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Positron impact ionization of CH$_4$

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Abstract

We have used two distorted wave models to calculate positron impact ionization of CH$_4$. In the first one we used Gaussian molecular target representations and in the second we assumed that the target is a sum of independent atoms. We found that our molecular model works better than the "independent atoms" model.
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1. Introduction

Total cross-sections for ionization by positrons have been measured for H$_2$ [1,2], N$_2$ [3], O$_2$ [4], CO [5], CO$_2$ [5,6] and for a number of organic molecules [7]. The calculations for this process have been limited to diatomic molecular targets using the distorted wave approach. Recent papers by Campeanu et al. [8–11] showed that good agreement with experimental measurements can be obtained with the CPE (Coulomb plus plane waves with full energy range) distorted wave model, using Gaussian target wave functions. This model was also used in the case of CO$_2$ but produced results well above the experiment. For CO$_2$ better theoretical results were obtained with an "independent atoms" CPE model.

2. Theory

The calculational method for positron impact ionization of a linear molecule has been described in detail elsewhere [8,9,11]. Below we give a brief description of the method and emphasize the theoretical approach in the case of CH$_4$.

The triple differential cross-section for the ionization of a molecule by positron impact may be written as

$$\frac{d^3\sigma}{d\hat{\mathbf{k}}_f \, d\hat{\mathbf{k}}_e \, dE_e} = \sum_r \frac{(2\pi)^4}{E_i}|f_r|^2, \tag{1}$$

where E_i, is the energy of the incident positron; E_e, the energy of the ejected electron, while $\hat{\mathbf{k}}_e$ and $\hat{\mathbf{k}}_f$ stand for the direction of the momenta of the ejected electron and scattered positron, respectively. In the formula above the continuum wave functions are normalized in energy, and the energy is expressed in Rydbergs. The summation over r is done over all occupied molecular orbitals. The amplitude can be written as

$$f_r = \langle \phi_f(\mathbf{r_1})\phi_e(\mathbf{r_2})|V(r_{12})|\phi_i(\mathbf{r_1})\phi_r(\mathbf{r_2})\rangle, \tag{2}$$

where ϕ_i and ϕ_f stand for the wave function of the incident and scattered positron, respectively, ϕ_e is the wave function of the ejected electron, while ϕ_r describes the initial state (orbital) of the active electron. In the above amplitude $\mathbf{r_1}$ is the position vector of the positron, while $\mathbf{r_2}$ stands for the position vectors of the active electron.

The CPE model [12] is a simple model in which the ejected electron moves in the field of the positive charge of the residual ion, while the scattered positron is represented as a free particle. In this model we make a partial

wave expansion of the wave functions of the incident projectile, the scattered positron and the ejected electron. Further, in the calculation of the total cross-section, one has to integrate over the angles of the outgoing electron and positron as well as the energy of the electron as described in [12]. This model assumes that the electron orbitals in the residual molecular ion are the same as in the target molecule during the time of the collision.

The CH_4 molecule has a tetrahedral symmetry. We have considered the following two types of molecular orbitals: the $2a_1$ orbital (with the lowest energy among the valence orbitals) and the 3 equivalent $1t_2$ orbitals. The molecular orbitals are taken as linear combination of the C and the four H Gaussian orbitals;

$$\phi(x,y,z) = C_C\phi_C(x,y,z) + \sum_{i=1}^{4} C_{H_i}\phi_H(x - x_i, y - y_i, z - z_i),$$
(3)

x_i, y_i and z_i being the coordinates of the H atoms. The Gaussian orbitals have been constructed as contractions of Gaussian type functions, using the STO-3G basis set [13]. With this method we have obtained the following ionization energies: 24.81 eV in the case of the $2a_1$ molecular orbital and 14.16 eV for the $1t_1$ orbitals. We have used these ionization potentials in our calculations.

The CH_4 orbitals do not have cylindrical symmetry, as in case of the σ orbitals for linear molecules, and the expansion was done in a different way. We expanded the initial state wave function in terms of spherical harmonics in the molecular frame

$$\phi(\mathbf{r}) = \sum_{l_b\mu} c_{l_b\mu}(r)Y_{l_b\mu}(\hat{\mathbf{r}}),$$
(4)

where the coefficient is obtained by

$$c_{l_b\mu} = \int d\hat{\mathbf{r}} \, Y_{l_b\mu}(\hat{\mathbf{r}})\phi(\mathbf{r}).$$
(5)

Performing the transformation to the lab frame (denoted by prime) one obtains

$$Y_{l_b\mu}(\hat{\mathbf{r}}) = \sum_{m_b} Y_{l_b m_b}(\hat{\mathbf{r}}')D_{m_b\mu}^{l_b}(\alpha, \beta, \gamma),$$
(6)

where the $D_{m_b\mu}^{l_b}(\alpha, \beta, \gamma)$ are the matrix elements of the rotation operator for the rotation of the frame through the Euler angles (α, β, γ). The orbital in the lab frame will be

$$\phi(\mathbf{r}') = \sum_{l_b m_b} Y_{l_b m_b}(\hat{\mathbf{r}}') \sum_{\mu} c_{l_b\mu}(r)D_{m_b\mu}^{l_b}(\alpha, \beta, \gamma).$$
(7)

Further the method is identical with the method presented for linear molecules.

Our current work includes the "independent atoms" CPE model which we introduced in [11] in order to improve our results for CO_2. In this model the cross-sections for ionization of each of the constituent atoms has been calculated separately within the CPE approximation [12], using the same Gaussian wave functions as for the molecular calculation, and the cross-section for the molecule has been obtained by summing the atomic contributions.

3. Results and discussion

We present the contributions from the various partial waves for the two CH_4 orbitals in Table 1. As the table shows, the first orbital is almost spherically symmetric; the $l_b = 0$ (i.e. monopole) term dominates and it has only a negligible $l_b = 3$ (i.e. octupole) contribution. The second orbital has a mainly dipole ($l_b = 1$) character; it also has significant quadrupole ($l_b = 2$) and some octupole ($l_b = 3$) contributions.

Fig. 1 shows our CH_4 total ionization cross-sections compared with the experimental measurements of Bluhme et al. [5]. As for CO and CO_2 [11] we present both our molecular CPE and independent atoms CPE results.

Our results show that the "independent atoms" CPE model overestimates the ionization cross-sections for positron impact energies lower than about 800 eV. The disagreement with the experiment is maximum near the peak where it exceeds the experimental measurements by

Table 1
Partial ionization cross-sections (in 10^{-16} cm^2) for the two types of CH_4 valence orbitals for 100 eV positron impact

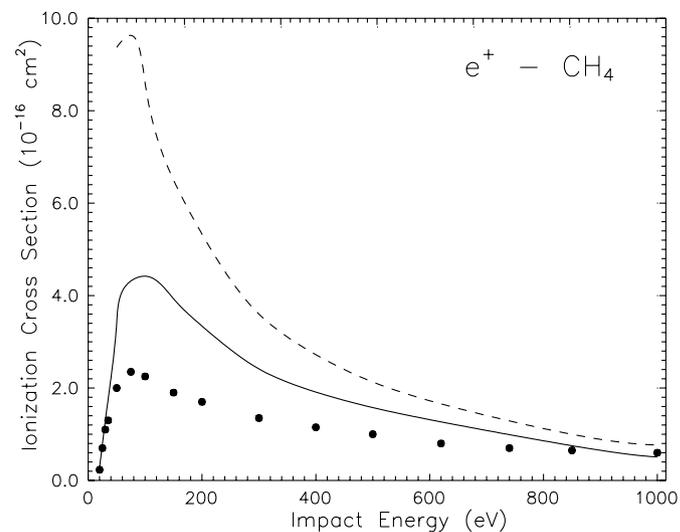| Orbital	l_b				Total orbital
	0	1	2	3	
$2a_1$	1.25	0	0	6.4×10^{-4}	1.25
$3 \times 1t_2$	0	2.92	0.24	1.5×10^{-2}	3.18
Total l_b	1.25	2.92	0.24	0.016	4.43

Fig. 1. Total cross-sections for positron impact ionization of CH_4 as a function of the positron impact energy. The experimental points are from Bluhme et al. [5]. Our molecular and independent atoms CPE model results are represented by the continuous and dashed curves, respectively.

a factor of 4. This disagreement is significantly higher than for CO and CO_2 [11].

Fig. 1 also shows that for CH_4 the molecular CPE model overestimates the results for impact energies below 700 eV but the disagreement with the experiment is much smaller than for the "independent atoms" CPE model. The disagreement reaches a maximum of about 80% near the peak. The CPE molecular model was in very good agreement with the experiments for all diatomic linear molecules that we examined [8–11], but it seems to fail for larger molecules such as CO_2 and CH_4.

There is however a distinction between these two cases. While for CO_2 the CPE molecular model overestimates the ionization cross-sections for all impact energies larger than 100 eV [11], for CH_4 the disagreement with the experiment is a maximum near the peak and decreases to zero for large impact energies. The reason for this difference is most likely related to different limitations of our theoretical model. In the case of CO_2 the initial wave function is a multicentered function, while the final state has been described by a Coulomb function centered at the origin. This limitation of the theoretical model is so severe that for CO_2 the "independent atoms" CPE model produces better results than the molecular CPE model [11]. In the case of CH_4 the contribution to the molecular orbitals from the atoms which are not centered at the origin (the H atoms) are less important than in the case of CO_2. The major contribution to the molecular orbitals comes from the C atom so that the error in using a Coulomb function centered at the origin is less severe in this case. This results in the CPE model giving better results than the "independent atoms" model in the present work.

4. Conclusions

Our previous calculations indicate that our simple CPE ionization model using Gaussian representations of the molecular targets works well, not only for homonuclear diatomic molecules [8–10], but also for heteronuclear diatomic molecules such as CO [11]. For the larger CO_2 and CH_4 molecules we cannot obtain such a good agreement with the experiment because of limitations in our theoretical model.

The "independent atoms" CPE model produces results in good agreement with the experiment only for high impact energies, and in general it is less accurate than a molecular CPE model. The exception is the case of CO_2, where a limitation of our molecular CPE model makes the "independent atoms" CPE model the better choice.

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