

Temperature effect on the microscopic hydration structures of phenol cation
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Temperature effects on the hydration structure is very important to understand microscopic nature of the hydrogen bond network. One of the temperature effects on the hydration structure in the cluster is a change in relative populations among the isomers. In the present study, we have carried out ultraviolet photodissociation spectroscopy of hydrated phenol cation trapped in the temperature-variable ion trap. We have succeeded in observing a clear change in the relative populations between the isomers having distinct hydration structures. The temperature-dependence observed is well interpreted by flexibility of the hydration structures of the isomers obtained by theoretical calculations.

Introduction

Hydrogen bond plays an important role in various chemical and biological process. To investigate the microscopic nature of hydrogen bond, a large number of spectroscopic studies of the gas-phase molecular clusters have been carried out and hydration structures of various systems have been determined so far. Since hydration structures are flexible in nature, temperature effect is very important. One of the temperature effects on the microscopic hydration structure is a change in relative populations among the isomers. In the present study, we have carried out ultraviolet (UV) photodissociation (PD) spectroscopy of hydrated phenol cation, $[\text{PhOH}(\text{H}_2\text{O})_5]^+$, trapped in our temperature-variable 22-pole ion trap. We have succeeded in observing a clear temperature dependence of the relative populations of the isomers having distinct hydration structures. Possible hydration structures of the clusters are obtained by density functional theory (DFT) calculations. The relative populations of the isomers are also estimated by statistical mechanically based on the results of the DFT calculation. In the present paper, we would like to discuss the temperature effect on the hydration structure of $[\text{PhOH}(\text{H}_2\text{O})_5]^+$ based on the experimental and theoretical results.

Experimental and computational details

In the present study, we used our temperature-variable 22-pole ion trap apparatus [1]. The hydrated phenol cation clusters were generated by the combination of laser ionization and supersonic expansion techniques. The clusters produced were mass-separated by the first quadrupole mass filter and then introduced into the 22-pole ion trap. The ions in the trap were temperature-controlled by the He buffer gas cooling method. After the achievement of the thermal equilibrium condition, UV laser light was irradiated to the clusters. The photofragment ions were mass-analyzed and detected by the second quadrupole mass analyzer. Possible hydration structures of isomers of $[\text{PhOH}(\text{H}_2\text{O})_5]^+$ were obtained by the DFT calculation at $\omega\text{B97X-D/6-311++G(3df,3pd)}$ level. We also estimated Gibbs energy of the isomers at various temperatures based on statistical mechanics. Then relative populations of the isomers were obtained assuming the Boltzmann distribution.

Results and Discussion

In the present study, we evaluated the vibrational temperatures of the ions in the trap based on the relative intensities of hot bands in the electronic spectra of phenol-trimethylamine cation, $[\text{PhOH-TMA}]^+$. Since a proton of the phenol moiety is transferred to trimethylamine side, the chromophore of the UV transition is a phenoxy radical in the cluster. The UV transition observed in the present study corresponds to the D_3 - D_0 transition of the phenoxy radical. As a result, vibrational temperatures of the $[\text{PhOH-TMA}]^+$ are almost the same as the temperature of the trap except for the case when the temperature of the trap is set below 30 K. The vibrational temperature of 30 K is the lowest one achieved in our trap.

Then, we measured the UV photodissociation spectrum of $[\text{PhOH}(\text{H}_2\text{O})_5]^+$ at vibrational temperatures from 30 to 150 K. In Figure 1, the spectra observed at 30 K and 150 K are shown. In the spectra measured at 30 K, only one isomers are observed. Hereafter, this isomer is referred to as isomer A. As the temperature elevates, another isomer is observed in the spectra. In Figure 1(b), the 0-0 band of a newly appeared species (isomer B) is denoted as B. The intensity of the 0-0 band of the isomer B is larger than that of the isomer A. This indicates an inversion of the relative populations between the isomers A and B occurs around at 150 K. Anyway, these spectra clearly indicates the change in the relative population between the two isomers along the temperature elevation.

Possible structures of the isomers A and B are also shown in Figure 1. They have distinct hydration structures and are expected to exhibit different temperature dependence in the relative populations. The isomer B has a flexible chain type hydration structure, which indicates a large entropic contribution in the temperature dependence. On the other hand, the hydration structure of the isomer A involves ring type structure. It should be less flexible than the chain type structures. Thus, the inversion of the relative population experimentally observed around 150 K is qualitatively interpreted by the difference in the flexibility of the hydration structures of the isomers A and B.

Details of the discussion will be presented in the paper.

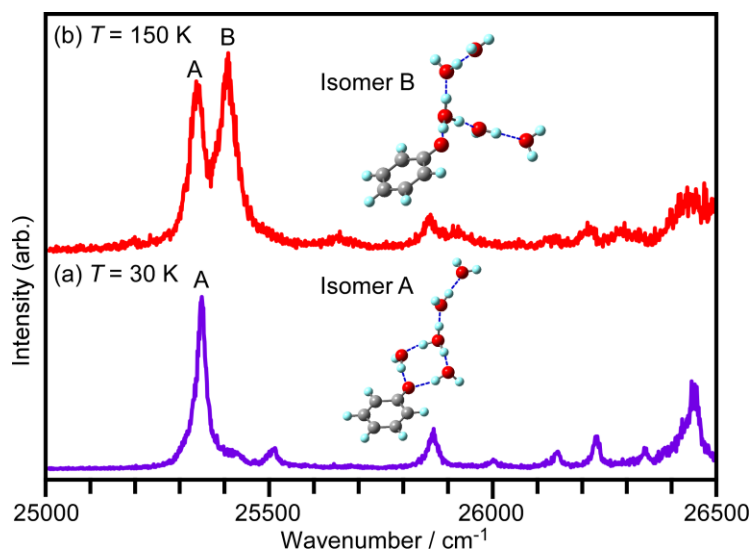


Figure 1. Photodissociation spectra of $[\text{PhOH}(\text{H}_2\text{O})_5]^+$ measured at (a) $T = 30$ K and (b) $T = 150$ K. Possible hydration structures of the isomers A and B are inserted.