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Near threshold vibrational excitation of molecules by positron impact: A projection operator approach

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Abstract

We report vibrational excitation ($v_i = 0 \to v_f = 1$) cross-sections for positron scattering by H_2 and model calculations for the ($v_i = 0 \to v_f = 1$) excitation of the C–C symmetric stretch mode of C_2H_2. The Feshbach projection operator formalism was employed to vibrationally resolve the fixed-nuclei phase shifts obtained with the Schwinger multichannel method. The near threshold behavior of H_2 and C_2H_2 significantly differ in the sense that no low lying singularity (either virtual or bound state) was found for the former, while a e^+-acetylene virtual state was found at the equilibrium geometry (this virtual state becomes a bound state upon stretching the molecule). For C_2H_2, we also performed model calculations comparing excitation cross-sections arising from virtual ($-i\kappa_0$) and bound ($+i\kappa_0$) states symmetrically located around the origin of the complex momentum plane (i.e. having the same κ_0). The virtual state is seen to significantly couple to vibrations, and similar cross-sections were obtained for shallow bound and virtual states.

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1. Introduction

Though in principle low energy electrons and positrons would not be expected to efficiently excite vibrational degrees of freedom of molecules, due to the small projectile masses, considerable energy transfer to vibrations usually takes place when the light particles are trapped in metastable states. Resonantly enhanced dissociation and vibrational excitation have long been observed in electron–molecule collisions, but only in the present decade a similar mechanism [1,2] was proposed to explain the very large annihilation rates of polyatomics [2–7]. The experimental evidence of vibrationally enhanced annihilation [3–5] and the first measurements of vibrationally resolved cross-sections [8,9] have attracted a lot of attention to the couplings between positron and nuclear degrees of freedom.

The recent experimental findings motivated our group, so far focused on fixed-nuclei elastic collisions [10,13–19] and electronic excitation [20,21], to develop a method to vibrationally resolve e^+–molecule collisions [11]. Our approach is based on the Feshbach projection operator formalism [12], which has long been employed in studies of long lived e^-–molecule compounds (resonances, virtual and bound states) [22]. The formalism describes the collision as the capture of the projectile in a temporary ion state, which eventually decays into a scattering channel, by decomposing the scattering wave function into a discrete state and a background continuum, with the former embedded and coupled to the latter. The formation of the transient launches the nuclei onto a complex and energy-dependent potential surface arising from the discrete–continuum coupling, and long lived transients significantly release energy into the nuclear degrees of freedom. The application of this well established approach to positron collisions is timely in view of the increasing interest on vibration dynamics.

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We report near threshold excitation of symmetry preserving (infrared inactive) vibrational modes of hydrogen and acetylene by positron impact. Though our formulation is more general, we focus on the *s*-wave contribution since it would be expected to be dominant at low energies, according to the Wigner threshold law [23]. We also present a discussion, based on model calculations, on the contribution of virtual and bound states to the *s*-wave cross-section, though estimates of the annihilation parameter (Z_{eff}) will be discussed elsewhere [24].

2. Theory

The Schrödinger equation for positron–molecule scattering is given by

$$H|\Psi_{\mathbf{k}_i v_i}\rangle = E|\Psi_{\mathbf{k}_i v_i}\rangle, \tag{1}$$

where $\mathbf{k}_i$ and v_i denote the incident positron wave vector and the initial vibrational eigenstate of the target, respectively. The Hamiltonian

$$H = K + H_{\text{ele}} = K + H_0 + V \tag{2}$$

is comprised by the nuclear kinetic energy operator (K), the positron–molecule scattering potential (V) and the electronic interaction-free Hamiltonian (H_0), given by the sum of the positron kinetic energy and the N-electron target Hamiltonian,

$$H_0 = -\frac{1}{2}\nabla_{\text{p}}^2 + H_N, \tag{3}$$

with the nuclear repulsion included in the latter. For simplicity, we restrict the formulation to a single vibrational mode and a single energy-allowed electronic channel (the target ground state). Formulations of the projection operator approach [12] accounting for target vibrations have long been proposed [25–30] and rely on a Born–Oppenheimer [31] electronic discrete state, $\phi_{\text{d}}(\mathbf{R}, \mathbf{r}_{\text{p}}; \rho)$, that uniquely defines the projectors $\mathcal{Q} = |\phi_{\text{d}}\rangle\langle\phi_{\text{d}}|$ and $\mathcal{P} = (1 - \mathcal{Q})$. In the present context, ϕ_{d} is an (N+1)-particle state including the positron ($\mathbf{r}_{\text{p}}$) and the N target electrons, $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$, and the semicolon $(;\rho)$ denotes parametric dependence on the nuclear coordinate ρ. Though the discrete e^+–molecule state would not exist in principle, since it would always be unstable against annihilation, the annihilation width is very small and can be neglected in comparison with the capture (decay) width associated with the coupling of ϕ_{d} to the continuum. The discrete state may also decay into the positronium formation channel, but this process can be safely disregarded in the low collision energies of interest, well below the Ps formation threshold.

The decomposition of the scattering wave function, $(\mathcal{P} + \mathcal{Q})|\Psi^{(+)}_{\mathbf{k}_i v_i}\rangle = |\Psi^{\mathcal{P}}_{\mathbf{k}_i v_i}\rangle + |\Psi^{\mathcal{Q}}_{\mathbf{k}_i v_i}\rangle$, splits up the T matrix, and the vibrational excitation cross-section becomes [12,26,32]

$$\sigma_{v_i \to v_f} = \frac{(2\pi)^3}{E}\left| T^{\text{bg}}_{v_f, v_i} + \left\langle \eta_{v_f} \left| U^*_{E_f} \frac{1}{E - K - V_{\text{opt}}(E - \widetilde{H}_N)} U_E \right| \eta_{v_i} \right\rangle \right|^2, \tag{4}$$

where $T^{\text{bg}}_{v_f, v_i}$ accounts for background scattering in the $\mathcal{P}$ space, $|\eta_v\rangle$ is a vibrational eigenstate of the target, and E (E_f) is the incoming (outgoing) positron energy. $U_E(\rho)$ is the angle-averaged positron capture (decay) amplitude (i.e. the $\mathcal{Q}$–$\mathcal{P}$ coupling matrix element), and the optical potential is given by [32]

$$V_{\text{opt}}(E - \widetilde{H}_N) = V_0(\rho) + \epsilon_{\text{d}}(\rho) + \Delta(E - \widetilde{H}_N) - \frac{\text{i}}{2}\Gamma(E - \widetilde{H}_N), \tag{5}$$

where

$$\widetilde{H}_N = K + V_0(\rho) \tag{6}$$

is the vibrational Hamiltonian of the target (V_0 is the ground state potential energy surface), and

$$\epsilon_{\text{d}}(\rho) = \langle\phi_{\text{d}}|H_{\text{ele}}|\phi_{\text{d}}\rangle - V_0(\rho) \tag{7}$$

is the relative energy of the discrete state with respect to the electronic ground state of the target; the electronic Hamiltonian (H_{ele}) is given in Eq. (2). Δ and Γ are the real and imaginary parts, respectively, of a complex, nonlocal and energy-dependent potential arising from the coupling of the discrete state (ϕ_{d}) to the continuum of background scattering states. The width Γ is related to the discrete–continuum decay probability and the level shift Δ contributes to the real part of the optical potential surface ($V_0 + \epsilon_{\text{d}} + \Delta$). Explicitly [32],

$$\Gamma(E - \widetilde{H}_N) = 2\pi \int k\text{d}k \int \text{d}\hat{\mathbf{k}}\, U_{\mathbf{k}} \delta\left(E - \widetilde{H}_N - \frac{k^2}{2}\right) U^*_{\mathbf{k}}, \tag{8}$$

and

$$\Delta(E - \widetilde{H}_N) = \frac{1}{2\pi} p \int \text{d}E' \frac{\Gamma(E' - \widetilde{H}_N)}{E - E' - \widetilde{H}_N}, \tag{9}$$

where the Cauchy principal value is indicated in Eq. (9).

2.1. Implementation

Though Eq. (4) is essentially exact, its calculation is not an easy task because the complex potential (V_{opt}) is energy-dependent and nonlocal in configuration space (it depends on the nuclear kinetic energy K through $\widetilde{H}_N$). The energy dependence of the complex potential is known to be important in near threshold scattering [33,34] and should not be neglected here. To avoid the scaling of the numerical effort, we employ a model description based on the work of Domcke et al. [32,34]. The decomposition of the fixed-nuclei T matrix is equivalent to the decomposition of the fixed-nuclei eigenphase sum

$$\delta(E) = \delta_{\text{bg}}(E) + \delta_{\text{d}}(E), \tag{10}$$