

Addendum to “Dynamical coupling effects in the vibrational excitation of H₂ and N₂ colliding with positrons”

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The present work revisits the calculations of nanoscopic quantum processes from a beam of low-energy positrons impinging on molecular hydrogen gas and focuses on the vibrational excitation processes from energy-transfer collisions. Earlier calculations were found to contain a numerical error in the chosen interaction forces, while the present corrected results are seen to agree very well with recently published experimental data.

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I. INTRODUCTION

The measurement of partial and total inelastic cross sections, leading to vibrational excitations of the molecular targets in the ambient gas, is currently one of the major areas of interest in the study of positron low-energy collisions [1]. Corresponding theoretical research regarding the microscopic mechanism involved and computational tests of the methods in relation to the experimental findings is also a very active subject where several attempts have been made for predicting the few partial inelastic cross sections yielded by measurements [2,3].

In a recent study [4] involving direct inclusion of the dynamical coupling between the impinging positrons and the vibrational motion of the gaseous diatomic targets, we have analyzed the behavior of the integral cross sections for H₂ and N₂ molecules. We looked at the scattering process in the low-energy regime and computed both elastic and vibrationally inelastic cross sections for collision energies between ~1.0 and 8.0 eV. Because of a numerical error in the case of the H₂ molecular target, the results for this system turned out to be very small. We therefore repeat here the above computations and correct the numerical error, thus modifying the final values of the cross sections, as we shall discuss below.

II. THEORETICAL MODEL

To solve the scattering of low-energy positrons off a vibrating-rotating molecular target, in its electronic ground state, requires first to write down expansions of both the total Hamiltonian and its molecular rovibrational wave functions within a selected coupling scheme that in turn guides the choice of the unknown expansion coefficients [4].

In a body-fixed (BF) vibrational close-coupling (VCC) scheme (BFVCC), the total Hamiltonian can be written as

$$H^{\text{BFVCC}} = H(\mathbf{r}_p) + H_{\text{el}}(\mathbf{r}_e) + H_{\text{vib}}(\mathbf{R}) + V_{p\text{-mol}}(\mathbf{r}_p, \mathbf{r}_e, \mathbf{R}), \quad (1)$$

where \mathbf{r}_p is the 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. $H(\mathbf{r}_p)$ is the kinetic-energy operator for the impinging positron, and $H_{\text{vib}}(\mathbf{R})$ and $H_{\text{el}}(\mathbf{r}_e)$ are the vibrational and electronic Hamiltonians, respectively.

$V_{p\text{-mol}}(\mathbf{r}_p, \mathbf{r}_e, \mathbf{R})$ represents the positron-molecule interaction. It is to be noted here that in the BFVCC scheme the rotational part $H_{\text{rot}}(\hat{\mathbf{R}})$ of the full Hamiltonian is neglected because of the BF frame that is being employed [5]. The wave function of the BFVCC representation is now expanded as

$$\Psi^{\text{BFVCC}} = \psi_0(\mathbf{r}_e|\mathbf{R}) \sum_{\nu, l} \phi_{\nu}(\mathbf{R}) u_{\nu l, \nu_0 l_0}^{\Lambda}(\mathbf{r}_p) (r_p^{-1}) Y_{l\Lambda}(\hat{\mathbf{r}}_p), \quad (2)$$

where $\psi_0(\mathbf{r}_e|\mathbf{R})$ 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 number. $Y_{l\Lambda}(\hat{\mathbf{r}}_p)$ denotes the angular part of the positron wave function, l is its orbital angular momentum, and Λ is the projection of l along the internuclear axis $\Lambda = l \cdot \hat{\mathbf{R}}$. In the BFVCC scheme this quantity is a good quantum number (constant of motion). Here $u_{\nu l, \nu_0 l_0}^{\Lambda}(r_p)$ is the radial part of the positron wave function, where $(\nu_0 l_0)$ denotes the particular initial channel that has been selected.

The main computational task is now that of solving the ensuing coupled equations

$$\left\{ \frac{d^2}{dr_p^2} - \frac{l(l+1)}{r_p^2} + k_v^2 \right\} u_{\nu l, \nu_0 l_0}^{\Lambda}(\mathbf{r}_p) = 2 \sum_{\nu', l'} V_{\nu l, \nu' l'}^{\Lambda}(\mathbf{r}_p) u_{\nu' l', \nu_0 l_0}^{\Lambda}(\mathbf{r}_p), \quad (3)$$

with

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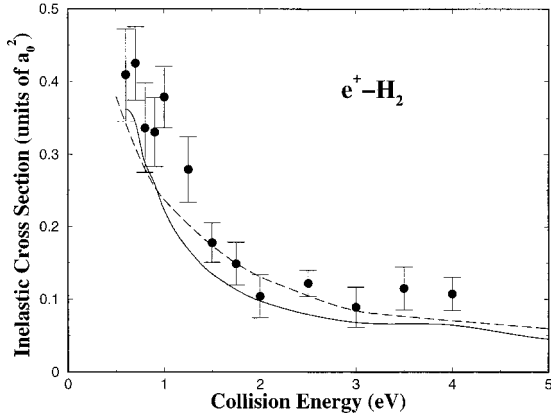


FIG. 1. Computed and measured partial integral cross sections for the $(0 \rightarrow 1)$ vibrationally inelastic process. The solid circles are the experiments from Ref. [7], and the dashed lines are the results from earlier calculations [8]. Our calculations are given by the solid line.

$$V_{\nu l, \nu' l'}^{\Lambda}(\mathbf{r}_p) = \sum_{\lambda} \langle \phi_{\nu}(\mathbf{R}) | V_{\lambda}(r_p | \mathbf{R}) | \phi_{\nu'}(\mathbf{R}) \rangle g_{\lambda}^{\Lambda}(l l'), \quad (4)$$

with $g_{\lambda}^{\Lambda}(l l')$ being a collection of angular factors coupling the relevant angular momenta [4] and

$$k_{\nu}^2 = 2(E - \varepsilon_{\nu}). \quad (5)$$

Here ε_{ν} is the energy of the ν th vibrational state. The V_{λ} coefficients are obtained from the expression

$$\begin{aligned} & \langle \psi_0(\mathbf{r}_e | \mathbf{R}) V_{p\text{-mol}}(\mathbf{r}_p, \mathbf{r}_e, \mathbf{R}) | \psi_0(\mathbf{r}_e | \mathbf{R}) \rangle_{\mathbf{r}_e} \\ &= \sum_{\lambda} V_{\lambda}(r_p | \mathbf{R}) P_{\lambda}(\hat{\mathbf{r}}_p \cdot \hat{\mathbf{R}}), \end{aligned} \quad (6)$$

TABLE I. Computed elastic and inelastic partial integral cross sections using the BF-VCC scheme described in the present work. Energy in units of eV and cross sections in atomic units. $[-n] = 10^{-n}$.

	0-0	0-1	0-2	0-3
0.5	30.23			
0.6	25.82	0.362		
0.7	22.40	0.344		
0.8	19.71	0.288		
0.9	17.49	0.259		
1.0	15.77	0.223		
1.25	12.52	0.169	0.134[-2]	
1.5	10.35	0.135	0.117[-02]	0.159[-03]
2.0	7.74	0.0976	0.769[-03]	0.155[-03]
2.5	6.31	0.079	0.566[-03]	0.131[-03]
3.0	5.45	0.0681	0.467[-03]	0.110[-03]
4.0	4.52	0.0644	0.396[-03]	0.864[-04]
5.0	4.03	0.0452	0.374[-03]	0.732[-04]
6.0	3.72	0.038	0.356[-03]	0.630[-04]

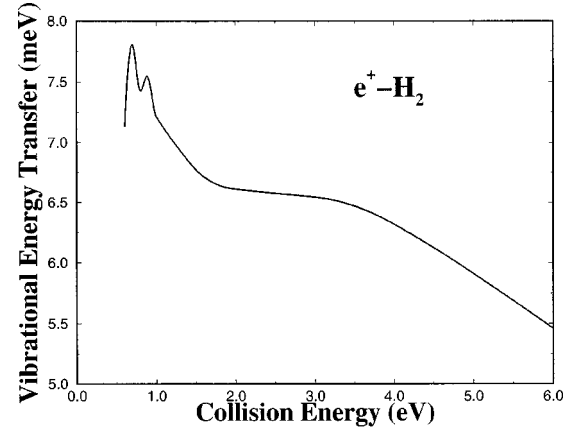


FIG. 2. Computed average vibrational energy-transfer values [4], in units of meV, as a function of collision energy.

and the vibrational wave functions of the molecular target are obtained as discussed in [4].

The solution of the coupled equations (3), subject to the usual asymptotic boundary conditions, gives the T matrix elements $T_{\nu l, \nu_0 l_0}$, and from it we get the partial integral vibrational excitation cross sections

$$\sigma(\nu_0 \rightarrow \nu) = \frac{\pi}{k_{\nu}^2} \sum_{\Lambda} \sum_{l l_0} |T_{\nu l, \nu_0 l_0}^{\Lambda}|^2. \quad (7)$$

III. COMPUTED RESULTS

One of the crucial elements for the evaluation of the coupling matrix elements of Eq. (4) is to have realistic knowledge of the dependence of the dipole polarizability of the target molecule on the changes of its internuclear distances. For the hydrogen molecule we have employed the computed values of α_0 and α_2 as a function of $R_{\text{H-H}}$ which have been given in the earlier work of Morrison and Saha [6]. The error of our previous calculations [4] was due to having actually employed incorrect units for the $\alpha_0(R)$ and $\alpha_2(R)$ computed values. The present results restored the correct files and therefore describe the effects on the coupling terms of Eq. (4) of using the values of Ref. [6] for α_0 and α_2 .

That a realistic treatment of the long-range part of the V_{cp} interaction affects very markedly the final inelastic data can be seen from the inelastic cross sections reported in Fig. 1: they are now a factor of 10^2 larger than those given by Fig. 5(a) of Ref. [4] of our earlier calculations. The actual values of the cross sections are given in Table I.

It is interesting to note that a comparison of our computed cross sections for the $(0 \rightarrow 1)$ excitation process with very recent experimental data [7] (which suggested the present study) and with earlier model calculations [8] clearly indicates that the present, corrected cross sections now follow very well the shape of the measurements both at low energy and all the way up to 4.0 eV. They also turn out to be very close to them in absolute values, thus allowing us to see more directly the strong influence on the positron scattering dynamics afforded by long-range polarization contributions within the body-fixed, vibrational close-coupled treatment of

this work. It is also interesting to note here that the new experiments of Ref. [7] include data on the vibrational excitation of the CO molecule which show also very good agreement with our earlier calculations on the same system [3], thereby confirming the essential reliability of our BF-VCC approach to positron-molecule inelastic processes.

The data of Fig. 2 now report the behavior of the average vibrational energy transfer (see Ref. [4] for its definition) as a function of collision energy. We now see much larger values than those of Fig. 7(a) in Ref. [4] and the presence of low-energy enhancement possibly due to nuclear-excited resonances at the opening of the $v=1$ level and below the $v=2$ excited level of the target molecule. Furthermore, the efficiency of the energy-transfer process decreases with in-

creasing collision energy, as is usually expected for this system [8,9].

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