



## Research paper

## Quantum dynamics study on the binding of a positron to vibrationally excited states of hydrogen cyanide molecule

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## ABSTRACT

We present computational results of vibrationally enhanced positron annihilation in the  $e^+ + \text{HCN}/\text{DCN}$  collisions within a local complex potential model. Vibrationally elastic and inelastic cross sections and effective annihilation rates were calculated by solving a time-dependent complex-potential Schrödinger equation under the *ab initio* potential energy surface for the positron attached HCN molecule,  $[\text{HCN}; e^+]$ , with multi-component configuration interaction level (Kita and Tachikawa, 2014). We discuss the effect of vibrational excitation on the positron affinities from the obtained vibrational resonance features.

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## 1. Introduction

Positrons have been widely used to probe negatively charged vacancy defects in bulk materials and also to detect cancer sites in human bodies using a positron-emission-tomography (PET) technique as an important medical application [1,2]. In spite of these widely-used applications of positrons, detailed interaction between positrons and molecules including positron binding mechanisms has not yet been fully understood from a viewpoint of molecular science. However, due to recent experimental developments to produce a high-resolution low-energy positron beam by Surko's group [3–5], it is becoming uncovered that many molecules including organic compounds can bind positrons with the corresponding binding energies (or positron affinities) being in a range of a few meV to ~300 meV depending on their molecular properties. In particular, it has been found that the magnitude of the measured positron binding energy roughly correlates with the molecular polarizability and permanent dipole moment of the molecule [6–9]. Notice that those positron binding energies are indirectly measured through the Feshbach-type resonance process, where a positron is transiently trapped to the molecule in the specific vibrationally excited state.

In order to understand detailed positron binding mechanisms in molecules at an atomic level, it should be highly important to compare experimental results with theoretical prediction. There have been some theoretical attempts to understand positron binding phenomena in molecules. The most important conclusion of the previous theoretical studies is that the electron-positron dynamical correlation is playing a crucial role for positron binding in molecules. Various methodologies including multi-component molecular orbital Hartree-Fock [10,11], many-body perturbation [12,13], configuration interaction [14–16], explicitly correlated Gaussian wave functions [17–19], and *ab initio* quantum Monte Carlo methods [20–23], have been so far applied. We should notice here that these first-principles *ab initio* calculations were carried out at the equilibrium structure under the fixed nuclei based on the Born-Oppenheimer approximation. Recently, the theoretical works of vibrational averaged positron binding is also reported under the multi-component *ab initio* potential energy surface for the positron attached molecule [24–29]. In addition to these electronic/positronic-structure-based studies, it should be mentioned that positron annihilation enhancement through the coupling between vibrational deformation of the molecular structure and virtual state formation was previously studied by Nishimura and Gianturco [30–32]; however, their study was based on a fixed-nuclei model and vibrational dynamics has not been explicitly taken into account.

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In this paper, we report results of quantum scattering dynamics calculations for the  $e^+ + \text{HCN}/\text{DCN}$  collision processes using a vertical positron affinity surface, which has been recently obtained as a function of the molecular geometry from the truncated multi-component configuration interaction level of *ab initio* calculations [26]. According to the calculations, the vertical positron affinity value is highly dependent on the molecular geometry. Interestingly, it was found that vibrational excitation of the CN and CH stretching modes enhances the positron affinity compared to that at the HCN equilibrium structure. This conclusion is very important since, as mentioned above, positron binding energies have been experimentally measured through the vibrationally excited state Feshbach resonances of molecules, providing some cautions for determining accurate positron binding energies [26–29]. Since the HCN molecule has only three degrees of freedom, one can perform quantum dynamics calculations without reducing its dimensionality. Unfortunately, positron beam experiments have not yet been performed for HCN/DCN; however, we believe that the present dynamics calculations may provide a good theoretical model for understanding the effect of molecular vibration on positron binding.

We here employ the local-complex-potential (LCP) model [33–42], which is based on a Born-Oppenheimer picture, to understand the dynamics of vibrational excitation and positron annihilation process. Within the simplest LCP model, the nuclear motions are governed by the complex-valued potential energy surface of  $V(\mathbf{Q}) - i\Gamma(\mathbf{Q})/2$ , where  $V$  and  $\Gamma$  are real and imaginary parts, respectively, and are functions of the nuclear coordinates  $\mathbf{Q}$ . Notice that  $V$  and  $\Gamma$  respectively correspond to the positronic resonance energy position and its resonance width determining the positron capture/detachment lifetime at a given nuclear configuration, where these two quantities are assumed to be independent of positron collision energy.

## 2. Method

The nuclear dynamics of resonant positron attachment within the LCP approximation can be described by the following time-dependent Schrodinger equation (with  $\hbar = 1$ ) as

$$i \frac{\partial \psi(R, r, \theta, t)}{\partial t} = \left[ T_N(R, r, \theta) + V(R, r, \theta) - \frac{i}{2} \Gamma(R, r, \theta) \right] \psi(R, r, \theta, t) \quad (1)$$

where  $T_N$  is the nuclear kinetic operator and  $(R, r, \theta)$  denote a set of the standard Jacobi coordinates for the H + CN configuration with  $R$  ( $= R_{\text{H-CN}}$ ) and  $r$  ( $= r_{\text{CN}}$ ) being the radial coordinates and  $\theta$  being the angular coordinate. Here, the electronic/positronic potential energy surface is given by  $V - i\Gamma/2$ , where  $V$  is the real part of the energy and  $\Gamma$  is the resonance width determining the positron capture/detachment lifetime. All the calculations presented here were done with  $J = 0$ , where  $J$  is the total angular momentum of the triatomic HCN system. The time-dependent wave packet  $\psi$  is propagated in time with the following initial condition [38,40],

$$\psi(R, r, \theta, t = 0) = \phi_{v_i}(R, r, \theta) = \sqrt{\frac{\Gamma(R, r, \theta)}{2\pi}} \chi_{v_i}(R, r, \theta) \quad (2)$$

where  $\chi_{v_i}$  is the vibrational wavefunction of HCN in the  $v_i$ -th vibrational state. The vibrationally elastic and inelastic cross sections can be calculated from the following equation as [40]

$$\sigma_{v_i \rightarrow v_f} = \frac{4\pi^3}{k^2} \left| \int_{-\infty}^{\infty} \phi_{v_f}(R, r, \theta) \exp(iEt) \psi(R, r, \theta, t) dt \right|^2 \quad (3)$$

where  $k$  is the wave vector corresponding to the initial positron collision energy. Similarly, the positron annihilation rate  $Z_{\text{eff}}$ , which

can be expressed as an effective number of electrons per molecule, is written as [40]

$$Z_{\text{eff}} = \frac{2\pi^2}{k} \int_{-\infty}^{\infty} \psi(R, r, \theta, t) \rho_d(R, r, \theta) \exp(iEt) \psi(R, r, \theta, t = 0) dt \quad (4)$$

$$\sim \frac{2\pi^2}{k} \rho_d \int_{-\infty}^{\infty} \psi(R, r, \theta, t) \exp(iEt) \psi(R, r, \theta, t = 0) dt$$

where  $\rho_d$  is the electron density at the positron position. In principle, the electron density should be parametrically dependent on the nuclear coordinates; however, we here assume that  $\rho_d$  is a constant value. Thus,  $Z_{\text{eff}}$  is simply determined by the Franck-Condon factor as described in Eq. (4).

The positronic/electronic potential energy surface  $V$  in eq. (1) is written as

$$V(R, r, \theta) = V^n(R, r, \theta) - E^{\text{PA}}(R, r, \theta) \quad (5)$$

where  $V^n$  is the potential energy surface of the neutral HCN molecule. We have employed the potential energy surface developed by Bowman et al. on the basis of the *ab initio* CCSD(T)-level electronic structure calculations [43].  $E^{\text{PA}}$  is the vertical positron affinity surface and its functional form is simply approximated as

$$E^{\text{PA}}(R, r, \theta) = E_0^{\text{PA}} + a_0(R - R_e) + a_1(R - R_e)^2 + a_2(r - r_e) + a_3(r - r_e)^2 + a_4(1 - \cos \theta) + a_5(R - R_e)(r - r_e) + a_6(R - R_e)(1 - \cos \theta) \quad (6)$$

where  $E_0^{\text{PA}}$  (39.5 meV) is the positron affinity value at the HCN equilibrium structure ( $R_e, r_e, \theta = 0$ ). We [26] have previously calculated the PA values of HCN at a total of 2810 geometric grid points. The parameters  $a_0$ – $a_6$  were determined from a least-square fitting to these calculated PA values ( $a_0 = 42.855$ ,  $a_1 = 21.714$ ,  $a_2 = 16.789$ ,  $a_3 = -13.991$ ,  $a_4 = -96.942$ ,  $a_5 = 2.297$ , and  $a_6 = -13.23$ ). This fitting yielded the root-mean-square deviation and the maximum deviation to be 6.5 meV and 49.0 meV, respectively.

As for the resonance width function, we here employ the simple form,  $\Gamma(R, r, \theta) = \alpha \exp[-\beta E^{\text{PA}}(R, r, \theta)]$ , which is a function of the positron affinity value given in Eq. (6) in order to reduce the number of empirical parameters as much as possible. Although this functional form cannot describe the Wigner threshold law behavior appropriately, this form has been chosen so as that a positron can be effectively captured around the potential energy region where the positron affinity is small. In this work,  $\alpha$  and  $\beta$  are chosen to be 50 meV and  $0.08 \text{ meV}^{-1}$ , respectively, in most of the present calculation. The parameter dependence on the computed results will be also given later. It should be mentioned that the above resonance width can be written as  $\Gamma = \Gamma^c + \Gamma^a$ , where  $\Gamma^c$  and  $\Gamma^a$  are the positron capture/detachment and annihilation widths, respectively. Theoretical work by Gribakin and Lee previously shows that the total resonance width  $\Gamma$  is exclusively determined by  $\Gamma^c$  due to the  $\Gamma^c \gg \Gamma^a$  relation [44].

In order to numerically solve the time-dependent Schrodinger equation of Eq. (1), we have used the standard discrete-variable-r representation (DVR) grid basis functions for all the Jacobi internal coordinates [45]. The standard sine DVR functions were used for the  $R$  and  $r$  radial degrees of freedom, while the Legendre DVR function was used for the angular  $\theta$  coordinate. The wave packet was propagated by using the standard split-operator method for time-evolution, where the action of the exponential containing the radial kinetic energy operator was carried out using the fast-Fourier transform (FFT) algorithm [46–49]. The numerical parameters used in this study were carefully chosen from extensive convergence tests including vibrational energy states of HCN/DCN, and scattering cross sections and annihilation rates. The present calculations were done with the grid size of 128, 128, and 60 for the  $R$  [2–4.5  $a_0$ ],  $r$  [1.8–3.8  $a_0$ ], and  $\theta$  [0–180 deg.] coordinates ( $a_0$  is the Bohr radius), respectively. We have carried out the calculations with a larger size of 256, 256, and 80, and

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