarbon sum parameter in water, for example, the well known DIN 38409 (H18) method [1] was developed using Freon-113 as solvent and infrared spectrometry, but this was withdrawn in the year 2000 according to an EU guideline because of the ozone destruction potential of the solvent. The replacement standard ISO 9377-2 is still problematic, due to the complicated sample preparation and the small range of detectable hydrocarbons using gas chromatography. In 2011 the ASTM D7678 method [2] was published, which is based on the use of cyclohexane as solvent and infrared quantum cascade laser spectroscopy. Here, we report on the use of a fiber-optic probe equipped with silver-halide fibers for waveguiding and a diamond micro-prism for ATR-measurements [3, 4]. A library of ATR-spectra of solvents, vegetable oils, biodiesel and various mineral oil products was established, which can be used for product identification. Besides the quantitative assay of hydrocarbons in cyclohexane, also the quantification of biodiesel in mineral diesel was tested using multivariate calibration methods based on partial least squares (PLS). The performance of three different fiber-optic probes has been compared for the evaluation of calibration transferability.

Keywords: infrared ATR spectroscopy; fiber-optics; hydrocarbon assay; environmental chemistry

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COMPARISON OF DIFFERENT MEASUREMENT TECHNIQUES FOR THE INFRARED SPECTROSCOPIC CHARACTERISATION OF BACTERIA

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The fast and accurate analysis of microorganisms is more in demand today than ever before. Especially, in medical sciences appropriate novel efficient methods are needed [1, 2], because of the essential identification of multi-resistant germs and contagious pathogens, which must be seen in conjunction with an increasingly mobile world population. Spectra of dry-films of *Pseudomonas fluorescens,* which were recorded with a fiber-optic ATR-probe equipped with a diamond micro-prism, were compared with spectra recorded in transmission on CaF_2- and ZnSe-windows, as well as on PE-foils. Furthermore, ATR-spectra of *Pseudomonas putida*, *Bacillus subtilis*, *Micrococcus luteus*, *Escherichia coli* were recorded for the compilation of a first spectral library. The detection limit with spectra recorded using the ATR-probe was less than 1 μg of dry mass.

Dendrograms were calculated based on a hierarchical cluster analysis, for which the spectral distances between the individual microorganisms using the specific interval of 1200 – 900 cm^{-1} were optimal. Beside investigations on the spectral reproducibility, the influence of storage with down freezing and warming-up on the bacterial mass and of different nutrient agars on the spectra of *Eschericha coli* and *Bacillus subtilis* was also tested. At last, a comparison between spectra of bacteria measured with the ATR-technique and spectra measured with dried bacteria on ZnSe-windows, which were provided by the Robert Koch-Institute in Berlin, was performed and identification using the ATR-spectra was successful even with the transmission spectral library exploited after vector normalisation using spectral data from 1600 – 900 cm^{-1}.

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SOLVENT INFLUENCE ON THE ELECTRONIC SPECTRA OF 1,6-DIPHENYL-1,3,5-HEXATRIENE IN TERNARY SOLUTIONS

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DPH (1,6-diphenyl-1,3,5-hexatriene) is a small uncharged molecule with a rod-like structure that absorbs and emits with high efficiency. DPH become, in the lasts decades, one of the most frequently used cromophore for its role in appreciation of microviscosity and anisotropy of the heterogeneous microsystems. DPH is used in fluidity estimation of the model and natural membranes because in hydrated environment does not show fluorescence but it show fluorescence in lipid bilayer.

Photochemical and spectral characteristics of DPH depend on environmental factors such as the temperature, solvent nature, etc. The higher of the solvent refractive index, the greater the red-shift of the DPH absorptions bands is. The solvents with high polarizability lead to a high fluorescence yield. Therefore, DPH is frequently used as an indicator of the degree of order in lipid microsystems.

The study about the solvent influence on the DPH electronic spectra is realized in this paper in order to analyze different comportment of this molecule in the protic and non-protic solvents.

The spectral shifts measured in electronic spectra are discussed on the basis of the theories regarding the solvent influence on absorption and fluorescence electronic bands.

Keywords: 1,6-Diphenyl-1,3,5-Hexatriene, electronic spectra, spectral shifts

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CONCENTRATION INFLUENCE OF FLUORESCENT DPH PROBE ON THE STRUCTURE AND MOBILITY POPC MODEL MEMBRANES: A MOLECULAR DYNAMICS STUDY

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DPH (1,6-diphenyl-1,3,5-hexatriene) is one of the most used fluorescent molecule of the hydrophobic domain of membranes. Their fluorescence polarization is high in the absence of rotational motion and is sensitive to reorientation of the long axis resulting from interactions with surrounding lipids. The steady-state anisotropy depends both on the fluorescence lifetime and order parameter.

The aim of the present study was to asses by means of computational methods (molecular dynamic simulation) for both the preference of the DPH molecule for the orientation and location in different regions of the bilayer and the influence of the concentration of DPH on the structure and dynamics of 1-palmitoyl - 2 - oleoylphosphocholine (POPC) membranes. Several parameters were followed during the course of the simulations which included area/lipid, ordering of acyl chains and rotational and lateral diffusion of phospholipids molecules and the orientation preference of the inserted DPH molecules. The simulated time interval exceeded at least one order of magnitude the DPH fluorescent lifetime.

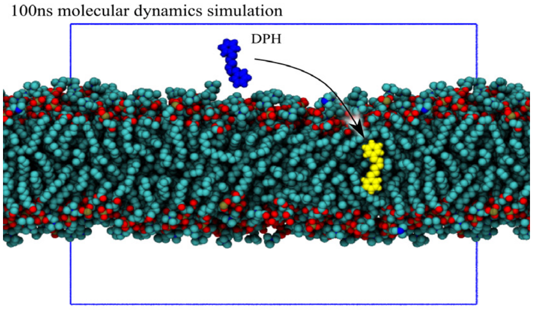

Fig.1 Snapshot of DPH insertion in POPC bilayer

DPH was found to influence wide range of membrane properties in a dependend manner concentration. The effects are maximal in the proximity of the fluorophore. The action of DPH is to increase the acyl chain order especially in high concentration regime.

Keywords: 1,6-Diphenyl-1,3,5-Hexatriene; molecular dynamics; 1-palmitoyl-2– oleoylphosphocholine (POPC);

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Acknowledgments: This research was financially supported by European Social Fund –„Cristofor I. Simionescu" Postdoctoral Fellowship Programme (ID POSDRU/89/1.5/S/55216), Sectoral Operational Programme Human Resources Development 2007 – 2013.

THE INFLUENCE OF MOLECULE-METAL JUNCTION TO CHARGE AND SPIN TRANSPORT THROUGH SMALL MOLECULES

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Pertinent applications are envisaged for organic-based electronics, including on-chip nanolabs, molecular transistors, memories, logic-gates, and other spin-driven technologies.

Using state of the art Non-Equilibrium Green Functions (NEGF) – Density Functional Theory (DFT), the charge and spin transport through small prototype molecules is addressed. Different types of anchoring atoms are used to connect the molecular system to (110) Cu leads. The results show no rectification in the case of symmetric systems, while for the different anchoring to the metallic leads small rectification is present.

The computed transmission function (T(E)) and projected density of states (PDOS) show metallic behavior near Fermi level, mainly due to nitrogen and/or sulfur atoms. The phenyl aromatic ring contributes to transport in a 2 eV wide window under the Fermi level and in sharp peaks above 2 eV (the Fermi level is set to 0 eV).

RI acknowledges financial support through Sectoral Operational Programme for Human Resources Development 2007-2013, co-financed by the European Social Fund, under the project number POSDRU/107/1.5/S/76841. Calculations were carried out at the National Institute for Research and Development of Isotopic and Molecular Technologies.

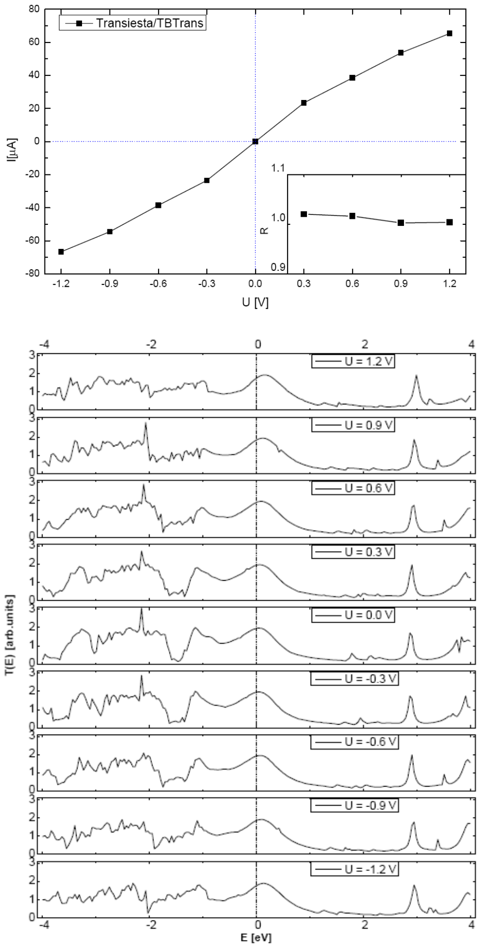

Fig.1 The I-V curve (top) and the transmission (bottom) for nitrogen-anchored phenyl group.

Keywords: quantum transport; Non-Equilibrium Green Functions; Density Functional Theory.

THEORETICAL STUDIES OF SOME PYRIDINE MOLECULAR COMPLEXES

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The molecular parameters and vibration spectrum of pyridine and its molecular complexes with methyl alcohol and ethyl alcohol have been analysed by using the methods from molecular programs [1, 2].

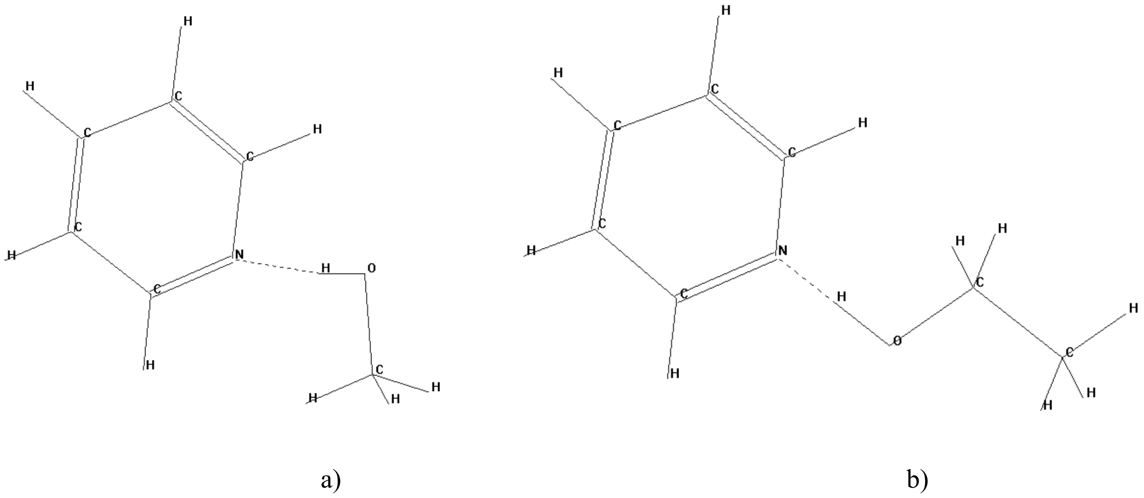

Fig. 1. The structural formulas of the studied molecular complexes a) pyridine and methanol, b) pyridine and ethanol (dotted line – hydrogen bond)

The investigated molecules were considered in the ground state. The bond lengths, atomic charges, the dipole moments, the polarizabilities and the energies of HUMO and LUMO levels were computed [3].

The theoretical frequencies obtained were correlated with the computed atomic charges. These results will be used to establish the behaviour of the selected complexes after the formation of hydrogen bonds.

Keywords: Vibration spectrum, pyridine, molecular complexes.

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RAMAN SPECTROSCOPY AND DEPOLARIZATION MEASUREMENTS OF ATMOSPHERIC GASES

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Raman spectroscopy has become an important method of diagnostics and monitoring of physical / chemical parameters of a medium. For example, Raman LIDAR has gained significance in monitoring air pollution. However, for quantitative interpretation and evaluation of Raman signals the absolute value of the scattering cross-sections needs to be known. The related Raman polarizability tensors of molecules can be accessed experimentally via the measurement of the wavenumber-dependent depolarization ratio, $\rho(\nu)$, which is associated with the isotropic and anisotropic contributions to the various Raman bands. Note that polarizability properties also find their way into the characterization of optical refractivity, Rayleigh scattering and collision-induced infrared activity; and can be helpful in studies of the symmetry of probe molecules, assignment of molecular vibrations, distinguishing between fundamentals, overtones, binary combinations, identification of isotopologues, etc.

Traditionally, the depolarization ratio is measured as the ratio of scattered light intensities $I_{VH}(\nu)$ and $I_{VV}(\nu)$, i.e. $\rho(\nu) = I_{VH}(\nu)/I_{VV}(\nu)$, where $I_{VV}(\nu)$ and $I_{VH}(\nu)$ are the intensities of the scattered light with polarizations parallel and perpendicular to the polarization plane of the incident laser beam, respectively. However, precise depolarization ratio measurements are notoriously problematic, often being hampered by poor signal-to-noise ratios and line overlap in the spectra, and by difficult-to-gauge contributions from optical components in the light passes and from solid-angle geometry. Recently, we have proposed a measurement approach which addresses all the aforementioned issues [1], and which has been successfully applied in comparing theoretical ratios with measured data for the hydrogen isotopologues in relation to the **K**arlsruhe **TRI**tium **N**eutrino experiment (KATRIN) [2].

Here we report on our studies in applying the aforementioned methodology of precise Raman depolarization measurements to atmospheric gases, namely the majority gases N_2 and O_2, and the trace gases H_2, CO_2, H_2O and CH_4. These measurements were performed for the majority of Raman branches of the various vibrational modes, up to Raman shifts of about 4500 cm^{-1}. The results are compared to other measurements reported in the literature and to theoretical values.

In addition to deriving depolarization ratios and polarizability tensor components we successfully applied the knowledge of these quantities to extract relative isotopologue and hot-band contributions from the spectra. For example, for atmospheric nitrogen we measured the isotopologue ratio $[^{14}N^{15}N] / [^{14}N_2] = 0.00721(18)$, which precisely matches the expected theoretical value of 0.00726 based on natural terrestrial isotope abundance [3], and nearly reaches the sensitivity of the best optical spectroscopy measurements for deviations in ^{15}N abundance [4].

Keywords: *Raman spectroscopy; atmospheric gases; depolarization ratios*

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FT IR SPECTROSCOPIC STUDY OF HYDROGEN BONDING AND SOLVENT INDUCED FREQUENCY SHIFTS OF N-t-BUTYL ACETAMIDE

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This paper reports the results of FT IR study of N-t-butyl acetamide in carbontetrachloride solution and in presence of 8 different molecules as H acceptors. Frequency shifts of carbonyl stretcing vibration ν(C=O) of N-t-butyl acetamide in 8 different organic solvents was also investigated. The spectroscopic characteristics for N-H...O hydrogen bonded complexes are given. Also, the equilibrium constants for 1 : 1 complex formation , at 25^{0}C were determined using IR and measurements. The wavenumbers of carbonyl stretcing vibration ν(C=O) were correlated with the solvent acceptor number (AN) and the linear solvation energy relationships (LSER).

Keywords: Hydrogen bonding, N-t-butyl acetamide, Solvent effect

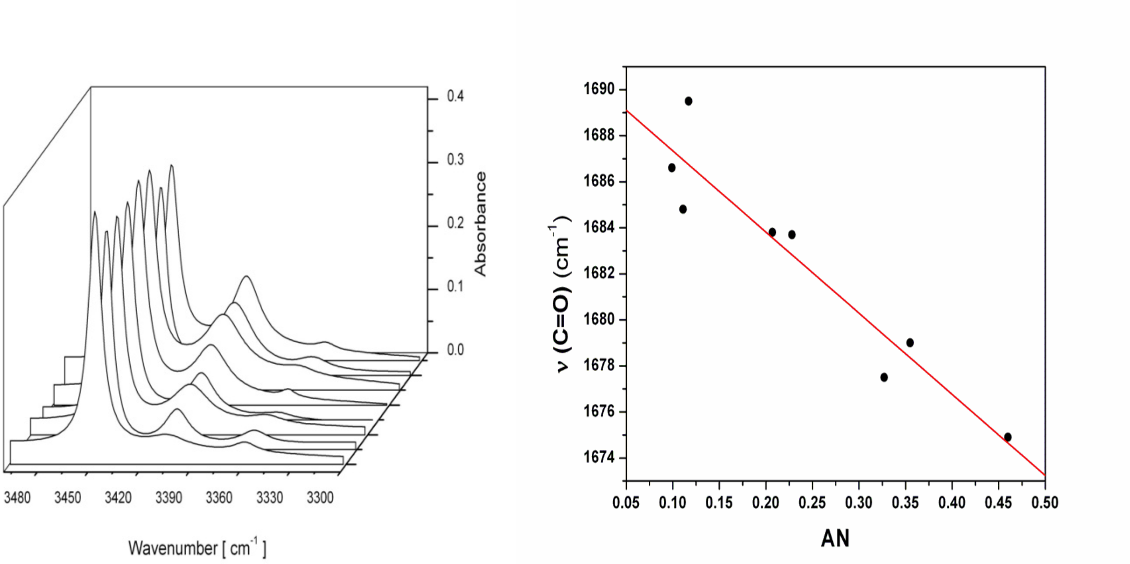

Figure 1 IR spectra of N-t-butyl acetamide hydrogen bonded complexes with ethyl acetate, and Correlation of the experimentally obtained wavenumbers of NTBA absorption maxima versus the Gutman acceptor number AN for all solvents used.

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CONFORMATIONAL AND VIBRATIONAL SPECTRAL ANALYSES OF GLYCYL-GLUTAMINE DIPEPTIDE, BASED ON IR, RAMAN AND DFT CALCULATIONS

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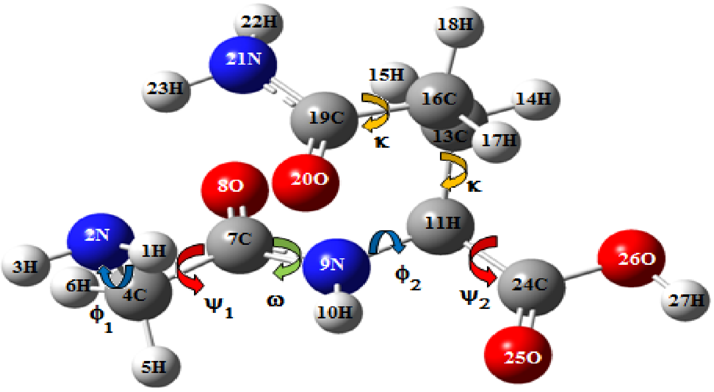
Glycyl-glutamine (Gly-Gln) dipeptide is an inhibitory neuropeptide that is derived from β-endorphin. It inhibits morphine conditioned place preference, tolerence, dependence and withdrawal. Gly-Gln dipeptide consist of 27 atoms and has 75 vibrational modes. In this work, firstly, conformational analysis have been performed for neutral Glycyl-glutamine dipeptide in order to determine the most preferable structures. The low energy conformations in different 360 conformers have been obtained by using the Ramachandran maps. Afterwards, the geometrical parameters of obtained stable conformations were used as starting parameters for DFT calculations. The molecular structure of Gly-Gln dipeptide, in the ground electronic state (in vacuum) was optimized by density functional theory method with B3LYP functional and using 6-31++G(d,p) basis set. The dimeric forms of the dipeptide were also formed and energetically preferred conformations of dimers were investigated using the same method and the same level of theory. The fundamental vibrational wavenumbers, IR intensities and Raman activities of the global conformation of monomeric and dimeric forms of the dipeptide were calculated and compared with the experimental vibrational spectra of solid Gly-Gln dipeptide.The assignments of the vibrational spectra were performed on the basis of the Potential Energy Distribution (PED) of the vibrational modes, calculated with Gar2ped program. Intra-hydrogen bonding interaction of monomeric, and inter- and intra- hydrogen bonding interactions of dimeric forms of dipeptide are determined.



Glycyl-glutamine dipeptide

CONFORMATIONAL AND STRUCTURAL STUDIES OF N-PROPYLAMINE FROM TEMPERATURE DEPENDENT RAMAN AND FAR INFRARED SPECTRA OF XENON SOLUTIONS AND AB INITIO CALCULATIONS

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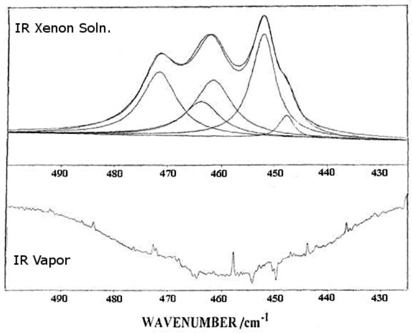
Many organoamines are very important biochemicals which play important roles in many areas. Their conformations and structures have been investigated over the years by several different techniques particularly microwave, infrared, and Raman spectra as well as electron diffraction data. A significant number of these studies for the enthalpy difference determinations between conformers were done in solution by infrared and/or Raman spectra. However, amines readily form dimers or larger associated species. Therefore, it is necessary to carry out these studies in very dilute solutions or in the gas phase to obtain reproducible results when varying the temperatures for enthalpy difference determinations, but variable temperature measurements in the gas phase results in very difficult experiments. However, we have found that we can overcome many of the difficulties by using rare gas solutions with very long liquid cells, i.e. 8 cm long, and the infrared technique as shown in Fig. 1. We have now extended this technique to the Raman spectra. Recently, we have been investigating the conformation stability and determined the structural parameters of several organoamines[1-2]. These studies clearly indicate that the enthalpy difference between the *gauche* and *trans* conformers of the NH_2 moiety will need to be determined experimentally rather than by theoretical predictions for organoprimary amines. It is of scientific interest to determine the effect of substituting one or more of the hydrogen atoms on β-carbon. One of the earliest molecules of this type studied was n-propylamine, $CH_3CH_2CH_2NH_2$[3] for which the conformational stability was determined. The most stable conformer was determined to be the trans-trans form but this determination was for the solid. However, the most stable conformer in the gas or the liquid need not be the same as found in the solid so it is of interest to obtain the relative stabilities of the five possible conformers of n-propylamine in the gaseous state. The order of stability and enthalpy differences have been obtained by utilizing variable temperature (-60 to -100 °C) studies of xenon solutions of n-propylamine by recording Raman spectra from 1175 to 625 cm^{-1} and infrared spectra from 600 to 40 cm^{-1}. To support the spectroscopic studies we have carried out more extensive *ab initio* calculations by utilizing a variety of basis sets. The results will be discussed and compared to the corresponding properties of some similar molecules wherever possible.



Keywords: conformational stability; Raman; vibrational assignment; n-propylamine; xenon solutions

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THE ABSORPTION AND FLUORESCENCE SPECTRA OF SOME SELECTED SYNTHETIC CYCLIC CHALCONE ANALOGUES IN ORGANIC SOLVENTS: SOLVENT AND SUBSTITUENT EFFECT

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This paper reports the absorption and fluorescence spectral properties of some selected synthetic cyclic chalcone analogues studied in various polar and nonpolar organic solvents. The studied compounds are E-2-1- benzosuberone (1a), E-2-(4'- methoxy)-1- benzosuberone (1b) and E-2-(4'-dimethylamino)-1- benzosuberone (1c). The small angle between the excited-singlet state and the ground-state dipole moment is also reported. The spectral shifts are interpreted in terms of change in the mobility of π- electrons, caused by the nature and positions of the substituents groups linked. A plausible explanation has also been offered for the observed relatively highly fluorescent nature of the (1c) molecule and the higher polarity it exhibit in the excited state compared to (1b) and (1a) in terms of their value of excited singlet state dipole moment. These results were observed also by fluorescence spectroscopy. The highest fluorescence of compounds(1c) have been obtained in chloroform.

Keywords: benzosuberone,synthetic cyclic chalcone analogues, absorption and fluorescence spectroscopy, fluorescence, organic solvents, excited singlet state and ground state dipole moment.

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JET COOLED ROTATIONAL STUDIES OF β-AMINOISOBUTYRIC ACID AND NIR-INDUCED CONFORMATIONAL ISOMERIZATION OF THE COMPOUND IN SOLID NITROGEN

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β-Aminoisobutyric acid (BAIBA) is a non-proteinogenic amino acid, whose occurrence in nature was established as early as in 1951.[1] It is a thymine and antiretroviral thymine analogues zidovudine (AZT) and stavudine (d4T) catabolite, which has been found to increase fatty acid oxidation in liver and reduce the gain of body fat mass in mice.[2,3] BAIBA is also a partial agonist at the glycine receptor (GlyR), competitively inhibiting glycine responses at low concentration.[4] It has been recently found that a common binding site for all amino acid agonists and antagonists exists in GlyR, at which the functional consequences of binding depend on the particular conformation the amino acid ligand adopts within the binding pocket.[4]

BAIBA is extremely flexible from the conformational point of view, presenting four internal rotation axes that can give rise to conformational isomerism (Figure). This characteristic shall be relevant in determining its physical and chemical properties, as well as its bioactivity. Nevertheless, no conformational studies on AIB have been reported hitherto.

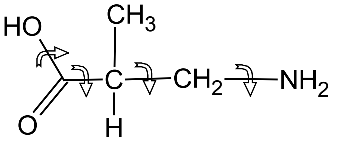

Fig. Schematic representation of BAIBA, showing the conformationally relevant internal rotation axes.

In this study, BAIBA has been studied in isolation conditions in the gas phase and trapped into a cryogenic matrix. A solid sample (m.p. ~180 ºC), was vaporized by laser ablation and investigated through their rotational spectra in a supersonic expansion using two different spectroscopy techniques: broadband chirped pulse Fourier transform microwave spectroscopy (CP-FTMW)[5] and conventional molecular beam Fourier transform microwave spectroscopy (MB-FTMW).[6] Conformers with structures of two types could be successfully identified by the comparison of the experimental rotational and ^{14}N nuclear quadrupole coupling constants with those predicted theoretically: type I, bearing a OH···N intramolecular hydrogen bond and its carboxylic group in the *cis* geometry (H–O–C–C dihedral ~0º), and type II, having a NH···O= bond and the *trans* arrangement of the carboxylic group. These two types of conformers could also be trapped from the gas phase into cryogenic matrices, and probed by infrared spectroscopy. *In situ* irradiation of AIB isolated in N_2 matrix, using near-infrared radiation tuned at the frequency of the 1st O–H stretching overtone of type II conformers (at ~6930 cm^{-1}), allowed to convert selectively these forms into type I conformers. Interpretation of the experimental results was supported by quantum chemical calculations undertaken at different levels of approximation.

Keywords: BAIBA; Microwave spectra; Matrix-Isolation FTIR Spectroscopy; NIR-Induced rotamerization.

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A STRUCTURAL AND VIBRATIONAL INVESTIGATION OF ZINC DIFLUOROMETHYLSULFONYL COMBINING THE FTIR AND RAMAN SPECTRA WITH AB-INITIO CALCULATIONS

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We have studied the structural and vibrational properties of a new compound used as reagent for the innate difluoromethylation of organic substrates via a radical process, the zinc difluoromethylsulfonyl salt (DFMS), $Zn(SO_2CF_2H)_2$, by means of infrared and Raman spectroscopies and *ab-initio* calculations. Recently, this compound was reported by Fujiwara *et al.* [1] as an air-stable white powder that can be easily prepared and it is an optimum precursor for the CF_2H radical. The molecular structure is observed in the Figure 1.

In this study, the corresponding geometries for the compound were calculated using the Gaussian 03 [2] program at HF and B3LYP theory levels while the harmonic vibrational frequencies for the optimized geometries of the compound were calculated using Lanl2dz, Lanl2MB, DGDZVP and DGDZVP2 basis sets. Then, for a complete assignment of the infrared and Raman spectra, DFT calculations were combined with Pulay´s Scaled Quantum Mechanics Force Field (SQMFF) methodology [3] in order to fit the theoretical wavenumber values to the experimental ones. Here, a complete assignment of the observed bands for the title molecule was performed.

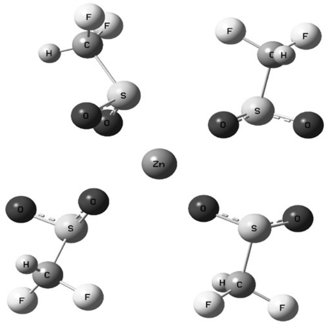

Fig.1 Theoretical structure of zinc difluoromethylsulfonyl

The nature of the Zn-O and Zn←O bonds and the topological properties of the compound were investigated and analysed by means of Natural Bond Order (NBO) [4] and *Bader's* Atoms in Molecules theory (AIM) [5], respectively. Additionally, the force constants were performed for the compound and then analyzed and compared with results obtained for similar compounds.

Keywords: zinc difluoromethylsulfonyl salt, Infrared spectrum, molecular structure, force field.

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H-BONDED CLUSTERS IN THE TRIMETHYLAMINE (TMA)/WATER SYSTEM

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The environmentally important interaction products of trimethylamine (TMA) and water molecules have been observed by Matrix Isolation Fourier Transform Infrared Spectroscopy (MIS-FTIR). Infrared spectra of solid argon matrix layers, in which both TMA and H_2O molecules were entrapped as impurities, were analyzed for bands in the ν(O-H) region, not seen in matrix layers containing either of the parent molecules alone. Results were interpreted on the basis of the emergence of several spectral band pairs and their red shifts from the position of the matrix isolated H_2O monomers as compared to semi-empirically scaled frequencies from the B3LYP/aug-cc-pVTZ calculations and empirical correlations with a large body of data on H-bonded complexes.

Bands were assigned to a complex cluster of two TMA molecules flanking a closed ring of four H-bonded H_2O molecules. The formation of this cluster is argued to be formed in the vapor phase (as opposed to being a result of diffusion of species in the matrix layer) and is related to its large stabilization energy (enthalpy) due to strong cooperative effects in its H-bond system.

COMPLEXATION AND IONIZATION IN THE SAME MATRIX LAYER

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The atmospherically important interaction products of sulfuric acid and ammonia molecules have been firstly observed by Matrix Isolation Fourier Transform Infrared Spectroscopy (MISFTIR). Infrared spectra of solid argon matrix layers, in which both H_2SO_4 and NH_3 molecules were entrapped as impurities, were analyzed for bands not seen in matrix layers containing either of the parent molecules alone. Results were interpreted on the basis of spectral changes induced by experimental conditions and by semi-empirically scaled frequencies from the B3LYP/aug-ccpVTZ and B3LYP/aug-cc-pVQZ calculations. Bands were assigned to complexes of the $H_2SO_4{*}NH_3$ and $H_2SO_4{*}[NH_3]_2$ general formulae. They differ significantly: the 1:1 $H_2SO4{*}NH_3$ complex is a strongly hydrogen bonded complex, an analog of the $H_2SO_4{*}H_2O$ complex, studied previously. For the 1:2 $H_2SO_4{*}[NH_3]_2$ complex, spectral results indicate an almost complete proton transfer forming a complex of essentially the two ionic moieties HSO_4^- and $[H_3N\cdots H\cdots NH_3]^+$, an analog of the $[H_2O\cdots H\cdots OH_2]^+$ "Zundel ion".

VIBRATIONAL AND THEORETICAL STUDIES OF Nd(III) AND Ce(III) COMPLEXES WITH OROTIC ACID

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Orotic acid (OA) has unique properties which render it a key biological compound involved in the biosynthesis of pyrimidine bases in living organisms [1]. Besides exhibiting bacteriostatic and cytostatic properties, this compound has attracted growing attention as the carrier for certain metal ions and for its behavior as a multidentate ligand [2]. The coordination chemistry of OA and its metal complexes with various therapeutic (including anticancer) effects, represent an active field of research in the recent years [1-4].

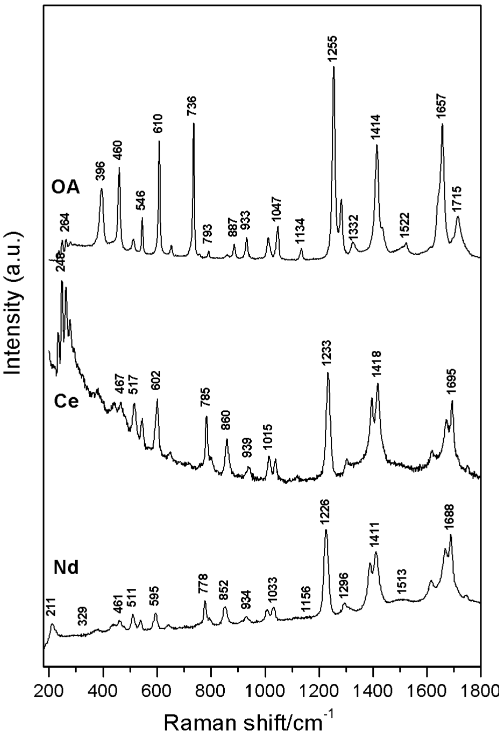

Fig.1 Experimental Raman spectra of (from top to bottom) orotic acid (OA), Ce(III)-OA and Nd(III)-OA complexes

Promising results of lanthanide complexes with biologically active ligands as cytotoxic agents prompted us to synthesize and investigate the new complexes of Nd(III) and Ce(III) with orotic acid. These complexes have been characterized spectroscopically by using IR and Raman techniques, coupled with quantum chemical calculations performed in the framework of density functional theory (DFT). Such methods have been shown previously as optimum tools for electronic structure calculations on molecular complexes [5]. For geometry optimizations and vibrational spectra calculations we used the hybrid B3LYP exchange correlation functional with the cc-pVDZ basis set for C, O, N and H atoms and SDD effective potential and basis set for Nd and Ce atoms.

As shown in Fig.1, marker bands for ligand binding to lanthanide ions are observed at 595 and 778 cm^{-1} for Nd(III) complex and at 602 and 785 cm^{-1} for Ce(III) complex. Both of them correspond to ν(M-O) stretching modes, with M= Nd or Ce, coupled with carboxylate groups in plane deformations. The ligand binding modes in these new complexes were elucidated by DFT geometries optimizations. It is concluded that in both complexes the metal ion is four-coordinated with bonds to two oxygen atoms from the carboxylate of the first orotate ligand, to one carboxyl oxygen of the second orotate ligand and to one O atom from an hydroxyl anion. All the metal-oxygen distances are slightly shorter for the Nd(III) complex compared to the Ce(III) complex.

Keywords: Nd(III)-OA and Ce(III)-OA complexes; Orotic acid; IR; Raman; DFT

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TREATMENT OF NONSTEROIDAL ANTIINFLAMMATORY DRUGS IN RHEUMATOLOGY. SPECTROFLUORESCENCE STUDY

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Arthritis is a joint disorder featuring inflammation. Rheumatoid arthritis is totally different and results from inflammation of the joints that have been attacked because of a faulty immune system. Nonsteroidal anti-inflammatory drugs (NSAIDs) are medications that are used to reduce pain as well as inflammation in the joints.

The aim of the study is to evaluate the mechanism of competition between phenylbutazone (PBZ) and ketoprofen (KP), two drugs recommended for the treatment of rheumatoid arthritis, in binding to bovine (BSA) and human (HSA) serum album, in high affinity binding site on the basis of quenching fluorescence method. The effect of the displacement of PBZ or KP from the complex has been presented on the basis of the comparison of the quenching curves and binding constants for the binary and tertiary systems.

The association constants K_a [M^{-1}] of binary PBZ-SA, KP-SA and tertiary PBZ-KP-SA complexes as well as the number of the class of binding sites were determined with the use of one- and two-component Scatchard model. Quenching fluorescence of serum albumin in the presence of the both drugs has been characterized by a modified Stern-Volmer nonlinear regression equation, from which dynamic K [M^{-1}] and static V [M^{-1}] quenching constants were determined.

The study of competition between PBZ and KP in binding to serum albumin shows the most important problems of combination treatment. It indicates the change of both drugs affinity to serum albumin in the ternary systems which should be taken into account in the multi-drug therapy.

Keywords: competition; spectrofluorescence; human serum albumin

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DETERMINATION OF THE SPECIFIC INTERACTION OF PCB'S AND HUMAN SERUM ALBUMIN. IN VITRO SPECTROSCOPIC STUDIES

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The binding parameters such as binding constants, quenching constants, number of binding sites for the independent class of binding sites or fractional accessible protein fluorescence for three congeners of polychlorinated biphenyls (PCB 118, PCB 126 and 153) in complex with human serum albumin (HSA) - the most abundant of the plasma protein, were determined using fluorescence technique. Polychlorinated biphenyls (PCBs) comprise organochlorine derivatives in body tissues. PCBs are dangerous due to its bioaccumulation in fat tissues and highly persistent in living organisms.

The binding parameters for the system HSA-PCB 118, HSA-PCB 126 and HSA-PCB 183 excited at λ_{ex} 280 nm were compared with that excited at 295 nm. Binding (K_B) and quenching (static and dynamic) constants for analyzed complexes were calculated on the base on Scatchard and non-linear regression on the basis of two-component Scatchard model with algorithm Lavenberg–Marquardt and Stern-Volmer method, respectively.

Keywords: PCB; binding; fluorescence

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This work was supported by the Grants from Medical University of Silesia: KNW-1-008/N/1/0 and KNW-1-050/P/1/0.

BINDING OF ASPIRIN TO SERUM ALBUMIN AND α_1-ACID GLYCOPROTEIN: A COMPARATIVE STUDY

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The interaction of aspirin (ASA, acetylsalicylic acid - analgesic, antipyretic and anti-inflammatory drug), with human serum albumin (HSA), bovine serum albumin (BSA) and α_1-acid glycoprotein (AGP) were studied by fluorescence spectroscopy technique under simulated physiological conditions. The binding parameters: binding constants, quenching constants, number of binding sites for the independent class of binding sites or fractional accessible protein fluorescence for HSA-ASA, BSA-ASA and AGP-ASA complexes were determined. It was found that ASA bounds to HSA near to tryptophanyl residue (Trp-214) in IIA subdomain. The same, Trp-214 group is engaged to binding of ASA in BSA molecule, but additionally it was found that Trp-135 located in IB subdomain participates in ASA interaction. Tyrosil groups from IB, IIB and/or IIIA subdomain play minor binding function. Surrounding of Trp-22 and Trp-160 in AGP is responsible for an independent binding of ASA, but main binding site for ASA on AGP was determined in hydrophobic pocket close to Trp-25. The results demonstrate that ASA bounds to analysed albumin in two classes of binding site with binding constants (K_a) equal $0{,}91 \times 10^4$ and $0{,}10 \times 10^4$ [M^{-1}] for BSA-ASA complex and $3{,}71 \times 10^4$ and $1{,}04 \times 10^4$ [M^{-1}] for HSA-ASA complex. AGP bounds ASA in one class of binding site with $K_a = 0{,}86 \times 10^4$ [M^{-1}]. An estimation of binding ability of albumin and α_1-acid glycoprotein is necessary in patients with hipo- or analbuminemia.

Keywords: ASA; binding; fluorescence

Acknowledgements:
This work was supported by the Grants from Medical University of Silesia: KNW-1-008/N/1/0 and KNW-1-050/P/1/0.

THE EFFECT OF GLYCATION OF PROTEIN ON THE KETOPROFEN BINDING

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Reducing sugars such as glucose, fructose, galactose with a lot of proteins (e.g. albumin, haemoglobin or collagen) are entering the nonenzymatic reaction of glycation which results in a glycated protein. The aim of this studies was to obtain the glycated human (gHSA) and bovine (gBSA) serum albumin i.e. advanced glycation endproducts – AGEs. This study has also shown the influence of glycation on ketoprofen (KTP) and serum albumins (human and bovine) complexes *in vitro*.

Ketoprofen is the propionic acid class of non-steroidal anti-inflammatory drug with analgesic and antipyretic effects. This drug is widely available and used in nowadays society. The interaction of ketoprofen with glycated (KTP - gHSA, KTP - gBSA) and native (KTP - HSA, KTP - BSA) albumins was investigated using quenching fluorescence technique.

The fluorescence analysis showed that KTP forms π - π complex with aromatic amino acid residues of glycated and non-glycated albumins. The complex formation is accompanied by dynamic and static quenching fluorescence of both albumins. The main binding site for KTP on albumins was found to be located in the hydrophobic IIA and/or IIIA subdomain where the Trps were placed. The analysis allowed for a designation of association constants K_a [M^{-1}] and quenching constants K_Q [M^{-1}] in the presence of ketoprofen. The higher values of K_a [M^{-1}] and K_Q [M^{-1}] were observed for human glycated (gHSA) serum albumin than for non-glycated (HSA) serum albumin. This allows for a suggestion that the transport of the drug may be altered in the patients with hyperglycemia.

Keywords: non-enzymatic glycation; AGEs; serum albumin; fluorescence study

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EXPERIMENTAL (FTIR AND NMR SPECTRA) AND THEORETICAL (DFT) STUDY OF NOVEL FLAVANONES

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The aim of this work is to characterize some novel flavanones by vibrational and NMR spectroscopies in conjunction with Density Functional Theory (DFT) calculations, in order to establish their structures and electronic properties. Quantum mechanical calculations of energies, geometries and vibrational wavenumbers in the ground state were carried out using hybrid functional B3LYP (Becke three parameter hybrid functional combined with Lee–Yang–Parr correlation functional) with 6-311G(d,p) as basis set. On the basis of agreement between the calculated and experimental results, assignments of all the fundamental vibrational modes of studied flavanones were examined. In addition, the molecular electrostatic potential map, the frontier molecular orbitals and the HOMO-LUMO gap of studied compounds are calculated and analyzed in order to estimate the possible paths for electron transport.

The calculation of NMR spectra of studied flavanones was performed using the GIAO (Gauge-Including Atomic Orbitals) method, [1], with the hybrid B3LYP, WP04 [2], WPC04, [2], and PBE1PBE [3] functionals in conjunction with 6-311++G(d,p) and aug-cc-pVDZ basis sets. Theoretical ^{13}C and ^{1}H chemical shift values (with respect to TMS) were reported and compared with experimental data, showing a very good agreement both for ^{13}C and ^{1}H. For each studied compound the DFT calculation revealed that there are two stable diastereoisomers.

Keywords: flavanone; DFT; FTIR; NMR; B3LYP; PBE0; WP04; WPC04.

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ORIGIN OF FLUORESCENCE LOSS IN BENZOYL-SUBSTITUTED PYRROLOPYRIDAZINES BY TIME-DEPENDENT DFT

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Excited states of several substituted pyrrolo[1,2-b]piridazines (5-aza-indolizines) were investigated by Time-Dependent Density Functional Theory (TDDFT) to provide an insight into the mechanism(s) responsible to intrinsic fluorescence loss in benzoyl-substituted derivatives. As recently reported [1], quantum yield drops from 0.70-0.90 to about 0.06-0.10 when an esther group on the pyrrolic ring is replaced with para-substituded benzoyl.

To provide an unbiased description of electronic transitions, both vertical excitation and vertical emission energies were computed using several hybrid functionals with different amounts of exact exchange as well as with range corrected variants. Configurational Interaction (CI) computations were carried on for comparison.

Vertical excitation energies computed in selected solvents for all the compounds being investigated were found to agree within 0.2-0.3 eV with the experimental data reported in [1]. A systematic and relatively large overestimation of vertical excitation energies (underestimation of maximum absorption wavelength) was found, as expected, in case of functionals with a large amount of Hartree-Fock exchange as well as when using CI.

In case of benzoyl-substituted derivatives, geometry optimization of the first excited state gives two different results if started from two slightly different initial conformations. However, both excited states are found to be "dark states", having essentially a n-π* local excitation (LE) and intramolecular charge transfer (ICT) π-π* character, respectively. It is not the case of highly-fluorescent esther or amide substituted pyrrolo[1,2-b]pyridazines where the first singlet excited state is found to have a LE π- π* character. Moreover, the ICT state found in benzoyl-pyrrolo[1,2-b]pyridazine is predicted to be 0.2-0.5 eV lower than the LE counterpart not only by normal hybrid functionals as PBE0 and B3LYP, which are likely to give spurious CT states [2], but also by functionals with large amount of HF exchange as BH&HLYP and even CI, the last being susceptible to bias the results against CT states with more than 1 eV [3].

Keywords: pyrrolodiazine; fluorescence; TDDFT; excited states; charge transfer;

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THE SPECTROPHOTOMETRIC STUDY OF THE BINDING OF VITAMIN E TO WATER+DIALKYL SULFOXIDE/AOT/HEPTAN REVERSED MICELLES

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The UV-Vis absorption spectroscopy is a suitable technique to provide direct information on the location of vitamin E in the water/ sodium bis (2-ethylhexyl) sulfosuccinate (AOT)/heptane system[1]. These observations provided to develop an elegant approach for studying the local microenvironments of vitamin E in micelles and membranes. In our earlier work [2] the effect of dimethyl sulfoxide (DMSO) and its diethyl sulfoxide (DESO) as a polar cosolvents on the binding of vitamin E to water + DMSO(DESO) containing reversed micelles of AOT has been investigated by a spectrophotometric method.

In the present work we extend this approach to study the effect of the other dialkyl sulfoxides such as dipropyl-, diizopropyl- and dibutyl- sulfoxides (DPSO, DiPSO, DBSO) as a polar cosolvents on the binding of vitamin E to water + dialkyl sulfoxide (DASO) containing reversed micelles AOT. The high values of dielectric constants of DASO and the peculiar strong intermolecular interactions between sulfoxides' and water molecules, especially in the concentration range used in this work provide an additional background to assume that in fact DASO are remaining in the micellar core. In addition one has to take into account that the solubility of DASO in heptane is negligible.

We recorded the UV-spectra for all DASO /water mixtures, at fixed R=[H_2O]/[AOT] , equals to 10 . Our investigations were restricted with one fixed R as we are interested to reveal the effect of polar cosolvent DPSO, DiPSO and DBSO as well as due to restricted solubility of vitamin E in aqueous solutions of these sulfoxides.

The distribution constants (K) of vitamin E in the presence of 1sulfoxide/5water (volume ratio) mixtures were 6.9; 7.0 and 8.1 for DiPSO, DPSO and DBSO respectively. Thus one can conclude that in comparison with pure water (K = 6.8 [1]) sulfoxide promotes the binding ability of vitamin E and the increase of solubilized amount of vitamin E in micelles.

Keywords: *Vitamin E; Reversed micelles; Dialkylsulfoxides; UV–Vis spectroscopy*

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FTIR INVESTIGATION OF INTERACTION BETWEEN POLY(MALIC ACID) DERIVATIVES AND DPPC LIPOSOMES

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Polymeric nanoparticles are currently generating increased interest in the field of targeted drug delivery. These nanoparticles have to be biodegradable with non toxic degradable products. Poly(malic acid) (PMLA) can be a promising candidate for drug carrier nanoparticles. In the presented study the effect of low molecular weight PMLA, as model degradation product, on dipalmitoylphosphatidylcholine (DPPC) model membranes was investigated. Liposomes, containing lipid bilayers as basic structural units are frequently used as model cell membranes and as drug delivery vehicles, as well.

To obtain information about possible interactions between PMLA and lipid molecules ATR-FTIR spectra of fully hydrated DPPC/PMLA systems were measured at room temperature. The spectral regions selected for investigation are: the symmetric CH_2 stretching vibration (2588-2580 cm^{-1}), the carbonyl stretching mode C=O (1800-1680 cm^{-1}) and the phosphate head group vibration region (1260-1000 cm^{-1}). No notable change was evidenced in ν_sCH_2 frequency by the presence of PMLA in the DPPC system, meaning that poly(malic acid) has any effect on the lipid order and packing under our experimental conditions.

The phosphate and carbonyl frequencies are widely used as sensors for hydration changes at the interface region or at the head group. Regarding the C=O stretching of ester carbonyl groups, in the case of DPPC/PMLA/water system with rather high acidity (pH=2.2), the relative intensity of non-hydrogen bonded C=O band becomes slightly higher compared to the "pure" DPPC/water liposomes. In the presence of PBS buffer, however, this phenomenon is suppressed. Assuming that no change in alkyl region occurs, the variation in overall band shape of the C=O band can be related to change in the "secondary hydration shell" of the lipid. This might contribute to variations of the dipole potential of the lipid membrane surface.

Investigating the $\nu_{as}PO_2^-$ stretching mode in DPPC/PMLA dry film spectra, the H-bonded PO_2^- asymmetric stretching band of phosphate moiety is still present (at 1222 cm^{-1}) and its intensity increases with increasing concentration of PMLA. One can presume that the occurring free OH groups of degraded poly(malic acid) might mimic the hydration water.

Computer simulation of molecular interactions in DPPC/PMLA system via modeling its measured infrared spectra was also done using *ab initio* and density functional (DFT) calculations, as well as molecular mechanics (MM).

LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS) AND MASS SPECTROSCOPY (MS) ANALYSIS OF CULTURAL HERITAGE MATERIALS

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Laser-induced breakdown spectroscopy (LIBS) and laser ablation time-of-flight mass spectrometry (TOF-MS) are used, on the basis of a hybrid experimental set-up, for the characterization of materials relevant to cultural heritage. A number of commercially available pigments and paint formulations were used in this study. Optical emission spectra, obtained by LIBS, lead to rapid, straightforward identification of the elemental content of the paint samples while mass spectra yield, additionally to elemental analysis, complementary isotopic analysis and, more importantly, identification of molecules and molecular fragments, permitting a more complete structural and compositional characterization of composite materials.

Keywords: Laser Induced Breakdown Spectroscopy; Mass Spectrometry; paint

THE CHIRI PROGRAM: ATOMIC CHARGES FROM IR INTENSITY

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Atomic charge is one of the most elusive and arbitrary molecular parameter and its reliable description is extremely important to investigate the physical properties of molecular systems as a function of their intra and intermolecular environment. Different schemes were and are proposed but most of them share an intrinsic weakness, since they cannot be related to any experimentally measurable property. In the past, some models were developed for a parametrization of experimental IR intensities, giving a direct connection between charges and experimental data. GAPT [1] and IR charges [2-4] in particular are defined on the basis of Atomic Polar Tensors (APTs). While GAPT charges have some weakness [3] but are very easy-to-use, the lack of a general procedure to get IR charges, hindered their application: this is one of the reasons of the little use of IR charges, which have been applied in a very limited number of cases and only by a small number of experts in the field.

We present here a method to extract IR charges from suitable DFT/ab-initio computed APT components, in comparison with other common methods. The procedure adopted and its implementation in the (freely-available) CHIRI program is also reported [4]. Thanks to this program, IR charges can be now readily gathered also by non-experts, provided that APTs from a quantum chemical calculation of the IR spectrum are available. The method has been applied for the calculation of IR charges of about 50 molecules: it describes accurately peculiar intramolecular interactions, providing a picture of the molecular charge distribution coherent with the chemical intuition. A nice agreement is also found with Hirshfeld [5] and CHELPG charges [6]. On this basis, we propose IR charges as a reliable, physically sound and easily accessible alternative to other charge parameters currently adopted. Furthermore, the model presented can be used also to extract information on charge fluxes, offering a detailed description of both static and dynamic molecular charge distribution. This work opens the way to many possible follow-ups, such as the analysis of IR charge values of a wider variety of molecular systems and the systematic investigation of the dependence of IR charges on the computational method adopted.

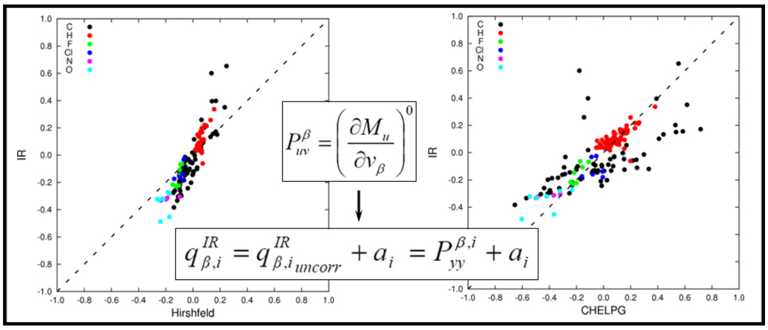

Fig.1 Correlation plot between IR charges, Hirsheld and CHELPG charges.

Keywords: atomic charges; atomic polar tensor; DFT calculations; infrared spectroscopy.

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BINDING MODES OF A DBTAA DERIVATIVE WITH DNA/RNA POLYNUCLEOTIDES REVEALED BY SERS

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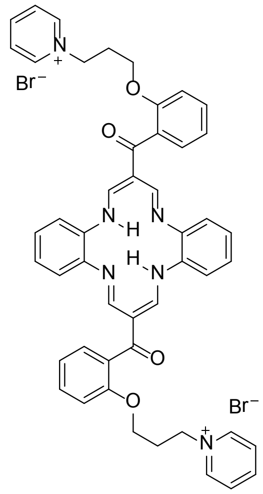

Fig.1 Molecular structure of the DBTAA derivative

Owing to their structural resemblance to porphyrins, widely known for their diversity of interactions with DNA, dibenzotetraaza[14]annulenes (DBTAA) have attracted much attention as molecules having potential nucleic acid binding ability. The molecular structure of newly synthesized derivatives suggests that the planar DBTAA core can easily intercalate between the base pairs, while long and flexible substituents at *meso* positions of the macrocycle can facilitate groove binding [1],[2].

Binding modes of the DBTAA derivative with synthetic DNA and RNA were studied using surface enhanced Raman spectroscopy (SERS). Changes in SERS intensity and appearance of new bands in spectra were attributed to different complexes formed between the DBTAA molecules and polynucleotides. Intercalation was revealed as the dominant binding mode of the annulene derivative with poly dGdC-poly dGdC and poly rA-poly rU, whereas binding within the minor groove of poly dAdT-poly dAdT was also considered. When all the dominant binding sites were occupied, SERS spectra indicated that the small molecules bind on the outside of the DNA analogues, while exist mainly as free molecules in equimolar ratio with the synthetic RNA polynucleotide, implying higher affinity for DNA than for RNA.

Keywords: surface-enhanced Raman spectroscopy; annulene; polynucleotide; binding

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KINETICS STUDIES OF SERS HOT-SPOTS FORMATION

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Surface-enhanced Raman (SERS) spectroscopy combines chemical specificity of vibrational spectroscopy with detection limits competing with those of fluorescence. Enormous SERS enhancement enables even single-molecule studies and implies great analytical potential. Although SERS effect amplifies Raman scattering of all analyte molecules adsorbed on the SERS-active nanostructures, the most important contribution comes from the analytes trapped in “hot-spots” [1], i.e. junctions or gaps between closely spaced and confined nanostructures. In the case of colloids, the hot-spots are formed by aggregation of nanoparticles (NPs) induced by the analyte itself or by an aggregating agent. Formation of hot-spots has important consequences for spectral properties of the analyte and affects its photophysics and photochemistry. Extremely strong electromagnetic field in dynamically evolving hot-spots and reorientation of the analyte causes temporal alteration in the SERS spectra [2] which complicates analyte identification in more complex systems.

The aim of the present study is to provide better insight into the dynamics of the hot-spots formation and the SERS enhancement mechanisms taking place in. For that purpose, temporal evolution of the SERS spectra was studied as a function of aggregation state by using 441.6 and 532 nm excitations being in resonance with surface plasmons of non-aggregated and aggregated Ag NPs, respectively. Several analytes differing in their spectral properties (absorption and fluorescence) and abilities to induce aggregation of the Ag NPs were tested, i.e. tetracationic Zn(II)- and Cu(II)-5,10,15,20-*tetrakis*(1-methyl-4-pyridyl) porphyrins and dicationic 4,4’-vinylene-bis(1-methylpyridinium). Tight aggregation and hot-spot formation was controlled by addition of chlorides into the Ag NPs containing the analyte at different concentrations. The SERS spectra were acquired as temporal series with short time sampling. Advanced SVD-based methods [2] were used for quantitative analysis and comparison of the SERS spectra obtained at different excitations and from the SERS systems considerably differing in their aggregation states and optical densities. The temporal evolutions of the SERS signals were correlated with the corresponding temporal evolutions of their surface plasmon extinction spectra. Besides the kinetic measurements in the large-scale samples, formation of the hot-spot at microscopic level was studied using Raman microspectroscopy and microfluidic devices [3]. Effect of the dynamics of the hot-spot formation to the SERS enhancement, spectral features of the analyte and signal stability, as well as morphology of the active sites speculated from the time-evolution of the analyte spectra are presented and discussed.

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Keywords: Surface-enhanced Raman spectroscopy, hot-spots formation, kinetics studies

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CHEMICALS DETECTION IN FRUIT CONSERVATION TREATMENT USING SURFACE-ENHANCED RAMAN SCATTERING

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Currently, the UE regulation selected the maximum levels for certain pesticides in products of plant origin [1] and certainly adequate sensitive techniques are required, with low costs and if possible in a nondestructive manner.

Surface-enhanced Raman Spectroscopy (SERS) deeply fulfill these requirements as a sensitive technique for detection trace amounts of organic compounds, contaminants, pesticides and many others.

Thiabendazole (TBZ), [2-(4-thiazolyl) benzimidazole], C10H7N3S is a chemical fungicide species and parasiticide largely used in vegetables and fruits treatment to prevent mold, blight, and other diseases for long transportation and deposit.

TBZ is also used as a food additive, a preservative with E number E233 (INS number 233). For example, it is applied to bananas to ensure freshness, and is a common ingredient in the waxes applied to the skins of citrus fruits.

In this paper we present a complete vibrational characterization of the TBZ, both theoretically and experimental, using Raman and SERS spectroscopy in conjunction with the DFT calculation.

Complete vibrational characterization is provided in order to correctly assign the SERS signal in various conditions regarding the pH [2] or concentration. The pH dependence and concentration dependence Raman spectra of TBZ respectively have been recorded and discussed. It has been proved that the TBZ could provide quality SERS signal in a large concentration range, as shown in the fig.1.

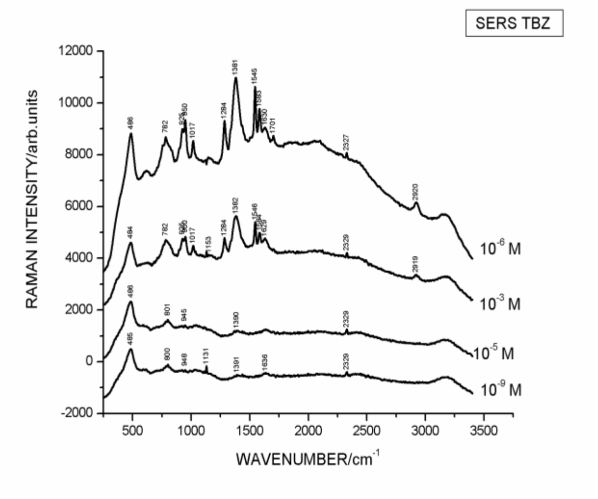

Fig1.SERS spectra of the TBZ in different concentrations

We succeeded in detecting the TBZ species on a large range of concentrations from 10^{-3} M to 10^{-9} M using silver colloidal nanoparticles. The TBZ species exhibit two basic spectral shapes, one for the 10^{-3} M to 10^{-5} M, other for the 10^{-6} M to 10^{-9} M concentration range. In first case the prominent SERS bands are observed at 486 cm^{-1}, 1382 cm^{-1}, 1546 cm^{-1}, whereas at lower case at 1701 cm^{-1} and 2920 cm^{-1}.

In order to detect the TBZ signal in fruits particularly bananas, orange, apples we took into account the possible interferences from the beta carotene (1155 cm^{-1}, 1523 cm^{-1}) that could change TBZ signal.

Upon optimization, the high quality SERS signal could be acquired in 5 seconds. Based on the data we proposed several strategies to detect the TBZ in the fruit species.

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SURFACE-ENHANCED RAMAN SCATTERING OF GENOMIC DNA FROM LEAVES OF DIFFERENT PLANT SPECIES

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In biochemical fields, plant DNA might be used to explore the interaction between DNA and small molecules, which is important in connection with probing the accurate local structure of DNA and with understanding the natural DNA-mediated biological mechanisms [1].

Ultrasensitive Raman measurements of nucleic acids are possible through exploiting the effect of surface-enhanced Raman scattering (SERS).

In this work, surface-enhanced Raman spectra of genomic DNAs from leaves of different plant species, were recorded and discussed, respectively, in the 200-1800 cm^{-1} spectral range.

SERS signatures, spectroscopic band assignments and structural interpretations of these plant genomic DNAs are reported. SERS spectra of nucleic acids are compared here with caution, because these signals are time-dependent.

Bands of dG, dA, dT, dC residues, backbone, deoxyribose moiety, PO_2^- symmetric stretch and [dT(C=O)] group, respectively, characteristic to genomic DNAs from different leaf tissues, are presented in detail [2]. We have identified in this data set, SERS spectra which show well resolved bands, providing rich structural information.

Keywords: Surface-enhanced Raman scattering (SERS), Genomic DNA, In vitro grown plant species

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SPECTRAL STUDY ON THE HOST-GUEST INTERACTION APPLICATION IN TARGETED DRUG DELIVERY

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Cyclodextrins are known for their capacity to form inclusion complexes with lipophilic drug molecules or molecule part [1], the resulted complexed pharmaceutical product presenting modified physico-chemical properties. A broad spectrum antibiotic with low solubility in aqueous solutions, used mainly for the treatment of tuberculosis, is Rifampicin (RIF). A way to enhance rifampicin's apparent solubility is by encapsulate the hydrophobic part of the molecule in the apolar cavity of the host β-Cyclodextrin (βCD). The aim of this study was to investigate the formation of RIF-(βCD) inclusion complex and further, the ability of these complexes to attach onto magnetic nanoparticles (such as Fe_3O_4) intended for drug delivery applications. Thus, such systems could be useful for targeting and releasing the drug at specific sites, by eliminating the solubility problems associated with this antibiotic, allowing higher drug concentration at the infection site and, in the same, time minimizing systemic side effects. For this purpose, first we analyzed the complexation efficiency between rifampicin and native β-Cyclodextrin in a range of pH values in buffer solution. For each case the analysis of electronic absorption spectra was carried out also. The optimal inclusion complex was obtained for RIF-βCD 1:1 molar ratio for pH > 7.0 – when rifampicin passes in anionic form, favoring the formation of the RIF-βCD inclusion complex (mediated by the piperazin group, which is deprotonated at high pH) [2]. The obtained complex was investigated spectrally, using ^{1}HNMR and IR spectroscopy; by performing X-Ray diffraction upon the powder samples, it was confirmed the interaction between the host (βCD) and the guest antibiotic. Based on these results and the recent scientific reports – revealing that magnetic nanoparticles can be stabilized in aqueous medium with molecules such as native βCD [3] - we synthesized magnetic nanoparticles by chemical precipitation followed by their dispersion in aqueous medium by stabilization with RIF-βCD. The analysis of the microstructural properties of the newly obtained products was carried out by XRD and IR which confirmed the formation of magnetic core / RIF-βCD shell systems with an average diameter of 13 nm. The magnetic characterization of the colloidal nanoparticles was accomplished based on Vibrating Sample Magnetometry (VSM), evidencing the possibility of their manipulation with applied external magnetic field. Further studies on the influence of βCD on the antimycotic activity of rifampicin correlated with *in vitro* monitoring of the drug release rate in water simulating the intercellular medium are planned in the near future.

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Keywords: rifampicin; β-Cyclodextrin; magnetic nanoparticles

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SPECTRAL AND QUANTUM CHEMICAL INVESTIGATION OF PHTHALAZINIUM-DIBENZOYL METHYLIDE

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Phthalazinium-dibenzoyl methylide (PDM) is a stable zwitterionic compound from the ylides class, used mainly as an acid-base indicator and in the synthesis of new heterocycle compounds [1]. Though numerous studies were devoted to the investigation of cycloimmonium ylides, there is not enough data on the ylide derivative such as PDM.

The spectral behavior of PDM molecule, as well as the estimation of the solute-solvent intermolecular interactions based on solvent shift approach, is presented in the frame of this study, the experimental results being correlated with quantum chemical calculations based on molecular orbital theory [2].

The electronic absorption spectra of PDM were recorded at room temperature in 20 binary solutions of different polarities, the changes induced by the solvent nature upon the wavenumber in the maximum of the intramolecular charge transfer band in the visible range being disscused. It was found that the PDM molecule can be used as probe able to measure, due to the hypsochromic shift, the intensity of the intermolecular interactions in solutions. Based on the obtained experimental data, the contribution of the intermolecular interactions of universal type was estimated by applying a mathematical model that correlates the spectral shift with functions of the solvent parameters (refractive index and dielectric constant).

In order to gain a deeper insight on its structural features, the molecular structure and reactivity of the PDM molecule was also analyzed from a theoretical point of view, using the semi-empirical method implemented in the molecular modeling programe HyperChem. The microscopic parameters characterizing the PDM molecule in the ground state – such as dipole moment, polarizability etc. - were estimated in order to calculate the same parameters in the excited state, based on the experimental data resulted from the solvatochromic analysis. Furthermore, the behavior of the PDM molecule in the first solvation sphere was also estimated from the semi-empirical calculations by applying the periodic box method – the electro-optical parameters, the energies of the frontier orbitals and the electronic spectra being predicted. The data obtained from the molecular modeling of the PDM geometry was found to be in good agreement with the experimental results.

Acknowledgements: This research was partially supported by the project "The transnational network of integrated management for postdoctoral research in the field of Science Communication. Institutional construction (post-doctoral school) and fellowship programme (CommScie)", Code POSDRU/89/1.5/S/63663.

Keywords: cycloimmonium ylide; electronic spectra; semi-empirical calculation

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POTENTIAL ENERGY SURFACES OF Π-CONJUGATED MOLECULES CALCULATED USING DFT-D AND DFT-DCP METHODS

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Charge and energy transport of π-conjugated molecules are strongly influenced by their intermolecular interactions and mutual orientation [1]. Thus, for a rational design of supramolecular functionalities, detailed knowledge of the intermolecular interactions is mandatory.

In this study we were interested to elaborate a protocol for locating the local and global minima on the PES of the TCNQ and 4F-TCNQ dimmers and to simulate a noncontact atomic force microscopy experiment by means of DFT calculations (NC-AFM DFT) using CO-Pentacene complex as a test case.[2] Such results are of paramount importance for understanding the aggregation of molecules in liquid phase and to explain their packing in solid state.

The rigid and relaxed potential energy surfaces of TCNQ, 4F-TCNQ dimers and CO-Pentacene complex have been investigated at B3LYP-D/6-31G(d) level of theory.

Global minimum on the relaxed PES are characterized by D$_e$=-0.467 eV for TCNQ and -0.608 eV for 4F-TCNQ. Different local minima identified for the two dimers are within 100 meV higher in energy than the global one. While the global minimum for TCNQ has a structure displaced along the long axis of the molecule by 2.078 Å, without any displacement along the Y axis, for 4F-TCNQ the global minimum on the relaxed PES corresponds to a structure displaced both on X (2.183 Å) and Y (3.583 Å) axes.

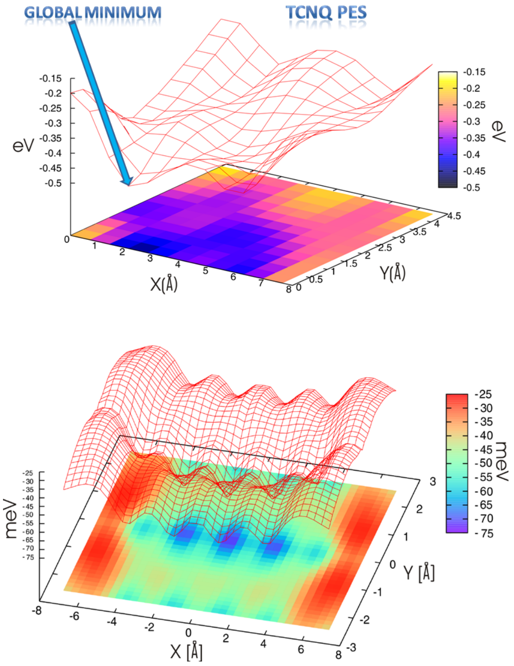

Fig.1 Relaxed PES of TCNQ (upper panel) and CO-Pentacene complex (lower panel)

For the NC-AFM DFT simulations the global minimum is characterized by D$_e$= 73 meV and a equilibrium distance measured between the central carbon ring of penacene and the C atom of CO molecule of 4.126 Å. As in the NC-AFM experiments our NC-AFM DFT approach was able to clearly resolve the image of the pentacene molecule absorbed to a Cu(111) substrate.

Keywords: TCNQ; 4F-TCNQ; Pentacene-CO complex; DFT-D

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STRUCTURAL AND VIBRATIONAL SPECTROSCOPIC ELUCIDATION OF SULPIRIDE IN SOLID STATE

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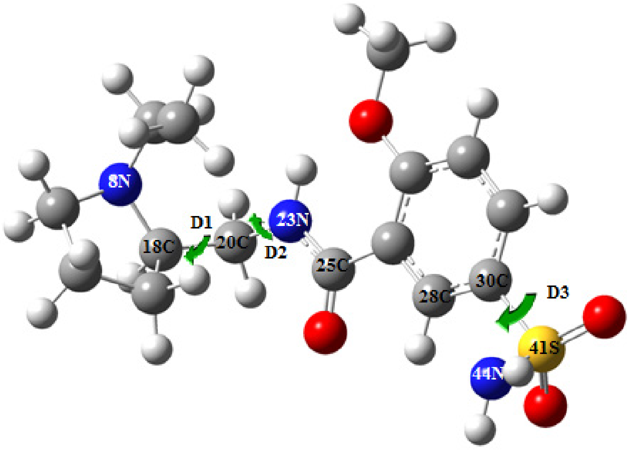
Sulpiride with the chemical formula 5-(aminosulfonyl)-*N*-[(1-ethyl-2-pyrrolidinyl)ethyl]-2-methoxy-benzamide ($C_{15}H_{23}N_3O_4S$) is a substituted benzamide class usually used to help treat the symptoms of psychosis, schizophrenia and major depressive disorder. It is known as a neuroleptic or antipsychotic drug.

In this study the theoretically possible stable conformers of free sulpiride molecule in electronically ground state were searched by means of torsion potential energy surfaces scan studies through dihedral angles **D_1**(8N, 18C, 20C, 23N), **D_2** (18C, 20C, 23N, 25C) and **D_3** (28C, 30C, 41S, 44N). The 1728 and 432 different conformations were searched with the three and two dihedral angles by using AM1 and DFT methods, respectively. The molecular structure of sulpiride, in the ground electronic state (in vacuum) was optimized by density functional theory method with B3LYP functional and using 6-31++G(d,p) basis set. The energetically preferred conformations of dimers were also investigated using the same method and the same level of theory. Raman and IR (4000-400cm^{-1}) spectra of sulpiride have been recorded in the solid state. The theoretical vibrational spectra of sulpiride in its monomeric and dimeric forms have been reported. The assignment of the bands was based on the Potential Energy Distribution data using GAR2PED program. Purpose of this work is to investigate the structural and vibrational characteristics of monomeric and dimeric structures of sulpiride molecule.



Sulpiride

SIMULATED VIBRO-ROTATIONAL FUNDAMENTAL BAND OF HCL DILUTED IN DENSE AR

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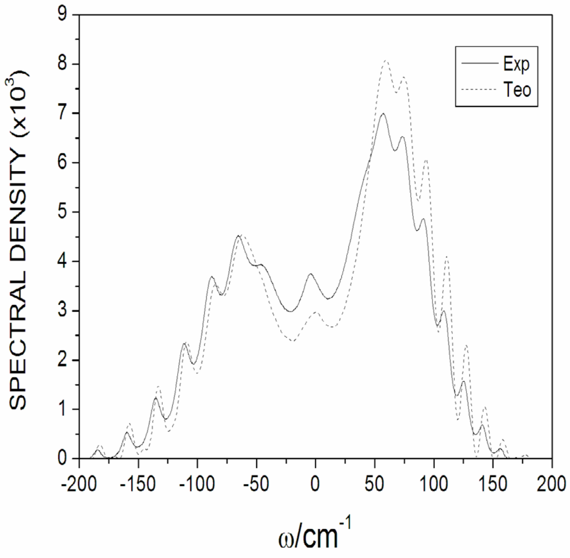
We have recently developed a quantum-classical stochastic simulation to explain the line shape of the fundamental band of HCl in dense Ar [1]. In this simulation the rotation was considered from a quantum point of view while the translation degrees of freedom were treated classically as an stochastic thermal bath. We have calculated the pure rotational spectral density by making use of this model in accordance that the hypothesis that the main features of the fundamental band shape are associated to the rotational degrees of freedom.

Later we have improved the stochastic simulation by developing a mixed quantum-classical dynamical simulation, in which the HCl diatomic environment was described by means of molecular dynamics, including more realistic details of the Ar dense phase.

In this work it is presented an analysis of the fundamental band of HCl in dense Ar, which includes the effects associated to the diatomic vibrational degrees of freedom. In this case both rotational and vibrational degrees of freedom are described by means of a quantum approach which allows to analyze, among others, the red shift of the whole band; the pure vibrational broadening of the vibro-rotational lines, and the line mixing effects associated to the line coupling which are included in the quantum-classical dynamic simulation



The binary HCl-Ar potential has been divided into an isotropic part depending of both diatomic vibration and bath translation, which is responsible for pure vibrational dephasing, and an anisotropic part depending on rotation and translation, which produce line broadening, line mixing and hence the basic characteristics of the line shape. Both calculated and experimental fundamental band of HCl for dense Ar at T=190 K [2] are shown in the figure, where the zero frequency corresponds to the non perturbed fundamental gas phase transition.

Keywords: Mixed quantum-classical dynamics;simulation;spectroscopy

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COMPARISON OF STRUCTURE AND DYNAMICS OF HUMAN HAPTOGLOBIN PHENOTYPES MONITORED BY VIBRATIONAL SPECTROSCOPY

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Human haptoglobin (Hp) is a glycoprotein from a blood serum which plays an important role in an immune system and in response to shock conditions. Haptoglobin is able to bind free hemoglobin in blood and prevent its metabolisation in kidneys [1]. This mechanism can also serve as a defense against bacteria (by reducing the availability of iron). Differences on Hp concentration in blood serve as a marker of different diseases, including cancer, inflammation, liver failure, hemolysis or infarct. Hp consists of two light (83 or 142 amino acids) and two heavy chains (243 amino acids) connected by disulphide bridges. The glycoprotein can occur in two allelic forms Hp1 and Hp2, therefore we can find three different phenotypes in a human population – Hp1-1 (88 kDa), Hp1-2 (107 kDa) and Hp2-2 (116 kDa) – having different hemoglobin affinity.

3D Hp structures are not available. Existing structures are based only on homology modeling [2, 3]. Several experiments were performed to prove that Hp1-1 changes structure after a heat-shock. The process leads to an increase of ordered structure and solvent accessible surface with respect to Hp chaperone-like activity [2].

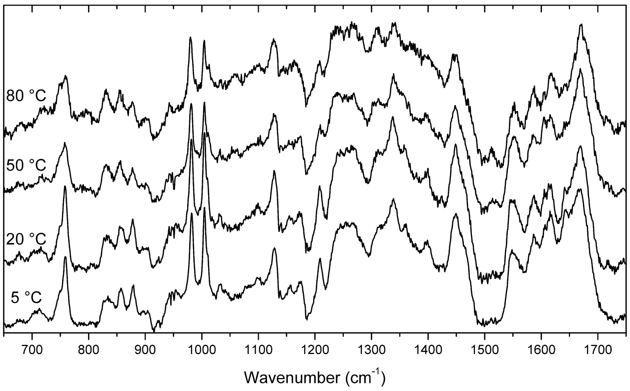

Fig.1 Raman spectra of thermal denaturation of Hp1-1

Here we examine different structural and dynamical behavior of Hp1-1 and Hp2-2 phenotypes by Raman and infrared (IR) spectroscopy. Irreversible dynamics of each of the phenotypes was monitored in the temperature range from 5 to 80 °C with 5 °C steps (see Fig. 1). The spectral series were analyzed by factor analysis and 2D correlation analysis. The comparative analysis using heterospectral 2D correlation analysis between Raman and IR series as well as between the phenotypes was performed to elucidate key changes leading to chaperone-like activity [2] as well as to point on structural differences. Structure of Hp in native state and after the heat-shock condition was followed among others by Raman optical activity and circular dichroism to obtain more detailed image of differences. This contributes to better understanding of different phenotypes [3] in the human population as well as it points on the structural role of the prolonged light chain in Hp2-2.

Acknowledgement: The work was supported by the Grant Agency of Charles University (No. 102-10/253054).
Keywords: Heat shock proteins; Infrared spectroscopy; Raman spectroscopy; Raman optical activity

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ANTIMICROBIAL PEPTIDE FROM EUSOCIAL BEE *Halictus sexcinctus* INTERACTING WITH MODEL MEMBRANES

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There are many already known antimicrobial peptides (AMPs) with considerable therapeutic potential but their exact mechanism of action still remains a matter of controversy [1]. AMPs interact with cytoplasmatic membrane and their amphiphatic structure plays an important role in this process. Simple models of membrane penetration involve formation of pores or dissolving membrane in a detergent-like manner. These processes lead to breakdown of the transmembrane potential causing leakage of cell content and finally the cell death. [2] The mechanism of antibacterial action probably includes recognition and specific interaction with bacterial cell membranes inducing lipid clustering or lipid phase separation [3].

Halictine-1 (Hal-1) a linear antibacterial dodecapeptide isolated from the venom of the eusocial bee *Halictus sexcinctus* [4] – has been subjected to a detailed spectroscopic study including circular dichroism, fluorescence and vibrational spectroscopy. We investigated Hal-1's ability to adopt an amphiphatic α-helical structure upon interaction with model lipid based bacterial membranes (phosphatidylcholine/phosphatidylglycerol based large and small unilamellar vesicles, sodium dodecylsulfate micelles) and/or helix inducing components (trifluoroethanol). It was found that Hal-1 responds sensitively to composition of the membrane model and to peptide/lipid ratio. Amphipathic nature of the helical Hal-1 seems to favour flat charged surfaces of the model lipid particles over the non-directional interaction with trifluoroethanol. Increasing fraction of polyproline II type conformation was detected at low peptide/lipid ratios.

Keywords: antibacterial peptides, halictine, micelle, liposome, circular dichroism, infrared spectroscopy

Acknowledgements.
The Grant Agency of the Czech Republic is gratefully acknowledged for support (No. 208/10/0376).

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PHYSICO-CHEMICAL (SPECTROSCOPIC: FT-IR, RAMAN, UV AND ^{1}H, ^{13}C NMR) STUDIES OF Mn(II), Fe(III), Co(II), Cu(II), Zn(II), Cd(II) VANILLATES

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Vanillic acid, one of the naturally occurring methoxy-derivatives of hydroxybenzoic acid, possesses antioxidant and anti-inflammatory properties [1]. In our previous works the specific effect of various metals on the electronic structure of benzoic acid derivatives has been investigated [2,3]. The aim of the present study was to determine the influence of Mn(II), Fe(III), Co(II), Cu(II), Zn(II), Cd(II) ions on the electronic charge distribution of vanillic acid. In this research FT-IR, FT-Raman, UV and ^{1}H, ^{13}C NMR spectra for vanillic acid and its complexes were recorded and analyzed. Differences in the wavenumbers and positions of bands in the IR and Raman spectra as well as chemical shifts in NMR spectra of complexes in comparison with ligand were observed. These results suggest that selected metal cations affect the biochemical properties of vanillic acid.

Keywords: Vanillic acid; Spectroscopic studies; Electronic structure

This work was supported by grant no. N N312 111838

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SPECTROSCOPY OF ISOMERIC PYRIDINEDICARBOXYLIC ACIDS AND THEIR SODIUM SALTS. MICROBIOLOGICAL STUDIES

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Alkali metals ions slightly affect the electronic change distribution in benzene carboxylic acids [1]. This work was focused on the investigation of influence of sodium ion on the molecular structure of such ligands as isomers of pyridinedicarboxylic acid. Six isomers of pyridinedicarboxylic acid : 2,3-pdca; 2,4-pdca; 2,5-pdca; 2,6-pdca; 3,4-pdca; 3,5-pdca and their sodium salts were studied with use of IR and Raman spectroscopy. In order to assign accurately vibration bands on IR and Raman spectra theoretical calculations in Gaussian 03 W with use of graphical overlay Gauss View 4.1.2. were also collected and compared with experimental ones. The spectral assignments were done on the basis of the literature data.

Elementary and thermal analysis showed that obtained sodium salts of six isomers were hydrated compounds described with general formula: $Na_2L{\cdot}nH_2O$ where $L=C_3H_3N(COO^-)_2$ and n= from 1 to 6. The spectroscopic studies led to conclusions concerning the distribution of the electronic charge in the each isomer of the acid. Replacement of the carboxylic group hydrogen with a sodium ion brings about some characteristic changes in the IR and Raman spectra of these salts in comparison with the spectra of the acids. IR spectra of salts show presence of asymmetric COO^- stretching vibrations at about 1600 cm^{-1} and symmetric COO^- vibrations at about 1400 cm^{-1} [2],[3]. Theoretical investigations were essential in ascribing position of bands for C=N vibrations, while there are contradictory literature data for pyridinedicarboxylic acids. They showed that bands for C=N vibrations cannot be assigned only for ν(C=N) vibrations but always are connected with ring vibrations. On the basis of presented data we may discuss the effect of substituent position in the ring on the electronic system of sodium pyridinedicarboxylates. The estimation of the electronic charge distribution in sodium complexes allows us to interpret more precisely the mechanism by which sodium ion affect the biochemical properties of pyridinedicarboxylate ligands. Microbiological data were collected for chosen five bacteria strain: *Escherichia coli* (PCM 2268), *Pseudomonas aeruginosa* (PCM 2270), *Staphylococcus aureus* (PCM 2267), *Proteus vulgaris* (PCM 2269), *Bacillus subtilis* (PCM 2021) and fungus *Candida albicans* (PCM 2566). These analysis showed that sodium salts very strong inhibits specially *Proteus vulgaris* (PCM 2269) and *Candida albicans* (PCM 2566). Broth bouillons with strains and fungus were vaccinated with six isomers of pyridinedicarboxylic acid and their sodium salts. Sodium complex of 2,6-pdca ligand revealed its potential antibacterial properties. All results will be published soon.

Keywords: Pyridinedicarboxylic acids; Spectroscopy; Microbiology.

This work was supported by S/WBiIŚ/1/2012

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VIBRONIC COUPLINGS IN OPTICALLY NONLINEAR *N*–BENZYL–2–METHYL–4–NITROANILINE CRYSTAL STUDIED BY RESONANCE RAMAN AND UV–VIS SPECTROSCOPY

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The occurrence of second harmonic generation (SHG) in benzene derivatives crystals requires a non–centric crystal lattice and intramolecular charge transfer (ICT) from an electron–donor to an electron–acceptor group (push–pull molecules). It was theoretically and experimentally established that vibronic couplings amplify static optically nonlinear (NLO) responses [1,2] and the intermolecular charge transfer via hydrogen bonds (HBs) may also enhance the hyperpolarizability of the molecules [3].

The optically nonlinear *N*–benzyl–2–methyl–4–nitroaniline (BNA) crystal reveals the high efficiency of second harmonic generation (SHG) [4], widely tunable THz generation in 0.1–15 THz range [5] and electro–optic effect [6]. In the orthorhombic BNA crystal [4,7] there are intermolecular N – H ··· O (3.309Å) hydrogen bonds (HBs), extending in two different directions with the resultant parallel to the polar axis *c*, which are responsible for crystal stability [7].

The orthorhombic BNA crystal was excited with six lines 488.0, 496.5, 514.5, 530.9, 568.2, 647.1 nm from Ar–Kr laser and the resonance Raman spectra were recorded in the 15–3500 cm^{-1} range in order to find resonance excitation profiles (REPs) and to recognize the vibronic couplings while UV–Vis–NIR reflection spectra, transformed into absorption, for BNA powder, were recorded in the 5000–50000 cm^{-1} region to find transitions correlated with inter– and intramolecular charge transfers. The UV–Vis results are compared with those of the semi–empirical quantum chemical calculations [8] while REPs are compared with those found for BNA precursor, 2–methyl–4–nitroaniline (MNA) [9]. The conjugation between lattice and fundamental vibrations correlated with HBs as well as vibronic couplings are discussed as the important factor towards the origin of SHG in the BNA crystal.

Keywords: resonance excitation profiles, hydrogen bonds, inter– and intramolecular charge transfers

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STRUCTURAL STUDIES OF 2-PHENYL-THIAZOLE-4-YL-METHYL-QUINOLINIUM IODINE

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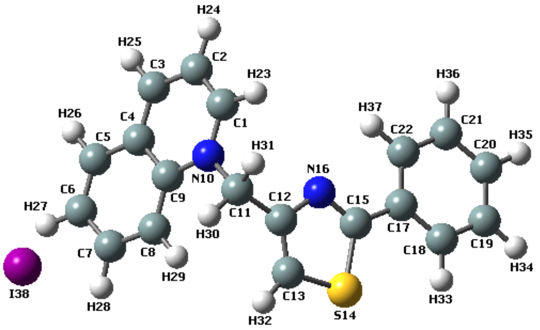
The synthesis of 2-phenyl-thiazole-4-yl-methyl-quinolinium iodide compound (2PTMQI) was performed by the alkylation of some nitrogen heterocycles, with halogen compounds, having in their structure 2-Aryl-thiazolic system [1,2]. The bactericide activity of the new compound has been evaluated against two strains of germs: *Staphylococcus aureus* and *Pseudomonas aeruginosa*.

In this work, experimental methods (NMR, FT-IR and Raman spectroscopies, and X-ray diffraction technique) coupled with quantum chemical calculations based on density functional theory (DFT) are used for structural and electronic characterization of phenyl-thiazole-4-yl-methyl-quinolinium iodide compound (2PTMQI).



Molecular structure and atom numbering scheme of 2PTMQI

X-ray diffraction technique indicates that 2PTMQI crystallized in the triclinic space group *P-1*, with Z=2 and cell parameters: a = 8.044(4)Å, b = 8.479(4)Å, c = 13.559(6)Å, α = 82.078(8)^{o}, β = 83.526(8)^{o} and γ = 74.350(7)^{o}.

The lowest energy conformer of this compound in gas phase was obtained by a potential energy surface scan performed at B3LYP/6-31G(d) level of theory.

The molecular vibrations of 2PTMQI were investigated by FT-IR, FT-Raman and SERS spectroscopies and a complete assignment of the experimental vibrational bands was possible on the basis of B3LYP/6-31G(d) calculations. The molecular electrostatic potential of this molecule has been calculated and used for predicting site candidates of electrophilic attack. By Raman and SERS spectroscopies, coupled with DFT calculations it was shown that this molecule adsorbs to the silver colloid through the sulfur atom.

^{1}H and ^{13}C NMR spectra of 2PTMQI were obtained in DMSO solution and they were also calculated using the GIAO (Gauge-Including Atomic Orbitals) method and by considering the solvent effects within the PCM solvation model. For a reliable prediction of the ^{13}C NMR spectrum of the investigated compound in DMSO solution, it is essential to use a correlation consistent basis set (cc-pVDZ) for carbon atoms.

Keywords: NMR, FT-IR, Raman, X-ray diffraction, DFT

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INVESTIGATION OF THE COMPLEXES BETWEEN DNA AND CHROMOSOMAL PROTEINS USING IR/VCD SPECTROSCOPY

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Interaction between DNA and two chromosomal proteins, HMGB1 and H1, have been studied. HMGB1 is a non-histone chromosomal protein. It is the most abundant member of HMGB (*High Mobility Group Box*) super family. One of the characteristic features of the HMGB proteins is a structural and functional motif, called HMGB-domain. This domain is responsible for DNA-binding activity of the HMGB-proteins. It was found that the HMGB-domains demonstrate structure specific binding to DNA. Among the typical targets of the proteins are pre-bent DNA structures, local distortions of the double helix, adducts of anti-cancer drug cisplatin etc. Although the HMGB-domains have been identified in various architectural and regulatory chromatin proteins their particular role in the living cell remains unclear. Another protein we studied was linker histone H1. Linker histones bind DNA on the entrances/exits of the nucleosomes and they are responsible for the structural organization of the chromatin.

Conventional spectroscopic approaches, such as UV circular dichroism (CD) are not very informative for the investigation of large supra molecular DNA-protein complexes. The major limitation of this technique is the considerable light scattering in the systems. To overcome this restriction we applied a combination of UV and IR absorption and CD spectroscopies. DNA-protein complexes were studied at different protein to DNA ratios in presence of divalent cations Ca^{2+}, Mg_{2+}, Mn^{2+}. The vibrational modes of the DNA bases and sugar-phosphate backbone were analyzed in the regions of 1800-1600 and 1300-800 cm^{-1} respectively. The experiments were performed in H_2O and D_2O solutions. The supra molecular structure of the complexes was visualized using atomic force microscopy.

Keywords: Circular Dichroism;UV/IR spectroscopy; DNA; chromatin; HMGB1; linker histone H1;

VIBRATIONAL SPECTROSCOPY OF THIOPHENE-FULLERENE DYADS

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Organic semiconductors are of high interest for applications as electronic components in photovoltaic devices. The mechanical flexibility, ease of processing, and low cost are only a few of their advantages [1].

One of the defining features of the organic photovoltaic devices (OPV) is the charge transfer originating from photo induced electronic transfer. The relative position between donor and acceptor molecules is critical for this process to occur. One of the best ways to optimize the relative position of the two components of the system is reported to be to covalently bond the parts [2].

In this study, we have investigated by DFT calculations the structural properties and the infrared and Raman-active vibrations of chemically bonded dyads of the fullerene C60 (acting as electron-acceptor) and thiophene-based molecules (acting as electron-donors). The 6-31g(d,p) basis set and the PBE and B3LYP exchange-correlation functionals have been employed throughout.

Specifically, we have considered six dyads with thiophene chains of increasing length in order to discern regularities and unambiguously assign the vibrational modes to the experimental spectral features. On the other hand, the results are aimed at matching the spectroscopic patterns with future charge transfer calculations, in which the length of the donor chain is expected to affect the efficiency of the transfer.

The geometry optimizations of the dyads reveal equilibrium donor-acceptor positions depending manifestly on the thiophene length, with the latter tending to bend about the fullerene. Both structural and spectral properties are compared with experimental and theoretical data from the literature. The agreement with experiments that we achieved is superior to previous publications.

Keywords: ab initio, infrared, Raman, dyads, OPV

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CHITOSAN-COATED ANISOTROPIC SILVER NANOPARTICLES AS A NOVEL CLASS OF SERS NANO-TAGS INSIDE LIVING CELLS

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There is an urgent need of new strategies for noninvasive diagnostic and monitoring of pathological conditions within the human body. The approach of combining the unique physical properties of noble-metal nanoparticles with their chemical specificity and easy way of conjugation opens new routes toward innovative methods of diagnosis and imaging inside living organisms. The nanoparticles of anisotropic shape bring an enormous potential for such applications because they give plasmon resonances within the near-infrared (NIR) optical window, transparent for biological tissue [1]. In addition, the sharp geometries they present can efficiently amplify the electromagnetic field around them, enabling anisotropic nanoparticles to be exploited as reproducible and highly sensitive surface-enhanced Raman scattering (SERS) nano-tags inside living cells [2]. We have recently developed a two-steps approach to prepare anisotropic silver nanoparticles enveloped in a shell of chitosan biopolymer. Taking the advantage of high stability of as-prepared chitosan-coated silver nanoparticles, a versatile dual plasmonic sensor was demonstrated in solution by combining localized surface plasmon resonance (LSPR) and SERS abilities [3]. Herein, we report new results which prove the potential of chitosan-coated anisotropic silver nanoparticles to act as SERS-active tags inside living cells. The SERS nano-tags were designed using *para*-aminothiophenol (*p*-ATP) as Raman active molecule. As prepared nano-tags were found to be highly stable under a wide range of environmental conditions (such as storage time, different pH, increased temperature), to be easily internalized by the cells and to be detectable inside living cells under a wide window of excitation wavelengths, ranging from visible to NIR. The fabricated plasmonic nanoparticles with endowed biocompatibility by chitosan coating can hold significant potential for diagnosis and imaging inside living organisms.

Keywords: SERS-tags; anisotropic silver nanoparticles; chitosan

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SPECTROSCOPIC AND THEORETICAL STUDY ON ALKALI METAL PHENYLACETATES

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Relationship between molecular structure and biological activity of chemical compound was intensively studied [1,2]. Phenylacetic acid is one of biological active ligand from the series $C_6H_5COO^-$, $C_6H_5CH_2COO^-$, $C_6H_5C_2H_2COO^-$. Benzoate, phenylacetate and phenylpropionate were intermediates in the methanogenic degradation of rice straw [3]. There are some papers about antioxidative and antiradical properties of phenylacetic acid [4,5]. It seems to be interesting to study on molecular structure of some phenylacetates.

In this work the influence of lithium, sodium, potassium, rubidium and cesium cations on the electronic system of phenylacetic acid was studied. The FT-IR and ^1H and ^{13}C NMR spectra were recorded for studied compounds. Characteristic shifts in IR and NMR spectra along phenylacetates of alkali metal salts were observed. Good correlations between the wavenumbers of the vibrational bands in the IR spectra of phenylacetates and some alkali metal parameters such as ionic potential, electronegativity, inverse of atomic mass, atomic radius and ionization energy were found for alkali metal phenylacetates. The density functional hybrid method B3LYP with 6-311++G** basis set was used to calculate optimized geometrical structures of studied compounds. Aromaticity indices, atomic charges, dipole moments and energies were calculated as well as the wavenumbers and intensities of IR spectra and chemical shifts in NMR spectra. The theoretical parameters were compared to experimental characteristic of alkali metal phenylacetates.

Keywords: alkali metal phenylacetates, IR, Raman, NMR, DFT

Acknowledgments
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SPECTROSCOPIC (FT-IR, FT-RAMAN, 1H AND 13C NMR), THERMOGRAVIMETRIC AND THEORETICAL STUDIES OF GENTISIC ACID AND SODIUM, COPPER(II) AND CADMIUM(II) GENTISATES

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Gentisic acid (2,5-dihydroxybenzoic acid) belongs to the group of phenolic acids, substances that naturally occur in fruit, vegetables, nuts, seeds, flowers and some herb beverages. There are no reports in literature about copper and cadmium gentisates. Although Ashidate et al. [1] mention that gentisic acid had only minimal copper chelating activity basing on UV spectra without publishing any data. In the present study the synthesis of above mentioned complexes and the investigation using vibrational spectroscopy, thermogravimetry analysis as well as chemical-quantum calculations data are described. Gentisic acid and its sodium salt were used to comparison with the results obtained for copper and cadmium complexes.

Sodium, copper(II) and cadmium(II) gentisates were synthesized and analyzed. Spectroscopic properties and molecular structures of studied compounds were determined using different complementary methods: FT-IR, FT-Raman, elementary analysis, thermogravimetric analysis and quantum-mechanical calculations. Analysis of the experimental IR and Raman spectra are confirmed by the results of chemical quantum calculations. Good correlation between experimental and theoretical FT-IR spectra was obtained. Elementary analysis was done for cadmium and copper gentisates. Obtained results were confirmed by thermogravimetric studies. The elementary and thermal analysis data were used to define formulas of obtained compounds ($[Cu(C_7H_5O_4)_2]\bullet 4H_2O$ and $[Cd(C_7H_5O_4)_2]\bullet 4H_2O$). On the basis of FT-IR data the type of coordination of COO- group by metal ions in synthesized complexes was suggested. According to the spectroscopic criteria the carboxylate group in cadmium gentisate is monodentate, whereas in copper gentisate seems to be bidentate chelating.

Keywords: sodium, copper and cadmium gentisates, FT-IR, FT-Raman, NMR, thermogravimetry, DFT, molecular structure

Acknowledgments
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STRUCTURAL CHANGES OF BETA-CAROTENE AND SOME RETINOID PHARMACEUTICALS INDUCED BY ENVIRONMENTAL FACTORS

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Carotenoids are natural antioxidant agents, pigments, and precursors of vitamin A. They have a beneficial effect on human health and are often used to cure skin diseases, problems with visual perception and immune system [1]. β-carotene is usually added as an element of vitamins and a supplement in a great number of food products, whereas retinoids are used as active components of tablets in the treatment of dermatological conditions.

Carotenoids consist of a long polyene chain (a system of conjugated double bonds) that is responsible for strong Raman signal. There are three characteristic bands in Raman spectra of these compounds: two of high intensity in the region of 1500 – 1550 cm^{-1} and 1150 – 1170 cm^{-1} due to stretching modes of C=C and C–C bonds (ν_1 and ν_2), respectively, and a band of medium intensity in the range of 1000 – 1020 cm^{-1} due to in-plane rocking modes of CH_3 groups attached to the polyene chain (ν_3) [2]. Furthermore, the position of ν_1 depends strongly on the length and terminal substituents of the polyene chain of carotenoids/retinoids as well as on their interaction with the environment [3].

Raman spectra of β-carotene and some retinoids (retinoic acid, isotretinoin, and etretinate) were collected from common pharmaceuticals (Betakaroten, Curacne, and Tigason) and interpreted on the basis of the characteristic bands. The influence of various factors on the position of Raman bands in β-carotene and etretinate spectra was investigated. For etretinate, solvents of various polarity and acidity were used to study the influence of environmental factors on its structure. Small bands' shifts were explained as being a result of compound aggregation and hydrolysis. Additionally, temperature stress was applied to investigate structural changes in β-carotene molecules. Raman spectra of synthetic β-carotene were studied in temperature range of -150 – +150°C. The observed changes were shown to be related to the β-carotene conformers' population in each temperature. Furthermore, the asymmetry of the ν_1 band was observed and explained by means of the band shape analysis.

The experimental vibrational spectra and electronic structures of all compounds were interpreted based on calculated models obtained using quantum-chemical methods. The most important conformers of β-carotene were analyzed to explain the influence of temperature stress on bands shifts. Retinoid conformers were calculated to compare theoretical and experimental spectra.

Keywords: β-carotene; retinoic acid; isotretinoin; etretinate; aggregation; solvent effect; temperature stress

Acknowledgement
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FT-IR IMAGING AND FT-RAMAN MAPPING OF Ni-HYPERACCUMULATING AND NON-HYPERACCUMULATING GENOTYPES OF *SENECIO CORONATUS*

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Most plants growing on metal-rich soils exclude metals from their shoots. However, about 2% of plants inhabiting these soils accumulate large quantities of heavy metals in their shoots: a phenomenon known as hyperaccumulation. *Senecio coronatus* (Thunb.) Harv. Asteraceae, is widespread in grasslands in South Africa but is also found on ultramafic outcrops. Populations of *S. coronatus* occurring on ultramafic soils represent Ni-hyperaccumulating and non-hyperaccumulating genotypes. They differ in terms of Ni uptake and show distinct cytological differences [1].

The identification and quantitative determination of plant components are usually performed using chromatographic methods that require destructive plant material compound extraction. Thus, it is impossible to investigate compound distribution at the cellular level. However, this limitation can be overcome by the use of vibrational spectroscopy methods such as Infrared and Raman spectroscopy. Furthermore, the simultaneous determination of several components *in situ* is possible when using the infrared imaging and Raman mapping techniques. Both techniques have been successfully applied for the nondestructive investigation of natural compounds [2,3].

Two genotypes of *S. coronatus* (a Ni hyperaccumulator and a non-hyperaccumulator) growing on ultramafic outcrops were investigated by FT-IR imaging and FT-Raman mapping to identify main components in both genotypes and show chemical differences between them. Additionally, the distribution of observed components in plant leaves and roots was determined to point out tissues that are the most valuable source of each compound. Spectra of both genotypes were found to be quite different from each other and the tissue dependent distribution of plant components was observed. The main emphasis was put on cytological differences between the genotypes, especially such as specialized cells which occur only in roots of the hyperaccumulating one. *S. coronatus* genotypes are also interesting in terms of the presence of copious material (lipids, alkaloids, and terpenoids) accumulated as deposits within air spaces.

Keywords: FT-IR imaging; FT-Raman mapping; Ni-hyperaccumulation; Senecio coronatus

Acknowledgement
The research was supported by the International PhD-studies program at the Faculty of Chemistry Jagiellonian University within the Foundation for Polish Science MPD Program co-financed by the EU European Regional Development Fund.

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VIBRATIONAL STUDY OF 2-[2,6-DICHLOROPHENYLIMINO] IMIDAZOLIDINE BASED ON DFT CALCULATIONS AND SQMFF METHODOLOGY

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We have studied the theoretical structural and vibrational properties of a vasodilator broadly used in hypertensive therapy, the 2-[2,6-dichlorophenylimino] imidazolidine compound, by using the experimental vibrational spectra and the Density Functional Theory (DFT). Calculations with Pople's basis set show that three conformers for the title molecule were theoretically determined in the gas phase, in accordance with the previously reported structural study by *Remko et a.l* [1], and probably those structures are present in the solid phase. The molecular structures are observed in the Figure 1.

Theoretical study of structure, p*K*a, lipophilicity, solubility, absorption, and polar surface area of this compound were published at the B3LYP/6-31+G** and B3P86/TZP methods [1]. In this study, the corresponding geometries for the compound were calculated using the Gaussian 03 [2] program at B3LYP theory level while the harmonic vibrational frequencies for the optimized geometries of the compound were calculated using 6-31G* and 6-311++G** basis sets in the approximation of the isolated molecule. Then, for a complete assignment of the infrared and Raman spectra, DFT calculations were combined with Pulay´s Scaled Quantum Mechanics Force Field (SQMFF) methodology [3] in order to fit the theoretical wavenumber values to the experimental ones. Here, a complete assignment of the observed bands for the title molecule was performed.

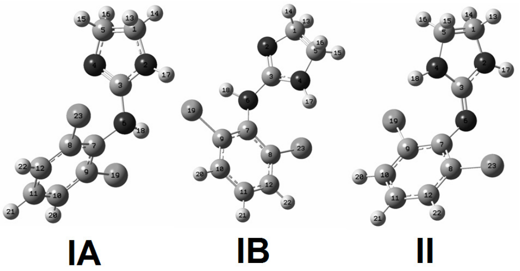

Fig.1 Theoretical structures of 2-[2,6-dichlorophenylimino] imidazolidine

In addition, the topological properties and the magnitude of the intramolecular interactions [4], the reaction path for the interconversion between the tautomers, the force constants and the frontier molecular orbitals were performed for the compound and then analyzed and compared with the results obtained for similar compounds [5,6].

Keywords: 2-[2,6-dichlorophenylimino]imidazolidine, Infrared spectrum, molecular structure, force field.

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LOW-WAVENUMBER RAMAN SCATTERING STUDY OF INCLUSION PHENOMENA IN BETA-CYCLODEXTRINS: EFFECT ON THE BOSON PEAK

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Cyclodextrins (CD) are well known in supramolecular chemistry as effective host organic systems able of encapsulating a wide variety of guest molecules in their hydrophobic cavity via non-covalent interactions [1]. The understanding of molecular mechanisms leading to the formation of these supramolecular assemblies is a topic of growing interest in physical chemistry, also in view of the rational design of new smart systems for bio-molecular encapsulation.

Here we report the study on the effect of the inclusion process of the anti-inflammatory drug ibuprofen (IBP), in both its enantiomeric forms, on the low-frequency vibrational dynamics of different types of native and modified cyclodextrins, probed by inelastic light scattering experiments. In particular, we inspect the low-frequency Raman spectra of IBP-CD inclusion complexes, focusing on the modifications occurring on the so-called "boson peak" (BP), a prominent feature typically observed in low-frequency inelastic neutron and Raman scattering spectra of amorphous materials and connected to significant physical parameters, including the elastic properties of the system in the mesoscopic range. These results will be compared with those obtained by inelastic neutron scattering experiments and by investigation of the vibrational dynamics of complexes in the high-frequency regime [2-4] with the aim to provide a detailed picture of the host-guest interactions involved in the equilibrium processes of the host-guest complex formation.

Keywords: Boson peak; cyclodextrin; Raman spectroscopy

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MOLECULAR STRUCTURE OF PHENYL- AND PHENOXYACETIC ACIDS – SPECTROSCOPIC AND THEORETICAL STUDY

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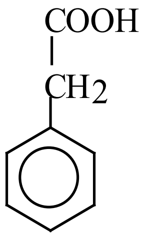
Phenylacetic (PNA) and phenoxyacetic acid (PAA) are biologically active compounds. They have antimicrobial, anticancer, antitumour, analgesic and anti-inflammatory bioactivity. They might be used as plant growth regulators as well as inhibitors of tillage [1]. In previous papers we analyzed the effect of substituents on the electronic structure of the aromatic ring of benzoic acid derivatives [2-3]. In this paper the study of chemical compounds with carboxyl group, which is not directly linked up the ring is presented. In phenylacetic acid molecule COOH group connects with the ring by the methylene group (-CH_2-) however in phenoxyacetic acid additionally by the ether group (-O-). The changes in physical, chemical and biological properties of them decided about their effect on the biological systems.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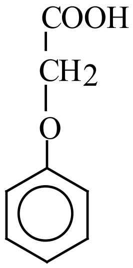
PAA

The FT-IR, FT-Raman and ^1H and ^{13}C NMR spectra were recorded for studied compounds in comparison with benzoic acid . The density functional hybrid method DFT (B3LYP/ 6-311++G**) was used to calculate optimized geometrical structures of studied compounds. Aromaticity indices, atomic charges, dipole moments and energies were calculated as well as the wavenumbers and intensities of IR spectra and chemical shifts in NMR spectra. The theoretical parameters were compared to experimental characteristic of phenyl- and phenoxyacetic acids.

Keywords: phenylacetic acid, phenoxyacetic acid, IR, Raman, NMR, DFT calculations

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EXPERIMENTAL AND THEORETICAL STUDY ON BENZOIC ACID DERIVATIVES

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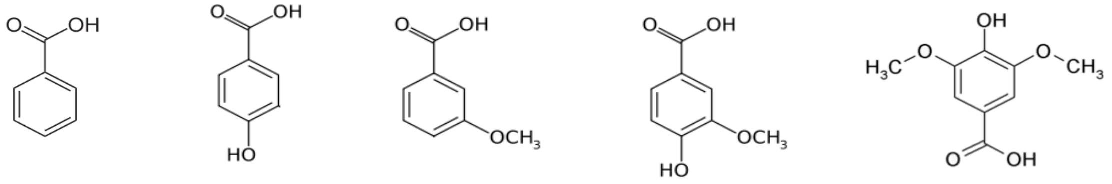
Benzoic acid derivatives are widely used as industrial chemicals, agrochemicals, pharmaceuticals and consumer products. Those of them with hydroxy and methoxy groups in molecule are known to have various biological activites [1-3].

Benzoic (BA), p-hydroxybenzoic (HBA), m-methoxybenzoic (MBA), vanilic (VA) and syringic (SGA) acids (Fig. 1) were studied using both experimental and theoretical tools.



BA HBA MBA VA SGA

Fig.1 Structural formula and codes of studied compounds

The vibrational (FT-IR, FT-Raman) and ^{1}H and ^{13}C NMR spectra of benzoic acid derivatives were recorded. Characteristic shifts and changes in intensities of bands along the studied series were observed. The changes of chemical shifts of protons (^{1}H NMR) and carbons (^{13}C NMR) in the series of studied compounds were observed too.

Optimized geometrical structures of studied compounds were obtained by B3LYP method using 6-311++G** basis set. Aromaticity indices, atomic charges, dipole moments and energies were calculated. The theoretical chemical shifts in ^{1}H and ^{13}C NMR spectra and theoretical wavenumbers and intensities of IR and Raman spectra were determined. The calculated parameters were compared to experimental characteristic of studied compounds.

Keywords: p-hydroxybenzoic acid; m-methoxybenzoic acid; vanilic acid; syringic acid, IR, Raman, NMR, DFT

Acknowledgments

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PLASMONIC PROPERTIES AND SURFACE ENHANCED RAMAN SCATTERING ON LINEAR ARRAYS OF GOLD HALF-SHELLS

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Surface enhanced Raman scattering (SERS) is a spectroscopic technique by which the Raman scattering from molecules absorbed on nanostructured metallic surfaces is several orders of magnitude (10^6-10^{12} or even more) stronger than that of free molecules. This feature is very exciting because it enables the detection and identification of very low analyte concentrations, down to the single molecule level [1]. This is possible by exploiting the enhanced electromagnetic fields at the metal surface, determined by the excitation of surface plasmons. Highly enhanced fields and high SERS enhancement factors are favoured by the presence of nanoscale roughness, as edges, apexex, corners, or gaps on the metallic nanostructure surface [2]. To have a good reproducibility of their SERS response, their size, shape, dispersity and organization need to be controlled, preferably over large surface areas. Currently, there is still a lack of SERS substrates which simultaneously satisfy these requirements, therefore the development of applications benefiting from the high sensitivity of the SERS technique is hampered.

In this work we describe an original approach to obtain nanostructured noble metal surfaces comprising linear chains of noble-metal semi-shells. By employing convective self-assembly (CSA) on a highly available and affordable substrate as template (grooves on DVDs), we obtained well defined, unidirectional lattices of polystyrene (PS) nanospheres (500 nm diameter). These are then used as templates for gold film deposition. Scanning electron microscopy (SEM), atomic force microscopy, optical transmission and reflectivity are employed to characterize the gold half-shell linear arrays. Their capability as SERS substrates is assessed by confocal Raman micro-spectroscopy under multiple excitation laser lines. These linear half-shell arrays can prove useful for developing SERS-based optical sensors. The presented studies will also further the current understanding of the optical properties and SERS behaviour of so-called Metal-Film over Nanospheres, a confirmed class of efficient and cost-effective SERS substrates [3,4].

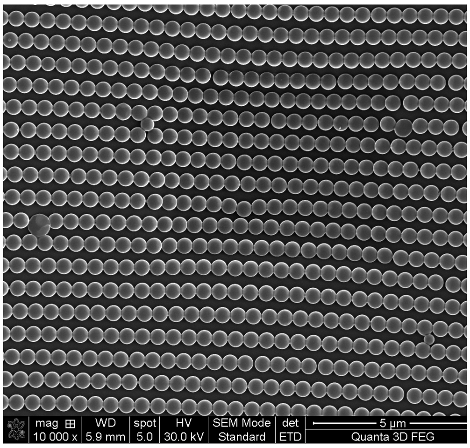

Fig.1 Scanning electron microscopy image of a linear array of gold half-shells.

Acknowledgement. This work was supported by CNCSIS–UEFISCSU, project Number PNII ID PCCE 129/2008

Keywords: surface enhanced Raman scattering; gold semi-shells; optical sensors

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RAMAN SPECTROSCOPY FOR IDENTIFICATION OF DIFFERENT CELL CULTURE CONTROLS AND VIRUS INFECTED

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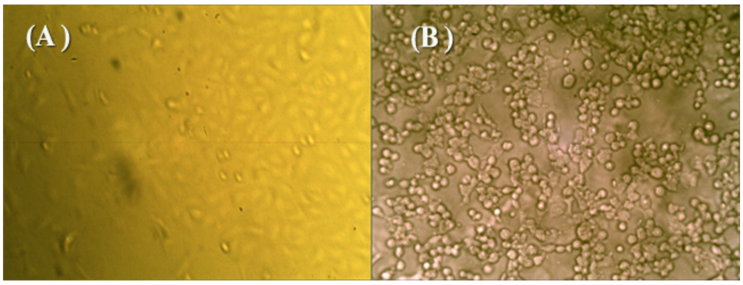

Fig. 1: A) control Vero uninfected cells.
B) Vero cells infected with HSV1

In general, viruses are involved in various clinical diseases in humans and animals. For instance, MuSV causes cancer in mice while HSV-1 is mainly involved in human cutaneous disorders. Early detection of these viral infections is critical for its successful therapy. The routine techniques used for the identification and detection of these viral infections are time consuming and highly costs. Therefore there is a need for developing a rapid, sensitive and simple technique for the identification of these infections.

Features of Raman spectroscopy like, sensitivity, rapidity and reliability make it ideal to investigate biological systems. It has been used to track changes between normal and abnormal cells and tissues in medicine and biology. In this study we investigated control NIH/3T3 fibroblast cells and malignant fibroblast cells transformed by murine sarcoma virus (NIH-MuSV), control Vero cells (Fig. 1A) and infected Vero cells with herpes simplex virus type 1 (HSV-1) (Fig1.B). These biological systems were identified and characterized using Raman spectroscopy and multi-variate analysis: principle component analysis (PCA) and linear discriminant analysis (LDA).

Cell culture is considered as an ideal model for the detection and identification of specific biomarkers related to the mentioned viral disorders due to its homogeneity and a complete control of most factors affecting its growth.

Keywords: RAMAN SPECTROSCOPY, PCA, LDA, CELL LINE, VIRAL INFECTIONS.

SERS OF PORPHYRINS FROM REGULAR METAL NANOSTRUCTURES

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Surface-enhanced Raman scattering (SERS) is an extremely sensitive spectroscopic technique that enhances Raman signal of molecules adsorbed on rough metal surfaces [1]. Routine (bio)analytical, (bio)sensing and medical SERS applications require sensitive and spectrally reproducible SERS-active surfaces [2]. Rationally designed regular metal nanostructures fabricated by nanosphere lithography (NSL) and biotemplating can fulfill above mentioned criteria. NSL is based on self-assembly of a monolayer of polystyrene or silica nanospheres on a solid substrate serving as a template for deposition of metal. Metal deposited in a compact layer onto the nanosphere template forms a surface called "film over nanosphere" (FON) [3]. Properties of FON can be adapted by functionalization so that FONs can be applied as efficient biosensors [3]. Nanobowl array is another example of surfaces based on NSL. The FON is peeled off the glass substrate and the nanosphere template is removed [4]. Advantage of this surface could be sharp edges of the nanobowls providing higher SERS enhancement.

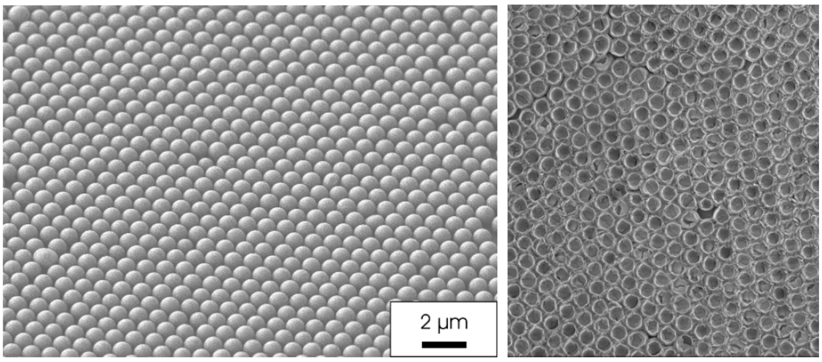

Fig. 1 SEM micrographs of AuFON (20 nm of gold) – left, and Au nanobowls (40 nm of gold) - right

In this contribution gold and silver FONs (Fig. 1, left) and nanobowl arrays (Fig. 1, right) were prepared and tested using SERS microspectroscopy. Good SERS spectra of testing biomolecule 5,10,15,20-tetrakis(1-methyl-4-pyridyl)porphyrin were obtained. Sensitivity, spectral reproducibility and (bio)analytical potential of these SERS surfaces were compared.

Keywords: SERS; film over nanosphere; nanobowls; porphyrin

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SPECTROSCOPIC INVESTIGATION AND ASSESSMENT OF METHYLENE BLUE LOADED GOLD-PLURONIC NANOPARTICLES FOR APPLICATION IN PHOTODYNAMIC THERAPY

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Methylene blue (MB) is a well-known photosensitizing drug employed in numerous biomedical applications, including photodynamic therapy (PDT). However, the excellent photochemical properties of MB, including the high quantum yield of intersystem crossing and singlet oxygen generation, are hindered in biological media, due to the formation of colorless leukomethylene blue which has negligible photodynamic activity.

In this work, we incorporated MB molecules into the polymeric shell of gold-Pluronic hybrid nanoparticles, preserving in this way its photodynamic effectiveness and obtaining multifunctional nanoparticles able to serve as therapeutic agents by photo-activation and, simultaneously, as sensitive spectroscopic probes. We demonstrated by combined detection through Surface Enhanced Raman Spectroscopy (SERS) and fluorescence measurements, that MB molecules are located in the whole polymeric shell, intercalated between the polymeric chains and also in the close proximity to the nanoparticle surface. Furthermore, we demonstrated the ability of the attached MB molecules to generate singlet oxygen, the main factor that mediates cytotoxicity in PDT.

Biological experiments were further conducted by incubating a line of cancer cells with hybrid nanoparticles *in vitro*. First verification of nanoparticles uptake by cells revealed an extranuclear, intracellular localization of the particles as imaged both by dark field images and measured by optical scattering spectra. Nanotoxicity tests proved a high biocompatibility of the particles, even at relatively high concentration and long-time (>48 h) exposure in dark. To achieve PDT we irradiated the nanoparticles inside cells using 660 nm light which overlaps the absorption band of MB molecules. Evaluation of phototoxicity by PDT showed that the photochemical destruction appears only in the irradiated spots and only in the presence of photosenzitizer tagged hybrid nanoparticles. Moreover, we found that the ability photosenzitizer tagged hybrid nanoparticles to kill cancer cells is superior to MB PDT treatment alone.

As a result, by integrating SERS, fluorescence and photosensitizing properties, the preparation of MB loaded gold-Pluronic hybrids represents a valuable development in field of multifunctional nanomaterials.

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Keywords: Multifunctional; Gold; Pluronic; Methylene Blue

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PHOTOPHYSICAL STUDY OF Zn PHTHALOCYANINE IN SOLVENT MIXTURES

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Photophysical properties of phthalocyanines are important in photodynamic therapy, where these compounds are used as photosensitizing agents. After their accumulation in the tumor, the photosensitizers are exposed to a light flux of specific wavelength. A photosensitizer absorbs light and produces active species *via* proper intermolecular excitation transfer processes. Among active species is the oxygen molecule in its first electronic excited state - singlet oxygen - that destroys nearby cancer cells. Optimisation of singlet oxygen generation is the way to the success of this kind of therapy.

Results on the measurement of photophysical properties of Zn Phthalocyanine (ZnPc) in different solvent mixtures as water/dimethyl sulfoxide and benzene/dimethyl sulfoxide are reported.

By using steady state absorption and laser induced fluorescence (LIF) spectroscopy techniques, parameters such as absorbance and quantum yield of fluorescence were determined function of water mole fraction in the solvent mixtures (Fig. 1).

The lifetime and quantum yield of photogenerated singlet oxygen behavior versus solvents rate were determined by the measurement of the time resolved phosphorescence of O_2 molecule at 1270 nm. This was generated *via* energy transfer from excited ZnPc molecule by the third harmonic of a pulsed Nd:YAG laser.

The data obtained were compared with the results obtained by time resolved laser photoacoustic spectroscopy measurements.

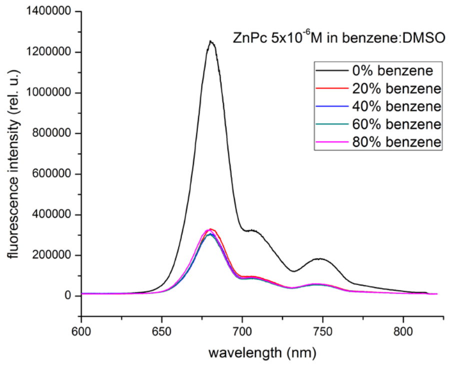

Fig. 1 LIF spectra of ZnPc 5x10^{-6} M solvated in benzene/DMSO mixtures.

Keywords: phthalocyanines; photophysics; singlet oxygen

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RAMAN SCATTERING STUDY OF 1-AMINOPYRENE DERIVATIVES

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N-triazinylated derivatives of 1-aminopyrene were shown to exhibit interesting photophysical properties, particularly the strong dependence of their fluorescence quantum yields on solvent polarity [1]. Recently, semiempirical calculations [2] indicated that when chlorine substituents are attached to the triazine ring, the nonradiative deexcitation can proceed via charge-transfer states. However, there has not been found any direct evidence of these states yet.

In this study, we tried to find support for the transition charge-transfer states in these compounds by measurement of resonance Raman scattering intensities which are known to reflect the dynamics of the excited state [3]. For this purpose, three compounds differing in the number of chlorine substituents were chosen, namely N-(4,6-dimethoxy-1,3,5-triazin-2-yl)-1-aminopyrene (APyTM2, Fig.1), N-(4-methoxy-6-chloro-1,3,5-triazin-2-yl)-1-aminopyrene (APyTCM) and N-(4,6-dichloro-1,3,5-triazin-2-yl)-1-aminopyrene (APyTC2).

We present a comparison of resonance Raman spectra of these compounds excited at 355 nm, i.e. at the maximum of their first absorption band, to normal Raman spectra measured by excitation at 632 nm. The assignment of the normal modes has been performed using the calculation of vibrational frequencies by DFT (B3LYP functional, split-valence basis set) method as implemented in Gaussian 09 software package [4]. In addition, we discuss the differences in surface-enhanced Raman spectra of these compounds obtained from aggregated silver colloidal particles.

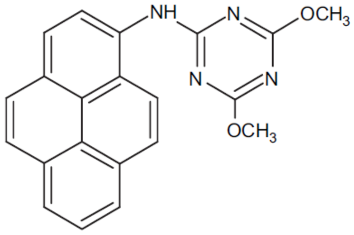

Fig.1 APyTM2 structure

Keywords: Aminopyrene,Charge-transfer, Resonance Raman, DFT, SERS

Acknowledgement
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SERS MONITORING OF NEW CHEMOTERAPEUTIC AGENT BASED ON DOXORUBICIN LOADED GOLD NANOPARTICLES

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The adsorption of the molecules on the metal surface can be considered as a *mimic* of drug adsorption process. Adsorption of the molecules on the metallic surface with nanometer structure give intense Raman spectra (SERS) determined by two main mechanism; electromagnetic and chemical one [1]. SERS has the advantages of chemical specificity, which help to overcome background problems affecting fluorescence spectroscopy in transient signals.

Controlling the stability of chemotherapeutic system based on metallic nanoparticles is a key aspect that must be addressed for medical applications of nanotechnology. In this sense, the ability of gelatin biopolymer to act as both reducing and stabilizing agent in the synthesis of gold nanoparticles (GNPs) was investigated here in order to synthesize a new chemotherapeutic system both stable and biocompatible.

We propose a completely green method for "one pot" synthesis of GNPs with controlled size by varying the gelatin and gold ions concentrations. The as synthesized GNPs were characterized in order to establish the role of gelatin concentration on the size, charge and stability of GNPs.

The biosynthesized GNPs were subsequently conjugated with doxorubicin (DOX) - a chemotherapeutic drug, then the DOX-GNPs system was monitored by surface plasmon resonance spectroscopy (LSPR), dynamic light scattering (DLS), surface-enhanced Raman spectroscopy (SERS), zeta potential and fluorescence measurements in order to characterize it and monitor the adsorption of doxorubicin on gold surface.

The SERS investigation of this novel DOX-GNPs system is a necessary step in order to further exploit it as a drug delivery carrier. Due to the highly biocompatible surface of biosynthesized GNPs, the DOX-GNPs complex can be used in biological media without further processing.

Acknowledgement:
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Keywords: SERS; Nanoparticles; Biosynthesis chemotherapeutic system.

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TAMOXIFEN AND CURCUMIN BINDING TO SERUM ALBUMIN. SPECTROSCOPIC STUDY

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During long term therapy, such as chemopreventive or anticancer therapy, the combination of several drugs could be necessary. Combination of tamoxifen (TMX) and curcumin (CUR) could be more effective with lower toxicity than each agent alone in use for the treatment of breast cancer. Binding of drugs to serum albumin is an important factor, which determines toxicity and therapeutic dosage of the drugs. The competition between two drugs for the binding site on albumin can result in a decrease in binding and an increase in the concentration of free biologically active fraction of drug in combination therapy.

The aim of the study was to examine the binding of tamoxifen and curcumin to human serum albumin and competition between them using fluorescence spectroscopy.

Quenching curves and the values of the binding parameters (binding constants, quenching constants, the number of drug molecules bound to binding site) indicate that TMX and CUR bound to human serum albumin (HSA). One binding site in the tertiary structure of HSA for both TMX and CUR was found.

A blue shift by 45 nm of fluorescence emission maximum of CUR in the presence of HSA shows that the binding of the drug to HSA was accompanied by an alteration of the hydrophobicity of the microenvironment.

Keywords: Tamoxifen, Curcumin, Fluorescence

Acknowledgements: This work was supported by the Grants from Medical University of Silesia: KNW-1-055/D/1/0 and KNW-1-050/P/1/0.

THE IR STUDY OF HUMIC ACIDS EXTRACTED FROM SEDIMENT AT GOCZAŁKOWICE DAM RESERVOIR BEFORE AND AFTER FLOOD

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The aim of this study was to estimate the effect of flood, which took place in 2010 on the Vistula River, on the properties of humic substances extracted from sediments collected at the Goczałkowice Reservoir. On the basis of the analysis of infrared (IR) spectra the influence of flood on the ability of humic acids to form metal complexes was estimated.

Sediment samples were collected from four places at the Goczałkowice Reservoir before (June 2009 and August 2009) and after flood (June 2010). Humic acids were extracted from sediment samples by alkaline extraction. Humic acids were studied by the infrared spectroscopy that allowed to identify characteristic functional groups of humic acids. A comparison of the relative intensity of absorption bands at $\nu = 1720$ cm^{-1}, typical for the carbonyl groups of carboxylic acids, aldehydes and ketones, and $\nu = 1650$-1610 cm^{-1}, corresponding to the asymmetric vibrations of dissociated carboxylic group or carboxyl group stretching vibrations of bonds between carbon atoms of aromatic rings, allows to evaluate the ability of extracted humic acids to form metal complexes.

The obtained IR spectra of humic acids extracted from sediments collected before and after flood, revealed the following absorption bands: $\nu_{\text{OH and/or NH}}$=3500-3300 cm^{-1}, $\nu_{\text{C-H}}$=2930 cm^{-1}, $\nu_{\text{C-H}}$=2850 cm^{-1}, $\nu_{\text{C=O}}$=1720 cm^{-1}, $\nu_{\text{C=C and/or COO-}}$=1650-1610 cm^{-1}, ν_{NH}=1540 cm^{-1}, $\nu_{\text{C-H}}$=1450 cm^{-1}, $\nu_{\text{C=O}}$=1080-1030 cm^{-1}, $\nu_{\text{C-H}}$=880-750 cm^{-1}.

It was found that the absorption band at about $\nu = 1720$ cm^{-1} of the IR spectra of humic acids extracted from sediments collected before flood is clearly visible, while it is much less intense or completely disappears in the IR spectra of humic acids extracted from sediment collected after the flood. The decrease of the intensity of the absorption band at $\nu = 1720$ cm^{-1} and the increase of the intensity of the absorption band $\nu = 1650$-1610 cm^{-1} on the IR spectra of humic acids extracted from sediments after the flood, may be an evidence of the increase in the ability of humic acids to form metal complexes. It can be said on the basis of previous findings that there is a correlation between the formation of metal complexes and the maturity of humic acids extracted from sediments [1-2]. Therefore, a simple analysis of changes of the intensity of absorption bands $\nu = 1720$ cm^{-1} and $\nu = 1650$-1610 cm^{-1} in the IR spectra allows to estimate the ability of humic substances to form metal complexes and their maturity.

Keywords: IR spectroscopy, Humic acids, Sediments

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THE USE OF UV/VIS AND EPR SPECTROSCOPY TO STUDY OF HUMIC ACIDS EXTRACTED FROM SEWAGE SLUDGE

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The sewage treatment process leads to the formation of large quantities of sewage sludge. Sewage sludge, if they meet health standards, can be used for remediation of soil or converted to compost. Agricultural value of sewage sludge would be assessed by their ability to form humus. Therefore it is important to determine the properties and maturity of humic acids extracted from sewage sludge collected at different stages of sewage treatment.

UV/Vis and EPR spectroscopy was used for these characteristics. The sludge samples were taken from the raw sewage sludge, the nitrification chamber, the denitrification chamber and sludge drying bed after the press from biologic-mechanical plant in Skoczów. Humic acids were extracted from sewage sludge by alkaline extraction.

On the basis of an increase of E_4/E_6 parameter in UV/Vis spectra it can be concluded that during the treatment process the intensity of oxidation and enrichment of humic acids with the oxygen functional groups increases. On the basis of UV/Vis spectra it can be also concluded that with the progress of treatment process, there is a change of parameters: E_2/E_3, E_3/E_4, E_{350}/E_{450}, E_2/E_4, E_2/E_6 that indicates the change in the degree of aromatization of extracted humic acid. These results confirm the intensification of the humification processes during the wastewater treatment process.

The EPR analysis, i.e. determination of the parameter g and the concentration of free radicals confirms the results of the UV/Vis spectroscopy. Results of the UV/Vis and EPR spectroscopy show that during the wastewater treatment process, humic acids extracted from sludge after the press are enriched with oxygen functional groups.

Keywords: UV/Vis, EPR, Humic acids

Acknowledgement: This work was supported by the Ministry of Science and Higher Education in Poland, University of Silesia (project No N N204 1932 33; BW/ICh/10/11) and Medical University of Silesia (KWN-1-050/P/1/0), Poland.

TOWARD AN ACCURATE LINE LIST OF THE C_2 MOLECULE

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C_2 is one of the fundamental radicals appearing abundantly in flames, combustion sources and hydrocarbon discharges. It has been observed in extraterrestrial sources, such as carbon stars, comets and protoplanetary nebulae. Theoretical computations are crucial for the interpretation of the experimental spectra and the simulation of interstellar media. In order to obtain the spectra of C_2 ab initio electronic structure and nuclear motion computations were performed within the Born-Oppenheimer approximation.

Firstly, potential energy curves (PEC) were calculated for six electronic states of C_2 over the internuclear separation region from 0.08 nm to 0.21 nm using the full valence complete active space self-consistent field (CASSCF) method followed by the valence internally contracted multireference configuration interaction (icMRCI) approach in combination with the aug-cc-pV5Z correlation-consistent basis set. The PEC calculations were carried out with MOLPRO 2009.1 program package. After taking into account the spin-orbit coupling terms with an in-house program the PECs were fitted to experimental (ro)vibrational energy levels. Employing the numerical PECs (ro)vibrational energy levels were computed using the LEVEL 8.0 program, followed by the computation of line strengths and (ro) vibrational intensities.

The calculated (ro)vibrational energy levels, transitions and intensities, forming a line list, are in excellent agreement with experimentally derived values for all investigated states of the C_2 molecule.

Keywords: nuclear motion computation; spin-orbit coupling; (ro)vibrational intensity; C_2

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SURFACE-ENHANCED RAMAN SCATTERING AND DFT INVESTIGATION OF 1,5-DIPHENYLCARBAZIDE AND ITS METAL COMPLEXES WITH Mn(II), Fe(III), Cu(II) AND Pb(II)

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Metal ions determination represents an area of interest in several fields, like environmental protection, food safety or clinical diagnostics. Analytical methodologies for direct determination of metal ions were established over the last decades including atomic absorption or emission spectroscopy and mass spectrometry. Although these methods are sensitive and accurate, they require tedious sample pre-treatment and expensive equipment. Thus, a significant increase in the development of optical chemical sensors for heavy metals has been noted in the last years, aiming to their routinely production, low cost, high selectivity and sensitivity.

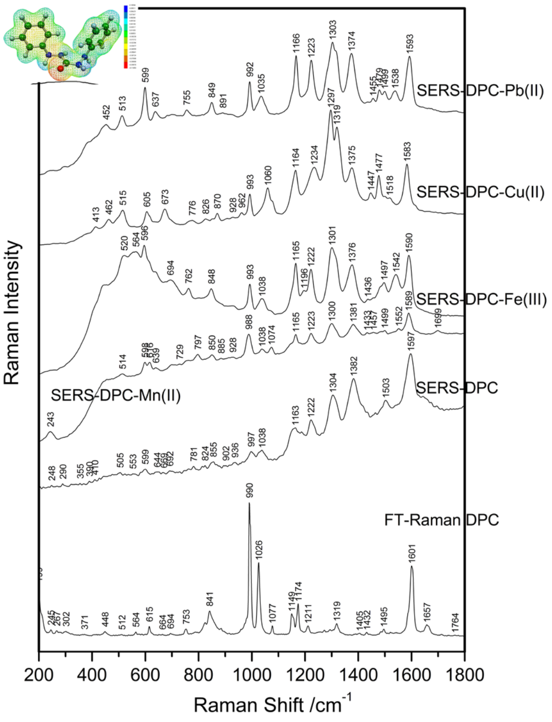

Figure 1. FT-Raman and SERS spectra of DPC. SERS spectra of DPC-Mn(II), Fe(III), Cu(II) and Pb(II) complexes, prepared at DPC:metal salts 2:1 molar ratio.

In this work, SERS spectroscopy is used in conjunction with quantum chemical calculations in order to characterize the molecular structure, electronic properties and vibrational energies of the 1,5-diphenylcarbazide (DPC) molecule and its complexes with Mn(II), Fe(III), Cu(II) and Pb(II). Thus, Raman and SERS spectra of DPC, as well as the SERS spectra of the Mn(II), Fe(III), Cu(II) and Pb(II) complexes of DPC, were assigned using DFT calculations with the hybrid B3LYP exchange-correlation functional using the standard 6-31G(d) basis set.

The SERS spectra of DPC and of its metal chelates were recorded using HeNe laser emitting at 633 nm and hydroxylamine reduced silver colloid [1].

The experimental vibrational bands were assigned to the calculated normal modes and a very good correlation was achieved between the experimental and theoretical data.

DPC complexes with Mn(II), Fe(III), Cu(II) and Pb(II) are differentiated by their SERS spectra, each metal complex showing a particular SERS spectral fingerprint (Fig. 1).

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STRUCTURE AND SPECTROSCOPIC PROPERTIES OF 4-AMINO-PYRIDINIUM-1-PROPIO BETAINE HYDROBROMIDE HEMIHYDRATE

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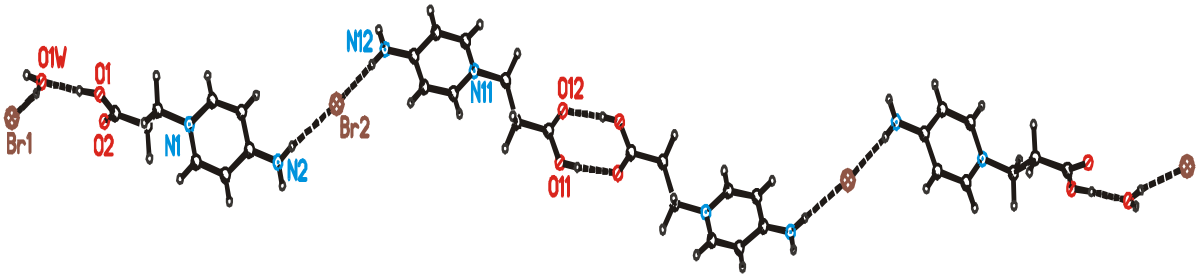
The structure of 4-amino-1-(2-carboxyethyl)pyridinium bromide hemihydrate has been studied by X-ray diffraction, B3LYP/6-311++G(d,p) calculations, FTIR and NMR spectra.



The crystals are monoclinic, space group P2$_1$/*c*. In the crystal a unique association of carboxyl group of 4-amino-1-(2-carboxyethyl)pyridinium cation is present, where one of two symmetric-independent groups is H-bonded to another, one forming a centrosymmetric dimer, and the second symmetry-independent groups is H-bonded to a water molecule. The crystal is built of chains, formed by the Br$^-$-H$_2$O-cation-Br$^-$-cation-cation-Br-cation-H$_2$O-Br$^-$ links, bifurcated at the Br anions and water molecules, each involved in three hydrogen bonds. The probable assignments of the anharmonic experimental vibrational frequencies of the investigated compound are based on the calculated frequencies in vacuum Correlations between the experimental ^{13}C and ^{1}H NMR chemical shifts (δ_{exp}) and the GIAO/B3LYP/6-311++G(d,p) calculated magnetic isotropic shielding constant (σ_{calc}) in D$_2$O, $\delta_{exp} = a + b \cdot \sigma_{calc}$, are reported.

Keywords: 4-amino-1-(2-carboxyethyl)pyridinium bromide hemihydrat; X-ray diffraction; FTIR and NMR spectra; DFT calculations

FT-IR SPECTROSCOPY ANALYSES FOR RESPONSE OF *CLOSTRIDIUM* STRAINS IN CONVERTING ENZYMATICALLY HYDROLYZED HAY

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Cellulose containing materials, such as hay, is widely distributed and can be used as a natural source of carbohydrates in microorganisms producing biofuel (int. al. butanol). Production of acetone, butanol and ethanol (ABE) from the fermentation of clostridia is a common technology. However, reliable and rapid methods for selection of *Clostridium* spp. with the highest potential to convert enzymatically hydrolyzed cellulose materials to ABE are still not available. It is known that formation of ABE product is dependent on the morphological and macromolecular composition of the cells [1]. The aim of this study was to evaluate the chemical composition of *Clostridium acetobutylicum* ATCC®824™*, C. beijerinckii* DSM 6422 and *C. tetanomorphum* ATCC®49273™ during the adaptation process for fermentation of enzymatically hydrolyzed hay by FT-IR spectroscopy.

The adaptation of clostridia was performed by the re-inoculation of cells in a new medium with small amount of enzymatically hydrolyzed hay. The amount of substrate in an artificial medium was increased by 5 % once per 24 hours. FT-IR spectra of biomass samples were recorded on a VERTEX 70 with HTS-XT extension (BRUKER, Germany). The data were processed by OPUS 6.5 software. The substrate degradation coefficient for *C. acetobutylicum* and *C. tetanomorphum* strains was estimated as 0.008 h^{-1} (P = −0.84 and −0.98, correspondingly) at 37 °C on the artificial medium without no hydrolyzed hay. Although the substrate degradation coefficient of *C. beijerinckii* was higher (0.047 h^{-1}, P= −0.83), with the increase of hydrolyzed hay concentration in the media, the total degradation rate of substrate by *C. acetobutylicum* and *C. tetanomorphum* decreased, whereas, it did not change significantly for *C. beijerinckii*. Depending on the composition of growth medium, growth phase and fermentation time, the FT-IR spectra of the clostridia showed to be qualitatively and quantitatively different in several spectral regions. *C. acetobutylicum* and *C. tetanomorphum* showed small but well pronounced absorption peak at 1737 cm^{-1}, identifying the biopolymer poly-β-hydroxybutyrate (PHB) by ester carbonyl stretch and a number of strong bands at wavenumber values between 1450 and 1000 cm^{-1} due to methyl (CH_3) and methylene (CH_2) deformations and C-O stretches. Indeed PHB was not identified in any of IR spectra of *C. beijerinckii*, the strain for which the substrate degradation rate was not inhibited by addition of hydrolyzed hay.

The study showed that FT-IR spectroscopy can be a quick and sensitive method for the characterization of clostridia during the adaptation to a specific growth media and thereby allows to select the correct strain for the highest product ABE yield in the fermentation.

Keywords: FT-IR spectroscopy, ABE fermentation; Clostridium strain; hydrolyzed hay

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AcknowledgmentThis work has been supported by European Regional Development Fund Project No. 2010/0300/ 2DP/2.1.1.1.0/10/APIA/VIAA/165„The production of a new generation of biofuel - biobutanol from agricultural waste"

NAKED - EYE AND SERS DETECTION OF SOME POLLUTANTS IN WATER BY INDUCING CONTROLLED AGGREGATION OF GOLD NANOPARTICLES

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Environmental pollution has become a serious problem for the last decades since human activity produces huge amounts of contaminants every second. Heavy metals are among the most widespread and dangerous pollutants released as a result of industrial activity. Many studies have been focused on developing selective and sensitive sensors for reliable screenings of heavy ions in water, air or soil. Most of them rely on the modification of optical properties of noble metal nanoparticles (NPs) such as nonlinear optical properties (NLO) or surface plasmon resonance in the presence of specific analytes, as well as on the ability NPs to enhance various spectroscopic signature of nearby analyte [1, 2].

In this work we demonstrate a sensitive approach for rapid detection of Zn^{2+} ions in water without using any chelating ligands. Actually the manipulation of the surface charges of gold nanoparticles (GNPs) as function of Zn^{2+} ions concentration induces GNRs aggregation which can be readout more rapidly than any cross-linking process, leading to faster assays. Indeed, we show that the presence of very low amount of Zn^{2+} ions in gold colloidal suspension leads to a controlled aggregation of GNPs, yielding a dramatic color change of colloidal suspension which can be observed via the naked eye. Specifically, the detection of Zn^{2+} ions based on the colorimetric response of GNPs as function of the ionic strength of water solution can be achieved with simple visual inspection in less than 3 minutes

The GNPs assemblies formed in solution in the presence of Zn^{2+} ions were successively analyzed by transmission electron microscopy (TEM) and X-ray diffraction (XRD) and further exploited as surface-enhanced Raman scattering (SERS) substrates. The assessment of SERS detection of organic pollutants in water has been performed with a portable Raman spectrometer operating at 785 nm laser line and para-aminothiophenol (p-ATP) molecule used as a model analyte. We demonstrate both experimentally and theoretically that the assembled gold nanostructures support high field localization for the ultrasensitive detection of a wide variety of analytes such as chelating agents, thiols, and different aromatic compounds.

Acknowledgements *This work was supported by CNCSIS –UEFISCSU, project number PNII - ID_PCCE_312/2008.*

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INFLUENCE OF CHLORIDE IONS AND LASER WAVELENGTH ON THE SERS SPECTRUM OF PARA-AMINOTHIOPHENOL

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Despite numerous studies on para-aminothiophenol (p-ATP) the appearance of the non-totally symmetric modes in the SERS spectrum remains a subject of debate. The literature presents two explanations for these bands. Several studies explain the non-totally symmetric modes of p-ATP in the SERS spectrum as a consequence of a charge transfer. For this, different laser wavelengths were used, to fit resonant or non-resonant conditions, or modifying the surface potential of the metal substrate.[1]

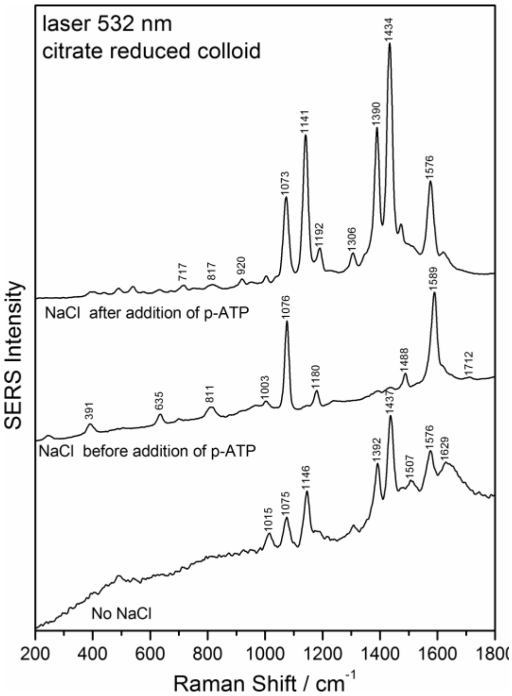

Fig.1. Chloride ions influence on SERS spectra of p-ATP.

Also, several studies sustain the appearance of the non-totally symmetric modes of p-ATP in the SERS spectrum by formation of dimers, due to surface catalytic-coupling reactions. For this statement, detailed experiments were performed, including DFT calculations and NMR spectroscopy for proving the new species.[2]

In this study it was found that using the 532 nm excitation laser line, the non-totally symmetric modes are present in the SERS spectrum. Decreasing the energy of the laser photons these modes decrease in intensity, being absent when using the 785 nm laser line. This behavior can be simply explained by a charge transfer model.

Also, it was found that the addition of NaCl before or after p-ATP is determinant for the presence of the non-totally symmetric modes of p-ATP in the SERS spectrum (see Fig.1). Thus, it was observed that using the citrate reduced silver colloid, without the addition of NaCl, the non-totally symmetric modes of p-ATP are present in the SERS spectrum. The addition of NaCl after p-ATP is already adsorbed on the colloidal silver surface, the non-totally symmetric modes of p-ATP are further enhanced in the SERS spectrum, most probably due to the aggregation of the silver particles.

If NaCl is added before the addition of p-ATP to the silver colloid, the SERS spectrum appears additionally enhanced, but the non-totally symmetric modes of p-ATP are absent. Thus, in the dimer formation model, the chloride ions avoid the formation of dimers, due to the change of the surface potential.

Concluding, both, surface potential and laser excitation wavelength are determinant in the dimer formation.

Keywords: para-aminothiophenol, SERS, chloride, dimer, charge-transfer

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OPTICS OF LIDAR SYSTEM USED FOR SPECTROSCOPIC MONITORING OF AIR POLLUTION

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LIDAR is an active remote sensing system being employed for studying's atmosphere in terms of aerosol distribution, extinction and back-scattering coefficients, optical depth and temperature. The determination of aerosol and clouds optical properties using the LIDAR system is based on the detection of the atmospheric returns (i.e. backscatter light) and their further analysis [1].

The LIDAR system is based on the patented micro-LIDAR system developed within ROLINET (ROmanian LIdar NETwork). The transmitter is a Nd:YAG laser used for generating laser pulses at 1064, 532 and 355 nm wavelength with 200μJ, 100 μJ and respectively 35 μJ per pulse The pulse repetition rate is variable up to 30 Hz. The three laser beams are emitted co-axially and expanded 5 times before being transmitted into the atmosphere. The initial divergence of the 6 mm laser beam diameter of 0,75 mrad is thus improved 5 times by using a 3λ beam expander (BE) resulting thus a single beam of 30 mm diameter and a final low divergence of 0,15 mrad. The lidar transmitter features offer the possibility to perform measurements up to high altitudes up to 12 km during daytime and as high as 15 km during nighttime for just one minute integration time and keeping an extremely high resolution as 7.5 m for example. The LIDAR receiver is based on a 3D mounting Newtonian configuration telescope being equipped with a 406 mm diameter primary mirror and a combined focal length of 1829 mm. An opto-mechanical detection module composed by LIDAR optimized detectors (Photomultipliers - PMT's for UV and VIS optical range) and a transient recorder provided by Licel GmbH are used to select and detect the backscattered optical signals [2].

For the LIDAR system, a matrix formalism in Gaussian approximation is developed in this paper. It involves the construction of a ray transfer matrix that describes the optical system. The matrix formalism is essential for LIDAR phenomena modeling to better understand the physics of the atmosphere and the air pollution. Also, the matrix formalism is used in the design of a new optical LIDAR system configuration in order to have other possibilities for atmospheric investigations [3].

This work was supported by the European Social Fund in Romania, under the responsibility of the Managing Authority for the Sectorial Operational Programme for Human Resources Development 2007-2013 [grant POSDRU/CPP 107/DMI 1.5/S/78342].

Keywords: spectroscopic technique, Lidar, matrix formalism

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FTIR SPECTROSCOPIC MONITORING OF *IN SITU* METABOLIC CHANGES IN BACTERIA RELATED TO POLYHYDROXYALKANOATE ACCUMULATION

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Many bacteria can accumulate carbon-and-energy storage compounds as intracellular granules of polyhydroxyalkanoates (PHAs). These polyesters, besides their important role in bacterial survival under stresses, are of industrial importance as environmentally friendly biodegradable plastics. For plant-growth-promoting rhizobacteria (PGPR), the trait of PHA accumulation is of great ecological importance [1, 2]. In this work, accumulation and properties of poly-3-hydroxybutyrate (PHB, a ubiquitous PHA representative) were studied in cells of the PGPR *Azospirillum brasilense* (ecologically different strains Sp7 and Sp245 [1–3]) and, for comparison, in the phytopathogen *Pectobacterium atrosepticum* strain SCRI1043 (formerly known as *Erwinia carotovora* ssp. *atroseptica* SCRI1043) [4]. The bacteria were grown under various environmental stresses (sublethal concentrations of heavy metals, cryogenic treatment or low growth temperatures, unfavourable carbon/nitrogen sources), and their effects on PHB accumulation were compared. Fourier transform infrared (FTIR) spectroscopy in the diffuse reflectance mode (DRIFT) was used in quantitative analysis for intracellular PHB [1]. Besides differences in PHB accumulation rates under various environmental factors found for epiphytic and endophytic strains of *A. brasilense* [1,3], DRIFT spectroscopy was sensitive to the degree of crystallinity of intracellular PHB [5], which was found to change upon prolonged growth under stresses and/or conditions of nutrient limitation. This is related to different PHB enzymatic hydrolysis rates dependent on its crystallinity, which is of paramount ecological importance for cells. Thus, FTIR (and, in particular, DRIFT) spectroscopy applied in microbial ecology is advantageous for detecting and monitoring intracellular accumulation of PHA and its *in situ* properties as a function of environmental conditions.

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Keywords: FTIR spectroscopy; Polyhydroxyalkanoates; Microbial ecology

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A SPECTROSCOPIC STUDY OF SULFAMETHOXAZOLE ADSORBED ON SILVER NANOPARTICLES

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Sulfamethoxazole (N'-(5-methyl-3-isoxazolyl) sulfanilamide) (SMX) is used as an agent to treat urinary tract infections.

The Raman and SERS spectra of SMX (adsorbed on silver colloid) (Fig. 1) were assigned on the basis of DFT calculations at B3LYP/6-31G(d) level of theory.

The SERS and Raman measurements were performed using the 532 nm Nd:YAG laser line and a silver colloid prepared by Lee-Meisel method [1] at pH 13.

In the Raman spectrum of the aqueous solution, the most intense band is located at 1599 (calc. 1595) cm^{-1}, a combination of stretching vibration of the benzene ring and a bending deformation of the amino group, while the band at 1123 (calc. 1098) cm^{-1} is assigned to the symmetric stretching of the SO_2 group. Another intense band is due to the stretching vibration of CH from the isoxazole ring and is seen at 3145 (calc. 3157) cm^{-1}.

The SERS spectrum is dominated by the band situated at 1526 cm^{-1}, which in the Raman spectrum can be seen at 1599 cm^{-1}. The superposition of the CN, CC stretching vibrations of isoxazole ring appears at 1589 (calc. 1609) cm^{-1}. The band at 1629 (calc. 1629) cm^{-1} is related to bending deformation of the amino group. The symmetric stretching vibrations of sulphonyl can be also seen in the SERS spectrum at 1114 (calc. 1098) cm^{-1}.

Based on the analysis of SERS and Raman spectra and considering the MEP of the molecule we concluded that SMX is absorbed in its neutral form, with the isoxazole ring and sulphonyl group perpendicular to the silver surface, while the benzene ring and the amino group are adsorbed in a tilted orientation.

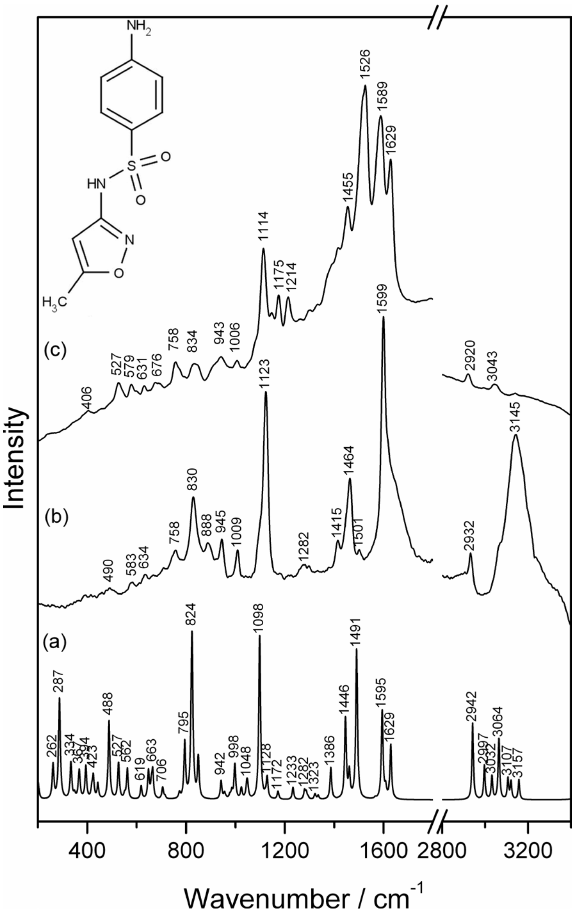

Fig.1 Calculated Raman spectrum of gas-phase SMX (a) experimental Raman spectrum of SMX in aqueous solution (b) and SERS spectrum of SMX adsorbed on colloidal particles (c)

Keywords: sulfamethoxazole, Raman, SERS, DFT

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RAMAN SPECTRUM OF AMINOPROPYLSILANETRIOL IN VAPOR

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Aminopropylsilanetriol (APST) is one of the most frequently used organofunctional silane coupling agents. This molecule also emerges through the hydrolysis of other alkoxysilanes as a product of hydrolysis. Because of its two functional groups located at the opposite molecular sites, it can react with organic polymers as well as with inorganic substrates and fillers. Conformational stability and vibrations of APST has been investigated using DFT calculations [1], [2], but the vibrational spectra were recorded only for water solution and condensed, polymerized structure. In this work we present Raman spectrum of APST in vapor phase.

In order to get Raman spectra of vaporized APST the following procedure was used: 25% water solution of APST was filled in glass capillary and frozen in liquid nitrogen bath. The capillary was then connected to the vacuum pump in order to evacuate all the air above the sample. After evacuation the capillary was sealed and left at room temperature. Raman spectra of solid, solution and of the evaporated sample above solution were recorded at room temperature (Fig. 1)

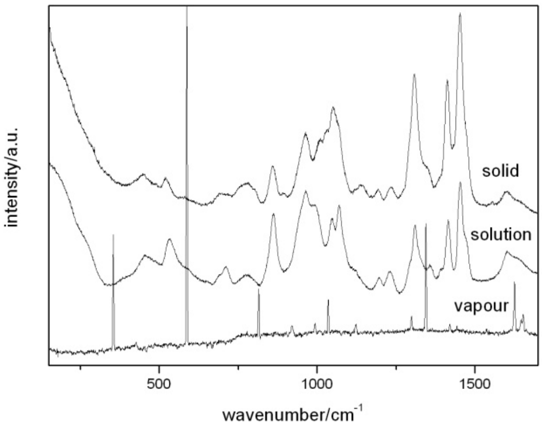

Fig. 1 Raman spectra of APST

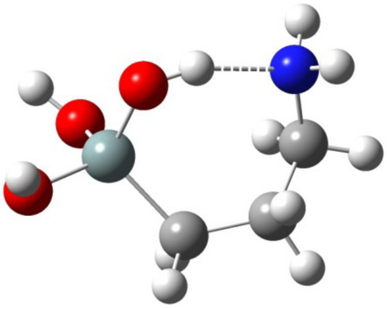

Fig. 2 Molecular structure of APST

Recorded spectra of vapor differ very much from those of solution and solid and we undertook DFT study in order to explain the differences. Unlike the molecule in the aqueous solution, where the most stable conformation is the one with straight propyl chain, in the vapor phase the propyl chain is bent to form intramolecular hydrogen bond $H_2N\cdots OH$ (Fig. 2).

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STRUCTURAL STUDIES OF Ag CONTAINING THIN FILMS OF TiO_2 – SiO_2 AND Al_2O_3- TiO_2 SYSTEMS DEPOSITED BY SOL-GEL METHOD

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FTIR spectroscopic structural studies of thin films of TiO_2 - SiO_2 and Al_2O_3- TiO_2 systems containing Ag nanoparticles were presented in this work. Thin films were synthesized by sol-gel method as separate one-component TiO_2, SiO_2 or Al_2O_3 layers or as two-component TiO_2-SiO_2 or Al_2O_3- TiO_2 ones. Silver nanoparticles were incorporated into the structure from SiO_2 sol, deposited as an additional layer. All thin films were deposited on steel by deeping and pulling out method.

Titania-silica and alumina-silica thin films are applied as anticorrosive layers in many branches, especially in medical ones. The addition of silver Ag gives them also particulate antibacterial properties, what is important from the medical application..

The FTIR spectroscopy, the XRD diffraction and the SEM microscopy together with the EDX method were applied to investigate the structure and microstructure of synthesized samples.

The structural studies allow to describe and compare the structure and morphology of thin films, as well those Ag free as Ag containing ones. In the FTIR spectra, the band observed at about 613 cm^{-1} is connected with the presence of non-tetrahedral cation (Ag) in the structure and thus is observed only in Ag containing materials. Bands due to the vibrations of Al-O and Si-O connections enabled to determined the coordination of Al and Si in synthesized samples.

The financial support of the AGH University of Mining and Metallurgy, grant No 11. 11. 160. 258

THE FTIR SPECTROSCOPY STUDIES OF ONE-COMPONENT AND MULTI-COMPONENT GELS IN Al_2O_3-TiO_2, Al_2O_3-SiO_2, TiO_2-SiO_2 AND Al_2O_3-TiO_2-SiO_2 SYSTEMS

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The structural spectroscopic studies of Al_2O_3-, TiO_2- and SiO_2 one -component gels as well as multi-component ones of Al_2O_3-TiO_2, Al_2O_3-SiO_2, TiO_2-SiO_2 and Al_2O_3 -TiO_2 - SiO_2 system were presented. All samples were obtained by sol-gel method applying different precursors of Al_2O_3, TiO_2 or SiO_2 oxides and were annealed in three different temperatures: 500°C, 800°C and 1000°C, in air. The main aim was to observe the influence of different type precursors, temperature and the chemical composition of particular samples on their structure. The FTIR spectroscopy together with the XRD Diffraction and the SEM Microscopy were applied to investigate the structure and microstructure of synthesized materials.

According to the diffraction patterns, an amorphous phase was observed in all samples up to 500°C and was decreasing with the rising temperature of the annealing. In Al_2O_3- SiO_2 gels, Aerosil® as a precursor of SiO_2 caused faster Al_2O_3 crystallization then TEOS (tetraethylorthosilicate). In all materials containing TiO_2, the crystallization of different polymorphs of TiO_2 was slower and begun in much higher temperatures in multi-component gels of Al_2O_3-TiO_2-SiO_2 system then in one-component sample. The FTIR spectra of all synthesized materials containing Al_2O_3 allowed to observe bands due to the vibrations of Al-O connections of Al in octahedral coordination, in spite of applied precursors.

The financial support of the AGH University of Mining and Metallurgy, grant No 11. 11. 160. 258

SYNTHESIS, CHARACTERIZATION AND THEORETICAL STUDY OF 2,2'-(1,2-PHENYLENEBIS(AZAN-1-YL-1-YLIDENE))BIS(METHAN-1-YL-1-YLIDENE)BIS(4-BROMOPHENOL)

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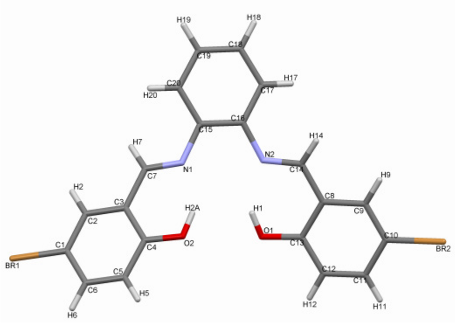
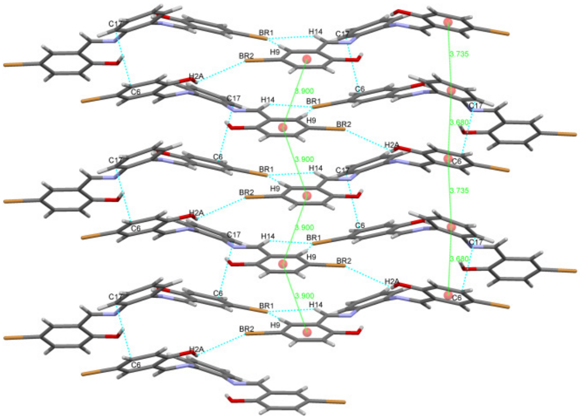
The title Schiff-base compound namely 2,2'-(1,2-phenylenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis(4-bromophenol), **L3**, has been synthesized and characterized byFT-IR and single crystal X-ray diffractiontechniques. The FT-IR (4000-400 cm^{-1}) spectrum as a KBr pellet and far-infrared (600-30 cm^{-1}) spectrum between polyethylene plates as nujol mulls of the compound was recorded via a Bruker Optics IFS 66v/s FT-IR spectrometer with 2 cm^{-1} resolution in vacuum. Single crystal structure data were collected on a Bruker Kappa APEXII CCD area detector diffractometer using Mo K$_{\alpha}$ radition (k = 0.71073 Å) at 105 (2) °K. The title compound **L3** crystallizes in the orthorhombic system with space group of Pbca. The molecule forms a two dimensional chains by strong C-H…Br and π…π interactions.Thespectra were interpreted with the aid of normal coordinate analysis based on the density functional theory using Ab initio and DFT calculation methods and basis set combination.In general calculated geometric parameters are in good agreement with those obtained from experimental data. FT-IR spectroscopy confirms the functional groups, particularly (C=N) imine group of the compound.





Keywords: FT-IR Spectroscopy, Single crystal structure, DFT

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STRUCTURAL PROPERTIES OF TiO_2/WO_3/NOBLE METAL BASED SYSTEMS BY SPECTROSCOPIC INVESTIGATIONS

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The investigation of titania based semiconductor shows a considerable interest among the scientific community, in principal due to their (photo)catalytic properties. The loading of noble metal nanoparticles on TiO_2 based semiconductors, e.g. Au, Pt or Ag, was proved to improve the (photo)catalytic performances as a consequence of both the structural alterations and charge transfer that occur at the noble metal-semiconductor interface [1]. The same boundary changes are usually present when heterogeneous semiconductors are in contact, e.g. TiO_2/WO_3 [2].

Therefore, in the present study our interest was focused on determining the structural changes that occur in different boundary zones of the nanoparticles TiO_2/WO_3/Au and TiO_2/WO_3/Pt by using Raman, Diffuse Reflectance UV-VIS (DR-UV-VIS) and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopic techniques.

Based on the complementary information derived from the recorded spectra structural particularities related to the structural units of the constituent oxides, bond length and coordination number of the titania and tungsten atoms are acquired. The investigations of these binary and ternary composites will deliver valuable information related to the interface quality and chemical environment of the atoms situated at the contact zones.

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Keywords: Raman spectroscopy, DR-UV-VIS spectroscopy, EXAFS spectroscopy.

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ASSESSING THE CHEMICAL POLLUTANTS DETECTION AND THEIR PHOTODEGRADATION BY SPECTROSCOPIC METHODS

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Aerogels are solid materials with exciting properties such as low refractive indices (<1.1), extremely low densities (up to 95% of their volume is air), and very high specific surface areas (often > 600m^2/g) [1]. Titanium dioxide based aerogels combine the above mentioned properties with those of TiO_2: high photosensitivity, non-toxic nature, large band-gap and stability.

By incorporating Au nanoparticles into the TiO_2 aerogel network improved photocatalytic performances were obtained [2], because the Au nanoparticles act as electron traps, facilitating electron-hole separation and promoting interfacial electron transfer process [3]. Also, the use of different Au nanoparticles concentration should induce significant modifications to the structure and morphology of the porous samples and, consequently to their photocatalytic performances.

On the other hand, the existence of noble metal nanoparticles into the TiO_2 porous matrix should allow the detection of water pollutants by SERS. Several studies related about the benefit of the Raman enhancement and used various types of noble metal surfaces or different structural environments containing noble metals for the detection of pollutant molecules [4, 5].

In this work we evaluated by SERS and UV-vis spectroscopy the detection ability and the photodecomposition of organic pollutants exhibited by some porous nanocomposites based on TiO_2 aerogels containing different amounts of Au nanoparticles of 16 nm in size. The morphological (BET, TEM) and structural (Raman, UV-vis diffuse reflectance spectroscopy) particularities of the obtained porous composites were also discussed in order to correlate them with the revealed photocatalytic activities and SERS detection abilities.

Keywords: SERS; photocatalytic activity; Au nanoparticles;

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APPLICATION OF INFRARED AND RAMAN SPECTRA IN THE STUDIES OF HEAVY METAL CATIONS SORPTION ON ZEOLITES

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This work presents the results of spectroscopic studies (MIR, FIR and Raman) of zeolites structures (belonging to different structural groups) after heavy metal cations (Ag^+, Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+} and Cr^{3+}) immobilization from aqueous solutions. The sorption has been conducted on sodium forms of natural chabazite, mordenite, ferrierite and clinoptilolite as well as on syntetic zeolite A and Y.

It was proven those heavy metal cations' sorption causes changes in the both infrared and Raman spectra of zeolites. Changes in the bands are analyzed in terms of the contributions of the bands corresponding to the characteristic ring units (SBU) of the aluminosillicate framework. Based on the changes, a scale of sorption and a kind of mechanism in the process (ion exchange and/or chemisorption) can be established.

The most significant changes have been determined in the region of pseudolattice vibrations (800–500 cm^{-1}). Cation exchange in the zeolite structure changes the degree of ring deformation, which results in intensities' modification of the MIR and Raman band associated with ring-opening vibrations. On the other hand, introduction of heavy metal cations into the structure of zeolites has caused the considerable modification of bands due to Me-O vibrations in FIR spectra. Relations between both the intensities and the positions of the characteristic ring and Me-O vibrations bands and a kind of cation in the structure have been observed. In all cases, systematic changes, connected with the type of cation (its chemical character) and its concentration in the initial solution have been revealed. Based on changes in the spectra due to the immobilization of heavy metal ions, a scale of the sorption can be established.

Results of IR and Raman spectroscopic studies have been compared with those obtained by atomic absorption spectroscopy (AAS), from which the proportion of ion exchange to chemisorption in the process and the effective cation exchange capacity of the individual samples have been estimated.

Financial support this work was provided by Polish Ministry of Science and Higher Education under grant no. N 507 316 536.

Keywords: zeolite; IR spectra; Raman spectra

IR AND RAMAN SPECTRA OF ZEOLITES FROM DIFFERENT STRUCTURAL GROUPS

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This work presents the results of spectroscopic studies (MIR, FIR and Raman) of zeolites (mainly natural) belonging to the seven major structural groups. Interpretation of vibrational spectra has been based on the identification of the bands associated with typical SBU vibrations. On the grounds of the previous works [1, 2], in which, based on *ab initio* calculations, visualization of vibration obtained for the structural units composed of single and double 4- and 6-membered rings had been analyzed, the bands have been assigned. Identification of these bands provides information related to the construction of the aluminosilicate framework of zeolites as well as about influence of exchangeable cations on the spectra.

Characteristic ring vibrations have been observed in the infrared and Raman spectra in the region of pseudolattice vibrations (400–800 cm^{-1}). On the other hand, in the FIR spectra the bands corresponding to the characteristic ring and Me–O vibrations have been observed. These rings occur in pseudomolecular complexes (built of alumino- and silicooxygen tetrahedra) which constitute the secondary building units (SBU) and form spatial framework of the zeolite. Changes the positions of the band toward lower wave numbers with increasing number of ring members have been observed. Additionally, influence of non-tetrahedral cations on the positions of above bands has been determined. Relationship between presences in the zeolite's spectrum of the bands connected with normal vibration of SBU and its membership to the appropriate structural groups has been proved.

Financial support this work was provided by Polish Ministry of Science and Higher Education under grant no. N 507 316 536.

Keywords: zeolite; SBU; IR spectra; Raman spectra

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TRANSPARENCY AND ABSORPTION EDGES OF SOME NEW COPOLYIMIDES CONTAINING SILOXANE AND ALICYCLIC UNITS

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Polyimides have become one of the most important and versatile classes of high performance polymers due to excellent mechanical and thermal properties [1]. Incorporation of flexible siloxane sequences into thermally stable polyimides has been shown to yield several attractive properties while retaining many of the excellent properties of the corresponding polyimide homopolymers [2]. The polyimide-based block copolymers possess good processability, low water absorption, atomic oxygen resistance, low dielectric constants, and excellent adhesion. Thus, this type of materials is attractive candidates for microelectronics as interlevel dielectrics, passivation layers or alignment layers for liquid crystals [3]. However, in the latter application, low refractive index, high transparency and reduced dielectric constant are required. In this context, the proposed approach to improve these properties consists in lowering the compound's polarizability by introduction into the polyimide structure of bulky, flexible and alicyclic dianhydride moieties and siloxane-based aliphatic diamine residues.

In the present study, the synthesis of new copolyimides by polycondensation reaction of epiclon (5-(2,5-dioxotetrahydrofurfuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic acid anhydride), as a cycloaliphatic dianhydride, together with two diamines, namely 1,3-bis(3-aminopropyltetramethyl)disiloxane and 4,4'-oxydianiline is reported. Some properties of these polymers, such as solubility, thermal stability, refractive index and dielectric constant are investigated. Optical characteristics in the ultraviolet, visible and near infrared spectral range are evaluated. The influence of the type and content of diamine residues on the transmission spectra and position of the absorption edge is discussed. To obtain the energy gap and other energies describing the absorption edge, the method proposed by Tauc for amorphous materials is applied. On the basis of these values, the influence of copolymer chain structure and structural disorder on the optical properties and probable electronic transitions has been considered.

Keywords: copolyimide; siloxane; alicyclic; transparency

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ANTIBIOTICS LOADING AND RELEASE FROM BONE IMPLANT SCAFFOLDS FOR THE PREVENTION OF INFECTIONS

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Sol-gel derived bioactive glass matrices have great success in orthopedic surgery and dentistry [1]. To prevent bacterial colonization and infection at the treatment site [2] of the bone implant scaffold, direct adsorption of the antibiotics on the matrix was evaluated. This loading procedure is more favorable for local administration due to its longer and steadier release time [3].

The bioactive glass matrices were prepared using the sol-gel method. After drying, the samples were milled and sieved, in order to obtain particles below 40 µm size. Three different antibiotics were used in this study: tetracycline, neomycin and streptomycin. The loading experiments were carried out at 37°C, in falcon tubes. For each antibiotic 0.25 g bioactive glass was immersed in a bath of 10 ml phosphate buffer (PBS) containing 70 mg antibiotic. After 4 hours the glass particles soaked in antibiotic enriched PBS solutions were filtered and rinsed with fresh PBS several times to remove the unattached antibiotic. Surface area and pore volume evaluation by Brunauer-Emmitt-Teller (BET) was performed before and after drugs loading.

To estimate the amount of loaded drug, UV-Vis and fluorescence spectroscopies were performed on the PBS collected solutions after functionalization. The time dependent antibiotic release was investigated by antimicrobial tests performed on the antibiotic loaded samples according to the inhibitory effect on both Gram positive and Gram negative bacteria compared to the pure bioactive glass.

Keywords: Sol-gel, UV-Vis, Fluorescence, Antimicrobial study

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ONE STEP SYNTHESIS OF GOLD NANOPARTICLES USING POLYETHYLENE GLYCOL

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The high interest in the development of new strategies for the synthesis of metal nanoparticles originates from their quantum scale dimension, that leads to particular electronic and optical properties, and thus having various applications in the fields of physics, materials science, chemistry, biotechnology, and medicine.

Gold is essentially inert and nontoxic, gold nanoparticles (GNPs) being therefore preferred in biomedical applications, like biochemical sensing, biological imaging, drug delivery and cancer treatment.[1,3]

In this study, we report a very effective and simple one step synthesis method for surface-enhanced Raman scattering (SERS) active gold colloids by reduction and stabilization with short and long chain polyethylene glycol, PEG200 and PEG10000, respectively. Depending on the mixing rate during the synthesis, the mean size of the gold nanoparticles (GNPs) can be controlled between 15 and 60 nm. The obtained colloids have been characterized by UV-Vis spectroscopy, transmission electron microscopy (TEM), and SERS. TEM micrographs reveal spherical nanoparticles with an average diameter of 15 nm, and polygonal particles with a mean size of 60 nm for the gold colloid with the absorption maximum at 520 nm and 562 nm, respectively.

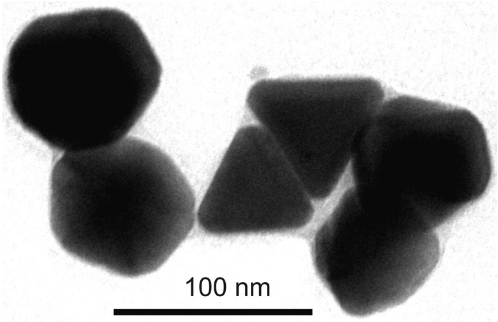

Fig.1. TEM micrography of the 60 nm colloidal GNPs.

The nanoparticle geometry influences drastically the position of the absorption maximum. While the 15 nm particles have an expected absorption maximum at 520 nm, for the 60 nm diameter GNPs a shift to higher wavelengths of the absorption maximum is observed. For spherical 60 nm GNPs an absorption maximum at ~535 nm is expected.[4,5] However, the PEG reduced GNPs show an absorption maximum at ~560 nm. The shift to higher wavelengths of the absorption maximum is most probably due to the polygonal geometry of the PEG reduced GNPs (see Fig.1).

The SERS activity of these new gold colloids was found to be comparable to that of conventional gold colloid obtained by citrate reduction, as shown by the SERS spectra of various analytes, using the 633 and 785 nm laser lines.

Keywords: Gold nanoparticles; polyethylene glycol; SERS

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CRYSTALLIZATION OF SILICATE-PHOSPHATE GLASSES OF $NaCaPO_4$–SiO_2 SYSTEM

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The fragility is the most characteristic feature of bioactive silicate-phosphate glasses of $NaCaPO_4$-SiO_2 system, which greatly limits its application. Improvement of the mechanical strength of glass can be achieved by a partial devitrification to obtain the glass-crystalline materials. However growth of crystalline phases very adversely affects the bioactivity of the glasses. It is therefore necessary to provide full control over the process. Uncontrolled growth of crystalline phases can be reduced by using a glass phase separation phenomenon in the silicate-phosphate glasses because boundaries of inclusion-matrix phase may be a barrier limiting the growth of crystalline phases. Based on DSC examinations it has been found out that crystallization of the glasses of $NaCaPO_4$–SiO_2 system is a multistep process. The presence of several clearly separated exothermic peaks in DSC curves of investigated glasses makes it possible to crystallize only the inclusions with the matrix remaining amorphous or vice versa. Conducted detailed X-ray and spectroscopic (MIR, Raman) studies of the materials obtained by annealing in a gradient furnace (in the temperature specified on the basis of DSC) showed that separately crystallized inclusions and matrix. Therefore, the use of the glass phase separation phenomenon can be obtained bioactive glass-crystalline materials by pre-established sizes of the crystalline phase.

This work was funded by the National Center of Science under the project number DEC-2011/01/N/ST8/07425.

Keywords: glass structure; direct crystallization; glass-ceramics

BROADBAND DIELECTRIC RELAXATION OF NEW QUATERNIZED POLYSULFONE

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Electronic properties of a new quaternized polysulfone (PSFP) - obtained by the quaternization reaction of chloromethylated polysulfone with triphenylphosphine - were investigated.

Dielectric spectroscopy measurements provided information on changes in the dielectric constant and dielectric loss, for different frequencies and temperatures. The dielectric constants (ε') increased with temperature, due to the increase of total polarization, arising from dipoles orientation and trapped charge carriers, and decreased with increasing frequency, due to dielectric dispersion, as a result of the lag of molecules behind the alternation of the electric field at higher frequency [1]. Thus, for the studied sample, the dielectric constant depends on the main chain and on the pendant group. On the other hand, the pendant groups reduced the electronic conjugation from the main chain and resulted in lower values of ε', comparatively with the unmodified polysulfone. Moreover, triphenylphosphonium from the side groups reduces more the electronic conjugation from the main chain, lower values of ε' and lower slopes of $\log\varepsilon$' *versus* temperature thus resulting.

The dielectric loss behavior for PSFP sample exhibits two types of relaxation, β and γ, the latter relaxation being more visible. α relaxation does not appear in quaternized polysulfones because of the losses caused by increased conductivity. In addition, the thermal decomposition temperatures of quaternized polysulfones do not exceed 150ºC, while that of polysulfone is approximately 400ºC [2]. In the case of γ transition, a relatively broad distribution of the relaxation times and a symmetrical dielectric dispersion is evidenced.

Keywords: Quaternized polysulfone; Dielectric loss; Dielectric dispersion

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SURFACE MODIFICATIONS OF ALUMINA/ ZIRCONIA BIOCERAMICS UPON DIFFERENT FLUORIDE-BASED TREATMENTS

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The administration of complex fluorides as compared with NaF suggests the possibility of using them as effective agents in dental caries prevention in human populations [1]. For example, stannous fluoride converts the calcium mineral apatite into fluorapatite, which makes tooth enamel more resistant to bacteria generated acid attacks. In toothpastes containing calcium minerals, sodium fluoride becomes ineffective over time while stannous fluoride remains effective in strengthening tooth enamel. Stannous fluoride has been shown to be more effective than sodium fluoride in reducing the incidence of dental caries and controlling gingivitis [2]. In the present study, the surface modifications of alumina and alumina/zirconia bioceramics are investigated upon different treatments with sodium tetrafluoroborate and stannous fluoride respectively. The proposed bioceramics are designed for orthopedic and dental implants, being prepared by a novel technique – Spark Plasma Sintering [3]. By using complementary spectroscopic tools such as ATR FTIR and XPS, the chemical changes on the surface before and after fluoride treatment are discussed in terms of their effectiveness. Qualitative and quantitative results show that the proposed bioceramics are more sensitive to SnF_2 treatment, because on their surface is retained a larger amount of fluorine following the treatment with stannous fluoride, compared to fluorine amount detected after the treatment with sodium tetrafluoroborate.

Keywords: alumina zirconia, surface treatment, ATR FTIR, XPS.

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STRUCTURAL AND OPTICAL PROPERTIES IN GADOLINIUM-ALUMINIUM-LEAD-GERMANATE QUATERNARY GLASSES

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Glasses in the quaternary system $5Al_2O_3 \cdot [xGd_2O_3 \cdot (100-x)(7GeO_2 \cdot 3PbO)]$ with $0 \le x \le 40$mol% have been prepared from melt quenching method. In this paper, we investigated structural and optical properties in gadolinium-alumino-lead-germanate glasses through investigations of FTIR (Fourier-Transform Infrared Spectroscopy) and UV-VIS (Ultra-Violet) spectroscopy.

The observations presented in these mechanisms show that by increasing of Gd_2O_3 content up to 40mol%, the glass network modification has taken place mainly in the germanate part, while the excess of oxygen can be accommodated in the host network by the creation of shorter rings of $[Ge_2O_7]$ structural units and the formation of $[AlO_4]$ structural units. The affinity pronounced of the gadolinium cations towards germanate structural units produces the formation of the $Gd_2Ge_2O_7$ crystalline phase.

The UV-VIS spectroscopy data show the charge transfer transitions of Pb^{+2}-O^{-2}, Al^{+3}-O^{-2} and Gd^{+3}-O^{-2}, respectively. The additional absorption in the range 300 to 600nm was attributed to other types of defects such as: non-bridging oxygen ions, change in valency of ions and other color centers.

The values of the direct optical band gap of the glasses are determined from the optical absorption spectra. By increasing of Gd_2O_3 content in the glass matrix, the optical band gap energy increases indicating changes of the lattice parameters by Gd_2O_3 incorporation.

RAMAN SPECTROSCOPIC STUDY OF ANCIENT GLASS BEADS FOUND IN THAILAND

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Various colors of glass beads excavated at different archaeological sites in Thailand, such as Khlong Thom, Hor-Ek and Au-Thong were characterized non-destructively using Raman, X-ray fluorescence and optical absorption spectroscopy to determine the glass composition and the glass production technology in ancient time. The Raman spectra and XRF analysis classified that they were mostly alkali-based glass matrix. Some were high lead-bearing glass. Theirs compositions were similar as Mediterranean, Islamic and Indian glasses, but higher concentration of aluminum. The colors were affected from transition metal ions' contents, such as copper, iron and manganese. Optical absorption spectra showed that various shades of colors due to the different in oxidation states. Tin and lead were mostly found in the opaque color samples, especially the red opaque. SEM micrographs showed more corroded and flaked microstructure. Comparison in the glass compositions, it can be assumed that there was some technology production which related between these sites and other sites in Asia; South-East Asia, South Asia, East Asia and Asia Minor. These information led to obtain knowledge of the historical link of the long distance trade and exchange networks in the ancient time both land and maritime.

Keywords: Thai Ancient glass bead; Raman, XRF, SEM

THE COMPLEX OF N-METHYLPIPERIDINE BETAINE WITH SQUARIC ACID. STRUCTURAL, SPECTROSCOPIC AND THEORETICAL STUDIES.

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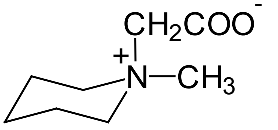
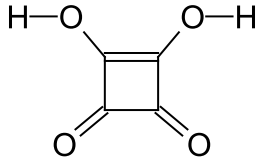
The crystal complex between the *N*-methylpiperidine betaine (MPB) and squaric acid (H_2SQ) is formed at the 1:1 ratio. The crystals are orthorhombic, space group *Pbca*. H_2SQ and MPB are linked by two non-equivalent O-H···O hydrogen bonds of 2.472(1) and 2.508(2) Å.



N-methylpiperidine betaine
(MPB)



Squaric acid
(H_2SQ)

In MPB a methyl group occupies the equatorial position, while the bulky CH_2COO^- substituent is at the axial one. Such orientation of the substituents around the quaternary nitrogen atom is a more profitable for C-H···O contacts between MPB and H_2SQ molecules. The MPB molecule is surrounded by four H_2SQ molecules. The solid-state FTIR spectrum is consistent with the X-ray results. The ^{1}H chemical shift of the CH_3 group confirms its equatorial position at the quaternary nitrogen atom, while the ^{13}C chemical shift of the COO carbon atom suggests that proton is not transferred from H_2SQ to MPB. The geometry of the optimized structures of the MPB·H_2SQ complex at the B3LYP/6-31G(d,p) level of theory, in a vacuum and solvated by water, have been used to calculate harmonic IR frequencies and to predict the chemical shifts in H_2O.

Keywords: N-methylpiperidine betaine, Conformation, Squaric acid, Hydrogen bonds, FTIR and NMR spectra, DFT calculations

KERR EFFECT IN POLY-γ-BENZYL-L- GLUTAMATE (PBG) SOLUTIONS

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The macromolecules may form ordered systems by orientation interactions in concentrated solutions or in gels, similar to liquid crystals or three dimensional networks with properties of solids. The external electrostatic field additionally orders the macromolecules by dipolar interactions, increasing the solutions anisotropy.

Poly-γ-benzyl-L-glutamate (PBG) is a dipolar macromolecule most widely studied due to its solubility in a large variety of organic solvents. The visible PBG birefringence in different solvents was measured as function of the external electrostatic field intensity by using very simple laboratory devices. The influence of the PBG concentration in solution, of the solvent nature and also of the external field intensity on the analyzed solutions' Kerr constant was carefully studied.

The increase in the anisotropy of the PBG solutions with the electrostatic field intensity was emphasized in our studies.

Keywords: Poly-γ-benzyl-L-glutamate; Kerr constant; external electrostatic field.

Acknowledgement

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BIREFRINGENCE AND DICHROISM OF POLY (VINYL ALCOHOL) STRETCHED FOILS CONTAINING PYRIDAZINIUM YLID MOLECULES

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Poly (vinyl alcohol) (PVA) foils have different applications in medical purposes and could be used as health indicators when they show dichroic properties.
The visible birefringence of the stretched PVA foils between crossed polarizers was determined from the channeled spectrum obtained in transmitted light. The PVA stretched foils' birefringence dependence on the thickness and the degree of stretching was carefully studied.

The rod-like or planar polyatomic molecules included in PVA films induce dichroic properties by ordering in the stretching process. Our purpose was to search the dichroism of the colored PVA foils and to establish the influence of the nature and concentration of dichroic molecules and also of the degree of stretching on the dichroic properties of the polymer foils.

Planar pyridazinium-ylids were included in polymer gel and the dichroism of the obtained dried and stretched foils was measured by using the visible intramolecular charge transfer (ICT) absorption band. The transition dipole corresponding to this absorption band is oriented along the ylid bond for symmetrically-substituted carbanion and it offers information about the orientation of the ylid molecules under the stretching process. The orientation of the electronic transition moment was also obtained from the dichroism studies in the case of some asymmetrical-substituted carbanion pyridazinium-ylids. The dichroic ratio induced by stretching was considered as an indicator of the order degree of the spectrally active molecules in the polymer foils.

The studies regarding foil dichroism are very important in spectroscopy of the complex molecules from the point of view of their structural characterization in parallel with the theoretical results obtained by computational methods. Quantum chemical calculations applied to the dichroic molecules in free space and in polymer foils attested our experimental results.

Keywords: PVA colored foils, birefringence, dichroism, ICT visible band of pyridazinium ylids.

The financial support of the European Social Fund – "Cristofor I. Simionescu" Postdoctoral Fellowship Programme (ID POSDRU/89/1.5/S/55216), Sectorial Operational Programme Human Resources Development 2007 – 2013 is acknowledged

HOW THE VARNISH LAYERS CAN MODIFY THE LIGHT SCATTERED AND REFLECTED BY PICTURAL SURFACES

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In our previous papers some changes of the spectral composition of the emergent light were observed for the varnished pictorial surfaces compared with the unvarnished ones. Consequently, the varnish layers can modify the artistic message. Some optical phenomena such as light scattering, reflection and total reflection must be considered when the spectral composition of the emergent light is simulated. The incidence angle, the layer thickness, the type of other resins and also the optical properties of the pictorial surfaces are important factors for the visual aspect of the varnished pictures. Finally, a general equation which expresses the emergent light composition versus the spectral composition of the incident light was obtained and simulated for different pictorial surfaces by various resins.

SPECTRAL STUDY OF 3,3',3'',3'''-((1E,1'E,1''E,1'''E)-([1,1'-BIPHENYL]-3,3',4,4'-TETRAYLTETRAKIS(AZANYLYLIDENE))TETRAKIS (METHANYLYLIDENE))TETRAKIS(NAPHTHALEN-2-OL),(NAFTALDAB),IN CONDENSED MEDIA

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Structural and spectral properties of 3,3',3'',3'''-((1E,1'E,1''E,1'''E)-([1,1'-biphenyl]-3,3',4,4'-tetrayltetrakis(azanylylidene)) tetrakis(methanylylidene))tetrakis (naphthalen-2-ol), (naftaldab), were investigated by theoretical and experimental methods.

The planar, polycyclic structure of naftaldab and the presence of the heteroatoms with lone pair electrons (participating to hyper-conjugation) determine the specific properties of the studied molecule. Theoretical investigations were made by using *ab initio* and DFT methods in order to elucidate the structure, spectral properties and solvent influence on them.

The electronic absorption spectra of naftaldab were recorded by UV VIS Hitachi U-2001 spectrophotometer. A solvatochromic study in solvents with various physico-chemical properties has been achieved in order to establish the nature of intermolecular interactions in naftaldab solutions.

The ability of naftaldab to orient in polymer foils was studied in poly (vinyl alcool) films which become anisotropic by stretching in warm heating conditions. The polymeric chains become ordered in the stretching process. Consequently, the PVA foils containing naftaldab become dichroic (spectral absorptions of the radiations linearly polarized on two perpendicular directions are different). The dichroic properties depend on the foil thickness and on the degree of stretching. The directions of the polarizations are parallel respectively perpendicular on the foil stretching direction.

The electronic absorption band of naftaldab (with maximum at 18700 cm^{-1}) has been utilized as indicator of dichroic ratio of the PVA containing naftaldab foil estimated by using the absorbencies in the maximum of the visible band of naftaldab for linearly polarized radiations acting parallel and perpendicularly on the stretching direction.

The dichroic ratio is an indicator of the degree of order of the naftaldab molecules parallel to the plane containing the stretching direction. The molecular degree of order increases with the increasing of the degree of stretching.

Keywords: naftaldab*, stretched PVA colored foils, dichroism, degree of order*

Acknowledgement

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DOPING OF FERROMAGNETIC MOTT INSULATORS: TOWARDS THE CONTROL OF TUNNEL AND COLOSSAL MAGNETORESISTANCES

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During the last quarter of century, magnetoresistance, *i.e.* change of electrical resistance in response to an applied magnetic field, has been at the heart of major scientific and technological breakthroughs. On the one hand, the discovery of the negative Giant Magnetoresistance (GMR) [1, 2] and Tunnelling Magnetoresistance (TMR) effects in magnetic multilayers has triggered the development of a new field in science and technology: *the spintronics*. Unlike conventional electronics based solely on the electronic charge, spintronics uses both the charge and spin of the electron. In a typical geometry inducing the GMR and TMR effects, in both cases, a very thin (≈ 1 to 4 nm) non-magnetic metal (GMR) or diamagnetic insulator (TMR) is sandwiched between two ferromagnetic (FM) metals. In GMR (TMR) devices, the standard (tunnel) transverse electrical resistance of the device is all the more low that both FM layers (1) have parallel magnetic moments and (2) contain electrons fully polarized at the Fermi energy. While (1) can be tuned by application of a magnetic field, the degree of polarization of electron is fully material-dependent. On the other hand, the discovery of a huge negative magnetoresistance effect in the perovskites manganites $La_{l-x}AE_xMnO_3$ (AE = Ca, Sr, Ba) [3] has initiated an intense activity of research within the community of solid state physics. This effect, termed "colossal" magnetoresistance (CMR), may exceed by more than three orders of magnitude the typical GMR values of magnetic multilayers. However, despite its very large value, the CMR effect in manganites has been only scarcely used in applications so far. A general strategy that allows obtaining materials showing either a CMR effect or a half-metal ferromagnet character is therefore highly needed. To the best of our knowledge, such a strategy does not exist today.

This study propose to check the validity of an original strategy allowing a rational research of compounds with either (i) a negative Colossal Magnetoresistance (CMR) or (ii) a half-metal ferromagnetic character inclined to show negative magnetoresistance in appropriate geometries or (iii) the coexistence of both effects. This strategy is based on our recent discovery of a colossal magnetoresistance (CMR) in the lacunar spinel GaV_4S_8 and its rationalization by a general theoretical model describing the magneto-transport properties of doped multiband ferromagnetic Mott insulators. The general character of the model strongly suggests that such a CMR effect should be retrieved in other multiband ferromagnetic Mott insulators after appropriate doping. This class of materials is also of special interest since they may easily display a half-metal ferromagnetic full spin polarization of carriers at the Fermi level.

Keywords: colossal magnetoresistance; ferromagnetic Mott insulator;

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INFLUENCE OF THE AIRY-FRESNEL TRANSMITTANCES ON THE MICHELSON INTERFERENCE PATTERNS OBTAINED WITH A ROTATING CELL FILLED WITH A UNIAXIAL LIQUID CRYSTAL

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Measurement of the main refractive indices and of the optical linear birefringence has been one of the standard tools in the study of anisotropic properties of materials for nearly two centuries [1, 2]. For this kind of measurement, a range of experimental techniques using polarized light (interferometry, polarimetry, polarizing microscopy, elipsometry, etc.) were optimized and applied in the study of the anisotropic materials such as solid crystals, organic tissues, strained glasses, polymers, liquid crystals, etc [2]. Among these techniques the most sensitive and accurate are those based on using the interferometers; this technique has been successfully applied to study the solid transparent samples [3]. For the liquid crystals kept in rotating cells, the main difficulty which appears is determined by the multilayer structure of the sample; the multiple internal reflections on the layers surfaces and the multi-beam interference have important influences both on the amplitude of recorded signals and on the angular positions of maxima and minima of interference found in the scanned interference patterns. The aim of the present theoretical and experimental study is to improve the theoretical model used for processing the signals recorded from the interference patterns obtained with a rotating liquid crystal cell placed in one arm of a Michelson interferometer. To increase the accuracy, the influence of the Airy-Fresnel transmittances and the Airy phase shift [4] are included in the theoretical model used for processing the recorded signals. In order to test the model, the technique is being used to determine the main refractive indices of 5CB liquid crystal. The obtained results are discussed considering the possibility of using the technique presented here in determining the main refractive indices for biaxial liquid crystals such as an organosiloxane low-generation liquid crystalline dendrimer which exhibits both the uniaxial (N_U) and the biaxial (N_B) nematic phases detected by several other experimental techniques [5].

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Keywords: interferometry; main refractive indices; biaxial nematic phase; uniaxial nematic phase; dendrimer;

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DETAILED INVESTIGATION OF BETA-CYCLODEXTRIN INCLUSION COMPLEX WITH DESFERRIOXAMINE B CHELATOR

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Desferrioxamine B, H3dfb, otherwise known as deferoxamine of desferal, is a naturally occurring trishydroxamic acid synthesized and secreted by several species of microorganisms. The deprotonated hydroxamic acids are capable to complete the coordination shell of iron(III) forming an hexadenate ligand [1,2]. Actually, H3dfb is the only chelator of iron used clinically to treat disorders related to iron overload and pathological iron deposition in man. However, H3dfb presents the disadvantage of its parenteral administration due to low intestinal absorption in the case of oral administration. An effective way to improve this situation could be by preparing a supramolecular inclusion compound with cyclodextrins.

To investigate this possibility, in this work, we analyzed the inclusion compound of beta-cyclodextrin (b-CD) with desferrioxamine B in solution by proton NMR spectrometry and molecular dynamics. An upfield shift of the H5 protons of beta-CD, located inside the cavity, was observed when the molar ratio [H_3dfb]/[b-CD] increases. Using the continuous variation method a 1:1 stoichiometry is proposed. With this hypothesis the association constant is calculated using a nonlinear least-square regression analysis [3,4]. A molecular dynamics trajectory has been also calculated and analyzed and supports the experimental results.

Keywords: NMR spectroscopy; molecular dynamics;inclusion compounds

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BTEX EXPOSURE ASSESSMENT OF AMBIENT AIR

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The aim of the present work was to develop a gas chromatography-mass spectrometric (GC/MS) method, using an isotopic labeled internal standard for the quantitative analysis of benzene (B), toluene (T), ethyl benzene (E), and o-, m-, p-xylenes (X) levels in ambient air. BTEX are toxic compounds with high impact on human health. The method was applied for BTEX levels determination in the indoor/outdoor air.

The method developed for BTEX determinations in indoor air is simple and rapid with a high selectivity and specificity due to the mass spectrometer operating in the SIM mode, which allowed the peak deconvolution of benzene and its deuterated analogue internal standard. SIM mode offers higher sensitivity than scan mode.

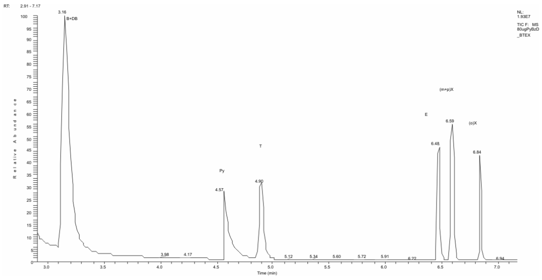

Fig. 1 BTEX separation by SIM-GC/MS

The method proved to be simple and fast, with good linearity, precision and accuracy, its validation demonstrating the capacity to reliably identify and measure the BTEX compounds.

Keywords: GC/MS; SIM; isotopic labeled.

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FREE AMINO ACIDS STUDY DURING SALAMI FERMENTATION

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The purpose of this study was to establish a fast and reliable experimental protocol for the analysis of free amino acids from dry fermented salami, using [^{15}N]-methionine as internal standard. Batches containing 0.3% glucono delta-lactone (GDL) and 0.05% sodium ascorbate (ASC), and batches containing only 0.1 % sodium ascorbate were manufactured. The content of free amino acids was measured at different time intervals over 45 days of storage.

The study of starter cultures and the influence of salt concentration, ripening time and the different curing ingredients are important in the quality of fermented sausages[1]. Free amino acids content is directly related to the meat flavor and taste. Meat consumers and processors are interested in the development of efficient and economical technology for processing meat into a product that is palatable and reasonable in cost [2]. A gas chromatography - mass spectrometric (GC/MS) technique was used for the quantitative characterization of amino acids in different steps of salami processing.

The extraction procedure of free amino acids was followed by a two-step derivatization method for the analysis of the free amino acids. Differences in amino acid levels were measured at different time interval days of storage. The free amino acids have increased significantly with the storage time, especially in GDL variety. Glutamic acid (Glu), valine (Val), histidine (His) and alanine (Ala) were the most abundant while cysteine (Cys) was generally low. The developed isotopic dilution GC/MS quantitative method showed good validation parameters, linearity, precision, accuracy, LOD. The method proved to be very helpful in the fermentation process study.

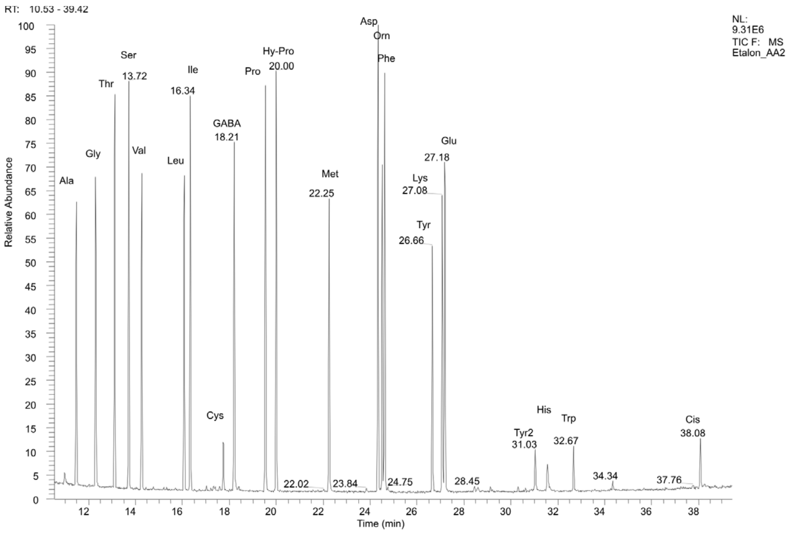

Fig.1 The TIC chromatogram of a standard solution of amino acids (10µg·mL^{-1})

Keywords: amino acids, dry fermented salami, GC-MS.

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STUDY OF INTERACTION BETWEEN CALCIUM PHOSPHATES AND TITANATE NANOTUBES

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Titanium and titanium alloys are regularly used for orthopaedic implants due of their resistant to corrosion, mechanical properties and biocompatibility. However, they are not bioactive and can not be directly bonded to the living bone tissues. There have been attempts to improve the bioactivity of titanium by surface modification of implant. Calcium phosphates (CaPs) are frequently used as coating material for orthopaedic and dental implants since they are both bioactive and biocompatible although their mechanical properties are not adequate [1]. To improve the mechanical properties of CaP, some authors added nanotubes (mostly TiO_2 and carbon), but in such procedures the additional processing of nanotubes is necessary [2, 3]. The aim of this work is to study the interaction of CaP with titanate ($H_2Ti_3O_7$) nanotubes (TiNT) that could be utilized for improving CaP mechanical properties.

Calcium phosphates are prepared biomimeticaly in the presence of TiNT and its phase development was studied by Fourier transform infrared spectroscopy (FTIR) and micro-Raman spectroscopy. Raman spectroscopy is suitable to study CaP+TiNT system because the most of Raman bands of CaP are in the part of spectrum where there are no intense bands of titanate nanotubes. The kinetic of phase changes in the mixed system was compared with the behaviour of system with pure CaP.

It was shown that Raman spectroscopy is more suitable for study of CaP+TiNT system then FTIR since it is easy to recognize the difference in the vibrational spectra of amorphous calcium phosphate (ACP), octacalcium phosphate (OP) and apatites. Moreover, the advantage of Raman spectroscopy is that the sample can be analyzed without the need of prior dehydration and has superior spatial resolution.

We observed that the transition from amorphous calcium phosphate (ACP) to octacalcium phosphate (OCP) was considerably faster in the case of addition of titanate nanotubes. The rate of phase development from ACP to the thermodynamically more stable apatites will be discussed in the relation to the amount of the TiNT in the reaction system.

Keywords: calcium phosphates; titanate nanotubes; Raman spectroscopy, FTIR

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EVALUATION OF CHEESE WHEY LACTOSE CONCENTRATION IN *E. COLI* HYDROGEN FERMENTATION BY FT-IR SPECTROSCOPY

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Cheese whey is a dairy industry by-product and a special waste with high lactose content, and a raw material for production of various biofuels, like ethanol, methane, bio-butanol and hydrogen. The aim of our study was to use FT-IR spectroscopy for estimation of the lactose concentration in whey and in *Escherichia coli* hydrogen fermentation

E coli JM 109 and *E. coli* BW25113 *hyaB hybC hycA fdoG frdC ldhA aceE* strains were tested for hydrogen gas production using cheese whey as substrate. Hydrogen concentrations in liquid and gaseous environments were measured with two experimental systems for quantitative measurements of hydrogen yield and rate. For hydrogen analysis in the gas phase the RGAPro-100 mass-spectrometer connected to the experimental test-system was used. FT-IR spectra of lactose, cheese whey, fermentation supernatant and *E. coli* biomass samples were recorded on a VERTEX 70 with HTS-XT extension (BRUKER, Germany) over the range 4000 - 600 cm^{-1}. Data processed with OPUS 6.5. As the characteristic peak of lactose was used one at 1042 cm^{-1}. Lactose concentration calibration curve created using Quant 1.

The results of FT-IR spectral quantitative analysis of different whey samples (raw, concentrated, ultra filtrated, stored at temperatures 4-21 ^{o}C or frozen for 1-21 days) showed that ultra filtrated or concentrated whey should be stored in a fridge to maintain the lactose concentration. While raw whey for storage should be centrifuged to overcome the growth of biomass and fermentation by indefinite microflora. The second derivative spectra were used for lactose measurements in fermentation broth. The lowest lactose concentration to be detected by FT-IR spectroscopy was 1.1 %. Measurement of lactose concentration during fermentation allows to follow its conversion by *E.coli*, and thus establishes the amount of whey that bacteria can metabolize.

This study showed that FT-IR spectroscopy being is a time-saving method is helpful for lactose concentration measurements and optimization of hydrogen fermentation. As well as, an assessment was developed to establish whether *E coli* JM 109 and *E. coli* BW25113 *hyaB hybC hycA fdoG frdC ldhA aceE* lactose consumption is viable possibility for bio-hydrogen production.

Keywords: FT-IR spectroscopy, lactose cheese whey, E. coli, hydrogen fermentation

Acknowledgments ERAF project No. 2010//0298/2DP/2.1.1.1.0/10/APIA/VIAA/157 “Technologies for biogas production from agricultural and dairy wastes” and prof. T. K. Wood (USA) for *E. coli* BW2511.

EFFECT OF GLUTARALDEHYDE ON HEMOGLOBIN ADSORPTION ONTO SILVER CONTAINING BIOACTIVE GLASS

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Silver containing bioactive glasses can be considered as implant suitable materials that combine the bioactivity and biocompatibility of Si-Ca based systems with the antibacterial properties of silver [1]. One important aspect that has to be considered in investigating the biocompatibility of such systems is its response in terms of interactions with protein. The protein formed layer on a biomaterial surface provides the topographical and chemical cues to guide cells, and increase the biomaterial ability to support and foster cells attachment. In this respect, one approach is to load inorganic substrates, e.g. ceramics and glasses, with biomolecules, e.g. proteins, to stimulate cell adhesion and spreading onto the material surface. Surface modification with protein agent coupling, e.g. glutaraldehyde (GA) is an effective approach to provide accessible and chemical functional groups for protein immobilization and to couple proteins without losing their conformational functionality [2].

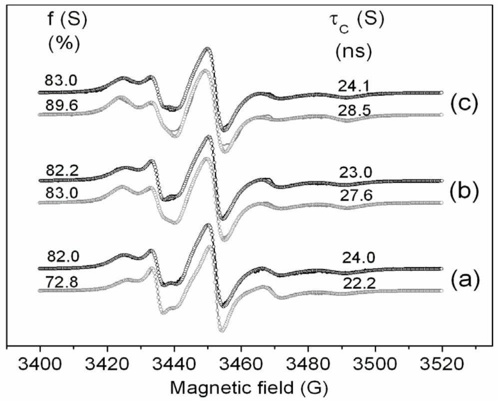

Fig.1 Experimental and simulated cw-EPR spectra of hemoglobin adsorbed on bioactive glass with 0% Ag (a), 2% Ag (b), 8 % Ag (c), with (black) and without (gray) GA.

To date, the effect of GA on protein immobilization onto bioactive glasses was poorly investigated. Therefore, the present study aims to investigate the influence of silver and GA in adsorption of horse hemoglobin on sol-gel derived bioactive glasses belonging to $56SiO_2\cdot(40-x)CaO\cdot4P_2O_5\cdot xAg_2O$ system, with x = 0, 2 and 8 mol%. For this purpose, both the pristine and surface modified samples were investigated before and after protein attachment, by site directed spin labelling combined with electron paramagnetic resonance (EPR), X-ray photoelectron spectroscopy (XPS), specific surface analysis and scanning electron microscopy (SEM). The mobility of the spin label side chain was determined from the EPR spectral line shape. From EPR spectra simulations were determined the values of rotational correlational times and the fraction of the immobilized spin labels (Fig. 1). The concentration of the attached protein was estimated by calculating the area of the EPR absorption spectrum, which is directly proportional to the spin concentration in the sample. The obtained values, correlated with the results obtained by XPS and SEM images, have shown that silver enhances hemoglobin adsorption, while GA influences the stability of protein attachment.

Keywords: surface functionalization, glutaraldehyde, antimicrobial, protein adsorption, EPR

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ELECTRONIC SPECTRA OF ZIRCONIUM DIOXIDE

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Zirconium dioxide (ZrO_2) is a molecule of astrophysical interest and its monoxide, ZrO is an important component in atmospheres of certain late type stars [1-5]. ZrO has considerable significance in distinguishing M and S-type stars [6], as it is one of the main absorption features in the spectra of S-type stars [7]. In stars with a very high mass loss rate, Zirconium dioxide, ZrO_2 clusters may form in large enough quantities to play a role as seed particle in dust formation processes [8]. Further, ZrO_2 is an important material with applications in microelectronics, catalysis and ceramics.

The electronic spectra of a cold molecular beam of ZrO_2 have been investigated using mass-resolved resonance enhanced multi photon ionization and laser induced fluorescence spectroscopy [9]. ZrO_2 was produced by laser ablation of a pure zirconium rod in the presence of a supersonic expanding mixture of approximately 5% O_2 in either helium or argon. The spectra were recorded in the region 17 000 cm^{-1} to 21 000 cm^{-1} and the bands assigned to the $A^1B_2 \leftarrow X^1A_1$ transition, whereby the origin and harmonic vibrational constants for the A^1B_2 state were determined. Further, the dispersed fluorescence of few bands were recorded to obtain vibrational parameters for the X^1A_1 state. A comparison is also made with isovalent TiO_2 [10].

Keywords: Electronic Spectroscopy; ZrO_2; REMPI; LIF

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PKU MONITORING BY ISOTOPIC DILUTION GC/MS METHOD

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In the present study we have developed an isotopic dilution (ID) GC-MS method for monitoring patients suffering from phenylketonuria (PKU). Untreated, PKU leads to progressive mental retardation, accompanied by other neurological manifestations as seizures and gait abnormalities [1]. Rapid medical intervention is essential for a successful outcome.

Valine (Val), leucine (Leu), proline (Pro), phenylalanine (Phe) and tyrosine (Tyr) were quantitatively determined from dried blood spot samples of 8 mm diameter (20µL of blood). The amino acids were extracted with 200µL methanol/HCl 0.1%, for 1h at 4°C [2], and 0.5µg of ^{15}N-Met was added to each 100µL of extract. A two-step derivatization procedure was applied: esterification with butanol/HCl 3M, and acetylation with trifluoroacetic anhydride. Target amino acids were separated and analyzed by GC/MS, in selected ion monitoring (SIM) mode (Fig.1). Quantitative analysis was performed by regression curve method.

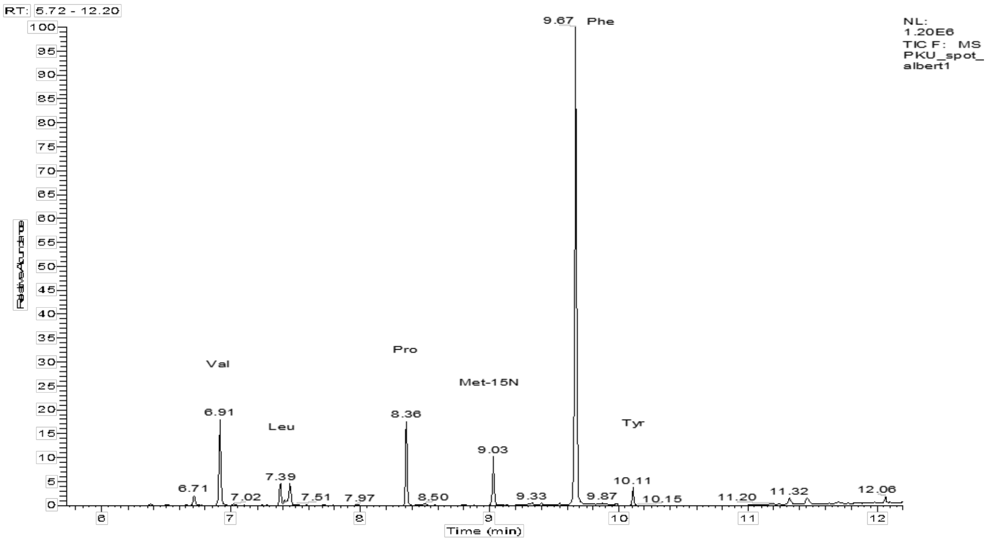

Fig.1 The SIM GC-MS chromatogram of a blood spot sample obtained from a PKU patient

Good chromatographic separation of the amino acids of interest and good validation parameters (linearity, precision and accuracy) were obtained.

The method is simple, reliable and also allows diagnosis of other metabolic diseases, such as maple syrup urine disease (MSUD) and hyperprolinemia (HP).

Keywords: Phenylketonuria; GC/MS; Isotopic dilution

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GC/MS ANALYSIS OF FATTY ACIDS IN TROUT PLASMA AND MEAT

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The purpose of this study was to develop and validate a GC-MS method to determine the fatty acid composition of rainbow trout (*Oncorhynchus mykiss*) plasma and meat.

The fatty acids were extracted from 0.5 mL of plasma by adding 0.5 mL chloroform:methanol 2:1 (v:v) [1]. The solution was shaken vigorously for 30 s, at room temperature. 1 g of trout meat was crushed with 1 g of quartz sand in a ceramic dish and homogenized with 5 mL distilled water. After centrifugation for 5 min, the supernatant was collected and the fatty acids were extracted by using the same solvent extraction conditions as for plasma. The lipids were converted to corresponding FAMEs (fatty acids methyl esters) by esterification of the carboxylic functions with 200 µL methanol/HCl 3M for 20 min at 80°C. Undecaenoic acid (C11:1) was used as internal standard.

Gas chromatography coupled to mass spectrometry (GC-MS) is an excellent technique for fatty acids identification and quantitation [2]. The nutritional quality of fish species can be evaluated from the fatty acid profile and by determining the eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) proportions (Fig. 1).

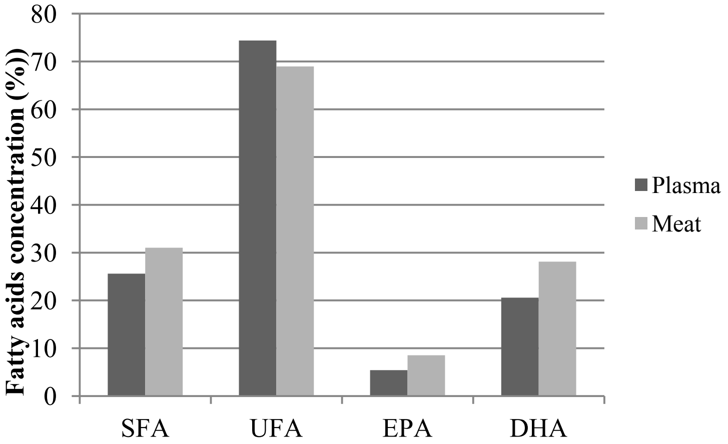

Fig.1 Saturated fatty acids (SFA), unsaturated fatty acids (UFA) and the omega-3 fatty acids: EPA and DHA, identified in trout plasma and meat.

The GC-MS method developed here is simple and good validation parameters (precision and accuracy) were obtained. The method was applied to study seasonal variation of trout fatty acids.

Keywords: GC/MS; FAME; Omega-3 fatty acids

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MORPHOLOGICAL MODIFICATION OF SOME POLYIMIDE PRECURSORS BASED ON ALICYCLIC DIANHYDRIDES BY A LYOTROPIC LIQUID CRYSTAL MATRIX

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Blends of hydroxypropyl cellulose (HPC) in lyotropic phase in different ratios with poly(amic acid)s (PAA)s based on epiclon (5-(2,5-dioxotetrahydrofurfuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic acid anhydride) and on bicyclo[2.2.2.]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BOCA) have been prepared. The possibility of using the inherent long-range ordering tendencies of the host liquid crystal itself (its pattern-forming properties) as a template [1], to produce positionally ordered polymer microstructures, has been investigated. This method could lead to materials with better properties in terms of elasticity and flexibility. The detailed surface morphology of the PAA/HPC films was examined by polarized light microscopy (PLM) and atomic force microscopy (AFM). The specific interactions, such as the hydrogen bonds between PAA and the liquid crystalline component were used for stabilization of the resulting morphology. The band texture, typical for lyotropic HPC solutions [2] was observed from atomic force microscopy images of PAA/HPC, evidencing different intensities and dimensions. This morphology was distinguished even at high PAA content and it was also maintained after HPC removal with a selective solvent. These results lie at the basis of future investigations concerning high performance mixed alignment layers used in display devices with tuned morphology.

Keywords: polyimide; alicyclic; liquid crystal; nanostructuration

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SPECTROSCOPIC ANALYSES OF POROUS NANOCOMPOSITES BASED ON TIO_2 AND AG NANOPARTICLES

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Aerogels based on TiO_2 are porous semiconductors with interesting properties such as low refractive indices, low thermal loss coefficients, high photosensitivity and large band-gap energy [1]. These properties make them attractive for diverse applications in solar energy conversion, pigments and electronic devices as well as in photocatalysis [2].

With the purpose of obtaining a high number of noble metal–semiconductor contacts, without dramatically altering the porous character of the samples, Ag nanoparticles were incorporated into the TiO_2 aerogel. This could lead to a change of the composites electronic structure via plasmon-induced charge separation [3], thus modifying its band-gap energy. It is well-known that collective oscillations of electrons are induced on the Ag nanoparticle surface by incident light. In the Ag–TiO_2 interfacial region, the oscillating electrons may be influenced by the electric field of the existent charge layer causing the transport of electrons to TiO_2 particles, modifying the electronic structure in such a way that the absorption spectrum shifts to the visible region.

The structural changes induced by the contact between noble metal and TiO_2 particles could certainly represent an additional cause for the appearance of different band-gap energy values. One should also mention that, in such heterogeneous systems, a transfer of electrons from TiO_2 towards Ag nanoparticles concurrently occurs, as a result of Fermi-level equilibration established between the systems [2,3].

In this study, Ag nanoparticles of various dimensions (~ 18, 45, 55 nm) were loaded into the TiO_2 aerogel matrix with the aim of modifying the band-gap energy of the nanocomposites and their structural and morphological properties.

The band-gap energy was determined with UV-vis diffuse reflectance spectroscopy. Raman spectroscopy and X-ray diffraction supply structural details about TiO_2-Ag composites. It was found that the band-gap energy values are related to the size of the Ag nanoparticles loaded into the TiO_2 aerogel matrix that also influences the structural and morphological particularities of the composites.

Keywords: TiO_2 aerogel; Ag nanoparticles; band-gap energy;

Acknowledgments: This work was supported by CNCSIS-UEFISCSU, project number PN II-RU-TE 81/2010.

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A GREEN APPROACH TO THE SYNTHESIS OF GRAPHENE OXIDE/REDUCED GRAPHENE OXIDE-GOLD NANOPARTICLES HYBRIDS

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Graphene- a monolayer of sp^2 –hybridized carbon, arranged in a honeycomb lattice, has received considerable attention due to its unique two-dimensional (2D) structure and remarkable physical and chemical properties [1]. Recently, a new class of graphene-based hybrid materials have aroused a great interest due to the novel properties resulted from combination of graphenes with different nanomaterials (e.g. magnetic nanoparticles, noble metal nanoparticles). Many methods for Au-graphene hybrid material have been developed. However, the main challenge consists in avoidance of hybrids aggregation by π-π staking between graphene nanosheets as well as the use of toxic chemicals (e.g. hydrazine) for graphene and/or gold reduction [2].

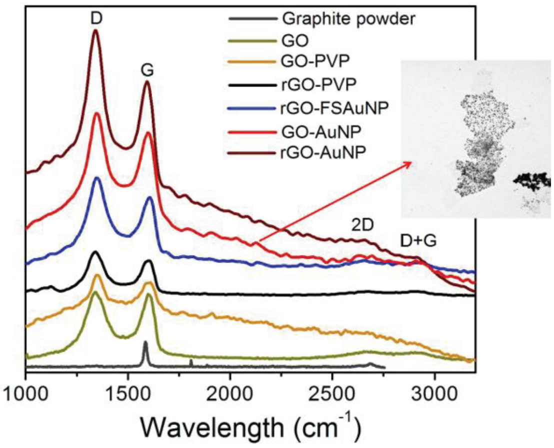

Fig. 1 Raman spectra of graphite powder (a), graphene oxide (GO) (b), graphene oxide-PVP composite (GO-PVP) (c), reduced graphene oxide-PVP composite (rGO-PVP) (d), reduced graphene oxide-flower shaped AuNP hybrid (rGO-FSAuNP) (e), graphene oxide-AuNP hybrid (GO-AuNP) (f), reduced graphene oxide-AuNP hybrid (rGO-AuNP) and the corresponding TEM image of GO-AuNP hybrid.

In this study a green approach to the synthesis of aqueous stable gold nanoparticles-reduced graphene oxide hybrids (AuNP-rGO) was reported, by employing graphene oxide (GO) as precursor, Poly(vinyl-pyrrolidone)(PVP) as AuNP-rGO hybrid stabilizer and/or GO reducer, and L-ascorbic acid (L-AA) as gold ions reducer. The results show that the presence of oxygen-containing functionalities on GO sheets plays an important role in growth of AuNP. Moreover, the shape of AuNP depends of the temperature of gold ions reduction: when reaction is performed at room temperature, the flower shaped AuNP are obtained, but in case of heating, the AuNP are most spherical. The as obtained hybrids could find a wide range of applications.

Keywords: Graphene oxide; Poly(vinyl-pyrrolidone); L-ascorbic acid; Hybrid material.

Acknowledgements: *This work was supported by CNCSIS-UEFISCDI, project number PNII-ID PCCE 129/2008 and Sectoral Operational Programme for Human Resources Development 2007-2013, co-financed by the European Social Fund, under the project number POSDRU/107/1.5/S/76841 with the title „Modern Doctoral Studies: Internationalization and Interdisciplinarity"*

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TEMPERATURE MODULATED DIELECTRIC SPECTROSCOPY IN THE TRANSITION REGIONS OF ALYCICLIC STRUCTURES

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Two polyimides, poly(DOCDA-ODA) and oly(DOCDA-p-BAPS), obtained from an alicyclic and flexible dianhydride, namely 5-(2,5-dioxotetrahydrofurfuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic acid anhydride (DOCDA) and an aromatic diamines 4,4'-oxydianiline (ODA) or 4-(4-((4-(4-aminophenoxy) phenyl)sulfonyl)phenoxy (p-BAPS) were synthesized and analysed by dielectric spectroscopy. The AC-dielectric properties of polyimides, such as dielectrical constant, ε', and dielectric loss, ε'', were measured in the - 200 - 250 °C temperature and 1 Hz - 1 MHz frequency ranges. Figure 1 exhibits the variation of dielectric loss with frequency and temperature, where two types of relaxation appear, γ - between - 100 °C ÷ 15 °C, and -85 ÷ 25 °C, and β - between 90 ÷ 160 °C and 50 ÷120 °C for poly(DOCDA-ODA) and poly(DOCDA-p-BAPS), respectively.

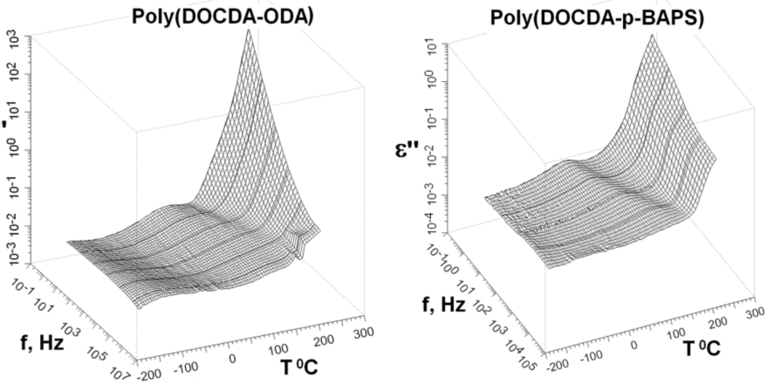

Fig. 1. Frequency and temperature dependencies of the dielectric loss for poly(DOCDA-ODA) and poly(DOCDA-p-BAPS)

Detailed spectrum results allowed evaluation of relaxation times, correlated with maximum frequency for dielectric relaxation, and of activation energies of γ and β relaxation. Taking into consideration that the strength and frequency of relaxation depend on the characteristic properties of dipolar and ionic relaxation, the study can also provide some information on the modification of local relaxation: in the case of γ relaxation a relatively broad distribution of the relaxation times and a asymmetrical dielectric dispersion appears, and in the case of β relaxation a broad distribution and a symmetrical dielectric dispersion appear for both samples. Also, the lower flexibility of the poly(DOCDA-p-BAPS) sample will reduce the mobility of the side groups, decreasing dielectric loss. The results were correlated with the chemical structure of polyimides and with other properties, such as flexibility and hydrophobicity. It has been showed that the factors that contribute to the interactions in the polyimide systems can be controlled for improving the some properties, for subsequent microelectronic applications, in which relatively low permittivity and high thermal stability are required.

Acknowledgements: The authors express their gratitude to Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number: PN-II-ID-PCE-2011-3-0937 – Phase 2012, for the financial support

Keywords: Dielectric spectroscopy; Relaxation phenomena; Alicyclic structures

SYNTHESIS, SPECTROSCOPIC AND CONFORMATIONAL STUDY OF SOME UREAS DERIVED FROM *N*-METHYLPIPERAZINE

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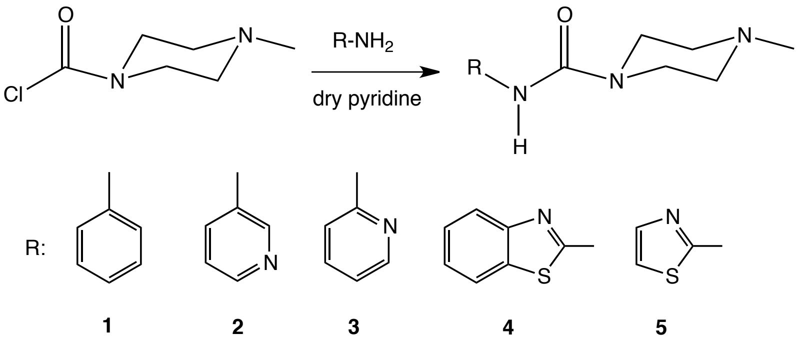
Substituted piperazines are common motifs in a large number of compounds with biological activity. Furthermore, *N*-urea and *N,N'*-bis-urea piperazine derivatives have interesting therapeutic indications. As a part of a research program related to the synthesis and structural study of potential pharmacologically interesting compounds we have focused our attention on the preparation of some tri-substituted ureas derived from *N*-methylpiperazine (**1**-**5**).



There has been a continuous interest in applying IR and NMR spectroscopies in characterizing the conformational equilibrium in different types of substituted ureas. The interest is determined besides by the biological activities of many representatives of these classes of compounds, by the closeness of their structure with the structure of amides.

Compounds **1**-**5** have been obtained starting from 4-methyl-1-piperazine carbonyl chloride and the corresponding amine.

A detailed study by ^{1}H, ^{13}C and IR spectroscopy has been done to determine the preferred conformations in solution. The assignments of proton and carbon resonances have been made on the basis of the literature data for related systems.

From the ^{1}H and ^{13}C NMR data it can be deduced that compounds **1**-**5**, in $CDCl_3$, show a preferred conformation where the *N*-CH_3 group is in equatorial position. The presence of one signal for axial and equatorial protons of the piperazine ring suggests a conformational dynamic for this ring. Besides, the equivalence of the C2 and C6 protons and also the C2 and C6 accounts for rotation around the N-CO bond.

The infrared spectra of compounds **1**-**5** in $CDCl_3$ and in a very dilute CCl_4 solution in the stretching NH region showed a very weak-weak band at 3431-3462 cm^{-1} and 3447-3470 cm^{-1}, respectively, which is assigned to a planar *trans* conformation according to literature data for tri-substituted ureas. The ν (C=O) in $CDCl_3$ appeared in the expected region at 1655-1660 cm^{-1}.

The comparison of solid (in KBr) and $CDCl_3$ solution results suggest the presence in the solid state of NH···O intermolecular bonds in compounds **1** and **4** and NH···N$_{\text{heterocyclic}}$ in compounds **2**, **3** and **5**.

Keywords: Tri-substituted ureas; Piperazine; Spectroscopy; Conformational Analysis

IR AND RAMAN SPECTRA OF 3-AMINOPROPYLTRIMETHOXYSILYL-MODIFIED SILICA GEL: QUALITATIVE ANALYSIS

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3-Aminopropyltrimethoxysilane (APTMS) and 3-aminopropyltriethoxysilane (APTES) are molecules with two functional groups that can be used as spacer (coupling agent), particularly on silica gel [1, 2]. Its methoxy or ethoxy groups undergo nucleophilic substitution with the –OH groups from the silica gel resulting in a Si-O-Si linkage leaving the amino group for further coupling to molecules, e.g., transition-metal complexes for applications as heterogeneous catalysts [3].

In this work we used transmission and diffuse reflectance IR techniques, together with MicroRaman technique to reveal the changes in the spectra of silica-gel before and after the chemisorption of APTMS on its surface. We also present our result on the possibility to attach molecules possessing catalytic properties on silica-gel modified with APTMS. The main indication that chemisorption of APTMS molecules on the silica-gel surface occurred is the observation of the lowering in the intensity of the absorption band in the OH stretching region (cf. Fig. 1). Comparison of the IR and Raman absorption bands in the CH_2 stretching region with published data [4] indicates that complete substitution under the experimental conditions has occurred. The comparison of the recorded Raman spectra with literature data [5, 6] and the performed non-linear curve fitting indicate the possible band due to the newly formed siloxy bond. Attachment of molecules possessing catalytic properties is also investigated and proved to occur.

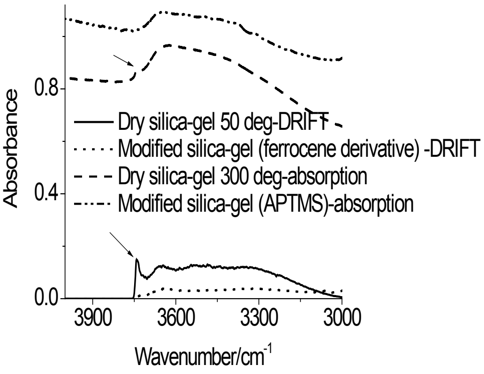

Fig.1 DRIFT and absorbance IR spectra of dried and modified silica gel. The arrows indicate the OH stretching band of the "free" OH groups in silica-gel.

Keywords: 3-Aminopropyltrimethoxysilane; Modified Silica-gel; IR and Raman spectra

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SPECTROSCOPIC INVESTIGATION OF P_2O_5-CdO-Li_2O GLASS SYSTEM – AS ESR DOSIMETER MATERIAL

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Many researches have focused on phosphate glasses in the last years due to theirs diversified applications in technology, medicine, as biomaterials and in clinical dosimetry [1].

In the present work a systematic IR, Raman and ESR study of the P_2O_5-CdO-Li_2O glass system where done in order to develop a suitable material for ESR dosimetry.

The ESR technique has shown to be considerably promising for high dose gamma measurements and it is currently employed in dosimetry and several materials are suitable for this purpose. Among these, some types of phosphate glasses were chosen.

The radiation induced hole centers in alkali phosphate glasses are characterized by the ESR hyperfine doublet of ^{31}P isotope (nuclear spin= ½) and were studied by different authors [2-3]. They found that the efficiency of the generation of electron and hole centers depends on the glass composition and is almost independent of the type of ionizing radiation source.

Glass dosimeters are important means for the various different high-dose level applications, e.g. for medical, industrial and food irradiation purposes.

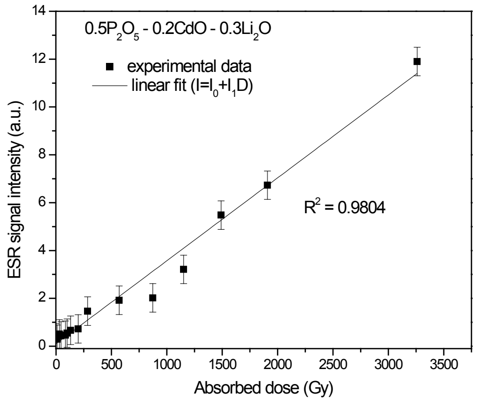

Fig.1. The linear dose response relationship for one of the studied glasses.

The predominant absorption band from IR spectra is attributed to the symmetric stretching vibrations of P=O double bonds. Raman spectra of the studied glasses contain also typical phosphate glasses bands. Thus the band at ~701 cm^{-1} is assigned to symmetric stretching mode of P–O–P bridging oxygens, $(POP)_{sym}$, between Q^3 phosphate tetrahedral and that from ~1164 cm^{-1} is attributed to symmetric stretching mode of O-P-O non-bridging oxygen (NBO), $(PO_2)_{sym}$, indicating the formation of Q^2 phosphate tetrahedron. Infrared and Raman investigation revealed a local network structure mainly based on Q^2 and Q^3 tetrahendrons connected by P-O-P linkages. A linear dependence (Fig.1) was obtained by representing the ESR signal intensity versus the absorbed doses in the range 100 – 3000 Gy, which proves that the glass system could be successfully used as ESR dosimeter.

Keywords: P_2O_5-CdO-Li_2O glasses, IR, Raman, ESR

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STRUCTURAL AND MICTROSTRUCTURAL STUDIES OF BLACK GLASSES OBTAINED ON THE BASIS OF LADDER LIKE SILSESQUIOXANES

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Obtaining homogenous glasses from Si-O-C system by classical melting of resource kit is very difficult due to the decomposition of the material and oxidation process. This problem can be solved by means of pyrolysis of ladder-like silsesquioxanes. Using of ladder-like silsesquioxanes with different ratio of T: D groups allows us to easily control the amount of carbon introduced into the glass structure. This is extremely important for the homogeneity of the glasses.

Main objective of this work was to conduct detailed structural (XRD, FIR, MIR, Raman, MAS NMR) and microstructural studies of black glasses obtained from ladder-like silsesquioxanes. Conducted XRD and far infrared (FIR) research showed that obtained materials are fully amorphous. Based on microscopic studies (SEM with EDX) it was ascertained that received glasses are homogenous.

Detailed structural research in middle infrared (MIR), Raman and MAS NMR allowed to say that obtained amorphous materials of v-SiO_2 structure contain the Si-C bonds – homogeneous black glasses.

Keywords: Black glasses; Ladder like silsesquioxanes; SiOC.

Acknowledgements
This work was supported by Polish Ministry of Science and Higher Education under project ‘‘Silsesquioxanes as ceramic precursors" 2659/B/T02/2011/40.

INTERACTIONS ANALYSIS BETWEEN FURAZOLIDONE AND EXCIPIENTS IN SOLID DOSAGE FORMS

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Furazolidone, 3-(5-Nitrofurfurylidineamino)-2-oxazolidinone, is a synthetic nitrofuran derivative, therapeutically effective as a bactericidal agent. Excipients are important components of pharmaceutical formulations and they can take an active part in the improvement of the characteristics of the pharmaceutical formulations.

In order to investigate the possible interactions between furazolidone and excipients in tablets formulations, differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis completed by X-ray powder diffraction (XRPD) and Fourier transform infrared spectroscopy (FTIR) were used for compatibility studies.

Based on their frequent use in preformulations, four different excipients: lactose (monohydrate and anhydre), magnesium stearate, talc and amidone were blended with furazolidone. The samples were prepared by mixing the analyte and excipients in a proportion of 1:1 and 1:0.25 (w:w).

The presence of the melting and of the decomposition signals of the pure furazolidon and of the corresponding excipients in the DSC traces and of characteristic mass losses steps, respectively in the TG curves supported the absence of incompatibility between furazolidone and excipients in the physical mixtures. XRPD patterns and FTIR spectra sustained these results, because they did not show evidence on interaction in the solid state between bioactive substance and excipient.

Based on the results supplied by DSC/TG, XRPD and FTIR, all excipients were found to be compatible with furazolidone, so they can be used in formulation of the slow release tablets.

Keywords: furazolidone, compatibility, DSC, TG, XRPD, FTIR.

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EFFECT OF HEAVY HALOGEN ATOM IN BIOLUMINESCENT REACTIONS

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Bioluminescence processes taking place in luminous organisms, are enzymatic chemiluminecent reactions resulted in formation of bioluminescent emitters (enzyme bound chromophores) in their fluorescent states and light emitting. Quantum yields of bioluminescent reactions are high – up to 50%. Effect of heavy halogen atoms in bioluminescent reactions was studied. Potassium halides (KCl, KBr, and KI) and a series of homologous xanthene dyes with halogen substituents (fluorescein, eosin Y, and erythrosin B) were chosen for experiments. Bioluminescent reactions of firefly (*Luciola mingrelica*), marine coelenterate (*Obelia longissima*), and marine bacteria (*Photobacterium leiognathi*) were used as objects of investigations. Two mechanisms of the halogen' influence were examined: (1) the physics effect of external heavy atom based on spin-orbital interactions in electron-excited structures, and (2) the biochemical effect, i.e. interactions with the enzymes resulting in changes of enzymatic activity. The physics effect was evaluated using photoexcitation of model fluorescent compounds (flavinmononucleotide, firefly luciferin and coelenteramide) with similar structure to the bioluminescent emitters. The bioluminescent and photoluminescent inhibition coefficients were calculated and compared for the luminous organisms to evaluate the relative contributions of the two mechanisms. The biochemical mechanism was found to be determinant.

Interactions of halogenated compounds and enzymes were studied using xanthene dyes. Mechanisms of bioluminescence quenching – energy transfer processes, collisional interactions, and enzyme-dye binding – were under consideration. Changes of bioluminescent spectra in the presence of the dyes were analyzed. Interactions of the dyes with enzymes were studied using fluorescence characteristics of the dyes in steady-state and time-resolved experiments. The dependences of fluorescence anisotropy of enzyme-bound dyes, the average fluorescence lifetime, and the number of exponential components in fluorescence decay on the atomic weight of halogen substituents were demonstrated. The results are discussed in terms of 'dark effect of heavy halogen atom' in the process of enzyme-dye binding; hydrophobic interactions were supposed to be responsible for the effect

Bacterial bioluminescent reaction was shown to be most sensitive to heavy halogen atoms involved into molecular structure; hence, it is suitable for construction of sensors to monitor toxicity of halogenated compounds

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EPR STUDY ON TETRACYCLINE LOADING AND RELEASE FROM A POROUS HOST MATRIX

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One of the most serious problems related to the procedure of introducing an implant into a body is the infection that can develop after the surgery treatment. In order to diminish the bacteriological risk associated with the implant materials, the addition of an antimicrobial drug such as tetracycline can be considered due to its broad antibiotic spectrum together with bone resorption inhibition and anti-inflammatory action [1]. In this respect, both the amount of tetracycline as well as details concerning its structure in adsorbed state and after release, are of great importance. This kind of information can be achieved by using electron paramagnetic resonance (EPR) spectroscopy: the intensity of EPR spectra is proportional with the spin concentration in the sample, while the line shape analysis can offer information about the polarity and mobility of the existing free radicals in the sample.

The aim of this study is to obtain information on tetracycline amount loaded and released from a bioactive glass matrix, and also information about tetracycline structural modification. In certain conditions tetracycline suffers structural changes that lead to appearance of nitroxide radicals, being thus possible to be studied by EPR spectroscopy. The obtained cw-EPR spectra recorded in liquid state before and after loading and release were simulated by using Easy Spin software [2]. The obtained rotational correlation times were in the nanoseconds range, and even shorter, leading to EPR spectra characterized by small line widths of the center lines and small apparent hyperfine splitting.

Keywords: tetracycline, EPR, spectra simulations

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STRUCTURAL CHANGES OF As_2Se_3 NANOLAYERS STUDIED BY SYNCHROTRON RADIATION PHOTOELECTRON AND SURFACE-ENHANCED RAMAN SPECTROSCOPY

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Light-induced structural changes on atomic and molecular scales, the effect of air exposure on surface structure and types and concentrations of different structural units (s.u.) and/or molecular fragments before and after laser irradiation were investigated in As_2Se_3 thin films by means of synchrotron radiation photoelectron and surface-enhanced Raman spectroscopy.

The influence of air and near bandgap laser irradiation on the surface structure of the As_2Se_3 nanolayers was studied. The As 3d and Se 3d photoemission peaks of the irradiated samples show significant differences in shape and position in comparison with those obtained for non-irradiated amorphous films. The experimental data were processed and quantified by curve fitting and the As 3d, Se 3d, C 1s and O 1s core-level components were analyzed in detail. The relative contribution of the As, Se, C and O atoms being in different chemical states to the whole As 3d, Se 3d, C 1s and O 1s signals, their structural origin, as well as their relation to the As_2Se_3 structure in surface and subsurface nanolayers before and after laser irradiation were also determined.

It was observed that near bandgap laser irradiation leads to significant redistribution of concentrations of As- and Se-centered s. u. on the sample surface: the amount of As-**Se**-Se and **As**-3Se components increases, while the **As**-rich Se-**As**-2As and 2Se-**As**-As s.u. disappear from the irradiated sample. These transformations indicate formation of new As-Se and Se-Se bonds and simultaneous breaking of As-As bonds during the light treatment.

Chalcogen enrichment in the top surface layers was also supported by the surface-enhanced Raman spectroscopy performed on As_2Se_3 nanolayers. The complex band in the micro-Raman spectra of amorphous films contains a peak at ~218 cm^{-1}, characteristic for either As-Se or As-As stretching vibrations and a shoulder at ~250 cm^{-1}, originating from Se-Se bond vibrations. Comparison with the ordinary micro-Raman spectra shows, that the intensity of the 250 cm^{-1} Raman band considerably increases in the surface-enhanced Raman spectra of As_2Se_3.

The induced structural changes on the surface of As_2Se_3 nanolayers under the ambient conditions and laser irradiation in air were interpreted using a new atomic model, in the frames of which the structural rearrangements were analysed and discussed in detail.

Keywords: synchrotron radiation photoelectron spectroscopy; surface-enhanced Raman spectroscopy; As_2Se_3 *nanolayers*

ELECTROCHEMICAL ETCHING OF SILICON-ON-INSULATOR LAYERS USING DC AND AC CURRENTS

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Etching of silicon-on-insulator (SOI) wafers is of scientific and technological challenge due to the nature of etching process itself, as well as due to the possible application of such silicon in development of new sensors. In this study we have electrochemically etched commercially available SOI wafers consisting of 40 μm thick device layer with resistivity ρ=20 Ωcm, separated from the 460 μm thick handle with resistivity ρ=10 Ωcm, with 1.5 μm thick SiO_2 layer. The etching process was carried out in an ethanolic solution of hydrofluoric acid with the volume concentration 1:1, by using different currents and etching time. Prepared samples were analyzed by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), optical microscopy, Raman and photoluminescence (PL) spectroscopy.

The differences in the structural and optical properties of the samples formed by etching with DC and AC currents were observed [1]. SEM images and EDS analysis of the samples etched with DC current showed that the device layer is covered with regular circular cavities of different sizes composed mainly of SiO_2. Raman spectra of these samples showed no significant shift of c-Si peak while PL spectra showed intense luminescence over the entire surface. When etched with AC current the surface of the samples exhibited island-like porous structures which show extremely intensive photoluminescence. SEM images showed that these islands consist of sponge-like mesoporous structures. Raman spectra exhibited substantial shift of TO(Γ) silicon peak, which is attributed to both the silicon nanostructures, that should exists within these structures, and the developed stress [2], caused by air oxidation of these sponge-like structures.

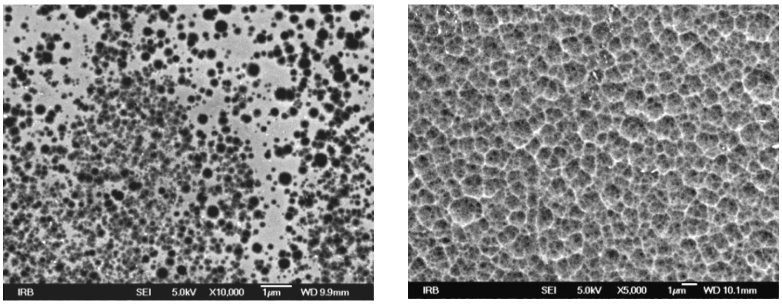

Fig.1 The surface of SOI wafers etched with DC current (left) and sponge-like mesoporous structures obtained with AC current (right)

Keywords: Silicon on insulator; porous silicon; SEM; EDS; photoluminescence; Raman spectroscopy; AC; DC

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FORMATION OF α-FeOOH, $AgFeO_2$ AND Ag_2O FROM THE MIXED $Fe(NO_3)_3$-$AgNO_3$ SOLUTIONS AT HIGH pH

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Precipitation of iron oxyhydroxide goethite (α-FeOOH), ternary Ag(I)-Fe(III) oxide silver ferrite ($AgFeO_2$) and silver(I) oxide (Ag_2O) from the mixed $Fe(NO_3)_3$-$AgNO_3$ solutions in a whole $[Fe^{3+}]:[Ag^{+}]$ concentration ratio range at high pH was investigated using X-ray powder diffraction (XRD), ^{57}Fe Mössbauer and FT-IR spectroscopies and field emission scanning electron microscopy (FE-SEM). Strong organic alkali tetramethylammonium hydroxide (TMAH) was used as a precipitating agent [1].

Monodispersed lath-like α-FeOOH particles were formed from a pure $Fe(NO_3)_3$ solution. The presence of Ag^+ ions influenced the formation of the delafossite-type oxide $AgFeO_2$ [2-4] beside α-FeOOH. The positions of XRD and Mössbauer lines suggested no significant incorporation of Ag^+ ions into the structure of α-FeOOH. FE-SEM revealed spherical and irregular $AgFeO_2$ nanoparticles and no significant change in the size and shape of α-FeOOH lath-like particles in these samples. In the precipitation system with the initial $[Fe^{3+}]:[Ag^{+}]$ concentration ratio of 50:50 almost exclusively $AgFeO_2$ nanoparticles 20-30 nm in diameter were formed (Figs. 1 and 2). These nanoparticles may have potentially useful magnetic and electrical properties. In the systems with a higher concentration of Ag^+ ions mixtures of $AgFeO_2$ and Ag_2O were formed. Single phase Ag_2O precipitated from a pure $AgNO_3$ solution.

Keywords: goethite; silver ferrite; silver oxide; TMAH; ^{57}Fe Mössbauer spectroscopy

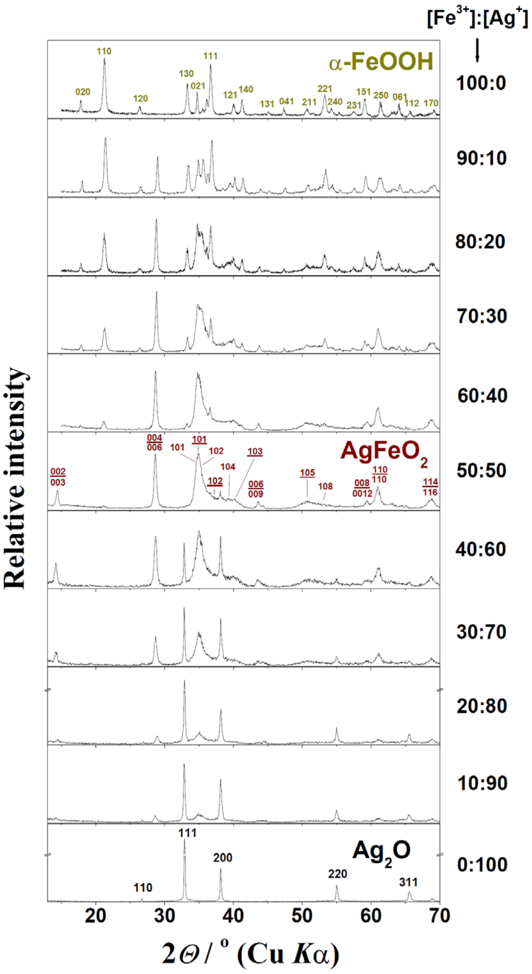

Fig. 1 XRD patterns of obtained samples with indicated initial $[Fe^{3+}]:[Ag^{+}]$ ratio

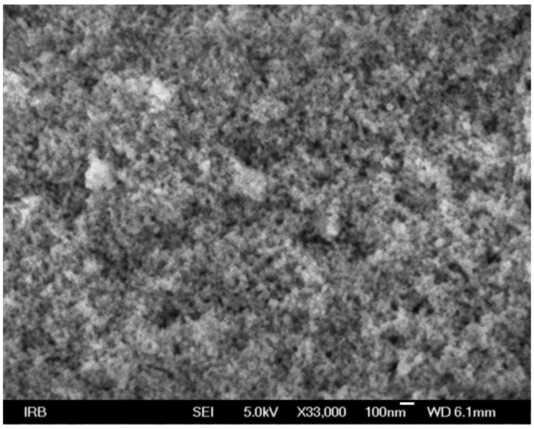

Fig. 2 FE-SEM image of $AgFeO_2$ nanoparticles formed at $[Fe^{3+}]:[Ag^{+}]$ ratio 50:50

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FABRICATION OF ORDERED PYRAMIDAL-SHAPED PLASMONIC SUBSTRATE FOR DETECTION AND QUANTITATIVE ANALYSIS USING SURFACE-ENHANCED RAMAN SPECTROSCOPY

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Surface-enhanced Raman spectroscopy (SERS) has emerged as an invaluable, ultrasensitive and highly specific tool for the detection and characterization of molecular probes adsorbed onto plasmonic nanostructures, becoming the method of choice for biosensing applications. However, the development of applications capable of quantitative analysis using SERS requires plasmonic substrates exhibiting highly reproducible enhanced Raman signal of the probe molecule over the entire detection area. A solution for these requirements is provided by developing periodically ordered metallic nanostructures.

In this work we present a rather simple approach for the fabrication of periodically ordered pyramidal-shaped metallic nanostructures. The polymer template for the plasmonic substrate was fabricated employing Nanoimprint Lithography (NIL), using a simple Digital Versatile Disc (DVD) as the initial mold. The first step consisted in transferring the negative image of the DVD to a polyvinyl alcohol (PVA) hydrogel film at 100 °C, which was used subsequently as the stamp. For fabricating the pyramidal-shaped template, a polycarbonate thermoplastic polymer was textured using the obtained PVA stamp. After detachment, the polyvinyl alcohol stamp was rotated with 90° and the second imprinting of the thermoplastic polymer was made yielding the periodically ordered pyramidal-shaped structure (see Figure 1). This technique represents a low-cost alternative to the classical lithography techniques, allowing the fabrication over large areas (~cm^2) of periodically ordered nanostructures in a controlled and reproducible manner.

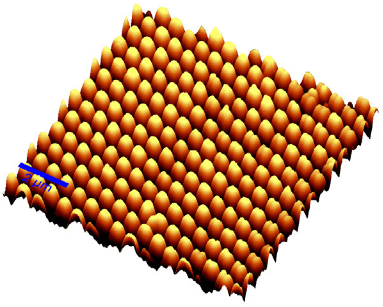

Figure 1 A) AFM image of ordered pyramidal shape substrate

The fabricated structure offers great potential for application in the detection and quantitative analysis of specific biomolecular interactions using the SERS technique. In this view, we are interested in exploiting the fabricated structure for the detection and quantitative analysis with high sensitivity of relevant biomolecules (*e.g.* urea) and antigen-antibody interaction (*e.g.* biotin-streptavidin). This approach offers the possibility to develop novel biosensors capable of detection and quantitative analysis of relevant biomolecules at extremely low concentrations.

Keywords: Biosensor; ordered plasmonic substrate; surface-enhanced raman spectroscopy

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CONFORMATIONAL CHANGES OF FIBRINOGEN ADSORBED ON BIOACTIVE GLASSES STUDIED BY FTIR SPECTROSCOPY

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Protein adsorption is a complex process involving van der Waals, hydrophobic and electrostatic interactions, and hydrogen bonding. It is accepted that the adsorption of the proteins on biomaterials surface leads to conformational changes with the extent of variation dependent on protein stability and protein-surface interaction [1, 2]. The infrared (IR) spectroscopy is a valuable tool used to investigate the protein structure. The sensitivity of the amide I vibration makes possible to determine the secondary structure alterations of the protein using IR [3]. The aim of this study was to determine the effects of changing the SiO_2/P_2O_5 amounts in bioactive glasses based on SiO_2-CaO-P_2O_5 on the adsorption behavior of fibrinogen on their surface.

The glass compositions $(64-x)SiO_2\cdot(36-x)CaO\cdot 2xP_2O_5$ (x=0, 1, 2, 3, 4) were prepared by sol-gel method. After aging at room temperature, under atmospheric conditions, the dried gel was annealed at 700°C in air for 3 h. In order to facilitate protein adsorption, the surface of the samples was functionalized with 3-aminopropyl-triethoxysilane [4]. The specific surface area and pores volume for the functionalized bioactive glasses were determined from sorption measurements performed in multipoint mod, and the values obtained were in the range 47.73-92.14 m^2/g and 0.21-0.24 ml/g, respectively. The functionalized samples were immersed in fibrinogen solution for 1 h at room temperature.

The changes occurred in secondary structure of fibrinogen after adsorption on bioactive glasses were assessed by fitting the amide I band with component bands after identifying their position with second derivative and then the determined values were correlated with those found in similar related studies [1]. In order to determine the covering degree of the samples with fibrinogen layer FT-IR imaging measurements were performed. The intensity distribution of the amide I (1650 cm^{-1}) and amide II (1550 cm^{-1}) band vibrations, recorded from the same area, was correlated with the fibrinogen distribution on the bioactive glass surfaces.

Keywords: FTIR, bioactive glass, protein adsorption

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THERMAL DECOMPOSITION OF Ni(II)-ACETATE and Ni(II)-LACTATE SALTS

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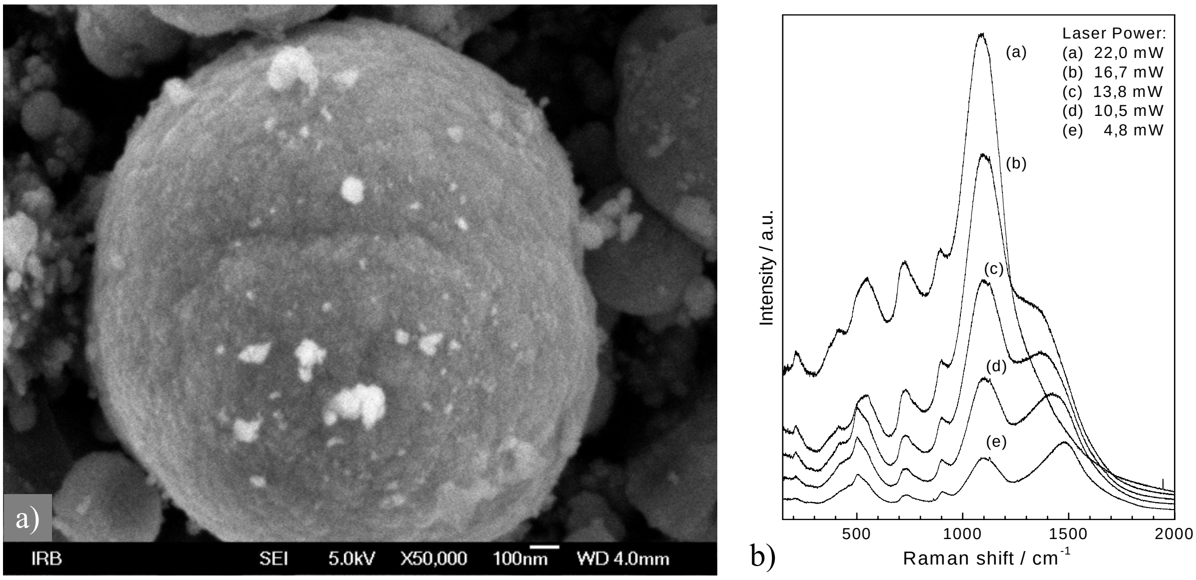
Nickel oxide (NiO; mineral name: bunsenite) has found an important applications in the form of thin films or powders. NiO films can be utilized as electrochromic material. Au-doped NiO film can be utilized as transparent electrode in optoelectronic devices, whereas Li-doped NiO film is potential gas sensor. NiO powders are used as starting material in the production of ferrite, (Ni, Zn)Fe_2O_4, thermistors and varistors or other products. The methods used in the synthesis of NiO powders are generally based on the thermal decomposition of Ni-salts, chemical precipitation of NiOOH combined with its thermal decomposition, hydrothermal treatment of NiOOH at high temperatures and sol-gel procedure.

In the present work the thermal decompositions of Ni-acetate and Ni-lactate salts were monitored using spectroscopic techniques: Raman, FT-IR and UV/Vis/NIR. Phase compositions of the powders produced were determined with XRD, whereas the shape and size of particles were determined with FE-SEM. Ni-organic salts were thermally treated in laboratory oven in contact with air, up to 800°C. It was found that NiO particles were accompanied with metallic nickel. Metallic nickel oxidized with increase of the temperature and prolonged time of heating. FE-SEM inspection also showed that the starting morphology of Ni-organic salts had a certain influence on the morphology of NiO particles. The changes in Raman, FT-IR and UV/Vis/NIR spectra were discussed.



(a) Agregate of nanoparticles obtained by thermal treatment of $Ni(CH_3COO)_2 \times 4H_2O$ in air at 400°C for 2h and (b) corresponding Raman spectra obtained at various powers of the laser excitation source

SIMVASTATIN-EXCIPIENTS INTERACTION ANALYSIS

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Simvastatin (SIM) (Fig. 1) is a hypolipidemic drug used to control elevated cholesterol, or hypercholesterolemia. It is a member of the statin class of pharmaceuticals.

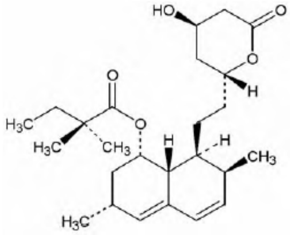

Fig. 1. Chemical structure of simvastatin

A pharmaceutical formulation is considered adequate when no drug-excipient interactions or between two excipients are found.

The aim of this work was to investigate the compatibility of SIM with the pharmaceutical excipients used in slow release tablets preformulations (20 mg/cp), by using thermoanalytical techniques (differential scanning calorimetry (DSC) and thermogravimetry (TG)), X-ray powder diffraction (XRPD) method and Fourier transform infrared spectroscopy (FTIR).

Physical mixtures of SIM: cellulose, lactose in a molar ratio of 1:1 and SIM: ascorbic acid, magnesium stearate, citric acid, talc in molar ratio of 1:0.25 were studied.

One can observe that the X-Ray powder diffraction patterns for samples obtained by mechanical mixture of bioactive compound with different ingredients are sum of patterns corresponding to each component, i.e. no new compound is formed; there are no interactions (physical or chemical between drug and excipients).

FTIR spectra supported these results, because no evidence of interaction in the solid state was found.

The melting and the decomposition DSC signals of the pure SIM and of the corresponding excipients and the unchanged mass losses steps, respectively present in the TG curves demonstrated the absence of interactions between SIM and excipients in the pharmaceutical formulations.

Based on the results supplied by DSC/TG, XRPD and FTIR, all the employed excipients were found to be compatible with SIM, so they can be used in formulation of the slow release tablets.

Keywords: Simvastatin, slow release tablets, compatibility, DSC, TG, XRPD, FTIR.

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POLYETHYLENE GLYCOL REDUCED GOLD NANOPARTICLES FOR DOXORUBICIN DRUG DELIVERY

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Doxorubicin is an anticancer drug widely used in breast cancer therapy. Its mechanism of action is to intercalate between base pairs in DNA helix having as a result the prevention of DNA replication, and thus the inhibition of protein synthesis.

There are several facts that limited the success of doxorubicin as a chemotherapeutic drug. It has a nonspecific distribution that generates adverse effects, a short biological half-life and develops quickly drug resistance.[1] This is the reason why there is a need for a specific delivery system.

In this study, the biocompatibility of novel polyethylene-glycol (PEG) synthesized gold nanoparticles (GNPs) [2] and their possibility as doxorubicin drug carrier was assessed. For this, Hs578T breast cancer cells were treated with doxorubicin, PEG-GNPs and doxorubicin adsorbed to PEG-GNPs. The results show that PEG-GNPs present a very low cytotoxicity, whereas at a 0.1 µM drug concentration the doxorubicin-PEG-GNPs complex shows a much higher cytotoxicity, compared to the free doxorubicin drug (see Fig.1). Thus, when adsorbed to PEG-GNPs, a lower doxorubicin concentration is enough to achieve the same therapeutic effect, as in the case of free doxorubicin. Therefore, the new doxorubicin-PEG-GNPs complex is promising for applications in cancer therapy.

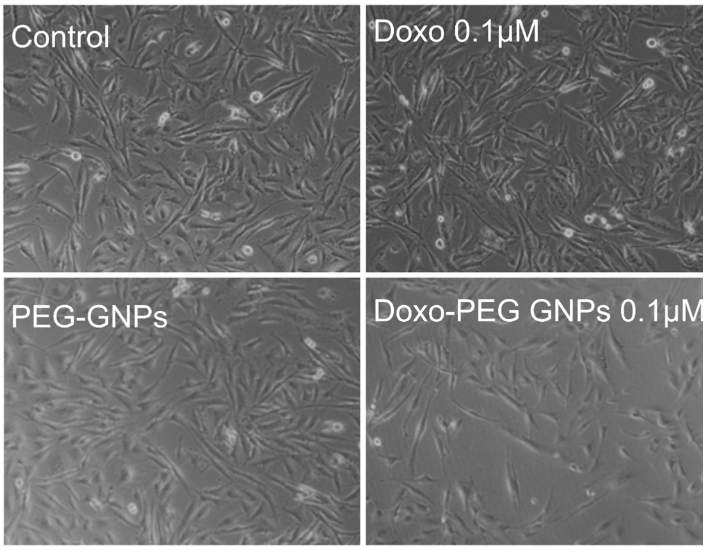

Fig.1. Cellular viability after treatment with doxorubicin, PEG-GNPs and doxorubicin-PEG-GNPs.

Keywords: Gold nanoparticles; polyethylene glycol; doxorubicin; Hs578T breast cancer cells

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ORGANIC SALTS OF GUANAZOLE – SEEKING FOR NEW MATERIALS FOR SECOND HARMONIC GENERATION

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The study of organic salts of guanazole was motivated by the previously prepared compounds based on the triazole [1-4] with the useful non-linear properties. Four novel organic salts of 3,5-diamino-1,2,4-triazole (Fig. 1) with malonic acid, glutaric acids, adipic acid and L-malic acid have been prepared and X-ray structural analyses have been performed within our project focused on preparation of new non-linear optical materials. The salts guanazolium(1+) hydrogen adipate and guanazolium(1+) hydrogen L-malate crystallize in the non-centrosymmetric space groups monoclinic *Cc* and orthorhombic $P2_12_12_1$, respectively. Unfortunately, the remaining two salts guanazilum(1+) hydrogen malonate and guanazolium(1+) hydrogen glutarate belong to the centrosymmetric triclinic space group *P*-1.

All salts were also characterised by the methods of vibrational spectroscopy (FTIR and FT Raman). The interpretation of the vibrational spectra is based on the DFT calculations according to experience with the similar organic molecules [3, 4].

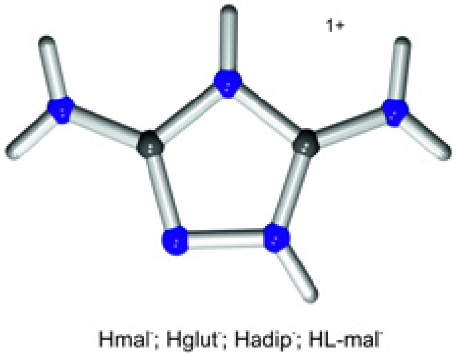

Fig 1: Scheme of salts of guanazolium(1+)

Keywords: Guananzole; Crystal structure; Second harmonic generation

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Acknowledgement
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PECULIARITIES OF SPECTRAL STRUCTURE OF EXTRINSIC MOLECULAR CRYSTALS AT LOW TEMPERATURES

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It is known that luminescence and absorption spectra of organic molecules dissolved in normal paraffins have at low temperatures multiplet quasi-line structure (Shpolskyi effect). Each component of the multiplet corresponds to a specific impurity center that is characterized by method of introduction of an impurity molecule to crystalline cell of a solvent. It is found as well that in spectra of related compounds with same geometrical dimensions and shapes, in the same solvent, quite different characters of multiplets are observed. This points out the fact that the nature of multiplet structure in electronic spectra is not finally clarified.

A similar (multiplet) structure has been observed by us at T = 4.2 K in absorption and luminescence spectra of some extrinsic molecular crystals. In particular, in phosphorescence spectra of benzophenone with admixture of dibrombenzophenone 2 series of narrow intensive bands are observed, with λ^1_{00} = 414.12 nm and λ^2_{00} = 415.88 nm, to those 2 impurity centers correspond. At increase of temperature up to 20K, both band series completely disappear from the spectrum.

Two impurity centers are formed as well in naphthalene crystal with impurity molecules of its mono-displacement. To each center its own band series in absorption and fluorescence spectra corresponds, initial bands of those are in resonance coincidence. In the Table respective distances $\Delta\nu_{1,2}$ between series are given.

Compounds $\Delta\nu_{1,2}$ (sm^{-1})	Compounds $\Delta\nu_{1,2}$ (sm^{-1})
α – fluoronaphthalene - 30	β – fluoronaphthalene - 96
α – chloronaphthalene - 10	β – chloronaphthalene - 52
α – bromonaphthalene - –	β – bromonaphthalene - 30

At study of experimental data the following properties of naphthalene crystal and impurity molecules are taken into account:

- most of naphthalene derivatives form displacement solid solutions in naphthalene crystals;
- in the naphthalene molecule 4 equivalent in energy positions of hydrogen atom exist, those are replaced by heteroatoms;
- point symmetry groups of an impurity molecule and of the crystal are sub-groups of a point symmetry group of a naphthalene molecule D_{2h},

Based on the symmetry of a free naphthalene molecule, impurity and naphthalene crystal it is shown that the number of impurity centres formed in the naphthalene crystal with impurities of naphthalene monosubstituted is determined by the formula $m = \frac{N \cdot n'}{N' \cdot n}$, where N and N' are the symmetry point group orders of the naphthalene molecule and the crystal, respectively, and n and n′ - degrees of intrinsic symmetry of position of the substitute of a free and an included to crystal impurity molecule.

The method described was used for analysis of spectral structure of molecular crystals of benzol, anthracene and naphthalene with mono- and poly-displacement impurities of those. Calculation data are in agreement with experimental results.

ASSESSMENT OF MOLECULAR INTERACTIONS OF INCLUSION COMPLEXES BETWEEN OF TWO CARDIOVASCULAR DRUGS –CYCLODEXTRIN

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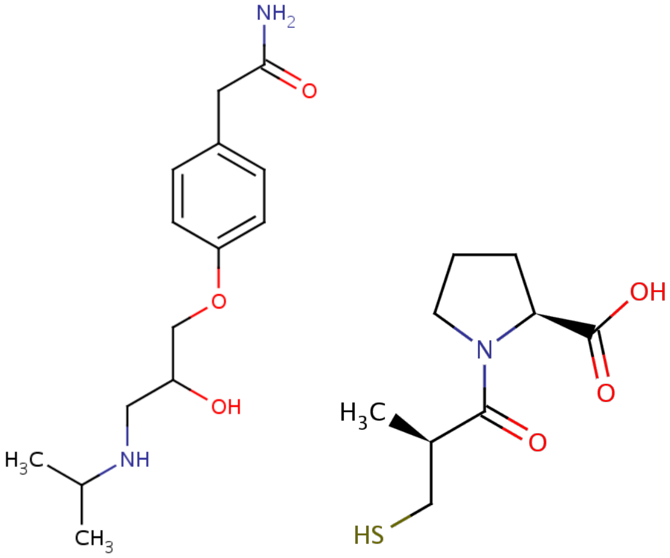
Molecular complexation with artificial receptors has become an increasingly used method in many technological areas and research fields. Among the different proposed methods, molecular complexation with cyclodextrins (CDs) is generally accepted as one of the most efficient.

The purpose of our research is to investigate and characterize the complexation thermodynamics of various cyclodextrins (α-cyclodextrin, β-cyclodextrin and hydroxypropyl - β-cyclodextrin) with atenolol and captopril using isothermal titration calorimetry (ITC) and to relate the thermodynamic parameters with the structure, by measuring ^{1}H NMR spectra of the inclusion complex.

ITC is one of the most relevant calorimetric techniques designed to investigate the physical basis of molecular interactions [1]. A single well-designed experiment can provide complete thermodynamic characterization of a binding reaction, including the equilibrium constant K, the Gibbs free energy ΔG, the reaction enthalpy ΔH, the entropic effect ΔS and reaction stoichiometry (n).

^{1}H NMR experiments were performed on a Brucker Avance III 500. The outcome used to characterize the cyclodextrins - cardiovascular drugs complexes were the chemical shifts of all the protons from the investigated macromolecular structures. The experimental data allows us to determine the reaction stoichiometry and to calculate the association constant K of the guest–host complexes. The stoichiometry of the complexes was determined by the continuous variation method (Job plot) [2].



Molecular structures of atenolol (left) and captopril (right).

Keywords: cyclodextrins, cardiovascular drugs, ITC calorimetry, ^{1}H NMR

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THE EFFECT OF TRIS BUFFER ON DPPC/WATER MODEL MEMBRANE STRUCTURE: DSC, SAXS AND FTIR STUDY

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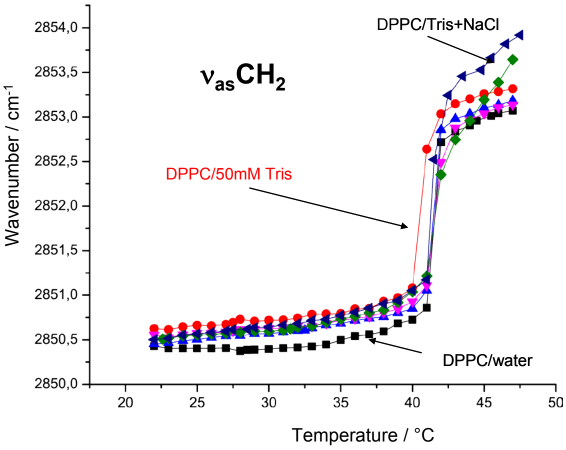
In order to explain the complex biological membrane functions, simplified model-membranes are often employed. Phospholipids are one of the major components of biological membranes and they are frequently used as model systems. By dispersing phospholipid molecules in water, uni- or multilamellar vesicles/liposomes are formed with potential application in nanomedicine as drug delivery vehicles, too. In this context, the effect of foreign molecules (ions, buffer systems, drugs) on the structure of the lipid/water two component systems is of great interest.

In this study we explored the structural properties of liposomes consisting of *dipalmitoyl phosphatidylcholine* (*DPPC*), one of the dominating lipids of human cell membranes, and water studied in *Tris (tris(hydroxymethyl)aminomethane) buffer* of different concentrations. Differential scanning calorimetry (DSC), small angle X-ray diffraction (SAXS) and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) has been employed to explore structural changes evoked by the presence of Tris molecules in structural characteristic of DPPC/water system. DSC study revealed the ionic character of interaction between DPPC and Tris molecules. Small angle X-ray diffraction (SAXS) curves showed a decay of lamellar structures in the presence of Tris, indicated by the broadening of diffraction peaks measured at gel phase (26°C). Moreover, at rippled gel and liquid crystalline phases the 'unbinding' of lamellae occurs. Addition of NaCl to the system, however, results in recovering of lamellar structure with ordered, periodical organization.



Temperature dependent FTIR investigations revealed also a small perturbation of acyl chain packing of DPPC bilayers caused by the presence of Tris molecules. The joint presence of Tris and NaCl molecules, however, cause a secondary phase transition above the main phase transition of DPPC bilayers (~46°C) with an increased *gauche/trans* conformers ratio of the acyl chains. Spectral features of phosphate headgroup vibrations were also changed, proving an interaction between phosphate diester group of DPPC and Tris molecules.

As a result of our systematic study an unexpected perturbation of Tris buffer on DPPC/water system was established. The combination of the applied experimental methods proved to be suitable for investigation of complex structural and thermotropic behaviour of DPPC/water model systems.

THE CRYSTALLINITY INVESTIGATIONS OF BIOMETAL COMPLEXES WITH DIFFERENT EXOPOLYSACCHARIDES

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Linear pullulan and branched dextran are microbial exopolysaccharides having several applications in the agriculture, food, cosmetic, chemical and pharmaceutical industries [1]. Moreover, these biopolymers are the subjects of theoretical studies as the representatives of macromolecules differing in the type of glycosidic linkage. In the case of dextran, the occurrence of the α-(1→6)-glycosidic bond provides for an increase of chain mobility. The pullulan structure is intermediate between amylose and dextran structures because of the co-existence of both α-(1→4) and α-(1→6) linkages in a single compound. Complexes of Cu(II) and Co(II) ion with reduced low-molar dextran and pullulan (RLMD and RLMP, M_w 5000–6000 g/mol) were synthesized in the water solutions, at the boiling temperature and at different pH values (7−13.5). FTIR microspectroscopy systems, ATR-FTIR spectrometer Bruker Tensor-27 in conjunction with a FTIR Bruker Hyperion-1000/2000 microscopy attachment equipped with a 15× objective and a 250-μm liquid nitrogen cooled MCT detector with the range of the IR spectrum from 4000–400 cm^{-1}, and resolution of 4 cm^{-1}, were used in this work. The crystalline/amorphous state of the powders was examined at room temperature. All the diffraction data (Cu K_α, 1.5418 Å) were collected on a θ:θ Bruker Axs D8 Advance vertical scan diffractometer; the generator was operated at 40 kV and 40 mA. The diffractometer was equipped with a Ni filter and a linear Position Sensitive Detector (PSD), with the following optics: primary and secondary Soller slits, 2.3 and 2.5°, respectively; divergence slit, 0.3°; receiving slit, 8 mm. The investigations of the crystallinity of polysaccharide complexes by means of FTIR and X-ray diffraction (XRD) are rare in literature. Here, we report the results of FTIR and preliminary XRD crystallographic characterization of Cu(II) and Co(II) ion complexes with RLMD and RLMP. The bands at about 1050 cm^{-1} and 1020 cm^{-1} found for both polysaccharides and their complexes, as well as in the spectra of polysaccharide starch, were shown to relate to the crystalline and amorphous phases, respectively [1,2]. The results of the FTIR spectroscopic study allowed one to suggest a predominant crystalline form of Cu(II) complexes, and amorphous form of Co(II) complexes. The results of preliminary XRD crystallographic characterization showed the poor crystallinity of Cu(II) complexes, in comparison with amorphous form of Co(II) complexes. The FTIR results are in accordance with those of XRD, and the FTIR technique is thus a useful method for detecting the crystallinity/amorphicity of such complexes.

Keywords: Crystallinity; FTIR; XRD

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MICROSTRUCTURAL CHARACTERISATIONS OF DIFFERENT Mn-OXIDE NANOPARTICLES USED AS MODELS IN TOXICITY STUDIES

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Mn-oxide microstructures were investigated with XRD, FT-IR, TEM, FE SEM and EDS techniques. The oxidation of the aqueous solutions of manganese (II) chloride by hydrogen peroxide was employed to synthesize pure 20-30-nm pseudospherical hausmannite (Mn_3O_4) nanoparticles and manganite (γ-MnOOH) nanowires. The α-MnO_2 nanotubes and nanorods were hydrothermally synthesized starting from $KMnO_4$ precursor, then modified with the addition of divalent metal cations Mn^{2+}, Cu^{2+}, Ni^{2+} and Fe^{2+}. The modification with Mn^{2+} induced the transformation of α-MnO_2 nanotube into 3D β-MnO_2 (pyrolusite) prismatic nanoparticles, whereas the low-crystalline α-MnO_2 nanorods were transformed into disc-like γ-MnO_2 nanoparticles. The modification with Cu^{2+} and Ni^{2+} induced the structural transformation of α-MnO_2 into a mixture of MnO_2 polymorphs. The modification with Cu^{2+} decreased, whereas the modification with Ni^{2+} improved the crystallinity of MnO_2. The modification with Fe^{2+} induced the structural transformation of α-MnO_2 into γ-MnO_2, a decrease in crystallinity and the segregation of α-Fe_2O_3 (hematite). Thus the modification of MnO_2 with Fe^{2+} (Mn^{2+}) divalent metal cations that can be oxidised into Fe^{3+} (Mn^{4+}) by a $KMnO_4$ precursor differs significantly in comparison with, in this case, non-oxidizable cations such as Cu^{2+} and Ni^{2+}. On the other hand, the advantage that the modification of MnO_2 with Mn^{2+} produces chemically identical compounds with different morphology can be used as a model system for toxicity study. In this work the preliminary measurements of intracellular oxidative stress in epithelial cells induced by manganese oxide nanoparticles are reported.

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SYNTHESIS AND LONG-TERM PHASE STABILITY OF Mn_3O_4 NANOPARTICLES

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The synthesis and long-term phase stability of hausmannite (Mn_3O_4) nanoparticles were investigated. The experimental techniques used were XRD, FT-IR, Raman, UV/Vis and FE-SEM. Mn_3O_4 nanoparticles were synthesized by (a) precipitation from $Mn(NO_3)_2$ and NH_4OH solutions and ageing of suspensions obtained at 160 or 20 ^{o}C, and (b) precipitation from $MnCl_2$ solution with addition of H_2O_2 and NH_4OH solutions and ageing of suspensions obtained at 90 or 20 ^{o}C. The order of adding H_2O_2 or NH_4OH influenced the phase composition of the precipitate. A combination of XRD, Raman and FT-IR techniques was useful in investigating the long-term phase stability of Mn_3O_4 and changes in the nonstoichiometry of these particles. The IR bands recorded in the range 623 to 635 cm^{-1} can be assigned to the nonstoichiometry of these particles. It was shown that the IR bands at 1085, 1115 and 1150 cm^{-1} corresponding to OH^- vibrations can be used in the interpretation of a very early stage of the phase transformation $Mn_3O_4 \rightarrow \gamma$-MnOOH. The appearance of an IR band (shoulder) in FT-IR spectra in the range 594 to 599 cm^{-1} was discussed in terms of a possible presence of very fine γ-MnOOH particles in traces and restricted to the surface of Mn_3O_4 nanoparticles. The water (moisture) adsorbed on Mn_3O_4 particles plays a key role in the phase transformation Mn3O4 → γ-MnOOH. Other parameters related to the synthesis route also play a certain role in this phase transformation. UV/Vis spectra were briefly discussed.

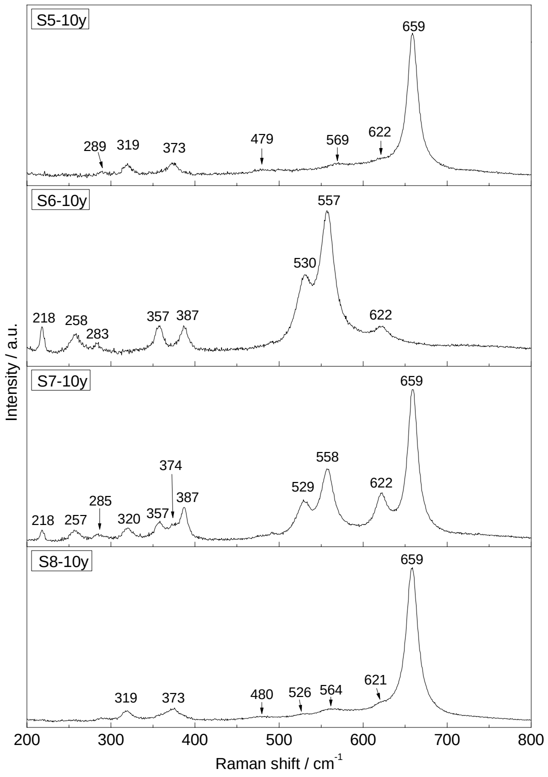

Fig. 1. Raman spectra of the long-term aged Mn-oxides prepared by different synthesis route. Spectra were recorded at 20 ^{o}C.

UV-PHOTO GRAFTING OF POLYETHYLENE TEREPHTHALATEME MBRANES WITH GLUCOSE TO OBTAIN SURFACE MOLECULARLY IMPRINTED POLYMERS

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The focus of this research is to demonstrate that utilizing UV irradiation a polymeric substrate will be grafted and surface molecularly imprinted polymers (SMIPs) will be obtain for the use in drug delivery systems (DDS). Advantages of these SMIPs for drug delivery applications include their low cost, ease of sample preparation, surface uniformity of the device and the possibility to improve kinetics of drug release into human body from DDS with different forms and shapes. Commercial Polyethylene terephthalate (PET) membranes with thickness = 120 µm were UV-photo-grafted with Glucose using a Hg vapour lamp HBO-200, at room temperature, in the presence of air. Three different preparation methods were applied for PET surface photo-grafting. **Method I**: UV irradiation of the films immersed in a homogeneous mixture of monomer/template solution, for 15, 30 and 60 minutes. **Method II:** The polymeric substrates are first UV irradiated, than immersed for 24 hours in monomer/template solution. **Method III:** The polymeric films were first immersed in monomer/template solution for 24 hours than UV irradiated. The solution monomer/template consists in: 2mM Aam (acrylamide), 80mM MBAAm (N,N'-Methylene-bis-acrylamide), 2mM Glucose, 1% wt Benzophenone and water.

AFM, ATR and XPS studies were made in order to determine and optimize the grafting conditions in which UV- photo grafting process takes place, without significant decomposition or damage of the material, to achieve new SMIPs with PET, as substrate. Surface energy, degree of grafting and a preliminary evaluations of *in vitro* drug release and binding affinity from the obtained SMIPs were also made in this study. After removal of the template from the obtained grafted films, the polymers were dried and the reloading capacity was evaluated using swelling equilibrium method. These preliminary evaluations of drug release from the obtained SMIPs were made to investigate the physical parameters needed and the mechanisms involved in obtaining optimal properties that influence the swelling of polymer matrix, release and reloading of the drug.

Based on this study we elucidate the best conditions in which PET films can be grafted using these three methods to obtain improved surface of polymer, demonstrating that using physical grafting methods we can obtain performance SMIPs cheap, rapidly and easily without involve complicate chemical synthesis, that can be successfully applied in biomedical field..

Keywords: UV-photo grafting, Surface molecularly imprinted, degree of grafting, binding affinity.

SPECTRAL STUDIES OF DONEPEZIL RELEASE FROM STRECHED PVA POLYMER FILMS

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The focus of this research is to obtain poly vinyl alcohol (PVA) polymer foils containing Donepezil in different concentration, in order to use in controlled released of drug in the palliative treatment of mild to moderate Alzheimer's disease. Moreover, the influence of polymeric foils stretching degrees on drug release was analyzed using spectrophotometer measurements.

Aiming to evidence the stretching degrees of PVA foils influence on drug release the membranes containing Donepezil in different concentration were obtained, than characterized. The morphology of pure PVA, PVA with drug, and polymeric films with Donepezil with different stretching degrees was investigated using AFM technique and roughness was calculated for each film. The contact angles of the samples were evaluated with KSV CAM 101 (Instruments Ltd., U.S.), using the sessile drop technique with water and ethanol. The critical surface tension, work of adhesion, and surface polarity of the studied PVA foils were also calculated.

In vitro evaluations of drug release from the obtained polymeric foils was made for different stretching degrees. In this method the absorbance of few standard Donepezil solution with different concentrations were measured using 6505 UV-VIS Spectrophotometer (Selected Science Ltd. England), at 268 nm, and the calibration curve was constructed. *In vitro* release studies of the drug were carried out by placing a dried and loaded sample in 20 mL bi-distilled water (and also in buffer solution with pH= 2, 4, 5,5) taken in a beaker at room temperature. After different time interval, the drug loaded polymer was removed from the first beaker and transferred to the next beaker containing 20 mL bi-distilled water at room temperature. The absorbance of the solution was measured at 268 nm in each case, and the amount of drug release after each time interval was calculated and a cumulative addition was made. The mechanism involved in drug release process was evaluated using Korsmeyer-Peppas empirical equation. Surface roughness and profile of drug release are strong affected by the initial drug load, and stretching degree of PVA foils.

Based on this study we demonstrate the dependence of release profile on the quality of polymeric foils containing Donepezil and we elucidate how stretching degree of polymer films can improve the kinetics of drug release into human body.

Keywords: stretched degree, drug release, surface polarity, surface roughness

SPECTROSCOPIC PROPERTIES OF π-HYDROGEN BOND COMPLEXES OF SUBSTITUTED BENZENES

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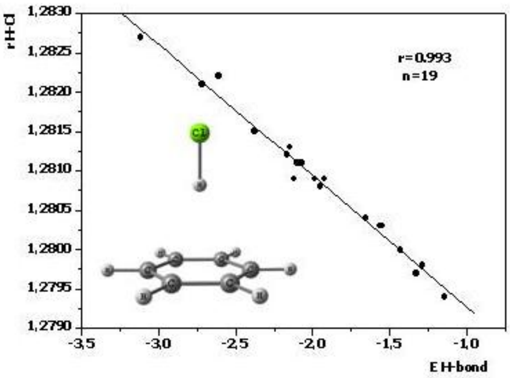
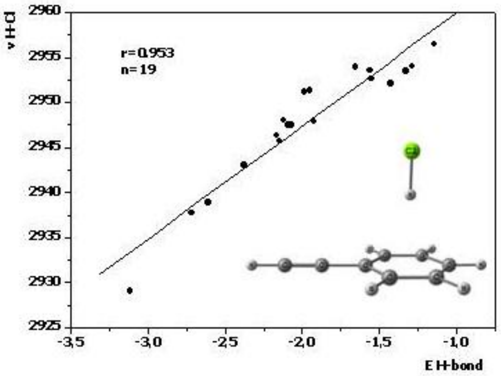
The formation of a hydrogen bond between a model proton donor (HCl) and the aromatic π-electronic system in benzene and a series of monosubstituted derivatives possessing symmetry Cs or higher is examined by theoretical DFT computations at MO6-2X/6-311+G(2d,2p). The calculated H-Cl stretching frequencies and r(H-Cl) bond lengths are correlated with the BSSE corrected energies of π-hydrogen bond formation. Good correlations are established between complexation energies (ΔE) and ν(H-Cl) as well as between ΔE and r(H-Cl). Extension of the series with additional phenylacetylenes derivatives (under the same symmetry constraints) further improves the correlations found. The established dependence between a spectroscopic property, ν(H-Cl), and the energy of π-hydrogen bond formation offers a possible approach for experimental studies of such complexes.





FTIR INVESTIGATION OF THE O-H···Xe INTERACTION IN SIMPLE CARBOXYLIC ACIDS IN SOLID XENON

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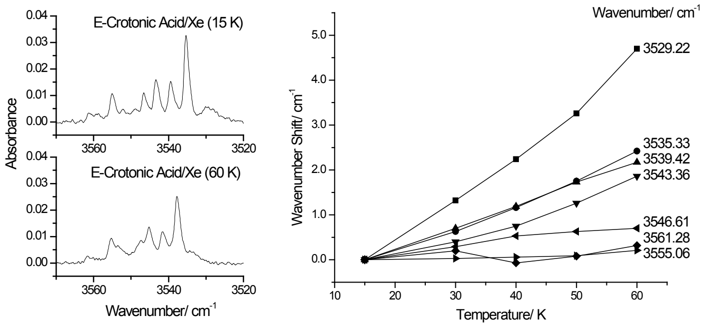
Matrix isolation FTIR spectroscopy is a widely used technique for the investigation of trapped molecules in solid state matrices, noble gases being generally used as host atoms because of their assumed inertness. However, it is well known that noble gases do indeed interact with the trapped molecules in a clearly observable way. Under appropriate conditions, covalently-bound noble gas containing compounds can even be produced [1,2]. Among the stable noble gases, xenon is able to interact stronger with the guest molecules than the smaller members of the family. Due to its large polarizability, the xenon atoms may efficiently interact with the trapped species through different mechanisms, included H-bond like interactions and dispersion [3,4]. Several recent studies have indicated that the O-H···Xe specific interaction appears to be particularly relevant and manifests itself spectroscopically in a well defined way, since the OH stretching vibration is known to be particularly sensitive to surroundings [5,6].

In the present study, the OH stretching spectral region of the infrared spectra of a series of simple carboxylic acids in solid xenon was investigated as a function of temperature (within the 10-60 K region). The spectra of all studied carboxylic acids are characterized by extensive site splitting, resulting from trapping of the guest molecules in matrix-sites with different morphology or different orientation of the guest molecules in the matrix cage [7]. Upon increasing the temperature of the matrix, the OH stretching bands undergo a general frequency blue-shift, while a decrease of temperature leads to the opposite behavior. The frequency shifts with temperature were found to be reversible. Furthermore, the shifts exhibited by the different OH stretching band site-components were found to be more pronounced for the components occurring at lower frequencies. These results indicated the prevalence of the O-H···Xe specific interaction for the guest molecules trapped in the sites associated with the lower frequency OH stretching band site-components (see the Figure). Such experimental evidence is in agreement with both experimental and theoretical results pointing to the increased stabilization and larger OH stretching frequency red-shifts upon interaction with a xenon atom for the carboxylic acid / xenon dimer bearing a specific H-bond like O-H···Xe interaction [3,4].



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ALGINATE A SOLUTION FOR KITCHEN AND MORE?

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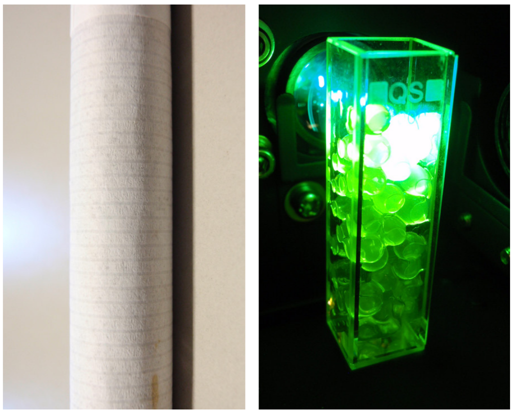
Alginic acid is a substance produced by algae. It is one of the natural products which can be seen as renewable resource. This has best conditions to be a tool in the human world. The salts from the alginic acid the alginates are used for different purposes because it is on the level of a food. One very popular application of alginate is the use of it in the molecular kitchen. In the molecular kitchen droplets of juices or cheese balls are produced. The juice droplets have the appearance of the fish eggs – caviar. A chemistry based caviar is the appearance of illuminated caviar. As to see in the picture fluoresceine diluted in water was dropped into the alginate solution to form balls. The balls were filled into a cell (polished on four sides) and were excited with 460 nm in an instrument for the fluorescence spectroscopy. Part of the same picture shows a cigarette paper. The cigarette paper with its burning rings, which should cause a continuously burn down of the cigarette.



These burn rings supported the ugly situation that when not under control it caused fires, fatalities and injuries To avoid such accidents the European Community introduced in November 2011 new regulations. The regulation forced the cigarette producers to change the behavior of the cigarette paper. This cigarette paper has now to have two zones of substances which will work like self-extinguishing when it is not actively smoked.

And here the alginate plays an important role. It is used as material for the two bands on the paper. For the industry it is important to have an analysis technique which can do a quick and non destructive measurement for an efficient quality control of such bands on paper. This form of control is possible with the FTIR measurement technique in combination with a single reflection measurement unit. The infrared spectra of paper and alginate are different enough to establish a method.

Keywords:Alginate, Fluoresceine, FTIR, ATR, cigarette, paper

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THE ANTIMUTAGENIC PROPERTIES OF BILE PIGMENTS: ECD AND VCD STUDY

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Bile pigments, bilirubin and biliverdin are tetrapyrrolic, dicarboxylic acids, product of the heme metabolism. In the past, it was believed that bilirubin possess negative role on the human organism. However, in recent studies it was shown that bile pigments are not simply by-products of heme catabolism, but also physiologically important molecules which exhibit significant antimutagenic, antioxidant and anticomplement properties. It was found that the antimutagenic activity of the pigments is closely related with the type of mutagen [1], but there are no studies explaining the mechanism of interaction between bile pigments and mutagens.

Electronic circular dichroism (ECD) and vibration circular dichroism (VCD) are the methods inherently sensitive to the structure of chiral substances. This techniques help to find out connections between 3D structure of bile pigments and its anti-mutagenic effects. It was shown by ECD and VCD that the bile pigments and mutagens are bounded in spectrally characterized associates.

In this work were used two structural analogs of mutagens, planar heterocyclic amines (2-aminofluorene and 2,7-diaminofluorene) and a non-planar polycyclic nitro-amine (2,4,7-trinitrofluorenone).

In addition to bilirubin and biliverdin, the cyclic tetrapyrrolic derivative (chlorin-e6) was used which possesses the intrinsic chirality without fast racemization which simplifies the observation by circular dichroism techniques.

Because bilirubin and biliverdin easily racemize in solution, proteins (human and bovine serum albumins) were used as chiral matrices, which selectively recognize one of the pigment enantiomers. Such system composed of serum albumins as matrices and bile pigments approximated a real system for degradation of mutagens in the blood serum.

Keywords: Bile pigment, Antimutagen, Circular dichroism

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MÖSSBAUER SPECTROSCOPY WITH A HIGH VELOCITY RESOLUTION APPLIED FOR THE STUDY OF METEORITIC IRON-BEARING MINERALS

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Various meteorites (iron, stony-iron and stone meteorites) contain iron-bearing minerals such as kamacite and taenite (Fe-Ni alloys), olivine (Fe, Mg)$_2$SiO$_4$, pyroxene (Fe, Mg, Ca)SiO$_3$, troilite FeS, schreibersite (Fe,Ni)$_3$P and so on. These minerals were formed in unique space conditions which cannot be reproduced in terrestrial conditions. Therefore, these minerals are interesting for understanding their physical features. Mössbauer spectroscopy is a useful tool for analysis of the iron-bearing minerals and used for a long time in these investigations. These studies showed complicated Mössbauer spectra of the majority of minerals. Therefore, further development of these studies can be carried out using Mössbauer spectroscopy with a high velocity resolution. This technique permits us to measure Mössbauer spectra in 4096 channels which can be better fitted (see [1, 2]).

In this work we consider some recent results in the study of some meteoritic minerals using Mössbauer spectroscopy with a high velocity resolution. Study of ordinary chondrites Farmington L5 and Tzarev L5 demonstrated the possibility to reveal spectral components related to crystallographycally nonequivalent M1 and M2 sites occupied by Fe^{2+} and Mg^{2+} in both olivine and pyroxene (Fig. 1a). Further study of olivine extracted from Omolon and Seymchan pallasites (Fig. 1b) showed small variations of the hyperfine parameters of the ^{57}Fe in the corresponded nonequivalent sites of both olivines. Mössbauer spectra of schreibersite samples extracted from Sikhote-Alin iron meteorite with three crystallographically nonequivalent M1, M2 and M3 sites occupied by Fe and Ni were analyzed using various numbers of components (Fig. 1c). These components were related to the ^{57}Fe in the M1, M2 and M3 sites with further evaluation of Fe and Ni occupations in schreibersite samples. Study of Chinga iron meteorite samples from visually different zones on saw cut of meteorite fragment demonstrated complicated Mössbauer spectra (Fig. 1d) with some differences of the fit.

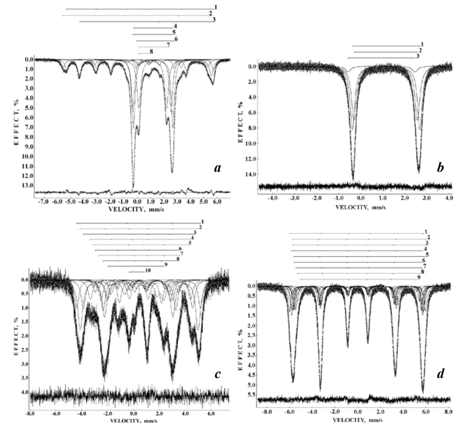

Fig.1 Mössbauer spectra of Farmington L5 (***a***), olivine from Seymchan (***b***), schreibersite from Sikhote-Alin (***c***) and Chinga metal (***d***) measured with a high velocity resolution. T=295 K.

Application of Mössbauer spectroscopy with a high velocity resolution for study of meteoritic minerals demonstrated larger number of spectral components revealed from the fit in comparison with that revealed from the spectra measured with a low velocity resolution.

This work was supported in part by the Federal Grant-in-Aid Program «Human Capital for Science and Education in Innovative Russia» (Governmental Contracts No. P1154 & No.14.740.11.1006).

Keywords: Mössbauer spectroscopy; Iron-bearing minerals; Meteorite

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STRUCTURAL STABILITY OF RNA HAIRPINS

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RNA hairpins play an important role in numerous cellular processes, including the viral replication cycles, due to the rich potential of the hairpin loops for diverse intermolecular interactions. We have focused our attention on two hairpins inside the genome of Human Immunodeficiency Virus type 1 (HIV-1). Trans-activation response (TAR) element causes a dramatic increase of the viral transcription efficiency [1] and the dimerization initiation site (DIS) is essential for dimerization of the genome and its subsequent encapsidation [2], which is crucial for the virus replication. Oligonucleotide therapies against HIV-1 are targeting on these hairpins, because of evolutionary conservativeness of their sequences. Blocking of the binding site of the hairpin by a kissing interaction with a proper synthetic RNA segment (aptamer) may significantly decrease the virus infectivity. RNA hairpin aptamer (R06) specific for the TAR hairpin was already found by SELEX technique [3], [4].

Both apical TAR and DIS hairpins are representatives of stable hairpin-loops with more than four nucleotides in the loop. Our first task was to characterize their structure and flexibility in aqueous environment and their dependence on the presence of monovalent and divalent ions, namely magnesium, that are generally regarded as stabilizers of RNA structural motifs. We employed methods of temperature dependent UV absorption and Raman spectra and their multivariate analysis, and differential scanning microcalorimetry.

Two temperature-induced transitions were unambiguously revealed from factor analysis of optical spectra of the apical part of TAR hairpin [5] and of the R06 aptamer as well. The high-temperature transition was interpreted as a temperature-induced disintegration of the stem and the hairpin opening. The weaker low-temperature transition, which was more pronounced for R06 than for TAR hairpin, was interpreted as a temperature induced change of the loop geometry. Spectral changes connected with the low-temperature transition indicate opening of the intraloop hydrogen bonds, weakened conformational regularity of the loop and a slight release of the regular A-type duplex geometry of the stem. Magnesium ions were found to affect the transition in the low-temperature region but not the hairpin opening.

Two DIS hairpins can form a kissing complex or an extended duplex. It was thus necessary to perform the same measurements with analog oligonucleotides containing sequence modifications allowing only duplex formation, in order to separate characteristics which belong to the kissing complex.

Acknowledgement: This work was supported by the Grant Agency of Charles University (project 50910), and the Czech Science Foundation (project 202/09/0193).

Keywords: RNA hairpin, Raman spectroscopy, UV absorption

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RADIATION INDUCED TOPOTACTIC [2+2] DIMERISATION OF ACRYLATE DERIVATIVES AMONG THE LAYERS OF A CaFe LAYERED DOUBLE HYDROXIDE FOLLOWED BY IR SPECTROSCOPY

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The family of layered double hydroxides (LDHs) is a class of (mostly) synthetic anionic layered clays with positively charged layers due to the partial isomorphous substitution of divalent cations for trivalent ones. The positive charges are balanced by inorganic or organic anions. The host–guest system may be viewed as a nanoreactor with reactants, where the appropriately functionalised organic guest anions may react with each other in the confined space of the LDH. Double-bonded systems may take part in, *e.g.,* light-induced cyclisation [1], when four-membered ring may form with more or less randomly oriented substituents in the solid sate without the LDH, while the LDH host may exert shape selectivity. For experimental trials the host–guest systems must be prepared and appropriately characterised first, then changes occurring on irradiation may be followed by IR spectroscopy. Results of this work are described below.

The host material was an LDH containing Ca(II) and Fe(III) in 3:1 molar ratio, prepared by the co-precipitation method. *E*-3-phenylpropenoate (**1**), *E*-4'-nitrophenyl-propenoate (**2**), *E*-3(2'-thienyl)propenoate (**3**), *E*-2,3-dimethylpropenoate (**4**), *E*-3(4'-chloro-benzoyl)propenoate (**5**), *E*-3(2',5'-difluorophenyl)propenoate (**6**), *E*-2-cyano-3(4'-hydroxy-phenyl)propenoate (**7**) or *E*-3(4'-imidazoyl)propenoate (**8**) anions were the guests. For intercalation, the dehydration-rehydration method was applied. The obtained nanohybrids were studied by powder X-ray diffractometry (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray fluorescence (EDX) coupled to the SEM instrument as well as FT-IR spectroscopy. Molecular modelling was used for visualising the possible spatial arrangement of the organic anions. Intercalated samples as well as the pristine acrylate salts in the solid state were subjected to UV-light irradiation. The resulting structures were elucidated by FT-IR spectroscopy.

Characterisation measurements unambiguously revealed that intercalation was successful. The layered structure of the host remained intact (SEM), the introduced acrylate derivatives did not decompose (FT-IR spectroscopy), and they were among the layers (XRD and SEM) and were evenly distributed (elemental map from SEM–EDX). Upon irradiation at room temperature there was no reaction for the intercalated samples containing the (**4**), (**5**), (**7**) and (**8**) anions, but [2+2] cyclisation took place for those having the (**1**), (**2**), (**3**) and (**6**) ones. These anions underwent [2+2] cyclisation in the solid state without the LDH host as well, just as the pristine (**4**), (**8**) anions. The events and the exerted selectivities observed for the reactions in the confined environment are rationalised with the aid of molecular modelling.

Keywords: intercalation in CaFe layered double hydroxide; acrylate derivatives; characterisation; UV irradiation induced [2+2] topotactic cyclisation; selectivity in the confined space

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CONFORMATIONAL PROPERTIES OF A PYRIDYL-SUBSTITUTED CINNAMIC ACID STUDIED BY NMR MEASUREMENTS AND COMPUTATIONS

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The conformational properties of *Z*-α-pyridyl cinnamic acid in solution have been studied by NMR measurements. Complete signal assignment was carried out and 2D NOESY measurements in three solvents were also performed. Before detailed measurements, however, the conformational space was explored computationally using *ab initio* calculations [1]. Results of this combined approach are detailed in this work.

The model compound was synthesised with modified Perkin condensation [2], was purified with column chromatography and was recrystallised until reaching constant melting point. Its NMR parameters were obtained in three solvents of significantly altering characteristics (DMSO(d_6) – dipolar aprotic solvent, methanol(d_4) – polar, protic solvent and chloroform(d) – apolar, aprotic solvent) on a Bruker DRX 500 instrument. The ^{1}H NMR spectrum in all solvents displayed signals only at the high chemical shift region, in dmso(d_6) even the proton signal of the carboxylic function appeared at 12.96 ppm. The aromatic and olefinic protons resonated in a narrow (approximately 2 ppm wide) chemical shift region at the low-field end of the spectrum. Although the ^{1}H NMR spectrum and coupling constant modulated ^{13}C NMR spectrum (JMOD) revealed the chemical shift of some characteristic functionalities (carboxylic, non-protonated aromatic resonances), 1D NMR spectra did not provide sufficient evidence to make unambiguous assignment because of the severe overlap of resonances in certain cases. 2D chemical shift correlation spectra were used to assign resonances. Homonuclear COSY spectrum was used to identify the proton resonances in isolated spin systems (phenyl, pyridyl); moreover, the olefin proton appeared as a singlet in the aromatic region. The ^{13}C NMR signals were assigned with the use of heteronuclear chemical shift correlation spectrum on the basis of the established ^{1}H NMR chemical shifts. Furthermore, 2D heteronuclear multiple bond experiment (HMBC) provided the connectivity information between different functionalities within the molecule.

Scouting computations predicted that full conjugation was overruled by steric interactions of the substituents, *i.e.,* many conformers were found and the rotation of the aromatic rings were either completely free or only partially restricted. The solution state conformation was monitored with the 2D NOESY experiment. The solvent change introduced very small, but significant chemical shift changes in the spectra. NOESY measurements verified indeed that in all three solvents the pyridyl group was virtually freely rotating.

Keywords: α-pyridyl cinnamic acid; 1D and 2D NMR measurements; ab initio molecular modeling

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èSTRUCTURAL AND SPECTRAL STUDIES OF [ISO]-QUINOLINIUM CARBOETHOXY METHYLID (iQCEM)

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The cycloimmonium ylids are molecules with applicability in organic chemistry and in pharmacy for obtaining new heterocyclic compounds. Among those ones, the molecules of in [iso]-Quinolinium CarboEthoxy Methylid (iQCEM) having zwitterionic nature are frequently used in chemistry as acid-basic indicators and for getting new heterocyclic structures.

The structural and electro-optical features of [iso]-Quinolinium CarboEthoxy Methylid (iQCEM) were established on the basis of HyperChem 8.0.6. The optimized geometry, the atomic charges, the length of the covalent bonds, the dipole moment and polarizability in the ground electronic state, the energetic characteristics of the molecule were calculated with this program.

In order to estimate the dipole moment in the excited state of iQCEM, a solvent study based upon the existent theories on the simple liquids was made.

The studied molecules have a visible charge transfer electronic absorption band, very sensitive to the solvent nature. Some binary and ternary solutions of iQCEM in various solvents were spectrally studied. The dependence of the wavenumber in the maximum of the intramolecular charge transfer (ICT) visible absorption band upon the electric permittivity was obtained. The electric dipole moment of iQCEM has been estimated using the solvatochromic effect, in the limits of the Mc.Rae theory.

Keywords: iso-Quinolinium CarboEthoxy Methylid, optimized geometry, intramolecular charge transfer, visible absorption band, solvent electric permittivity, electric dipole momentum.

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INVESTIGATION OF THE STRUCTURAL CHANGES INDUCED BY RARE EARTH ADDITION TO THE SPRAY-DRY TITANOSILICATE MICROSPHERES

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Materials with high refractive index, low density and good transparency in visible region are in demand as optical lenses especially for glasses [1].

The aim of the present study is to synthesize by means of sol-gel combined with spray-drying methods titanosilicate microspheres (titanium:silica 1:1 atomic ratio) with rare earth addition and to obtain by vibrational (Raman) and electronic resonance spectroscopies specific data about the local structure and structural changes induced by lanthanum content in the prepared samples. Scanning electron microscopy (SEM) was used in order to examine the morphology of the microspheres before and after thermal treatment. The SEM images show that the prepared microspheres are very well defined and have spherical shape with a diameter less than 5 μm and they keep their sphericity even when nanocrystals are developed.

Microspheres were prepared from tetraethoxysilane (TEOS), titanium izopropoxide (TIP), lanthanum nitrate hexahydrate and gadolinium(III) nitrate in a low lanthanum content range ($La_2O_3 \leq 10$mol%). The as-prepared microspheres were found to be non-crystalline confirmed by X-ray diffraction (XRD) patterns. From the XRD patterns there were also identified the crystalline phases formed in polycrystalline microspheres obtained after thermal treatments.

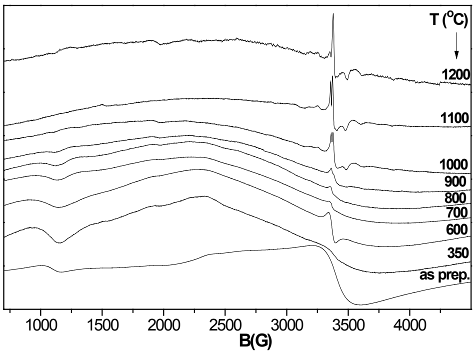

Fig.1 EPR spectra of Ti:Si 1:1 system

The Gd^{3+} ions were used as paramagnetic resonance centres, as they are sensitive to their surrounding and able to inform about the structural changes which may occur in their vicinity. The electron paramagnetic resonance (EPR) [2] spectra indicate that the thermal annealing process play a significant role in the formation of additionally paramagnetic centers.

Keywords: Sol gel; spray dry; microspheres; rare earth; nanocrystals; Raman; EPR; XRD; SEM.

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THE INFLUENCE OF SELENIUM OXIDE ON THE LOCAL ORDER AND BIOCOMPATIBILITY OF BIOACTIVE GLASSES

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Bioactive glasses SiO_2-CaO-P_2O_5 with an optimum ratio of the compounds are promising bioactive and biocompatible systems. In interaction with biologic environments, these glasses allow both developing the generation of bone matrix and bone growth. Moreover the bioactivity of these glasses can be stimulated by thermal treatment in terms of apatite phase development. As the cells do not attach directly to the substrate, but they can bind to the proteins that are adsorbed onto the scaffold's surface, the tissue engineering scaffolds must be functionalized with protein first in order to establish the biocompatibility.

This study proposes the analysis of $xSeO_2\cdot(100-x)[61SiO_2\cdot30CaO\cdot9P_2O_5]$ biomaterial with x = 0, 1, 3, 5, 10% mol, synthesized by sol-gel process. Selenium is known as an important trace for the human body, an essential component of a key antioxidant enzyme, necessary for normal growth and development with a significant role in detoxification of heavy metals (such as mercury) and antibodies production by the immune system. Therefore, the addition of selenium oxide into the matrix improves the bioactive glass properties.

The aim of this study is to synthesize the SiO_2-CaO-P_2O_5-SeO_2 bioactive materials and to investigate them by means of vibrational spectroscopies (Raman, FTIR) the microstructural properties and protein absorption in order to clarify biocompatibility and the influence of selenium addition and thermal treatment on the matrix. The structural characterization was completed by thermal analysis (DTA, TGA), X-ray diffraction (XRD), and energy dispersive X-ray analysis (EDAX) and scanning electron microscopy (SEM). The thermal behavior of these bioactive materials determines the optimal thermal treatment temperature of the samples and also the temperature of the maximum crystallization process. XRD data point out the amorphous structure of as prepared samples and also the apatite nanocrystals development after thermal treatment above 300°C. Further information regarding the elemental composition was obtained by EDAX analysis. In order to establish the biocompatibility, the surface was functionalized with protein and the surface absorption was investigated by means of vibrational spectroscopic technique such as Fourier Transform Infrared (FT-IR) [1] spectroscopy. FT-IR is a suitable method to elucidate the amino acid side-chains involved in the adsorption process and to investigate the structural changes of the secondary structure of the protein upon the adsorption process [2]. By comparing the FT-IR spectra of SiO_2-CaO-P_2O_5 and SiO_2-CaO-P_2O_5-SeO_2 systems with those of protein functionalized ones and also with the bulk protein one can emphasize the binding of the protein to the bioactive materials surface.

Keywords: selenium oxide; apatite; protein adsorption; FT-IR;Raman; DTA-TGA; XRD; SEM; EDAX

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OPTICAL SPECTROSCOPY OF ETHYNE-LINKED PORPHYRIN FILMS

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Thin films of ethyne-linked porphyrin dimers [1] are investigated mainly by means of spectroscopic ellipsometry in the NIR-Vis spectral range. The porphyrin films are prepared by organic molecular beam deposition in high-vacuum conditions on silicon substrates covered by the native oxide. For a better understanding of the optical behaviour of the porphyrin dimers, their corresponding monomers are additionally characterized. The dielectric functions of both monomers and dimers are derived from ellipsometrical measurements by employing a three-phase optical model. The optical response of the ethyne-linked dimers in solution is characterized by red-shifts of the first absorption structure, Q-band (at ca. 650 nm), and a split in the Soret (B) band. In dimer films the most significant variations are the loss of relative intensity of the B-band at ca. 420 nm and a faint low energy tail of the Q-region. These evidences may suggest that the conjugation in the multilayers is most probably lowered.

Keywords: ellipsometry; porphyrin; dimer; thin films; silicon.

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PREPARATION OF MESOPOROUS SILICA LAYERS BY POLYCONDENSATION OF OCTAHYDRIDOOCTASILSESQUIOXANE (T_8^H)

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Many applications need materials with a porosity greater than in the zeolite and considerably smaller than the microporous materials – mesoporous materials. In this paper we propose to obtain mesoporous silica layers by hydrolytic polycondensation of octahydridooctasilsesquioxanes (T_8^H). Such a procedure allows to obtained a silica layers completely devoid of organic substituents, but having an ordered structure of the siloxane bonds, leading to the creation of mesopores.

Materials were obtained as bulk material and as layers on steel substrate.
Structure of the obtained materials was identified on the basis of detailed spectroscopic and x-ray studies. Carried out structural studies (XRD, MIR) of obtained materials revealed that the reaction of hydrolytic polycondensation of (T_8^H) leads to amorphous silica

The size and pore distribution were measured using nitrogen adsorption methods (BJH). Based on structural and microstructural (SEM, AFM) analysis and BET investigation we can say that amorphous mesoporous silica layers on steel substrate can be obtained through hydrolytic polycondensation of T_8^H.

Keywords: S*ilsesquioxanes; Mesoporous materials; Thin layers*

Acknowledgements
This work was supported by Polish Ministry of Science and Higher Education under project ‘‘Silsesquioxanes as ceramic precursors" 2659/B/T02/2011/40.

INFLUENCE OF EXPERIMENTAL CONDITIONS ON THE MICROSTRUCTURE OF HEMATITE PARTICLES PRECIPITATED BY FORCED HYDROLYSIS OF $FeCl_3$ SOLUTIONS

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Hematite (α-Fe_2O_3) particles have found various applications, for example, as pigments, fillers, gas sensors and photocatalysts, in anticorrosion protective paints or in synthesis of magnetic oxide ceramics. There are various methods of the production of α-Fe_2O_3 particles. Forced hydrolysis of $FeCl_3$ solutions is simple way to precipitate α-Fe_2O_3 particles.

The influence of experimental conditions on the forced hydrolysis of $FeCl_3$ solutions and specifically the effect of amidosulfonic acid on the microstructure of precipitates were investigated. Precipitates were analysed with XRD, ^{57}Fe Mössbauer, FT-IR and UV/Vis spectroscopies, as well as with FE-SEM. The phase transformation β-FeOOH → α-Fe_2O_3 was accelerated with increase the temperature of hydrolysis, whereas the adding of amidosulfonic acid at the start of the hydrolysis of Fe^{3+} ions suppressed the phase transformation β-FeOOH → α-Fe_2O_3 or decrease a crystallinity at 120 and 160 °C. The size and shape of hematite particles were strongly dependent on $FeCl_3$ concentration, temperature and presence of sulfonate/sulfate groups. Preferential adsorption of sulfonate/sulfate groups influenced the hematite crystal growth direction. The aggregation effect was also noticed in the formation of hematite particles.

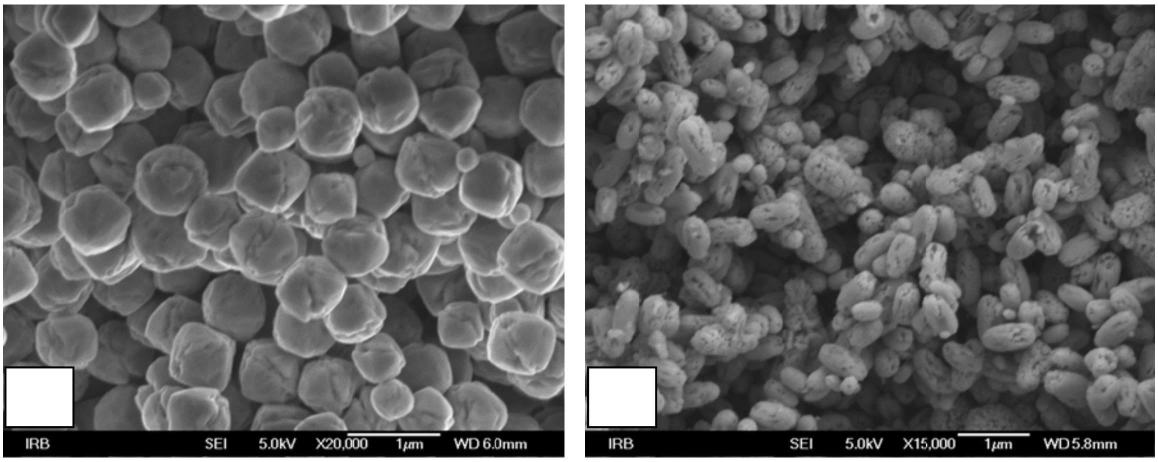

Fig. 1. FE-SEM images of α-Fe_2O_3 particles precipitated by forced hydrolysis of 0.05 M $FeCl_3$ solution at 160 °C, (a) in the absence and (b) in the presence of amidosulfonic acid.

DEGREE OF CONVERSION AND MICROHARDNESS OF DENTAL COMPOSITE RESIN MATERIALS

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Dental composite resins (CR), comprised of resin matrix and inorganic fillers, are commonly used materials for the replacement of hard dental tissues. The light initiated conversion of resin monomers into a polymer network is never complete, and residual unreacted monomers can cause adverse biological reactions and weakening of the mechanical properties. Therefore, the degree of conversion (DC) is often tested property which gives much information about the CR. Among a number of methods utilized for the determination of the DC, Fourier transform infrared spectroscopy (FT-IR) and microhardness (MH) are often used. In past, studies have determined the positive correlation of DC values determined by MH and FT-IR measurements. The aim of the study was to establish whether MH values can be used instead of FTIR for determination of DC of contemporary CR.

Two nano-hybrid CR: Tetric EvoCeram (TEC; Ivoclar Vivadent, Liechtenstein) and IPS Empress Direct (ED; Ivoclar Vivadent) and one submicron-hybrid CR – Charisma Opal (CO; Heraeus Kulzer, Germany) were tested. For FT-IR measurements, CR samples (n=10, d=1cm, thickness 0.1 mm) were polymerized using a Bluephase G2 LED curing unit (Ivoclar Vivadent) in high power mode (1200 mW/cm^2) for 30 s. The uncured samples were pressed into KBr pellets (d=1cm) using spectroscopically pure KBr. DC of polymerized samples was determined by Fourier transform spectrometer Mo. 2000 (Perkin Elmer, UK). Spectra of paired un-polymerized and polymerized composite specimens were recorded in a transmission mode at room temperature, corrected by subtracting the background and then converted into the absorbance mode. A total of 22 scans per sample were measured at a resolution of 4 cm^{-1}. DC was calculated as the % change in the equivalent aliphatic (1638 cm^{-1})/aromatic (1610 cm^{-1}) molar ratios of cured and uncured samples. MH samples (n=10) were placed between Mylar films and pressed between two steel plates to 0.85mm thickness. Vickers MH was measured using Leitz Miniload 2 Microhardness Tester (Leitz, Germany), load 5 and 10 g. The data were analyzed using ANOVA and Tukey's post hoc test ($p<0.05$).

The DC results indicate that CO was the highest polymerized material (62.20%) in comparison to TEC (58.85%) and ED (58.78%). Opposite, ED was significantly hardest material (24.49) when compared to CO (17.81) and TEC (20.05).

The amount of fillers in all tested CR was 55-59 vol%, but the composition and size of fillers varied widely. Lower DC of TEC and ED could be attributed to the medium size of particles (550 and 400 nm, respectively), similar to the output wavelength of the polymerization unit (385-515 nm), which usually contributes to higher light scattering and consequently lower polymerization. Since the CO was the material with the highest DC, but also with the lowest MH, it can be concluded that the DC of new CR formulations with the addition of nano-fillers cannot be estimated through the MH data.

This study was supported by MZOS projects 065-0352851-0410, 098-0982904-2952 and 035-0352851-2854, Republic of Croatia.

Keywords: composite resins; Fourier transform infrared spectroscopy; degree of conversion

COMPARISON OF COMPUTED THERMODYNAMIC AND SPECTRAL PARAMETERS OF H-BOND WITH EXPERIMENTAL DATA

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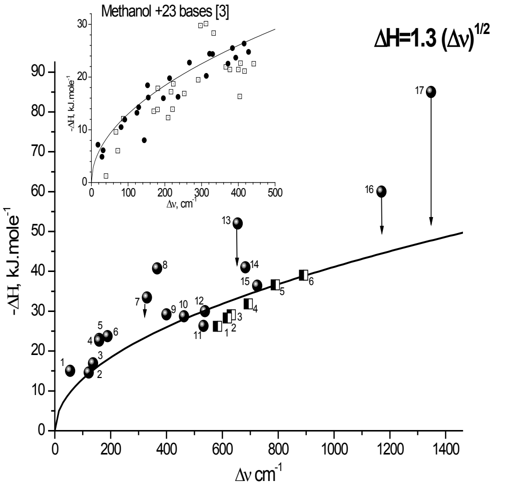
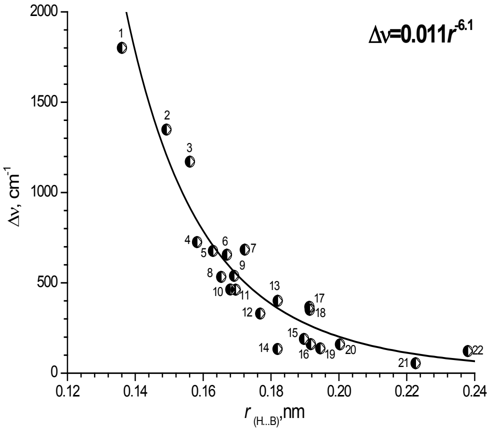
H-bond energies, distances and red shifts, computed by various methods are compared with corresponding well established empirical correlations of these parameters [1-3] . The latter are presented as solid lines on the Figures. Over twenty different H-bonds computed in the last 10 years are shown with individual symbols.





Despite the scattering, the computations confirm the empirical correlations. On the other side these correlations can more reliably verify the computational methods of choice.

The suggested earlier correlation of H-bond energy with the H-bond length as a power function [2] fits experimental data better than the exponential function suggested in ref. [4.].

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STRUCTURAL AND PHYSICAL - CHEMICAL STUDY OF THE NEW KEGGIN POLYOXOMETALATES WITH MIXED ADDENDA

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Polyoxometalates are metal-oxygen clusters that exhibit a fascinating variety of structures and properties, including size, shape, charge, density, acidity, redox states, stability, solubility etc.

The new complexes, which correspond to the formula $K_{5-6}[Z^{2+,\ 3+}PVM_{10}O_{39}(H_2O)]\cdot xH_2O$; M = W^{6+}, Mo^{6+}, Z = Mn^{2+}(**1**), Fe^{3+}(**2**), Co^{2+}(**3**), Ni^{2+}(**4**), Cu^{2+}(**5**) were synthesized from α-$[PVM_{10}O_{39}]^{8-}$; M = W^{6+}(**L$_1$**), Mo^{6+} (**L$_2$**) and investigated by means of elemental analyses, thermogravimetric, X-ray diffraction and spectroscopic (FT-IR, UV−Vis, EPR) methods.

Using X-Cell computer program, X-ray powder diffraction patterns were indexed. The crystallographic system and unit cell parameters were determined. The calculated densities obtained from unit cell volume and molecular weights are reasonable values for compounds of this type.

By comparing the FT-IR spectra for ligand **L$_1$** and for complexes **1**, **2, 3, 4** and **5** we determined that the coordination of Z metal ions take place through the O_c and O_e oxygen atoms from corner-sharing and edge-sharing octahedra. The shift of the $\nu_{as}(P\text{-}O_i)$ antisymmetric stretching vibration, the main band of the ligand, towards higher energies in complexes indicates that the coordination increases the cohesion of the monolacunary ligand structure.

Visible spectra of complexes **3, 4** and **5** show the characteristic d-d electron transfer bands of Co^{2+}, Ni^{2+} and Cu^{2+} ions in octahedral field. However, the expected transition bands are not found in the spectrum of complex **1** and **2**. The d-d transitions of the Fe^{3+} and Mn^{2+} ions are totally masked which indicates that the two metal ions are involved in the charge transfer.

The powder EPR spectra obtained in the X band at room temperature are typical for monomeric species.

Keywords: polyoxometalates, TMSPs, FT-IR, UV-Vis, EPR spectroscopies

OXYGEN EFFECTS ON PORPHYCENE AND PORPHYRIN NEAR-INFRARED LUMINESCENCE KINETICS

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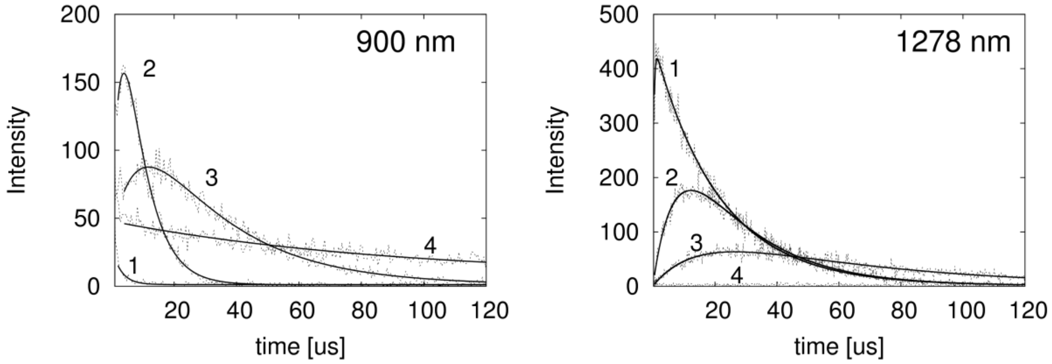
Singlet oxygen (1O2), the lowest excited state of molecular oxygen, participates in many important biological processes and can be employed in a variety of applications such as photodynamic therapy. One possible way of achieving oxygen excitation is by photosensitization, namely the generation of 1O2 by energy transfer from excited states of other molecules, which are therefore referred to as photosensitizers. Porphyrins form a very important group of photosensitizers. Porphycenes, structural isomers of porphyrins, are outstanding candidates for second-generation photosensitizers for photodynamic therapy [1] due to substantially increased intensity of the Q-bands.

In this contribution, tetra-propyl-porphycene (TPrPo), dissolved in either tetrahydrofuran or in toluene, is studied by means of time- and spectrally-resolved NIR luminescence spectroscopy. A surprising dependence of the luminescence kinetics on oxygen concentration was observed in both solvents and for a wide range of observation wavelengths (800 – 1100 nm). The figure below shows a series of luminescence traces of TPrPo solutions at 900 nm and at 1278 nm for a sample with oxygen concentration gradually decreasing from high (number 1; air-saturated) to very low oxygen concentration (number 4). Surprisingly, the kinetics at 900 nm for intermediate oxygen concentrations show a rise-component whose rate constant depends on the concentration of oxygen. The singlet oxygen kinetics at 1278 nm can be satisfactorily fitted by two exponentials. The rise-component was not detected in the parent tetraphenylporphyrin solutions. On the other hand, the presence of rise-section was mentioned previously for air-saturated water-soluble porphyrin TMPyP [2]. The results suggest the formation of a transient complex between the triplet photosensitizer and oxygen. This work provides a more detailed understanding of the interactions between photosensitizers and oxygen.



Keywords: Phosphorescence; Photosensitizer; Porphycene; Singlet oxygen

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MONITORING THE HEALING PROCESS OF RAT BONES USING RAMAN SPECTROSCOPY

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The aim of this study was to investigate the influence of stable gastric pentadecapeptide BPC 157 on femoral head osteonecrosis in rats using Raman spectroscopy. The sample preparation procedure involved interrupted blood supply and drainage of epiphysis, cut ligament, incisedperiosteum, violent luxation, and thereby healing instability and soft tissue damage. Three different groups of rats were defined, the group treated with BPC 157 (10µg;10ng/kg/daily), the control group and the group of healthy animals. The effects were assessed after 3 and 6 weeks. Radiological and microscopical assessment showed that in control group rats femoral heads were completely destroyed, with injury level increasing from third to sixth week, while in treated group animals the development of femoral head osteonecrosis was attenuated. In particular, vasculary deprived femoral heads of all BPC 157 treated rats more or less retained their hemispherical profile at both third and sixth week.

Spectroscopy measurements were performed using Perkin Elmer Spectrum GX FT Raman spectrometer with 4 cm^{-1} resolution. Excitation was NdYaG laser at 1064 nm wavelength and used laser power was 500 mW. The samples were mounted on universal holder so that the effected side of femoral head was exposed to the excitation laser light. The exposed surface was about 3 mm in diameter. Approximately 10 spectra, with 100 scans each, were recorded from different spots on samples surface. We had 3 samples from each defined group from animals sacrificed after 6 weeks, and 2 samples from each defined group from animals sacrifice dafter 3 weeks.

All spectra were baseline corrected and normalized to amid I band because we have noticed that the band intensity of the amide I was the least changed for all recorded spectra. After that, those spectra were analyzed with student t-test to extract spectral regions where statistically significant difference between the treated, control and healthy group was observed. The most prominent difference between the treated and control group was observed in spectral region between 900 – 1100 cm^{-1} (mineral metric). Spectra analysis also revealed the difference between samples from animals sacrificed after three and six weeks. The difference in prominent band at 960 cm^{-1}, which is assigned to PO_4^{3-} stretching (ν_1) vibrations [1], was more emphasized in spectra recorded from samples acquired from animals sacrificed after 6 weeks. In addition, principle component analysis (PCA) was applied on recorded spectra. PCA results confirmed that the mineral spectral sub region contributes the most to the difference between defined groups.

Keywords:Raman spectroscopy; BPC-157, bone healing

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MATRIX ISOLATION STUDY OF THE NICOTINE MONOMER

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Nicotine, $C_{10}H_{14}N_2$, is an infamous alkaloid present in tobacco, known for its psychoactive properties as an agonist of the cholinergic nervous system [1-3]. The physicochemical properties of this molecule have been studied since the 19th century [4].

Several thermochemical and spectroscopic studies on nicotine in condensed phase, as well as on neat and hydrated protonated nicotine ions were already carried out [5]. However, experiments in condensed phases, in which crystal or solvent effects are present, do not unveil the intrinsic conformational preferences of nicotine. Such characterization is only possible for monomeric molecules, either in the gas phase or for molecules embedded into a “non-interactive” environment.

Previous theoretical data on the compound predict that in gas phase, at physiological temperature (37 ºC), the *cis* and *trans* conformers should be almost equally populated, while in solutions only one (*trans*) conformer should exist [6]. Nevertheless, no detailed conformational study on nicotine has been reported hitherto. Nicotine molecule possesses three degrees of conformational freedom: (i) rotation between the pyrrolidine and pyridine rings (which defines the *cis* and *trans* conformations); (ii) pseudorotation of the pyrrolidine ring; and (iii) orientation of the methyl group (axial or equatorial) relatively the pyrrolidine ring. It is then a quite flexible molecule, prone to exhibit a variety of conformations, which can be expected to be relevant to the bioactivity of the compound.

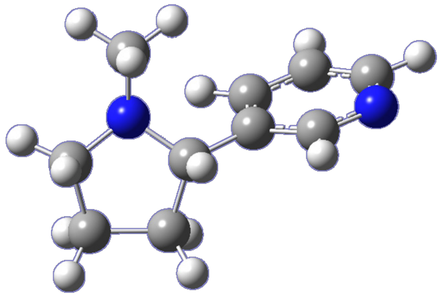

Fig.1 The most stable conformer of nicotine.

Taking this into account, the present work is, to the best of our knowledge, the pioneer effort to unravel the structures of nicotine conformers using noble-gas matrix isolation technique coupled with FTIR spectroscopy. Results of our experiments are interpreted based on comparison with theoretical calculations of vibrational spectra for the nicotine conformers.

Acknowledgment. FCT grant (SFRH/BD/44443/2008) is acknowledged.

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STRUCTURAL FEATURES OF Fe(II) HYDROXO COMPLEXES IN EXTREMELY CONCENTRATED NaOH SOLUTIONS

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Fe(II) compounds are highly sensitive to oxidation, thus much care has to be exercised if one wants to maintain this low oxidation state in aqueous solution. Therefore, it is not surprising that their hydroxo complex formation properties have been less frequently studied than that of Fe(III) [1]. It is especially true for such complexes in solutions with extremely high concentrations of base ($[OH^-]_T > 0.1$ M). In the experimental work leading to this contribution, the solution structure of Fe(II) hydroxo complexes forming in strongly alkaline solutions was studied with a variety of methods. The solubility of the complexes was found to be rather low, *i.e.* solid material was precipitated from the solutions. The structure of the precipitates obtained at various base (*e.g.,* NaOH, KOH and CsOH) concentrations was investigated as well. Results of this study are communicated in the followings.

For the preparation of the Fe(II) hydroxo solution complexes extremely concentrated NaOH solutions were used (up to 20 M). For structural studies, in a purpose built apparatus, UV-VIS spectroscopy was applied. For studying the structural features of the precipitates FT-IR and Raman spectroscopies were used, while XAS measurements helped to elucidate the coordination geometries of the complexes both in solution and in the solid state.

The varying color of the solutions containing Fe(II) complexes depending on the concentrations of the NaOH solutions used for their preparation clearly indicated that the structure of the complexes formed varied with NaOH concentration in this OH^--concentration range. UV-Vis as well as XAS measurements verified this visual observation. FT-IR, Raman as well as XAS measurements performed on the solid precipitates allowed to learn about structural details: oxidation state of the central ion, coordination numbers as well as geometric arrangements.

It has been proven that a combination of spectroscopic methods, if purpose-built cuvette is applied, provides with adequate information on the structure of oxygen-sensitive not so easily accessible materials like Fe(II) hydroxo complexes obtained from extremely concentrated NaOH solution.

Keywords: Fe(II) hydroxo complexes; structural features in solution and the solid state; UV-Vis, FT-IR, Raman and XAS measurements

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FIRST PRINCIPLE STUDIES OF ELECTRONIC STRUCTURE AND BONDING PROPERTIES OF CHOSEN PHENYL LADDER-LIKE SILSESQUIOXANE CLUSTERS

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The results of theoretical analysis of molecular structure and bonding in relation to experimental IR spectra of chosen ladder-like phenyl silsesquioxane clusters are presented. The methods used in this analysis – the Bader's Quantum Theory of Atoms in Molecules [1] and bond order models (as defined by Pauling[2], Bader[1], Cioslowski and Mixon[3]), applied to topological properties of the electron density, obtained from *ab initio* calculations carried out by Gaussian09 [4], as well as Brown's Bond Valence Model [5] (bonds valences and strengths and bond and overall strains, calculated for molecular structure and bonds lengths data obtained in *ab initio* calculations) are described.

DFT calculations for several ladder-like phenyl silsesquioxane molecules were performed. The molecules were subjected to energy minimization procedure in the Gaussian 09 program using the B98 (DFT) method and a set 6-31G (d) of basic functions [4]. As a result the frequencies and intensities of vibrational modes together with the displacement vectors of the atoms were obtained. Based on the calculated frequencies (scaled using the scale factor of 0.9608) and intensities, respective infrared spectra were constructed assuming a 30 cm^{-1} band half-width.

Detailed analysis of the obtained results (IR spectra, bond critical points, bond orders, electron density topology) carried out from the point of view of cluster size and spatial conformation in relation to experimentally obtained IR spectra is presented.

Keywords: Ladder-like structure; Silsesquioxane

Acknowledgements

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CHARACTERIZATION OF METAMORPHIC AND WEATHERING PROCESSES IN CHLORITE AND MICA GROUP MINERALS BY MICRO-RAMAN AND IR SPECTROSCOPIES

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Currently, modern analytical methods offering high spatial resolution (such as microprobe analysis) as well as various micro-spectroscopies becomes the standard mineralogical tools for identification of minerals and for monitoring of their transitions. Such techniques are indispensable for mineralogists because they allow to identify precisely and characterize minerals, which are usually inhomogeneous and differ a little bit on a composition. A distinct advantage of micro-spectroscopic techniques is that they offer a possibility for monitoring of various transitions and processes (also metamorphic or weathering) at the micrometer level, contrary to the standard analytical methods dedicated to powder analysis and giving only the knowledge on averaged chemical composition.

For presented herein investigations two different rock-forming minerals was chosen as an representative of chlorite group (thuringite) and mica group (biotite) minerals. Both, chlorites with the general chemical formula $(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6$ as well as biotite $K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$ are the members of phyllosilicates. All samples were collected from outcrops of low-grade metamorphism rocks e.g. muscovite-biotite-chlorite schists in the area of Kotlina village, Kamienica Range, Izery Mts (Sudetes, SW Poland).

Chlorites and biotites are well known as methastable minerals able to undergo chemical transformations and breakdown (as a result of metamorphic, hydrothermal or metasomatic processes) even under rather low pressures and temperatures (metamorphism of so called epi zone). They are also very susceptible to weathering.

The vibrational spectra of pure non-changed chlorites and biotites as well as intermediate phases such as chloritized biotite and chlorite containing biotite relicts were acquired. Coexistence of these various phases directly proved that the biotite chloritisation process occurs in investigated samples. Described transformation of reached in Fe and Mg biotite into the chlorite results from metamorphism and weathering. Presented above interpretation of vibrational spectra was supported by polarized light-microscopy observations on thin layers and by microprobe analysis (SEM-WDS). Performed investigations showed that both middle IR and Raman spectroscopies may be successfully applied for monitoring of the metamorphic and weathering processes. The vibrational modes assigned to stretching of hydroxyl or Me-OH groups seems to be especially attractive to analyze a degree of biotite into chlorite conversion. A presence of mentioned bands and the their relative intensities give information about the progress of chloritisation process on the non-destructive and quick way.

Keywords: Biotite; Chlorite; Mica

Acknowledgement
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STRUCTURAL INVESTIGATION OF BISMUTH BASED PHOSPHATE GLASSES CONTAINING VANADIUM IONS

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Bismuth based glasses attracted a lot of interest due to their important applications in the field of glass ceramics, layers for optical and electronic devices, thermal and mechanical sensors, reflecting windows, or as super conductors. Despite the fact that Bi_2O_3 is not a classical glass former, due to its high polarizability and small field strength of Bi^{3+} ions, in the presence of conventional glass formers (such as B_2O_3, PbO, SiO_2) it may build a glass network of [BiO_n] pyramids. The structural role played by Bi_2O_3 in glasses is complicated and poorly understood. This is because the [BiO_n] polyhedra are highly distorted due to the lone pair electrons. It is reported that Bi_2O_3 occupies both network-forming and network-modifying positions in oxide glasses and therefore, the physical properties of glasses (containing Bi_2O_3) exhibit discontinuous changes [1, 2].

The addition of vanadyl ion VO^{2+} is useful to characterize the glass local structure. The VO^{2+} ion, like other transitional metals, provide information about many specific aspects as the geometry of structural units of the glass network or the character of chemical bonds in glasses.

ESR and vibrational investigations were made on $xV_2O_5(1-x)[0.8P_2O_5 - 0.2Bi_2O_3]$ system, with $0 \leq x \leq 50$ mol %, prepared using reagent grade purity V_2O_5, $(NH_4)_2$ HPO_4 and Bi_2O_3 in suitable proportion.

ESR spectra of these glasses (Fig.1) are considered a superposition of a well-resolved super hyperfine structure typical for isolated vanadium ions and a broad line characteristic for associated ions. The dipole-dipole interactions exist between paramagnetic ions until x = 5 mol % and the super exchange interactions prevail at high V_2O_5 content (x>10mol %).

Complementary to ESR measurements, IR and Raman spectra show that the addition of TM oxides leads to the depolymerization of the phosphate network; in consequence V_2O_5 acts as network modifier [3].

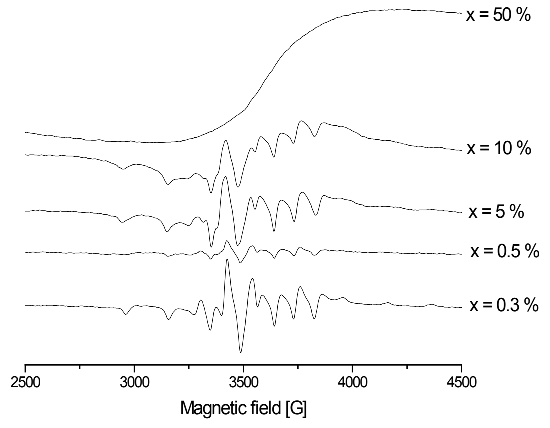

Fig.1. ESR spectra of $xV_2O_5(1-x)[0.8P_2O-0.2\ Bi_2O_3]$ glass system

IR and Raman investigations showed also that the studied glasses contain two types of structural units, pyramidal BiO_3 and octahedral BiO_6 units in variable proportions.

Keywords: P_2O_5-V_2O_5-Bi_2O_3 glasses, IR, Raman, ESR

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SPECTROSCOPIC INVESTIGATION OF SOME BLACK CARBON-PVA DOPED MEMBRANES GAMMA IRRADIATED

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The effect of black carbon particles on the structure and optical properties of poly vinyl alcohol (PVA) was investigated by UV-VIS, Raman and XRD methods before and after gamma irradiation. Small concentrations of black carbon produce great modification of UV-VIS absorption. Above 30% black-carbon concentration the samples becomes almost opaque in UV domain. After irradiation at D = 5500 Gy, only small modifications on the UV absorption properties were observed.

The X rays difractograms contains the specific peak of PVA at $2\theta = 19^0$ and other peaks at $2\theta = 23.4^0$, 24.3^0, 25.2^0 characteristic to black-carbon. The amplitude of those peaks increases with the concentration of carbon. The difractograms are very similar after irradiation.

Raman spectra of doped membranes show the characteristic vibration bands of the black-carbon. Only small modification of the amplitude of these bands appears after irradiation without frequency shift. The spectroscopic measurements indicate a relatively high chemical stability of the polymeric membranes at these doses of radiation.

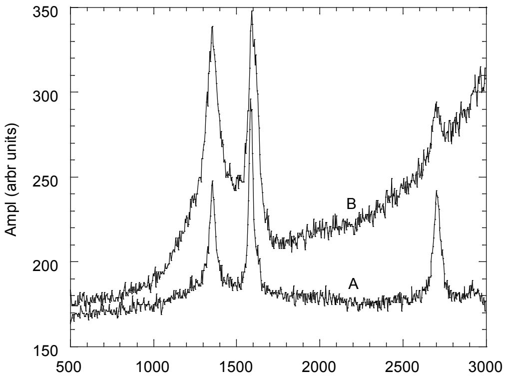

Fig. 1 Raman spectra of PVA membranes doped with 30% black carbon before irradiation (curve B) and after irradiation at 5500 Gy (curve A)

Keywords: Poly (vinyl alcohol); black carbon; Gamma irradiation

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SOLID SOLUTIONS IN THE ZrO_2-TiO_2 SYSTEM PREPARED BY LOW-TEMPERATURE SOL-GEL SYNTHESIS

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Amorphous precursors of the ZrO_2-TiO_2 system at the ZrO_2-rich side of the concentration range were prepared by low temperature hydrolysis and polycondensation reaction of zirconium and titanium n-propoxide. Dried samples were calcined in air at different temperatures up to 1100 °C and analyzed at room temperature using X-ray powder diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy and field emission scanning electron microscopy (FE SEM). The Zr/Ti molar ratio in the obtained products was determined by energy-dispersive X-ray spectrometry (EDS). The results of phase analysis showed that the incorporation of Ti^{4+} ions has very small influence on the stabilization of high-temperature tetragonal polymorph of ZrO_2. Monoclinic ZrO_2-type phase was dominant in the products obtained after crystallization of the amorphous precursors (samples calcined at temperatures below 800 °C) with up to 20 mol% of TiO_2. However, the amount of phase structurally closely related to tetragonal ZrO_2 significantly increase and become dominant in the product with 20 mol% of TiO_2 subjected to temperature treatment at 1000 °C. The incorporation of 30 or more (up to 50) mol% of Ti^{4+} ions causes formation of srilankite-type phase. Precise determination of lattice parameters, performed using the whole-powder-pattern decomposition method, showed that the lattice parameters a and c in the orthorhombic srilankite lattice approach each other with the decrease of titanium content, which indicate gradual transition to phase structurally closely related to tetragonal ZrO_2. Thermal behavior of the amorphous precursors was also examined by differential thermal analysis and thermogravimetric measurement. The crystallization temperature of the amorphous precursors increased with an increase in the TiO_2 content, from 410 °C (0 mol% of TiO_2) to 680 °C (40 mol% of TiO_2).

Keywords: ZrO_2-TiO_2, XRD, Raman spectroscopy, FE-SEM, EDS

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ASSESMENT OF THE BETULIN CONTENT IN THE *BETULA PENDULA ROTH* BIRCH BARK FROM ROMANIAN FLORA

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Vibrational spectroscopy analysis of the betulin and its derivative species found in the outer bark of the birch tree has been conducted in order to asses the ability of the FT-Raman and FT-IR techniques for direct evaluation of the betulin content in Romanian birch flora resources. Our previous work reported the complete vibrational characterization of several pentacyclic triterpenes, betulinic acid, betulin [1] and their new pharmaceutical formulation as guest-host complex [2] or betulin-based nanoemulsion [3]. Pentacyclic triterpenes revealed important therapeutical activities and depending on the dose, triterpenes can produce antiinflammatory, cytoprotective, antitumor and apoptotic effects. Although abundant in the birch tree, the Romanian potential resource for the increased demand of product has been completely ignored. Triterpene species although rather expensive, are largely used in pharmacetucal trials and research. Here we expand the study to prospect the environmental evaluation of the pentacyclic triterpene local resourses. A number of 17 different bark sample species from 7 representative trees from the northern part of the country, namely the forest area of Vatra Dornei, have been characterized. The spectral data were assigned, analysed and compared concerning the relative intensity of the triterpene specific bands versus non triterpene bands (lignin, cellulose) observed in the vibrational spectra of the raw bark. FT-IR and Raman analysis of staistically relevant samples from the *Runc Hill*, the *Black Hill* and *Park – Vatra Dornei* allowed to evaluate the best source regarding the content of betulin. Fig. 1 presents the FT-IR spectra of the outer bark from *Runc Hill*, the *Black Hill* and *Park – Vatra Dornei*.The signal revealed different hydration status (water band versus triterpene bands) as well as different relative intensities of the revealed dominant bands at 1030, 1455,1644, 1716, 2850, 2920, 3339 cm^{-1}. These bands were assigned [1] to pure betulin as main compound of the birch bark. Taking into account the relative intensity ratios of the Raman bands at 1643 and 1601 cm^{-1}, we concluded that the best area was *Runc Hill* with ratio values between 0,914 and 1,168. We could classify and characterize the samples regarding the content of pentacyclic triterpenes DR 2 OUT (sample two out from Runc Hill) sample showed highest betulin content.Such results are crucial for the prediction of the best harvesting area, taking into account the environmental factors for the selection of optimal genotypes directly in the field,with appropriate portable Raman equipment.

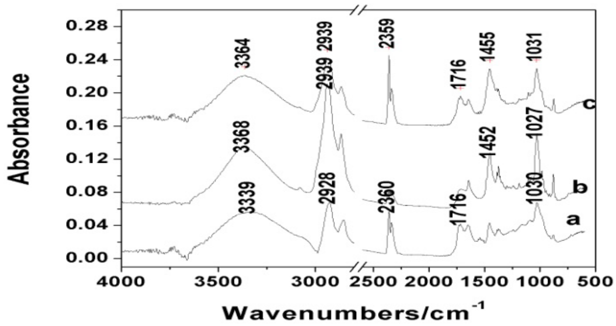

Fig. 1 Representative ATR-FT-IR spectra of the outer bark collected from *Runc Hill* (a) , *Black Hill* (b) and *Park-Vatra Dornei* locations from Romania

Keywords:FT-IR, FT-Raman, betulin, Romanian birch bark

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STUDY ON MAGNETIC AND STRUCTURAL PROPERTIES OF SM-CO THIN FILMS

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The miniaturization of magnetic data storage devices forces the modern technology to store bits of information on increasingly smaller units of magnetic material. In this sense thin Sm-Co films are attractive as they allow thermal stability even in nanometer ordered grains. Sm-Co films were deposited by dc magnetron sputtering on Cu seedlayers that were deposited on thermally oxidized Si(001) wafers. The microstructure of the thin films was investigated by X-ray diffraction and electron microscopy, while the magnetic properties such as remanent magnetization and coercive field were analyzed by VSM measurements. Here, we present a systematic study of the influence of Co-Sm film thickness and annealing conditions (deposition on pre-heated substrates or post-annealing) on the structural and related magnetic properties. We observe an increase in coercivity with increasing thickness of the Co-Sm film. This behavior is accounted to the internal stress induced by the lattice mismatch between the Cu seedlayer and the Sm-Co film for the as-deposited films at room temperature。 In contrast, for deposition on pre-heated substrates the coercivity is strictly related to the phase formation of the Sm-Co.

SPECTROSCOPIC INVESTIGATIONS OF PROTEIN ATTACHMENT ON THE SURFACE OF MONTMORILLONITE – POLY(VINYL ALCOHOL) NANOCOMPOSITES

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Clay mineral / polymer nanocomposites are a new class of materials investigated and used in many domains including biomaterials for tissue engineering and drug delivery systems. These specific applications imply studies of the material's behavior in physiological fluids *in vivo* or culture mediums *in vitro* considering that the living cells cannot interact directly with foreign materials, but they readily attach to the adsorbed layer of proteins. The concentration, distribution, and mobility of the adsorbed protein layer on a surface are clue factors to understand the biological response of a substrate [1]. Nanocomposites (NCs) synthesized from a montmorillonite clay mineral (MMT) and poly(vinyl alcohol) (PVA) by solution intercalation method with three different clay-polymer weight ratios were characterized by structural, morphologic, thermal and spectroscopic techniques. Structural characterization by powder X-ray diffraction analysis allowed to evaluate the dispersion of the clay nanoparticles within the polymer matrix by monitoring the position and shape of the basal reflections from the silicate layers. The thermogravimetric (TG) and differential thermal analysis (DTA) results pointed out the NCs thermal stability and the influence of clay-polymer weight ratios on transition temperatures. NCs and MMT morphologies were investigated using Transmission Electron Microscopy and Atomic Force Microscopy. X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared (FTIR) spectroscopy analyses were performed on PVA, MMT and NCs. To investigate the protein attachment to the surface of the NCs the materials were immersed in simulated physiological fluid enriched with protein. From XPS analysis the attachment of the protein is confirmed in recording N1s photoelectron peak of the amino groups, the C1s peak changes and also in decreasing of intensity of photoelectron peaks specific to the matrix elements (Al, Si etc.) [2]. The O1s and C1s core level peaks were deconvoluted into components of similar Lorentzian-Gaussian contributions in order to identify the type of bonds formed by oxygen and carbon atoms, based on the binding energies of the components obtained from deconvolution. By FTIR spectroscopy the protein attachement to the material surface was evidenced by amide I and amide II vibrational bands [3].

Keywords: polymer-clay nanocomposites, protein attachment, XRD, DTA/TG, TEM, BET, FTIR, XPS.

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SPECTROSCOPIC INVESTIGATION OF PVA-TiO$_2$ MEMBRANES GAMMA IRRADIATED

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The modifications induced by gamma radiation on microscopic scale of poly vinyl alcohol (PVA) membranes doped with different amounts of titan dioxide (TiO$_2$) were observed by ESR and XRD spectroscopies. The ESR spectra show the apparition of a strong signal characteristic to free electrons, after gamma irradiation (Fig. 1). This signal is associated with the breaking of the polymeric chain of PVA induced by radiation and apparition of free radicals. The concentration of free radicals increases with the dose of radiation and was calculated from the area of the signal. The TiO$_2$ dopant doesn't affect the processes of apparition of free radicals.

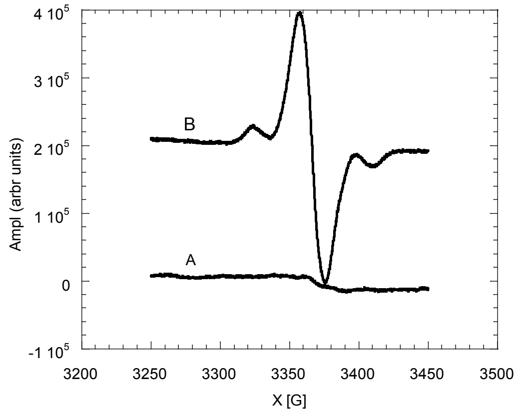

Fig. 1 ESR spectra of PVA membranes containing 20% TiO2 before irradiation (curve A) and after irradiation at 20 KGy (curve B)

For a given dose of radiation the ESR spectra of samples with different concentrations of TiO$_2$ are very similar, that indicates only minor effect of the dopant on the breaking chain processes and apparition of free radicals.

XRD difractograms contain the specific peak at $2\theta = 29^0$ characteristic for PVA [1] and many peaks at $2\theta = 38,2^0$, $56,4^0$, $74,5^0$, $86,4^0$ characteristic for TiO$_2$ [2]. Small modifications of the amplitude of these lines are observed after irradiation. This behavior is associated with an ordering effect of the polymeric chains induced by irradiation.

Keywords: Poly (vinyl alcohol); TiO$_2$ system; Gamma irradiation

Acknowledgement
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LOCALIZED GROWTH OF GOLD NANOPARTICLES FROM Au(I) AND Au(II) PRECURSORS USING LASER IRRADIATION

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When embedded in transparent solid matrices, the nonlinear optical properties of gold nanoparticles (GNPs) make them attractive for applications such as optical telecommunications, data storage, optical computing and information processing [1]. Whereas a large number of synthetic routes have been developed to obtain GNPs in the liquid phase with controlled sizes and shapes, their inclusion in solid host matrices [2] is not at all a trivial task.

In the present work, a direct and space-selective formation of GNPs was obtained within a transparent mesoporous silica host matrix post-doped with appropriate Au(III) and Au(I) precursors. This synthesis was carried out using laser irradiation which provided a localized growth of the GNPs.

The choice of these precursors made it possible to obtain reproducible microarrays of spherical and non-aggregated GNPs without the addition of either reducing or capping agents to the system. The synthesis method described consists of three steps: impregnation of the sol-gel-derived matrices with the gold precursors, irradiation and then removal of the precursors from the matrices by washing. The different phases of the process were followed spectroscopically by means of Raman spectroscopy, TEM, UV-vis absorption spectroscopy, x-ray diffraction and transmission electron microscopy.

The irradiations were carried out with both continuous wave lasers (λ = 266 and 532 nm) and a pulsed laser (λ =800 nm; pulse: 120 fs; repetition rate: 1KHz), which made it possible to fabricate 2D and 3D microarrays of gold nanoparticles, respectively. The presence of GNPs in the irradiated sample was confirmed by UV-vis absorption spectroscopy and x-ray diffraction and the gradual change in the matrix and in the chemical precursors were followed using micro Raman spectroscopy. TEM analysis showed that the GNPs obtained are spherical and that clustering is avoided thanks to the mesoporous nature of the matrix.

The washed samples were tested for thermal resistance: it was shown that the GNP microarrays obtained are able to resist until up to at least 500°C with no observable gold diffusion outside the irradiated areas. The evolution of the Localized Surface Plasmon resonance band with temperature was followed using UV-visible spectroscopy.

Keywords: Gold nanoparticles; Localized growth; Laser radiation; Silica matrix

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SPONTANEOUS IONISATION OF PHENOTHIAZINE UPON ADSORPTION ON LAPONITE CLAY MINERAL

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The mere mixing of phenothiazine (PTZ) with laponite clay material induces the spontaneous ionization of the heterocyclic molecule upon adsorption. Due to their particularly low ionization potential values (I.P. = 6.7 eV), the mere adsorption of the molecules on the surface of the clay is the key parameter to generate the radical cation ($PTZ^{\bullet+}$). However, the presence of water between the laponite sheets prevents the penetration of phenothiazine molecules into the pores. Consequently, in order to allow the molecule sorption within the porous void space, two different experimental approaches have been carried out in liquid phase using acetone or in solid phase under argon atmosphere. Sorption and ionization processes of PTZ are followed by using diffuse reflectance UV-visible absorption (DRUVv) and Raman scattering spectroscopies.

In the solid phase, the mere mixing of PTZ with dehydrated laponite induces PTZ spontaneous ionization and radical cation formation. The $PTZ^{\bullet+}$ features are found to develop gradually with time over several days. Moreover, the spectral data show that a second PTZ ionization occurs at longer times leading to the formation in high yield of very stable PTZ^{2+} dication. In the presence of acetone, the water molecules are replaced by acetone molecules and due to higher PTZ solubility in acetone than in water, PTZ is found to penetrate into the pores of laponite. After acetone evaporation, the DRUVv and Raman spectra indicate that the sorption process takes place much faster than in solid phase and leads also to the formation of dication in high quantity.

In addition, comparison is made between the data obtained in the presence of water and under anhydrous conditions. It appears clearly that in the presence of water, sorption occurs only on the external surface and induces only $PTZ^{\bullet+}$. In contrast, with acetone or under argon in the solid phase, the $PTZ^{\bullet+}$ moiety initially created evolves rapidly to the dication. These results are in total agreement with the data recently reported in zeolites [1,2] and demonstrate that the dication formation requires high confinement to take place.

The very long-lived charge-separated states obtained upon ionization are explained by the negatively or positively charged surface of laponite. The clay is assumed to stabilize the radical cation and dication species while the Na^+ charge-compensating cations might trap the ejected electrons and hinder rapid recombination.

Keywords: Laponite; Phenothiazine; Spontaneous ionization; UV-visible; Raman

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EFFECT OF DOPED ATOM MAGNETISM ON ELECRTONIC TRANSPORT THROUGH $C_{59}X$ AND $C_{69}X$ ($X=B$ AND N) MOLECULAR JUNCTIONS

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In this paper, a theoretical study of the spin-polarized quantum transport through the C_nX molecular junction is presented applying the Keldysh nonequilibrium Green's function formalism. The effects of the contacts, doped atom and cage type and the gate and bias voltages on the spin-polarized quantum transport through the C_nX molecular junction are considered in calculations. In the calculations are indicated that the spin-dependent local density of states of the C_nX molecules are the cause of magnetic moment on every carbon atom in the vicinity of the doped atom. Also, the spin polarization can reaches as high as about 100% with the proper selections of the bias and gate voltages.

Keywords: Transport; Fullerene; Nonequilibrium Green's function

STRUCTURAL ANALYSIS OF INSULIN LOADED SILICA MICROPARTICLES

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Insulin is a therapeutic protein of great interest for its broad use in the treatment of diabetes mellitus. Several attempts have been proposed to improve oral bioavailability of insulin, among them microencapsulation represents a promising concept [1].

Bioactive molecules can be easily encapsulated within silica particles by means of sol-gel polymerization method. Sol-gel enables the production of nanoparticles with homogeneous protein distribution and permit ambient temperature processing necessary for handling biomolecules. The silica matrix can effectively isolate individual biomolecules preventing aggregation and protein denaturation by limiting the movement of the protein within the matrix [2]. A controlled release is achieved by restricting diffusion of encapsulated insulin out of the particles, by tailoring the internal porosity structure of the particles. This process was adapted by combining sol-gel chemistry with freeze-drying and spray-drying, to produce microparticles with different porosity. Although spray-drying is a very efficient one-step process for production of microparticles with controlled characteristics and narrow particle size distribution [3], it remains questionable the integrity of the insulin structure after encapsulation. The main objective of the present study was to determine whether insulin loaded in silica matrixes suffers structural changes. The shape and surface morphologies of the silica microparticles were investigated by Scanning Electron Microscopy (SEM) (Fig.1). The insulin secondary structure was assessed using Fourier Transform Infrared Spectroscopy (FTIR). The results indicated a high structural integrity of insulin in sol-gel derived particles. The stability and integrity of insulin was evidenced also with Differential Scanning Calorimeter (DSC). Site-directed spin labelling (SDSL) in combination with Electron Paramagnetic Resonance (EPR) spectroscopy was also used to provide structural and dynamic information.

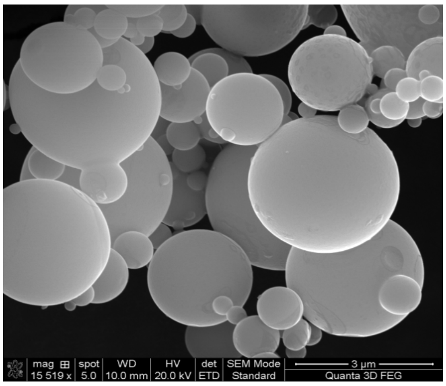

Fig. 1. Shape and surface morphology of the silica spray dried microspheres.

Keywords: drug loading; insulin; silica; FTIR; DSC; SEM; EPR

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LASER PERFORMANCE AND SPECTROSCOPIC PROPERTIES OF Yb-DOPED Lu_2O_3 AND YAG CERAMICS

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Since the first laser oscillation achieved in 2003 [1], several efforts have been focused on Yb-doped transparent polycrystalline ceramics, which are nowadays considered a strategic material for the development of innovative diode-pumped solid-state-laser able to reach high average powers and pulse with a short time duration [2].

The excellent results achieved can be explained considering both the intrinsic characteristic of Ytterbium ions (Yb) and ceramic matrices. As a matter of fact, Yb^{3+} has only two manifolds, $^2F_{5/2}$ and $^2F_{7/2}$, which reduce the quantum defects determining a relatively low thermal load, a long lifetime of the upper state of the laser transition and a wide range of tunability. The ceramic matrices, if compared with the corresponding crystalline materials, show comparable optical qualities, higher uniformity in the distribution of dopants, better thermo-mechanical properties. Moreover, ceramics have a shorter processing time and lower processing temperature, which result particularly advantageous for two cubic sesquioxides as Lu_2O_3 and Sc_2O_3. Due to their high melting point (above 2400 °C) only recently they have been grown in small-size crystals with good optical quality. Sesquioxides are has been considered very promising host matrices because of their high undoped thermal conductivity (up to 12 W/mK).

We present an in-deep spectroscopic investigation and the laser performance achieved by two different A/R coated Yb-doped ceramics as Lu_2O_3 and YAG. The pumping wavelength as well as the concentration of dopants have been opportunely chosen in order to have an almost comparable absorption coefficient and thermal conductivity [3]. In particular, $Yb:Lu_2O_3$ [4,5] is pumped at 968 nm while Yb:YAG [6] at 933 nm. Both are longitudinally pumped in *quasi*-CW (Duty Factor of 20%) at room temperature. The doping levels are 1% *at.* (Lu_2O_3) and 0.7% *at.* (YAG), respectively.

To focus on the laser performance, with both samples we measured the output power as a function of the absorption pump power and we estimated the corresponding slope efficiency. An almost comparable values of the output power is measured while the slope efficiency is found to be higher in Yb:YAG.

Keywords: Solid-state lasers; Ytterbium laser materials; Rare earth solid-state lasers

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SOLID-STATE MAS NMR STUDY OF SOME MIDDLE BRONZE AGE POTTERY

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For many millenniums ceramics was the main material used for storage or food preparation. Archaeological sites usually contain large amounts of pottery, which can be used for cultural and chronological assessment.

Nuclear Magnetic Resonance Spectroscopy applied to Bronze Age ceramics can be useful for cultural framing of the monument, determination of the technology or the relationship with neighboring and contemporary civilization.

In this study solid-state MAS NMR has been used to monitor the composition and phases of different ceramic fragments belonging to Middle Bronze Age found in archaeological sites from Costişa and Siliştea, Neamţ County, Romania.

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Keywords: NMR; Ceramics; Archaeology; Pottery

MULTI-SCALE SPECTROSCOPIC ANALYSIS ON PRECIOUS STONES

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We report here the results of a non-destructive, multi-scale spectroscopic investigation, performed at elemental and microscopic (molecular) level, on a set of precious stones, i.e. sedimentary and metamorphic rocks, widely used as building blocks historical constructions and sculptures [1, 2].

The elemental analysis was carried out by X-ray fluorescence (XRF), whereas the molecular characterization was achieved by Raman and FT-IR spectroscopy. In most cases, portable instrumentation was used, whose advantages for the *in situ* analysis were put into evidence.

The aim of the present study was, first of all, to understand if samples that appear similar from a macroscopic observation exhibit differences in their elemental and molecular properties.

Again, we propose to create a chemical database for precious marbles, that could be a source for future work of non-destructive characterization for valuable stone materials.

Keywords: portable XRF; portable Raman; non-destructive methods; precious stones

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SPECTROSCOPIC STUDIES ON THE RECIPROCAL INFLUENCE BETWEEN VITAMIN C AND ENTRAPING SILICATE MATRIX

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Vitamin C also named L-ascorbic acid is widely necessary in the metabolism of living being. It increases the organism resistance against microorganisms and participates in the antibodies formation, having an important role also in teeth and bone strengthening or wound healing [1]. Ascorbate is synthesized by almost all living organism one exception being the humans [2]. All species that do not synthesize ascorbate require it in the diet. The excess of ascorbic acid taken orally may cause gastric irritation and also renal problems (kidney stones) because is metabolized in oxalic acid. The property of vitamin C to support calcium absorption and collagen formation [1] could make this compound a candidate in bone tissue regeneration, introduced locally, together with bioactive glasses.

The purpose of this study was to entrap vitamin C in a silicate glass matrix and evaluate its influence on the glass matrix but also vice versa - the influence of the glass composition on the structure of vitamin C.

For this reason a silicate glass was prepared using the sol-gel method because it allows the incorporation of determined amounts of vitamin C and does not need high temperatures for the glass network formation.

Spectroscopic method like FTIR was used to investigate vitamin C, silicate glass and the composition formed from the two materials to see the local structural changes that induce one to another.

Release studies of Vitamin C from the silicate matrix were made by immersing the composites in distillated water for a longer period of time. Liquid phase from these samples was removed periodically and analyzed by means of UV-Vis spectroscopy. This spectroscopic method was also used for solid samples analysis before and after immersion in water.

Keywords: vitamin C entrappment; silicate matrix; FTIR, UV-Vis

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USE OF INFRARED SPECTROSCOPY FOR CHARACTERISATION OF ADHESIVE TAPES

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Adhesive tapes are often subject of forensic examination as they are used by offenders to bind a victim as well as to prepare explosive charges or to seal threatening letters. Examination of adhesive tapes is performed in order to identify the kind of the tape and to define their probable producer. It includes application of optical methods which enable one to observe its structure, colour, thickness, width, birefringence or fluorescence as well as chemical analysis - of both glue (adhesive) and backing of the tape - providing mainly information of their polymer components. Infrared spectroscopy (IR) could be used for these purposes [1]. An attempt was made to evaluate the usefulness of the IR method in differentiation of adhesive tapes for forensic purposes and in classification of the samples.

About 50 adhesive tapes of different types (packing, office and electrical tapes) and makes were examined. All tapes were purchased from supermarkets and stores. The infrared spectra of backings and glues of tapes were recorded on Digilab FTS 40Pro spectrometer combined with UMA 500 microscope in transmission mode. On the basis of the obtained IR spectra it was possible to identify the main polymers and fillers and to classify tapes into particular groups. On the base of chemical contents of backings the tapes were classified into one of 4 groups and on the base of the type of glue also into 4 groups. Within each group small differences were observed, which were originated from the presence of minor components of the sample, making possible to create subgroups. The majority of tapes contained polyethylene or polypropylene backing and styrene butadiene rubber glue. It was possible to differentiate 27 tapes from the whole set of the examined samples.

It was found that IR spectroscopy providing crucial information about polymer content is useful for identification of adhesive tapes found at the crime scene and enables one to classify samples into several chemical classes. IR method, together with a more sensitive method, e.g. pyrolysis gas chromatography (Py-GC/MS) analyzing the thermal destruction products, may provide a better discriminations of the studied tapes.

Keywords: adhesive tapes; Raman spectroscopy; classification;

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EXAMINATION OF CAR PAINT SAMPLES OF THE SAME COLOR USING VIS MICROSPECTROMETRY FOR FORENSIC NEEDS

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VIS spectrophotometry allows an objective measurement of color as opposed to the subjective results of visual color comparison. In this paper the usefulness of this method for comparison of car paint traces of the same color and the same or different shade was studied for forensic purposes. Sixteen samples of solid and metallic bright and dark red paints taken from different cars were examined. Each sample was measured in reflectance mode both via the top layer and directly on a cross-section of the paint chip using a light beam falling perpendicular to the top surface of the sample in the reflectance mode and on cross-section. J&M TIDAS microspectrometer combined with a C. Zeiss Axioplan 2 microscope was used to perform measurements in both reflectance and transmittance mode. The spectral range was 380–780 nm. Each paint fragment was exposed to measurements in 10 different places, the obtained spectra were averaged and the final spectrum was characterized in accordance with the CIELAB model, L, a^*, b^* coordinates.

On the basis of the obtained results the hypothesis has been made that discrimination of car paints of the same color is conditioned not by kind, number and even contents of the colorful pigments, but rather by morphology of a paint layer, i.e. by size, shape, orientation and distribution of the pigment grains in a paint resin. A criterion allowing two samples of the same shade to be distinguished was established.

Keywords: Paint; VIS spectroscopy; Discrimination

Acknowledgments
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AMYLOID FORMATION STUDIED BY IR 2DCOS-MOVING LAPSE

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Amyloidosis is characterized by the abnormal self-assembly and deposition of proteinaceous material into insoluble ordered aggregates. There are several pathologies associated with this aggregates, known as "protein misfolding" disorders. In many proteins, when heated at high temperature and low pH, a series of structural changes resulting in the formation of fibrillar structures are produced. Insulin is a model of fibril formation that has produced a wealth of biochemical and structural data. The time-course of fibril formation can be followed by infrared spectroscopy looking at the appearance of a characteristic band in the amide I region. The kinetics is triggered by temperature at 70 ºC and pH at 2.0.The infrared spectrum shows, that after a lag time (concentration-dependent), β-turns and α-helix bands decrease first whereas the random coil component increases. Later, a band at 1626 cm^{-1}, associated with extended chains, replaces the random coil component. Infrared 2D-COS has been applied to different stages of the process. Since an intense band appears, the synchronous map does not give much information, because it is obscured by the predominance of this peak. In order to extract more information from the correlation maps, we have developed an approach that we call “2DCOS-moving lapse” that allow us to follow the process without the disturbance produced by the aggregation band. In this approach, we take a window of ten spectra and move this interval one spectrum at a time along the perturbation. Then, maps can be studied at different incubation times, e.g. before random coil formation and at different stages in the random coil-fibril exchange. The maps obtained indicate a two-step process with a first stage associated with an opening of the protein driven by destabilization of β-turns, located in the outer part of the protein, and a second part where the fibril is formed.

Acknowledgments

This work was supported in part by the Spanish Ministerio de Educación y Ciencia (grant No. BFU 2010-22103)

ASSEMBLING MOLECULES ON NANOPARTICLES AND NANOSTRUCTURED SURFACES

Octavian Popescu

Romanian Academy and Babeș-Bolyai University Cluj-Napoca

The workshop is organized in the frame of the research program PCCE321/2008.

CONFOCAL 3D AND TOPOGRAPHIC RAMAN IMAGING

Ute Schmidt and Lena Welter

Witec Germany

Confocal Raman microscopy combines extremely sensitive Raman spectroscopy with high resolution optical microscopy, leading to chemical images with diffraction limited 3D resolution. For large area investigations on rough and inclined samples True Surface Microscopy provides the ability to acquire topographic Raman images along the true surface of the sample. The aim of this workshop is to explain the principle of confocal and True Surface Raman imaging and to outline the various fields of applications of the techniques.

HIGH PERFORMANCE SPECTROMETRY SOLUTIONS FROM THERMO FISHER SCIENTIFIC

THERMO SCIENTIFIC SPECTROSCOPY SOLUTIONS FOR UV-VIS, FT-IR AND RAMAN

Steve Reynolds

Sales Manager Molecular FTIR, NIR and Raman spectroscopy products, Thermo Fisher Scientific

A NEW CONCEPT FOR MOLECULAR SPECTROSCOPY: THERMO SCIENTIFIC NICOLET iS50 FT-IR SPECTROMETER

Bruno Beccard

FTIR & Raman Product Specialist, Thermo Fisher Scientific

Over recent years, there has been more and more need for easy-to-use, flexible yet powerful analysis systems. Hyphenation has become a keyword. The Thermo Scientific Nicolet iS50 FT-IR Spectrometer combines ease of use with various FTIR and Raman sampling techniques, including GCIR and TGA IR in a small footprint instrument.

EXPANDING CAPABILITIES: MULTIPLE CHANNELS ACQUISITION AND STEP SCAN

Bruno Beccard

FTIR & Raman Product Specialist, Thermo Fisher Scientific

Since the end of the 1980's, alternate techniques have been used for enhancing capabilities for surface studies, such as PEM IRRAS. These dual modulation techniques expand into chiral molecule studies through VCD. Step scan is a way to eliminate Fourier frequencies. It can be used for a variety of applications including time resolved spectroscopy as well as simultaneous multiple modulations.

MICROSCOPY OR MICROSPECTROSCOPY

Bruno Beccard

FTIR & Raman Product Specialist, Thermo Fisher Scientific

FTIR and Raman microscopy are aimed at getting spectrum and thus identification of small samples, or portions of samples. This also can be used to follow concentration profile along a line or an XY area. Image processing can also be part of the picture, especially with use of chemometric techniques. While sharing a lot, FTIR and Raman microspectroscopies have their respective fields of excellence.

MEASURING OF SOLID SAMPLES IN REFLEXION AND TRANSMISSION WITH A HIGH END UV/VIS SYSTEM.

Erich Heiden[1] and Dan Bulik[2]

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[2]*Managing Director, Berd Trading srl, Thermo Fisher Scientific Distributor in Romania for Spectroscopy Products*

Learn how Reflection measurements can be easier to perform and to achieve quicker, more accurate results. Applications like “Tauc” calculations; color measurement, and Haze are becoming much more simple.

COLE-PARMER PICOSPIN™-45 BENCHTOP NMR SPECTROMETER – REVOLUTION IN LOW FIELD NMR SPECTROSCOPY

Janusz M. Kossakowski

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LIGHT INDUCED REACTIONS IN CRYOGENIC MATRICES

Rui Fausto

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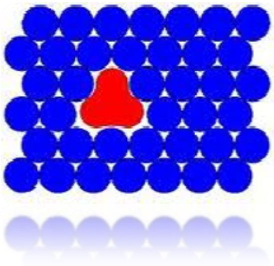
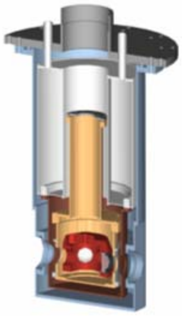


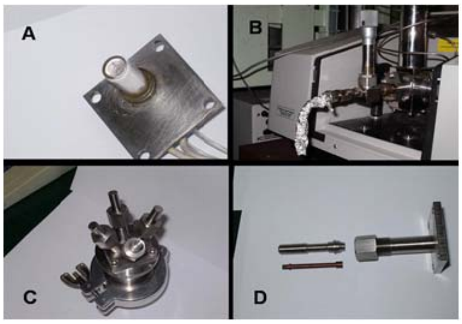
- The fundamentals of the matrix isolation technique will be presented, and its main advantages in the study of chemical reactivity described.
- Examples of its use in the investigation of photochemical (UV-induced) and hot-vibrational chemistry (IR-induced) processes will be given and discussed.
- These examples will include conformational isomerizations, rearrangements, fragmentations and molecular aggregation.

This lecture will stress the power of the matrix isolation technique, coupled with infrared spectroscopy, to study chemical reactivity.

Since its invention by George Pimentel in 1954 [1], matrix isolation has been given an enormous contribution to the study of molecular reactivity. Nowadays, the investigation of light induced reactions in cryogenic matrices is a hot topic of research both in chemistry and physics [2]. For example, interesting chemical systems with potential application as molecular optical devices have been described [3-5], and new materials, such as stable covalently bound noble gas containing molecules, have been produced and characterized [2,6]. Moreover, in recent years, besides the more classic photochemical processes involving UV-visible excitation and electronic excited states, studies have also included hot vibrational chemistry processes, in which vibrationally excited molecules in their ground electronic state undergo chemical transformations upon IR excitation. Matrix-isolation spectroscopy has been the main technique used in these investigations, revealing itself to be specially powerful in the identification of reaction intermediates and establishment of reaction mechanisms. Interestingly, the success of this approach may also be ascribed to the concomitant development of computational chemistry, which provides sound theoretical foundations for the interpretation of the experimental data, and the availability at relatively low cost of tunable lasers that could be used as adequate irradiation sources to investigate specific processes in an elegant and powerful way.

Besides a general introduction to matrix isolation, in this lecture a series of case studies will be presented which illustrate the use of the method in the investigation of chemical processes induced by both UV-visible and IR light.





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