Effects of vibrational anharmonicity and inter-mode couplings on the binding energy of a positron to molecules

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Abstract. We theoretically analyzed the effect of the anharmonicity and the inter-mode couplings of molecular vibrations on a positron affinity (PA), which is the binding energy of a positron to HCN and CH$_2$O molecules. Based on different theoretical approaches for describing vibrational wave functions, we confirmed that (i) not only the anharmonicity but also the inter-mode couplings on potential energy surface are indispensable for the accurate calculation of PA values, and (ii) the effect of inter-mode couplings on a positron affinity surface is sufficiently weaker than that on potential energy surface.

1. Introductions
Positrons are widely used in both scientific and technological areas such as physics, chemistry, material science, medicine, and their interdisciplinary areas [1, 2]. The understanding of the fundamental processes of positrons in materials is expected to provide useful information for the interaction of the positron with surfaces, bulk materials, and polymers, as investigated using techniques such as Doppler broadening of positron annihilation radiation, angular correlation of annihilation radiation, positron annihilation lifetime spectroscopy, etc.

A positron affinity (PA), which is a binding energy of a positron to an atom or molecule, is one of the most important properties for positron-attached systems as well as an annihilation rate. Surko and co-workers have succeeded in measuring the experimental PA values for many molecular species such as hydrocarbons, alcohols, nitriles, aldehydes, etc. using the vibrational Feshbach resonance (VFR) technique [3-6]. In VFR processes, a positron molecular complex can be formed at vibrational excited states of the molecule by absorbing the excess energy of an incident positron. Thus, the effect of molecular vibrations could have an important role on the binding of a positron in this phenomenon.

Recently, we have theoretically demonstrated the effect of molecular vibrations on the PA values of hydrogen cyanide (HCN) and formaldehyde (CH$_2$O) molecules [7, 8] using ab initio multi-component molecular orbital and vibrational quantum Monte Carlo methods. For both molecules, vibrational excitations cause a drastic change in molecular PA values, and such PA variations mainly arise from the change in molecular permanent dipole moments by the excitations. The details of anharmonicity and inter-mode couplings of molecular vibrations, however, have not been discussed from a quantitative point of view, yet. In the present study, we discussed the PA values of HCN and CH$_2$O molecules at vibrational excited states using different theoretical approaches for describing vibrational wave functions, in order to elucidate the effect of the anharmonicity and the inter-mode couplings of molecular vibrations on the positron binding to the molecules.
2. Method
In order to estimate molecular PA values including the effect of molecular vibrations, we employed the vibrational averaged scheme [7]. The vibrational averaged PA value (PA\textsubscript{v}) are defined as
\[PA_v = \frac{\int \Psi_v(Q) PA(Q) |\Psi_v(Q)|^2 dQ}{\int |\Psi_v(Q)|^2 dQ},\]
where Q = (Q, Q, ..., Q\textsubscript{v}) means vibrational normal mode coordinates, \Psi_v the \(v\)\textsuperscript{th} vibrational wave function of a parent molecule, and PA(Q) the following vertical PA at a given Q:
\[PA(Q) = E^M(Q) - E^{[M;e^+]}(Q),\]
where \(E^M\) and \(E^{[M;e^+]}\) are total energies of a parent molecule (M) and its positronic complex ([M;e^+]), respectively. The PA\textsubscript{v} value corresponds to the weighted average of vertical PA values with vibrational probability density function (|\Psi_v|^2). The vibrational wave function is assumed to be the form of products of modal functions \(\phi\) as \(\Psi_v = \prod_{\text{all modes}} \phi\). We employed three different methods to obtain modal functions: (i) vibrational quantum Monte Carlo (VQMC) method [7], (ii) Störmer-Levy-Oshida (SLO) method [10], and (iii) harmonic approximation (HA). We note here that VQMC method can take both the anharmonicity and the inter-mode couplings on potential energy surface (PES) into account under the mean-field approximations. The SLO method is one of numerical solvers to obtain the accurate solution of one-dimensional Schrödinger equation, and thus the solutions includes the effect of one-dimensional anharmonicity along each vibrational coordinate. The HA method includes neither the anharmonicity nor the inter-mode couplings. In order to calculate PA(Q) values, the multi-component molecular orbital (MC_MO) method [9] was used in this study. Since a PA value is defined at a given position in a multi-dimensional space (Q-space), PA(Q) in Eq. (2) has the form of multi-dimensional surface like PES, and contains multi-dimensional contributions (or inter-mode couplings). In order to discuss the inter-mode couplings on PA(Q) surface (positron affinity surface, PAS) as well as PES, we also calculated PA values containing only one-dimensional contributions along each vibrational coordinate with VQMC wave functions.

In the vertical PA calculations, we employed the truncated singly and doubly excited configuration interaction (CISD) method for a positron-attached molecule, where three types of excitations, (i) single electronic, (ii) single positronic, and (iii) simultaneous single electronic - single positronic excitation configurations are included. The 6-31++G(2df,2pd) and [15s15p3d2/1g] Gaussian-type functions (GTFs) were employed for electronic and positronic basis sets, respectively, for [HCN;e^+] system. For [CH\textsubscript{2}O;e^+] system, the electronic and positronic basis sets are the 6-31+G(3d2f) and [12s8p6d2f] GTFs, respectively. The exponents of the positronic GTFs were determined by the even-tempered scheme. These basis sets were constructed as reproducing the accurate vertical PA values obtained with diffusion Monte Carlo calculations at equilibrium geometries of HCN and CH\textsubscript{2}O molecules [8, 11].

In the potential energy calculations, CCSD(T) (coupled-cluster singles and doubles with perturbative triples) with Dunning’s augmented correlation consistent polarized valence triple-zeta (aug-cc-pVTZ) basis set was used for HCN molecule. The four-dimensional PES was construct by a potential energy table consisting of 14,695 grid points. For CH\textsubscript{2}O molecule, the CCSD/aug-cc-pVTZ level of \textit{ab initio} calculation was used. A six-dimensional PES of CH\textsubscript{2}O molecule was truncated by 3-mode representation technique [12] which includes inter-mode couplings up to third order. The total number of the grid points is 33,476.

3. Results and Discussion
The PA\textsubscript{v} values of HCN molecule obtained with different vibrational wave functions are summarized in Table 1. As reported in our previous paper [7], VQMC results show that the excitations of the CN and CH stretching modes enhance the PA value compared to the value at the ground state, while that
of the bending mode deenhances it. The largest PA enhancement is found for the excited states of the CH stretching mode. Such PA variations can be described qualitatively even with the vibrational wave functions by SLO and HA methods. From a quantitative point of view, however, HA method significantly underestimates the PA variations in all vibrational excitations. For instance, the PA variation from the ground state value ($\Delta PA$) by the lowest CH stretching excitation is calculated as +3.07 meV with VQMC method, while the variation is estimated as only +0.42 meV with HA method. The vibrational wave function by SLO method can improve the quantitative accuracy of PA variations, but still considerably underestimate PA variations by the vibrational excitations of the bending modes. The $\Delta PA$ by the lowest bending excitation is calculated as $-1.72$ meV with VQMC method, while the variation is estimated as $-0.31$ meV with SLO method. Using the linear regression analysis (LRA) used in our previous study [7], we also confirmed that these PA variations with SLO and HA methods are mainly due to the change in the permanent dipole moment by vibrational excitations. Although the quantitative accuracy of SLO and HA methods is lower than that of VQMC method, the origin of such PA variations is consistent with the previous VQMC results.

The mean error (ME) and mean absolute error (MAE) from VQMC results for SLO and HA methods are also given in Table 1. The ME and MAE are here defined by the average of $PA_{v}^{(SLO/HA)} - PA_{v}^{(VQMC)}$ and its absolute value over all states, respectively. The ME of SLO method is the positive value of $+1.35$ meV meaning that the method tends to overestimate PA values totally, while the HA gives the negative ME value of $-1.38$ meV meaning the underestimation of PA values. The MAE with SLO method is lower than that of HA method, but is greater than 1 meV. These results mean that not only the anharmonicity but also the inter-mode couplings on potential energy surface are indispensable for the quantitative estimation of PA values of HCN molecule. Table 1 also show the PA value including only one-dimensional contributions on PAS with VQMC wave function ($PA_{v}^{(1D)}$). The ME and MAE for $PA_{v}^{(1D)}$ values are calculated as $\approx 0.00$ meV (less than $1\mu$eV) and 0.14 meV, respectively. These small ME and MAE values mean that the effect of inter-mode couplings on PAS is sufficiently weaker than that on PES.

| State | VQMC | SLO | HA |
|-------|------|-----|-----|
| $X_{1,2}^{a}$ | $PA_{v}^{(VQMC)}$ | $\Delta PA$ | $PA_{v}^{(1D)}$ | $\Delta PA$ | $PA_{v}^{(SLO)}$ | $\Delta PA$ | $PA_{v}^{(HA)}$ | $\Delta PA$ |
| GS   | 39.95 ±0.01 | − | 39.95 | − | 40.96 | − | 39.51 | − |
| 1    | 38.23 ±0.01 | −1.72 | 38.29 | −1.66 | 40.65 | −0.31 | 39.14 | −0.38 |
| 2    | 40.88 ±0.01 | +0.93 | 40.92 | +0.98 | 42.09 | +1.13 | 39.80 | +0.29 |
| 3    | 43.02 ±0.01 | +3.07 | 42.79 | +2.84 | 43.42 | +2.47 | 39.94 | +0.42 |
| 1    | 36.99 ±0.01 | −2.96 | 37.40 | −2.55 | 40.41 | −0.54 | 38.82 | −0.69 |
| 2    | 41.93 ±0.01 | +1.98 | 41.88 | +1.93 | 43.26 | +2.30 | 40.09 | +0.58 |
| 3    | 46.34 ±0.02 | +6.39 | 46.12 | +6.17 | 45.99 | +5.03 | 40.35 | +0.84 |

Mean error from VQMC results: $\approx 0.00$ meV ($1.35$ meV) and 0.14 meV, respectively. These small ME and MAE values mean that the effect of inter-mode couplings on PAS is sufficiently weaker than that on PES.

The $PA_{v}$ values of CH$_2$O molecule obtained with different vibrational wave functions are summarized in Table 2. In the case of CH$_2$O molecule, the excitations of modes 2 (C=O stretching), 3

Table 1. Vibrational averaged positron affinity ($PA_{v}$) values of HCN molecule at the ground (GS), fundamental tone ($X_{1}$), and lowest overtone ($X_{2}$) states using the vibrational wave functions obtained with variational Monte Carlo method (VQMC), Störmer-Levy-Oshida method (SLO), and harmonic approximation (HA). The $PA_{v}$ variation from each ground state ($\Delta PA$) are also shown. Unit in meV.

$X$ denotes a vibrational mode: "1" means the bending mode, "2" CN stretching mode, and "3" CH stretching mode.

$^a$ All the data from Ref. [7]. The error means the standard error of Monte Carlo samplings.

$^b$ The inter-mode couplings of PA surface is not included.
(CH\textsubscript{2} bending), and 6 (CH\textsubscript{2} rocking) tend to enhance the vibrational PA\textsubscript{v} value, while those of modes 1 (symmetric C–H stretching), 4 (out-of-plane bending), and 5 (anti-symmetric C–H stretching) tend to deenhance it. Among all vibrational modes, the C=O stretching mode gives the largest contribution to the enhancement of PA\textsubscript{v} value [8]. The \( \Delta \)PA values with the SLO and HA methods are qualitatively consistent with those with VQMC method for the excited states of modes 1, 2, 4, and 5 which have the absolute \( \Delta \)PA values greater than about 1 meV.

The HA method gives the negative ME values as \(-1.05\) meV which means the method totally tends to underestimate PA\textsubscript{v} values. Although the SLO method gives the small ME value of \(-0.10\) meV, such tendency might be due to an accidental cancellation of errors. In fact, the MAE value of SLO method is close to 1 meV. As in the case of HCN molecule, the smallest MAE value is found for PA\textsubscript{v}\textsuperscript{(1D)} values.

From these results, we again confirmed that (i) the both the anharmonicity and the inter-mode couplings on PES are indispensable for the quantitative estimation of PA values of CH\textsubscript{2}O molecule, and (ii) the effect of inter-mode couplings on PA surface is sufficiently weaker than that on PES.

Finally, we make a comment on the origin of PA variations at different theoretical level. As shown in our previous work [8], the PA enhancement/deenhancement of CH\textsubscript{2}O molecule mainly arise from the change in the permanent dipole moments by vibrational excitations. The PA\textsubscript{v}\textsuperscript{(HA)} variations, however, could not be described by the change in the dipole moment (the \( R^2 \) value in LRA is less than 0.2). Thus, the potential anharmonicity must be essentially indispensable for describing the vibrational states of CH\textsubscript{2}O molecule. Although the LRA results for PA\textsubscript{v}\textsuperscript{(SLO)} and PA\textsubscript{v}\textsuperscript{(1D)} values are consistent with VQMC results, the SLO method, in which the inter-mode couplings on PES is neglected, qualitatively fail to describe PA variations at the excited states of CH\textsubscript{2} bending and rocking modes as mentioned above.

### Table 2. Vibrational averaged positron affinity values of CH\textsubscript{2}O molecule. All abbreviations are defined in Table 1. Unit in meV.

| State | \( X_{1,2} \) | \( \text{VQMC} \) | \( \Delta \text{PA} \) | \( \text{PA}_{v}^{\text{(1D)}} \) | \( \Delta \text{PA} \) | \( \text{PA}_{v}^{\text{(SLO)}} \) | \( \Delta \text{PA} \) | \( \text{PA}_{v}^{\text{(HA)}} \) | \( \Delta \text{PA} \) |
|-------|------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| GS    | 25.78±0.03 | -1.27           | 25.66           | -1.32           | 25.67           | -1.12           | 25.02           | -0.04           |                 |
| 1     | 24.51±0.02 | +4.91           | 30.54           | +4.88           | 30.40           | +4.73           | 27.28           | +2.22           |
| 2     | 30.69±0.06 | +0.25           | 25.95           | +0.29           | 25.31           | +0.36           | 24.77           | -0.29           |
| 3     | 26.03±0.03 | -0.90           | 24.82           | -0.84           | 24.50           | -1.16           | 23.87           | -1.19           |
| 4     | 23.60±0.02 | -2.18           | 23.33           | -2.34           | 24.95           | -0.72           | 24.31           | -0.75           |
| 5     | 25.91±0.03 | +0.13           | 25.81           | +0.15           | 25.47           | -0.19           | 24.86           | -0.19           |
| 1     | 23.57±0.02 | -2.21           | 23.31           | -2.35           | 23.45           | -2.22           | 24.96           | -0.09           |
| 2     | 36.07±0.08 | +10.29          | 35.87           | +10.21          | 35.16           | +9.50           | 29.50           | +4.44           |
| 3     | 26.06±0.04 | +0.28           | 26.02           | +0.36           | 24.99           | -0.67           | 24.51           | -0.55           |
| 4     | 24.08±0.03 | -1.70           | 24.07           | -1.59           | 23.43           | -2.23           | 22.75           | -2.31           |
| 5     | 21.43±0.01 | -4.35           | 20.87           | -4.79           | 24.28           | -1.38           | 23.58           | -1.48           |
| 6     | 26.14±0.03 | +0.36           | 26.08           | +0.42           | 25.29           | -0.37           | 24.68           | -0.38           |

Mean error from VQMC results: \(-0.16\) meV
Mean absolute error from VQMC results: 0.16 meV

\( X \) denotes a vibrational mode: “1” symmetric CH stretching, “2” CO stretching, “3” CH\textsubscript{2} bending, “4” out-of-plane bending, “5” anti-symmetric CH stretching, and “6” CH\textsubscript{2} rocking.

\( b \) All data from Ref. [8]. The error means the standard error of Monte Carlo samplings.

\( c \) The inter-mode couplings of PA surface is not included.
4. Conclusion
In order to elucidate the effect of the anharmonicity and the inter-mode couplings of molecular vibrations on the positron binding to HCN and CH₂O molecules, we theoretically analyzed the vibrational averaged positron affinity (PA) of both molecules using the vibrational wave functions obtained with three different theoretical methods: (i) vibrational quantum Monte Carlo method which includes the effects of both anharmonicity and inter-mode couplings under the mean-field approximation, (ii) Störmer-Levy-Oshida method which takes the effect of only the one-dimensional anharmonicity along each vibrational coordinate into account, and (iii) the harmonic approximation which does not include both effects. For both molecules, our results show that not only the anharmonicity but also the inter-mode couplings on potential energy surface are indispensable for the quantitative estimation of PA values. We also confirmed that the effect of inter-mode couplings on a positron affinity surface are sufficiently weaker than that on a potential energy surface.

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