Electronic excitation of N_2 by positron impact

Puspitapallab Chaudhuri, Márcio T. do N. Varella, Claudia R. C. de Carvalho, and Marco A. P. Lima
Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas (UNICAMP), 3083-970 Campinas, São Paulo, Brazil
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We present cross sections of electronic excitation of nitrogen molecule (N_2) by positron impact using the Schwinger multichannel method. Our calculated cross sections are compared with the recent and the only available experimental data of Sullivan *et al.* [Phys. Rev. Lett. **87**, 073201 (2001)]. Present theoretical results for excitation to the $a\ ^1\Pi_g$ states do not reproduce the near-threshold structure observed in the experimental data.

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I. INTRODUCTION

The interaction of positron with matter has long been a subject of intense research in the fields of both experimental and theoretical atomic and molecular physics. However, in the last decade, with the availability of highly efficient buffer-gas positron accumulation technique (Penning-Malmberg trap) [1] and new innovative developments in trap based beams [1,2] it is now possible to create cold, bright low-energy monochromatic positron beam. This high resolution ($\Delta E \sim 25$ meV full width at half maximum) [1] beam of positrons can be utilized to perform highly sophisticated scattering experiments where measurements of state-resolved absolute cross sections for electronic, or vibrational, excitations are realizable with much accuracy. These new techniques and subsequent measurements of cross sections besides being directly applicable in various other areas serve as a strong motivation for the theorists to extend their calculations to explore specific areas of atomic and molecular interaction with matter.

One such specific area is the excitation of electronic states of molecules by positron impact. Theoretical studies on the electronic excitation of molecules are limited. To our knowledge, there are reported results only for H_2 [3,4] and N_2 [5]. Nitrogen has an important application in experimental physics as it is widely used as an effective buffer gas in Penning traps in order to cool and capture positrons. Highly energized positrons coming out of a radioactive source lose energy in the trap by means of inelastic collisions with nitrogen molecules [6]. These low-energy positrons are then used in a variety of areas such as material science, atomic and molecular physics, and plasma physics [6]. A theoretical investigation on the electronic excitation of N_2 is essential to understand the physical mechanism of this important trapping process in positron accumulators. Moreover, the measurements of absolute cross sections for these states might, in turn, enhance the modeling capabilities of efficient positron traps [7].

Recently, Sullivan *et al.* [1] reported, for the first time, measurements of absolute cross sections for the positron impact excitation to the $a'\ ^1\Sigma_u^-$ and $a\ ^1\Pi_g$ states of N_2. They found a striking near-threshold enhancement in the $a\ ^1\Pi_g$ excitation cross section which strongly encourages a more detailed investigation. Even though the authors did not discuss the nature of the observed structure, the fact that it may be a core-excited shape resonance (i.e., a shape resonance associated with an excited state) is quite relevant. Positron scattering resonances have been elusive [8], except for the N_2 experimental data under discussion. However distinct vibrational Feshbach resonances have recently been observed in positron annihilation in molecules [9]. Resonances in positron-atom (or molecule) scattering are expected to be rare due to the nature of the positron-target interaction. While modern techniques have provided suitable positron beams to find possible resonances, the repulsive character of the static interaction potential seems to prevent the formation of a legitimate resonant state. We recently reported a three-channel calculation for the excitation to the $a\ ^1\Pi_g$ states [5] which did not reproduce the near-threshold (possibly resonant) structure observed in the experimental data [1]. Nevertheless, this calculation was rather crude since it disregarded important dynamical aspects, such as the distortion of the target due to the positron field (polarization effects) and the existence of open excited collision channels other than the $a\ ^1\Pi_g$ states. Moreover, the excited states were described through the improved-virtual-orbital (IVO) approximation [10], unable to provide a fair description of excitation thresholds. In this paper, we present a more elaborate *ab initio* theoretical calculation of the $a\ ^1\Pi_g$ excitation cross section of N_2, aiming to elucidate the origin of the experimentally observed prominent structure.

II. THEORY

In the present work we have used the Schwinger multichannel method (SMC) for positrons. The method has been discussed quite elaborately in several previous publications [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

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

with

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

In the above expressions, $S^-_{k_{i,f}}$ is a solution of the unperturbed Hamiltonian (molecular Hamiltonian plus the kinetic energy operator for the incident positron), V is the interaction potential between the incident positron and the molecular target, and $|\chi_m\rangle$ 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 $(P+Q=1)$; $\hat{H}$ is the collision energy minus the full scattering Hamiltonian; and $G_P^{(+)}$ is the free-particle Green's function projected onto P space.

III. COMPUTATIONAL ASPECTS

The Cartesian Gaussian basis set used for both bound state and scattering calculations was given previously [14], without any contraction. The ground state of the target was described through the single-determinant Hartree-Fock (HF) framework, while the IVO approximation (out of the $3\sigma_g$ orbital) was used for unoccupied orbitals. The nuclei were held fixed throughout the collision (fixed-nuclei approximation). In this work we addressed six-channel (6C) calculations including excitation to the $a'\ ^1\Sigma_u^-$, $a\ ^1\Pi_g$, and $w\ ^1\Delta_u$ states, plus the elastic (ground state) channel. In our previous work [5], $a\ ^1\Pi_g$ excited states were obtained by promoting an electron to IVO particle orbitals. However, both $a'\ ^1\Sigma_u^-$ and $w\ ^1\Delta_u$ states can only be described through linear combinations of singly excited Slater determinants (apart from spin) and it is therefore unlikely to obtain a fair description of the N_2 spectrum in the IVO fashion. Hence, we improved the SMC computational codes to describe excited states of the target by means of linear combinations of singly excited states, the so-called single-excitation configuration-interaction (CIS) approximation. In this new version, the SMC scattering wave function is written as

$$\Psi^{(+)}_{\tilde{k}_i} = P\Psi^{(+)}_{\tilde{k}_i} + Q\Psi^{(+)}_{\tilde{k}_i} = \sum_{m=0}^{N_{open}} \sum_n c^{(+)}_{mn}\Phi_m\varphi^m_n + \sum_{p>N_{open}} \sum_q c^{(+)}_{pq}\Phi_p\varphi^p_q, \quad (4)$$

with

$$\Phi_j = \sum_{\alpha=1}^{N_{as}} a_{j\alpha}\phi^j_\alpha, \quad j \geqslant 1. \quad (5)$$

In Eq. (4), Φ_i are target states, φ^i_j are positron scattering orbitals, $c^{(+)}_{kl}$ are variational coefficients, and N_{open} is the number of energetically open electronic collision channels. The ground state of the target (Φ_0) is given by a single Slater determinant. The open excited states (P space), on the other hand, are described by linear combinations of singly excited Slater determinants (ϕ^j_α), according to Eq. (5). N_{as} is the dimension of the active space used in the CIS expansion and $a_{j\alpha}$ are the related coefficients. The closed excited states of the target (Q space) may be described in either way (single-determinant or CIS approximation) or by a combination of both. In the calculations performed, we set $N_{as}=6$, with five states belonging to the open-channel (P) space and one to the closed-channel (Q) space. The active space was composed by $3\sigma_g \rightarrow 1\pi_{gx,y}$ and $1\pi_{ux,y} \rightarrow 1\pi_{gx,y}$ single excitations, giving rise to $a'\ ^1\Sigma_u^-$, $a\ ^1\Pi_g$, and $w\ ^1\Delta_u$ excited states.

By direct use of IVO orbitals, the thresholds were quite poor and the $3\sigma_g^1 1\pi_g^1$ ($a\ ^1\Pi_g$) and $1\pi_u^1 1\pi_g^1$ ($a'\ ^1\Sigma_u^-$ and $w\ ^1\Delta_u$) states were interchanged [5,14]. Unfortunately, CIS expansions (we have used $N_{as}=6,32,48$) were not able to overcome this problem, leading to an $a\ ^1\Pi_g$ threshold lying above the $w\ ^1\Delta_u$ one. It is opportune to observe that the HF approximation spuriously packs the $3\sigma_g$ orbital of N_2. As a result, the $1\pi_u$ becomes the highest occupied orbital, thus overestimating the ionization potential of the $^2\Sigma$ ion [15]. Our result (namely, the interchange between $a\ ^1\Pi_g$ and $w\ ^1\Delta_u$ thresholds) is indeed related with a too compact $3\sigma_g$ orbital. A straight solution for this problem would be a large CI calculation, including at least double excitations. However, such procedure could not be carried out with our current computational codes. We thus tried to improve the electronic spectrum of the molecule by manually mixing the occupied $3\sigma_g$ orbital with the unoccupied $4\sigma_g$ one, obtaining mixed orbitals of the kind

$$3\sigma_g' = c_1 3\sigma_g \pm c_2 4\sigma_g, \qquad 4\sigma_g' = \pm c_2 3\sigma_g - c_1 4\sigma_g, \quad (6)$$

where c_1 and c_2 are mixing coefficients. This comes out to be a simple but effective compromisation between computational cost and labor of calculation and qualitative accuracy of the results. The net effect of the mixing is to make the occupied $3\sigma_g$ orbital more diffuse. The choices of the mixing coefficients and of the sign convention are of course arbitrary. For each sign convention, we made several attempts taking linear combinations of the two orbitals in different proportions setting an error margin of ±3 % with respect to the experimental excitation thresholds and thereby obtained different sets of mixed orbitals. All trial choices lead to similar cross sections in exploratory scattering calculations and we selected $c_1=\sqrt{0.90}$ and $c_2=\sqrt{0.10}$ as the working values. The different sign conventions, on the other hand, are not equivalent because they imply qualitatively different charge densities for the target. We therefore decided to work with three different basis sets: namely, unmixed HF orbitals (HFO), which are simply the original $3\sigma_g$ and $4\sigma_g$ orbitals ($4\sigma_g$ is actually an IVO); mixed bonding orbitals (BO), given by the upper sign convention in Eq. (6); and mixed antibonding orbitals (ABO), given by the lower sign convention in Eq. (6). The excitation thresholds and ionization potentials for different orbital sets are given in Table I.

IV. RESULTS AND DISCUSSION

In a previous paper [5], we called attention to the fact that simple SMC close-coupling calculations, in which the configuration space is composed by a few excited states without properly describing the polarization effects and the competi-

TABLE I. Excitation thresholds (ET) and ionization potentials (IP) in units of eV. HFO, BO, and ABO indicate different orbital sets (see text). The $^2\Sigma$ and $^2\Pi$ ion states are obtained by removing one electron from $3\sigma_g$ and $1\pi_u$ orbitals, respectively.

	ET			IP	
	$a'\ ^1\Sigma_u^-$	$a\ ^1\Pi_g$	$w\ ^1\Delta_u$	$^2\Sigma$	$^2\Pi$
Experiment	8.399	8.549	8.890	15.6	17.0
HFO	8.608	10.347	9.178	17.3	16.8
ABO	8.701	8.769	9.272	15.9	17.3
BO	8.613	8.721	9.184	17.3	19.7

tion among collision channels, could be affected by spurious numerical resonances. In short, the underlying mechanism leading to such spurious structures would be as follows. In some configurations associated with diffuse scattering orbitals, the positron would be far from the target, leading to very small potential matrix elements, $V_{mn}=\langle\chi_m|V|\chi_n\rangle$. Since the d_{mn} matrix, given in Eq. (2), must be inverted according to Eq. (1), these nearly zero matrix elements give rise to numerical resonances (bumps) in the scattering amplitude. In order to overcome such problem, we developed a technique to remove the troublesome configurations. It may be outlined as follows (details are given elsewhere [5]).

(i) By switching off the polarization effects ($Q\hat{H}Q$) and the second-order term $VG_P^{(+)}V$ in Eq. (3), the SMC provides a basis-set representation of the first Born approximation (FBA). Usually, the spurious resonances show up in the basis-set FBA. (As a matter of fact, no physical resonance should be noticed in the FBA.)

(ii) By diagonalizing the V_{mn} matrix, the configurations weakly coupled by the potential (that is, the eigenvectors of V_{mn} associated with small eigenvalues) may be sorted out and removed from the configuration space. In practice, the weakly coupled eigenvectors are taken out until a fairly good agreement between basis-set FBA and actual FBA scattering calculations is achieved.

(iii) Basis-set FBA scattering calculations performed with such reduced configuration spaces become free of spurious resonances, but the comparison with actual FBA calculations is hindered by a poor description of higher partial waves ($l \geqslant 3$). A closure procedure, in which the lower partial waves ($l \leqslant 2$) are obtained with the basis-set FBA procedure and the higher ones come from actual FBA calculations, turned out to be an efficient way for overcoming this problem [5].

(iv) For the SMC calculation, however, we diagonalized the operator $\bar{V}_{mn}=PVP+Q\hat{H}Q$ because the configurations belonging to the Q space would give rise to zero eigenvalues if the latter term was neglected.

To check numerical instabilities of the SMC method, we have removed configurations corresponding to near-zero eigenvalues of $\bar{V}$. Note, however, that $\bar{V}$ depends on energy through $\hat{H}$ and this would produce an energy dependent basis set. To avoid this, we have used a fixed value of energy for selection of the configuration space (corresponding to a $\hat{H}$ with an impact energy of 21 eV—an energy above the studied energy range 9.5–20 eV). To study a possible dependence on the choice of the $\hat{H}$ energy in $\bar{V}$, we have also carried out a calculation using a fixed energy of 9 eV (an energy just below the studied energy range) and found no difference between the results obtained with the two choices. Below we present only the set of results corresponding $\bar{V}$ configurations obtained with the fixed impact energy of 21 eV. The closure procedure was also used to improve higher partial waves ($l \geqslant 3$).

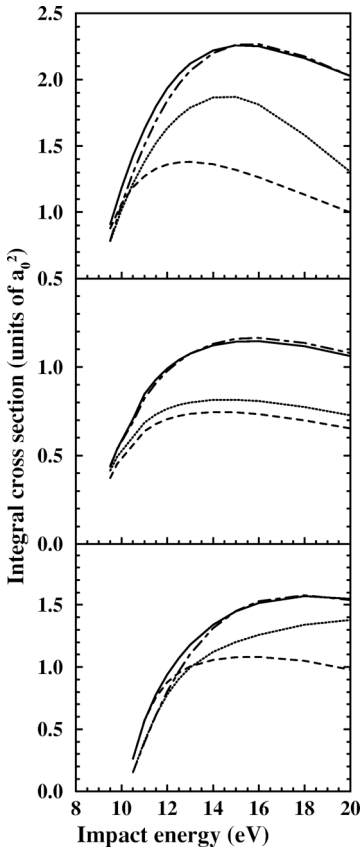

FIG. 1. Integral cross section for the excitation to the $a\ ^1\Pi_g$ states of N_2 by positron impact. Results obtained with different orbital sets are presented in different panels. Lower panel, HFO; central panel, ABO; and upper panel, BO. In each panel, the legend is as follows: dotted line, CUT1 calculation; dashed line, CUT2 calculation; dot-dashed line, CUT1+closure calculation; and solid line, CUT2+closure calculation.

Spurious resonances were indeed observed in present 6C calculations. For each orbital set (HFO, BO, and ABO) configurations were taken out according to two thresholds (all configurations with eigenvalues—absolute values—below this threshold were eliminated). The first one, hereafter referred to as CUT1, was chosen to remove only the troublesome configurations. The second one (CUT2) removed some extra configurations in order to allow a stability check. In Fig. 1 we present the calculated excitation cross section to the $a\ ^1\Pi_g$ states. For each orbital set, we show four different sets of calculations: CUT1, CUT2, CUT1+closure, and CUT2+closure. It is clear that CUT1 and CUT2 calculations provide similar cross sections near threshold, though some discrepancy is observed at higher energies. This is due to the

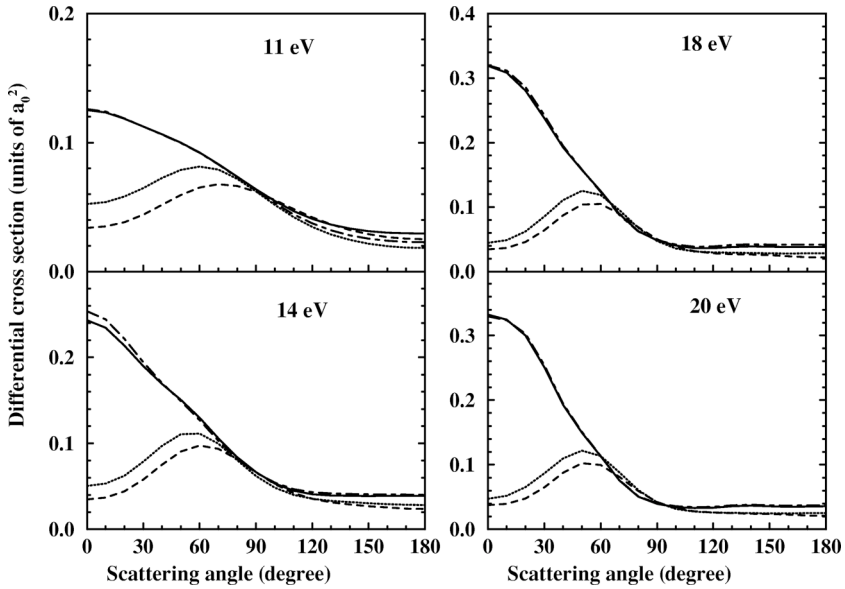

FIG. 2. Differential cross section for the excitation to the $a\ ^1\Pi_g$ states of N_2 by positron impact. Dotted lines, CUT1 calculation; dashed lines, CUT2 calculation; dot-dashed lines, CUT1+closure calculation; and solid lines, CUT2+closure calculation.

description of higher partial waves as revealed by the agreement between CUT1+closure and CUT2+closure calculations (and also by partial cross sections). This picture is confirmed by Fig. 2 where the corresponding differential cross sections (DCS), obtained with the ABO set are presented. (Though not shown here, HFO and BO sets present similar behavior.) At higher scattering angles ($\theta > 90°$), all approximations are fairly close to one another. In the vicinity of the forward scattering direction, on the other hand, higher partial waves become important and the closure procedure plays an important role. Even though CUT1 calculations always provide better cross sections at low scattering angles (as expected), there is significant contribution from the closure procedure in all cases. Hence, multichannel SMC calculations carried out with both thresholds are equivalent, if combined with the FBA. (In fact, the agreement is more than reasonable even without the closure procedure.) This is quite relevant because it indicates that spurious resonances may be removed without compromising the variational stability of scattering calculations.

Our results (CUT1-closure) are compared with experimental data of Ref. [1] in Fig. 3. In view of the arbitrary mixing of $3\sigma_g$ and $4\sigma_g$ orbitals it is a hard task to decide which orbital set is the most reliable. In view of its accurate excitation thresholds and ionization potentials (see Table I), the ABO set seems to be closer to the actual electronic density of N_2 molecule. Nevertheless, the most important feature of Fig. 3 is the fact that cross sections obtained with the three orbital sets are qualitatively similar. Even though some discrepancy in magnitude is noticed, no calculation was able to reproduce the experimental near-threshold structure. Our calculations (BO and ABO) provide a fair description of the collision dynamics in the sense that it includes all electronic states that are open around 11 eV, where the experimental structure is observed. The ordering of the states in the molecular spectrum is also correct and the excitation thresholds are in very good agreement with experiment. Moreover, the ionization potentials of the ABO set also agree with experimental values (see Table I). On the other hand, present calculations neglect the positronium formation channel and also lack of a thorough description of polarization effects. (Present elastic cross sections are far from the elastic-scattering calculation of Ref. [14] in which about 30 000 configurations were used to account for the distortion of the target during the collision.) While it is possible that polarization and positronium formation could affect the collision dynamics thus making the scattering potential attractive enough to bear a core-excited shape resonance, we point out that no excitation threshold is found around 11 eV. Usually, core-excited shape resonances (as well as Feshbach resonances) are associated with ion states with energies lying very close to the related parent (neutral) states. As a result, it seems

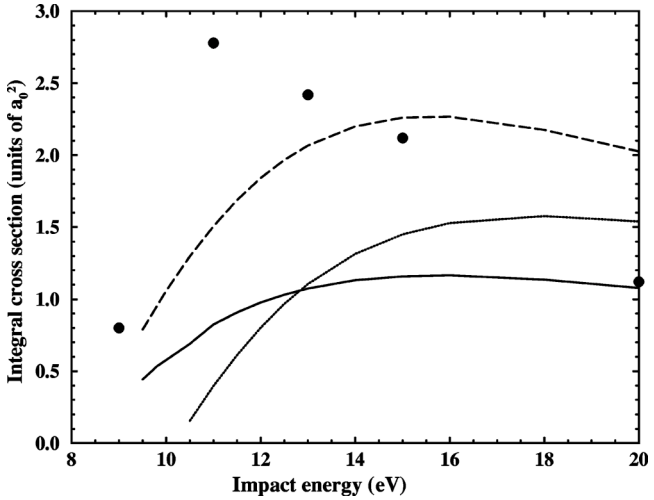

FIG. 3. Integral cross section for the excitation to the $a\ ^1\Pi_g$ states of N_2 by positron impact. Dotted line, HFO calculation; dashed line, BO calculation; solid line, ABO calculation; and bullets, experimental data of Ref. [1].

unlikely to find a N_2^+ state lying close to 11 eV. Finally, we observe that excitation cross sections to $a'\ ^1\Sigma_u^-$ and $w\ ^1\Delta_u$ states are not presented because our computational codes are not currently able to perform FBA calculation for CIS target states. (The $a\ ^1\Pi_g$ states may be described through single excitations and the related FBA calculations were carried out in this fashion.)

V. CONCLUSIONS

We have presented excitation cross sections to the $a\ ^1\Pi_g$, $a'\ ^1\Sigma_u^-$, and $w\ ^1\Delta_u$ states of N_2 Our 6C calculations took advantage of the CIS approximation in order to improve the molecular spectrum. However, our results did not reproduce the near-threshold (11 eV) enhancement observed in the experimental excitation cross section to the $a\ ^1\Pi_g$ states [1]. In fact, spurious resonances were observed in our calculations, but this was remedied by removing configurations weakly coupled by the scattering potential. In fact, analysis of the electronic excitation spectrum indicates that a core-excited shape resonance associated with the $a\ ^1\Pi_g$ states is not likely to take place.

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