



# Positron impact ionization of CO and CO<sub>2</sub>

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## Abstract

We have applied our CPE distorted wave model using Gaussian target representations to the heteronuclear molecules CO and CO<sub>2</sub>. We found that this theoretical model works well for CO, but for CO<sub>2</sub> better agreement with experimental measurements is obtained in the “independent atoms” model.

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## 1. Introduction

Total cross sections for ionization by positrons have been measured for H<sub>2</sub> [1,2], N<sub>2</sub> [3], O<sub>2</sub> [4], CO [5], CO<sub>2</sub> [5,6] and for a number of organic molecules [7]. So far calculations for this process have been limited to homonuclear molecular targets using the distorted wave approach. Recent papers by Campeanu et al. [8–10] 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. We have applied this approach in the current study of positron impact ionization of CO and

CO<sub>2</sub> and have investigated the results obtained using a simple ‘independent atom’ model as well.

## 2. Theory

The calculational method for electron impact ionization of a homonuclear molecule has been described in detail elsewhere [8,9]. Below we give a brief description of the method and emphasize the differences of the present calculations for heteronuclear molecules from those previously applied to homonuclear diatomic molecules.

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

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

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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. The summation over  $r$  is done over all occupied molecular orbitals. The amplitude can be written as

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

where  $\phi_i$  and  $\phi_f$  stand for the wavefunction of the incident and scattered positron respectively,  $\phi_e$  is the wavefunction of the ejected electron, while  $\phi_r$  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.

In our previous work [8,9] we found that our CPE model gave reliable results for positron impact ionization of homonuclear diatomic molecules. The CPE model [11] 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 wavefunctions 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 [11]. 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.

We have used Gaussian wavefunctions for the description of the ground state of the CO and CO<sub>2</sub> molecules with a basis set of 3 basis functions as described in [8,9].

In the case of CO the following molecular orbitals have been considered for the ionization process:  $\sigma_{2s}$ ,  $\sigma_{2s}^*$ ,  $\pi_{2p_x}$ ,  $\pi_{2p_y}$  and  $\sigma_{2p_z}$ . These orbitals are analogous to those of the N<sub>2</sub> molecule without the symmetries characteristic of the orbitals of a homonuclear molecule.

The  $\sigma$  orbitals are written as a linear combination of the C and O atomic orbitals

$$\phi_{\sigma_r}(\mathbf{r}_2) = C_O\phi_O^r(\mathbf{r}_2^O) + C_C\phi_C^r(\mathbf{r}_2^C), \quad (3)$$

$\mathbf{r}_2^O$  and  $\mathbf{r}_2^C$  being the electron coordinates relative to the O and C nuclei, respectively.  $\phi_O^r$  and  $\phi_C^r$  are  $sp_z$  hybrid orbitals obtained from Gaussian wavefunctions.

We expand these orbital as previously [8] in terms of Legendre polynomials

$$\phi_{\sigma_r}(\mathbf{r}_2) = \sum_{l_b} c_{l_b}^r(r_2, R) P_{l_b}(\cos \omega_2), \quad (4)$$

where  $\omega_2$  stands for the angle between  $\mathbf{r}_2$  and  $\mathbf{R}$ , the latter being the molecular axis. The expansion coefficients can be expressed with the following integral

$$c_{l_b}^r(r_2, R) = \frac{2l_b + 1}{2} \int_{-1}^{+1} d(\cos \omega_2) P_{l_b}(\cos \omega_2) \phi_{\sigma_r}(\mathbf{r}_2). \quad (5)$$

In order to separate the angular dependencies on the position of the electron and the orientation of the molecular axes, the Legendre polynomial is expanded in terms of spherical harmonics

$$P_{l_b}(\cos \omega_2) = \frac{4\pi}{2l_b + 1} \sum_{m_b} Y_{l_b m_b}^*(\hat{\mathbf{R}}) Y_{l_b m_b}(\hat{\mathbf{r}}_2). \quad (6)$$

By this method we have expressed the  $\sigma$  molecular orbital as a sum of products of a one-center (atomic) wavefunctions characterized by an angular momentum  $l_b$  and a spherical harmonic expressing the dependence on the orientation of the molecular axes

$$\phi_{\sigma_r}(\mathbf{r}_2) = \sum_{l_b m_b} \frac{4\pi}{2l_b + 1} c_{l_b}^r(r_2, R) Y_{l_b m_b}(\hat{\mathbf{r}}_2) Y_{l_b m_b}^*(\hat{\mathbf{R}}). \quad (7)$$

As described in [9], the method for  $\pi$  orbitals is slightly different, because they do not have spherical symmetry. Performing the expansion one obtains

$$\begin{aligned} \phi_{\pi}(\mathbf{r}_2) = & \sum_{l_b m_b} \sqrt{\frac{3}{2l_b + 1}} \sum_{\lambda} c_{\lambda}^r(r_2, R_0) C_{\lambda 0 1 0}^{l_b 0} C_{\lambda 0 1 m}^{l_b m_b} \\ & \times \sum_{\mu} Y_{l_b \mu}(\hat{\mathbf{r}}_2) D_{\mu m_b}^{l_b}(\alpha, \beta, \gamma), \end{aligned} \quad (8)$$

where  $C_{\lambda 0 1 m}^{l_b m_b}$  are the usual Clebsch–Gordan coefficients and  $D_{\mu m_b}^{l_b}(\alpha, \beta, \gamma)$  stands for the matrix element of the rotation operator which rotates the molecular frame through the Euler angles  $(\alpha, \beta, \gamma)$  into the laboratory frame.

In the usual experimental setup the orientation of the molecule in the laboratory frame is not detected, and for comparison with experiment we have to average the cross section over the angles of the molecular axis (1). By this procedure, taking into account

the orthogonality properties of the spherical harmonics (for  $\sigma$  orbitals) and of the rotation operator matrix elements (for  $\pi$  orbitals), the differential cross section may be written as a sum of cross sections characterized by a certain angular momentum of the initial state

$$\frac{d^3\sigma_{AV}}{d\hat{\mathbf{k}}_f d\hat{\mathbf{k}}_e dE_e} = \sum_r \sum_{l_b m_b} \frac{(2\pi)^4}{E_i} |f_r^{l_b m_b}|^2. \quad (9)$$

In the expression above we have denoted by  $f_r^{l_b m_b}$  the partial scattering amplitude for orbital  $r$  with the angular momentum of the initial state characterized by  $l_b$  and  $m_b$ .

The method for the linear and symmetric triatomic molecule,  $\text{CO}_2$ , is similar. In the case of  $\text{CO}_2$  the molecular axis  $R$  corresponds to the distance between the two oxygen atoms, which is about twice as long as the internuclear distance in  $\text{CO}$  (4.4 a.u. versus 2.16 a.u.). For this molecule the valence orbitals taken into account in the ionization calculation are  $3\sigma_g$ ,  $2\sigma_u$ ,  $4\sigma_g$ ,  $3\sigma_u$ ,  $1\pi_u$  and  $1\pi_g$ .

### 3. Results and discussion

Because  $\text{CO}$  does not have the symmetry of the previously studied homonuclear molecules, every term in the expansion over the angular momentum  $l_b$  makes a contribution to the ionization of each orbital (with the exception of the  $\pi$  orbital, which has no contribution for  $l_b = 0$ ). It is interesting to analyze the contribution from each orbital and each angular momentum  $l_b$  to the total cross section. Tables 1 and 2 list these contributions for two different impact energies, 100 eV and 1000 eV, respectively.

Taking into account only the  $l_b = 0$  term is equivalent to the spherical averaging of the wavefunction which was used in [12]. For the ionization of  $\text{H}_2$  this averaging did not introduce an appreciable error but in the case of  $\text{CO}$  terms with  $l_b > 0$  contribute significantly to the total cross section. Also, the relative contribution of different  $l_b$  terms vary with the impact energy. At higher energies the contributions from larger  $l_b$  values gain in importance as is evident in the comparison of the results in Tables 1 and 2. In addition, at the lower impact energy (100 eV) the contribution of the various orbitals to the total cross section increases with the decrease of the ionization potential

Table 1  
Contributions to the ionization cross section of  $\text{CO}$  at 100 eV

Orbital	$l_b$				Total orbital
	0	1	2	3	
$\sigma_{2s}$	0.28	0.03	0.04	$3 \times 10^{-4}$	0.35
$\sigma_{2s}^*$	0.08	0.32	0.11	$3 \times 10^{-5}$	0.51
$\pi_{2p_x} + \pi_{2p_y}$	0	0.64	0.008	0.04	0.69
$\sigma_{2p_z}$	1.10	0.13	0.27	0.001	1.50
Total $l_b$	1.46	1.12	0.43	0.04	3.05

Table 2  
Contributions to the ionization cross section of  $\text{CO}$  at 1000 eV

Orbital	$l_b$				Total orbital
	0	1	2	3	
$\sigma_{2s}$	0.39	0.45	1.07	0.03	1.95
$\sigma_{2s}^*$	0.39	0.64	0.50	0.005	1.54
$\pi_{2p_x} + \pi_{2p_y}$	0	1.34	0.09	0.48	1.91
$\sigma_{2p_z}$	1.34	0.22	0.96	0.004	2.53
Total $l_b$	2.13	2.66	2.62	0.52	7.93

Table 3  
Contributions to the ionization cross section of  $\text{CO}_2$  at 100 eV

Orbital	$l_b$				Total orbital
	0	1	2	3	
$3\sigma_g$	0.394	0	0.178	0	0.572
$2\sigma_u$	0	0.279	0	0.005	0.284
$4\sigma_g$	0.072	0	0.347	0	0.419
$3\sigma_u$	0	0.721	0	0.165	0.886
$1\pi_u$	0	2.66	0	0.043	2.703
$1\pi_g$	0	0	0.94	0	0.94
Total $l_b$	0.466	3.66	1.465	0.213	5.804

Table 4  
Contributions to the ionization cross section of  $\text{CO}_2$  at 1000 eV

Orbital	$l_b$				Total orbital
	0	1	2	3	
$3\sigma_g$	0.044	0	0.365	0	0.409
$2\sigma_u$	0	0.049	0	0.339	0.388
$4\sigma_g$	0.007	0	0.318	0	0.325
$3\sigma_u$	0	0.117	0	0.17	0.287
$1\pi_u$	0	0.862	0	0.047	0.909
$1\pi_g$	0	0	0.263	0	0.263
Total $l_b$	0.051	1.028	0.946	0.556	2.581

characteristic to the orbital, while at the higher impact energy (1000 eV) the influence of the ionization potential on the contribution is less important.

A similar analysis is done in Tables 3 and 4 for  $\text{CO}_2$ . As explained previously for the  $\text{N}_2$  molecule [9], in the expansion on  $l_b$  for gerade orbitals only the terms with even  $l_b$  are nonzero, while for ungerade orbitals only orbitals with odd  $l_b$  contribute. Moreover, the first nonzero contribution of the  $\pi_g$  orbital occurs for  $l_b = 2$ , the  $l_b = 0$  term being zero for orbitals with this symmetry.

As expected for a long molecule such as  $\text{CO}_2$ , the contribution of the  $l_b = 0$  term is very small even for small impact energies. A notable feature is the big contribution coming from the  $1\pi_u$  molecular orbital. This term contributes almost a half of the total cross section.

Figs. 1 and 2 show our total ionization cross sections results compared with the experimental measurements of Bluhme et al. [5]. We did not plot the  $\text{CO}_2$  measurements of Larichia and Moxom [6] as they correspond to impact energies below 25 eV. Fig. 1 shows that the CPE model produces very good agreement between our theoretical data and experimental data for CO. However, for  $\text{CO}_2$  the CPE model results are nearly 50% above the experimental measurements as shown in Fig. 2.

Given that the CPE model produces reliable results for smaller, diatomic molecules, the likely reason for the disagreement for  $\text{CO}_2$  is the fact that while the initial wavefunction is a multicentered function, the final state has been described by a Coulomb function centered at the origin. A possible solution would be to represent the ejected electron as a coulomb multicentered function, but that would make the calculations much more difficult. Here we have tried a simpler approach, the “independent atoms” CPE model. In this model the cross sections for ionization of each of the constituent atoms has been calculated separately within the CPE approximation [11], 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. In the “independent atoms” model the wavefunctions of the initial state and the final state have the same center of reference since we move the center of each atom to the origin of the coordinate system. The results of the “independent atoms” CPE model, included in Fig. 2, are in better agreement with the experimental data than the molecular CPE calculations for impact energies higher than 100 eV.

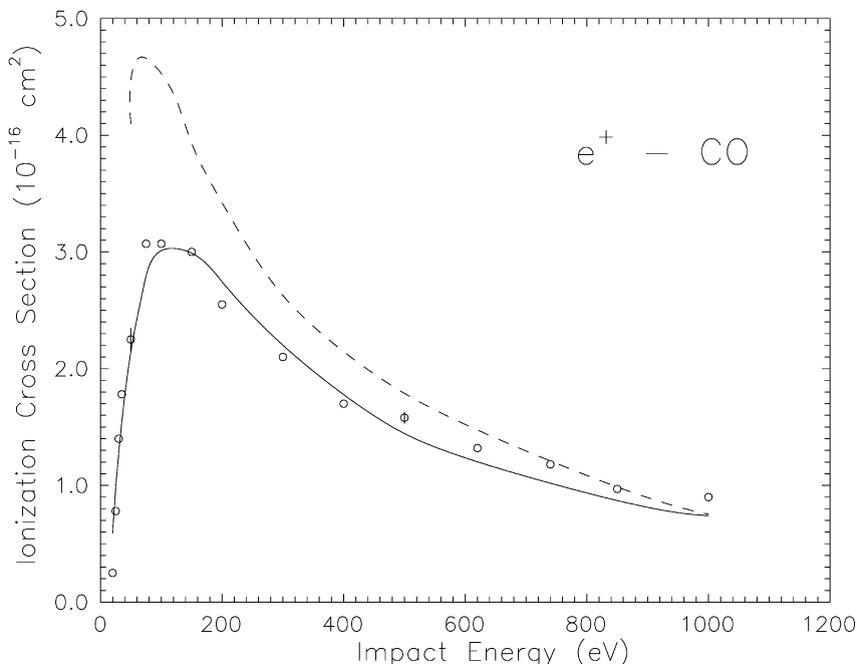


Fig. 1. Total cross sections for positron impact ionization of CO as a function of the positron impact energy. The experimental points are from Blume et al. [5]. Our molecular and independent atoms CPE model results are represented by the continuous and dashed curves, respectively.

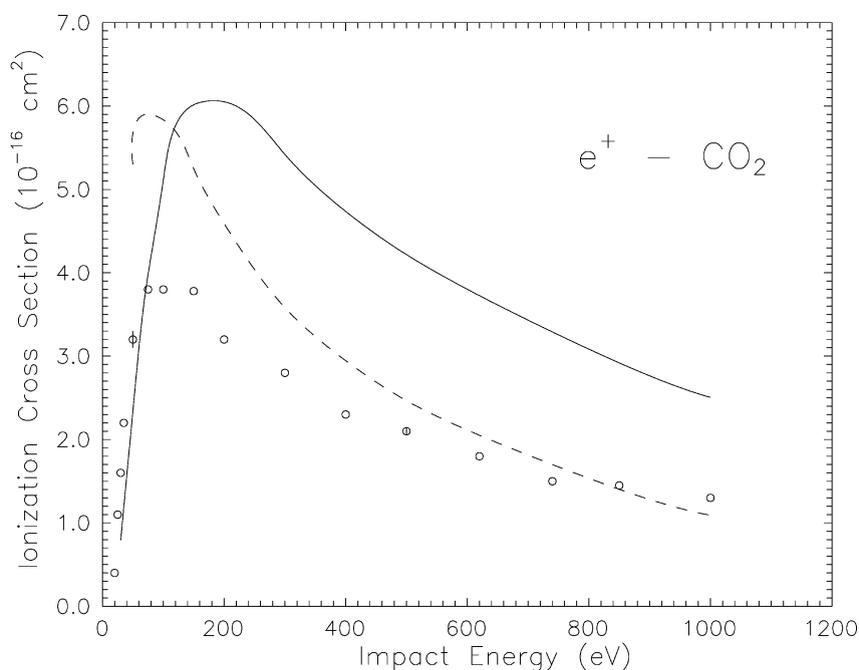


Fig. 2. As for Fig. 1 but for the positron impact ionization of CO<sub>2</sub>.

In order to check the validity of the “independent atoms” model we have also applied this to the ionization of CO. Fig. 1 shows that in this case the independent atoms model gives results which for impact energies above 200 eV are slightly higher than the molecular model but still in reasonable agreement with the experiment. For impact energies lower than 200 eV the independent atoms model produces ionization cross sections which are much higher than the molecular model and the experimental results.

Looking at the two figures it is interesting to observe the similarity in the shape of the “independent atoms” model curves and in their agreement with the experiment. This is not the case with the molecular model curves and we gave above an explanation on why our CO<sub>2</sub> molecular model results are not as accurate as in the CO case.

#### 4. Conclusions

Our calculations indicate that our simple CPE ionization model using Gaussian representations of the molecular targets works not only for homonuclear but also for heteronuclear diatomic molecules, such as

CO. For the larger CO<sub>2</sub> molecule, where the CPE molecular model appears to break down, better results for impact energies higher than 100 eV are obtained with an “independent atoms” CPE approximation. In the case of CO the “independent atoms” model produces ionization cross sections which, particularly for energies lower than 200 eV, are in worse agreement with the experiment than the molecular model. Further study is required to determine whether these outcomes apply more generally to other molecular systems.

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