

Vibrational excitation by positron collisions with molecular gases: a study of O₂ and NO targets

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Abstract. The scattering of slow positrons from O₂ and NO molecules is treated using exact static interactions and a model potential for correlation-polarisation forces. The quantum coupled equations for the elastic scattering are extended to vibrationally inelastic processes and the different excitation probabilities are evaluated. Comparison with existing experiments for the NO target indicates that the present calculations provide a realistic treatment of positron scattering below Ps formation and give computational estimates on the efficiency of such projectiles in producing vibrationally excited molecules in the ambient gas.

PACS. 34.50.Gb Electronic excitation and ionization of molecules; intermediate molecular states (including lifetimes, state mixing, etc.) – 34.80.Bm Elastic scattering of electrons by atoms and molecules

1 Introduction

At nonrelativistic velocities ($v \ll c$) the interaction of a positron with an electron or with a nucleus can be accurately represented by the Coulomb potential. Apart from the opposite sign of the interaction, the slow collisions of positrons with the electronuclear components of a stable molecule differ from those of an electron at least in two respects. Firstly, as the particles are different, the total wave function within a Born-Oppenheimer (BO) picture of the molecule with the nuclei held fixed in space (FN approximation) needs not be antisymmetrical and therefore there are no exchange terms in the final scattering amplitude. Secondly, the electron-positron pair can annihilate (subject to certain selection rules) into two emitted photons. In principle, this absorptive process modifies the potential acting between the electron and the positron by the addition of a positive imaginary part, but since the annihilation cross-section is much smaller than the cross-sections associated with characteristic molecular scattering, this modification of the Coulomb potential can be ignored.

When the collision processes are studied at energies which are low enough to be below the Positronium (Ps) formation energy for the target system, one could analyse the quantum dynamics of positron-molecule scattering by chiefly considering the consequences of the Coulomb potential as the main source of interaction.

Experiments involving the decay of positrons in atomic and molecular gases [1–3] are usually described as evolving through three distinct periods. The mean life associated with the first of them is very short and corresponds to the order of time in which an energetic positron slows down to energies below the ionization threshold of the ambient gas. The second is associated with a lifetime of the order which is expected when free annihilation into two photons occurs. The last period is usually much longer and corresponds to a mean lifetime of about 10^{-7} s. It is related to the slow three-photon decay of orthopositronium and is found to be practically independent of the ambient gas pressure.

It is therefore clear from the foregoing discussion that, at collision energies below the first excitation threshold of the gaseous molecules and also below the threshold for Ps formation, the annihilation rates of monoenergetic beams of positrons which are scattered from a container of gaseous molecular targets is chiefly controlled by the total wave function which describes elastic scattering of positrons by the ambient gas. The measurements of such quantities, and the development of the corresponding theoretical and computational tools, constitute our main source of information on the physics of positrons in molecular studies.

On the other hand, while the studies on atomic gases have a very long and detailed history [1, 2], the corresponding analysis of molecular systems is fairly recent and still coming from a more limited range of experiments [3, 4]. It therefore becomes increasingly more important to be able to provide theoretical models and computational procedures which can help us to obtain both the relevant wave

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functions and the corresponding cross-sections at the simpler level of the purely elastic processes. In the case of molecular targets an additional question, which would be useful to be able to answer, is the possible effect of vibrational excitation processes on the size of those “elastic” cross-sections where neither Ps formation nor annihilation are as yet processes of relevant size.

In the present work we have tried to answer some of the above questions in the case of polyelectronic diatomic targets for which, to our knowledge, no previous calculations exist nor computational attempts have been made before to include the dynamical coupling of the positron projectile with the molecular vibrational degrees of freedom. The following section briefly outlines our theoretical model for the interaction forces and for the vibrational dynamical coupling between the positron and a linear polyelectronic molecule. Section 3 presents our computational results and discusses their implications in the case of O₂ and NO as molecular targets. Section 4 summarizes our conclusions.

2 Interaction and dynamics

To describe the scattering of positrons by a vibrating molecule in its electronic ground state, one has to solve the familiar Schrödinger equation

$$(\mathcal{H} - E)\Psi = 0, \quad (1)$$

subject to the usual scattering boundary conditions. Here \mathcal{H} and Ψ are the total Hamiltonian and the total wave function of the electrons, nuclei and positron which constitute the system and E is the fixed total energy at which the process is meant to occur.

The expansion of this Hamiltonian and of the total wave function in terms of the total molecular Hamiltonian and of the molecular eigenfunctions plus the scattering positron depends now on the type of coupling scheme one wishes to employ (*e.g.*, see: M.A. Morrison [5]). In a Body-Fixed (BF) frame of reference one can write the total Hamiltonian as

$$\begin{aligned} \mathcal{H}^{\text{BF-VCC}} = & \mathcal{H}(\mathbf{r}_p) + \mathcal{H}_{\text{el}}(\mathbf{r}_e) + \mathcal{H}_{\text{vib}}(\mathbf{R}) \\ & + V_{\text{p-mol}}(\mathbf{r}_p, \mathbf{r}_e, \mathbf{R}), \end{aligned} \quad (2)$$

where \mathbf{r}_p is the scattering positron coordinate measured from the center of mass of the system, \mathbf{r}_e collectively denotes the molecular electronic coordinates and \mathbf{R} is the internuclear set of coordinates of the molecule. $\mathcal{H}(\mathbf{r}_p)$ is the kinetic energy operator for the impinging positron, $\mathcal{H}_{\text{vib}}(\mathbf{R})$ and $\mathcal{H}_{\text{el}}(\mathbf{r}_e)$ are the vibrational and the electronic Hamiltonian, respectively.

$V_{\text{p-mol}}(\mathbf{r}_p, \mathbf{r}_e, \mathbf{R})$ represents the positron-molecule interaction. It is to be noted here that in the BF-VCC scheme the rotational part, $\mathcal{H}_{\text{rot}}(\hat{R})$, from the full Hamiltonian has been neglected because the BF frame that is being employed is rigidly fixed to the molecular target [6, 7]. The total wave function of the BF-VCC representation

is now expanded in terms of molecular vibrational states of the diatomic target

$$\Psi^{\text{BF-VCC}} = \chi_0(\mathbf{r}_e|\mathbf{R}) \sum_{\nu,l} \phi_\nu(\mathbf{R}) u_{\nu l, \nu_0 l_0}^\wedge(r_p) 1/r_p Y_{l\wedge}(\hat{\mathbf{r}}_p), \quad (3)$$

$\chi_0(\mathbf{r}_e|\mathbf{R})$ is the ground-state electronic wave function (parametrically dependent on \mathbf{R}), ϕ_ν is the vibrational wave function of the molecule and ν labels the vibrational quantum state. $Y_{l\wedge}(\hat{\mathbf{r}}_p)$ denotes now the angular part of the positron wave function, where l is its orbital angular momentum and \wedge is the projection of l along the internuclear axis $\wedge = \mathbf{1} \cdot \hat{R}$. In the BF-VCC scheme for diatomic molecules this quantity is a good quantum number (constant of motion). The unknown function $u_{\nu l, \nu_0 l_0}^\wedge(r_p)$ is the radial part of the positron wave function, where $(\nu_0 l_0)$ denotes the particular initial channel which has been selected for the vibrational and angular momenta.

Using now equations (2) and (3) in the Schrödinger equation (1) one gets the corresponding BF-VCC coupled differential equations

$$\begin{aligned} \left\{ \frac{d^2}{dr_p^2} - \frac{l(l+1)}{r_p^2} + k_\nu^2 \right\} u_{\nu l, \nu_0 l_0}^\wedge(r_p) = \\ 2 \sum_{\nu' l'} V_{\nu l, \nu' l'}^\wedge(r_p) u_{\nu' l', \nu_0 l_0}^\wedge(r_p), \end{aligned} \quad (4)$$

with

$$V_{\nu l, \nu' l'}^\wedge(r_p) = \sum_\lambda \langle \phi_\nu(R) | V_\lambda(r_p | R) | \phi_{\nu'}(R) \rangle g_\lambda^\wedge(l l') \quad (5)$$

and

$$g_\lambda^\wedge(l l') = \left\{ \frac{2l' + 1}{2l + 1} \right\}^{1/2} C \left(\begin{matrix} \lambda & l' & l \\ 0 & \wedge & \wedge \end{matrix} \right) C \left(\begin{matrix} \lambda & l' & l \\ 0 & 0 & 0 \end{matrix} \right) \quad (6)$$

and

$$k_\nu^2 = 2(E - \varepsilon_\nu). \quad (7)$$

V_λ is obtained from the following expression:

$$\begin{aligned} \langle \chi_0(\mathbf{r}_e|\mathbf{R}) | V_{\text{p-mol}}(\mathbf{r}_p, \mathbf{r}_e, \mathbf{R}) | \chi_0(\mathbf{r}_e|\mathbf{R}) \rangle = \\ \sum_\lambda V_\lambda(r_p | R) P_\lambda(\hat{\mathbf{r}}_p \cdot \hat{R}). \end{aligned} \quad (8)$$

The C 's of equation (6) are the usual Clebsch-Gordan coefficients. The vibrational wave functions of the molecule can be obtained first by solving the following differential equation for the normal coordinate R :

$$\left\{ \frac{d^2}{dR^2} + 2\mu(\varepsilon_\nu - U^0(R)) \right\} \phi_\nu(R) = 0, \quad (9)$$

where μ is the reduced mass of the molecule and $U^0(R)$ comes from the ground electronic state, Ψ_0 , of the target which provides the potential supporting, the corresponding vibrational bound states.

The solution of the coupled equation (4) subject to the usual asymptotic boundary conditions finally yields the T matrix $T_{\nu l, \nu' l' 0}^{\wedge}$ and from it we can get the partial integral vibrational excitation cross-section using the following expression [7]:

$$\sigma_k(\nu_0 \rightarrow \nu) = \frac{\pi}{k_{\nu}^2} \sum_{\wedge} \sum_{l_0} |T_{\nu l, \nu' l' 0}^{\wedge}|^2 \quad (10)$$

for each transition of interest.

The scattering process treats the actual dynamical coupling between the vibrations of the molecule and the “local” kinetic energy of the impinging positron as acting during the evolution of the scattering state in equation (4). This is therefore a better approximation than the simpler vibrational adiabatic approach [8] whereby the convolution over vibrational levels, initial and final, is carried out only after the fixed nuclei rotation (FNR) problem has been solved.

If one starts by assuming the target molecule to be in its ground electronic state and at its equilibrium geometry the $V_{p\text{-mol}}$ potential of equation (2) describes the local static interaction between the impinging positive charge and the undistorted multipoles of the target, V_{st} , together with the polarisation effects that such charged projectile induces on the molecular charge distribution:

$$V_{p\text{-mol}} = V_{\text{st}}(\mathbf{r}_p) + V_{\text{pol}}(\mathbf{r}_p) = \sum_{\lambda=0}^{\lambda_{\text{max}}} [v_{\lambda}^{\text{st}}(r_p) + v_{\lambda}^{\text{pol}}(r_p)] P_{\lambda}(\cos\vartheta). \quad (11)$$

In the low-energy positron scattering, target polarisation effects usually play a crucial role in modelling the full $V_{p\text{-mol}}$ interaction [9,10]. It has been a common procedure to employ some parameter-dependent, simple functional form of the polarisation component which is made to behave correctly both in the asymptotic region and near the origin. However, the adjustable models are not always satisfactory and suffer from the problem of requiring some prior set of data to which the model can be adjusted. In addition, such empirical models cannot really predict the absolute values of the computed cross-sections.

If one decides instead to employ in the evaluation of the v_{λ}^{pol} more sophisticated *ab initio* calculations, there are still nontrivial difficulties with them. For example, a rigorous variational calculation where each target occupied molecular orbital (MO) fully relaxes in the presence of the projectile suffers severely from the problem of including correctly nonadiabatic effects at short distances without having to resort to fitting parameters. Furthermore, when one chooses an *R*-matrix type of approach [11] the polarisation effects have to be included by either constructing an optical potential using two-particle-one-hole excitations of the initially occupied target MOs or by employing additional polarisation pseudostates. Such approaches, however, are not easily amenable to a balanced introduction of polarisation forces over the whole range of relative distances sampled by the scattering process [12]. It is therefore often desirable to be able to find a simple,

but parameter-free, form of a local polarisation potential which behaves correctly both near the origin and in the asymptotic region.

The model that we have employed is obtained in the same spirit of an electron correlation-polarisation potential (V_{ecop}) introduced earlier on for electron-molecule collisions [13–15]. What we instead employ here is a further modification of that approach, which we call the V_{pcop} potential which treats the impinging positron as a positively charged impurity at a fixed distance in a homogeneous electron gas given, within the local-density-approximation (LDA), by a generalized Density Functional Theory (DFT) treatment [10,16]. This treatment had already been extended by us [17] to molecular targets and applied to various calculations of cross-sections below Ps formations. It has been discussed extensively before and we will therefore not repeat here its detailed description. Suffice it to say that the inner region of the interaction is given by such model while, beyond the inner region between the origin and $r_p \geq 8.0a_0$, the polarisation potential is taken to be accurately described by the leading dipole term of the molecular polarisation potential, $\alpha/2r_p^4$, where α could be either the parallel or the perpendicular dipole polarisability, α_{\perp} and α_{\parallel} , and it takes over the interaction for distances larger than the crossing point with the multipolar coefficients of the inner region expansion of each v_{λ}^{pol} of equation (11). The combination of the positron-electron correlation terms and the asymptotic polarisation terms therefore provides the global V_{pcop} correction to the V_{st} contribution of equation (11).

This parameter-free correlation-polarisation interaction is treated as energy independent since, at the low collision energies which we shall consider, the further non-adiabatic effects for positron scattering may not be very important due to the strong repulsive forces near the nuclear locations. Thus, contrary to what happens for electrons, we expect that the inelastic processes will be mainly sampling the outer regions of the molecular charge distribution.

3 Computational results

The starting point of the present calculations were the electronic wave functions for both systems fixed at their equilibrium internuclear distances and evaluated at the SCF-HF (Hartree-Fock) level using a multicenter expansion over Gaussian-type orbitals (GTOs). In particular, we employed the GAUSSIAN 94 suite of codes [18] and described the R_{eq} wave functions for O_2 and NO using a D95** 6d 10f basis set expansion for the former and the latter systems. The energy obtained were -149.65259 hartrees for O_2 ($R_{\text{eq}} = 2.866a_0$) and -129.27474 hartrees for NO ($R_{\text{eq}} = 2.173a_0$).

In order to achieve a reasonable estimate of their dipole polarisability values (α_0 and α_2 at R_{eq}), we employed the same basis sets but carried out the calculations by relaxing the orbital occupation constraints in order to allow for a better description of polarisation

effects. The values obtained at the equilibrium geometries were: $\alpha_0 = 10.71 a_0^3$, $\alpha_2 = 6.87 a_0^3$ for O_2 and $\alpha_0 = 10.41 a_0^3$, $\alpha_2 = 3.96 a_0^3$ for NO.

We have further computed the isolated molecular potential energy curves by carrying out another set of calculations for the O_2 molecule: in this case we used a much larger GTO basis set by employing a CC-PVTZ 6d 10f expansion and by repeating the calculations for a large number of internuclear distance values. They varied from 0.7 Å up to 2.5 Å in intervals of 0.15 Å. In the case of the NO target we chose instead to employ the analytical expression for the V_{NO} potential given in reference [19]. In each calculation we found that the use of five vibrational functions in the CC vibrational equations for each system was sufficient to reach 1% convergence in the inelastic and elastic cross-sections between the lowest three levels.

The single-center expansion (SCE) of the interaction potentials was carried out up to $\lambda_{\max} = 16$ for both O_2 and NO and for the V_{st} and V_{pcop} potentials. The radial integration of the coupled equations was extended up to 200 bohr for r_p and the matching with V_{pcop} occurred around $r_p \sim 8.0$ bohr.

The dependence of the dipole polarisabilities on internuclear distance was taken from the potential calculations discussed before. We have simply matched the asymptotic forms of the polarisation potential for each molecular internuclear distance to the V_{pcop} value at that distance and therefore generated values of $\alpha_0(R)$ and of $\alpha_2(R)$. Such values were in turn used in equation (8) to produce the long-range part of the coupling potentials between vibrational states of each target. The Λ index of the molecular states included in the sum to yield total cross-sections went from $\Lambda = 0$ (Σ state) up to $\Lambda = 8$ both for gerade and ungerade states of the scattered positron. The corresponding angular momentum values for the scattered positron were taken up to $l_{\max} = 11$. This meant that the maximum number of coupled channels for O_2 went up to 30 for both gerade and ungerade symmetries, while it went up to 55 coupled channels in the case of NO. The energy spacings between the lower vibrational levels of O_2 were found to be: $\Delta\varepsilon_{01} = 0.196$ eV, $\Delta\varepsilon_{02} = 0.392$ eV and $\Delta\varepsilon_{03} = 0.588$ eV. For the NO system the corresponding values were: $\Delta\varepsilon_{01} = 0.236$ eV, $\Delta\varepsilon_{02} = 0.472$ eV, $\Delta\varepsilon_{03} = 0.708$ eV.

A more specific idea on the behaviour of the various terms concurring to generate the full couplings of equations (5) and (11) is presented in Figures 1 and 2.

The results shown in Figure 1 present (on top) the two leading multipolar components of the V_{pcop} discussed in the main text for the O_2 molecule, at its equilibrium geometry, while the same results for the NO target are shown in the lower panel. We clearly see there that the short-range correlation correction cuts off the long-range polarisation terms and brings the full interaction to reach a finite value at the origin. It is also interesting to note that both systems show in the short-range region very similar behaviour of the correlation correction, while differing in the long-range parts due to the different polarisability values (larger for O_2 than for NO).

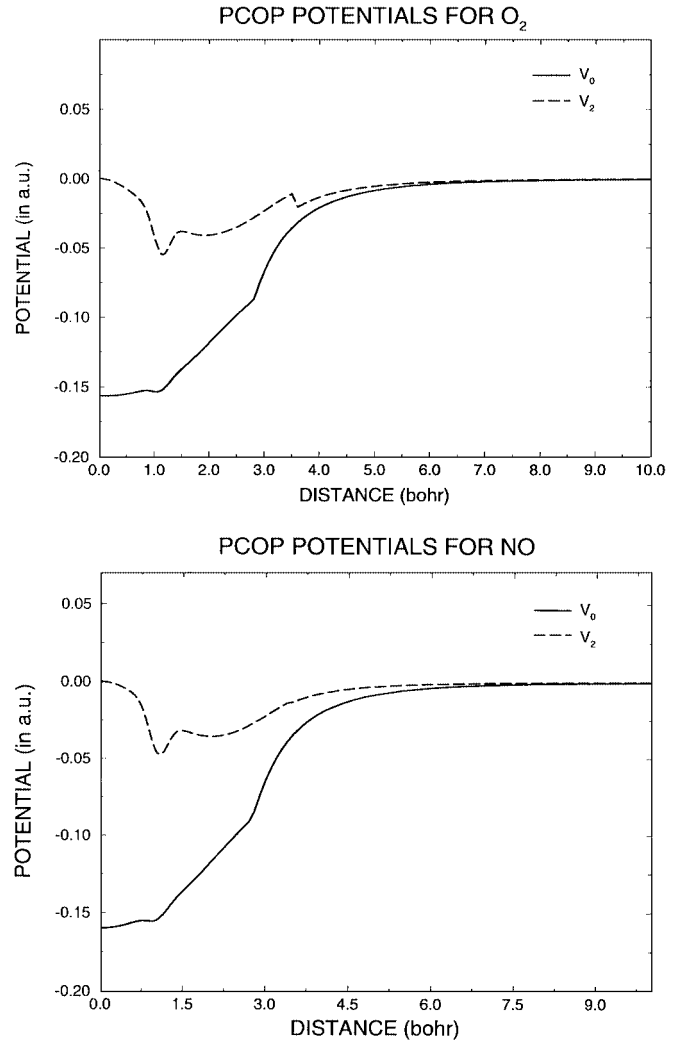


Fig. 1. Computed lowest multipolar coefficients for the V_{pcop} potential discussed in the main text. Upper panel: V_0 and V_2 components for the O_2 molecule. Lower panel: same components for the NO molecule.

A further, and marked, source of difference in the behaviour of the full interaction can be seen in Figure 2, where the static contributions are added to the same multipolar terms of Figure 1, thus resulting in the full potentials of equation (11) for the lower two multipolar coefficients. The O_2 target potential coefficients, seen in the upper part of Figure 2, clearly show the marked anisotropy of the charge distributions and the strongly repulsive effects as one approaches the position of the nuclear cusp: the V_2 coefficient is therefore stronger there than the spherical term and is much larger than that of NO at the same relative distance from the center of mass (c.o.m.). The potential coefficients for NO, on the other hand, reveal a less marked anisotropy and a further cusp effect from the fact that the two nuclei are now both away from the c.o.m. position: only the N position is shown in the figure. Furthermore, the lack of (g, u) symmetry in NO makes the V_1 term more important in the long-range region where the dipole interaction becomes dominant.

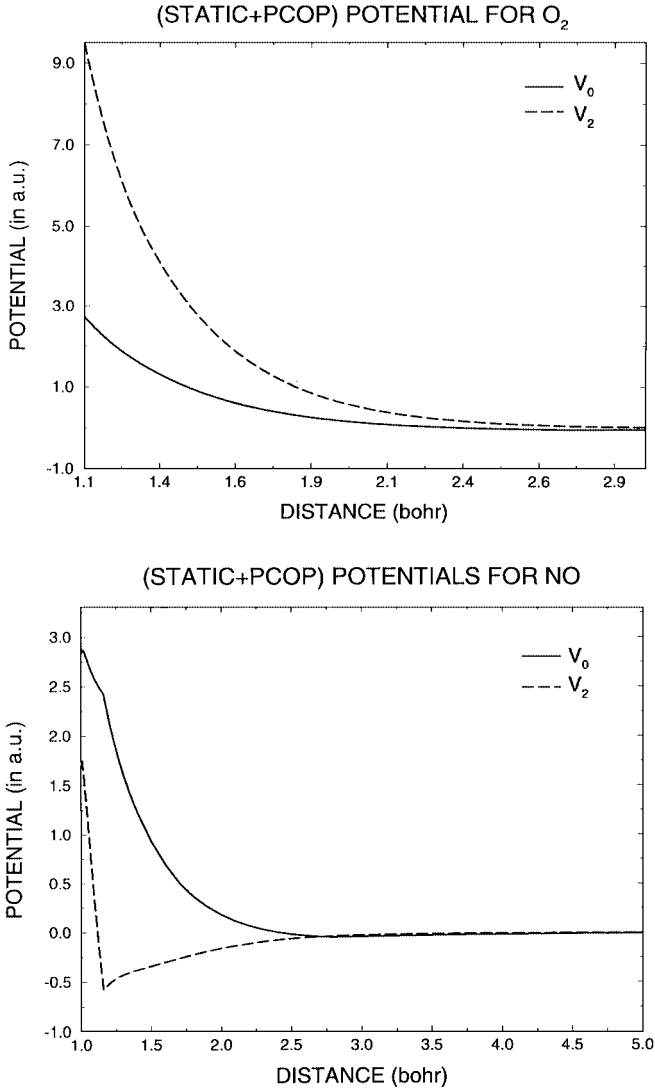


Fig. 2. Full interaction potential ($V_{st} + V_{pcop}$) computed for positron-molecule scattering. Upper panel: lowest two coefficients of its multipolar expansion for the O_2 molecule. Lower panel: lowest two coefficients of the same multipolar expansion for the NO molecule.

The computed potential couplings between molecular vibrations and the incoming positron, *i.e.* the coupling terms of equation (8), show the following behaviour:

- i) The coupling between nearest neighbours is by far the strongest in both molecules and for all the leading scattering states.
- ii) The range of action of the coupling is really very short: the impinging positron is capable of deforming the molecular charge distributions (hence the corresponding force constants) only when it comes well inside such charge and when the correlation-polarisation forces become important.
- iii) The coupling strengths for $\Delta\nu \geq 1$ decay very rapidly and both systems show negligible vibrational coupling effects (at least from the potential terms) when $\Delta\nu = 3$. Higher $\Delta\nu$ values are entirely negligible.

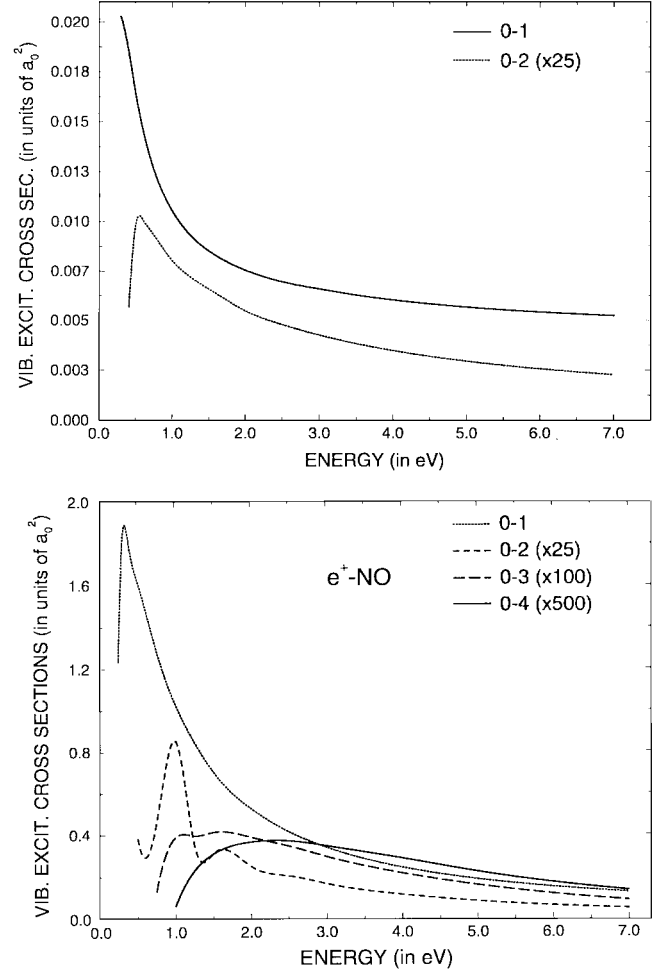


Fig. 3. Partial, integral vibrational excitation cross-sections computed for positron scattering from O_2 (upper panel) and from NO (lower panel). The different excitation probabilities are shown, in each panel, with some of them multiplied by the factors indicated near each in order to make them visible on the global scale.

We therefore see that, even for polyelectronic targets, the vibrational coupling induced by positron is rather small and appears to be, at least from the present computations, markedly smaller than in the case of electron scattering processes.

To further verify this point, we present in Figures 3 and 4 the computed, integral partial, vibrationally inelastic cross-sections within the range of collision energies before Ps formation. We also show in Figure 4 the average vibrational energy transfer values over the same range of collision energies. The latter quantity is defined as follows:

$$\langle \Delta E_{\text{vib}} \rangle_{\nu=0} = \frac{\sum_{\nu \neq 0} \sigma(\nu \rightarrow \nu' | k^2) \Delta \varepsilon_{\nu\nu'}}{\sum_{\nu=0}^{\nu'_{\text{max}}} \sigma(\nu \rightarrow \nu' | k^2)}, \quad (12)$$

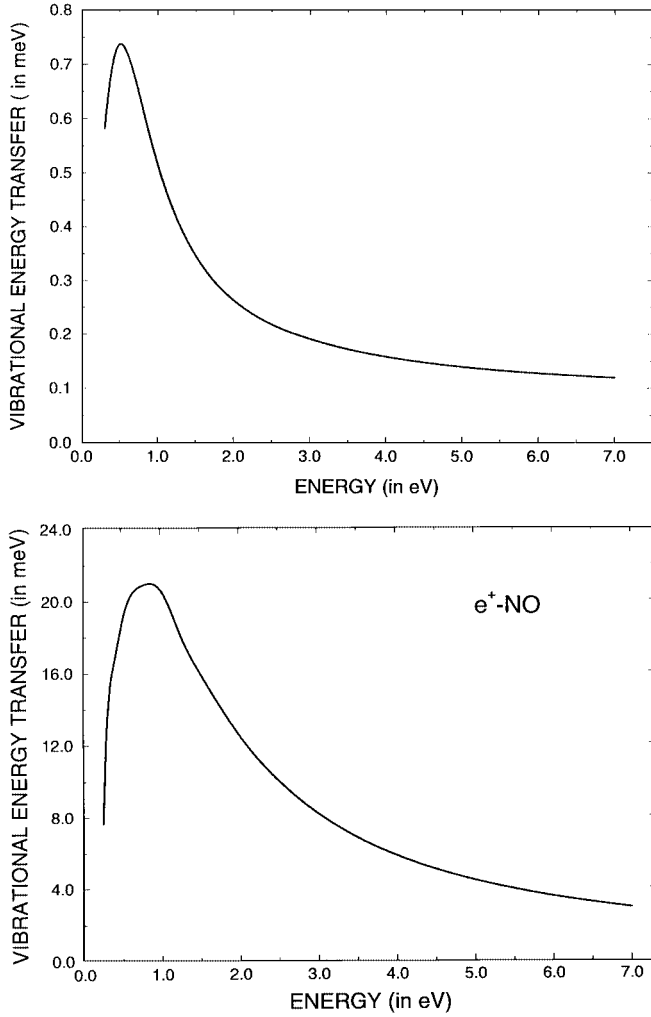


Fig. 4. Vibrational energy transfer values, as defined by equation (12) of the main text, computed for the O_2 molecule (top panel) and for the NO molecule (lower panel).

where we have considered the average excitation of the ambient molecular gases chiefly to occur from their lowest vibrational states ($\nu = 0$) [20].

It is interesting to note, when looking at the results shown in Figure 3, that the excitation of the $\nu' = 1$ vibrational level of NO is much larger (at the same collision energies) than that for the O_2 gas: between 2.0 and 5.0 eV, for instance, the excitation probability of NO varies between 0.2 and $0.4 a_0^2$, while that of O_2 is of the order of $0.7 \times 10^{-2} a_0$. Obviously the permanent dipole moment coupling of vibrational modes plays a rather important role in the former gas, as opposed to the latter, and therefore causes vibrational excitation over a much larger region of interaction. The corresponding coupling matrix elements for the NO target were, in fact, found to be much larger than those of O_2 . One should also note here that the present calculations of the coupling matrix elements of equation (5) include the static multipoles of the target molecules through the \mathbf{R} -dependence of V_{st} in equation (11). The present calculations also indicate that the excitation processes involving energy transfers of more

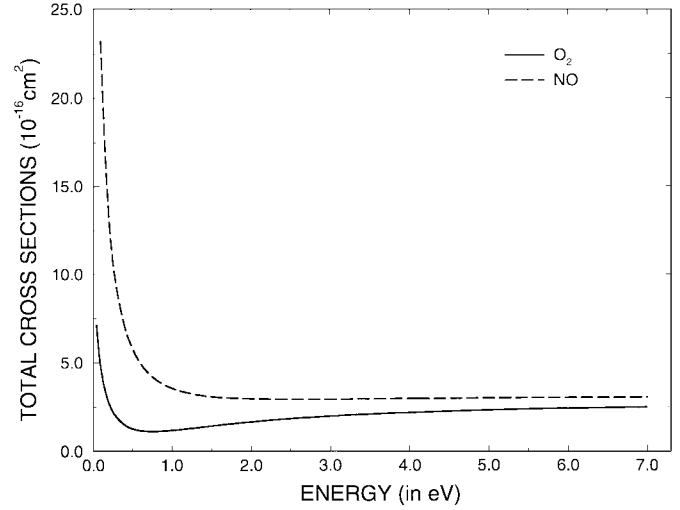


Fig. 5. Comparison of the computed total integral cross-sections (elastic + vibrationally inelastic) for the O_2 (solid line) and the NO (dashed line) molecules discussed in this work.

than one vibrational quantum are, for both molecules, markedly smaller than those for the $\Delta\nu = 1$ process. The positron perturbation, in fact, chiefly affects the outer regions of the bound electron wave functions because of the strong nuclear repulsion (see Fig. 2), hence we should expect that the deformation of the bond force constants induced by electron scattering becomes less effective in the case of positron dynamics and therefore makes the multiple excitation processes much less likely to happen.

This particular feature can be gleaned when we examine the computed values from equation (1) over the same range of collision energies (see the results of Fig. 4):

- i) The average energy transfer from positron scattering in the NO ambient gas is seen to be between 50 and 40 times larger than in the case of O_2 at the same collision energies.
- ii) Both molecular gases further show that, at the lower collision energies, the excitation process undergoes a very marked increase below $E_{coll} \sim 1$ eV and that such features could be related to the strong attractive wells exhibited by the inelastic coupling potentials (Fig. 3 and 4) associated to the $(0 \rightarrow 1)$ transitions. Thus, as the corresponding inelastic cross-sections of Figure 3 clearly show, the excitation probabilities could be increased by the presence of possible resonances induced by the coupling potentials which enter the scattering equation (4). This possibility has been qualitatively already suggested for the positron-oxygen system [21].

The differences between the two molecular gases are compared more directly in Figure 5, where we report the total integral cross-sections (elastic + vibrationally inelastic) for both molecules over the same range of collision energies. One clearly sees there that the polar NO gas is providing at low collision energies much larger cross-sections for positron scattering than those given by the O_2 molecule: the marked increase of the integral cross-sections as the collision energy decreases is definitely

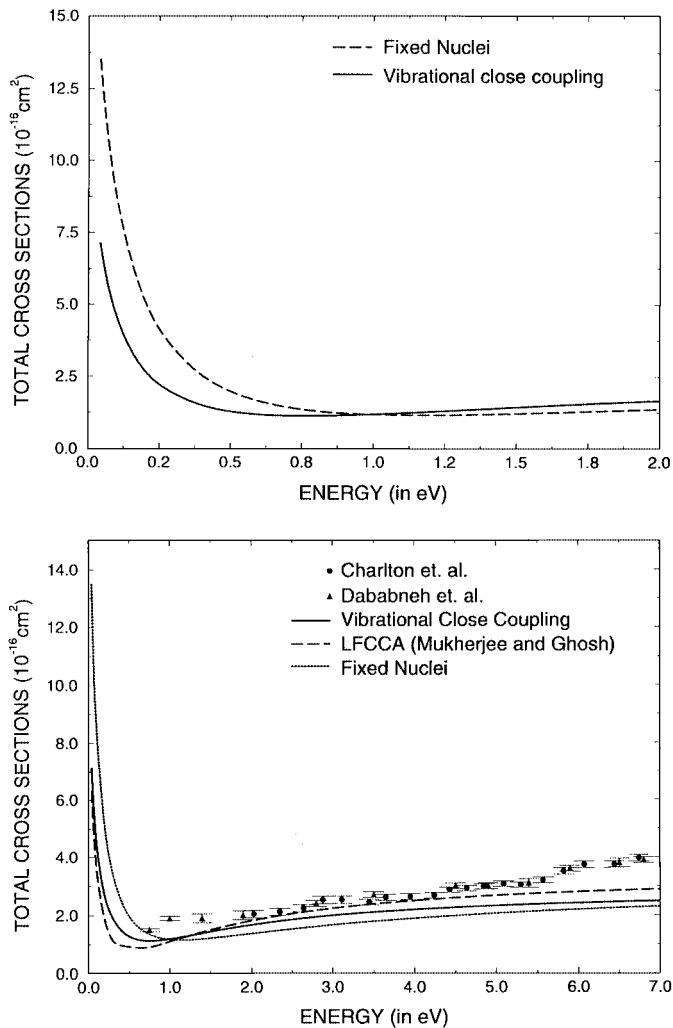


Fig. 6. Upper panel: comparison between the integral cross-sections computed for the NO molecule using different dynamical schemes. Dashed line: cross-sections obtained within the FN scheme discussed in the main text. Solid line: cross-sections obtained via the vibrational close coupling scheme presented in this work. Lower panel: calculations for the e^+ -O₂ scattering cross-sections compared with experiments (filled circles: from reference [14], filled triangles from reference [21]) and with earlier calculations (LFCCA from reference [22]). See text for the meaning of symbols.

stronger in the case of the polar target than in the case of O₂.

We have not found experimental data on positron scattering from NO, but data exist for the case of O₂ [21]. We can thus compare the latter measurements with our calculations in the lower panel of Figure 6, while we further show the results for the same molecule over a smaller range of energies in the upper panel of the same figure.

What we can compare in that figure, in fact, are the values of the integral cross-sections for e^+ -O₂ elastic (rotationally summed) scattering computed within the fixed-nuclei decoupling scheme (see before) and those of the total (elastic plus vibrationally inelastic) integral cross-

sections obtained with the coupled equations discussed above. We see that the effect of vibrational inelasticity is fairly marked at low energies, *i.e.* below 1.0 eV, although, when we move the higher collision energies, the vibrational inelasticity plays a minor but still significant role as it is shown to always affect the cross-section values.

The situation for the O₂ target can be further analysed by making use of both a comparison with existing experiments [21] and of earlier model calculations which considered explicitly the rotationally inelastic channels and carried out Laboratory Fixed (LF) close-coupled calculations (LFCCA) [22]. Our calculations at the FN level and for the vibrationally inelastic dynamics are also reported in the lower part of Figure 6. One can make the following observations:

- i) All computed cross-sections follow rather well the experimental data although still remaining smaller than the measurements.
- ii) The LFCCA calculations of reference [22] are larger than both the FN and the vibrational close-coupled results above the 1.0 eV value of collision energy. Given the different target wave function employed by [22], and their different polarisability values, it is however difficult to give any physical explanation for the differences with the present results.
- iii) The vibrational close-coupling cross-sections obtained in the present work are seen to remain larger than the FN cross-sections, thereby indicating that molecular vibrations, even in the case of positron scattering and at collision energies where Ps formation is not as yet significant, are playing a definite role in controlling the magnitude of the total cross-sections.
- iv) The disagreement which still exists between computed and measured cross-sections, however, may be indicative of the fact that for open-shell targets, the present-model correlation-polarisation interaction further needs to be refined, as we shall briefly discuss below.

4 Conclusions

In the present study we have carried out a model evaluation of the interaction forces between an ambient molecular gas and impinging slow positrons, considering collision energies up to the threshold of Ps formation. The main interest of the study was to examine out the importance of the molecular degrees of freedom which are accessible at those energies (chiefly rotational and vibrational) where the positron beam can be inelastically scattered within the gas. In particular, we have examined the role of the dynamical coupling between molecular nuclear motions and the positron during collisions.

The results from this study show that in a polar molecular gas like NO the contributions from the dipole transition moment in the short-range region of interaction dominate the $\Delta\nu = 1$ excitations, thereby making such inelastic processes much larger than in the case of nonpolar gases.

One should also bear in mind here that the scattering from polar targets, as is well known, requires in general the additional inclusion of corrections for the divergent behaviour in the low-energy region [23]. However, the inelastic cross-sections which we analyse here are removing such divergency because of the presence of off-diagonal potential terms [24].

The comparison of the e^+ -O₂ results with available experiments (no such data are available for NO collisions) indicate that our calculations are in fair agreement with them and therefore give us some measure of confidence for the corresponding cross-sections for the NO ambient gas.

One should also remember, however, that the present analysis intends to focus on the possible role played by vibrationally inelastic collisions in low-energy positron scattering and we have therefore disregarded, for the time being, other features of the positron interactions like the fact that both targets are open-shell systems, that electronic excitation might occur below the Ps formation threshold and that spin changes can occur during excitation [21]. If one were to fully include such effects, however, then the present model for V_{pcop} should be revised and modified. Such changes are deemed for the moment to be outside the scope of the present analysis.

In summary, the present study suggests that vibrationally inelastic channels do have a significant role for positron quenching in ambient molecular gases, especially at the very-low-energy regimes. It would be interesting to see if such channels also play a role when studying annihilation processes and the behaviour of Z_{eff} coefficients in polyatomic gases [25]. It will be the object of a further study which we are presently undertaking [26] in our group.

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