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Screening effects in the ionization of molecules by positrons

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Abstract

Theoretical DWBA calculations for the ionization of N_2, CO, CO_2 and CH_4 molecules are presented. Previous calculations are improved by calculating the wavefunctions of the ejected electron and of the positron in the spherically averaged, screened field of the molecule. Results for N_2 and CO are in very good agreement with the experimental data, while those for CO_2 and CH_4 need more improvement.
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1. Introduction

Positron impact ionization of molecules have been studied experimentally by several groups [1–4]. Previously we have made calculations for the direct ionization of the H_2, N_2, O_2, CO, CO_2 and CH_4 molecules in a wide energy range. We have applied the CPE (Coulomb plus plane waves with full energy range) model adopted to molecules. The initial state of the molecules have been described by multi-center Gaussian wavefuctions, while the final state of the ejected electron was described by Coulomb waves. For the incident and scattered positron plane waves or Coulomb waves were used. The results were in good agreement with the experiment for H_2 [5] and CO [6], while for CO_2 [6], N_2 [7], and CH_4 [8] theoretical results overestimated the experiments.

In order to improve the previous results, we have applied for these molecules the DWBA (distorted wave Born approximation) model, which describes the ionization process more realistically than the CPE model. In this approximation the wavefunctions of the ejected electron, and of the incident and scattered positron are calculated in a more realistic potential. The potential created by the nuclei and the bound electrons is spherically averaged, and the radial Schrödinger equation is solved numerically in this field. The effect of this screened po-

tential is investigated separately on the ejected electron and on the scattered positron.

2. Theory

In the present Letter, we investigate the positron impact ionization of the N_2, CO, CO_2 and CH_4 molecules. The detailed calculational method for these molecules has been described elsewhere [5–8]. Here we give a brief description of the method and emphasize the differences introduced by this Letter.

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

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

Here E_i is the energy of the incident positron, E_e the energy of the ejected electron, while $\hat{k}_e$ and $\hat{k}_f$ stand for the direction of the momenta of the ejected electron and scattered positron, respectively. The summation over r is done over all occupied molecular orbitals. The amplitude can be written as

$$f_r = \langle \phi_f(\vec{r}_1)\phi_e(\vec{r}_2) | V(r_{12}) | \phi_i(\vec{r}_1)\phi_r(\vec{r}_2) \rangle, \tag{2}$$

where ϕ_i and ϕ_f stand for the wavefunction of the incident and scattered positron respectively, ϕ_e is the wavefunction of the ejected electron, while ϕ_r describes the initial state of the active electron. In the above amplitude $\vec{r}_1$ is the position vector of the

positron, while $\vec{r}_2$ stands for the position vector of the active electron.

The ground state of the molecule has been described by Gaussian wavefunctions. In the case of linear molecules, the two-center or multi-center wavefunctions have been expanded in terms of Legendre polynomials:

$$\phi_r(\vec{r}_2) = \sum_{l_b} c_{l_b}(\vec{r}_2, \vec{R}_0) P_{l_b}(\cos\omega_2), \tag{3}$$

where $\vec{R}_0$ is the internuclear distance and ω_2 is the angle between $\vec{r}_2$ and $\vec{R}_0$. The expansion coefficients can be expressed with the following integral:

$$c_{l_b}(\vec{r}_2, \vec{R}_0) = \frac{2l_b + 1}{2} \int_{-1}^{1} d(\cos\omega_2) \, P_{l_b}(\cos\omega_2)\phi_r(\vec{r}_2). \tag{4}$$

For nonlinear molecules the initial state wave function has been expanded in terms of spherical harmonics without a cylindrical symmetry,

$$\phi_r(\vec{r}_2) = \sum_{l_b\mu} c_{l_b\mu}(r_2)Y_{l_b\mu}(\hat{r}_2), \tag{5}$$

where the expansion coefficient is obtained by

$$c_{l_b}(r_2) = \int d\hat{r}_2 \, Y_{l_b m_b}(\hat{r}_2)\phi_r(\vec{r}_2). \tag{6}$$

By this method [5–8] the triple differential cross section for the ionization of a molecule by positron impact may be expressed as a sum of cross sections characterized by a certain angular momentum of the initial state

$$\frac{d^3\sigma}{d\hat{k}_f \, d\hat{k}_e \, dE_e} = \sum_{r} \sum_{l_b m_b} \frac{(2\pi)^4}{E_i} |f_r^{l_b m_b}|^2, \tag{7}$$

where $f_r^{l_b m_b}$ denotes the partial scattering amplitude for orbital r with the angular momentum of the initial state characterized by l_b and m_b. Further, in the calculation of the total cross section, one has to integrate over the angles of the ejected electron and scattered positron as well as the energy of the ejected electron.

Previously calculated ionization cross sections were based on the CPE approximation. The CPE method assumes that if the scattered positron is faster than the ejected electron the positron moves in the field of the neutral molecule, while the ejected electron moves in the field of the positive ion. For the case when the ejected electron is faster than the scattered positron the electron moves in the field of two positive charges, while the positron moves in the field of the positive ion. The wavefunctions of the incident positron, the scattered positron and the ejected electron were expanded in terms of partial waves.

In the framework of the DWBA approximation method we have calculated ionization cross sections involving more realistic wavefunctions for the incident and scattered positron and the ejected electron. We have spherically averaged the real potentials created by the nuclei and the electrons. The wavefunctions of the continuum states were calculated numerically in these potentials. The radial part of the continuum states was obtained

by solving the radial Schrödinger equation using the Numerov method. The numerical wavefunctions have been normalized by employing the method of Burgess [9].

Spherically averaging the potential created by the electrons being on the orbital r we obtain

$$V_{\text{electrons}}^r(r') = -n_r \frac{1}{4\pi} \int \frac{|\phi_r(\vec{r}_2)|^2}{r_>} \, d\vec{r}_2, \tag{8}$$

where $r_>$ denotes the greater between r_2 and r' (the distance from the center of the considered sphere), while n_r is the number of the electrons on the orbital. The total potential created by all the electrons may be written as

$$V_{\text{electrons}} = \sum_{r} V_{\text{electrons}}^r(r'). \tag{9}$$

The real potential created by the nuclei has been spherically averaged as follows. The molecules have been 'rotated' in all directions around the center of mass. In the case of the N_2 molecule for example we obtain from this 'rotation' a sphere with radius $R_0/2$ and a uniform distribution of the nuclear charge on the surface of this sphere. Finally, the averaged potential created by the two nuclei of the N_2 molecule may be written as

$$V_{\text{nuclei}} = \begin{cases} \frac{2Z}{R_0/2}, & \text{for } r' < \frac{R_0}{2}, \\ \frac{2Z}{r'}, & \text{for } r' > \frac{R_0}{2}, \end{cases} \tag{10}$$

where Z is the atomic number.

We have applied the above method for all investigated molecules. For the CO_2 molecule we obtain a sphere with radius $R_0/2$ and a uniform distribution of the nuclear charge created by the O atoms, while the C atom were placed in the center of the sphere. For the CO molecule we obtain two spheres with different radii and the nuclear charge of the C atom was placed on the sphere with the greater radius. Finally, in the CH_4 case we obtain a sphere with the radius being equal with the distance between the C atom and one of the H atoms and the nuclear charge of the H atoms were placed on this sphere, while the C atom remains in the center.

Taking into account the expressions of (9) and (10) we obtain the resulting potential as the sum between these potentials, where the spherically averaged potential of the nuclei is screened by the spherically averaged potential created by the electrons:

$$V_x = V_{\text{nuclei}} + V_{\text{electrons}}, \tag{11}$$

where $x = i, f, e$. Here, the $x = i$ subscript denotes the potential used in the calculation of the wavefunction of the incident positron. When $x = f$, we have used the expression of (11) to calculate the wavefunction of the scattered positron, while in the $x = e$ case the wavefunction of the ejected electron was calculated.

Further, two models have gradually introduced the distortion of the incoming and outgoing waves in order to illustrate the effect of each change in the wave representation. The first model assumes that when the scattered positron is faster than the ejected electron the positron moves in the field of the neutral molecule and the electron moves in the spherically averaged

potential field created by the nuclei and by the remaining electrons (after the ionization). When the ejected electron is faster than the scattered positron the positron moves in the field of the positive ion, while the electron moves in the averaged potential created by the nuclei and the positron screened by the averaged field of the remaining electrons. In addition, the model assumes that the incident positron moves in the field of the neutral molecule. Using the above notations for the potentials, the mathematical representation of this model may be written as

$$V_i = 0,$$
$$\begin{cases} V_f = 0, \\ V_e = V_{\text{nuclei}} + V_{\text{electrons}}(-) \end{cases} \quad \text{for } E_f > E_e,$$
$$\begin{cases} V_f = \frac{1}{r'}, \\ V_e = V_{\text{nuclei}}(+) + V_{\text{electrons}}(-) \end{cases} \quad \text{for } E_e > E_f, \quad (12)$$

where $V_{\text{electrons}}(-)$ denotes the spherically averaged potential created by the remaining electrons and $V_{\text{nuclei}}(+)$ is the averaged potential created by the nuclei and the positron. E_f and E_e denotes the energies of the scattered positron and the ejected electron, respectively. We call this model the electron screening (ES) model, since the screened potentials have been used only for calculating the wavefunction of the ejected electron.

The second model assumes that when the scattered positron is faster than the ejected electron the positron moves in the averaged field of the nuclei and all electrons and the ejected electron moves in the averaged field of the nuclei and the remaining electrons. When the ejected electron is faster than the scattered positron the positron moves in the averaged field of the nuclei and the remaining electrons, while the ejected electron moves in the averaged field of the nuclei and the positron screened by the averaged field of the remaining electrons. In addition, the incoming positron moves in the averaged potential field of the nuclei and all electrons. Mathematically:

$$V_i = V_{\text{nuclei}} + V_{\text{electrons}},$$
$$\begin{cases} V_f = V_{\text{nuclei}} + V_{\text{electrons}}, \\ V_e = V_{\text{nuclei}} + V_{\text{electrons}}(-) \end{cases} \quad \text{for } E_f > E_e,$$
$$\begin{cases} V_f = V_{\text{nuclei}} + V_{\text{electrons}}(-), \\ V_e = V_{\text{nuclei}}(+) + V_{\text{electrons}}(-) \end{cases} \quad \text{for } E_e > E_f. \quad (13)$$

The notations used in Eqs. (13) are the same as in Eqs. (12). We have designated this model as total screening (TS) model, since the screened potentials have been used for calculating wavefunctions for both the incoming and outgoing particles.

3. Results and discussion

Figs. 1–4 show our total ionization cross sections results for the investigated molecules: N_2, CO, CO_2 and CH_4. In these figures we present results corresponding to models CPE, ES and TS together with the experimental data of Bluhme et al. [1].

In Fig. 1 we present the integrated cross sections for positron impact ionization of molecular nitrogen. Fig. 1 shows that the results obtained with the ES model are in very good agreement with the experimental measurements. For impact energies lower than 100 eV the results produced by the CPE model agrees well with the experimental data, while for impact energies larger
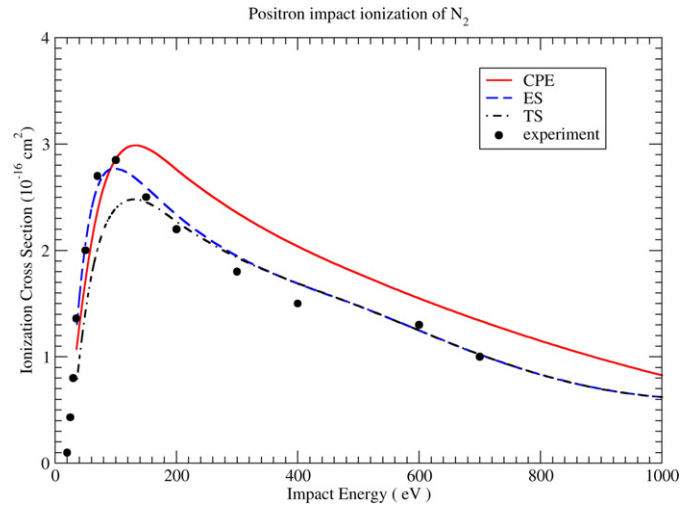

Fig. 1. Total cross sections for positron impact ionization of N_2 as a function of the positron impact energy. The experimental points are from Bluhme et al. [1].
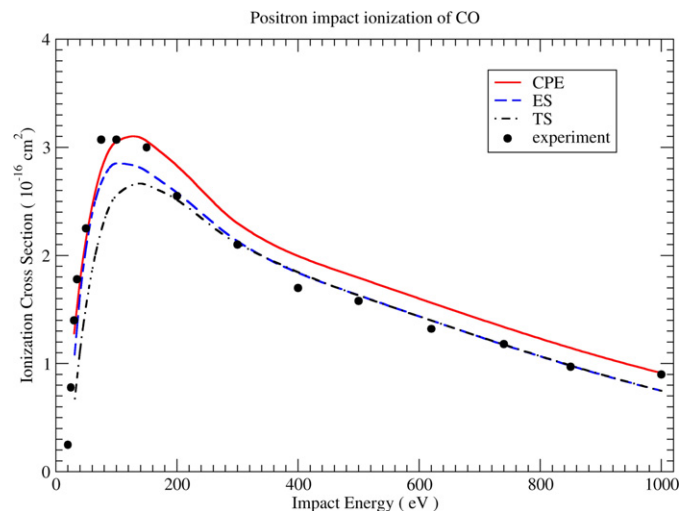

Fig. 2. Total cross sections for positron impact ionization of CO as a function of the positron impact energy. The experimental points are from Bluhme et al. [1].
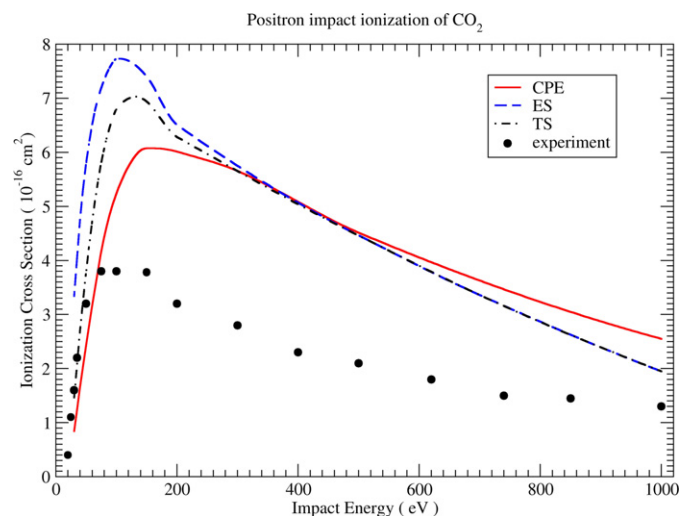

Fig. 3. Total cross sections for positron impact ionization of CO_2 as a function of the positron impact energy. The experimental points are from Bluhme et al. [1].
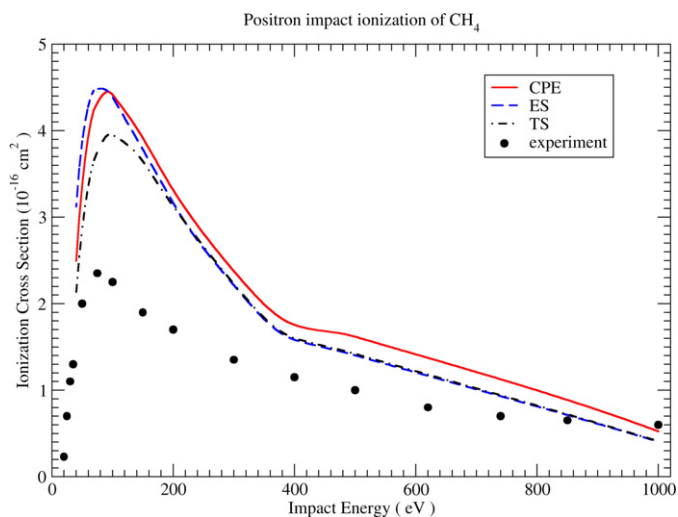
Fig. 4. Total cross sections for positron impact ionization of CH_4 as a function of the positron impact energy. The experimental points are from Bluhme et al. [1].

than 150 eV the results are above the experimental points. The TS model produces results that are different from those obtained with the ES model only in the region of the peak, where we found a minimal disagreement with the experiment.

Fig. 2 shows the results for the CO molecule. In this case, for impact energies larger than 200 eV, the ES and TS results are in better agreement with experimental data than the CPE results, but there are minimal differences. In the region of the peak and for small impact energies the CPE agrees well with the experiment, while the results produced by the ES and TS models are a slightly lower than those obtained with the CPE method.

In Fig. 3. are presented the results obtained for the CO_2 molecule. The figure shows that our screened potential models overestimate the experimental results. The disagreement is about 80%. The CPE model results are lower than those obtained with the ES and TS models, but they still are in bad agreement with experimental data (the disagreement is about 50%). This large discrepancy found for the CO_2 molecule should be explained by the large size of the molecule and by the fact that in our method have calculated the continuum wavefunction in a spherically symmetric (one-center) potential. A possible solution would be to represent the ejected electron as a multicentered function.

In the case of the CH_4 molecule the results are presented in Fig. 4. Our results show that the used models overestimate the ionization cross sections for positron impact energies lower than 800 eV. However, improvement has been found in the region of the peak, where the TS model produces lower results than the CPE and the ES models. Minimal improvement has been found in the case of the ES and TS models compared with the CPE results also for larger energies.

4. Conclusions

In this Letter we have refined our previous calculations for the positron impact ionization of several molecules. We have calculated the wavefunction of the ejected electron and the scattered positron in a spherically symmetric screened potential. In all cases studied the theoretical results were improved relative to the CPE model, where the wavefunctions were approximated by Coulomb or plane waves. This improvement is particularly clear at impact energies higher than 200 eV. Our new results for N_2 and CO are in very good agreement with the experiment, and in a reasonable agreement with the CH_4 measurements. The worse agreement between theory and experiment continues to exist for CO_2. As shown in [6], the cause of this disagreement is the large size of the molecule, and improvement for this target may be expected only if the ejected electron will be described by multi-center wavefunctions, similarly to the initial state.

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