Computing vibrational effects in low-energy positron scattering from polyatomic molecules: the H$_2$O and C$_2$H$_2$ stretching modes

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Abstract

We report a theoretical study and the computational results on vibrational excitations by positron impact of the polyatomic molecules CH$_4$ and C$_2$H$_2$ as examples. The study has been carried out using the body-fixed vibrational close-coupling (BF-VCC) method which is relevant for describing vibrationally inelastic processes in low-energy collisions. The interaction potential we employ to model the forces at play is described in detail and we also report our numerical techniques for solving the scattering equations. The cross-sections are obtained for the vibrational excitations of the symmetric ($v_1$) and the antisymmetric ($v_3$) stretching modes of the H$_2$O molecule and for the symmetric stretching ($v_1$) mode of C$_2$H$_2$, and they are compared with simpler available approximations.

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1. Introduction

The theoretical cross-sections for the vibrationally inelastic scattering of positrons (e$^+$) from water (H$_2$O) and acetylene (C$_2$H$_2$) molecules are here obtained for the first time and reported in detail below. This is an extension of our work on the vibrational excitation processes that occur in simple polyatomic molecules in the gas phase, induced either by positron [1–3] or by electron impact [4,5]. Since an incident positron is distinguishable from all the bound electrons of the molecular target, there is no effect from electron exchange a feature which needs instead to be considered in the case of electron scattering. Moreover, a positron has the additional possibility of taking up one of the electrons of the target molecule to form a positronium (Ps) atom, when the collision energy is above the threshold for the Ps formation energy (5.8 eV for H$_2$O and 4.6 eV for C$_2$H$_2$).

The H$_2$O molecule is a polar target that belongs to the $C_s$ point group and possesses three types of vibrational normal modes, i.e. the symmetric
stretching \((v_1)\), the bending \((v_2)\), and the antisymmetric stretching \((v_3)\) modes, all of which are infrared (IR) active. Therefore, the long-range interaction with a charged projectile is expected to be effective, especially because of the molecular permanent dipole moment. The vibrational excitation processes in the present molecules, considered as having only their low vibrational energy levels populated initially, could be treated as occurring separately through its different normal modes of vibration with different fundamental frequencies and symmetries. It is therefore interesting to try to understand how the separate vibrational excitation cross-sections depend on the feature of the specific mode without considering the mixing of the modes.

While, on the experimental side, total cross-sections for many types of atoms and molecules have been reported (see [6,7] and references quoted therein), to the authors’ knowledge, no measurement on vibrationally inelastic cross-sections for \(\text{H}_2\text{O}\) and \(\text{C}_2\text{H}_2\) molecules by positron collisions has been reported thus far. The last few years, however, have witnessed the development of a novel technique involving a magnetized beam of cold positrons, which allowed one to carry out measurements of absolute vibrationally inelastic cross-sections for \(\text{CF}_4\) [8], \(\text{CO}\), \(\text{CO}_2\), \(\text{H}_2\) [9] and \(\text{CH}_4\) [10]. These data have been measured at energies as low as 0.5 eV and up to several eV, with a greatly improved FWHM value of 18 meV. In the case of electron scattering off \(\text{H}_2\text{O}\) molecules, because of remarkable developments in experimental techniques, very recently measured electron energy loss spectra with 10 meV of FWHM have revealed that in this molecule the cross-section for the \(v_3\) mode is excited much less than the \(v_1\) at low scattering energies between 0.05 and 3 eV [11]. In the case of the positron, however, because that higher resolution required is not yet available, the excitations of the \(v_1\) and \(v_3\) modes cannot be completely resolved by the current quality of the measurements, nor have been attempted even as an unresolved peak.

These processes have thus stimulated the interest of theoreticians and spurred the formulation of computational methods which could provide predictions and explanations on how the phenomenon is occurring at the nanoscopic level. In this paper, we therefore report our computed cross-sections for the lowest excitations of \(\text{H}_2\text{O}\) molecules in both the \(v_1\) and \(v_3\) modes, and of \(\text{C}_2\text{H}_2\) for its symmetric stretching \((v_1)\) mode. We further discuss their features by comparing our findings with available approximate calculations on the same excitation processes.

The details of the present theory are described in the next section while the numerical techniques are presented in Section 3. In Section 4, we report the final cross-sections and discuss their behavior with reference to other available calculations. We give our preliminary conclusions in the last section of the paper. Atomic units (au) are used throughout the present analysis unless otherwise stated.

2. Theory

The details of the present theory have been already reported in our previous work [2,3], so we provide here to the reader only a brief reminder of it. In order to obtain vibrational excitation cross-sections for positron scattering from polyatomic molecules we need to solve the Schrödinger equation of the total system to yield the total wavefunction \(\Psi\) at a fixed value of the total energy \(E\). It should also be noted that no \(\text{Ps}\) formation channel is considered throughout the present calculations as this process is estimated to be fairly negligible at the energies we are considering.

We can also assume that the orientation of the target molecule is being kept fixed during the collision since molecular rotations are usually slower when compared with the velocity of the projectile. This is usually called the fixed-nuclear orientation (FNO) approximation [12], and corresponds to ignoring the rotational Hamiltonian of the total system. Then, the total wavefunction could be generally expanded as follows:

\[
\Psi(r_p|R) = r_p^{-1} \sum_{i,m} u_{i,m}(r_p) X_{i,v}(\mathbf{r}_p) \chi_a(R).
\]  

Here, \(\chi_a\) is the vibrational wavefunction of the molecule with the vibrational quantum number \(n \equiv (n_1, \ldots, n_N)\) with \(N\) representing the total number of normal vibrational modes of the target
molecule. The variables $\mathbf{R}$ and $\mathbf{r}_p$ now denote the molecular nuclear geometry and the position vector of the positron from the center-of-mass (c.o.m.) of the target, respectively. The unknown functions $u_{lvn}$ describe the radial coefficients of the wavefunction of the incident particle and the $X_n$ are the symmetry-adapted angular basis function [13]. In this paper, $v$ in Eq. (1) stands for the indices $(p\mu h)$ collectively, and $p$ stands for the chosen irreducible representation, $\mu$ distinguishes the component of the basis if its dimension is greater than one, and $h$ does that within the same set of $(p\mu)$.

After substituting Eq. (1) into the equation of the total collision system under the FNO approximation, we obtain for $u_{lvn}(r_p)$ a set of full close-coupling equations which now also include vibrational channels. These are also called the body-fixed vibrational close-coupling (BF-VCC) equations [1],

$$
\frac{d^2}{dr_p^2} + \frac{l(l+1)}{r_p^2} + k_n^2 u_{lvn}(r_p) = 2 \sum_{v'v''} \langle lvn|V|l'v'n'\rangle u_{l'v'n'}(r_p),
$$

(2)

where $k_n^2 = 2(E_0 - E_{n}^{\text{vib}})$ with $E_{n}^{\text{vib}}$ being the energy of the specific molecular vibration we are considering. Any of the elements of the interaction matrix in Eq. (2) is given by

$$
\langle lvn|V|l'v'n'\rangle = \sum_{l'v'n'} \int d\mathbf{R} \{ \xi_{l'v'n'}(\mathbf{R}) \}^* V_{l'v'n'}(r_p) \{ \xi_{lvn}(\mathbf{R}) \} 
\times \int d\mathbf{r}_p X_{l'v'n'}(\mathbf{r}_p)^* X_{lvn}(\mathbf{r}_p) X_{l'v'n'}(\mathbf{r}_p).
$$

(3)

This method is essentially a generalization of the method proposed long ago (called the ‘hybrid theory’) for the simple case of a diatomic molecule [14]. When solving Eq. (2) under the boundary conditions that the asymptotic form of $u_{l'v'n'}^{\text{in}}$ is represented by a sum containing the incident plane wave of the projectile and the outgoing spherical wave, we obtain the $K$-matrix elements. Therefore, the integral cross-section for the vibrationally inelastic scattering is given by

$$
Q(n \rightarrow n') = \frac{\pi}{k_n^2} \sum_{l'v'} \sum_{l''v''} |T_{l'v'n'}^{lvn}|^2,
$$

(4)

where $T_{l'v'n'}^{lvn}$ is the $T$-matrix element.

The interaction potential ($V$) between the impinging positron and the molecular target is represented here by us in the form of a local potential. Thus, $V$ is described by the sum of the repulsive electrostatic ($V_{n}^{\text{el}}$) and the attractive positron correlation-polarization ($V_{pp}^{\text{el}}$) terms. For the latter term, we have employed over the years [1] the simple parameter-free model potential, introduced by Boronski and Nieminen [15], in the short-range region of $r_p$, and have connected it smoothly with the asymptotic form of the polarization potential $-\alpha_0/2r_p^2$ with $\alpha_0$ being the spherical dipole polarization of the target.

In addition, one can also employ a simpler computational method which has often been employed to treat vibrational excitation. It is called the adiabatic nuclear vibration (ANV) approximation (see e.g. [16]) and in it, no direct positron dynamical coupling like in Eq. (3) is active during the scattering process. The $T$-matrix elements are thus obtained as simple expectation values with respect to the fixed-nuclei (FN) $T$-matrix for each specific normal mode of the target,

$$
T_{l'v'n'}^{lvn} = \int d\mathbf{R} \{ \xi_{l'v'n'}(\mathbf{R}) \}^* T_{l'v'n'}^{lvn}(\mathbf{R}) \{ \xi_{lvn}(\mathbf{R}) \}.
$$

(5)

3. Numerical details

The H$_2$O molecule is placed in $xz$-plane and the $z$-axis is taken along the $C_2$ symmetry axis with the oxygen atom on the positive side. The target wavefunctions of H$_2$O and C$_2$H$_2$ molecules were calculated at the self-consistent field level using the single-center expansion applied to a multiconfiguration Gaussian-type orbitals (GTOs) [17], and the basis set employed was given by the atomic and molecular orbital code GAUSSIAN 98 package [18]. The GTO basis sets we have chosen are those of D95* type which consist of, for the two molecules considered, (9s5p1d)/[4s2p1d] for oxygen, (9s5p)/[4s2p] for carbon, and (4s)/[2s] for hydrogen. The computed wavefunction of H$_2$O at the molecular equilibrium geometry (1.809 au of the O–H distance and 104.5° of the molecular angle), yields the dipole moment ($\mu_z$) and the total energy as $-2.299$
Debye (−1.85) and −76.0349 au, respectively: the number in brackets corresponds to the dipole experimental value. In the case of C2H2, the target wavefunction employed at the equilibrium geometry (C–H and C–C bond lengths are respectively 2.003 and 2.268 au) gives the total energy of −76.7992 au.

The terms of the multipolar expansion for the interaction potential in Eq. (3) were retained up to \( l_0 = 24 \), and the scattered wavefunction of the positron in Eq. (1) was expanded up to \( l = 12 \) for both the \( v_1 \) and the \( v_3 \) modes, and \( l_0 = 36 \) and \( l = 18 \), in the FN approximation, for the \( v_1 \) mode of C2H2. When solving Eq. (2) we have included the lowest two vibrational states of \( n = 0 \) and 1, assuming the vibrational wavefunctions to be that of the harmonic oscillator. The above parameters were found to describe to good numerical convergence the molecular anisotropy of the interaction. In order to solve the close-coupling equations by means of standard Green’s function techniques, Eq. (2) is rewritten as an integral equation, called a Volterra equation (for details, see [19–21]). For the polarizability of \( \alpha_0 \) which appears in the asymptotic region of the \( V_{pcp} \) term, we first obtain the values of \( \alpha_0 \) from the D95* type wavefunctions employed, and normalize our calculations to the experimental value of \( \alpha_0 \) (9.92 au for H2O and 28.68 au for C2H2) at the equilibrium geometry.

4. Discussion of results

The three panels shown in Fig. 1 report some of the computed quantities that are necessary to carry out the dynamical calculations described in the previous section. We describe there, in fact, the behavior of the dipole moment of H2O as a function of the coordinate changes for the two stretching modes we are studying. The top panel reports the behavior of the dipole component along the \( z \)-axis for the case of the symmetric stretching: the equilibrium computed value (−2.299 Debye) can be compared with the experimental value of −1.85 Debye, showing a difference of about 20%. The lower two panels report the corresponding variations for the two component (along the \( z \)- and \( x \)-axis) of the molecular dipole moments as a function of the antisymmetric stretching process: we see that our calculation reproduce correctly the dipole value (\( x \)-component) at the equilibrium geometry.

The calculation reported in Fig. 2 show the actual computed values of the \((0 \rightarrow 1)\) vibrationally inelastic cross-sections from their energy threshold and up to about 4 eV of collision energy. The following consideration could be made.

1. Both excitation cross-sections show very strong peaks of their cross-sections just above their respective threshold openings: the dominance of the charge–dipole coupling potential plus the polarizability effect obviously enhances the positron projectile excitation efficiency, a feature we had already detected for the IR active modes of CH4 molecule near their threshold openings [22].
2. Both excitation processes do not show any effect from closed channels since the inelastic cross-sections given within our essentially two-state picture are seen to have converged to their final values and to change very little when additional vibrational channels are included. This result also suggests that the system does not seem to have marked Feshbach-type resonances below the threshold openings.

3. The use of the more simplified computational scheme of Eq. (5), shown in the figure by the open circles, also indicates that an adiabatic physical picture of the inelastic process is giving the same results as those from the more rigorous BF-VCC calculations down to collision energies to threshold openings, where the cusp given by the latter method is only in part reproduced by ANV calculations.

4. The simpler Born calculations [12] also indicate the importance of the more sophisticated interaction potentials we have used in our work: their calculated \((v_1 + v_3)\) excitation cross-sections, open squares, are smaller than the BF-VCC and the ANV calculations at all the energies considered here and fail quite clearly to yield the threshold peak behaviors seen in the previous calculations.

5. Present conclusions

In this work we have presented quantum calculations for the vibrationally inelastic cross-sections of a polar and a nonpolar polyatomic
targets, i.e. for H\textsubscript{2}O and C\textsubscript{2}H\textsubscript{2}, obtained by positron impact at low collision energies. We have excluded in our treatment both the Ps formation channel and any other target excitation channel on the ground that, at the considered impact energies, those contributions are rather small [1].

The calculations included correctly the dynamical couplings between the impinging projectile and the stretching vibrations of the two kinds of molecules, limiting the present study to the symmetric and antisymmetric modes of water (v\textsubscript{1} + v\textsubscript{3}) and to the symmetric stretching mode of acetylene (v\textsubscript{1} mode). The interaction forces were obtained from a nonempirical description of the forces at play and the quantum coupled equations were solved within the molecular frame formation of the inelastic process (BF-VCC equations).

The present results clearly indicate the strong influence of structural factors on the excitation dynamics since the size of the inelastic cross-sections for the polar targets are more than a factor of 10 larger than those for the nonpolar molecule. Furthermore, the rather weak coupling between the positron and the vibrating molecules is underlined by three clear effects seen in the calculations: (i) the smaller size of the excitation cross-sections when compared with similar results for electron impact excitation in the low energy region [23], (ii) the fact that the close-coupling expansion over target vibrators is essentially given to convergence by a two-state expansion and (iii) that the adiabatic simplification provided by ANV model (see previous Section 3) produces excitation probabilities which are practically the same as the BF-VCC results unless the collision energies get very close to the excitation thresholds. A more extended analysis of the vibrational excitation for all three modes of the H\textsubscript{2}O molecule will be presented elsewhere [23].

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