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Accounts

Spectroscopic Study of Intracluster Proton Transfer in Small Size Hydrogen-Bonding Clusters of Phenol

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Spectroscopic studies of the hydrogen-bonding clusters of phenol were reviewed with an emphasis of the characterization of the cluster structures involving the proton transfer processes. Two experimental methods which were newly developed for the spectroscopy of the size selected clusters and their ions were described. Trapped ion photodissociation spectroscopy revealed that chromophore alternation occurs in the cluster cations with various proton-accepting molecules, such as NH_3 and H_2O. The infrared spectroscopy combined with the ionization detection was applied to the spectra of the OH vibrations which characterized the neutral clusters of phenol with water. The spectroscopic evidence of the ion-pair form of the neutral cluster is presented and the possibility of the intracluster acid-base reaction is discussed.

Spectroscopic study of molecular clusters has been advanced by various experimental methods combined with the supersonic expansion technique, which prepares clusters bound by van der Waals force or by hydrogen-bond under an isolated condition at very low temperature. New spectroscopic methods for the cluster studies have also promoted researches in cluster chemistry; these include geometrical structures, relaxation processes, dissociation processes, solvation and solvent effects, reaction intermediates, transition regions, and stereo-chemistry. The importance of the cluster chemistry is closely related to the statement that clusters represent a new phase of matter functioning in the region between gas and condensed phases. Some of the inherent nature of chemical reactions in the conventional phases may be revealed by researches in chemical processes occurring within clusters.

(i) A pair of molecules in a cluster are often thought to be a reaction precursor whose reaction is initiated by a *triggering* event such as electronic excitation or ionization. Reactions occurring in clusters are often similar to processes in the conventional phases.

(ii) The chemical reactivity depends on conformation and/or configuration of the intermolecular bonds, which is closely related to stereochemical processes. Some reactions may be specific to intracluster processes in which the geometrical structure allows the reaction to occur.

(iii) A molecule surrounded by a small number of other molecules represents a molecular model of a solute–solvent system in the condensed phase. Solvent effects in bulk systems may be pursued in terms of structure and dynamics of clusters.

Thus physicochemical studies of molecular clusters provide us with the information about common processes encountered in the conventional phases as well as processes specific to cluster chemistry which never happen in bulk systems.

Many spectroscopic studies have been done on hydrogen-bonded clusters.$^{1—39)}$ The clusters involving water molecules are of particular importance for the investigation of properties of aqueous solutions. The clusters involving ammonia are also well studied, especially their structures and dynamical properties. In hydrogen-bonding clusters, proton transfer is an important class of the intracluster chemical processes, since it is the most fundamental chemical reaction. Proton transfer occurring within the hydrogen-bonding clusters is closely related to processes associated with acid-base reactions in the condensed phases. The intracluster proton transfer represents one of the simplest reactions without perturbation by environment. The mechanism of an acid-base reaction can be investigated by stepwise clusterization of solvent molecules. In this respect the intracluster proton transfer is an ideal reaction for a molecular level investigation of chemical reactions.

In this paper, we present a review of our recent work concerning intracluster proton transfer in hydro-

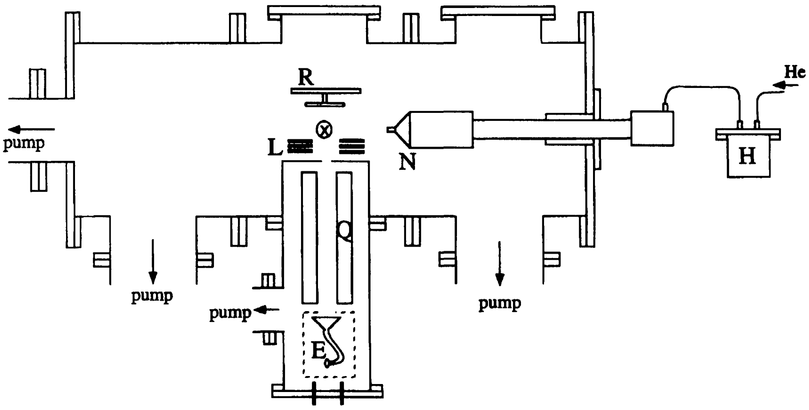


Fig. 1. Experimental schematic of REMPI spectroscopy. E, electron multiplier; H, sample housing; L, ion lenses; N, pulsed supersonic nozzle; Q, quadrupole mass filter; R, repeller. In the ion trap experiment R and L are replaced by an RF cell. Laser beams cross the jet stream at x point.

gen-bonding clusters of phenol. Since phenol is a prototype among many hydrogen-donating aromatics, studies of clusters of phenol with hydrogen-accepting molecules will contribute to the investigation of structure and dynamics of various hydrogen-bonding systems. First, we describe intracluster proton-transfer processes of the cluster cations of phenol with small numbers of basic molecules, such as ammonia, water, and others. The experimental methods are briefly described, since the size-selectivity is a key feature of the spectroscopy of a particular cluster species. We have recently proposed Trapped Ion Photodissociation (TIP) spectroscopy, which involves an ion storage technique, for mass-selected analysis of a particular cluster.[25] The proton transfer in the cluster ions can be identified as an alternation of their electronic transition. Stable forms of the cluster ions have been found for various clusters as a result of the spectral change associated with the chromophore alternation.[34,35] Similar chromophore switching was also investigated by changing the cluster size. The chromophore switching occurs for the clusters with the acceptors having proton affinity larger than 840 $\mathrm{kJ\,mol^{-1}}$.

Secondly, we describe the investigation of the neutral clusters of $[\mathrm{PhOH{-}(H_2O)}_n]$. The vibrational spectroscopy greatly contributes to investigation of cluster structures through the characterization of their key vibrations, such as OH vibrations. We have developed IR spectroscopy combined with an ionization detection, in which a particular cluster species is properly selected by resonantly enhanced multiphoton ionization (REMPI).[35] The neutral clusters of $[\mathrm{PhOH{-}(H_2O)}_n]$ in the electronic ground state were characterized by the vibrational spectra of the OH stretching vibrations of the phenol site as well as of the water sites. Remarkable frequency changes of the OH vibrations have been found as the cluster size increases. We have also found some evidence that an ion-pair form is created in the neutral cluster with $n=4$. Such a result suggests that the acid-base reaction takes place even in a small size cluster, and that the solvation of a few water molecules is good enough to stabilize the ion-pair form.[40] The system represents a molecular-level model of an aqueous solution of an acid, in which the heterolysis of the acidic compound is induced by intermolecular proton transfer.

Experimental Methods

Our experiments employed a tunable dye laser system and a vacuum chamber for REMPI studies, in which a supersonic nozzle and a quadrupole mass filter or a TOF mass spectrometer were used. Figure 1 shows a schematic view of the chamber. High sensitivity and species-selectivity are the major requirements of spectroscopy for the cluster study. A supersonic nozzle expansion, which is the most popular method as a cluster source, prepares a mixture of various clusters with respect to size and species, and their density in the expansion is usually very low. So a highly sensitive detection method is necessary for the spectroscopy of clusters with such a low concentration. In addition, the method should perform as a selective detection of a particular species in the mixture or should be combined with an additional technique to sustain the selectivity. REMPI is often used as a sensitive detection method but it is not fully appropriate without being combined with mass-selective equipment. The ionization often leads to fragmentation of the initially created cluster ion or to evaporation of a part of it. Such a fragmentation following ionization results in additional complications for the size selection. In spectroscopic studies, the mass selection after the ionization is thus also necessary in order to avoid the complications.

Figure 2 represents a brief view of an ion trap cell for the TIP spectroscopy which provides spectra of mass-selected cluster ions. Details of the ion trap cell were given elsewhere.[25,41] Among various ion storage techniques, this method is known to be a modification of quadrupole ion storage trap (QUISTOR).[42] The cell is composed of a ring electrode and two end caps used as the other electrode. Then, it is called cylindrical ion trap (CIT) cell.[43] A radio frequency (RF) electric potential with a d.c. bias is applied on the ring electrode with respect to the end cap electrode which is grounded. The mass selection of charged species can be performed by selecting appropriate voltages of the

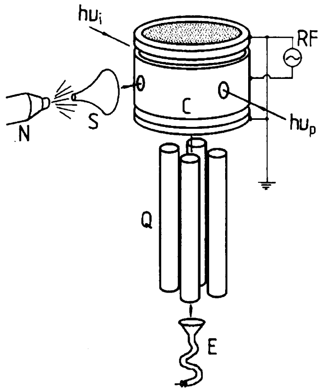


Fig. 2. Schematic view of the apparatus for the ion trap experiment. C, ion trap cell; E, electron multiplier; N, pulsed supersonic nozzle; Q, quadrupole mass filter; S, skimmer. RF voltage and DC bias are applied between the endcaps and the ring electrode. Molecular beam enters into the cell through a side hole of the ring electrode. Clusters in the molecular beam are ionized by the ionization laser ($h\nu_i$) and the trapped cluster ion is photodissociated by the probe laser ($h\nu_P$). The fragment ions run out spontaneously through a hole at the center of the bottom endcap and are analyzed by a quadraplor mass filter.

RF potential and of the d.c. bias as well as selecting the RF frequency. The molecular beam containing neutral clusters was introduced into the cell and the cluster was ionized with an UV laser for REMPI. The cluster ion of interest was trapped by a suitable condition of the electric potentials of the cell. Various fragment ions created upon the ionization can be removed from the cell during the storage. To observe the spectrum of the stored cluster ion, another laser pulse for electronic or vibrational excitation was introduced into the cell after a suitable storage time, typically several milliseconds. The excitation is usually followed by fragmentation, so that the fragment yield spectrum of the trapped species can be obtained as a function of the excitation laser frequency by monitoring an ion current due to a particular fragment. A quadrupole mass filter was used for the separation of the fragments. By this method we have produced a TIP spectrum which represents the mass-selected electronic spectra of particular cluster ions with the desired size.

Figure 3 shows a schematic diagram of IR spectroscopy for size-selective neutral clusters. An ion current generated by REMPI with an UV laser ($h\nu_{uv}$) was monitored as a measure of the ground state ($v''=0$) population of a particular cluster. The size selection was carried out by tuning $h\nu_{uv}$ at the resonance energy of the S_1–S_0 transition of the particular species. When an IR laser ($h\nu_{IR}$) induces the vibrational transition to the $v''=1$ level, the population of the $v''=0$ level is reduced so that the ion current is decreased. Thus, by scanning $h\nu_{IR}$ and by monitoring the ion current, the vibrational spectrum of the particular cluster is obtained as an ion dip spectrum; we call this method *ionization detected infrared spectroscopy* (IDIRS).[35] The tunable IR light used here was generated by the frequency difference generation with a nonlinear optical crystal ($LiNbO_3$).

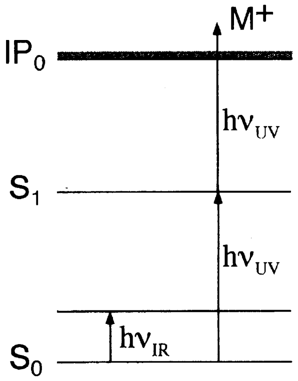


Fig. 3. Excitation scheme for ionization detected infrared spectroscopy. The IR laser is introduced prior to the UV laser by 50 ns.

Proton Transfer in the Cluster Cations

(a) Stable Forms of PhOH Cluster Ions. In hydrogen-bonding clusters it is useful to know where the proton or hydrogen atom of interest is. The proton location depends on the acidity of the proton donating molecule as well as on the proton affinity of the acceptor molecule. Let us consider an ion of a pair of molecules: AH and B. The cation $[AH–B]^+$ has two forms:

$$AH^+\cdots B \qquad A\cdots H^+B$$

which are connected through an isomerization coordinate with respect to intermolecular proton transfer. In condensed phases, such an intermolecular process is so sensitive to various perturbations due to solvation that the stable form of the ion may not be determined properly by the molecular properties of AH and B. In vapor phase, the stable form of the ions is often predicted by the fragment analysis in mass spectrometry. However, the analysis is not always adequate for the prediction of the correct form of the ion, as will be demonstrated below. In this section, we describe the identification of stable forms of the ions $[AH–B]^+$ by using spectroscopic methods combined with the mass-selection.

(i) $[PhOH–N(CH_3)_3]^+$. Figure 4 shows the TIP spectrum of the hydrogen-bonded complex ion of PhOH with $N(CH_3)_3$. The electronic spectrum was obtained by trapping $[PhOH–N(CH_3)_3]^+$, which is the complex ion with mass number of 132 amu, and by monitoring the yield of fragment $H^+N(CH_3)_3$ as a function of the laser frequency of the excitation.[25] Except for a spectral red shift, the spectrum with a characteristic vibronic structure was found to be quite similar to the absorption spectrum of phenoxy radical, PhO, which was reported by Tripathi and Schuler.[44] The result suggests that the cluster ion has a chromophore for the electronic transition similar to that of the neutral PhO, and consequently that the cluster consists of PhO and $H^+N(CH_3)_3$; that is, it appears as (Chart 1).

For the neutral states of the cluster, the fluorescence

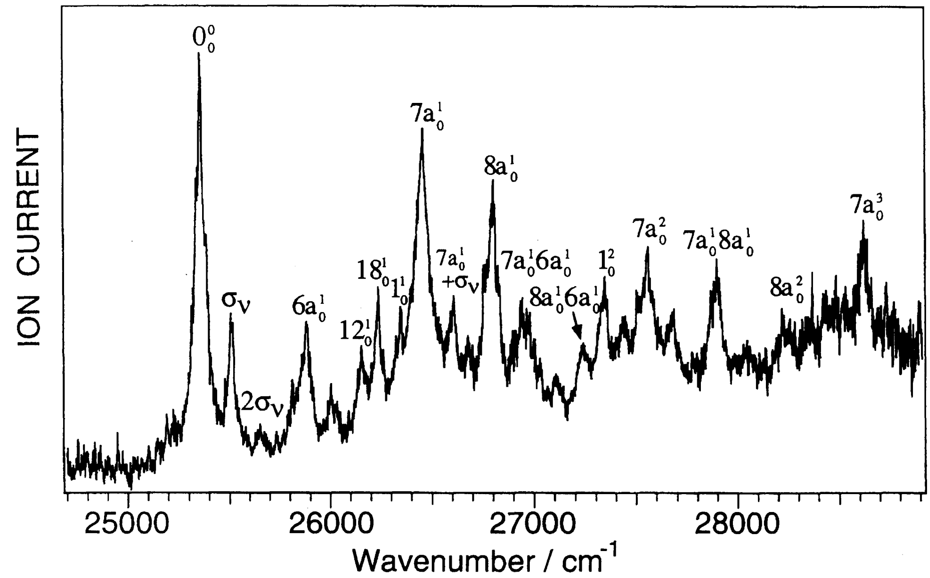


Fig. 4. Electronic spectrum of $[PhOH–N(CH_3)_3]^+$ obtained by TIP spectroscopy. Assignments of prominent vibronic bands are indicated as given in Ref. 39.

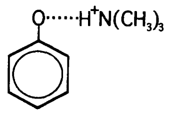


Chart 1.

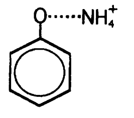


Chart 2.

spectroscopic studies revealed that the proton transfer does not occur in its S_1 and S_0 states,[7] though $N(CH_3)_3$ has a large proton affinity. In contrast, as shown in Fig. 5a, the proton transfer of the cluster ion has been expected from the fragmentation pattern after the photoionization; the $H^+N(CH_3)_3$ fragment is dominant, but no fragment of $PhOH^+$ appears in the mass spectrum. In ordinary mass spectrometry, the structure of an ion is often predicted from its fragmentation pattern. However, the structure analysis of the ion by using fragmentation is valid when the structure is the only form to exist. A misleading case of the fragment analysis is given below.

(ii) $[PhOH–NH_3]^+$. Figure 5b shows the mass spectrum after photoionization of the hydrogen-bonded complex of PhOH with NH_3: The $PhOH^+$ is the only fragment and no $NH_4{}^+$ appears.[8] With these results the ordinary fragment analysis predicts that the non-proton transfer form, that is, $[PhOH^+–NH_3]$ is feasible. However, the TIP spectrum obtained by trapping $[PhOH–NH_3]^+$ was found to be similar to that of $[PhO–H^+N(CH_3)_3]$ given in Fig. 4. The result indicates that $[PhOH–NH_3]^+$ has the PhO chromophore and appears as the proton transferred form,[34] that is, (Chart 2).

The disagreement between the two alternative structures can be understood if we assume that $[PhOH^+–NH_3]$ is a meta-stable form and $[PhO–NH_4{}^+]$ is the most stable form. Two forms represent the structures of the ion in both the potential wells which are separated by a potential barrier, as shown in Fig. 6. Each well is closely related with one of the two dissociation coordinates; one is R(OH····N) leading to $PhOH^+$ with NH_3 and the other is R(O····HN) leading to PhO with $NH_4{}^+$. There are several experimental and theoretical results used to drawing the energy diagram given in Fig. 6 : (i) the two dissociation limits are lying at about the same energy.[8,9] (ii) The dissociation limits are lower than the barrier top, which is estimated at about 1 eV above the ionization threshold.[8] (iii) The ionization followed by dissociation generates only the $PhOH^+$ fragment, but does not lead to the $NH_4{}^+$ fragment.[9,17]

Since the S_1 state of the neutral complex is known to be the non-transferred form,[8] the Franck–Condon (FC) region of the ion prepared by REMPI via S_1 occurs in the potential well of the non-transferred form. Because of the high barrier described above, the fragmentation following REMPI takes place only in the meta-stable well. Such dissociation characteristics were confirmed with the time-resolved REMPI spectroscopy done by Syage and co-workers;[23,24] the proton transfer is not fast enough in a time scale less than nanoseconds. The relatively slow rate of the proton transfer means that the effective mass of the proton transfer is much larger than the mass of the bare proton. Thus, various relaxations of the aromatic ring structure must be associated with the proton transfer. Because of the slow rate, the conversion from the meta-stable well to the stable well can not be identified by ordinary mass spectroscopy with a nanosecond time scale. On the other

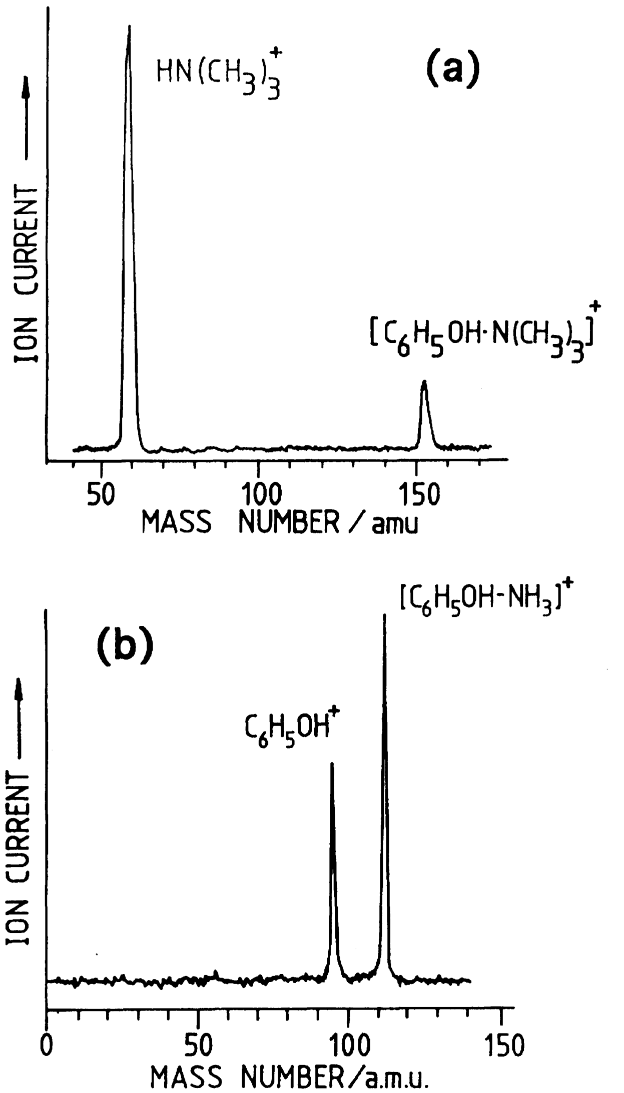


Fig. 5. Mass spectra of (a) [PhOH–N$(CH_3)_3$] and (b) [PhOH–NH_3] obtained after REMPI.

hand, the ion trapping of the complex ion allows enough time for the conversion to be completed. Since the TIP spectroscopy examines the electronic transition of the complex ion after the storage for several milliseconds, the proton-transferred form is formed and is properly identified. Thus, the stable structure of the cluster ions having a meta-stable form must be examined carefully with appropriate spectroscopic methods.

(iii) [PhOH–Ar]$^+$, [PhOH–H_2O]$^+$, and [PhOH–*p*-Dioxane]$^+$. In these complex ions, the proton transfer is not accompanied by fragmentation following ionization; mass spectra show that the PhOH$^+$ fragment is dominating. Figure 7 shows the TIP spectrum of [PhOH-Ar]$^+$, which is broad with no vibronic structure.[45] Since the proton transfer to argon atom is not expected in the present REMPI condition, the spectrum of [PhOH–Ar]$^+$ is unambiguously attributed to the electronic transition of phenol ion. Other complex ions showed the spectra similar to that of [PhOH–Ar]$^+$.

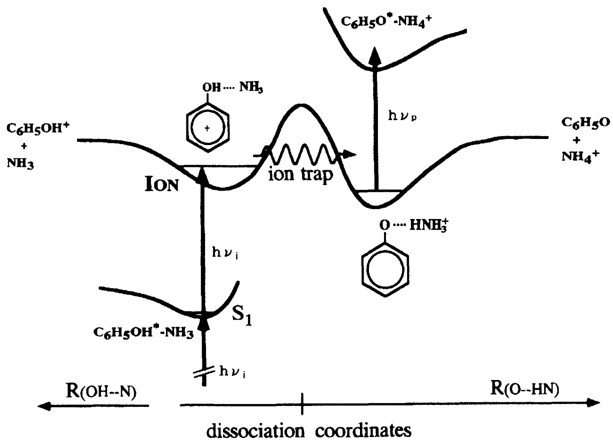


Fig. 6. Schematic energy diagram for the ionic state of [PhOH–NH_3]$^+$. There are two dissociation limits which are almost the same energy.

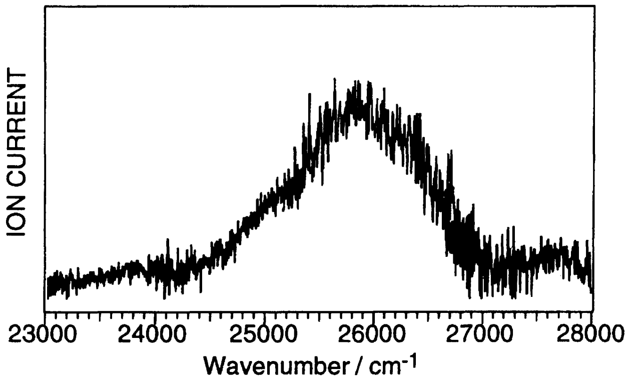


Fig. 7. Electronic spectrum of [PhOH–Ar]$^+$ obtained by TIP spectroscopy.

The similarity indicates that the spectra of these hydrogen-bonded complex ions are due to the electronic transition of the phenol ion chromophore. Thus the complexes with H_2O and with *p*-dioxane have the non-transferred form, in accord with the results from their mass spectra. The electronic structure of these complexes is no longer in the meta-stable form.

In Table 1, the results including the complexes with NH_3 and with the amine are summarized and the proton affinities (PA) of the accepting molecules are listed. We see that the chromophore change occurs at a threshold value of PA, at 840 kJ mol^{-1}. The chromophore switching between the proton transferred form and the non-transferred one is determined by the net value of the dissociation energy of $PhOH^+ \rightarrow PhO + H^+$ and PA of the acceptor. In the case of the complex with NH_3, the proton transfer seems to be quite critical. We may be able to control the proton transfer of the complex ions by selecting PA of the acceptor. Such a "*manipulation*" involving the chromophore switching can be realized in cluster ions with water molecules, as described in the following section.

(b) Size Dependence of Stable Form of [PhOH–$(H_2O)_n$]$^+$. In the spectroscopic studies

Table 1. Stable Forms of $[PhOH\cdots B]^+$ Ions and Proton Affinities of the Acceptors B

Proton acceptor B	*p*-Dioxane	Furan	$(H_2O)_n$ $n=1$	$n=2$	$n=3$	$n=4$	NH_3	$N(CH_3)_3$
Proton affinity ($kJ\,mol^{-1}$)	811	836	690	840	932	1003	886	970
Stable form	$\longleftarrow [PhOH^+\cdots B] \longrightarrow$ ||				$\longleftarrow [PhO\cdots H^+B] \longrightarrow$			

dealing with a number of different sizes of cluster ions, such as $[PhOH–(H_2O)_n]^+$, the TIP spectroscopy performs its neat function of the size-selection. Figure 8a is the mass spectrum observed just after the ionization of the molecular beam without ion trapping, showing that there is a heavy mixture of various cluster ions. In contrast, Fig. 8b is the mass spectrum obtained after the ion trapping. It is clear that a single species dominates in the cell and that the TIP spectrum is definitely originating from the trapped species. Figure 9 shows the TIP spectra of the clusters of $[PhOH–(H_2O)_n]^+$, representing a size dependence of the chromophore of their electronic transition.[45] The broad and structureless spectra of the $n=1$ and 2 clusters, reproduced in Figs. 9a and 9b, indicate that the $PhOH^+$ chromophore is responsible for them and that the ions must have the non-transferred structure as their stable form. On the other hand, the spectrum of the $n=3$ cluster, in Fig. 9c, exhibits a vibronic structure, indicating that the chromophore is switched to the PhO type and that the conversion to the proton transferred form occurs at $n=3$. In Fig. 9d, the spectrum involving the larger clusters with more than $n=4$ represents a quite similar vibronic structure to that of the complex with NH_3, except for a small spectral shift.

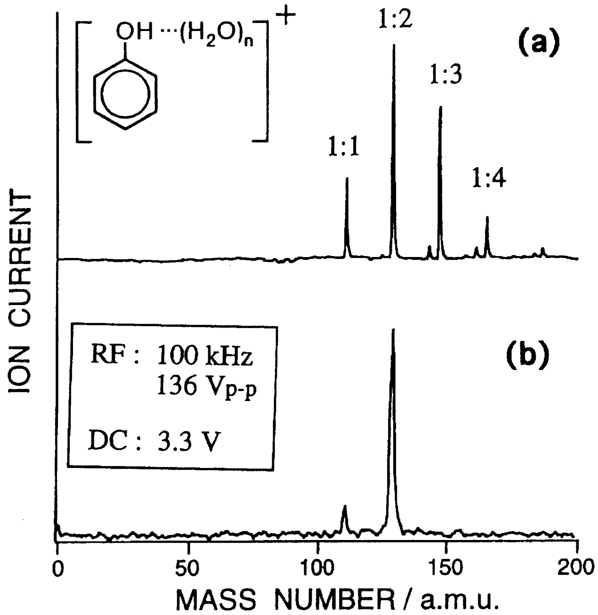


Fig. 8. (a) Mass spectrum obtained just after REMPI of $[PhOH–(H_2O)_n]$, indicating a mixture of the $(1:n)$ cluster ions. (b) Mass spectrum of trapped species in the ion trap cell, showing that the $(1:2)$ cluster ion is dominated under an appropriate trapping condition for the $n=2$ cluster ion. The trapping condition is indicted.

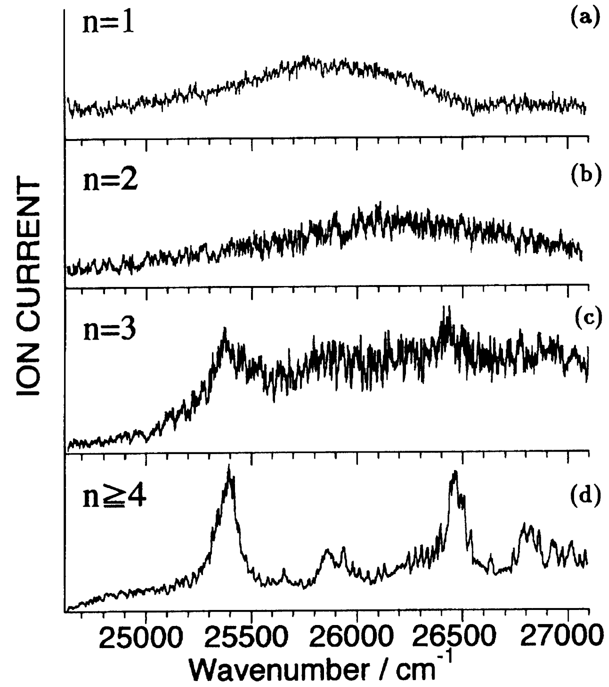


Fig. 9. Electronic spectra of $[PhOH–(H_2O)_n]^+$ obtained by TIP spectroscopy.

The size dependence of the cluster structure has been confirmed by IR spectroscopy of the trapped cluster ions,[46] in which vibrational spectra in the OH stretching vibrational region of the cluster ions are obtained. The comparison indicates that the bands of the $n=1$ and 2 ions are similar to those of the corresponding clusters of pure water, indicating that the structure should be the non-transferred form. On the other hand, the spectrum of $[PhOH–(H_2O)_3]^+$, is found to be very similar to the spectrum of the hydrated oxonium ion, $H^+(H_2O)_3$,[47—49] representing that the $n=3$ cluster ion must have the proton transferred structure as the stable form. Thus the conclusion obtained from the analysis of the electronic spectra has been confirmed by the

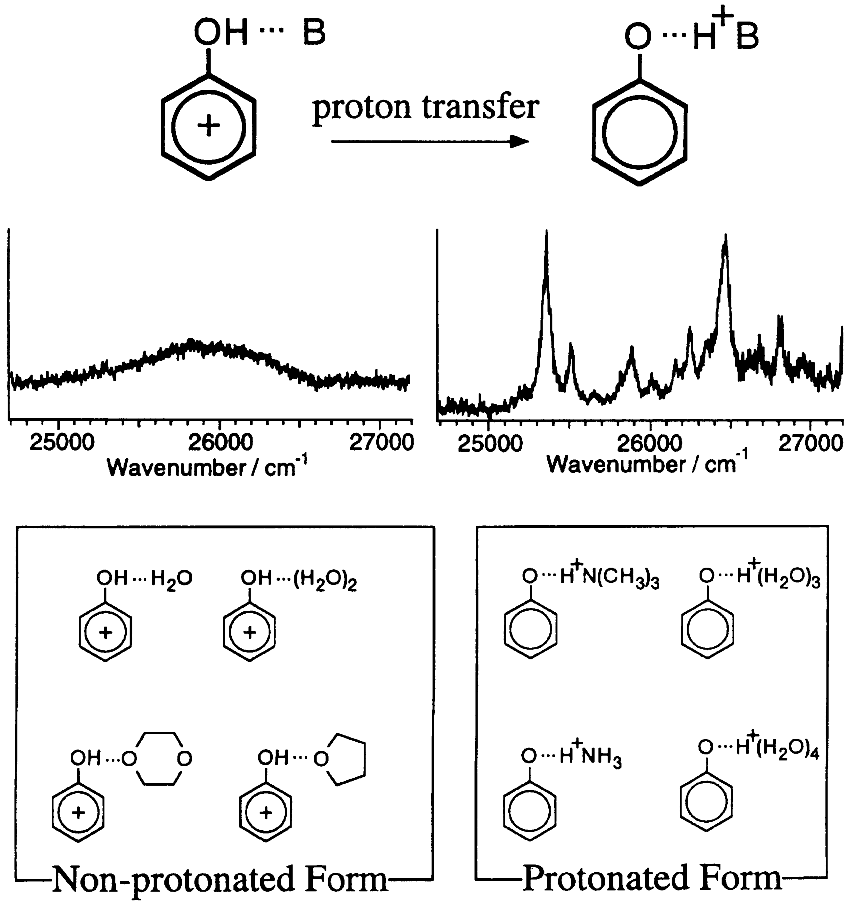


Fig. 11. Chromophore switching as revealed by the electronic spectra. Stable forms of the $[PhOH–B]^+$ are classified into two groups; the protonated and the non-protonated form.

vibrational spectroscopy. Both the results show that the chromophore switching takes place at n=3, that is, (Chart 3).

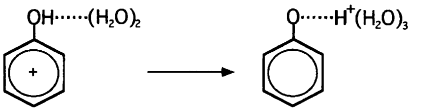


Chart 3.

The size dependence of the chromophore switching of $[PhOH–(H_2O)_n]^+$ may be understood in the following way, as illustrated in Fig. 10. As given in the figure, each ion is supposed to have two minima in the adiabatic potential along the dissociation coordinate: One of the wells corresponds to the non-transferred form and the other to the transferred one. With increasing n, the dissociation limits leading to PhO and $H^+(H_2O)_n$ are reduced with respect to the other limit, leading to $PhOH^+$ and $(H_2O)_n$, as indicated at the right in the figure. Since the well of the protonated form is closely correlated with the former limit, more stabilization will occur for the well with the increase of n. Though the potential surface must be given on the basis of theoretical calculations, this represents a qualitative interpretation of the size dependence of the chromophore switching.

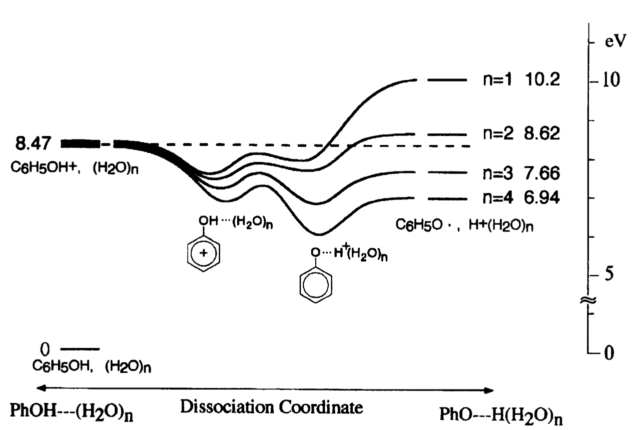


Fig. 10. Schematic energy diagram for the ionic state of $[PhOH–(H_2O)_n]^+$. Dissociation limits for PhO and $H^+(H_2O)_n$ are indicated with respected to the other limit for $PhOH^+$ and $(H_2O)_n$ at 8.47 eV.

Figure 11 summarizes the type of cluster ions classified by observing the characteristic chromophore. In Table 1, the stable forms of the cluster ions with various proton accepting partners, including the water clusters, are listed. It shows that a threshold for the chromophore switching exists at about PA=840 kJ mol^{-1} irrespective of the type of the proton accepting part-

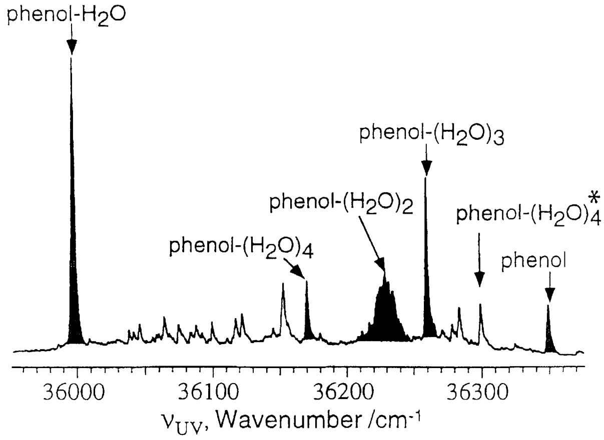


Fig. 12. The origin region of REMPI spectrum of the phenol–water system, showing the S_1–S_0 transition energies of bare phenol and of the [PhOH–$(H_2O)_n$] clusters for n=1—4. The spectrum was obtained by monitoring the total ion current.

ner. The result suggests that the intracluster proton transfer

$$[AH^+\cdots B] \longleftrightarrow [A\cdots H^+B]$$

is sensitive only to PA, but insensitive to other properties of the acceptor, such as its geometrical size. It also seems that the potential barrier height to the proton transfer is not affected by the molecular size of the partner, but is solely determined by the intramolecular property of the phenol moiety.

Proton Transfer in Neutral [PhOH–$(H_2O)_n$] Clusters

The vibrational spectroscopy is quite effective in the structural investigation of chemical compounds; in the case of the neutral clusters this requires the size selection to be satisfied. Phenol surrounded by water molecules is considered to be a microscopic model species in its aqueous solution. Various questions arise for the model with respect to hydrogen bond formation, size dependence, proton transfer, and acid-base reaction.

(a) IR Spectroscopy of the OH Vibrations. IR spectra of the neutral clusters of phenol with water, [PhOH–$(H_2O)_n$],[35] were obtained by the ionization detection method described in the previous section. The size selection is performed by tuning the ionization laser frequency at a particular resonance energy of the S_1–S_0 transition for REMPI of the cluster with a particular size. Figure 12 illustrates the REMPI spectrum of the phenol–water system, which represents the difference in the S_1–S_0 transition energies of individual clusters with n=0—4. The identification of the cluster size was performed by two-color REMPI/mass spectroscopy, reported by Stanley and Castleman, Jr.,[26] and their assignments are indicated in the figure. The bands with no assignment are due to vibronic bands of the known species.

Figure 13 shows the OH stretching region of the IR spectra of [PhOH–$(H_2O)_n$], for n=0—4.[35,40] In bare PhOH, as shown in (a) of the figure, the OH stretching vibration (ν_{OH}) appears at 3657 cm^{-1}. In [PhOH–H_2O], shown in (b), the ν_{OH} band exhibits a red shift by 133 cm^{-1} from the bare PhOH band, and two new bands attributed to the OH vibrations of the H_2O site appear at 3657 and 3748 cm^{-1}, which correspond to the symmetric stretching (ν_1) and the antisymmetric stretching (ν_3) vibrations of H_2O, respectively. The spectrum is the counterpart of the Raman spectrum given by Felker and coworkers,[30] who have developed the ionization detected Raman spectroscopy of clusters. The OH vibrations of the water site of the cluster can be compared to the IR spectrum of bare H_2O.[50] The ν_1 and ν_3 vibrations of [PhOH–(H_2O)] are very close to the corresponding vibrations of pure H_2O, although they are slightly shifted, by only a few wave numbers. On the other hand, the OH stretching of the PhOH site exhibits a remarkable red shifts. This indicates that the force field of the O–H bond of PhOH is substantially reduced by the hydrogen bonding, but only a little change of the force field occurs in the O–H bonds of the proton accepting H_2O site.

The IR spectra of the larger size clusters are also compared to those of the neat water clusters, [$(H_2O)_2$], [$(H_2O)_3$], and [$(H_2O)_4$], which have been reported by several groups.[50—53] The comparison reveals that the bands due to the water sites of [PhOH–$(H_2O)_n$] are very similar to the water clusters with corresponding sizes. It is worthwhile to note that the bands of [PhOH–$(H_2O)_2$] are similar to the corresponding bands of $(H_2O)_2$. As given in Fig. 14, there are two possibilities for [PhOH–$(H_2O)_2$], because this cluster can be considered to be a phenol derivative of $(H_2O)_3$ which is thought to be in a ring form. Actually the electronic spectroscopy of [PhOH–$(H_2O)_2$] done by Gonohe and others[6] emphasized that the second water molecule is bound as a hydrogen acceptor, suggesting a ring form. If the ring form is realized, the IR spectrum of [PhOH–$(H_2O)_2$] is expected to be similar to that of $(H_2O)_3$ but not to $(H_2O)_2$. The same is true for [PhOH–$(H_2O)_3$], because theoretical calculations predicted a ring form of $(H_2O)_4$.[54] On the other hand, the observed IR spectra suggest that the water sites of [PhOH–$(H_2O)_n$] are not significantly affected by the hydrogen-bonding of phenol. Therefore, we tentatively conclude that [PhOH–$(H_2O)_n$] has a structure such that the clusters are formed by hydrogen-bonds between PhOH and the water clusters. To obtain unambiguous assignments of the spectra, however, the force field calculations for the optimized cluster structures are strongly desired.

The figure shows a clear tendency of the band shifts of the vibrations; the OH stretching vibrations are classified into two groups. The bands remaining at 3710—

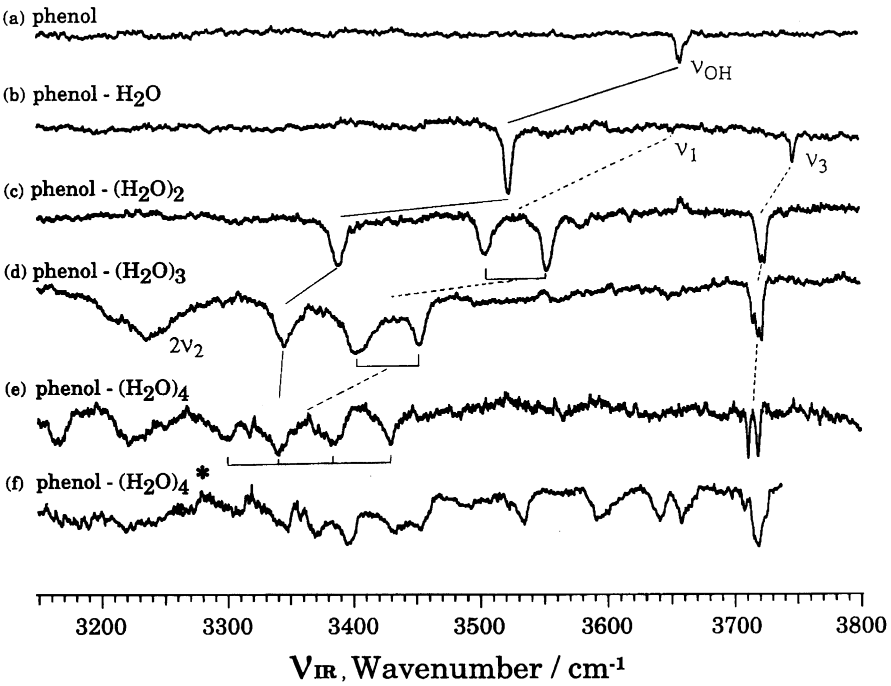


Fig. 13. Vibrational spectra of the OH region of bare phenol and of the [PhOH–$(H_2O)_n$] clusters for n=1—4, obtained by IDIR spectroscopy.

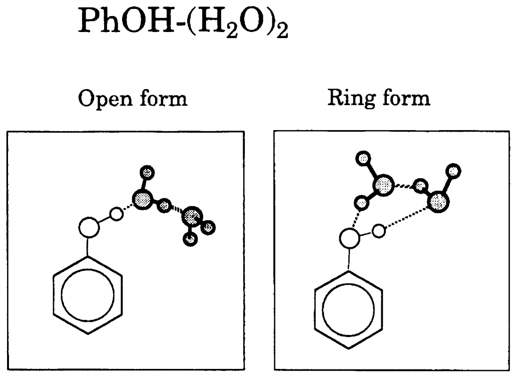


Fig. 14. Cluster forms of [PhOH–$(H_2O)_2$].

3750 cm^{-1} are in one group and the bands in the other group exhibit remarkable red shifts with characteristic splitting. The bands in the former group are due to the vibrations which are not significantly influenced by the hydrogen-bonding and those in the latter are due to the vibrations of the OH bonds responsible for the hydrogen-bonds. The extreme feature is seen in the [PhOH–$(H_2O)_4$] spectrum given in (e) of Fig. 13, representing a large separation between the two groups. The spectral range of 3500—3700 cm^{-1} seems to be a *window* region of the OH vibrations, where no band is allowed. Going to the larger clusters, we expect that the window becomes wider because the basicity of the water cluster site increases with the size n.

(b) Intracluster Acid- Base Reaction in [PhOH–$(H_2O)_4$]*. In spite of the general tendency of the OH vibrations described above, we have found that anomalous OH vibrations appear in the *window* region of a particular species of [PhOH–$(H_2O)_4$]*.[40] As shown in Fig. 13f, four new bands occur in the region when the band denoted by [PhOH–$(H_2O)_4$]* in Fig. 12 was chosen for REMPI. This band has been assigned as an isomer of the n=4 cluster by Catsleman, Jr. and co-workers.[26] The characteristic feature of the IR spectrum suggests that the cluster structure of this isomer should be substantially different from that of the other clusters.

To our surprise, the anomalous bands of this specific cluster were found to be quite similar to the spectrum observed for the hydrated oxonium ion, $H_3O^+(H_2O)_n$.

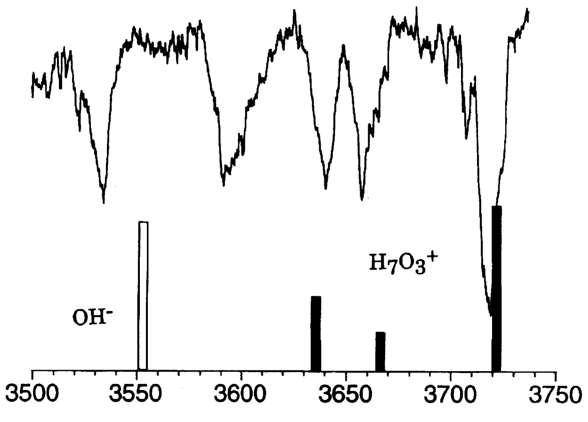


Fig. 15. Anomalous vibrations of [PhOH–$(H_2O)_4$]*. Histograms represent the three bands (dark bars) of $H^+(H_2O)_3$ reported in Ref. 46 and the OH^- band (open bar) observed in gas phase given in Ref. 53.

In Fig. 15, the spectrum of the region is reproduced and the band positions reported in the $H_7O_3{}^+$ spectrum are illustrated by dark bars as a histogram. The IR spectra of $H_3O^+(H_2O)_n$ for n=0—4 were first observed by Schwarz[47)] and recently by Lee's group.[48,49)] The frequencies of the bands in question are very close to those of the $H_7O_3{}^+$ spectrum and the intensities are also similar to each other. On the basis of the similarity, therefore, we have concluded that there exists an ionic part similar to $H_7O_3{}^+$ in $[PhOH-(H_2O)_4]^*$ even though the cluster is neutral in its ground state. The presence of the cationic moiety, $H_7O_3{}^+$, in the neutral cluster immediately leads to a consequence that there should be an anionic part in the cluster and that the cluster must be in an ion-pair form.

As is well known, such an ion-pair form of neutral clusters has been found in the electronically excited state.[10,14,22,27—29)] The pioneering study on the excited state proton transfer was done by Leutwyler and coworkers[10)] for the $[1\text{-Naphthol}-(NH_3)_n]$ clusters. By fluorescence spectroscopy as well as mass spectrometry, they found that the excited state proton transfer occurs in the clusters with $n \geqq 4$. Recently, other groups[15,29)] have reported that the threshold is at $n=3$. For the $[PhOH-(NH_3)_n]$ clusters, Jouvet and others[9,16)] investigated the ionization yield spectra by using two-color REMPI with mass spectrometry and found a threshold for the excited state proton transfer at $n=4$. The time-resolved spectroscopic study on the excited state proton transfer has been done by Syage and others,[37)] it involved a pump-probe method with picosecond lasers. They showed that a clear threshold is seen at $n=5$ for the $[PhOH-(NH_3)_n]$ clusters. In the electronically excited state, the acidity of phenol becomes larger than that of the ground state, so that the electronic excitation may induce the proton transfer. Thus the ion-pair form is expected to be feasible in the excited state.

Since aqueous solution of phenol is weakly acidic, $pK_a=9.82$ in the ground state, one expects that the electrolyte dissociation of phenol takes place in the cluster and the resulting phenolate anion may act as the counter part. In this case, the following structure is expected for the cluster in question:

$$[(PhO^-)-(H_2O)-(H_7O_3{}^+)] \quad \text{(Structure I)}$$

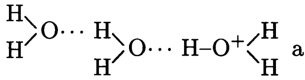
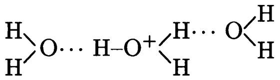
If this is the case, PhO^- is the chromophore of the electronic transition. The chromophore may bring a significant change of the electronic spectrum compared to that of the other clusters with the PhOH chromophore. Actually, in the case of the excited state proton transfer of $[1\text{-Naththol}-(NH_3)_n]$ clusters, the red shifted fluorescence was observed, which means that it originates from the naphtholate anion chromophore.[10,22)] As shown in Fig. 12, however, the electronic transition of $[PhOH-(H_2O)_4]^*$ occurs in the same region, showing that no substantial change of the chromophore takes place. So it is unlikely that the cluster has the form represented by Structure I.

The other possible form of the cluster is the following:

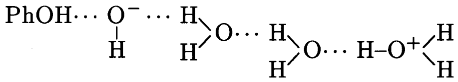
$$[PhOH-(OH^-)-(H_7O_3{}^+)] \quad \text{(Structure II)}$$

which originates from the electrolyte dissociation of water. In this case, the PhOH chromophore is left unchanged and a transition energy is expected similar to what is observed in the REMPI spectrum. In addition to this, another piece of evidence for Structure II is found in the IR spectrum. As illustrated in Fig. 15, there are two bands at 3591 and 3534 cm^{-1} in the region which are not attributed to $H_7O_3^+$. These bands are also found to be very close to the vibration of OH^-(3555 cm^{-1} in gas phase).[55)] Although the detailed assignment of the anomalous bands has to be carried out on the basis of the vibrational analysis for the cluster structures predicted by ab initio calculations, the close similarity among the vibrational spectra suggests that Structure II is responsible for the ion-pair form of the cluster.

Though the detailed structure of $H_7O_3{}^+$ is not fully known, one of the expecting forms is the following:


and


If this is the case, the following form is expected as the ion-pair structure of the cluster:



The two neutral H_2O molecules seems to be effective to shield the Coulombic potential between the two different charged parts, and PhOH seems to be a *spectator* bound to the ion-pair site.

The ion-pair form should also be examined from a thermodynamic point of view. The heterolysis of H_2O in the gas phase is an endothermic process with an extremely large enthalpy change;

$$H_2O \longrightarrow HO^- + H^+ \quad ;\Delta H(H_2O) = 1632 \ \text{kJ mol}^{-1}.^{56)}$$

The enthalpy changes of the successive solvation of H_2O onto the charged parts have been found in the literature:

$$\begin{aligned}&H^+(H_2O)_{n-1} + H_2O \longrightarrow H^+(H_2O)_n \quad ;\Delta H^+_{n,n-1}\\ &\Delta H^+_{0,1} = -691, \ \Delta H^+_{1,2} = -151,\\ &\Delta H^+_{2,3} = -93 \ \text{kJ mol}^{-1},^{57)}\end{aligned}$$

and

$$\begin{aligned}&OH^-(H_2O)_{n-1} + H_2O \longrightarrow OH^-(H_2O)_n \quad ;\Delta H^-_{n,n-1}\\ &\Delta H^-_{0,1} = -94, \ \Delta H^-_{1,2} = -69 \ \text{kJ mol}^{-1}.^{57)}\end{aligned}$$

From a thermodynamic point of view, it is unlikely that the complete electrolyte dissociation reaction takes place in the gas phase, because the solvation of four H_2O

molecules is not good enough to compensate the endothermic process with the extremely large $\Delta H(H_2O)$. In the cluster, however, the separation of the two charges is of the order of a few angstroms, so the Coulombic energy between them is substantially smaller than $\Delta H(H_2O)$ which is associated with the complete separation of the pair. In addition to this, the solvation of H_2O molecules onto both the charged moieties contributes to stabilize the ion-pair. Although a quantitative estimation is difficult, it is feasible that the ion-pair form can be stabilized by a small number of solvated water molecules in the $[PhOH–(H_2O)_4]$ cluster.

Though the ion-pair form is strongly suggested from the anomalous spectrum, the present assignment is based on the similarity between the positions of the anomalous IR bands and those of the hydrated oxoniun ions. To obtain a conclusive assignment of the bands, the band intensities as well as the vibrational frequencies must be analyzed more quantitatively. The same is true for the assignments of the bands observed for the species other than the ion-pair form. The theoretical investigations of the cluster structures are strongly desired: These involve geometrical optimization of the structure by ab initio calculations and the force field calculations of vibrational frequencies of the optimized structure. Thus an unambiguous confirmation of the ion-pair form will be given by the simulation of the observed vibrations on the basis of the theoretical analysis of the cluster structures.

Very recently, the vibrational spectroscopic study of the benzene–water clusters has been reported by Pribble and Zwier.[58] They observed the IR spectra of the OH stretching region of $[Benzene–(H_2O)_n]$ clusters for $n=1$—7, which are very similar to our results for the $[PhOH–(H_2O)_n]$ clusters. In their spectra of $[Benzene–(H_2O)_n]$ clusters, the spectral feature is normal for the clusters up to $n=5$, but a remarkable change of the feature occurs at $n=6$. In particular, the bands appearing in the *window* region of 3500—3750 cm^{-1} of $[Benzene–(H_2O)_6]$ are found to be very similar to the anomalous bands observed for $[PhOH–(H_2O)_4]^*$. A close comparison of the two spectra shows that the frequencies of most of the corresponding bands coincide within 10 cm^{-1}. According to their assignments based upon ab initio calculations of $(H_2O)_n$ clusters, the anomalous bands are due to the OH vibrations of the double donor H_2O site, in which both hydrogen atoms of H_2O are bound as hydrogen-donors; they called these vibrations double donor OH stretches. They emphasized that the double donor OH stretches are associated with the formation of a non-cyclic structure of the water cluster site. At the moment, we have not established that the similarity of the anomalous OH vibrations in both cases is due to the same origin. However, it seems that the close resemblance of the two spectra is not accidental, but is originating from a common reason arising from some property of the water clusters.

The ion-pair form is considered to be a precursor which leads to the acidity of the water solution of phenol, since further solvation of water molecules induces the real separation of the pair which leads to the acidity of the solution. This argument does not necessarily mean that Structure II represents an inherent property of pure water clusters, but it suggests that the ion-pair form of the water cluster site is created by the presence of phenol. A sequential formation of Structure II seems to be more likely; the heterolysis of phenol takes place first in the cluster, leading to Structure I. This form may act as a trigger for the next step of the relaxation of the cluster structure leading to Structure II, which is supposed to be more stable. An alternative interpretation is also possible: there is an equilibrium between Structure I and II and we are observing only the latter. Since the electronic transition of the former should appear in a different spectral region, the present IR spectroscopy combined with the electronic transition cannot detect the species classified as Structure I. These problems will be solved by further experimental studies.

Concluding Remarks

The novel experimental methods for spectroscopic analysis of molecular clusters contribute to reveal chemical processes occurring within the clusters. Intracluster proton transfer of hydrogen-bonding clusters of phenol has been examined as a good example for chemical reactions within clusters. The major conclusions are the following:

(1) Stable forms of $[PhOH–B]^+$ were investigated and classified. The threshold for the proton transfer occurs at PA=840 kJ mol^{-1}, irrespective of the acceptor B.

(2) In $[PhOH–(H_2O)_n]^+$, the conversion to the proton transferred form from the non-transferred takes place at $n=3$. The switching was confirmed by both electronic and vibrational spectroscopies.

(3) The vibrational spectra of the neutral clusters shows that $[PhOH–(H_2O)_n]$ ($n\leqq 4$) has a structure such that the clusters are formed by hydrogen-bonds between PhOH and the water clusters.

(4) The anomalous OH stretching vibrations of the isomer of $[PhOH–(H_2O)_4]$ indicates that the ion-pair structure originates from an intracluster acid–base reaction.

The results show that the intracluster proton transfer is not always similar to processes in the conventional phases but is sometimes specific to the clusters. In this respect, the solute–solvent model of clusters has to be examined more carefully and extensively. The electronic spectroscopy provides us with gross features, being based on differences in electronic structure. The vibrational spectroscopy carries a possibility of seeing more detailed geometrical structures through the analyses of the key vibrations. The spectroscopic results concerning intermolecular bonds are of particular importance in theoretical calculations of cluster structures, which will stimulate further cluster studies with more advanced spectroscopy. Through the present study we have emphasized that the processes occurring within small size clusters are important and that the molecules surrounded by a small number of solvent molecules have quite a significant role in the cluster chemistry.

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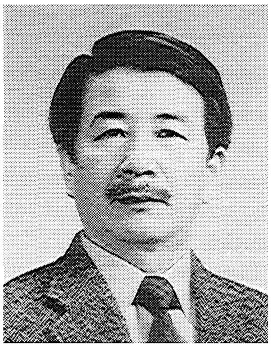

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