Infrared Photodissociation Spectroscopy of [Aniline−(Water)$_n$]$^+$ ($n = 1−8$): Structural Change from Branched and Cyclic to Proton-Transferred Forms

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Infrared photodissociation spectra of [aniline−(H$_2$O)$_n$]$^+$ ($n = 1−8$) are measured in the 2700−3800 cm^{-1} region. The spectra are interpreted with the aid of density functional theory calculations. The $n = 1$ ion has an N−H···O hydrogen bond. The spectrum of the $n = 2$ ion demonstrates a large perturbation to both of the NH oscillators, indicating the 1−1 structure where each NH bond is bound to a water molecule. For the $n = 3$ ion, the calculated spectrum of the 2−1 branched structure coincides well with the observed one. For the $n = 4$ ion, there exist three strong bands at 2960, 3100, and 3430 cm^{-1}, as well as a very weak one at 3550 cm^{-1}. The observed spectrum in the 3600−3800 cm^{-1} region is decomposed into four bands centered at 3640, 3698, 3710, and 3734 cm^{-1}. The 2−2 branched isomer is responsible for all the features except the 3550 and 3710 cm^{-1} bands. These two bands are due to another isomer with a five-membered ring. An infrared band characteristic of the $n = 5$ ion appears at 3684 cm^{-1}, which is not seen in the spectra of the $n = 1−4$ ions. This band is indicative of a ring structure and assigned to the free OH stretching vibration of the three-coordinated (double acceptor−single donor) H$_2$O. The $n = 5$ ion has the five-membered ring structure with the fifth water molecule bound to the terminal (double acceptor) H$_2$O. The observed spectra of the $n = 6−8$ ions show features quite different from those of the $n = 1−5$ ions; a very strong and broad band emerges around 3400 cm^{-1}, while no prominent bands appear below 3200 cm^{-1}. It is suggested that the $n = 6−8$ ions have proton-transferred structures.

1. Introduction

Aqueous clusters are important research objects in cluster science, because these clusters are thought to be a prototype of liquid phase chemistry of aqueous solutions. Spectroscopic studies of isolated gas phase clusters in combination with quantum chemical calculations provide detailed information on intermolecular interactions. Lee and co-workers have extensively investigated the infrared spectroscopy of protonated water clusters H$^+$(H$_2$O)$_{2−8}$.[1,2] These cluster ions were mass-selected and trapped in a radio frequency octopole ion trap. Irradiation with an infrared laser in the 2700−3900 cm^{-1} region induces fragmentation of the parent ions. Vibrational predissociation spectra of these cluster ions were measured by monitoring the yield of the fragment ions as a function of the laser frequency. They interpreted the observed spectra with the aid of ab initio molecular orbital calculations. In H$^+$(H$_2$O)$_{2−5}$, the ion core is H$_3$O$^+$. On the other hand, a proton-transfer intermediate, H$_5$O$_2$$^+$(H$_2$O)$_4$, was identified for the H$^+$(H$_2$O)$_6$ ion. The H$^+$(H$_2$O)$_{7, 8}$ ions also have the H$_5$O$_2$$^+$ unit as the ion core. They also studied the other protonated aqueous cluster ions, such as NH$_4$$^+$(H$_2$O)$_{2−7}$ and H$^+$(CH$_3$OH)(H$_2$O)$_{1−6}$.[3−6]

The infrared spectroscopy has been performed also for hydrated ions of aromatic molecules. Several groups have

investigated structures and intracluster proton-transfer reactions of aromatic cluster ions as a function of the number of water molecules. Solcà and Dopfer measured the infrared spectrum of a simple hydrated aromatic ion, [benzene−(H$_2$O)$_1$]$^+$, by the vibrational predissociation spectroscopy.[7] From the amount of the red shifts of the OH stretching bands, they concluded that the [benzene−(H$_2$O)$_1$]$^+$ ion has a bridged structure, in which the oxygen atom approaches benzene$^+$ in the aromatic plane to form hydrogen bonds with two protons of benzene$^+$. Miyazaki et al. compared the infrared photodissociation spectra of the same species prepared by two different methods.[8] More recently, they investigated larger clusters, [benzene−(H$_2$O)$_{2−6}$]$^+$, and demonstrated that one proton of benzene$^+$ is transferred to the water moiety in [benzene−(H$_2$O)$_{4−6}$]$^+$.[9] Vibrational spectra of [phenol−(H$_2$O)$_m$]$^+$ ($m = 1−3$ and an ensemble with $m \geq 4$) in the 3100−3800 cm^{-1} region were measured by Sawamura et al.[10] They suggested that the [phenol−(H$_2$O)$_{m\geq3}$]$^+$ clusters take the proton-transferred form, C$_6$H$_5$O···H$_3$O$^+$(H$_2$O)$_{m−1}$, while the [phenol−(H$_2$O)$_{1, 2}$]$^+$ ions possess the nonproton-transferred form, C$_6$H$_5$OH$^+$···(H$_2$O)$_{1,2}$. Kleinermanns and co-workers reexamined the same system and extended the measurements to larger clusters with $m = 7$ and 8.[11] They introduced the infrared photodissociation after resonant ionization technique. It was concluded from the experimental results that the [phenol−(H$_2$O)$_3$]$^+$ ion has the nonproton-transferred structure, whereas the proton-transferred structure is the most stable arrangement for [phenol−(H$_2$O)$_4$]$^+$. They also carried out ab initio calculations for the clusters with $m = 1−4$. Several minimum-energy

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structures were obtained for m = 3 and 4, including both proton-transferred and nonproton-transferred structures.

In this paper, we examine infrared photodissociation spectra of hydrated aniline ion clusters, [aniline−(H$_2$O)$_n$]$^+$, with n = 1−8, in the 2700−3800 cm^{-1} region. Previously, the infrared spectra of these clusters were reported by Nakanaga et al.[12,13] and by our group.[14] Nakanaga and Ito found an anomalous stability for [aniline−(H$_2$O)$_{4, 5}$]$^+$, as these ions are quite abundant in a mass spectrum of the aniline−water binary system.[13] From the results of the infrared photodissociation spectra in the 3200−3800 cm^{-1} region and density functional theory (DFT) calculations, they suggested that the [aniline−(H$_2$O)$_{4-6}$]$^+$ ions have a cyclic hydrogen bonding network, although the correspondence between the observed and calculated spectra seems to be ambiguous. They created the cluster ions using multiphoton ionization (MPI). In our experiment, we use electron-impact ionization in order to produce cluster ions whose configurations are located in most cases at the global minimum. We extend the measurement to a lower frequency of 2700 cm^{-1} and a larger cluster size of n = 8. This frequency extension enables us to see several new bands in the 2700−3200 cm^{-1} region. These bands have not been observed in the previous study,[12,13] and they are quite important to determine cluster structures. DFT calculations are carried out for optimizing the geometry and evaluating the vibrational frequency of the n = 1−5 clusters. By comparing the observed spectra with the calculated ones, the most stable structures of the n = 1−5 clusters are determined. In particular, spectral features in the 3600−3800 cm^{-1} region are shown to be informative for determining the cluster structures. We suggest the possibility of the proton transfer in the n = 6−8 ions on the basis of a drastic change of the observed spectra from n = 1−5 to n = 6−8.

2. Experimental and Computational Details

The infrared photodissociation spectra of [aniline−(water)$_n$]$^+$ (n = 1−8) are measured by using an ion guide spectrometer with two quadrupole mass filters.[15] Gas mixture of argon, aniline, and water is expanded into a vacuum chamber through a pulsed nozzle (General Valve Series 9) with a 0.80 mm orifice diameter. The total stagnation pressure is 2 × 10^5 Pa. Neutral clusters are ionized by an electron-impact ionizer situated near the exit of the nozzle. The electron kinetic energy is adjusted to 350 eV. After they are passed through a skimmer, the ionized clusters are introduced into the spectrometer. The parent ions are isolated by the first quadrupole mass filter. After deflection by 90° through an ion bender, the parent ions are led into a quadrupole ion guide and merged with a laser beam. The photoexcitation induces fragmentation of the parent ions. The resultant fragment ions are mass-analyzed by the second quadrupole mass filter and detected by a secondary electron multiplier tube. For normalizing the yields of the fragment ions, the power of the dissociation laser is monitored by a pyroelectric detector (Molectron P1-15H-CC). The infrared photodissociation spectra of the parent ions can be obtained by plotting the normalized yields of the fragment ions against the wavenumbers of the dissociation laser. A tunable infrared light source is an optical parametric oscillator system (Continuum Mirage 3000) pumped with a Nd:YAG laser (Continuum Powerlite 9010). The output energy is 1−2 mJ/pulse, and the line width is approximately 1 cm^{-1}.

DFT calculations are carried out for the n = 1−5 ions with the *Gaussian 98* program package.[16] Geometries of the clusters

TABLE 1: DFT-Calculated Absolute Energy (E, E_{zpve}), Relative Energy to the Most stable isomers (ΔE), and Binding Energy (E_{Bind}) of [Aniline−(H$_2$O)$_n$]$^+$ (n = 1−5)

species	E, hartree	E_{zpve},[a] hartree	ΔE,[b] cm^{-1}	E_{bind},[c] cm^{-1}
aniline$^+$	−287.353401	−287.236183		
H$_2$O	−76.420626	−76.399532		
1I	−363.807403	−363.665814		6606
2I	−440.257870	−440.092039	0	5858
2II	−440.254365	−440.088724	728	5130
3I	−516.703153	−516.513194	0	4746
3II	−516.701228	−516.510813	523	4223
3III	−516.697382	−516.508238	1088	3658
3IV	−516.697911	−516.508014	1137	3609
4I	−593.147609	−592.933504	0	4560
4II	−593.149299	−592.933268	52	4508
4III	−593.145857	−592.931604	417	4143
4IV	−593.139632	−592.925451	1767	2793
5I	−669.595985	−669.355509	0	4932
5II	−669.594846	−669.354084	313	4619
5III	−669.589923	−669.351250	935	3997

^{a} Corrected with zero-point vibrational energies. ^{b} Obtained after zero-point vibrational energy correction. ^{c} $E_{bind}(n) = -E_{zpve}(n) + E_{zpve}(n - 1) + E_{zpve}(H_2O)$, where $E_{zpve}(n - 1)$ is the energy of the most stable isomer of the (n − 1) ion.

are optimized and vibrational frequencies of the stable structures are evaluated at the B3LYP/cc-pVDZ level of theory. For calculating vibrational frequencies, we employ a scaling factor of 0.9676 for all the ions. Table 1 summarizes DFT-calculated absolute energy, relative energy to the most stable isomers, and binding energy. The binding energies calculated are in the range of 3609−6606 cm^{-1} except for isomer **4IV** (2793 cm^{-1}). In most cases, two photons are needed for dissociation of cold clusters. In our experimental apparatus, however, a multiphoton process hardly occurs because of the sparse photon density in the ion guide.[15] Therefore, the cluster ions are dissociated through one-photon absorption with assistance from internal energy.

3. Results and Discussion

3.1. Infrared Photodissociation Spectra of [Aniline−(H$_2$O)$_n$]$^+$ (n = 1−8). Figure 1 shows infrared photodissociation spectra of [aniline−(H$_2$O)$_n$]$^+$ (n = 1−8) in the 2700−3800 cm^{-1} region. The dissociation channel chosen for recording the spectra is the loss of one water molecule. The spectra of the clusters with n = 1 and 2 have already been reported in our previous paper.[14] All the clusters possess relatively sharp bands in the 3600−3800 cm^{-1} region. The spectra of the n = 6−8 clusters in the 3000−3600 cm^{-1} region show close resemblance to each other; one broad band exists around 3400 cm^{-1}. An expanded view of the spectra in the 3500−3800 cm^{-1} region is represented in Figure 2 (dots). These bands can be assigned to the free OH stretching vibrations. These spectra can be decomposed into an appropriate number of Lorentzian components (dotted curves). For the clusters with n = 1 and 2, we can reproduce the observed spectrum with two components. For the spectrum of the n = 3 ion, three Lorentzian components are necessary to reproduce the spectrum. It is possible to decompose the spectra of the n = 4−6 clusters into four components. On the other hand, the spectra of the n = 7 and 8 clusters can be decomposed into two components. Table 2 summarizes the observed frequencies of [aniline−(H$_2$O)$_n$]$^+$ (n = 1−5) with DFT calculated frequencies and assignments. For assigning the water molecules in the clusters, we use the following abbreviations to identify the positions: single acceptor (A), double acceptor (AA), single acceptor−single donor (AD), double acceptor−single donor (AAD).[2]
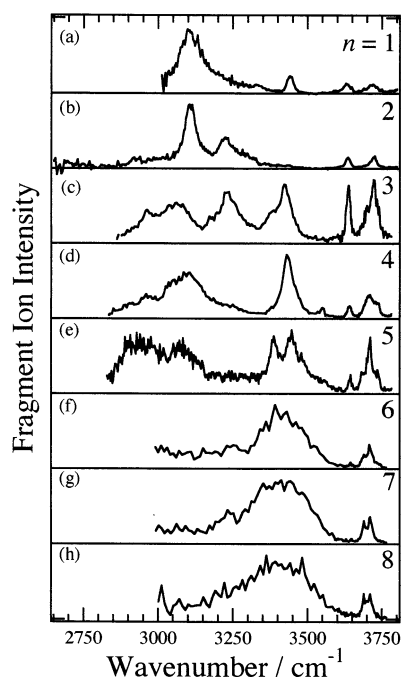
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Figure 1. Infrared photodissociation spectra of [aniline−$(H_2O)_n$]$^+$ ($n = 1-8$) in the 2700−3800 cm^{-1} region. Fragment ion monitored for the spectra of [aniline−$(H_2O)_n$]$^+$ is [aniline−$(H_2O)_{n-1}$]$^+$ (loss of one water molecule). All the spectra are normalized by the laser power.
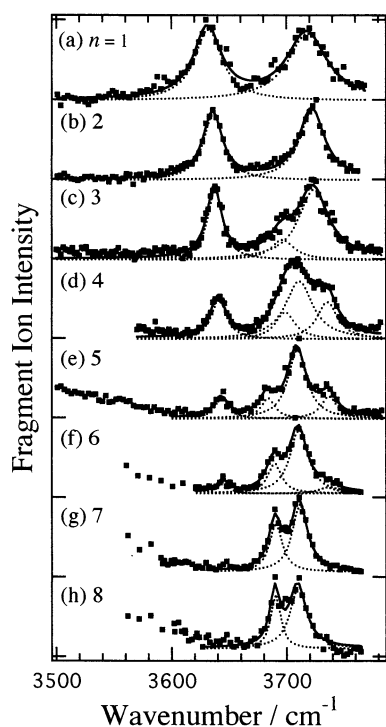

Figure 2. Enlarged view of the infrared photodissociation spectra of [aniline−$(H_2O)_n$]$^+$ ($n = 1-8$) in the 3500−3800 cm^{-1} region. The observed spectra (shown by dots) are decomposed into Lorentzian components (dotted curves). Solid curves represent the sum of the Lorentzian components.

Let us compare the infrared photodissociation spectra of [aniline−$(H_2O)_n$]$^+$ ($n = 1-6$) obtained in the present and previous[12,13] studies. Overall spectral features in the 3600−3800 cm^{-1} region are almost the same as those reported in the previous study. On the other hand, the previous spectra in the 3100−3600 cm^{-1} region disagree with the present ones.[13] The spectra reported by Nakanaga and Ito display bands at 3230

TABLE 2: Observed and Calculated Frequencies (cm^{-1}) and Assignments of the Infrared Spectra of [Aniline−$(H_2O)_n$]$^+$ ($n = 1-5$)

species	observed frequency, cm^{-1}	isomers	calcd frequency,^{a} cm^{-1}	assignments^b
$n = 1$	3105	**1I**	3047	bonded NH of aniline$^+$
	3440	**1I**	3467	free NH of aniline$^+$
	3630	**1I**	3628	sym free OH of H_2O (A)
	3715	**1I**	3715	asym free OH of H_2O (A)
$n = 2$	3105	**2I**	3092	sym bonded NH of aniline$^+$
	3225	**2I**	3205	asym bonded NH of aniline$^+$
	3635	**2I**	3630, 3631	sym free OH of H_2O (A)
	3725	**2I**	3719, 3719	asym free OH of H_2O (A)
$n = 3$	3070	**3I**	2945	bonded NH of aniline$^+$
	3230	**3I**	3192	bonded NH of aniline$^+$
	3420	**3I**	3319	bonded OH of H_2O (AD)
	3637^c	**3I**	3632, 3645	sym free OH of H_2O (A)
	3696^c	**3I**	3694	free OH of H_2O (AD)
	3723^c	**3I**	3722, 3736	asym free OH of H_2O (A)
$n = 4$	2960	**4I**	2959	sym. bonded NH of aniline$^+$
	3100	**4I**	3054	asym. bonded NH of aniline$^+$
	3430	**4I**	3337, 3338	bonded OH of H_2O (AD)
	3550	**4II**	3478, 3530	bonded OH of H_2O (AD)
	3640^c	**4I, 4II**	3646, 3646, 3609^d	sym. free OH of H_2O (A or AA^d)
	3698^c	**4I**	3696, 3696	free OH of H_2O (AD)
	3710^c	**4II**	3688, 3695, 3706	free OH of H_2O (AD)
	3734^c	**4I, 4II**	3738, 3738, 3694^d	asym. free OH of H_2O (A or AA^d)
$n = 5$	2940	**5I**	2816	bonded NH of aniline$^+$
	3070	**5I**	2983	bonded NH f aniline$^+$
	3387	**5I**	3233, 3252	bonded OH of H_2O (AAD) and H_2O (AD)
	3447	**5I**	3370	bonded OH of H_2O (AD)
	3480	**5I**	3454	bonded OH of H_2O (AAD) and H_2O (AD)
	3642^c	**5I**	3646	sym. free OH of H_2O (A)
	3684^c	**5I**	3667	free OH of H_2O (AAD)
	3708^c	**5I**	3689, 3691, 3703	free OH of H_2O (AD)
	3735^c	**5I**	3737	asym. free OH of H_2O (A)

^{a} A scaling factor of 0.9676 is used for all the frequencies. ^{b} The abbreviations used to represent the character of the water molecules in the clusters are the following: single acceptor (A), double acceptor (AA), single acceptor−single donor (AD), double acceptor−single donor (AAD). sym = symmetric. asym = asymmetric. ^{c} Obtained after deconvolution. ^{d} Values and assignments of isomer **4II**.

and 3447 ($n = 3$), 3240 and 3467 ($n = 4$), 3460 ($n = 5$), and 3400 cm^{-1} ($n = 6$) in the 3100−3600 cm^{-1} region.[13] It is probable that the disagreement comes from the different ways of ion production.[14] In the previous work, the cluster ions were produced via MPI of the neutral aniline/water clusters. In MPI processes, configurations of cluster ions that are similar to those
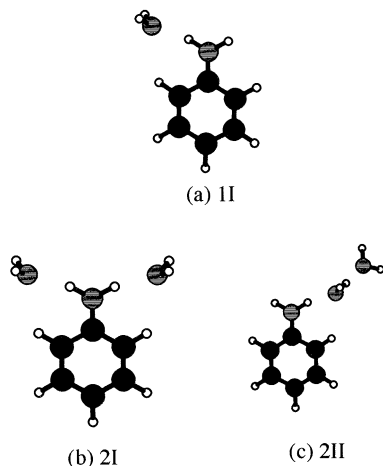
Figure 3. Structures of (a) [aniline−(H$_2$O)$_1$]$^+$ and (b, c) [aniline−(H$_2$O)$_2$]$^+$ optimized at the B3LYP/cc-pVDZ level of theory.
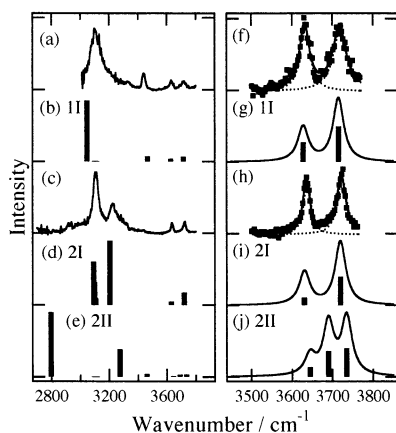

Figure 4. Overall and enlarged views of the infrared photodissociation spectra of (a, f) [aniline−(H$_2$O)$_1$]$^+$ and (c, h) [aniline−(H$_2$O)$_2$]$^+$. The calculated infrared spectra of the isomers (b, g) **1I**, (d, i) **2I**, and (e, j) **2II** are also shown by bars for comparison. In the enlarged view of the (g, i, j) calculated spectra, the solid curves represent convolution of the stick spectra with Lorentzian functions. The width of the Lorentzian functions is fixed to 32 cm^{-1} (fwhm).

of neutral precursors are mainly accessible.[7] These configurations may be located at local minima on the potential energy surfaces. When the barriers between the local minima and the global minimum are sufficiently high, the cluster ions with these configurations survive the isomerization to the lowest energy form and are probed by the subsequent spectroscopy. In the electron-impact ion source of our apparatus, the electron beam is introduced into the region close to the nozzle orifice; the cluster ions are probably produced via ionization of the aniline monomer followed by three-body association with water molecules. In such a case, the cluster ions are produced predominantly in their lowest energy form.[7]

3.2. [Aniline−(H$_2$O)$_{1,2}$]$^+$. Figure 3 shows the structures of [aniline−(H$_2$O)$_{1, 2}$]$^+$ optimized at the B3LYP/cc-pVDZ level. Figure 4 compares the observed spectra with the calculated ones for [aniline−(H$_2$O)$_{1,2}$]$^+$. Overall spectra are shown in the left part (Figure 4, parts a−e); an enlarged view of the spectra in the 3450−3850 cm^{-1} region is displayed in the right part (Figure 4, parts f−j). In the observed spectrum of [aniline−(H$_2$O)$_1$]$^+$ (Figure 4, part a), four bands are observed at 3105, 3440, 3630, and 3715 cm^{-1}. The positions and relative intensities of these bands are coincident with those calculated for isomer **1I** (Figure 3, part a); the calculation predicts four strong bands at 3047, 3467, 3628, and 3715 cm^{-1}. These four bands are assigned to

the hydrogen-bonded NH, free NH, symmetric free OH, and asymmetric free OH stretching vibrations, respectively. The observation of the hydrogen-bonded NH band furnishes further evidence for the N−H•••O-type hydrogen-bonded structure of [aniline−(H$_2$O)$_1$]$^+$ proposed earlier.[12] The observed spectrum of [aniline−(H$_2$O)$_1$]$^+$ in the 3450−3850 cm^{-1} region is decomposed into two Lorentzian components (dotted curves in Figure 4, part f). For easy comparison, we convolute each peak in the calculated spectrum (solid curve in Figure 4, part g) by a Lorentzian function (with a width of 32 cm^{-1}). It is clear that the calculation underestimates the intensity of the symmetric OH stretching band relative to the asymmetric one.

Parts b and c of Figure 3 depict the structures of [aniline−(H$_2$O)$_2$]$^+$ optimized at the B3LYP/cc-pVDZ level. In isomer **2I** (Figure 3, part b), each NH bond is bound to a water molecule. We call this structure a 1−1 branched form. In isomer **2II** (Figure 3, part c), one NH bond is bound to a water dimer and the other is free from intermolecular bond formation. Isomer **2I** is more stable than isomer **2II** by 728 cm^{-1}. The observed spectrum is exhibited in Figure 4, parts c (solid curve) and h (dots). Four distinct bands are located at 3105, 3225, 3635, and 3725 cm^{-1}. The calculated spectra are shown in Figure 4, parts d and i (isomer **2I**) and e and j (isomer **2II**). The observed spectrum agrees with the calculated one of isomer **2I**; there are two strong bands in the 3000−3400 cm^{-1} region. In the observed spectrum, no band is identified around 3440 cm^{-1}, where the free NH band of isomer **2II** is predicted to exist. In addition, any indications of absorption are not recognized around 2800 cm^{-1}, where the hydrogen-bonded NH band of isomer **2II** is expected. Therefore, we can exclude the contribution of isomer **2II** to the observed spectrum; all the features are proved due to the presence of isomer **2I**. Spectral features in the 3500−3800 cm^{-1} region also support this assignment. The observed spectrum has two maxima at 3635 and 3725 cm^{-1}. The calculated spectrum of isomer **2I** also shows two maxima at 3630 and 3719 cm^{-1}; these bands are the symmetric and asymmetric OH stretching vibrations of the water molecules. On the other hand, the spectrum of isomer **2II** (Figure 4, part j) displays the third maxima at 3690 cm^{-1} between the symmetric and asymmetric OH bands. This band is the free OH stretching vibration of the AD−H$_2$O in isomer **2II**. From the resemblance between the observed spectrum and the calculated one of isomer **2I** in the 3500−3800 cm^{-1} region, it is evidenced again that the predominant form of [aniline−(H$_2$O)$_2$]$^+$ is isomer **2I**. We assign the bands observed at 3105 and 3225 cm^{-1} to the symmetric and asymmetric stretching vibrations of the hydrogen-bonded NH$_2$ group, respectively. The 3635 and 3725 cm^{-1} bands are attributed to the symmetric and asymmetric OH stretching vibrations of the water molecules, respectively. It is noted that the calculation underestimates the intensity of the symmetric OH stretching band relative to the asymmetric one also for [aniline−(H$_2$O)$_2$]$^+$, as seen in Figure 4, part i. For $n = 2$, there seems to be a discrepancy in the NH stretching intensities between experiment (Figure 4, part c) and calculation (Figure 4, part d). According to the result of the vibrational frequency calculation, the symmetric NH stretching around 3100 cm^{-1} is coupled with the CH stretching vibrations; the infrared intensity of the symmetric NH stretching is divided into a few vibrational modes. The integrated intensity of the infrared bands around 3100 cm^{-1} is higher than the intensity of the asymmetric NH stretching, consistent with the experimental result.

3.3. [Aniline−(H$_2$O)$_3$]$^+$. Four structural isomers of [aniline−(H$_2$O)$_3$]$^+$ optimized by DFT calculations are illustrated in Figure
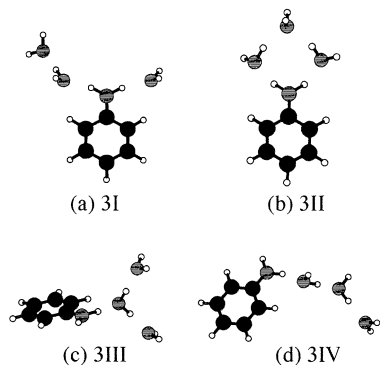
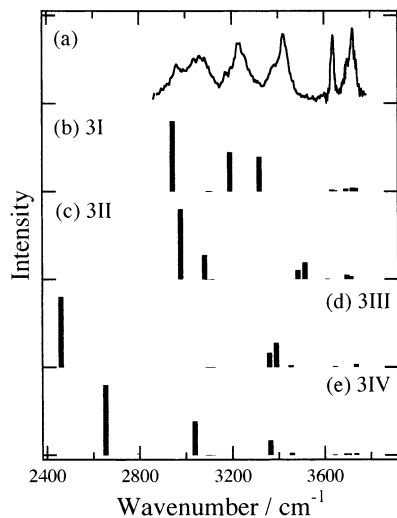**Figure 5.** Structures of [aniline$-$(H$_2$O)$_3$]$^+$ optimized at the B3LYP/cc-pVDZ level of theory.

Figure 6. (a) Infrared photodissociation spectrum of [aniline$-$(H$_2$O)$_3$]$^+$. (b$-$e) Calculated spectra of isomers **3I**$-$**3IV**.

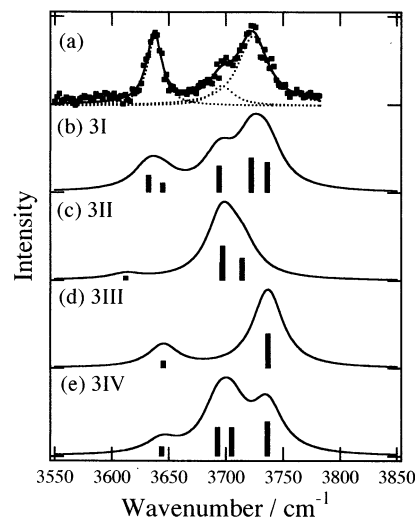**Figure 7.** Enlarged view of the observed (dots) and calculated (bars) spectra of [aniline$-$(H$_2$O)$_3$]$^+$ in the 3550$-$3850 cm^{-1} region. In the (b$-$e) calculated spectra, the solid curves represent convolution of the stick spectra by Lorentzian functions with a width of 32 cm^{-1} (fwhm).
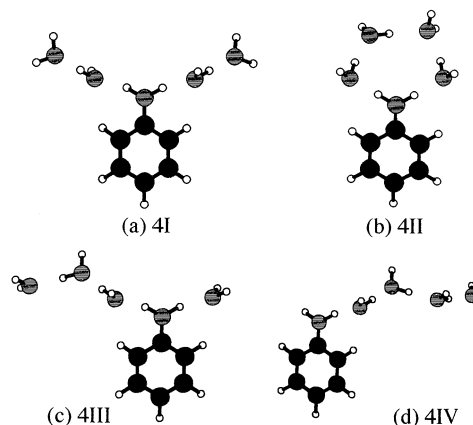

Figure 8. Structures of [aniline$-$(H$_2$O)$_4$]$^+$ optimized at the B3LYP/cc-pVDZ level of theory.

5. The 2$-$1 branched structure (isomer **3I**) is computed to be the lowest in energy as already found in the previous study.[13] Isomer **3II** has a four-membered ring that consists of the NH$_2$ group and three water molecules. Both isomers **3III** and **3IV** have a water trimer at one NH bond; the aniline ion is bound to the middle and terminal molecule of the water chain, respectively. Figure 6 compares the observed spectrum with the calculated ones of these isomers. The spectrum of isomer **3I** agrees well with the observed one; only isomer **3I** has three comparably strong bands in the 2800$-$3600 cm^{-1} region. Figure 7 displays an enlarged view of the spectra in the 3550$-$3850 cm^{-1} region. The observed spectrum has two maxima at 3637 and 3723 cm^{-1} and one weak hump at 3696 cm^{-1}: these features are decomposed into three Lorentzian components (dotted curves in Figure 7, part a). It is clear that the convoluted spectrum of isomer **3I** bears a fair resemblance to the observed band contour. In particular, the existence of the weak hump between the two maxima is reproduced in Figure 7, part b. Therefore, we conclude that the stable arrangement of [aniline$-$(H$_2$O)$_3$]$^+$ is the 2$-$1 branched structure (isomer **3I**). The bands observed at 3070 and 3230 cm^{-1} are assigned to the hydrogen-bonded NH stretching vibrations. The 3420 cm^{-1} band is attributed to the hydrogen-bonded OH stretching band of the AD$-$H$_2$O. The 3637 and 3723 cm^{-1} bands are ascribed to the symmetric and asymmetric free OH stretching bands of the A$-$H$_2$O, respectively. Finally, the band at 3696 cm^{-1} is the free OH vibration of the AD$-$H$_2$O.

3.4. [Aniline$-$(H$_2$O)$_4$]$^+$. Figure 8 shows the structures of [aniline$-$(H$_2$O)$_4$]$^+$ optimized at the B3LYP/cc-pVDZ level. The most stable structure is isomer **4I**, which has the 2$-$2 branched form. Isomer **4II** has a five-membered ring. In this structure, one water molecule acts as a terminator (double proton acceptor). The other chain structures (isomers **4III** and **4IV**) are less stable than isomers **4I** and **4II**. Figures 9 and 10 compare the observed spectrum with the calculated ones. In the observed spectrum (Figure 9, part a), three maxima emerge at 2960, 3100, and 3430 cm^{-1}. In addition to these strong bands, there is a very weak band at 3550 cm^{-1}. In the 3550$-$3850 cm^{-1} region, the observed spectrum (Figure 10, part a) shows two maxima at 3640 and 3710 cm^{-1} and a shoulder at 3734 cm^{-1}. As seen in Figure 9, part b, the calculated spectrum for isomer **4I** shows coincidence with the observed one in the 2800$-$3600 cm^{-1} region. The lowest frequency band and the next one are located within a range of 150 cm^{-1} in both the observed spectrum and the calculated one of isomer **4I**. Therefore, we suppose that the predominant form of [aniline$-$(H$_2$O)$_4$]$^+$ is isomer **4I**. However, the existence of the 3550 cm^{-1} band cannot be explained by the spectrum of isomer **4I**. In the enlarged view of the spectra in Figure 10, there is also a discrepancy between the observed spectrum and the calculated one of isomer **4I**. The calculation predicts three well-resolved bands in this region for isomer **4I** (Figure 10, part b). Another isomer is invoked to explain these discrepancies in the infrared spectra. DFT calculations predict that the second most stable form of [aniline$-$(H$_2$O)$_4$]$^+$ is isomer

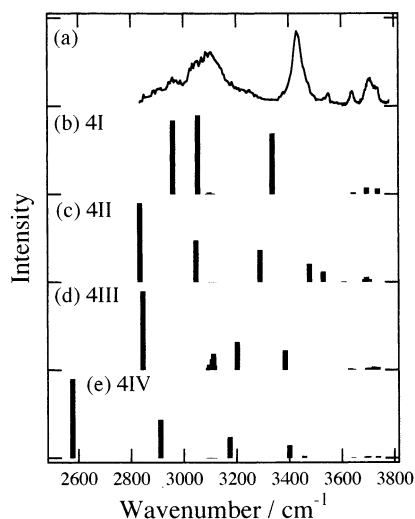[Aniline−(Water)$_n$]$^+$ ($n = 1−8$)

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Figure 9. (a) Infrared photodissociation spectrum of [aniline−(H$_2$O)$_4$]$^+$. (b−e) Calculated spectra of isomers **4I−4IV**.
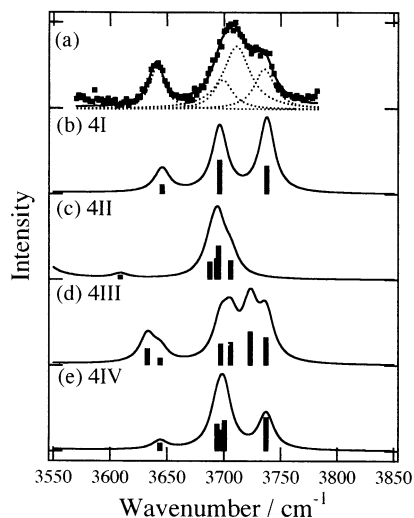

Figure 10. Enlarged view of the observed (dots) and calculated (bars) spectra of [aniline−(H$_2$O)$_4$]$^+$ in the 3550−3850 cm^{-1} region. In the calculated spectra (b−e), the solid curves represent convolution of the stick spectra by Lorentzian functions with a width of 16 cm^{-1} (fwhm).

4II. According to the frequency evaluation and the convolution of the stick spectrum with Lorentzian functions, isomer **4II** has one strong maximum at 3694 cm^{-1} (see Figure 10, part c). The observed spectrum in the 3550−3850 cm^{-1} region can be decomposed into four Lorentzian components centered at 3640, 3698, 3710, and 3734 cm^{-1}. The components at 3640, 3698, and 3734 cm^{-1} are assigned to isomer **4I**, because the band position and relative intensity are consistent with those of isomer **4I**. The 3710 cm^{-1} band originated from isomer **4III**.[17] As shown in Figure 9, part c, isomer **4II** has two bands in the 3400−3600 cm^{-1} region. Therefore, the band at 3550 cm^{-1} is assigned to the hydrogen-bonded OH stretching vibrations of isomer **4II**. We conclude that the main form of [aniline−(H$_2$O)$_4$]$^+$ is the 2−2 branched structure like that of isomer **4I** although the five-membered ring form (isomer **4II**) also exists under the present experimental conditions. The coexistence of isomers **4I** and **4II** is probable because DFT calculations indicate that the energy difference between these isomers is only 52 cm^{-1} (see Table 1).

It is of use to compare the infrared spectrum of [aniline−(H$_2$O)$_4$]$^+$ with those of H$^+$(H$_2$O)$_7$ reported by Lee and co-workers.[2] The spectrum of H$^+$(H$_2$O)$_7$ reveals four sharp
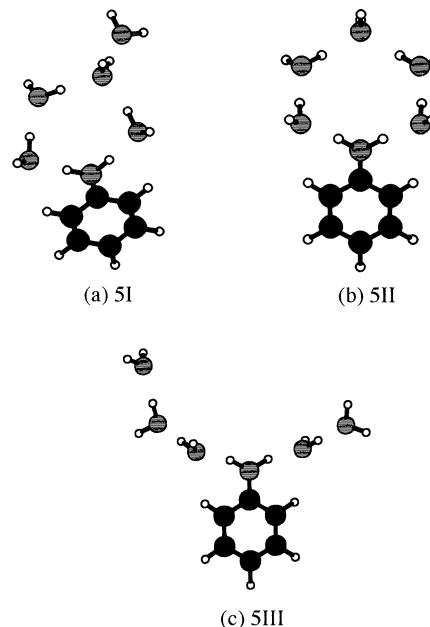
transitions at 3502, 3544, 3555, and 3581 cm^{-1} in the 3500−3600 cm^{-1} region. The widths of these bands are much narrower than those of the lower frequency hydrogen-bonded OH bands. It is generally true that less broadening and smaller red shifts indicate less softening of the OH stretching mode by hydrogen bonding. Such a situation is expected when two water molecules are hydrogen-bonded simultaneously to the oxygen atom of another water molecule. That is, the bands in the 3500−3600 cm^{-1} region show the existence of a terminal AA−H$_2$O in the clusters.[2] Bands in this region were assigned to the hydrogen-bonded OH stretching bands of the AD−H$_2$O of the five-membered ring isomers (structures **7VI** and **7X** in ref 2). In the spectrum of [aniline−(H$_2$O)$_4$]$^+$, there exists a very weak band at 3550 cm^{-1}. Because of the similarity of the band position to those of H$^+$(H$_2$O)$_7$, the band at 3550 cm^{-1} is ascribed to the hydrogen-bonded OH stretching vibrations of the five-membered ring isomer (isomer **4II**).

3.5. [Aniline−(H$_2$O)$_5$]$^+$. According to the results of the geometry optimization for [aniline−(H$_2$O)$_4$]$^+$, branched structures (in which the aniline$^+$ ion possesses almost equal number of water molecules at each NH bond) or cyclic structures may be stable for larger clusters with $n > 4$. We consider three structural isomers for [aniline−(H$_2$O)$_5$]$^+$. Figure 11 displays the structures of [aniline−(H$_2$O)$_5$]$^+$ optimized at the B3LYP/cc-pVDZ level. The most stable form is isomer **5I**. It has a five-membered ring, and the fifth water molecule is bound to the terminal water. Isomer **5II** has a six-membered ring structure. Isomer **5III** has a 3−2 branched structure. Figure 12 compares overall spectra of [aniline−(H$_2$O)$_5$]$^+$. The observed spectrum shows five maxima at 2940, 3070, 3387, 3447, and 3480 cm^{-1} in the 2800−3600 cm^{-1} region. The spectrum of isomer **5I** is similar to the observed one; the existence of two bands in the 2800−3200 cm^{-1} region is reproduced in Figure 12, part b. An enlarged view of the spectra is exhibited in Figure 13. The observed spectrum exhibits four maxima at 3642, 3684, 3708, and 3735 cm^{-1}. The band contour is decomposed into four Lorentzian components. The calculated spectrum of isomer **5I** (Figure 13, part b) well reproduces the existence of four maxima in the 3600−3800 cm^{-1} region. Therefore, we conclude that the predominant form of [aniline−(H$_2$O)$_5$]$^+$ produced in our

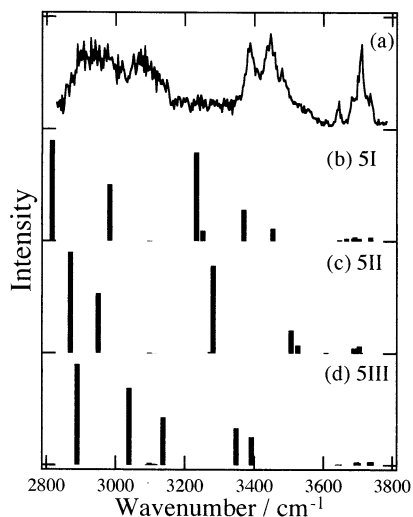**Figure 11.** Structures of [aniline−(H$_2$O)$_5$]$^+$ optimized at the B3LYP/cc-pVDZ level of theory.

Figure 12. (a) Infrared photodissociation spectrum of [aniline−$(H_2O)_5]^+$. (b−d) Calculated spectra of isomers **5I**−**5III**.
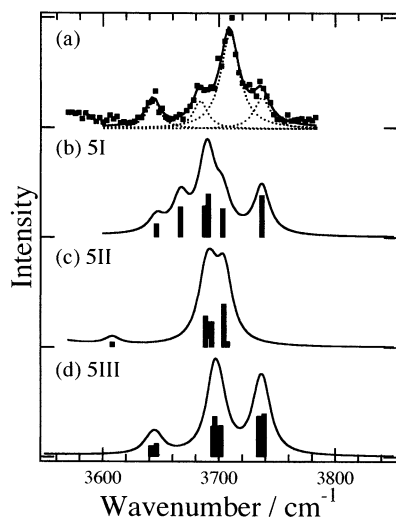

Figure 13. Enlarged view of the observed (dots) and calculated (bars) spectra of [aniline−$(H_2O)_5]^+$ in the 3550−3850 cm^{-1} region. In the (b−d) calculated spectra, the solid curves represent convolution of the stick spectra by Lorentzian functions with a width of 16 cm^{-1} (fwhm).

experiment is the five-membered ring structure (isomer **5I**). The bands observed at 2940 and 3070 cm^{-1} are assigned to the hydrogen-bonded NH stretching vibrations. The 3387, 3447, and 3480 cm^{-1} bands are ascribed to the hydrogen-bonded OH stretching vibrations. The bands at 3642 and 3735 cm^{-1} are the symmetric and asymmetric OH stretching bands, respectively. Finally, the bands at 3684 and 3708 cm^{-1} are ascribed to the free OH stretching vibrations.

It is worth comparing the results of [aniline−$(H_2O)_{1-5}]^+$ with those of other hydrated cluster ions. A characteristic of the observed spectrum for [aniline−$(H_2O)_5]^+$ is the 3684 cm^{-1} band. The band position is almost the same as those of the free OH bands of the three-coordinated AAD−H_2O in H$^+(H_2O)_{7,8}$, CH$_3$NH$_3^+(H_2O)_6$, and NH$_4^+(H_2O)_7$.[2,3] The existence of ring isomers is evidenced by this band. For the protonated water clusters, H$^+(H_2O)_m$, the clusters with $m \leq 6$ have noncyclic structures, because five or six water molecules cannot form a ring structure. On the other hand, the addition of one water molecule to H$^+(H_2O)_6$ induces a structural change from non-cyclic form to cyclic one. The H$^+(H_2O)_7$ ion has the five-membered ring form; the other two water molecules are bound to the OH groups that stick out of the ring. The two extra water

molecules stabilize the five-membered ring in the protonated water clusters. The [aniline−$(H_2O)_n]^+$ clusters have a similar tendency. According to the infrared spectra, the $n = 1$−4 clusters have the noncyclic structures, although the $n = 4$ ion has the additional cyclic isomer. The $n = 5$ ion has the fairly stable, five-membered ring. The calculations predict the five-membered cyclic structures for both $n = 4$ and 5 ions. The change in relative stability of the cyclic and noncyclic structures occurs for the $n = 4$ and 5 ions. In $n = 5$, the water molecule that closes the ring is AAD, while in $n = 4$ it is AA. The AAD must be substantially more stable than the AA. Therefore, one extra water molecule can stabilize the same five-membered ring in the case of the hydrated aniline ion clusters.

3.6. [Aniline−$(H_2O)_{6-8}]^+$. As shown in Figure 1, parts f−h, the spectra of the $n = 6$−8 clusters are very similar to each other. In the spectra of the $n = 2$−5 clusters, there are two bands that can be assigned to the NH stretching vibrations of the aniline$^+$ moiety in the region below 3350 cm^{-1}. The intensities of these bands are comparable to or larger than that of the OH stretching bands located in the region above 3350 cm^{-1}. On the other hand, the spectra of the $n = 6$−8 clusters show a very broad band around 3400 cm^{-1}; no noticeable band nor growing absorption is seen in the region below 3200 cm^{-1}. It is difficult to explain such a drastic change of the spectra by simple addition of water molecules to the smaller clusters. The [phenol−$(H_2O)_m]^+$ clusters with $m = 4$, 7, and 8 have the proton-transferred form.[11] The infrared spectra of these clusters display very broad band around 3430 cm^{-1}; the spectral features are very similar to those of [aniline−$(H_2O)_{6-8}]^+$. Therefore, it is probable that the proton of the NH bond is transferred to the water moiety in the $n = 6$−8 clusters. The detailed structural identification of the $n = 6$−8 clusters by DFT calculations may be very difficult, because a large number of isomers have to be considered. However, the infrared spectra in the 3500−3800 cm^{-1} region contain some structural information on the clusters. The spectra of the $n = 6$−8 clusters show two maxima around 3690 and 3710 cm^{-1}. On the basis of the assignments for the smaller clusters, these bands are assigned to the free OH stretching vibrations of water molecules involved in the ring formation. In particular, the former band is the free OH stretching of the three-coordinated AAD−H_2O, indicating the ring structures of the clusters. Consequently, the $n = 6$−8 clusters possibly have the proton-transferred structure with the ring of the hydroge-bonding network.

4. Conclusion

The infrared photodissociation spectra of the [aniline−$(H_2O)_n]^+$ ($n = 1$−8) ions have been measured in the 2700−3800 cm^{-1} region. The geometry optimization and vibrational frequency evaluation have been carried out at the B3LYP/cc-pVDZ level of theory for the $n = 1$−5 clusters. The [aniline−$(H_2O)_n]^+$ ($n = 1$−8) ions exhibit a variety of cluster structures. The success in revealing the cluster structures was made possible by the spectroscopic measurements on size-selected cluster ions coupled with DFT calculations. The number of the structural isomers that are necessary to explain the observed spectra of [aniline−$(H_2O)_n]^+$ is fairly smaller than that of other hydrated cluster ions, such as H$^+(H_2O)_m$.[2] This makes the discussion of the structures of [aniline−$(H_2O)_n]^+$ quite simple. The $n = 1$−3 ions have the noncyclic, branched structures. For $n = 4$, the 2−2 branched structure is the most stable form, although the five-membered ring structure also exists in our experiment. The $n = 5$ ion possesses the five-membered ring structure. The drastic change of the infrared spectra and the appearance of the

[Aniline−(Water)$_n$]$^+$ ($n = 1$−8)

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characteristic bands around 3690 cm^{-1} suggest that the $n = 6$−8 clusters have the proton-transferred structure with the ring of the hydrogen-bonding network.

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(17) There is a slight disagreement in the position between the decomposed component (3710 cm^{-1}) and the maximum predicted for isomer **4II** (3694 cm^{-1}). This is due to an improper choice of the scaling factor of 0.9676 for isomer **4II**. The symmetric free OH band of isomer **4II** emerges at 3609 cm^{-1}, which is lower than the observed frequency (3640 cm^{-1}). A better agreement of the band position is achieved, if one uses a scaling factor slightly larger than the present value for isomer **4II**.