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Infrared spectroscopy of the benzene–H₂O cluster cation: experimental study on the drastic structural change upon photoionization

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Abstract

Infrared photodissociation (IRPD) spectra of (benzene (Bz)–H₂O)⁺ was measured in the 3 μm region. The cluster cations produced by two different methods, resonant photoionization of the neutral cluster and collisions of the bare benzene cation with water molecules, gave the same IR spectrum. This fact indicates that the most stable isomer cluster cation was generated in both methods. The cluster cation was found to have the side structure bound by the charge–dipole interaction. These results demonstrate that the water molecule on the benzene C₆ axis in the neutral state is flipped to the side of the benzene ring upon the photoionization. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

It has been well known that π electrons on a conjugated system can accept hydrogen to form a weak hydrogen bond, that is, so-called π-hydrogen bond. π-hydrogen bonds play an important role in determining structures of proteins and crystals of organic molecules, etc., and many studies by using gas phase clusters have been carried out to reveal the nature of π-hydrogen bonds [1–5].

π-hydrogen bonded clusters with polar solvent molecules, such as water and methanol, have been

known to give rise to efficient fragmentation when the acceptor site of the clusters is ionized by resonance enhanced multiphoton ionization (REMPI) [1,3,4,6]. This efficient dissociation is easily understood by considering the strong repulsive force between the positive charge on the π system and the permanent dipole of the solvent. Because of this repulsion, the π-hydrogen-bonded structure is no longer a stable structure in the cationic ground state, and a totally different type of cluster structures is expected. Therefore photoionization of the neutral cluster is accompanied with a large displacement of the intermolecular coordinates because of the Franck–Condon restriction.

The benzene (Bz)–H₂O cluster is the most extensively studied π-hydrogen-bonded cluster [1,2,7–12]. It has been experimentally confirmed that the water molecule is symmetrically π-hydro-

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gen bonded on the center of the benzene ring, as shown in the Fig. 1. In the one-color REMPI via the S_1 state the fragmentation yield is about 90% [1,3]. Two theoretical analyses have been reported on the threshold ionization of this cluster. Courty et al. [13] analyzed the semiempirical potentials of neutral and cationic ground states, and they concluded that the formation of the stable $(\text{Bz-H}_2\text{O})^+$ cluster cation is ascribed to the classically forbidden region of the ground state wave function for the intermolecular vibrational motion. Later, Tachikawa and Igarashi [14] performed direct ab initio dynamics calculations. In their calculations, the trajectory started from the equilibrium point of the neutral cluster gives the stable cluster cation whereas that from the inner classical turning point leads to the dissociation of the cluster. In spite of differences in details, both the theoretical analyses predicted that the threshold photoionization of the neutral $\text{Bz-H}_2\text{O}$ cluster partly results in the production of the stable cluster cation accompanied by the significant changes in the cluster structure. Very recently, Tachikawa et al. [15] predicted the

detailed structure and vibrational frequencies of the $(\text{Bz-H}_2\text{O})^+$ cluster cation by using the density functional theory.

Though the previous theoretical calculations estimated that the $(\text{Bz-H}_2\text{O})^+$ cluster cation is mainly bound by the charge-dipole interaction instead of the π -hydrogen bond [13–15], there has been no experimental study on the structure of the cluster cation. In the present study, we carried out infrared (IR) spectroscopy of the $(\text{Bz-H}_2\text{O})^+$ cluster cation prepared by two distinct methods: one was the two-color REMPI in which the neutral $\text{Bz-H}_2\text{O}$ cluster in a supersonic jet was ionized via the S_1 state. The produced cluster cation is expected to reflect the Franck–Condon bright structure from the neutral cluster. The other was so-called ‘pick-up’ method in which a bare benzene cation was generated by the REMPI of neutral benzene and then following collisions with water molecules and carrier gas produce the cluster cation. In this method, the production of the most stable structure of the cluster cation is dominant [16,17]. We applied IR photodissociation (IRPD)

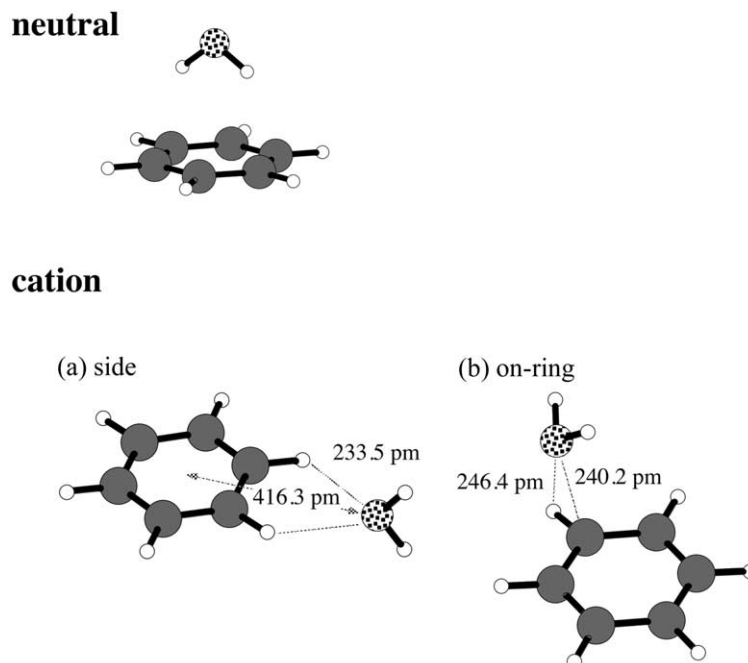


Fig. 1. Upper: stable structure of the $\text{Bz-H}_2\text{O}$ cluster in the neutral ground state [8]. Lower: Geometry optimized structures of (a) the side and (b) the on-ring structures of the $(\text{Bz-H}_2\text{O})^+$ cluster cation calculated at the B3LYP/6-31G(d,p) level of theory.

technique to detect weak IR absorption of the cluster cation. The structural change upon the photoionization of $\text{Bz-H}_2\text{O}$ is discussed based on the IR spectra of these cluster cations.

2. Experiment

In the REMPI preparation of the cluster cation, we recorded the IRPD spectrum of the size-selected $(\text{Bz-H}_2\text{O})^+$ cluster cation by using a Wiley–McLaren type time of flight mass spectrometer. Details of this technique have been described elsewhere [18]. Briefly, a jet expansion of a gaseous mixture of benzene, water and He is skimmed by a skimmer. The neutral $\text{Bz-H}_2\text{O}$ cluster formed in the molecular beam is ionized by two-color REMPI via the S_16^1 level ($38\,655\text{ cm}^{-1}$ [1]). The excess energy in the ionization is kept within 600 cm^{-1} above the appearance energy [13], by tuning of the wavelength of the ionization assist laser. After a delay time of 50 ns from the ionization, an IR light pulse is introduced for vibrational excitation. When the IR light is resonant on a vibrational level of the cluster cation, dissociation of the cluster cation occurs and the intensity of the parent cluster cation is depleted. Therefore, the IR spectrum of the cluster cation is obtained as a depletion spectrum by scanning the IR frequency while monitoring the intensity of the parent cluster cation.

On the other hand, in the pick-up preparation of the cluster cation we measured the IRPD spectrum of the $(\text{Bz-H}_2\text{O})^+$ cluster cation by using a tandem quadrupole mass spectrometer. Briefly, in the collisional region of a pulsed supersonic expansion of the gaseous mixture, a bare benzene molecule is first ionized by the one-color REMPI via the 6_0^1 transition ($38\,606\text{ cm}^{-1}$ [19]), and following collisions with water molecules and carrier He gas form various sizes of the $(\text{Bz-(H}_2\text{O)}_n)^+$ cluster cations ($n \geq 1$). The $n = 1$ cluster cation is size-selected by the first quadrupole mass filter, and is spatially focused into the center of a quadrupole ion lens. An IR light pulse is introduced into the quadrupole ion lens at the right angle to the ion beam. When the IR light is resonant on vibrational transitions of the cluster cation, the

vibrational excitation causes the fragmentation of the cluster cation. Both the parent cation and the fragment cation are introduced into the second quadrupole mass filter, and the fragment ion (Bz^+) is detected as a function of the IR wavelength. Thus the IRPD spectrum of the $(\text{Bz-H}_2\text{O})^+$ cluster cation is obtained. Details of the experimental apparatus will be described elsewhere [20]. Briefly, the apparatus is composed of an ion source chamber and a detection chamber containing the two quadrupole mass filters. Those quadrupole mass filters are connected with cylindrical ion lenses and a set of quadrupole ion lens. The pulsed valve in the source chamber and the mass filters and ion lenses in the detection chamber are colinearly aligned.

In both the experiments, benzene and water vapor at the room temperature is mixed with He of 3 atm in the stagnation pressure.

3. Results and discussion

Figs. 2a,b show the IRPD spectra of the $(\text{Bz-H}_2\text{O})^+$ cluster cation in the CH and OH stretching vibrational region. The cluster cation was prepared by (a) the REMPI and (b) the pick-up methods, respectively. These two IR spectra are clearly the same, indicating that the cluster cation of the same structure is produced in both the preparation methods. Because the pick-up method prefers to produce the most stable isomer of the cluster cation, this result demonstrates that the photoionization from the S_1 state, which has the on-top π -hydrogen-bonded structure as the neutral ground state, also leads to the production of the most stable cluster cation.

Three bands are seen at 3720 , 3635 and 3090 cm^{-1} in the IR spectra (the accuracy of the peak positions is $\pm 3\text{ cm}^{-1}$). They are clearly assigned to the anti-symmetric (ν_3) and the symmetric OH stretching vibration (ν_1) of the water site, and the CH stretching vibrations of the benzene cation site, respectively. The vibrational frequencies of the ν_1 and ν_3 modes are red-shifted by 22 and 36 cm^{-1} from those of the bare water molecule ((ν_1) 3657 , (ν_3) 3756 cm^{-1} in bare water [2]), respectively. In other 1:1 hydrated cluster

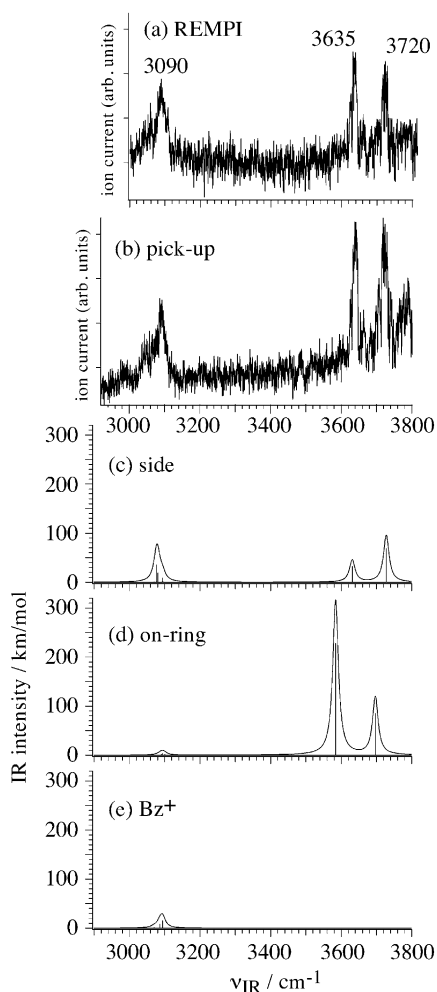


Fig. 2. (a,b) IRPD spectra of the $(\text{Bz-H}_2\text{O})^+$ cluster cation prepared by the REMPI method and the pick-up method, respectively (see text). (c,d) Simulated IR spectra of $(\text{Bz-H}_2\text{O})^+$ in the side and on-ring structures at the calculation level of B3LYP/6-31G(d,p), respectively. The calculated harmonic frequencies are scaled by a scaling factor of 0.956, and convoluted by a Lorentzian function of 20 cm^{-1} in FWHM. The stick spectra without the convolution are also shown. The ordinates of all the simulated spectra are in km/mol given to the stick spectra. (e) Simulated IR spectra of the bare benzene cation at the same level of calculation.

cations, the similar red-shifts of the ν_1 and ν_3 modes have been observed [21–24]. Moreover, a remarkable enhancement of the absorption intensity of the ν_1 band relative to the ν_3 band, which is commonly observed in hydrated cluster cations [21–24], is also seen in the spectra. It is also noticed

that the CH stretch band is found at nearly the same position as that of the bare benzene cation (3094 cm^{-1} [25,26]) although the band in the cluster is significantly broadened.

In the case of the neutral $\text{Bz-H}_2\text{O}$ cluster, complicated splittings of the OH stretch bands of the water site were found, and they are attributed to the coupling with the free rotation of the water molecule around the C_6 axis of the benzene molecule [2]. Such splittings of the OH bands disappear in the cluster cation spectra, suggesting that the rotation of the water molecule is inhibited in the $(\text{Bz-H}_2\text{O})^+$ cluster cation. As mentioned above, the intensity of the CH stretch band of the cluster cation is as strong as those of the OH stretch bands, although aromatic CH stretch strengths in molecular cations are generally much weaker than those of OH stretches [25,27]. This remarkable feature indicates that the water molecule gives distinct perturbations to the CH stretching vibrations of the benzene site in the cluster cation. It is quite contrary to the neutral $\text{Bz-H}_2\text{O}$ cluster, in which the water molecule on the benzene ring gives almost no perturbation to the CH stretch bands [10].

The stable structure of the $(\text{Bz-H}_2\text{O})^+$ cluster cation has been studied by theoretical calculations. Tachikawa and coworkers found out two geometry optimized structures, side and on-ring structures, by using the MP2/6-31G(d,p) level calculations [14]. They recently calculated the detailed structure and vibrational frequencies of the former isomer by means of the density functional theory [15]. We also carried out the B3LYP/6-31G(d,p) level calculations by using the GAUSSIAN 98 program package [28], and confirmed the results by Tachikawa and coworkers. The calculated structures of the two isomer cations are shown in Fig. 1 [29]. In both the structures, the orientation of the water molecule to the benzene ring is reversed from the neutral $\text{Bz-H}_2\text{O}$ cluster, in which both the hydrogen atoms of the water molecule face to the benzene ring plane to form the π -hydrogen bonds. The structures of the cluster cation show that the charge-dipole interaction is the main component of the intermolecular bond and the π -hydrogen bonds disappear upon the photoionization. At the B3LYP/6-31G(d,p) level

of the calculations, the total binding energy of the side structure is 3290 cm^{-1} and that of the on-ring structure is 3190 cm^{-1} (including the basis set superposition error and zero-point energy corrections). The side structure is slightly more stable than the on-ring structure (100 cm^{-1}). The previous MP2/6-31G(d,p) level calculations by Tachikawa and Igarashi [14] estimated that the side structure was more stable than the on-ring one about 1000 cm^{-1} . In both the calculations, the energy differences are so small that the most stable structure cannot be unequivocally determined only by the estimation of the stabilization energy. Therefore, the simulation of the IR spectra based on the optimized structures is expected to play a key role for structure determination of the cluster cation.

Figs. 2c,d show simulated IR spectra of the side and on-ring cluster cations, respectively. That of the bare benzene cation is also shown in Fig. 2e for comparison. These simulated IR spectra were obtained from the normal mode analyses of the stable structures at the same level. The scaling factor of 0.956 was applied to all the calculated harmonic frequencies. This value is determined to fit the experimental value of the CH stretch vibrations of the bare benzene cation [25,26]. The observed band positions of the OH and CH bands in the cluster cation are correctly reproduced in both the cluster structures. The intensity enhancement of the ν_1 mode of the water site relative to the ν_3 mode, which is commonly observed in hydrated cluster cations, is also well reproduced in both the structures [15]. On the other hand, a remarkable difference of the simulated IR spectra between the side and on-ring structures is seen in the relative intensities of the CH and the OH stretch bands. In the side structure, the intensities of the CH stretches are significantly enhanced in comparison with that of the bare benzene cation, and they are as strong as those of the OH stretches. This enhancement should be attributed to the local solvation of the CH bonds, which induces a permanent dipole and breakdown of the symmetry in the benzene cation site. These effects can also be regarded as the C–H–O type hydrogen bond formation. In the on-ring structure, on the other hand, the intensities of the CH stretches are as

weak as those of the bare benzene cation, reflecting the small perturbations to the in-plane stretching modes.

In the observed IR spectra of the $(\text{Bz-H}_2\text{O})^+$ cluster cation, the intensity of the CH stretch band is as strong as those of the OH stretch bands. This feature well agrees with the simulated IR spectrum (c) based on the side structure, while it is difficult to explain the remarkable enhancement of the CH stretch band intensity by using the on-ring structure model, as seen in the simulated IR spectrum (d). Therefore, it is reasonably concluded that the spectral carrier of the observed IR spectra has the side structure shown in Fig. 1.

The pick-up preparation of the cluster cation prefers the generation of the most stable isomer, while the REMPI preparation reflects the Franck–Condon overlap between the neutral and cationic states. In this study, we found that both the cluster cations generated by these two different methods show the same IR spectrum, which is attributed to the side structure. This result clearly demonstrates that the most stable structure of the $(\text{Bz-H}_2\text{O})^+$ cluster cation is the side structure bound by the charge–dipole interaction, and the water molecule located on the center of the benzene ring in the neutral ground state is flipped into the side of the benzene ring upon the resonant photoionization. This structural change corresponds to the domination of the charge–dipole interaction accompanied by the fission of the π -hydrogen bonds. Although this drastic structural change seems to be Franck–Condon forbidden, semiempirical and ab initio dynamics calculations have already predicted such phenomenon [13,14]. In this study, the first experimental evidence of the cluster structural change due to the charge–dipole interaction is presented.

Finally, it is worth to note that the drastic structural change upon the photoionization of $\text{Bz-H}_2\text{O}$ is quite contrary to the small changes found for the cases of on-top clusters of an aromatic molecule with Ar, which is bound by the dispersion force [16,17,30–33]. A typical example is the phenol-Ar cluster [16,17,30–32]. The Ar atom locates on the center of the aromatic ring in the neutral ground state of phenol-Ar, while Ar is bound to the hydrogen of the hydroxyl group in

the most stable structure of the cation, and the on-top structure similar to the neutral cluster is less stable in the cation [16,17]. Photoionization of phenol–Ar results only in the production of the less stable on-top cluster cation accompanied with the small structural change, and the generation of the H-bonded cluster cation is Franck–Condon forbidden [31]. Such a remarkable difference in the photoionization behavior of Bz–H₂O and phenol–Ar is originated in the presence of the permanent dipole of water; the vertical ionization of the π -hydrogen bonded on-top cluster causes strong repulsion between the positive charge in the phenyl ring and the permanent dipole of the water site. Photoionization of phenol–Ar lacks such repulsion force which drives drastic rearrangement of the cluster structure.

Note added in Proof

After this paper was accepted for publication, a paper by Solca and Dopfer was published [34]. They also reported IR spectroscopy of the (Bz–H₂O)⁺ cluster cation. Their study concentrated on the cluster cation produced in a pick-up type source, and they observed the spectra of (Bz–HDO)⁺ and (Bz–H₂O–N₂)⁺ for comparison.

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