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Positron impact ionization of molecular oxygen

R.I. Campeanu [a], V. Chis [b], L. Nagy [b,*], A.D. Stauffer [a]

[a] *Department of Physics and Astronomy, York University, Toronto, Canada*
[b] *Faculty of Physics, Babeş-Bolyai University, str. Kogălniceanu nr. 1, 400084 Cluj, Romania*

Abstract

We have carried out distorted wave calculations of positron ionization of molecular oxygen in order to compare with experimental measurements. In this work the oxygen molecule was represented by a Gaussian wave function which includes contributions from alpha and beta electrons. We find that our CPE model produces results which are in good agreement with the combined measurements for total ionization and positronium formation.
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1. Introduction

Positron impact ionization of molecules has been studied recently both experimentally and theoretically. Experimental total ionization cross sections were measured for H_2 [1,2], N_2 [3], CO [4], CO_2 [5] and for organic molecules [6]. For O_2 [7], the existing measurements of the total ionization cross sections include the contributions from Ps formation. However, for O_2 there are also unpublished Ps formation cross sections [8]. Most theoretical studies have dealt with positron impact ionization of molecular hydrogen. In this Letter we employ the distorted wave model CPE, using a two-center formalism and a Gaussian representation of the O_2 molecule, a method which we

used successfully for positron ionization of H_2 [9] and N_2 [10].

2. Theory

The theory was described in detail in [9] for the ionization of σ orbitals and in [10] for π orbitals. Here we give only a short outline of the theory and emphasize the particularities for the O_2 case. The triple differential cross section for the ionization of a homonuclear molecule by positron impact may be written as

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

where E_i is the energy of the projectile, E_e the energy of the ejected electron, while $\hat{\mathbf{k}}_{\mathbf{e}}$ and $\hat{\mathbf{k}}_{\mathbf{f}}$ stand for the

* Corresponding author.
 E-mail address: lnagy@phys.ubbcluj.ro (L. Nagy).

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

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

where ϕ_i and ϕ_f stand for the wavefunction of the incident and scattered positron respectively, ϕ_e is the wavefunction 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 vector of the active electron. We are assuming in this model that the electron orbitals in the residual molecular ion are the same as in the target molecule during the time of the collision.

The molecular orbital of the active electron is taken as a linear combination of Gaussian orbitals

$$\phi_r(\mathbf{r_2}) = N_r \left[\phi^{\mathrm{CGF}}(\mathbf{r_{a2}}) + \phi^{\mathrm{CGF}}(\mathbf{r_{b2}}) \right]. \tag{3}$$

The molecular orbitals in case of the oxygen molecule have been calculated in the unrestricted Hartree–Fock formalism (i.e., different spatial orbitals for electrons of α and β spin). This was necessary because O_2 is paramagnetic (on the last occupied orbital, 2p π_g, we have two electrons with the same orientation of the spin), and once the value of the magnetic spin quantum number of the molecule is fixed, the two spin directions are not equivalent. For each of the internal orbitals (2s σ_g, 2s σ_u, 2p σ_g, 2p π_u) we have considered separately the contributions from alpha and beta electrons. Using this approach we obtained an ionization potential of 11.20 eV, which is 7 percent smaller than the experimental value 12.04 eV.

In the calculations we have used the Gaussian 98 program package [11], with an STO-3G basis set [12]. Using this minimal basis set, only the 1s, 2s, and the three 2p atomic orbitals are considered for each of the two oxygen atoms. These basis functions are constructed as contractions of Gaussian primitives

$$\phi^{\mathrm{CGF}}(\mathbf{r}) = \sum_{p=1}^{L} d_p \phi_p^{\mathrm{GF}}(\alpha_p, \mathbf{r}r), \tag{4}$$

where L is the length of the contraction and d_p a contraction coefficient. The Gaussian primitives have

the general form

$$\phi^{\mathrm{GF}}(\alpha, \mathbf{r}) = N x^{l_x} y^{l_y} z^{l_z} e^{-\alpha\gamma^2 r^2}, \tag{5}$$

where the sum $l_x + l_y + l_z$ gives the angular momentum of the corresponding basis function, N is a normalization factor of the primitive and γ a scaling factor used to scale all the exponents in the related Gaussians. The normalization factor for a Gaussian primitive of an arbitrary angular momentum is given by

$$N = \left(\frac{2}{\pi}\right)^{3/4} \frac{2^{l_x+l_y+l_z}(\alpha\gamma^2)^{(2l_x+2l_y+2l_z+3)/4}}{[(2l_x-1)!!(2l_y-1)!!(2l_z-1)!!]^{1/2}}. \tag{6}$$

As described in our previous papers [9,10], in order to perform the angular integrals in the amplitude (2) analytically, the molecular orbital $\phi_r(\mathbf{r_2})$ is expanded in a Legendre series. The radial integral is performed numerically.

In the calculation of the total cross section, we must also integrate over the angles of the outgoing electron and positron as well as the energy of the ejected electron, as described in [13] for the atomic case.

3. Results and discussion

In Fig. 1 we present our direct ionization cross sections obtained with model CPE (the solid curve) together with the experimental data of the UCL group [7] and the Ps formation measurements from the Wayne State group [8]. This set of Ps formation measurements was considered as a lower limit on the true Ps formation cross sections [8]. It is interesting to note that both sets of experimental results show some structure at lower energies, a feature which was attributed to the coupling between the Ps formation and the excitation of O_2 by positron impact to the Schumann–Runge continuum [7]. The structure reported in the UCL experiment is wider than the structure seen in the Ps formation measurements and occurs at lower energies. These differences might be related to the addition in the UCL experiment of the coupling of the direct ionization channel, which at these impact energies is closed. Fig. 1 also shows that by adding our direct ionization cross sections to the lower limit set of Ps formation cross sections one obtains total ionization cross sections which agree well with the UCL data over the 17–26 eV interval. Note that while our direct
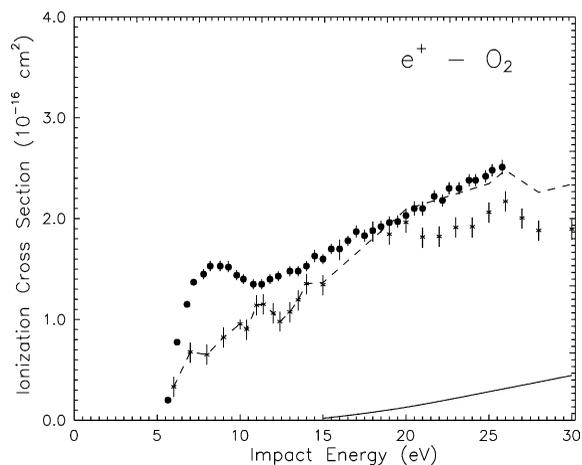
Fig. 1. Positron impact ionization of O_2 for low impact energies. The full circles correspond to the total ionization cross sections measured by Larrichia et al. [7], while the asterisks correspond to the lower limits of Ps formation as measured by the Wayne State group [8]. Our CPE results for direct ionization are represented by a continuous curve. The dashed curve corresponds to the addition of our CPE ionization cross sections to the Ps formation measurements from the Wayne State group.
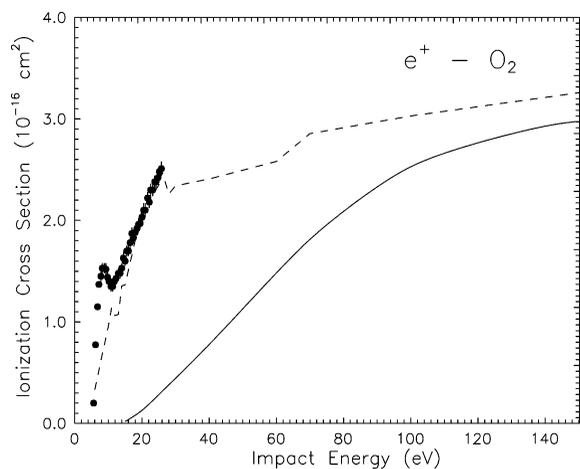

Fig. 2. Positron impact ionization of O_2 for intermediate impact energies. The experimental points and the curves are as in Fig. 1.

ionization CPE data were fitted with a spline curve, the dashed curve follows the structure corresponding to the Ps formation measurements.

Fig. 2 extends our theoretical data up to 150 eV. It would be interesting to see if our predictions can be confirmed by new direct ionization or total ionization measurements at higher energies.

4. Conclusions

This Letter utilizes the distorted-wave model CPE with a Gaussian wave representation for the molecular target to calculate positron impact direct ionization cross sections for O_2. Previously we have shown [9, 10] that this method can produce reliable data for positron ionization of H_2 and N_2. O_2 is a paramagnetic molecular target, which is sufficiently different from H_2 and N_2 to require a separate study.

Unfortunately to date there are no measurements of direct ionization for this molecular target. The comparison with the experiment can be done by using total ionization experimental data from UCL [7] and Ps formation measurements from the Wayne State group [8]. Also the range of impact energies for which the comparison can be made is quite small due to the fact that the UCL experiment obtained total ionization cross sections only for incident positrons slower than 26 eV. However, this Letter shows that our theoretical method can produce reliable data even for the more complex molecule O_2. The agreement between our direct ionization data together with the experimental Ps formations and the UCL total ionization data is quite impressive between 17–26 eV.

Our method can be extended readily to other complex molecules and we intend to examine other processes for which experimental data is available.

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