

Positron-attachment to acetonitrile, acetaldehyde, and acetone molecules: Vibrational enhancement of positron affinities with configuration interaction level of multi-component molecular orbital approach

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Abstract. To theoretically demonstrate the binding of a positron to acetonitrile, acetaldehyde, and acetone molecules, we have calculated the vibrational averaged positron affinity (PA) values along the local CN or CO vibrational contribution with the configuration interaction level of multi-component molecular orbital method. This method can take the electron-positron correlation contribution into account through single electronic - single positronic excitation configurations. The PA values are enhanced by including the local vibrational contribution from vertical PA values due to the anharmonicity of the potential. For acetonitrile, acetaldehyde, and acetone molecules, the PA values after averaging over the 1st vibrational state are 136, 55, and 96 meV, which can be compared with the corresponding experimental values of 180, 90, and 173 meV, respectively.

1. Introduction

A positron, which is the antiparticle of an electron, has same mass, same spin of an electron but positive charge. Positrons injected into a liquid or solid induce processes such as ionization or electronic excitation of atoms/molecules, the formation of a meta-stable bound state of a positron and an electron (positronium, Ps), and the formation of positronic molecular complexes, etc., before the positron undergoes pair-annihilation with an electron. Recently, the positron is studied in many areas such as physics, chemistry, material science, medicine, etc [1, 2]. In medical field, positron emission tomography (PET) is known to be a powerful tool as non-destructive scanning [3].

A number of binding energies of positron (positron affinities, PAs) to molecular species such as hydrocarbons, alcohols, and halogenated hydrocarbons have been experimentally reported by Surko and co-workers [4-10]. A positron should be able to form an infinite number of bound states with non-rotating molecules if the molecule has a dipole moment with a value greater than 1.625 Debye (the critical dipole moment, D_c) [11, 12]. Recently, Danielson *et al.* [8] have experimentally measured the PA values of acetonitrile, acetaldehyde, and acetone molecules as 180, 90, and 173 meV, respectively. We note here that they experimentally measured PA values via the vibrational Feshbach resonance in which a positronic molecular complex can be formed at the molecular vibrational excited states by absorbing the excess energy of an incident positron.

Meanwhile, the most theoretical works for the positron-binding molecules are on “polar” molecules with strong dipole moment such as alkali metal hydrides [13-16], carbonyl and aldehyde



species [17-19], some nitrile species [20-22], and so on. Recently, we have applied our multi-component molecular orbital (MC_MO) method [23-25] to positron-binding to some molecules, and shown the importance of vibrational contribution [19, 26]. We have already calculated the vertical PA values for acetonitrile, acetaldehyde, and acetone molecules as 135, 52, and 92 meV, respectively [19, 22]. To our knowledge, however, the theoretical analysis for acetonitrile, acetaldehyde, and acetone molecules including both electron-positron correlation and vibrational contribution has not been reported, yet.

In this study, thus, we would like to quantitatively analyse the PA values for acetonitrile, acetaldehyde, and acetone molecules. We will calculate vibrational averaged PA values including both the local CN or CO vibrational contribution and positron-electron correlation by configuration interaction treatment with our MC_MO scheme [23-25] for these species.

2. Theory

We show here a brief outline of the multi-component molecular orbital (MC_MO) method. The details are described in Refs. [23-25]. The non-relativistic Hamiltonian operator for a molecular system containing N_e electrons, N_{nuc} fixed nuclei, and a positron (p) is

$$H = -\frac{1}{2} \sum_i \nabla_i^2 - \frac{1}{2} \nabla_p^2 + \sum_i \sum_{j>i} \frac{1}{r_{ij}} - \sum_i \sum_I \frac{Z_I}{r_{iI}} - \sum_i \frac{1}{r_{ip}} + \sum_I \frac{Z_I}{r_{pI}}, \quad (1)$$

where the first and second terms are the kinetic energy operators for the electrons and positron, respectively. The other terms are the Coulomb interaction: Z_I is the charge of the I -th nucleus and the variables of r_{ij} , r_{ip} , etc. are the distances between particles.

The total wave function ($|\Psi_{\text{tot}}(\mathbf{R}_e, \mathbf{r}_p)\rangle$) of the positronic compound is given as a configuration interaction (CI) formalism of

$$\begin{aligned} |\Psi_{\text{tot}}(\mathbf{R}_e, \mathbf{r}_p)\rangle &= \sum_L |\Psi_L(\mathbf{R}_e, \mathbf{r}_p)\rangle C_L \\ &= |\Phi_0^e(\mathbf{R}_e)\rangle |\phi_0^p(\mathbf{r}_p)\rangle C_{(0,0)} + \left(\sum_{L_e} \sum_{L_p} \right) |\Phi_{L_e}^e(\mathbf{R}_e)\rangle |\phi_{L_p}^p(\mathbf{r}_p)\rangle C_{(L_e, L_p)}, \end{aligned} \quad (2)$$

where C_L ($C_{(L_e, L_p)}$) is the CI coefficient of L th configuration ($|\Psi_L(\mathbf{R}_e, \mathbf{r}_p)\rangle$) which consists of products of the L_e th electronic configuration of Slater determinant ($|\Phi_{L_e}^e(\mathbf{R}_e)\rangle$) and L_p th positronic orbital ($|\phi_{L_p}^p(\mathbf{r}_p)\rangle$). The variable $\mathbf{r}_p$ is the positronic coordinate, and $\mathbf{R}_e = (\mathbf{r}_1, \dots, \mathbf{r}_{N_e})$ the $3N_e$ -dimensional position vector consisting of the electronic coordinates.

If one treats only the first term of Eq. (2), one can easily derive the mean-field Hartree-Fock (HF) equations of the MC_MO method. Considering a closed shell electronic structure, the one-particle electronic and positronic Fock operators are as

$$f^e(\mathbf{r}_e) = h^e(\mathbf{r}_e) + \sum_i^{N_e/2} [2J_i(\mathbf{r}_e) - K_i(\mathbf{r}_e)] - J_p(\mathbf{r}_e), \quad (3)$$

$$f^p(\mathbf{r}_p) = h^p(\mathbf{r}_p) - \sum_i^{N_e/2} 2J_i(\mathbf{r}_p), \quad (4)$$

where $h^e(\mathbf{r}_e)$ is the one-particle operator, which contains the kinetic energy and Coulomb interaction potential with the nuclei, J_i is the Coulomb operator and K_i is the exchange operator. Expanding the molecular orbitals of the electrons and the positron as linear combinations of basis functions, one can obtain the multi-component electronic and positronic wave functions by solving the Roothaan equations simultaneously, and also obtain the HF energy.

The following CI matrix elements are calculated by modification of the graphical unitary group approximation (GUGA) technique for the positronic compound:

$$\begin{aligned}
 H_{LL'} &= \langle \Psi_L(\mathbf{R}_e, \mathbf{r}_p) | H | \Psi_{L'}(\mathbf{R}_e, \mathbf{r}_p) \rangle \\
 &= \left\langle \Phi_{L_e}^e(\mathbf{R}_e) \left| -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i \sum_{j>i} \frac{1}{r_{ij}} - \sum_i \sum_I \frac{Z_I}{r_{iI}} \right| \Phi_{L'_e}^e(\mathbf{R}_e) \right\rangle \left\langle \phi_{L_p}^p(\mathbf{r}_p) | \phi_{L'_p}^p(\mathbf{r}_p) \right\rangle \\
 &\quad + \left\langle \Phi_{L_e}^e(\mathbf{R}_e) | \Phi_{L'_e}^e(\mathbf{R}_e) \right\rangle \left\langle \phi_{L_p}^p(\mathbf{r}_p) \left| -\frac{1}{2} \nabla_p^2 + \sum_I \frac{Z_I}{r_{pI}} \right| \phi_{L'_p}^p(\mathbf{r}_p) \right\rangle \\
 &\quad - \left\langle \Phi_{L_e}^e(\mathbf{R}_e) \left| \left\langle \phi_{L_p}^p(\mathbf{r}_p) \left| \sum_i \frac{1}{r_{ip}} \right| \Phi_{L'_e}^e(\mathbf{R}_e) \right\rangle \right| \phi_{L'_p}^p(\mathbf{r}_p) \right\rangle,
 \end{aligned} \tag{5}$$

where the first, second, and third terms denote the contributions of electronic, positronic, and simultaneous electronic-positronic correlations, respectively. After diagonalization of the CI matrix of Eq. (5), one can obtain the CI wave function and its energy.

To calculate positron affinity (PA) values including the contribution of molecular vibrations, we employed the scheme proposed by Gianturco *et al.* [15]. In this scheme, the PA of parent molecules on vibrational states is assumed to be evaluated in the Born-Oppenheimer framework, i.e., within the picture of an immediate positron attachment to molecule at a given geometry, and be modulated by the vibrational wave function of parent molecule before the geometrical relaxation process due to the positron attachment occurs. Under the assumption, we can define the vibrational averaged PA of molecule X as

$$\text{PA}_\nu^X = \frac{\int_0^\infty \{E^X(\mathbf{R}) - E^{[X;e^+]}(\mathbf{R})\} |\psi_\nu^X(\mathbf{R})|^2 d\mathbf{R}}{\int_0^\infty |\psi_\nu^X(\mathbf{R})|^2 d\mathbf{R}}, \tag{6}$$

where $\mathbf{R}$ means the vibrational normal coordinate, $E^X(\mathbf{R})$ ($E^{[X;e^+]}(\mathbf{R})$) and $\psi_\nu^X(\mathbf{R})$ the total energy of molecule X (positron-attached molecule $[X; e^+]$) and the ν th local CN or CO vibrational wave function of molecule X, respectively. In the numerical integration of Eq. (6), we set the negative PA values as zero. Because of the limitation of our computational resources, we have calculated these molecules considering only the CN or CO local stretching modes.

3. Computational detail

First, we have optimized the geometry of the parent acetonitrile (CH_3CN), acetaldehyde (CH_3CHO), and acetone ($(\text{CH}_3)_2\text{CO}$) molecules at the HF/6-31++G(2df,2pd) level of calculation [19, 22]. Second, we have employed the single-point calculation for positron-attached complexes at the optimized equilibrium structures of the parent species. An even-tempered $[15s15p3d2f1g]$ GTF positronic basis set is employed with $\alpha_{i+1} = c \times \alpha_i$, where $c=3.1623$ and $\alpha_1 = 1.0 \times 10^{-6}$ for s - and p -type GTFs. The other positronic polarized GTF exponents are 0.31623, 0.1, 0.031623 for d -type, 0.31623, 0.01 for f -type, and 0.31623 for g -type GTFs. All positronic GTFs are centered on the oxygen or nitrogen nucleus. Note that the positronic basis set with small exponent value is indispensable for describing weakly bound positron. In all calculations, the centers of positronic basis sets were fixed on the oxygen or nitrogen nucleus with great electro-negativity. We have confirmed that the basis set center dependence was completely negligible since positronic basis sets were quite diffusive.

We have employed the truncated singly and doubly excited configuration interaction (CISD) levels, where three types of excitations, (i) single electronic, (ii) single positronic, and (iii) both single

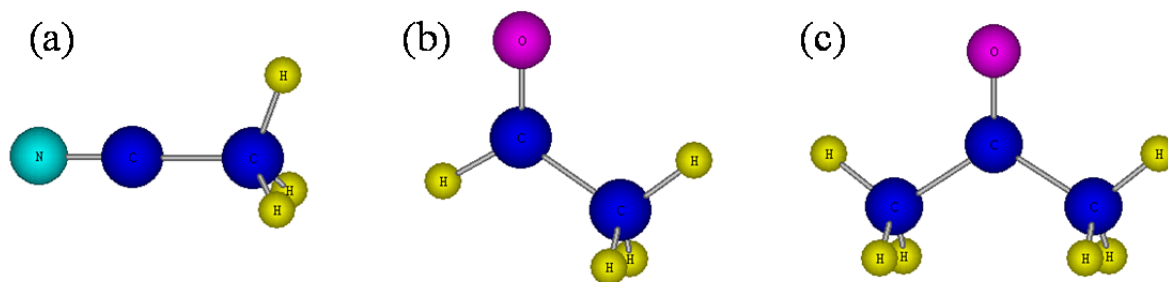


Figure 1. Optimized equilibrium geometries of (a) acetonitrile (CH_3CN), (b) acetaldehyde (CH_3CHO), and (c) acetone ($(\text{CH}_3)_2\text{CO}$) molecules at the HF/6-31++G(2df,2pd) level.

electronic - single positronic excitation configurations are included. We note here that our CISD level of calculation includes no pure electronic correlation contributions (no double electronic excitation terms) [17-20, 22]. Strictly speaking, more extension of the configuration space and the polarized basis functions will definitely improve the total energy and properties, since the CI expansion for positronic systems is known to converge slowly. Recently, however, we have already shown that the PA value for HCN molecule obtained with our CISD calculations [22] can be qualitatively compared to our previous quantum Monte Carlo (QMC) result [21], though our variational energy for the $[\text{HCN}; e^+]$ species is still higher than that obtained by QMC. Thus, we have decided to employ our truncated CISD level under the limitation of computational facilities.

Calculations of parent molecules were performed with GAUSSIAN 03 program package [27] and CI calculations of positronic compounds were carried out using our own program package of the MC_MO [28].

4. Results and discussion

4.1. Vertical positron affinity value

Figure 1 summarizes the optimized equilibrium geometries of acetonitrile (CH_3CN), acetaldehyde (CH_3CHO), and acetone ($(\text{CH}_3)_2\text{CO}$) molecules at the HF/6-31++G(2df,2pd) level. We note here that electrons are drawn toward the nitrogen (oxygen) atom from the carbon atom in these CN (CO) groups. We have employed single-point calculations for the positronic complexes of these carbonyl molecules with the fixed equilibrium geometries as shown in Figure 1. The PA values for acetonitrile, acetaldehyde, and acetone molecules are 135, 52, and 92 meV, respectively, which are highly correlated with the dipole moment values of 4.12, 3.13, and 3.27 debye for parent species [19, 22]. We note here that our calculated vertical PA values are smaller than the experimentally measured PA values of 180, 90, and 173 meV for these molecules, respectively [8].

4.2. Vibrational averaged positron affinity values

To discuss one of the reasons for the above differences between our calculated and corresponding experimental PA values, we have taken the vibrational contributions into account. Following ref. 15, we have evaluated the averaged PA values in the Born-Oppenheimer framework, i.e., within the model of an immediate positron attachment to these molecules at a given geometry, modulated by the vibrational wave function of the initial parent species before the relaxation process occurs.

In Table 1, first, we show the dipole moments and the vertical PA values ($E^X(R) - E^{[X;e^+]}(R)$) at various CN distances for acetonitrile molecule. Table 1 clearly demonstrates that the PA values become greater as the CN distance increases. This result correlates with the corresponding dipole moment values.

Next, we have solved the one-dimensional Schrödinger equation for nuclear wave functions on the potential energy curve of the local CN stretching coordinate. Figure 2 shows the potential energy

Table 1. Dipole moments (μ) and positron affinities (PA) at various CN distances (R_{CN}) in acetonitrile molecule.

$R_{\text{CN}}(\text{\AA})$	$\mu(\text{debye})$	PA(meV)
0.969	3.87	92
0.995	3.93	99
1.022	3.99	105
1.048	4.05	112
1.075	4.11	120
1.101	4.17	127
1.128	4.23	135
1.154	4.29	143
1.181	4.35	151
1.207	4.42	160
1.234	4.48	169
1.260	4.54	178
1.286	4.60	188
1.313	4.66	197
1.339	4.73	208

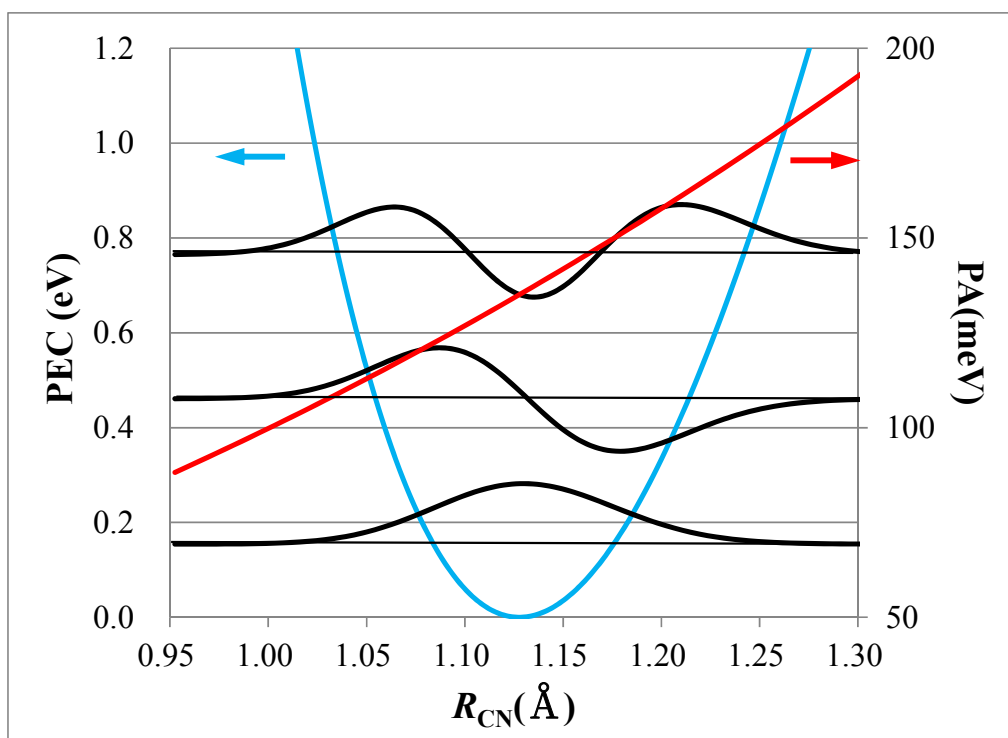


Figure 2. The one-dimensional potential energy curve (PEC, blue line on a left-handed side scale in eV) and positron affinity (PA, red line on a right-handed side scale in meV) values with respect to the local CN stretching coordinate for acetonitrile molecule. The corresponding 0th, 1st, and 2nd vibrational wave functions are also shown.

Table 2. Vibrational averaged PA values and R_{CN} (R_{CO}) distances for acetonitrile, acetaldehyde, and acetone molecules. Experimental PA values are also shown. Eq. means values at equilibrium position.

	Acetonitrile		Acetaldehyde		Acetone	
	PA(meV)	$R_{\text{CN}}(\text{\AA})$	PA(meV)	$R_{\text{CO}}(\text{\AA})$	PA(meV)	$R_{\text{CO}}(\text{\AA})$
Eq.	135	1.128	52	1.182	92	1.187
$\nu=0$	136	1.131	55	1.186	96	1.191
$\nu=1$	139	1.138	63	1.194	105	1.199
$\nu=2$	141	1.144	70	1.202	115	1.207
$\nu=3$	144	1.151	77	1.210	124	1.215
$\nu=4$	146	1.157	83	1.217	131	1.221
Exptl. ^[8]	180		90		173	

curve (PEC, on a left-handed side scale in eV), positron affinity (PA, on a right-handed side scale in meV) values, and 0th, 1st, and 2nd vibrational wave functions with respect to the local CN stretching coordinate. Our 0- $\rightarrow$ 1 vibrational excitation energy is 2474 cm^{-1} which is slightly smaller than the corresponding CN harmonic normal mode frequency of 2588 cm^{-1} with HF/6-31++G(2df,2pd) level [27], mainly due to the anharmonic effect and neglecting the motions of methyl group. The energies of the 0th, 1st, and 2nd vibrational states are 1244 , 3718 , and 6169 cm^{-1} (154 , 461 , and 765 meV), respectively. The expectation values of CN distance for these vibrational states are calculated to be 1.131 , 1.138 , and $1.144\text{ \AA}$, respectively. It should be noted that these values are longer than the corresponding equilibrium one of $1.128\text{ \AA}$, due to the anharmonicity of the potential energy curve.

In Table 2 calculated vibrational averaged PA values for acetonitrile, acetaldehyde, and acetone molecules are shown using Eq. (6). The $\text{PA}_{\nu}^{\text{CH}_3\text{CN}}$ values for $\nu=0$, 1 , and 2 are 136 , 139 , and 141 meV , respectively. Contrary to the alkali-halide cases [15], our $\text{PA}_{\nu}^{\text{CH}_3\text{CN}}$ value of 136 meV is slightly greater than the pure vertical PA value of 135 meV . Interestingly, the vibrational averaged PA value increases quickly with ν , since the expectation values of CN distance for $\nu=1$ and 2 are longer than that for $\nu=0$ due to the anharmonicity of the CN potential in Figure 2. Although the PA values are enhanced by including the local CN vibrational contribution, the correction is actually quite small. The inclusion of other vibrational degrees of freedom such as methyl group contribution and coupling between vibrational modes would be important for more quantitative discussion.

In Table 2 similar tendency is shown in acetaldehyde and acetone molecules; The $\text{PA}_{\nu}^{\text{CH}_3\text{CHO}}$ ($\text{PA}_{\nu}^{(\text{CH}_3)_2\text{CO}}$) values for $\nu=0$, 1 , and 2 are 55 , 63 , and 70 (96 , 105 , and 115) meV , respectively. These results imply that the experimental PA values should be greater than the vertical PA ones, since vibrationally excited states are included in forming positron-molecule bound states via Feshbach resonances in which a vibrational mode absorbs the excess energy.

We have found that the positron is trapped in the field of the dipole potential and the corresponding vertical PA values are all positive for acetonitrile, acetaldehyde, and acetone molecules. We have also found that the PA values are enhanced by including the local CN or CO vibrational contribution. The inclusion of other vibrational degrees of freedom and application to other molecules are quite interesting topics. Such studies are now in progress in our group.

5. Conclusion

We have elucidated the positron binding structure of acetonitrile, acetaldehyde, and acetone molecules with the configuration interaction scheme of multi-component molecular orbital calculations by including the local CN or CO vibrational contribution. Our vertical PA values for these molecules are

135, 52, and 92 meV, respectively, which are highly correlated with the dipole moment values of 4.12, 3.13, and 3.27 debye for the corresponding parent species. The PA values are enhanced by including the local vibrational contribution due to the anharmonicity of the potential. For acetonitrile, acetaldehyde, and acetone molecules, the PA values after averaging over the 1st vibrational state are 136, 55, and 96 meV, which can be compared with the corresponding experimental values of 180, 90, and 173 meV, respectively.

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