Electronic excitation of CO by positron impact

Euclimar P. da Silva
Departamento de Física, Universidade Federal do Ceará, 60455-760 Fortaleza, Ceará, Brazil

Márcio T. do N. Varella and Marco A. P. Lima
Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas (UNICAMP), 13083-970 Campinas, São Paulo, Brazil
(Received 10 May 2005; published 21 December 2005)

We report calculated cross sections for the electronic excitation of carbon monoxide by positron impact. The calculations were carried out with the Schwinger multichannel method and included six collision channels, namely the ground ($X\ ^1\Sigma^+$) and five electronically excited ($A\ ^1\Pi$, $I\ ^1\Sigma^-$ and $D\ ^1\Delta$) states. Present calculated excitation cross sections to the $A\ ^1\Pi$ state did not present any resonant features, being in this sense consistent with previous calculations for the isoelectronic nitrogen molecule. The experimental $a\ ^1\Pi_g$ excitation cross section of N_2 presented a resonantlike structure which would also be expected in the $A\ ^1\Pi$ excitation of CO. We discuss possible reasons for the disagreement between experiment and theory.

DOI: 10.1103/PhysRevA.72.062715 PACS number(s): 34.85.+x, 34.50.Fa, 34.50.Gb

I. INTRODUCTION

The development of high resolution ($\Delta E \sim 25$ meV FWHM) beam of positrons using the highly efficient buffer-gas positron accumulation technique (modified Penning-Malmberg trap) helped further the study of positron physics [1–3]. The bright low-energy monochromatic positron beam allows experimentalists to perform highly sophisticated scattering experiments where measurements of state-resolved absolute cross sections for electronic or vibrational excitations are possible. This experimental breakthrough finds useful applications in several other areas such as material science, atomic physics, plasma physics, and mass spectroscopy [4]. Moreover, they serve as a strong motivation for the theorists to extend their calculations to investigate in more detail the finer aspects of the scattering process in order to better understand the experimental findings and the underlying physical facts.

Recently, Surko and his collaborators performed a series of highly precise experiments on the electronic excitation of Ar, CO_2, H_2, and N_2 in the energy range from 5 to 30 eV [2]. Perhaps the most interesting experimental finding was a striking near-threshold enhancement in the $a\ ^1\Pi_g$ excitation cross section of nitrogen. Even though the authors did not discuss the nature of the observed structure, the fact that it may be a core-excited shape resonance is quite relevant [5]. Even though vibrational Feshbach resonances have been observed in low-energy positron collisions against polyatomics [6], it is generally accepted that the inherent repulsive nature of the static positron-target interaction seems to prevent the formation of legitimate shape resonances [7]. As a matter of fact, *ab initio* e^+-N_2 scattering calculations [8–10] did not reproduce the conspicuous resonant-like structure and the reasons for such discrepancy between theory and experiment are not well understood.

It should be recalled, however, that the occurrence of electron-molecule shape resonances is often associated with a low-lying virtual orbital leading to a metastable ion state. The incident electron may be trapped either in the field of the target ground state (potential scattering shape resonance) or in the field of some excited parent state (core-excited shape resonance). As a result, molecules with similar electronic structures usually present similar resonant features. This is indeed the case of the isoelectronic nitrogen and carbon monoxide molecules, whose electronic structures differ mostly due to the heteronuclear character of the latter. Both systems present well-known $^2\Pi$ shape resonances in the electronically elastic scattering channel associated with the virtual 2π orbitals. Since such analogy is not restricted to electron scattering, positron-impact excitation of carbon monoxide turns out to be a very attractive problem. In principle, a core-excited shape resonance noticeable in e^+-N_2 collisions could also be expected to occur in the e^+-CO system. We have therefore taken up the task of investigating the electronic excitation of CO theoretically, closely following the procedure used in previous work on nitrogen [8,9].

II. THEORY

We have calculated cross sections for the electronic excitation of CO to the $A\ ^1\Pi$, $I\ ^1\Sigma^-$, and $D\ ^1\Delta$ states by positron impact using the Schwinger multichannel method (SMC). Formal aspects of this approach are discussed in detail elsewhere [11–13]. Hence, we present no details here, but a few working expressions for the sake of completeness. The scattering amplitude is given by

$$f_{\vec{k}_i\vec{k}_f} = -\frac{1}{2\pi}\sum_{m,n}\langle S_{\vec{k}_f}|V|\chi_m\rangle(d^{-1})_{mn}\langle\chi_n|V|S_{\vec{k}_i}\rangle \tag{1}$$

where

$$d_{mn} = \langle\chi_m|A^{(+)}|\chi_n\rangle, \tag{2}$$

and

$$A^{(+)} = Q\hat{H}Q + PVP - VG_P^{(+)}V. \tag{3}$$

In the above expressions, $S_{\vec{k}_i}$ is a solution of the unperturbed Hamiltonian (molecular Hamiltonian plus the kinetic energy operator for the incident positron); V is the interaction poten-

tial between the incident positron and the molecular target; $|\chi_m\rangle$ is a *configuration* state, i.e., an $(N+1)$-particle variational trial function (the product of a target state and a positron scattering orbital). P and Q are, respectively, projection operators onto energetically open and closed electronic states of the target,

$$P = \sum_{l}^{open} |\Phi_l(\vec{r}_1, \ldots, \vec{r}_N)\rangle\langle\Phi_l(\vec{r}_1, \ldots, \vec{r}_N)|, \tag{4}$$

with

$$Q = 1 - P. \tag{5}$$

Finally, $\hat{H}$ is the collision energy minus the full scattering Hamiltonian and $G_P^{(+)}$ is the free-particle Green's function projected onto P space.

In the present implementation of the method, the target ground state is described with a single-determinant Hartree-Fock (HF) wave function. On the other hand, excited states are given by linear combinations of singly excited determinants, the so-called single-excitation configuration interaction (CIS) approximation. As a result, the SMC scattering wave function is written as

$$\Psi_{\vec{k}_i}^{(+)} = \sum_k c_{0k}^{(+)} \Phi_0 \varphi_k^0 + \sum_{m=1}^{N_{open}} \sum_n c_{mn}^{(+)} \Phi_m \varphi_n^m + \sum_{p>N_{open}} \sum_q c_{pq}^{(+)} \Phi_p \varphi_q^p, \tag{6}$$

with

$$\Phi_j = \sum_{\alpha=1}^{N_{as}} a_{j\alpha} \phi_\alpha, \quad j \geqslant 1. \tag{7}$$

In the expressions above, Φ_i are targets states, $i=0$ being the ground state, φ_j^i are positron scattering orbitals, $c_{ij}^{(+)}$ are variational coefficients, while N_{open} and N_{as} are, respectively, the number of energetically open electronic collision channels and the dimensions of the active space used in CIS expansions. In Eq. (7), ϕ_α are singly excited Slater determinants, $a_{j\alpha}$ are the variational coefficients of the CIS calculation, and the products $\Phi_i\varphi_{ij}$ correspond to the configurations denoted by χ_m in Eq. (1). The first term in the right-hand side of Eq. (6) is the so-called static approximation, in which the target is kept frozen in the ground state. Excited open collision channels are included in the second term, while the third accounts for polarization effects (closed-channel or Q space). Excited states belonging to the P (open-channel) space are always described with the CIS approximation, according to Eq. (7), while those belonging to the Q space may be described at either improved-virtual-orbital (IVO) [15] or CIS levels.

If the trial basis set is able to expand the interaction region (that is, if $\Sigma_m|\chi_m\rangle\langle\chi_m| \simeq 1$ where V is nonzero), the wave function in Eq. (6) would be expected to accurately describe correlation effects (polarization, virtual positronium formation), electronic excitation, and competition among open and closed collision channels. However, the truncated free-particle Green's function, $G_P^{(+)}$ in Eq. (3), cannot account for the positronium (Ps) formation channel, which is neglected in the present implementation of our theory.

TABLE I. Cartesian Gaussian basis set $\chi_{lmn}^{(\alpha)} = N_{lmn}(x-A_x)^l \times (y-A_y)^m (z-A_z)^n \exp(-\alpha|\vec{r}-\vec{A}|^2)$.

Center	Type	Exponent
C	s	5240.6353, 782.2048, 178.35083, 50.815942, 16.823562, 6.175776, 2.418049, 0.511900, 0.156590, 0.05, 0.02
C	p	18.84180, 4.159240, 1.206710, 0.385540, 0.121940, 0.045, 0.01
C	d	1.50, 0.75, 0.30
O	s	10662.285, 1599.7097, 364.72526, 103.65179, 33.905805, 12.287469, 4.756803, 1.004271, 0.300686, 0.10, 0.03
O	p	34.856463, 7.843131, 2.308269, 0.723164, 0.214882, 0.06, 0.02
O	d	1.70, 0.85, 0.34
CM[a]	s	0.010, 0.003
CM	p	0.09, 0.03, 0.01
CM	d	0.9, 0.3

[a]Chargeless dummy center placed on the center of mass.

III. COMPUTATIONAL ASPECTS

The Cartesian Gaussian basis set used for both bound state and scattering calculations are presented in Table I. It is a $[11s/7p]$ variant of a basis set given by Dunning [14], also being similar to the basis set used by Lima [16]. The unoccupied orbitals were calculated within the IVO framework [15] (out of the 5σ orbital). The ground state HF wave function provided an electronic energy of −135.292 802 Hartree. The nuclei were held fixed at the experimental equilibrium distance of the ground state ($R=2.132a_0$) [17] throughout the collision (fixed-nuclei approximation). Due to limitations in the computer codes, the molecule was treated as belonging to the C_{2v} point-group symmetry.

We have performed six-channel ($6C$) calculations including excitations to the $A\ ^1\Pi$, $I\ ^1\Sigma^-$, and $D\ ^1\Delta$ states, plus the elastic channel, $X\ ^1\Sigma^+$. In CIS expansions, the active space was composed by $5\sigma \rightarrow 2\pi_{x,y}$ and $1\pi_{x,y} \rightarrow 2\pi_{x,y}$ single excitations. Calculated excitation thresholds are shown in Table II along with experimental results [19]. We mention in passing that the somewhat large discrepancy observed for the $A\ ^1\Pi$ threshold (13.1%) is well understood. Due to the reduced active space, only one single excitation is found to

TABLE II. Excitation thresholds (in eV) for the six-state CIS approximation.

State	Experiment	CIS
$A\ ^1\Pi$ [18]	8.4	9.5
$I\ ^1\Sigma^-$ [19]	9.9	9.9
$D\ ^1\Delta$ [19]	10.5	10.3

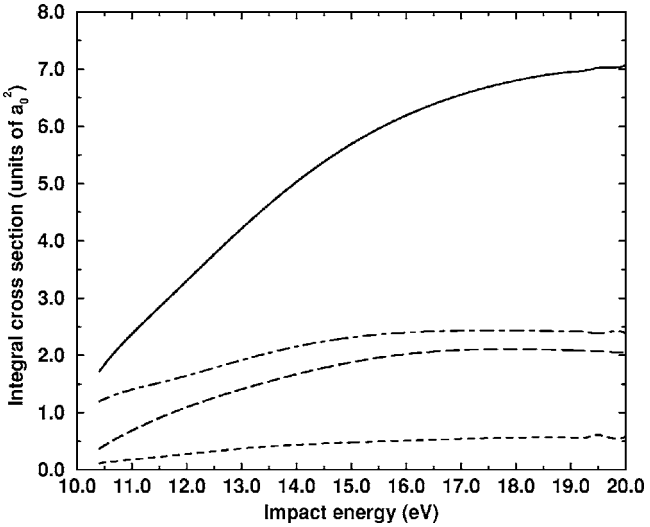

FIG. 1. Integral cross section for the electronic excitation to the $A\ ^1\Pi$ state of CO by positron impact. Solid line: Total cross section (summed over all symmetries). Also shown are the partial cross sections. Short dashed line, $^2\Sigma$ symmetry; dotted-dashed line, $^2\Pi$ symmetry; long dashed line, $^2\Delta$ symmetry.

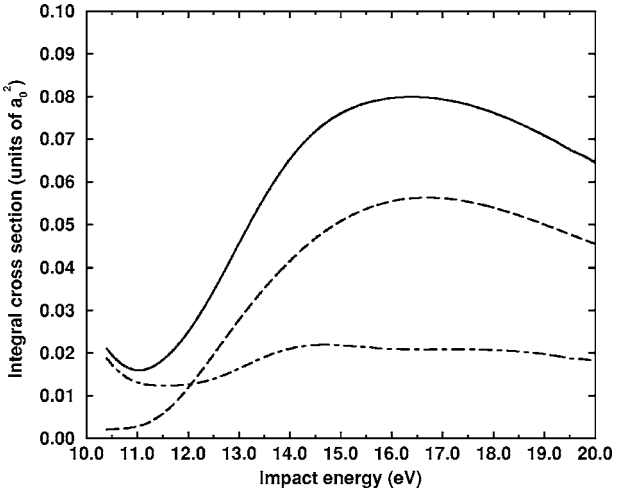

FIG. 2. Integral cross section for the electronic excitation to the $I\ ^1\Sigma^-$ state of CO by positron impact. Solid line: Total cross section (summed over all symmetries). Also shown are the partial cross sections. Dotted-dashed line, $^2\Pi$ symmetry; long dashed line, $^2\Delta$ symmetry.

contribute to each degenerate component of the $A\ ^1\Pi$ state. As a result, the CIS expansion is equivalent to the IVO approximation (for $A\ ^1\Pi_{x,y}$ states only). In previous calculations for N_2 [8,9], it was necessary to take linear combinations of $3\sigma_g$ and $4\sigma_g$ orbitals in order to well reproduce the experimental electronic excitation spectrum. The HF approximation is known to give rise to an overly compact $3\sigma_g$ orbital for nitrogen because the interaction that pushes $2\sigma_u$ and $3\sigma_g$ orbitals apart from each other is missing due to the symmetry constrain [20]. As a result, $3\sigma_g$ and $1\pi_u$ orbitals become interchanged. Fortunately, this drawback does not occur in the CO molecule because its heteronuclear character allows proper interaction between 4σ and 5σ orbitals (these are equivalent to $2\sigma_u$ and $3\sigma_g$ in nitrogen, respectively).

IV. RESULTS AND DISCUSSION

In previous publications [8,9] the occurrence of spurious (numerical) resonantlike structures in SMC calculations was discussed. In short, they may take place due to nearly linear-dependent configurations in the variational trial set, which lead to very small potential matrix elements, $\bar{V}_{mn} = \langle\chi_m|(PVP+Q\hat{H}Q)|\chi_n\rangle$. Once the d_{mn} matrix in Eq. (2) has to be inverted according to Eq. (1), these nearly zero matrix elements give rise to numerical resonances (bumps) in the scattering amplitude. Fortunately, this problem can be overcome by removing the troublesome configurations, as described in Refs. [8,9]. Essentially, an advantage is taken from the fact that only spurious resonances survive in the first Born approximation (FBA), thus allowing the identification of physical resonances. In present 6*C* calculations, such numerical features were found in the excitation cross sections to the $I\ ^1\Sigma^-$ and $D\ ^1\Delta$ states. These were successfully removed and the higher partial waves of the resulting scattering amplitudes were improved by combining the SMC approach ($l \leqslant 2$) with the FBA ($l \geqslant 3$) [8,9] for the the $A\ ^1\Pi$ and $D\ ^1\Delta$ states. The $I\ ^1\Sigma^-$ state was calculated only with the SMC approach ($l \leqslant 5$) since the FBA does not contribute in this case.

In Figs. 1–3, we present integral excitation cross sections to the $A\ ^1\Pi$, $I\ ^1\Sigma^-$, and $D\ ^1\Delta$ states, respectively. The symmetry decomposition of the cross sections is also shown. The structure noticed around 19.5 eV in the cross sections is due to the threshold of an extra collision channel. Out of six states composing the CIS active space, only five were treated as open channels (counting the degeneracies of $A\ ^1\Pi$ and $D\ ^1\Delta$ states). The sixth electronic state was always treated as belonging to Q space, even though it should be open above

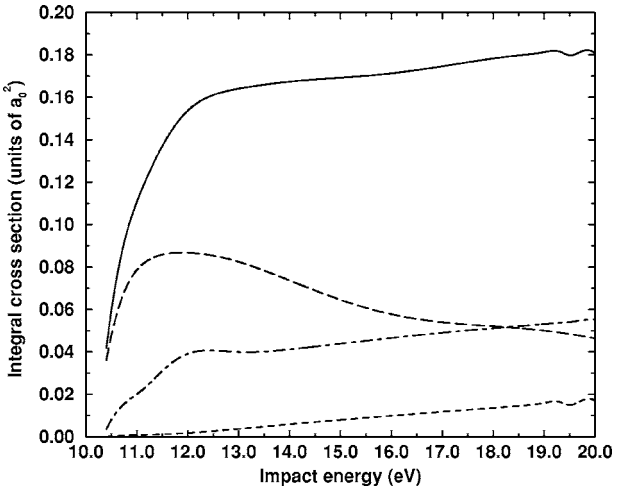

FIG. 3. Integral cross section for the electronic excitation to the $D\ ^1\Delta$ state of CO by positron impact. Solid line: Total cross section (summed over all symmetries). Also shown are the partial cross sections. Short dashed line, $^2\Sigma$ symmetry; dotted-dashed line, $^2\Pi$ symmetry; long dashed line, $^2\Delta$ symmetry.

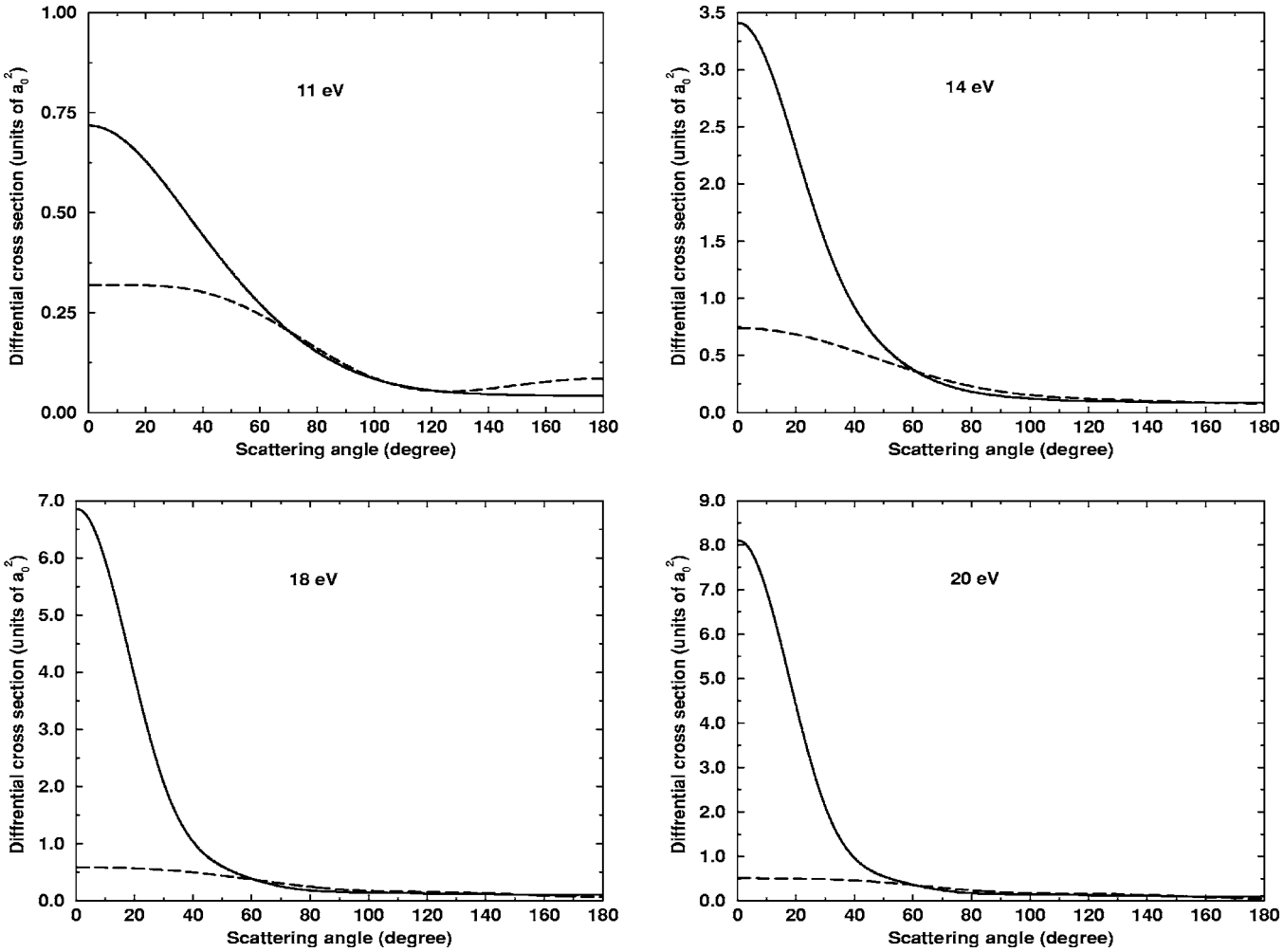

FIG. 4. Differential cross sections for the electronic excitation to the $A\ ^1\Pi$ state of CO by positron impact at 11, 14, 18, and 20 eV. Long dashed line, present results without the closure procedure (SMC only); solid line, present relsults with the closure procedure (SMC +FBA).

19 eV. The most relevant feature noticed in the present results is the structureless $A\ ^1\Pi$ excitation cross section. This behavior is consistent with previous calculations for N_2 [8,9], but it again raises the question about the nature of the near-threshold structure observed in the experimental $a\ ^1\Pi_g$ excitation cross section of nitrogen. From the theoretical standpoint, it could be claimed that present calculations (as well as those for N_2) do not take nuclear motion and the Ps formation channel into account. However, the presence of an extra electronic channel (namely, Ps formation) would either shorten the resonance lifetime, if it was strongly coupled to the resonant state, or hardly affect the resonance, if the coupling was weak. As a result, the Ps formation channel would not be expected to give rise to a core-excited shape resonance. In a similar fashion, nuclear motion should also broaden resonant features due to the inclusion of vibrational excitation (or dissociation) exit channels. Such resonance broadening associated with the improvement of fixed-nuclei cross sections is always observed in electron scattering calculations. In this sense, the absence of resonances in our calculations should not be credited to the lack of vibrational motion.

A question could also be raised about the role of polarization effects, poorly described in our calculations. In principle, polarization effects would be expected to shift (towards lower energies) core-excited shape resonances already noticed in close-coupling calculations, but not to give rise to such resonances. On the other hand, further inclusion of closed channels could give rise to Feshbach resonances, which would not be present in simple close-coupling calculations. This would be a plausible explanation for the discrepancy between theory and experiment, but it is not possible to come to a conclusion about the origin of the near-threshold enhancement in the electronic excitation of nitrogen based on our results. In addition, the experimental structure seems rather broad (>1 eV) in comparison with the widths observed in electron-scattering Feshbach resonances (typically, fractions of eV [21]), and the present level of description of the Q space does not allow the assignment of a parent state. On the other hand, our structureless cross sections could be understood on the basis of the interplay between polarization effects and Ps formation, in case the experimental feature was related to the latter, since the Ps formation threshold leading to a $^2\Pi$ ion is 10.2 eV [20].

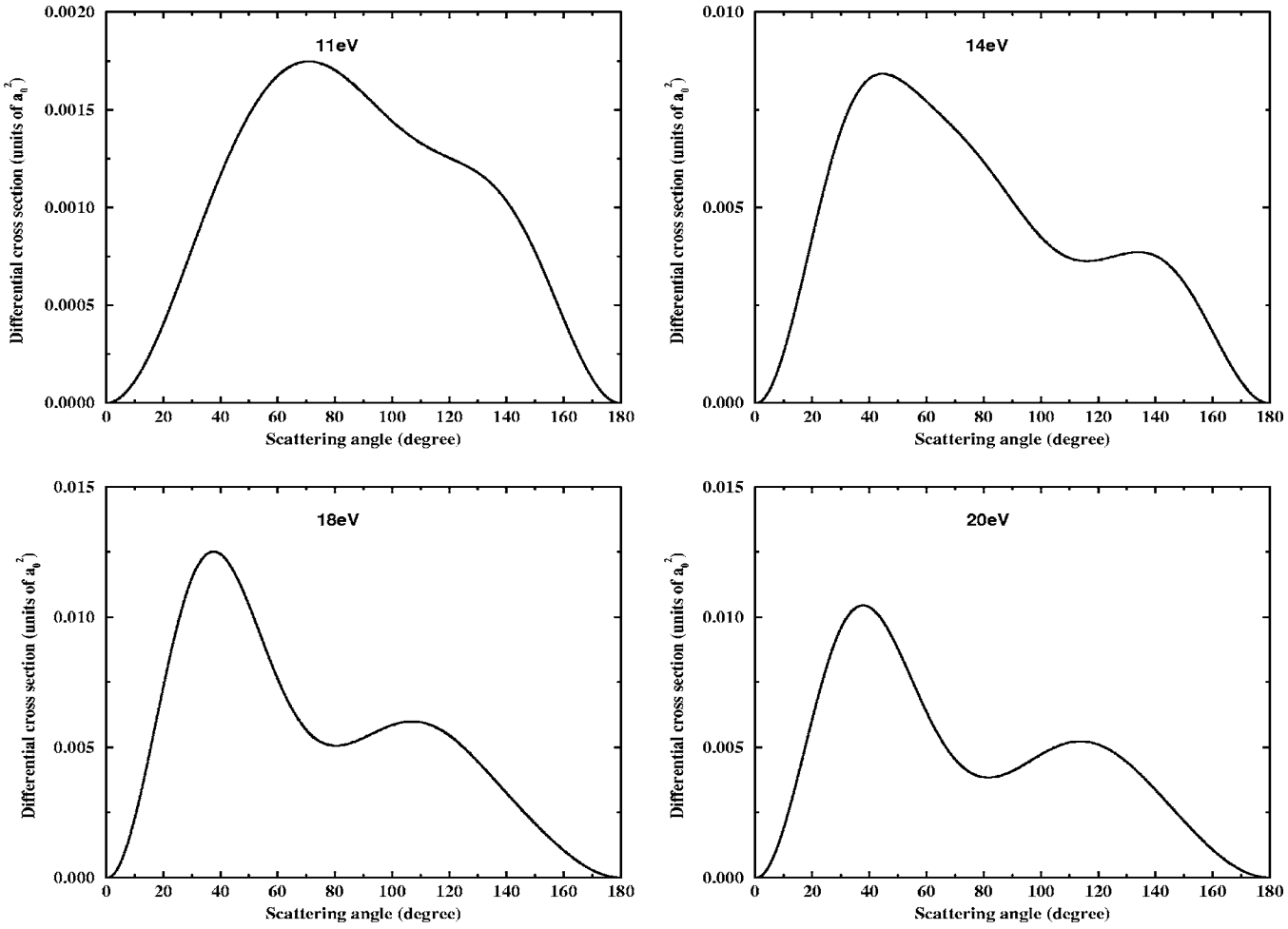

FIG. 5. Differential cross sections for the electronic excitation to the $I\ ^1\Sigma^-$ state of CO by positron impact at 11, 14, 18, and 20 eV. Solid line: present results without the Born closure (SMC only).

Though the experimental points are somewhat sparse, hindering a more precise assignment of the location of the feature, the $a\ ^1\Pi_g$ excitation cross section seems to peak between 10 and 11 eV [2]. Hence, it is possible that virtual Ps formation could enhance the cross section just below the threshold, and that loss of probability (to the Ps channel) could then make it smaller above the threshold. Such behavior would not be observed in our close-coupling calculations because the lack of polarization does not allow a proper description of virtual Ps. If this picture is correct, improving the closed-channel space would not remedy the absence of flux in the Ps channel above the threshold, but it would be expected to describe the rise of the cross section below the Ps threshold. For carbon monoxide, the Ps formation threshold associated with a $^2\Pi$ ion is also very close to 10.2 eV [20], and the same behavior would be expected in the excitation to the $A\ ^1\Pi$ state.

Finally, we mention in passing that the broad structure in the excitation cross section to the $I\ ^1\Sigma^-$ state (Fig. 2) should not be assigned to a resonance. Besides being rather broad, such a structure has a very small magnitude and should be strongly affected by the inclusion of polarization effects. Finally, we present in Figs. 4–6 the related differential cross sections (DCS) at selected energies for the sake of completeness. In Figs. 4 and 6 comparison is made between DCS obtained with and without the closure procedure, in which higher partial waves are calculated with the FBA [8,9]. At low scattering angles, where the contribution of higher partial waves is expected to be more important, there is remarkable improvement.

V. CONCLUSIONS

We have reported calculations for positron-impact excitation to the $A\ ^1\Pi$, $I\ ^1\Sigma^-$, and $D\ ^1\Delta$ states of CO. Present six-channel calculations resulted in structureless cross sections for excitation to the $A\ ^1\Pi$ state, which is consistent with previous calculations for N_2. Our results do not elucidate the origin of the structure experimentally observed in the $a^1\Pi_g$ excitation cross section of nitrogen, a feature that would also be expected in the $A\ ^1\Pi$ channel of CO. Since the inclusion of extra competing collision channels should not give rise to resonances, we do not expect that the absence of Ps formation and vibrational excitation channels would be responsible for the lack of near-threshold structures in our results. On the other hand, a thorough description of polarization effects could give rise to such structures if they were resonant in nature or related to the onset of Ps formation associated with $^2\Pi$ ions. The inclusion of polarization effects (through a

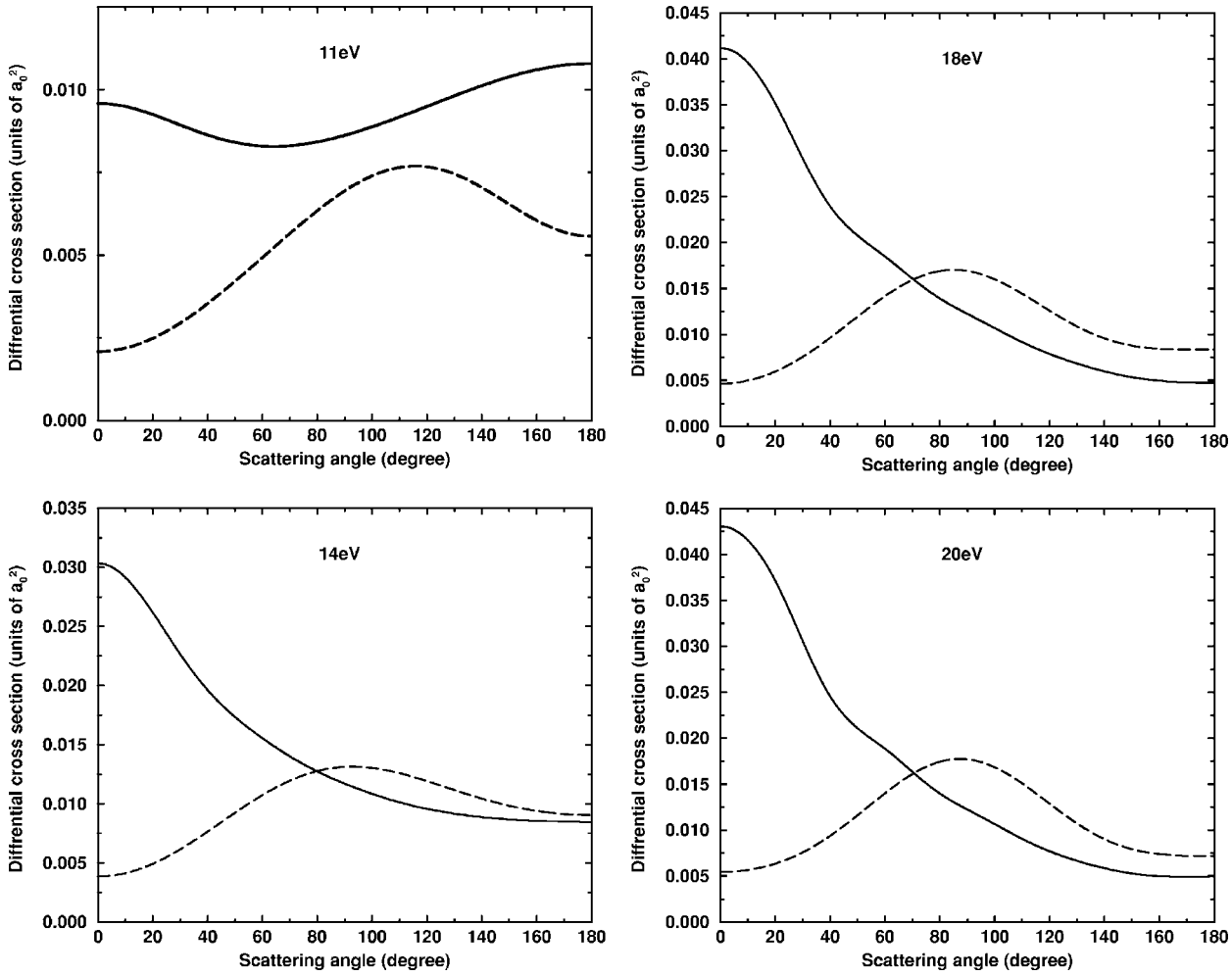

FIG. 6. Differential cross sections for the electronic excitation to the $D\ ^1\Delta$ state of CO by positron impact at 11, 14, 18, and 20 eV. Long dashed line, present results without the closure procedure (SMC only); solid line, present results with the closure procedure (SMC+FBA).

large Q space with virtual excitations out of the 2π orbital) is presently under way in our group, in order to check this assumption.

ACKNOWLEDGMENTS

This work was supported by the Brazilian agencies FAPESP and CNPq. Our calculations were performed at CENAPAD-SP. The authors would like to thank Professor Cliff Surko and Professor Stephen Buckman for discussions on virtual positronium formation during the XIII Workshop on Low-Energy Positron and Positronium Physics Workshop, 27-30 July 2005, held in Campinas, São Paulo, Brazil.

[1] S. J. Gilbert, J. P. Sullivan, R. Greaves, and C. M. Surko, Nucl. Instrum. Methods Phys. Res. B **171**, 81 (2000).

[2] J. P. Sullivan, J. P. Marler, S. J. Gilbert, S. J. Buckman, and C. M. Surko, Phys. Rev. Lett. **87**, 073201 (2001).

[3] J. P. Sullivan, S. J. Gilbert, and C. M. Surko, Phys. Rev. Lett. **86**, 1494 (2001).

[4] C. M. Surko, *New Directions in Antimatter Chemistry and Physics* (Kluwer Academic, Dordrecht, 2001), pp. 345–366.

[5] In electron scattering the terminology *Feshbach resonance* usually refers to a core-excited metastable ion whose energy lies below that of the parent state, while *core-excited shape resonance* to a metastable ion lying above its parent (see Ref. [21] below). Though the repulsive positron-molecule static potential is known to hinder shape resonances in elastic scattering, we keep the same terminology here to refer to the relative energies of the temporary ion and of the excited parent state of the neutral molecule. Note, however, that the parentage of core-excited ions often have mixed character (linear combination of configurations associated with open and closed parent states).

[6] S. J. Gilbert, L. D. Barnes, J. P. Sullivan, and C. M. Surko, Phys. Rev. Lett. **88**, 043201 (2002); *ibid.* **88**, 079901(E) (2002).

[7] J. P. Sullivan, S. J. Gilbert, S. J. Buckman, and C. M. Surko, J. Phys. B **34**, L467 (2001).

[8] P. Chaudhuri, M. T. do N. Varella, C. R. C. de Carvalho, and

M. A. P. Lima, Nucl. Instrum. Methods Phys. Res. B **221**, 69 (2004).
[9] P. Chaudhuri, Márcio T. do N. Varella, C. R. C. de Carvalho, and M. A. P. Lima, Phys. Rev. A **69**, 042703 (2004).
[10] T. N. Rescigno (private communication).
[11] J. S. E. Germano and M. A. P. Lima, Phys. Rev. A **47**, 3976 (1993).
[12] E. P. da Silva, J. S. E. Germano, and M. A. P. Lima, Phys. Rev. A **49**, R1527 (1994); Phys. Rev. Lett. **77**, 1028 (1996).
[13] E. P. da Silva, J. S. E. Germano, J. L. S. Lino, C. R. C. de Carvalho, A. P. P. Natalense, and M. A. P. Lima, Nucl. Instrum. Methods Phys. Res. B **143**, 140 (1998).
[14] T. H. Dunning, Jr., J. Chem. Phys. **53**, 5716 (1978).
[15] W. J. Hunt and W. A. Goddard III, Chem. Phys. Lett. **24**, 464 (1974).
[16] M. A. P. Lima, Ph.D. thesis, 1986, California Institute of Technology.
[17] J. Rose, T. Shibuya, and V. Mckoy, J. Chem. Phys. **58**, 74 (1973).
[18] V. Meyer, A. Skerbele, and E. Lassettre, J. Chem. Phys. **43**, 805 (1965).
[19] G. Herzberg, T. Hugo, S. Tilford, and J. Simmons, Can. J. Phys. **48**, 3004 (1970).
[20] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (McGraw-Hill, New York, 1989), pp. 194–197.
[21] G. J. Schulz, Rev. Mod. Phys. **45**, 423 (1973).