Ab initio study of the effect of molecular vibrations on the positron-binding to polyatomic molecules

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The positron, which is the anti-particle of the electron, is now widely used in both scientific and technological areas. The detail mechanism of such processes, however, is still unclear in the molecular level. A positron affinity (PA) value, which is a binding energy of a positron to an atom or molecule, has now been experimentally measured by Surko and co-workers for many molecular species such as acetaldehyde, acetone, and acetonitrile molecules [1], based on the vibrational Feshbach resonance by incident low-energy positrons. Thus, in order to elucidate the mechanism of the positron binding to molecules, the theoretical analysis including the effect of molecular vibrations is indispensable. In this study, we will show the effect of molecular vibrations on PA values, based on *ab initio* multi-component quantum Monte Carlo (QMC) [2] and molecular orbital (MCMO) [3] methods for the electronic and positronic wave functions simultaneously, and the anharmonic vibrational quantum Monte Carlo (QMC) method [4].

In order to analyze the PA value including the effect of molecular vibrations, we introduced vibrational averaged PA (PA_ν) defined by the following equation:

$$\mathrm{PA}_\nu \equiv \frac{\int \mathrm{PA}^{[X]}(\boldsymbol{Q})|\Psi_\nu(\boldsymbol{Q})|^2 \mathrm{d}\boldsymbol{Q}}{\int |\Psi_\nu(\boldsymbol{Q})|^2 \mathrm{d}\boldsymbol{Q}},$$

where $\boldsymbol{Q}$ is a set of vibrational coordinates and Ψ_ν is the vibrational wave function of the ν-th vibrational excited state. The $\mathrm{PA}^{[X]}(\boldsymbol{Q})$ is the vertical PA value at the molecular geometry $\boldsymbol{Q}$, defined by the total energy difference of the parent molecule (X) and its positron attached system ($[X;\mathrm{e}^+]$) as $\mathrm{PA}^{[X]}(\boldsymbol{Q}) \equiv E^{[X]}(\boldsymbol{Q}) - E^{[X;\mathrm{e}^+]}(\boldsymbol{Q})$. In this study, $E^{[X;\mathrm{e}^+]}(\boldsymbol{Q})$ and $\Psi_\nu(\boldsymbol{Q})$ were calculated with configuration interaction level of MCMO theory [3] and vibrational QMC method [4], respectively.

In the case of formaldehyde (CH_2O) molecule, the vertical PA value at the equilibrium position is predicted as +25(3) meV with QMC calculation. Applying the anharmonic vibrational analysis, the vibrational excitation of the C=O stretching mode enhances the PA value, whereas the excitation of CH_2 rocking mode deenhances it. We confirmed that such PA variations arise from the change in both permanent dipole moment and dipole-polarizability at each vibrational excited state. We will show some results of other larger molecules.

References

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