

LOW-ENERGY ROTATIONAL EXCITATION OF H₂ AND N₂ BY POSITRON IMPACT.

I - COMPUTED PARTIAL CROSS SECTIONS

J. A. Sabin del Valle¹, Instituto Superior de Tecnologías y Ciencias Aplicadas (InSTEC), Ciudad de La Habana, Cuba

S. Telega², Faculty of Applied Physics and Mathematics, Technical University of Gdansk, Poland

F.A. Gianturco^{*3}

^{1,2,3}Department of Chemistry and INFM, University of Rome "La Sapienza", Rome, Italy

ABSTRACT

Low-energy collisional excitation of rotations in H₂ and N₂ by impact with slow positrons in the gas phase is considered by carrying out a Space-Frame (SF) dynamical calculation at energies well below the positronium formation threshold.

RESUMEN

Se consideran excitaciones por colisiones de baja energía de rotaciones en H₂ y en N₂ por impacto con positrones lentos en la fase gaseosa llevándose a cabo un cálculo dinámico en el sistema de referencia espacial a energías bien por debajo del umbral de formación del positronium.

I. INTRODUCTION

The experimental and computational study of low-energy positron scattering from molecular gases, both diatomic species and polyatomic targets, has a relatively long history which is chiefly related to the fundamental interest in the consequences of positron annihilation in gases and in the effects of slowing down positron beams in several media of applied relevance [1-3].

One of the complications created by the use of antiparticles in low-energy processes is the existence of additional channels which are not present in the case of electron beams. Thus, we know of the possibility of forming the positronium (Ps) compound, that adds a distinct 'reactive' channel to the theoretical description of the above processes [1], or that the particle-antiparticle decay channel, whereby the pick off by the positron of a bound electron leads to the emission of 2 or 3 γ photons, can leave molecular cations within the gas and therefore strongly modify the collisional process. In the present study, however, we shall limit our analysis to collision energies where the above channels are either closed or contribute very little to the overall collisional event, thereby focussing our theoretical and computational discussion to the direct excitation of molecular rotational degrees of freedom by low-energy scattering with positrons in simple molecular gases.

II. THE SPACE-FRAME DYNAMICS

In the present calculations we shall treat the N₂ and H₂ molecular targets as rigid rotors, disregarding from the time being the effects of vibrational excitations during the rotational energy transfer collisions. Furthermore, as reported in the following Section, the interaction with the molecules will be described by a local, energy-independent effective potential between the impinging particle and each rotating target. The total scattering wavefunction can be expanded in terms of asymptotic target rotational states that, for the title molecules, are simple spherical rotors

$$H_{\text{rot}}(\hat{R}_{\text{eq}})Y_{jmj}(\hat{R}_{\text{eq}}) = \frac{\hbar^2}{2I}j(j+1)Y_{jmj}(\hat{R}_{\text{eq}}) \quad (1)$$

with I being the isolated molecule moment of inertia [4] and \hat{R}_{eq} the space orientation of the molecular bond, kept at its equilibrium value. Hence, the total scattering wave function is given as

$$\Psi_n(E, r_p, R_{\text{eq}}) = \sum_f u_{i \rightarrow f}(r_p, E)r_p^{-1}Y_f(\hat{R}_{\text{eq}}) \quad (2)$$

where $|f\rangle$ denotes the $|j'm_j\rangle$ final states of the molecule involved in the expansion and the $u_{i \rightarrow f}(r_p, E)$ are the channel components of the scattering wavefunction, to be determined by solving the usual Schrödinger equation subject to its

scattering boundary conditions. Here the scalar r_p is the scattered positron variable position from the molecular center of mass (c.o.m.)

$$u_{i \rightarrow f}(r_p) \rightarrow \delta_{if} h^{(-)}(r_p) - (k_i / k_f) S_{if} h^{(+)}(r_p) \text{ as } r_p \sim \infty \quad (3)$$

$h^{\pm}(r_p)$ is a pair or linearly independent free partial solutions. When they are chosen to be appropriate Riccati-Hankel functions, then the S_{if} coefficients become the elements of the reduced scattering matrix, often additionally labelled by the total angular momentum of the system: $J = j + l$, the latter l being the continuum electron partialwave component.

The $u_{i \rightarrow f}$ are in turn expanded in products of total angular momentum eigenfunctions and of radial functions $\phi_{\lambda\lambda'}^J(E, r_p)$, where J is the magnitude of the angular momentum and, $\lambda' = (j', l')$. The radial functions are in turn solutions of the familiar set of coupled, second order homogeneous differential equations (in the case of local interactions) [5,6]

$$(U^J(r_e))_{\lambda\lambda''} = 2 \sum_L f_L(l', j'; l'', j''; J) V_L(r_p) \quad (4)$$

where I is the unit matrix, Φ^J is the matrix of radial functions and

$$(I^2)_{\lambda\lambda''} = l'(l' + 1) \delta_{\lambda\lambda''} \quad (5)$$

$$(K^2)_{\lambda\lambda''} = k_j^2 \delta_{\lambda\lambda''} = (2)(E - E_j) \delta_{\lambda\lambda''} \quad (6)$$

$$(U^J(r_e))_{\lambda\lambda''} = 2 \sum_L f_L(l' j'; l'' j''; J) V_L(r_p) \quad (7)$$

where the $f_L(l' j'; l'' j''; J)$ are the well-known, real coefficients of Percival and Seaton [4] and the coupling between the asymptotic (adiabatic) target states is given by the radial matrix elements which we shall discuss in detail in the next Section. Since L is even and $f_L(l' j'; l'' j''; J)$ is real, the $U_{\lambda\lambda''}^J$ is nonzero only if $j' - j''$ is even, i.e. the matrix is block diagonal with two subblocks that contain only even values of $(l' + j')$ or only odd values of $(l' + j')$. Thus, when one starts from $j = 0$ it is only necessary to include those values of the partialwave index l for which $|J - j| \leq l \leq J + j$ and for which $l + J$ is even. When j_{\max} is the maximum value of j included in the expansion (2), then the f_L 's are zero for $L > 2j_{\max}$ when $j' < j_{\max}$ and $j < j_{\max}$.

We have recently developed [7] a suitable numerical algorithm that judiciously performs such controls along the radial evaluation process and modifies the size of the relevant S-matrix. We have called it the Modified Variable Phase Approximation (MVPA) and have employed it in the present case to solve the set of coupled equations (4).

Typically, for numerical convergence we needed to use the full coupling from about 10^{-3} Å (the initial integration point) out to 8.0 Å, then we could gradually reduce the K-matrix size out to 600 Å, for H_2 and out to 2000 Å, for N_2 . This essentially meant that, when we went beyond such size-values for the K-matrix we found that the corresponding cross section values changed by less than 10^{-3} Å², which is taken as our accuracy threshold for the final observables.

The total angular momentum values went up to 5 for H_2 and N_2 , while the target rotational basis was extended up to 16 for H_2 and up to 28 for N_2 . The rotational constant of the former target was taken to be 60.853 cm^{-1} , while it was only 2.01 cm^{-1} for the latter molecule. The multipolar coefficients of the potential expansion went up to $\lambda_{\max} = 18$ for the hydrogen target and to $\lambda_{\max} = 26$ for the nitrogen target. The corresponding partialwave angular momenta for the scattered electron therefore went up to $l_{\max} = 21$ for the H_2 molecule and up to $l_{\max} = 33$ for the N_2 molecule.

III. THE POSITRON-MOLECULE POTENTIAL

If one starts in the asymptotic region of the interaction, where charge overlap effects have vanished, one can immediately write the dipole leading term of the polarisation part of the full potential V_{pcp} [8]

$$V_{\text{pcp}}(r_p) \sim V_{\text{pol}}(r_p) = -\frac{1}{2r_p^4} \{ \alpha_0(R) + \alpha_2(R) P_2(\hat{R} \cdot \hat{r}_p) \} \quad (8)$$

where α_0 is the spherical dipole polarisability of the target molecule at its geometry R , α_2 is its non-spherical term and the Legendre polynomial depends on the molecular frame angle $\vartheta = \arccos(\hat{R} \cdot \hat{r}_p)$. We have employed experimental values for such quantities [9]. The present V_{pcp} is based on the correlation energy of a localized e^+ in an e^- gas, and its hybridization with the correct asymptotic form of equation (8). Earlier on [10,11] a similar approach was applied to the problem of a light impurity in an electron gas. In those methods, the electron gas is described by a set of interacting bosons representing the collective excitations in the random-phase-approximation. Further, Boronski and Nieminen [12] described the density-functional theory of the electron-positron system, and presented the results on the positron-electron correlation energy as a function of the density parameter r_s [10-12] for different $n_+(r_s)/n_-(r_s)$ ratios including the case of one positron in a homogeneous electron gas. Here n_+ and n_- denote the densities of positrons and electrons, respectively. It therefore follows that the total V_{pcp} potential for the e^+ -molecule system can now be assembled by writing

$$\begin{aligned}
V_{\text{pcp}}(r_p | R) &= V_{\text{corr}}(r_p | R) \text{ for } r_p < r_c \\
&= V_{\text{pol}}(r_p | R) \text{ for } r_p > r_c \quad (9)
\end{aligned}$$

The connecting parameter r_c is usually around $4.0a_0$ for the present system and varies depending on the chosen multipolar coefficient of the final expansion. The total e^+ -molecule interaction potential can now be obtained in a local form and will also include the exact electrostatic interaction $V_{\text{st}}(r_p)$

$$V_{\text{tot}}(r_p | R) = V_{\text{st}}(r_p | R) + V_{\text{pcp}}(r_p | R) \quad (10)$$

The latter interaction can be further expanded over the usual set of Legendre polynomials

$$V_{\text{tot}}(r_p | R) = \sum_{L=0}^{\infty} V_L(r_p | R) P_L(\hat{r}_p \cdot \hat{R}) \quad (11)$$

the coefficients only take even L values and provide the anisotropic coupling potential terms needed in the scattering eq.s where they are directly included in equation (7).

IV. ROTATIONALLY INELASTIC CROSS SECTIONS

The present results are reported in Figure 1 for both target molecules, with the calculations for the H_2 systems in its ground electronic state shown in the upper panel. The elastic, state-to-state cross sections from the initial level (the $\sigma_{0 \rightarrow 0}$ cross section) is seen to be by far the largest contribution to the process, and to rapidly decrease at low energies from very large values near zero energies. On the other hand, the quadrupole excitation cross section ($j_i = 0 \rightarrow j_f = 2$) is nearly two orders of magnitude smaller and grows to a higher energy plateau from very small threshold values. The same growth is also seen to occur for the ($j_i = 0 \rightarrow j_f = 4$) excitation cross sections, which are however even smaller in size and increase with energy at an even smaller rate. On the whole, we see that the slow positrons appear to be rather inefficient in exciting rotational levels in a molecule like H_2 that presents one of the largest rotational level spacings even at the lower- j states. We therefore expect rather slow cooling rates when H_2 is being used as a buffer gas for a positron beam.

A further indicator of the dominance of the direct quadrupole excitation potential for the present system is shown by the results reported in the upper panel of Figure 2. We show there the computed excitation cross sections from the $j = 0$ initial level up to the $j_f = 8$ final level. Two different collision energies are examined and the computed cross sections are given on a log scale. We clearly see that the excitation efficiency into the higher j_f levels increases with collision energy, as should be expected.

However, we also clearly see that the size of the corresponding cross sections drops dramatically for excitations beyond the direct quadrupolar term, i.e. for $j_f > 2$.

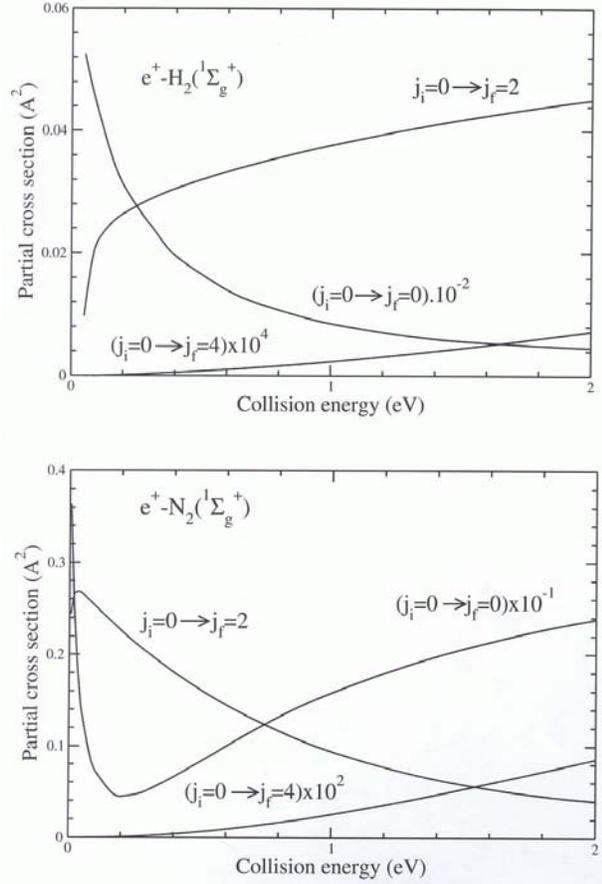


Figure 1. Computed state-to-state, partial integral cross sections for e^+ impact on H_2 (upper panel) and N_2 (lower panel). Some of the cross sections have been scaled to show them all within the same range (units of \AA^2).

Computed state-to-state, partial integral cross sections for e^+ impact on H_2 (upper panel) and N_2 (lower panel). Some of the cross sections have been scaled to show them all within the same range (units of \AA^2). The computed elastic and inelastic, state-to-state partial integral cross sections for positron impact on nitrogen molecules are reported in the lower panel of Figure 1.

One immediately notices that the cross sections are now much larger than in the case of H_2 and exhibit different behaviour as a function of collision energy. The elastic process, ($j_i = 0 \rightarrow j_f = 0$), now presents a marked Ramsauer minimum at low energies and grows to a large plateau of values as the energy increases. The inelastic cross sections, shown in the same panel, have opposite energy dependence and are both much larger than in the case of H_2 : the stronger angular anisotropy of the e^+ interaction with

N_2 compared with H_2 and the markedly smaller rotational constant of the former molecule compared to the latter (about 2 cm^{-1} versus about 60 cm^{-1}) are important factors which favour that direct angular momentum couplings cause larger excitations.

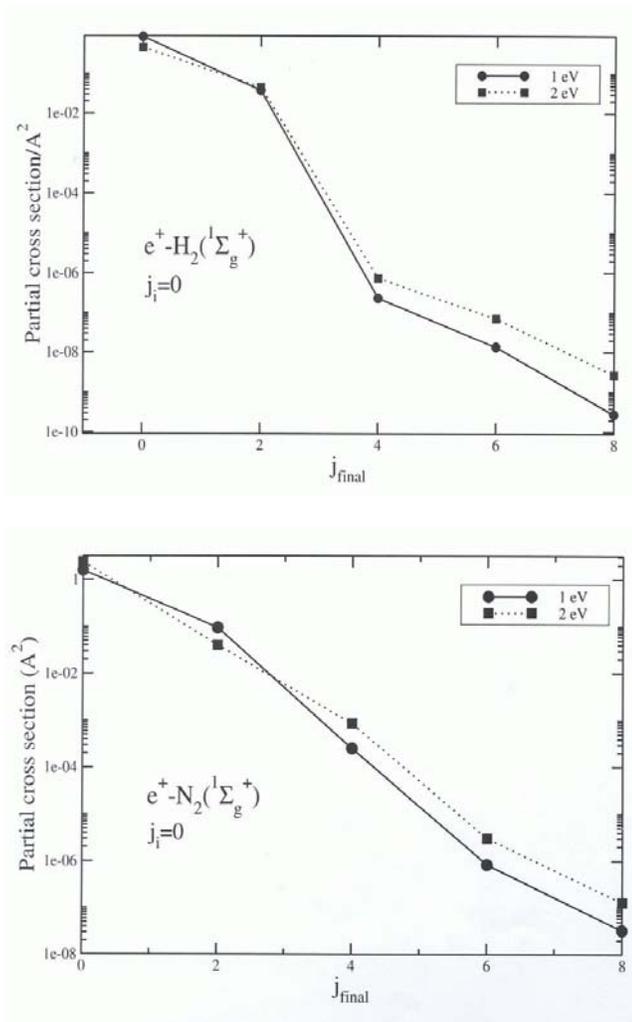


Figure 2. Partial, state-to-state integral cross sections for rotational excitation of H_2 (upper panel) and N_2 (lower panel) by positron impact. The curves in each panel refer to different collision energies. All transitions are from $j_i = 0$ into j_{final} values shown by the horizontal axis.

In one of the earlier papers [13] an approximate estimate of the $(0 \rightarrow 2)$ rotational excitation cross sections suggested a strong peak below 0.05 eV of collision energy. The further calculations in the SF frame of ref. [14] found it around 0.04 eV of collision energy: our present results place the same peak at 0.045 eV . All three results further suggest the size of the peak to be around 0.27 \AA^2 , showing good agreement between three very different estimates.

V. PRESENT CONCLUSIONS

In this work we have analysed in some detail the collisional heating of rotational internal energy in gaseous H_2 and N_2 interacting with a beam of slow positrons, and have limited our calculations to the partial, integral cross sections values. The computational analysis has been carried out within a Space Fixed quantum dynamics that couples the positron motion with the rotating molecular target via a non empirical, anisotropic interaction potential within the close-coupled expansion over rotor states described in Section II. The present results clearly indicate that the heating or cooling efficiency is larger for N_2 in comparison with H_2 , although the larger energy spacings of the latter molecule yield on the whole to larger amounts of energy being transferred between the leptonic projectile and the molecules of the gas. Particular attention has been given to testing numerical convergence by reaching cross section stability around about 0.1% , using the various numerical parameters described in Section IV.

VI. ACKNOWLEDGMENTS

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