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Infrared Spectroscopy of (Phenol)$_n^+$ ($n = 2-4$) and (Phenol−Benzene)$^+$ Cluster Ions

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Infrared and electronic spectra of size-selected phenol cluster ions, (phenol)$_n^+$ for n = 2−4, were observed by using dissociation spectroscopy combined with an ion trap technique. Vibrational spectra of the OH stretching region indicate that the dimer ion has an asymmetric form such that the ionic moiety acts as a proton donor and that the trimer and tetramer ions have noncyclic forms with respect to intermolecular hydrogen bonds. In the electronic spectra of (phenol)$_n^+$ in the range of 400−1600 nm was found no charge resonance transition except for a transition due to the local excitation of the phenol ion moiety. The result indicates that charge delocalization interaction between phenyl rings is not significant in these cluster ions. It was concluded that all the phenyl moieties in the trimer ion are bound by a linear chain of the OH···O hydrogen bonds, while a symmetric form with cyclic hydrogen bonds has been established for the neutral trimer. The OH stretching vibration of the hetero dimer ion of (phenol−benzene)$^+$ was also observed, in which the phenol ion is expected to be bound onto the benzene ring through a π-type hydrogen-bond. An extremely large red-shift and a substantial broadening of the OH band of the phenol ion moiety were found, and the results were discussed in respect to the characteristic feature of hydrogen-bonded OH vibrations of ionic clusters.

1. Introduction

Vibrational spectroscopic studies of size-selected clusters have recently become popular for the investigation of intermolecular binding structures which provide us with new materials for a microscopic view of condensed phases. Extensive studies of ionic species involving water clusters have been carried out by many research groups using infrared (IR) dissociation spectroscopy in combination with mass spectrometric methods.[1−5] Size-selected neutral clusters have also been investigated by spectroscopies combined with population-labeling methods,[5−14] as well as molecular-beam-scattering method.[15] Recent studies of neutral phenol clusters, (phenol)$_n$ for $n = 1-3$, reported by G. V. Hartland et al.[6] and by T. Ebata et al.,[9] have revealed that their hydrogen bond structures are closely related to the crystal structure of phenol, in which 3-fold screw axes of intermolecular hydrogen bonds are characteristic. Rotational coherence spectroscopy of the electronic transition of the dimer has been performed by L. L. Connell et al.,[16] providing its rotational constants for a precise structural analysis. It has been established for the dimer that two phenol molecules are inequivalently bound by a single hydrogen bond with a nonplanar conformation of two phenyl rings.[6,16] For the trimer, extensive vibrational spectroscopy, including polarization measurements of Raman spectra,[9] has established that the trimer has the symmetrically cyclic form, in which three phenol units are equivalently bound by intermolecular hydrogen bonds. It is a firm confirmation of the cyclic form for the trimer, which was first suggested by K. Fuke and K. Kaya in their multiphoton ionization spectroscopy.[17,18]

For the cluster ions of phenol, on the other hand, few studies have been reported so far; zero kinetic energy (ZEKE) photoelectron spectroscopy of the phenol dimer reported by O. Dopfer et al.[19] is the only report involving a structural investigation of the ionic state. The ZEKE spectrum exhibits vibrational structure with long progressions involving intermolecular vibrations, suggesting that a structural change is induced upon ionization of the neutral dimer. Such a structural change is of particular interest with respect to substantial changes in intermolecular interactions upon ionization: not only hydrogen bonds, but also phenyl ring interactions, are thought to be enhanced in the ionic state. Thus, different cluster structures can be expected for the cluster ions, because the intermolecular structure may be determined by a balance between these two kinds of intermolecular forces involving charged site(s). In the case of the benzene dimer, actually, it has been found that a sandwich form is feasible for the ionic state,[20] while a T-shaped form is evident for the neutral.[21−23]

In this paper, we report IR spectra of the phenol cluster ions, (phenol)$_n^+$ ($n = 2-4$), by using IR multiphoton dissociation spectroscopy combined with the ion trap technique which has been known to be effective for obtaining size-selected spectra of ionic species. In previous papers,[24,25] we applied the same spectroscopic method to characterize intermolecular structures of cluster ions of water-solvated phenol, [phenol−$(H_2O)_n$]$^+$. The intermolecular structures of the cluster ions have been examined with the observed spectra. Vibrational spectra of the OH stretching region and electronic spectra in the near ultraviolet region have demonstrated that the alternation of cluster forms with respect to proton transfer takes place at $n = 3$. In the present work, IR spectra show that the phenol dimer ion has the similar open form as that of the neutral dimer, in which the charged site acts as a proton donor and the neutral site appears to be a proton acceptor bound by a single hydrogen bond. On the other hand, the spectrum shows that the trimer ion is no longer cyclic, while the cyclic form is evident for the neutral trimer in its ground state. In order to investigate the phenyl ring interactions, we also observed electronic spectra of the trapped cluster ions. The electronic spectra show that there is no significant interaction of the charge delocalization between the phenyl rings in the trimer and the tetramer ions. Finally, the characteristic feature of the hydrogen-bonded OH stretching vibrations is examined by measuring the OH band of the heterodimer ion of phenol with benzene.

2. Experimental Section

The experimental apparatus of trapped ion photodissociation spectroscopy was described in previous papers.[24−26] The phenol

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cluster ions were prepared by using a channel nozzle system, which was also described in a previous paper.[25] A gaseous mixture of helium and phenol vapor was expanded through a pulsed channel nozzle with a channel orifice of 1 mm in radius and 15 mm in length. The channel orifice has a side hole of 2 mm diameter, which crossed the channel at right angles. Phenol was photoionized at the crossing point with an ultraviolet (UV) laser beam. The laser wavelength was fixed at the 0−0 band of the S_1-S_0 transition of phenol. The cluster ions were formed by collision among phenol ions under extensive collisions with He atoms in the channel orifice. The cluster ions were finally cooled down through the expansion from the nozzle into vacuum. A typical background pressure in the experimental region of the vacuum chamber was about 1×10^{-5} Torr. The stagnation pressure gas was typically 3 atm with a partial pressure of phenol of about 10 Torr. This preparation method of cluster ions is substantially more efficient than the direct photoionization of neutral clusters in jet expansions.[26] Heterodimer ions of (phenol−benzene)$^+$ were prepared in the same way by using helium gas with a trace of benzene vapor.

Cluster ions expanded from the nozzle were introduced into a cylindrical ion trap cell,[25] which was used for the size selection as well as for the ion storage. The cell was composed of a cylindrical electrode and two end-caps used as the other electrode. A radio frequency (RF) electric potential was applied to the cylindrical electrode with respect to the end-cap electrode which was grounded, so that the cell could be used as a quadrupole ion trap. The mass selection of cluster ions was performed by selecting an appropriate voltage and frequency for the RF potential. The cluster ions of interest were trapped in the cell by a suitable condition of the RF potential, and the other cluster ions were removed from the cell during the storage.

After the storing the cluster ions for about 1 ms, tunable IR or visible light was introduced into the trap cell. Dissociation following IR or visible light absorption is enhanced when the incident light frequency is resonant with the vibrational or electronic transitions of the cluster ions. The photodissociation fragments were spontaneously ejected from the trap cell because of the resulting disfavorable trapping conditions for them. Then, they were mass-selected by a quadrupole mass filter and detected by a channel electron multiplier. The ion current signal was processed by a boxcar integrator followed by a computer. Thus, the absorption spectra of the cluster ions can be observed by monitoring the yield of the dissociation fragments. The (phenol)$_n^+$ spectra were obtained by monitoring the (phenol)$_{n-1}^+$ fragment intensities as a function of the IR or visible light wavelength. The tunable IR light was generated by difference frequency mixing in a $LiNbO_3$ crystal, in which two light beams of the second harmonic of a Nd:YAG laser and a tunable dye laser pumped by the Nd:YAG laser were overlapped. The IR power was about 0.5 mJ with a spectral resolution of 1 cm^{-1}. Spectrograde benzene and phenol (98%) were purchased from Wako Chemical Industries, Ltd., and the latter was used after purification by vacuum sublimation.

3. Results and Discussion

3.1. Infrared Spectra of (Phenol)$_n^+$ for $n = 2-4$. Figure 1 shows IR multiphoton dissociation spectra of (a) (phenol)$_2^+$, (b) (phenol)$_3^+$, and (c) (phenol)$_4^+$, respectively. Mass spectra of the cluster ions trapped in the cell are reproduced in Figure 2, indicating that a single ionic species dominates for each trapping condition. Thus, the mass spectra certify that the observed IR spectra in Figure 1a−c are due to the size-selected phenol cluster ions.

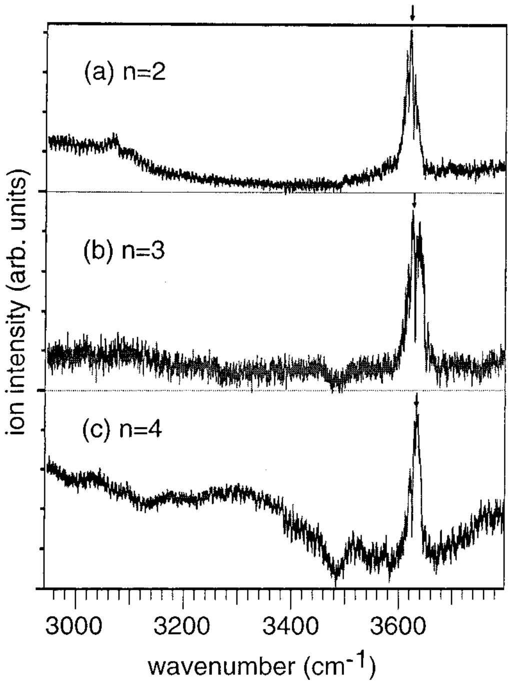

Figure 1. Infrared spectra of (phenol)$_n^+$ obtained by monitoring the (phenol)$_{n-1}^+$ fragment ion intensity as a function of the infrared wavelength, (a) (phenol)$_2^+$, (b) (phenol)$_3^+$, and (c) (phenol)$_4^+$, respectively. Sharp dips around the 3620 cm^{-1} are due to absorptions of rotational lines of water vapor along the optical path of the IR light. Marked positions with an arrow were taken as frequencies of their bands. Each spectrum was normalized with respect to the IR power. Since the ion detection efficiency was not constant for species, a comparison in intensities of different clusters cannot be made.

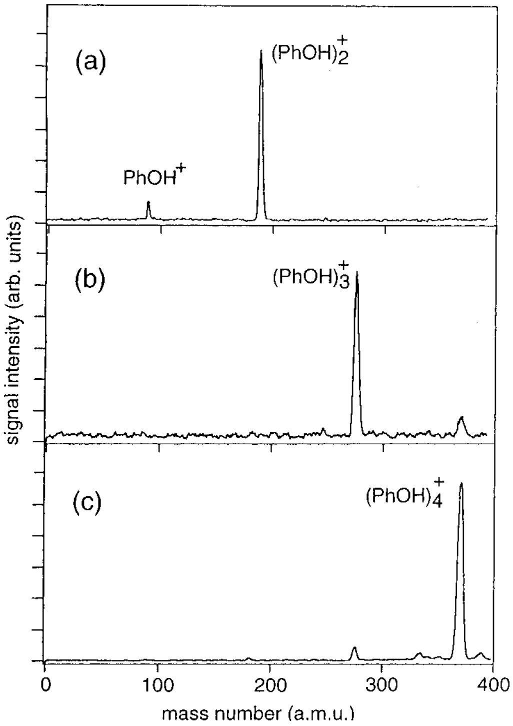

Figure 2. Mass spectra of the cluster ions stored in the trap cell under the different ion trap conditions which were suitable for trapping (a) (phenol)$_2^+$, (b) (phenol)$_3^+$, and (c) (phenol)$_4^+$. The dominated species in spectra a−c correspond to IR spectra of Figure 1a−c, respectively. Although undesired species were also stored, for example, phenol$^+$ in spectra a, their combination was so small that no significant contribution was seen in their IR spectra.

The IR spectrum of (phenol)$_2^+$, where an intense band is seen at 3620 ± 3 cm^{-1}, is essentially the same as the one reported in a previous paper.[24] In addition, an extremely broad band that peaked at about 3090 cm^{-1} is seen; we will discuss the origin of this band in a later section. First, we discuss the assignment of the intense band at 3620 cm^{-1} in Figure 1a. The frequency of this band is very close to the OH stretching frequency of the neutral phenol monomer[7,27] at 3657 cm^{-1}, but it is not close to the corresponding band of the phenol ion[22] at 3535 cm^{-1}. The result suggests that the observed band at 3620 cm^{-1} can be assigned to the OH stretching vibration of the neutral site of $(phenol)_2^+$.[28] As described previously, it has been established for the IR spectra of many hydrogen-bonded clusters and their ions that OH bands occurring in the range of 3600−3700 cm^{-1} correspond to the OH oscillators of acceptor sites,[12,24] which are not directly hydrogen-bonded. In hydrogen-bonding networks, such OH oscillators free from the direct hydrogen bond may be called "dangling OH bonds". In simulations of IR spectra of phenol−$(H_2O)_n$ clusters based on ab initio molecular orbital calculations,[29] it has been demonstrated that no significant change occurs in OH stretching frequencies for the dangling OH bonds of acceptor sites. Therefore, the observed band in Figure 1a is assigned to the free OH stretching vibration of the neutral phenol site which is acting as an acceptor of hydrogen bond in $(phenol)_2^+$. As a consequence, it is concluded that $(phenol)_2^+$ has an open structure, in which the two phenol sites are inequivalently bound, where the charged site appears as a proton donor and the neutral site acts as an acceptor. Since the proton donating ability, i.e., the acidity, is much larger in the phenol ion than in the neutral, it is quite reasonable that phenol ion takes the proton-donating site. Thus, it is seen that the inequivalent conformation of the two phenyl rings is preserved upon ionization. Then, the vibrational structure of the ZEKE spectrum[19] seems to represent other large geometrical changes without involving the ring conformation.

As seen in Figure 1b,c in the IR spectra of both $(phenol)_3^+$ and $(phenol)_4^+$, the intense bands appear at frequencies similar to that of $(phenol)_2^+$: the peak positions are 3627 ± 3 and 3632 ± 3 cm^{-1} for $(phenol)_3^+$ and $(phenol)_4^+$, respectively. These bands are obviously attributed to the free OH stretching vibrations of the neutral sites, indicating that at least one dangling OH bond is involved in these ions. The presence of the dangling OH bond is clear evidence for noncyclic structures for $(phenol)_3^+$ and $(phenol)_4^+$. On the other hand, no remarkable band but a broad and weak absorption appears in the region of 3000−3600 cm^{-1} of the $(phenol)_3^+$ spectrum. In the $(phenol)_4^+$ spectrum, an extremely broad absorption appears to be very similar to that of the case of $(phenol)_2^+$. The assignment of this broad absorption will be discussed later.

The noncyclic form of $(phenol)_3^+$ is in a sharp contrast to the cyclic form of the neutral trimer, $(phenol)_3$. The latter has recently been established by IR and stimulated Raman spectroscopic study;[9] all the OH stretching frequencies of $(phenol)_3$ are largely red-shifted from the dangling OH bond frequency region. It was also found that the OH bands split into two categories: one is IR active and the other is favored in the Raman spectrum. The depolarization ratio measurement of the Raman bands revealed that the latter corresponds to a totally symmetric vibration and the former to a non-totally symmetric vibration. This is firm evidence of the cyclic structure for the neutral trimer, which must associated with the C_3 point group.[9] For the neutral $(phenol)_4$, on the other hand, no direct evidence has been given so far. However, IR spectroscopic studies[12] and theoretical calculations[29] of hydrogen-bonded clusters, such as phenol−$(H_2O)_n$, represent the fact that cyclic forms are the most stable structures for the size of $n = 2-5$. In this respect, the similar cyclic form is also expected for $(phenol)_4$. Thus, the IR spectra obtained in this work indicate that the intermolecular structures of $(phenol)_3^+$ and $(phenol)_4^+$ are quite different from their corresponding neutral forms and represent the fact tht the cyclic structures are no longer favorable in these ions.

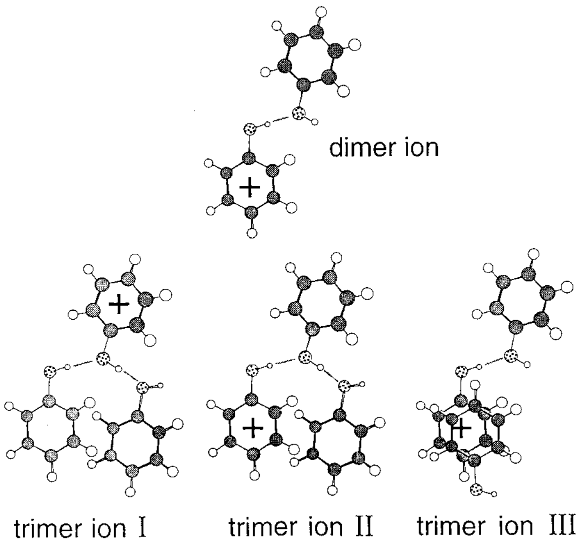

Figure 3. Schematic forms of phenol dimer and trimer ions.

3.2. Electronic Spectra of $(Phenol)_n^+$ for $n = 3$ and 4. For noncyclic structures of $(phenol)_3^+$, we have several candidates, as shown schematically in Figure 3, together with the form of $(phenol)_2^+$ characterized in this work. In $(phenol)_2^+$, the charge should be predominantly localized on the proton-donating site, as described above. In $(phenol)_3^+$, the charged site should also appear as a proton donor, because the acidity of phenol ion is larger than that of the neutral. The only requirement for noncyclic forms of $(phenol)_3^+$ is the presence of the dangling OH bond(s) in the hydrogen accepting site(s). Thus, three forms are found to be possible as given in Figure 3. In both forms I and II, a hydrogen bond chain is essential; the ionic moiety sits at the center of the chain for form I while at the end for form II. From a view point of the charge delocalization interaction among phenyl rings,[20] no intense band due to the charge resonance (CR) transition is expected from form I, because the distance between the phenyl rings is so large that the interaction between the ionic and the neutral moieties is insignificant. Form II may exhibit the CR transition because the phenyl ring interaction can be possible, even though the distance between the two rings is substantially restricted by the hydrogen bond chain. Form III is of hybrid type, consisting of the hydrogen-bonded dimer part and the third phenol molecule which is bound on the charged site through the phenyl ring interaction. An antiparallel sandwich conformation may optimize the interactions between the phenyl rings because of the dipole moment of phenol.

Discrimination of these forms can readily be carried out by observing the CR transition of the cluster ions. Figure 4a shows the electronic spectrum of $(phenol)_3^+$ in the visible and near IR region. In the case of a sandwich-type dimer ion of aromatic molecules, such as the benzene dimer ion,[20] a broad and extremely intense CR absorption is known to occur with its peak at around 900−1000 nm. In addition, a much weaker transition is seen at around 400 nm, which is associated with the local excitation (LE) due to a $(\pi-\pi)$ transition of the charged moiety. As shown in Figure 4a, on the other hand, the absorption intensity in the near IR region of $(phenol)_3^+$ is much weaker than that of the LE band seen at around 400 nm. Very recently, extensive measurements of the electronic transitions of $(phenol)_n^+$ for $n = 2-6$ have been performed by Nishi and co-workers.[30] Their results also show that absorption in the near IR region is extremely weak for the small size clusters.

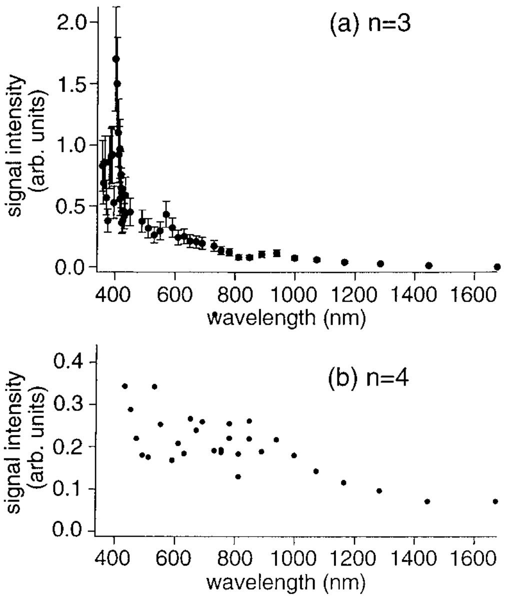

Figure 4. Electronic spectra of (a) $(\text{phenol})_3^+$ and (b) $(\text{phenol})_4^+$, obtained by monitoring the ion intensity of the $(\text{phenol})^+$ fragment. The intensity was normalized with respect to the incident laser power. Since the same fragment ion was detected, the scale units are the same in both spectra.

From the electronic spectrum, thus, form III is immediately ruled out from the candidates for the cluster form of $(\text{phenol})_3^+$. In the case of form II, it is not as clear as that in form III, because the phenyl ring interaction may be small. However, the possibility of form II also seems to be small for the following reason: since the transition dipole moment of the CR transition is extremely large compared to that of the LE transition, substantial intensity of the CR band is expected even with small overlap between the two phenyl rings. Thus, form II is also ruled out from the candidates. Therefore, it is suggested that form I is the most feasible form for $(\text{phenol})_3^+$, although it is tentative. The conclusion must be examined with a more elaborate study that includes theoretical calculations.

We also measured the electronic spectrum of $(\text{phenol})_4^+$ in the CR band region as shown in Figure 4b. The relative intensity of the CR band region of $(\text{phenol})_4^+$ is almost the same as that of $(\text{phenol})_3^+$, indicating the weakness of the phenyl ring interactions. Therefore, it is suggested that $(\text{phenol})_4^+$ has a similar form as $(\text{phenol})_3^+$ of form I. These results mean that the hydrogen bond formation is dominant over the phenyl interactions, at least, in the small-sized cluster ions.

3.3. Structure Change upon Ionization. Now, we have an interesting result with respect to different structures between the ionic clusters and the corresponding neutrals; that is, $(\text{phenol})_3$ has the cyclic form with equivalent phenyl groups, while $(\text{phenol})_3^+$ appears to have the chain form of hydrogen bonding with inequivalent moieties. The same may be true for $(\text{phenol})_4$ and its ion. We will discuss the substantial difference in their cluster forms, although a qualitative argument is involved. Let us confine our arguments to small-sized clusters such as the trimer or tetramer, where there is no chance of forming bicyclic structures with respect to the intermolecular hydrogen bonding. It is evident that the cyclic form has always a larger number of hydrogen bonds by one than that in the chain form. For small-sized clusters, however, all the intermolecular angles of O−H···O bonds are expected to be bent in their cyclic form, because the ordinary angle between the OH bond and the direction of the maximum distribution of the nonbonding electrons is larger than the angle expected for the cyclic form. Thus, the cyclic forms results in some stress to the intermolecular hydrogen bonds, while the chain forms do not have such a bond angle strain. Accordingly, it is noticed for the cyclic forms that the stabilization by the ring formation is reduced by the destabilization due to the angle stress. In neutral clusters, the stabilization energy of a single hydrogen bond is usually less than 10 kcal/mol.[31] Thus, the equilibrium structure of the neutral clusters may be optimized by a trade-off between the additional stabilization due to the extra bond and the destabilization due to the bond angle distortion, both of which accompany the ring formation. In the case of cluster ions, on the other hand, the stabilization energy of a single hydrogen bond involving the ionic moiety is several times larger[32] than that of the neutral site. A large stabilization energy can be obtained by forming a first bond between the ionic and neutral moieties. Therefore, the optimization of the intermolecular structure in cluster ions is merely given by forming a dominant hydrogen bond involving the ionic moiety without any bond angle distortion, resulting in the chain forms.

With respect of the above argument on the bond angle stress of the neutral trimer, it is seen that a related interpretation can be effective for the S_1-S_0 electronic spectra of the clusters including phenol. The S_1-S_0 electronic spectra[9,33−35] of $(\text{phenol})_3$, phenol−$(H_2O)_2$, and phenol−$(CH_3OH)_2$ all exhibit long progressions of intermolecular modes. Such a spectral feature indicates that a large structural change is involved due to the enhancement of the hydrogen bond strength upon electronic excitation. In terms of the trade-off between the angle distortion and the increase of hydrogen-bonding energy, a rearrangement of the cluster form is induced upon excitation, leading to a new equilibrium structure from that of the ground state trimer. Since ionization induces a much larger enhancement in the hydrogen bond strength than electronic excitation, a change from the cyclic form is feasible for the phenol trimer ion.

3.4. Disappearance of Hydrogen-Bonded OH Bands. In the IR spectra of $(\text{phenol})_n^+$, it is seen that no prominent band, except for an extremely broad absorption, occurs in the region of 3000−3600 cm^{-1}, where stretching vibrations of the hydrogen-bonded OH oscillators should appear. The disappearance of distinct bands due to hydrogen-bonded OH stretches is puzzling, because their IR absorption intensity is expected to be larger than that of the dangling OH oscillators.[4] A similar feature has also been found in the hydrogen-bonded OH stretching region of the cluster ions of the phenol−water and phenol−methanol systems. In a previous paper,[24] this characteristic feature of the hydrogen-bonded OH stretches was discussed with respect to the difference in dissociation yield because the spectra were observed by an indirect method involving IR multiphoton excitation followed by dissociation. The dissociation yield via hydrogen-bonded OH stretches may not be as good as that via the others, because that the former vibration has usually a large anharmonicity which causes a low absorption efficiency for the second IR photon. Fast intramolecular vibrational redistribution of the hydrogen-bonded OH vibrations might also lead to an inefficient absorption cross section of the second photon.[4] As was described in a previous paper,[24] it was suggested that a two-photon transition to the low-lying electronic excited state of the phenol ion site may be involved in the broad absorption appearing in 2900−3500 cm^{-1}. However, an alternative interpretation, that is, the broad absorption is due to the hydrogen-bonded OH bands, could be put forth. Because of the ambiguous assignment of the broad absorption, further extensive investigation has been requested for the bands appearing in the 3000−3600 cm^{-1} region of cluster ions having the hydrogen-bonded OH oscillators.

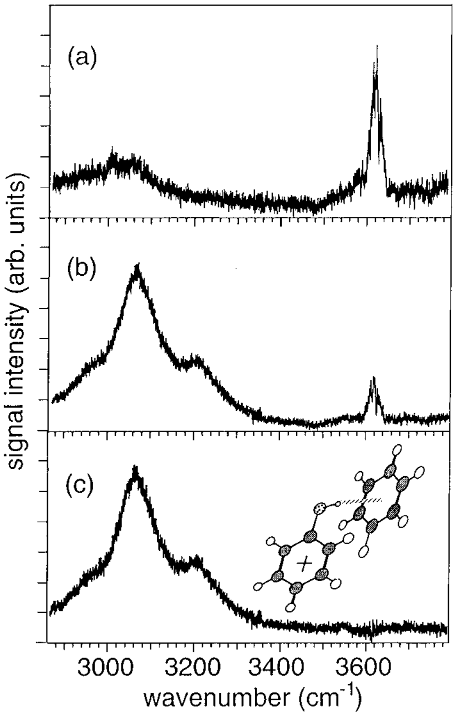

Figure 5. Infrared spectra of (a) $(\text{phenol})_2^+$ and (b) $(\text{phenol})_2^+$ with (phenol−benzene)$^+$, obtained by monitoring the phenol$^+$ fragment ion intensity as a function of the infrared wavelength. The difference between the spectra b and a is reproduced in spectra c. Schematic form of (phenol−benzene)$^+$ is illustrated in (c).

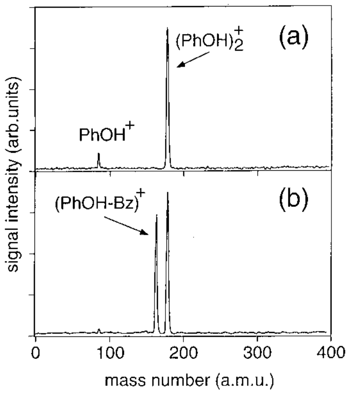

Figure 6. Mass spectra trapped in the trap cell; spectra a and b were taken under the conditions when IR spectra a and b in Figure 5 were observed, respectively.

In Figure 5b is illustrated an IR spectrum of cluster ions observed by a supersonic expansion of a mixture with phenol and benzene, where $(\text{phenol})_2^+$ and the phenol−benzene heterodimer ion (phenol−benzene)$^+$ were generated simultaneously. For comparison, the spectrum of $(\text{phenol})_2^+$ is reproduced in Figure 5a from Figure 1a. In Figure 6a,b are shown mass spectra of the trapped species in the ion trap cell when the spectra (a) and (b) in Figure 5 were observed, respectively. Since the mass resolution of the ion trap cell is not good enough for the separation of the species with 172 amu for (phenol−benzene)$^+$ from that with 188 amu for $(\text{phenol})_2^+$, the IR spectrum shown in Figure 5b represents the spectrum of the former ion overlaid by that of the latter. The spectrum of Figure 5b shows a peak at 3620 cm^{-1} and an intense absorption with a considerably broader feature at about 3060 cm^{-1} with shoulders on its both sides. It is easily seen that the peak at 3620 cm^{-1} coincides with that of Figure 5a within the experimental accuracy of the present work and that the band undoubtedly originates from $(\text{phenol})_2^+$. In Figure 5c is given the difference between the spectra 5a and 5b where the intensity of the spectrum 5a was reduced such that the peak height of the 3620 cm^{-1} band in spectra 5a is as high as the peak in spectra 5b. Thus, the subtracted result (5c) represents the IR spectrum due to (phenol−benzene).$^+$

It is well-known that π-electrons in unsaturated compounds, such as benzene, are effective as proton acceptors in a so-called π-type hydrogen bond.[6,8,31] A schematic view of the heterodimer ion bound by π-type hydrogen bond between phenol and benzene is illustrated in the insertion of Figure 5c. Since the ionization energy of phenol is substantially lower than that of benzene,[36] it is evident that the charge in the heterodimer ion is localized predominantly on the phenol side. In this heterodimer ion, therefore, only the OH bond of the phenol ion site appears to be a hydrogen-bonded OH oscillator. In this respect, the intense IR band peaked at about 3060 cm^{-1} in Figure 5c can uniquely be assigned to the absorption associated with the hydrogen-bonded OH stretching vibration of the phenol ion moiety. Since the OH frequency of the bare phenol ion has been known to be 3535 cm^{-1}, as described above, the difference of about 475 cm^{-1} is a "red" shift of the OH stretching vibration induced by the π-type hydrogen bond formation of the phenol ion. Thus, such a large frequency reduction, as well as an extremely broad feature, is associated with the hydrogen bond formation in the ionic clusters, even though the π-type hydrogen bond is substantially weaker than the σ-type hydrogen bond. In this respect, much larger frequency reduction and substantial broadening may easily be expected for the case of σ-type hydrogen bonding systems of phenol ion, such as for the $(\text{phenol})_2^+$ or $[\text{phenol}-(H_2O)_n]^+$ cases. For the ionic clusters, therefore, it is suggested that a drastic deformation of the potential of the OH stretching mode is induced by hydrogen bond formation, and that the force constant of the mode decreases so drastically that the OH stretching vibration of the ionic site cannot be uniquely identified. Though ab initio calculations of such an ionic species with an open shell electron configuration are not easily performed, theoretical investigations are heavily desired for analyzing hydrogen-bonded OH vibrations of the cluster ions in detail.

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