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Investigation of the Structure of the Ternary Cluster of Aniline−Water−Tetrahydrofuran and Its Cation by Infrared Depletion Spectroscopy

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Spectroscopic information of ternary aniline clusters which include water has been obtained for the first time by infrared depletion spectroscopy. The vibrational spectra of the NH and OH stretching region of aniline−water−tetrahydrofuran (THF) clusters and their cations were measured by using infrared (IR) depletion spectroscopy. The infrared spectrum of the neutral cluster showed four absorption bands at 3715 cm^{-1} (free OH), 3491 cm^{-1} (free NH), 3403 cm^{-1} (bonded OH), and 3376 cm^{-1} (bonded NH). Analysis of the frequency red shifts of these bands showed that this cluster has a chainlike structure; the NH bond of aniline interacts with the oxygen atom of water, and one OH group of water interacts with the oxygen atom of THF. In contrast, the aniline cation acted as a double donor of hydrogen in the cluster cation. The infrared spectrum of the cluster cation showed three absorption bands at 3722 cm^{-1} (antisymmetric stretching of OH), 3636 cm^{-1} (symmetric stretching of OH), and 3230 cm^{-1} (bonded NH). Analysis of the red shifts of the infrared bands showed that the main interactions were the hydrogen bond between the NH bond of aniline and the oxygen atom of THF and that between the NH bonds of aniline and the oxygen atom of water.

Introduction

Recent progress in the infrared (IR) spectroscopy of isolated clusters in supersonic jets has provided detailed information about the structure of molecular clusters. Infrared depletion spectroscopy, which is an IR−UV double resonance method, is particularly useful for clusters that include aromatic compounds, because this method uses the aromatic molecule as a UV chromophore.[1−3] Aniline is the simplest amine with an aromatic ring, thus making it a good model system for studying the hydrogen bond interactions of NH bonds. Numerous binary aniline complexes have been studied by infrared depletion spectroscopy.[4−11]

Water is the most important solvent, and many studies have been done on hydrogen-bonded water clusters.[13−18] However, only two studies have been done on the spectroscopy of aniline−water complex; one study was on the neutral complex by using Fourier transform microwave spectroscopy,[19] and the other was on the measurement of the cation complex by using infrared depletion spectroscopy.[5] No studies have been done on the aniline−water complex or related clusters by using REMPI (resonance-enhanced multiphoton ionization) spectroscopy. In a previous study, we were unable to observe the REMPI spectrum of the neutral aniline−water complex but were able to measure the infrared depletion spectrum of the aniline−water cation that originated from a larger aniline−$(H_2O)_n$ cluster.[5] The difficulty in observing the REMPI signal of the aniline−water complex is apparently due to the significant structural difference between the neutral and the cation complex, thus prohibiting the optical transition. In the neutral complex, the OH bond of water interacts with the lone pair of the nitrogen atom of aniline, whereas the NH bond of aniline cation interacts with the oxygen atom of water. When the neutral complex is ionized, the lone pair of aniline disappears, and the complex possibly decomposes into an aniline cation and water.

When we previously measured the REMPI spectrum of the larger water clusters,[5] we observed the enhancement of the aniline−water cation signal when there is a third molecule such as CO in the sample gas. This suggested that ternary clusters were generated in the molecular beam and that the aniline−water cation was generated by fragmentation of this complex cation. To study the hydrogen bond interaction of water in the aniline cluster, we measured the infrared spectrum of a ternary cluster, aniline−water−THF (tetrahydrofuran). THF is a common organic solvent, and recently, Chowdhury measured the infrared spectrum of the aniline−THF complex in the NH stretching region.[20] The proton affinity of THF is 831 kJ/mol,[21] which is between that of water (697 kJ/mol) and that of an amine molecule (NH_3: 853 kJ/mol),[21] and therefore, we expect a moderate hydrogen-bonding interaction with aniline. In the present work, we report the first observation of the REMPI and vibrational spectra of the ternary aniline−water−THF cluster. We also measured the infrared spectrum of its cluster cation and determined the structural differences between the neutral cluster and cluster cation.

Experimental Section

The infrared spectra of aniline−water−THF clusters were measured using a double resonance ion depletion technique that utilizes REMPI and infrared predissociation. Details of the experimental apparatus have been given elsewhere.[11]

The aniline−THF−water cluster was prepared in a supersonic expansion of a gaseous mixture of aniline, water, THF, and He (150 kPa). The gas mixture was prepared by passing He that contained traces of water vapor over a dilute solution of THF in aniline. The water vapor was introduced to the gas mixture by first exposing a gas cylinder to atmosphere for a few minutes and then evacuating and filling it with helium. This cylinder was then used as the helium source. The vapor pressure of water was kept at less than 100 Pa, because when it was increased to more than 100 Pa, a broad background signal appeared and the REMPI signal became unstable. The gas mixture was injected into a vacuum chamber through a pulse valve (General Valve, 0.8 mm inner diameter), which was operated at 10 Hz and was

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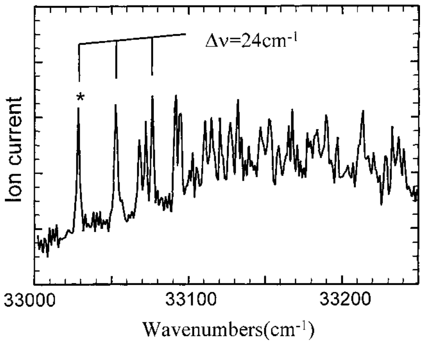

Figure 1. UV excitation spectrum of aniline−H_2O−THF measured by monitoring the mass signal of $M = 183$ (aniline−H_2O−THF^+).

open for 250 μs/pulse. The cluster beam was introduced into an ionization room through a molecular beam skimmer (1 mm inner diameter). The clusters were ionized by REMPI using a pulsed UV laser (duration time ∼ 5 ns) and then detected by using a linear TOF mass spectrometer. We used the S_1 state of the aniline−water−THF cluster for the first step in the REMPI process. To minimize the fragmentation of the larger aniline clusters, we used a glass filter to reduce the power of the UV laser to less than 100 μJ/pulse.

Infrared light was generated by a difference frequency mixing of the Nd:YAG fundamental with that of an IR dye laser (Spectra Physics Wex System). The output of the IR laser was 0.5−2 mJ/pulse, and the pulse duration was about 5 ns. The wavelength of the IR laser was calibrated by monitoring the wavelength of the dye laser using a wave meter (Burley WA4500). The reliability of the frequency measurement was estimated to be better than 1 cm^{-1}.

The infrared spectra of the aniline−water−THF complex and the corresponding cluster cation were measured using infrared depletion spectroscopy. In the case of the neutral cluster, infrared absorption was measured as the ion depletion induced by vibrational excitation. To accomplish this, the cluster beam was irradiated with an IR laser 50 ns before being irradiated with the UV laser. If the cluster absorbs an infrared photon, it will be excited into a vibrationally excited state. This excitation depletes the population of the clusters in the ground state, thus reducing the REMPI signal of the clusters. The infrared spectrum of the cluster cation was also measured by detecting the decrease in the ion current caused by the infrared predissociation of the cationic cluster. In this measurement, the cluster beam was irradiated with the IR laser 50 ns after being irradiated with the UV laser pulse.

We used ab initio MO calculations to help the investigations of the experimental results. The structure and frequency shifts of the NH and OH stretching vibrations of the neutral cluster were calculated using the Gaussian94 program with the B3LYP function and 6-31+G* basis set. The structure and the frequency of the cluster cation were calculated at the UHF/6-31+G* level due to the computer restriction.

Results and Discussion

Infrared Spectrum of the Neutral Cluster. Figure 1 shows the UV excitation spectrum of aniline−water−THF cluster that was measured by monitoring the mass signal of aniline−water−THF^+ ($m/z = 183$). A clear vibrational progression with the frequency difference of $\Delta\nu = 24$ cm^{-1} is evident in the 33 000−33 200 cm^{-1} region. On the basis of this figure, the band origin of the S_1−S_0 transition has been determined to be 33 029 cm^{-1}. The lower wavelength region (lower than 33 029 cm^{-1}) shows no band structure. The red shift of the band origin relative to that of aniline monomer is 1000 cm^{-1}.

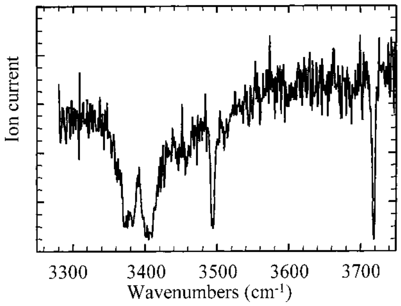

Figure 2. Infrared depletion spectrum of aniline−water−THF.

Figure 2 shows the infrared depletion spectrum of the aniline−water−THF cluster in the NH and OH stretching region measured with the UV laser set at the band origin of the S_1−S_0 band (33 029 cm^{-1}). The spectrum shows four strong absorption bands at 3715, 3491, 3403, and 3376 cm^{-1}. The bandwidth for each of the two absorption bands (3403 and 3376 cm^{-1}) was about 20 cm^{-1}, which is about four times larger than that for the other two bands (3715 and 3491 cm^{-1}). These spectral features strongly suggest that there are two hydrogen bonds as well as two free OH or NH bonds in the cluster.

Assignment of the Infrared Bands of the Neutral Cluster. We assigned the band observed at 3715 cm^{-1} to the OH stretching mode of free OH group, because the bandwidth was much smaller than that of the 3403 and 3376 cm^{-1} bands and the frequency was close to that observed for free OH groups in other clusters (3715 cm^{-1}).[13] On the basis of the same reasoning, we assigned the band observed at 3491 cm^{-1} to the free NH stretching vibration of aniline.

The assignment of the infrared bands at 3403 and 3376 cm^{-1} was not straightforward, because the frequencies of these bands were close and there has been no previous spectroscopic data for the OH vibrations in aniline cluster. We assigned the band at 3376 cm^{-1} to the NH stretching vibration considering the magnitude of the red shift from the corresponding band of aniline monomer. In the aniline monomer, there are two NH stretching vibrations at 3422 and 3508 cm^{-1}, which are assigned to the symmetric NH stretching vibration and antisymmetric NH stretching vibration, respectively. When one of the NH bond interacts with another molecule through an NH-σ interaction, the symmetric stretching vibration shows a large red shift and correlates to the stretching band of bonded NH and the antisymmetric stretching vibration shows a small red shift and correlates to the NH stretching mode of free NH. The relationship and the magnitude of the red shifts of NH stretching vibrations of aniline were discussed in ref 12, and the red shift of the NH stretching mode of bonded NH should be about 30 cm^{-1} or larger when the red shift of the stretching band of the free NH is 17 cm^{-1}. If we assigned the band at 3403 cm^{-1} to the bonded NH, the red shift would be only 19 cm^{-1}. Therefore, this absorption band at 3403 cm^{-1} cannot be assigned to the NH stretching mode but rather to the stretching vibration of the bonded OH group. Table 1 shows the assignments of the observed infrared bands.

Structure of the Neutral Cluster. The broad red-shifted absorption bands in the infrared spectrum of Figure 2 suggest that there are two hydrogen bonds in the cluster, an NH-σ type bond and OH-σ type bond. Because THF acts as a hydrogen bond acceptor, three possible structures satisfy this condition of two such hydrogen bands. (a) NH−OH−O structure: An NH bond interacts with the oxygen atom of water, and an OH

TABLE 1: Observed Frequencies of the NH and OH Stretching Vibrations of the Aniline−THF Complex and Aniline−Water−THF Clusters

	aniline−THF		aniline−THF−water	
	ν (cm^{-1})	$\Delta\nu^a$ (cm^{-1})	ν (cm^{-1})	$\Delta\nu^a$ (cm^{-1})
OH-free			3715	41
NH-free	3478	30	3491	17
OH-bonded			3403	254
NH-bonded	3369	53	3376	46

[a] Red shifts using corresponding bands of monomer (water, aniline) as a reference.

bond interacts with the oxygen atom of the THF. (b) OH−NH−O structure: An OH bond interacts with the nitrogen atom of aniline, and an NH bond interacts with the oxygen atom of the THF. (c) NH−O−HO structure: An NH bond and an OH bond interact with the oxygen atom of the THF. The oxygen atom of the THF accepts two hydrogen bonds.

Figure 3a−c shows the above three possible structures for aniline−water−THF clusters. Among these three structures, structure c seems to be unsuitable, for the oxygen atom of THF accepts two hydrogen bonds.

To discuss the structure of the cluster, we need to consider the UV and infrared spectra of the aniline−THF complex. Figure 4a shows the excitation spectrum measured by monitoring the mass channel $M = 165$ (aniline−THF$^+$). The broad background in the excitation spectrum seems to be the fragments of larger clusters. There are two different band progressions in the excitation spectrum. One band observed around the 33 000−33 200 cm^{-1} region we assigned to the aniline−water−THF cluster, as discussed above (see Figure 1). The other band observed in the 33 200−33 400 cm^{-1} region had a band progression of $\Delta\omega = 15.3$ cm^{-1} and was previously assigned to the aniline−THF complex by Chowdhury, who first observed the infrared spectrum of the aniline−THF complex.[20] We also measured the infrared depletion spectrum for this aniline−THF band (Figure 4a). Two absorption bands occurred at 3478 and 3369 cm^{-1}, which agree well with those observed by Chowdhury.[20] The band origin of $S_{1-}S_0$ of the aniline−THF complex is not clear from Figure 4a because it is overlapped by the signal of the aniline−water−THF cluster. The spectrum in Figure 4a shows complex features similar to those reported by Chowdhury, suggesting that his sample was contaminated with water.

Comparison with the Aniline−THF Cluster. To further confirm the assignments of both band progressions, we measured the infrared hole-burning spectra for each series in Figure 4a. The resulting spectrum in Figure 4b was obtained by setting the IR laser to 3491 cm^{-1}, which corresponds to the free NH stretching vibration of the aniline−water−THF cluster. The band progression assigned to aniline−water−THF was absent, confirming that the spectrum in Figure 1 should be assigned to a single species of the aniline−water−THF cluster. The infrared hole-burning spectrum in Figure 4c was obtained by setting the IR laser to 3476 cm^{-1}, which corresponds to the free NH stretching vibration of the aniline−THF complex. The band progression observed in the 33 200−33 400 cm^{-1} region was absent, confirming that the origin of this band is aniline−THF.

Chowdhury assigned the peak at 33 255 cm^{-1} (indicated by an asterisk in Figure 4b) to the 0−0 band of the aniline−THF complex and without any experimental evidence tentatively assigned the peaks observed at lower wavenumber region to the 1:2 cluster. However, the spectra in Figure 4 clearly show that the band origin of the aniline−THF complex is not at 33 255 cm^{-1} but at 33 238 cm^{-1}. The spectrum reported by Chowdhury resembles that of Figure 4a. This means that the peaks he assigned to the 1:2 complex should be assigned to the aniline−water−THF cluster. This result suggests that his sample was contaminated with water. However, his experimental results about the infrared spectrum were not affected by this contamination.

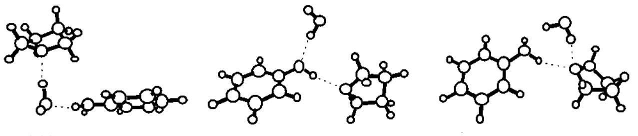
a) NH-OH-O b) OH-NH-O c) NH-O-HO

Figure 3. Calculated structures of the aniline−water−THF cluster having one NH-σ type and one OH-σ type hydrogen bond by Gaussian 94 (B3LYP method, 6-31+G* basis set): (a) NH−OH−O(THF) type; (b) OH−NH−O(THF) type; (c) NH−O(THF)−HO type. The oxygen atom of THF acts as a double acceptor (i.e., accepts two hydrogen bonds).

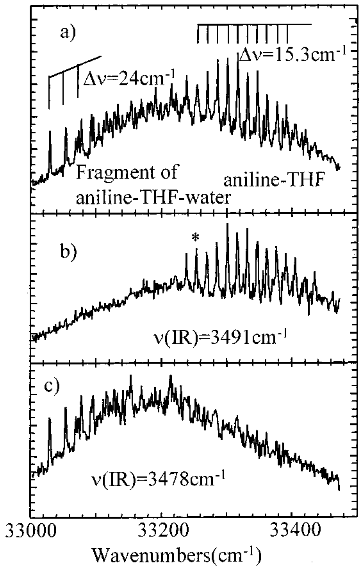

Figure 4. Excitation spectra measured by monitoring the mass signal of $M = 165$: (a) excitation spectrum measured without IR laser; (b) infrared hole-burning spectrum, with the frequency of the IR laser set at 3491 cm^{-1}; (c) frequency of the IR laser set at 3478 cm^{-1}.

Table 1 summarizes the observed infrared frequencies of the aniline−THF and aniline−water−THF clusters. The red shifts of the NH stretching vibration were smaller than those observed for the aniline−THF complex. If structure b is assumed, the red shifts of the NH bands would be larger than those of the aniline−THF complex, because the accumulation of hydrogen bonds tends to produce a larger red shift for the hydrogen-bonded system.[13] This suggests that the acceptor of the NH bond in the aniline−water−THF cluster differs from that in the aniline−THF complex. Namely, on the basis of the red shift of the NH stretching modes, structure a is preferred.

MO Calculation for the Neutral Cluster. To confirm our results about the assignments of the infrared spectrum and the stable structure of the cluster, we calculated the structure and frequency shifts of the NH and OH stretching vibrations by using the Gaussian94 program with the B3LYP function and 6-31+G* basis set. Table 2 shows the results for the aniline−THF complex. Because there is no ambiguity about the structure of this complex, we can estimate the reliability of the calculation of the ternary cluster of aniline−water−THF. Table 3 shows observed and calculated frequencies for the three possible structures of the aniline−THF−water cluster and shows the frequency shifts from the corresponding band of monomers. The following discussion is based on the frequency shifts rather than

TABLE 2: Observed and Calculated Red Shifts of the NH Stretching Modes for the Aniline−THF Complex[a]

	obsd		calcd	
	ν (cm^{-1})	$\Delta\nu^b$ (cm^{-1})	ν (cm^{-1})	$\Delta\nu^b$ (cm^{-1})
NH-free	3478(30)	30	3629	20.3
NH-bonded	3369(63)	63	3494.7	56.7

[a] B3LYP/6-31+G* was used in the calculation. [b] Red shifts using corresponding bands of monomer (water, aniline) as a reference.

the frequency itself, because the effect of the hydrogen bond interaction appears as the red shift of the NH or OH stretching vibration in the infrared spectrum. The original conformation of structure c in which two hydrogen bonds are assumed was found to be unstable, and there is another hydrogen bond interaction between the OH group of water and the nitrogen atom of aniline in the converged structure in the calculation. With this structural change, the calculated stabilization energy was still lower than that for either of the other two conformers. Because only two hydrogen bonds were observed in the cluster, structure c cannot be the observed conformer.

Comparison of the calculated and observed red shifts of the OH and NH stretching vibrations for structures a and b shows structure a to be the more probable structure from the following reasons. If we assumed that the observed structure was structure a, the calculation well reproduced the observed red shifts for the OH stretching modes and fairly well reproduced those for the NH stretching modes. On the other hand, if we assumed structure b, the calculation did not reproduce the red shifts of the NH stretching vibrations at all.

As discussed above, we have revealed that the aniline−water−THF cluster has a chainlike structure, where the NH bond interacts with the oxygen atom of the water and one OH group interacts with the oxygen atom of THF (Figure 3a). This structure differs from that observed for the aniline−water complex, where the main interaction is the hydrogen bond between the OH group and the nitrogen atom of aniline. This difference will be discussed further in the later part of this section (Structural Differences of Aniline Clusters).

Infrared Spectra of Cation Clusters. Figure 5a−c shows the infrared depletion spectra of the cations with $m/e = 93$ (aniline$^+$), 165 (aniline−THF$^+$), and 183 (aniline−water−THF$^+$), respectively. In this case, the cluster cation dissociates into fragments when it absorbs the infrared photon. A decrease in the signal corresponds to the dissociation of the cation induced by the infrared absorption, and an increase corresponds to the generation of cationic fragments from the larger clusters. The spectrum of the cation with $m/e = 111$ (aniline−H_2O^+) is not shown in Figure 5 because it was weak and did not show any significant response to the IR laser except the absorption band of aniline−H_2O^+ at 3440 cm^{-1}.

Figure 5c shows the spectrum of the aniline−water−THF$^+$ cluster. Two absorption bands occurred at 3638 and 3722 cm^{-1} in the OH stretching region, and a broad absorption band occurred at around 3200 cm^{-1}. Although the signal-to-noise ratio of the OH stretching bands was relatively poor, the frequencies of these bands agree well with the corresponding bands observed for the aniline−water complex.[5] This correspondence suggests that the interaction between the aniline cation and water should be a hydrogen bond between the NH group and the lone pair of water. Because no free NH stretching vibration was observed in the spectrum, the interaction between THF and the aniline cation also seems to be a hydrogen bond between the NH group and the oxygen atom of THF.

Figure 5b shows the dependence of the mass signal of aniline−THF$^+$ on the IR laser. The increase in the ion signal of aniline−THF$^+$ quantitatively corresponds to the decrease in the ion signal of the aniline−water−THF$^+$ cluster. This means that aniline−water−THF$^+$ dissociates into aniline−THF$^+$ and water when it absorbs an infrared photon, suggesting that aniline−THF$^+$ is more stable than aniline−H_2O^+. This agrees well with the difference in the proton affinities between THF (831 kJ/mol) and water (697 kJ/mol). An absorption band of aniline−THF$^+$ occurred at 3426 cm^{-1}, which we assigned to the stretching vibration of the free NH group of the aniline cation. The red shift of this mode for aniline−X$^+$ complexes is known to show a linear correlation with the proton affinity of X. The observed red-shift agrees with that expected from the correlation, further confirming the structure and the interaction type for this complex.

Structure of Cluster Cations. Table 4 compares the observed vibrational frequencies and the frequency red shifts of the aniline−THF$^+$ and aniline−water−THF$^+$ cluster cations with the calculated frequencies from ab initio MO calculation at the UHF/6-31+G* level based on theory (Gaussian 94). The results show that the observed and calculated frequencies agree relatively well for both of the cluster cations.

The calculations show that the band observed at 3230 cm^{-1} should be assigned to the stretching vibration of the NH group that interacts with water. This is the first observation of the stretching mode of a NH group interacting with water. This band was not observed in the aniline−H_2O^+ cation because this cation needed a multiphoton absorption of an infrared photon to dissociate the cation. In our experiments, only one infrared photon was needed to expel the water molecule. On the basis of this result, the hydrogen bond becomes weaker when both of the NH groups interact with proton acceptor, and the stabilization energy becomes less than 3200 cm^{-1} for the following reaction:

$$\text{aniline−water} - \text{THF}^+ \rightarrow \text{aniline−THF}^+ + \text{water}$$

Structural Differences in the Aniline Clusters. Figure 7 compares the observed structures of the aniline−water−THF and related clusters. The main interaction of the aniline−water−THF cluster differs from that of the cluster cation and also differs from that of the aniline−water complex.

The difference between the neutral clusters and the cationic clusters can be explained as follows. In a neutral cluster, the strength of the hydrogen bond of the NH group does not significantly differ from that of the OH group, and the structure that does not contain a double donor is preferred, namely, structure b in Figure 7. In contrast, the aniline cation is known to be a strong donor. Our experimental results show that aniline cation is still stronger than the OH of water even when the cation acts as a double donor (Figure 7c).

Explanation for the difference in structure between the aniline−water−THF cluster and the aniline−THF complex is not so straightforward. One reason for the difficulty is that we cannot deny the possibility of the existence of the OH−NH−X conformer (Figure 3b). Although we could not find this conformer in the REMPI spectrum, it might decompose when it is ionized, for the same reason that the aniline−water complex decomposes.[5] When the complex is ionized, the lone pair of the nitrogen atom disappears and the aniline cation becomes planar. There will be repulsive force between the positive charge of the ring and the proton of the OH group of water, possibly leading to the expulsion of the water molecule.

Our experimental results confirm that there is a stable conformer of the aniline−water−THF cluster with an NH−OH−X configuration and that the aniline−water complex has

TABLE 3: Calculated Frequencies of OH and NH Stretching Vibrations of Aniline−THF−Water Cluster[a]

	obsd. (cm^{-1})		structure a (cm^{-1}]		structure b (cm^{-1})		structure c (cm^{-1})	
	ν	$\Delta\nu^b$	ν	$\Delta\nu^b$	ν	$\Delta\nu^b$	ν	$\Delta\nu^b$
OH-free	3715	41	3820	39	3810	50	3731	128
OH-bonded	3403	254	3482	253	3452	283	3651	83
NH-free	3491	17	3619	30	3580	69	3607	42
NH-bonded	3376	46	3450	101	3412	140	3497	53
Δ*E*[c]			−3573		−3420		−2721	

[a] B3LYP/6-31+G* was used in the calculation. [b] Red shifts using the corresponding bands of monomer (water, aniline) as a reference. [c] Stabilization energy, corrected for zero-point energy.

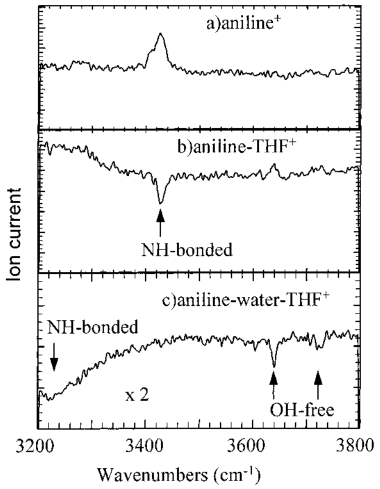

Figure 5. Infrared depletion spectra of aniline$^+$, aniline−THF$^+$ and aniline−water−THF$^+$ clusters: (a) aniline, $M = 93$; (b) aniline−THF$^+$, $M = 165$; (c) aniline−water−THF$^+$, $M = 183$.

TABLE 4: Observed and Calculated Vibrational Frequencies of Aniline−THF$^+$ and Aniline−Water−THF$^+$ Cluster Cation

	obsd		UHF/6-31+G*	
	ν (cm^{-1})	$\Delta\nu^a$ (cm^{-1})	ν (cm^{-1})	$\Delta\nu^a$ (cm^{-1})
Aniline−THF$^+$				
NH-free	3426	62	3823	51
NH-bonded			3412	344
Aniline−Water−THF$^+$				
OH antisym	3722	34	4152	38
OH sym	3638	19	4049	22
NH bonded (water)	3230	258	3667	207
NH bonded (THF)			3469	287

[a] Red shifts using the corresponding bands of monomer (water, aniline) as a reference.

no conformer of the NH−OH type complex.[19] On the basis of these two results, the relative stability of the complexes can be described as follows. The NH−OH type conformer is less stable than the OH−NH conformer of the aniline−water complex. The existence of a third molecule (e.g., THF), however, stabilizes the NH−OH−X type conformer more than the OH−NH−X type conformer. In other words, the accumulation of hydrogen bonds in the NH−OH−X conformer seems to have lower energy than that in the OH−NH−X conformer.

Conclusion

The vibrational spectra of the NH and OH stretching region of the ternary cluster of aniline−water−THF and its cation were measured using an infrared depletion technique.

Our analysis of the red shifts of these bands showed that the structure of the neutral cluster is linear, containing two hydrogen bonds, NH−OH−O(THF) (Figure 3a). This structure differs from that observed in the aniline−water complex (Figure 7a).

The cationic cluster was found to have a triangular structure, where the aniline cation acts as a double donor (Figure 6b).

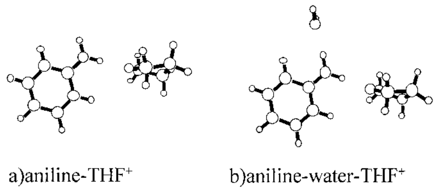

Figure 6. Calculated structures of the cationic aniline clusters: (a) aniline−THF$^+$ complex; b) aniline−water−THF$^+$ cluster.

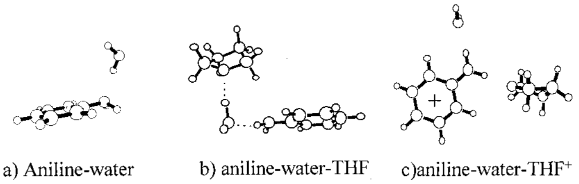

Figure 7. Structure of aniline−water clusters: (a) aniline−water; (b) aniline−water−THF; (c) aniline−water−THF$^+$.

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