Infrared photodissociation spectroscopy of aniline$^+$–(water)$_{1,2}$ and aniline$^+$–(methanol)$_{1,2}$

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Abstract

Infrared photodissociation spectra of the aniline ion solvated by water and methanol molecules are measured in the 2600–3800 cm^{-1} region. Substantially red-shifted and broadened transitions are distinctly observed at 3105 and 2915 cm^{-1} for aniline$^+$–(H_2O)$_1$ and aniline$^+$–(CH_3OH)$_1$, respectively, and assigned to the stretching vibration of the hydrogen-bonded NH oscillator of the aniline$^+$ moiety. The spectra of aniline$^+$–(H_2O)$_2$ and aniline$^+$–(CH_3OH)$_2$ demonstrate a large perturbation to both of the NH oscillators, indicating that each NH bond is bound to a solvent molecule in the most stable structure.

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1. Introduction

The characterization of ion–molecule complexes is of fundamental importance in understanding the nature of intermolecular interactions and exploring the microscopic details of solvation processes. To this end, ion–molecule complexes have been studied by mass spectrometry [1] and optical spectroscopy [2]. Vibrational spectroscopy is particularly useful for probing intermolecular interactions, because certain vibrational modes are quite sensitive to intermolecular perturbations. Lee and co-workers developed the vibrational predissociation spectroscopy of cluster ions and investigated the structures of $H_3O^+(H_2O)_n$ and $NH_4^+(NH_3)_n$ [3,4]. By using a similar technique, Lisy and co-workers studied the interaction between metal ions and solvent molecules [3,5].

Microsolvation of aromatic ions was also studied by several groups. The vibrational spectra showed that the phenol ion forms a σ-type hydrogen bond between the hydroxyl proton and the oxygen atom of solvent molecules such as water [6–8], methanol [6] and phenol [6,9]. All the prominent bands observed in the 2800–3800 cm^{-1} region of the spectra are ascribed to OH oscillators of the solvent part of the complexes; the transition of the proton-donating OH oscillator of the phenol moiety is not seen as a distinct band in the spectra. The vibrational frequency of the proton-donating OH group in phenol$^+$–H_2O was estimated only by theoretical calculations [8,10]. The vibrational spectra of the aniline ion also suggested the formation of a σ-type hydrogen bond with solvent molecules such as water [11,12], ammonia [13] and aniline [14]. However, the transition of the proton-donating NH oscillator of the aniline moiety was not detected in the region from 3100 to 3900 cm^{-1}. Thus, the nature of the ionic hydrogen bonds through the hydroxyl and amino groups has yet to be characterized directly by spectroscopic studies.

The observation of the transition due to the proton-donating oscillator is strongly desired for characterizing the interaction between an ion and a solvent and investigating the dynamics of vibrationally excited state leading to the predissociation of the complex. Recently, the 4-aminophenol$^+$–H_2O complex was studied by Gerhards and Unterberg [15]. They found the structure containing an N–H•••OH_2 hydrogen bond as one of the two isomers. The stretching vibration of the proton-donating NH oscillator of the 4-aminophenol$^+$ moiety was observed in the photodissociation spectrum. However, the extremely broad feature prevents the determination of precise values for the transition frequency and the band width.

The main purpose of this work is to observe the transitions due to the proton-donating NH oscillators of the aniline ion solvated by water and methanol molecules. The absence of the bands in the previous spectra for the aniline/water system may be due to a decrease in the laser intensity below 3300 cm^{-1} [11,12]. Therefore, we extend the measurement to the frequency region lower than the previous work, keeping the laser intensity almost constant. The absorption band originating from the proton-donating NH oscillator in aniline$^+$–H_2O is observed successfully; the spectral features confirm the structure of the complex proposed before [11]. However, the spectrum of aniline$^+$–$(H_2O)_2$ is different from the previous one [12]; the difference is explained by comparing the methods of preparing the complex. The spectra of aniline$^+$–$(CH_3OH)_{1,2}$ are obtained for the first time and interpreted with the aid of theoretical calculations.

2. Experimental and Computational

Infrared photodissociation spectra of aniline$^+$–$(H_2O)_{1,2}$ and aniline$^+$–$(CH_3OH)_{1,2}$ are measured by using a vacuum apparatus with two quadrupole mass filters and a quadrupole ion guide [16]. The solvated aniline ions are produced in an ion source of electron-impact type. The parent ions are isolated by the first quadrupole mass filter. After deflection by an ion bender, the ions are introduced into the ion guide and irradiated by an infrared laser (Continuum, Mirage 3000). The photoexcitation induces vibrational predissociation of the parent ions. After leaving the ion guide, the resultant fragment ions are analyzed by the second quadrupole mass filter and detected by a secondary electron multiplier tube. The photodissociation spectra are obtained from the yields of the fragment ions as a function of wavenumber of the infrared laser.

For aniline$^+$–$(CH_3OH)_{1,2}$, density functional theory (DFT) calculations are carried out with Gaussian 98 program package [17]. The geometries of the ions are optimized and the vibrational frequencies are evaluated at the B3LYP/cc-pVDZ level of theory.

3. Results and discussion

3.1. Aniline$^+$–$(H_2O)_{1,2}$

Nakanaga and co-workers have already reported the results of infrared spectroscopy and ab initio calculations of aniline$^+$–$(H_2O)_n$ with n = 1–6 [11,12]. Three absorption bands were observed at 3440, 3636 and 3715 cm^{-1} in the spectrum of aniline$^+$–$(H_2O)_1$ [11]. They assigned the latter two bands to the symmetric and antisymmetric OH-stretching vibrations of the water moiety, because the frequencies are close to those of the bare water molecule. Only one band (3440 cm^{-1}) was observed in the region of the NH-stretching vibrations. They attributed this band to the free NH oscillator of the aniline moiety, because the frequency is approximately equal to the average of the two NH-stretching frequencies of the bare aniline ion. From these results, they suggested that there is a hydrogen bond between one of the two NH bonds of aniline$^+$ and the oxygen atom of H_2O. Fig. 1a schematically illustrates the proposed structure of aniline$^+$–$(H_2O)_1$. The geometry optimized at the MP2/6-31G** level was consistent with the experimental results; the vibrational frequencies calculated were in reasonable agreement with the observed ones [11].

Fig. 2a shows the infrared photodissociation spectrum of aniline$^+$–$(H_2O)_1$ recorded in the present work. Four prominent bands are observed at 3105, 3440, 3630 and 3715 cm^{-1}. The positions of the latter three bands are in good agreement with those reported by Nakanaga et al., while the relative intensities of the bands in our spectrum are more reliable than those in the previous one obtained using the laser with decreasing intensity toward the lower frequency [11]. The most intense band is located at 3105 cm^{-1}, which was missed in the previous work probably due to low laser intensity below 3300 cm^{-1} [11]. The position and intensity of this band are consistent with those calculated for the hydrogen-bonded NH oscillator [11]. Therefore, we attribute this band to the NH oscillator of aniline$^+$ involved in the hydrogen bond. The observation of this band furnishes further evidence for the N–H•••O-type hydrogen-bonded structure of aniline$^+$–$(H_2O)_1$.

We have successfully observed a prominent band due to the proton-donating NH oscillator of the aniline$^+$ moiety in aniline$^+$–$(H_2O)_1$. For phenol$^+$–$(H_2O)_1$, on the other hand, the infrared spectrum shows very broad absorption extending from 2900 to 3400 cm^{-1} [6]; it is not obvious whether the feature is a part of the band of the proton-donating OH oscillator of phenol$^+$. The difference in the spectral feature is reasonably explained by the magnitude of the proton affinity of the anilino (C_6H_5NH) and phenoxy (C_6H_5O) radicals. Both of the aniline$^+$–$(H_2O)_1$ and phenol$^+$–$(H_2O)_1$ complexes have the σ-type hydrogen bond, N–H•••OH_2 and O–H•••OH_2, where the proton interlinks the anilino and phenoxy radicals with the water molecule. Positional balance of the proton should highly depend on the difference in the proton affinity between the radicals and water. Because the magnitude of the proton affinity of the anilino radical (950 kJ/mol) is larger than that of the phenoxy radical (858 kJ/mol) [18], the anilino radical attracts the proton more tightly than the phenoxy radical in the complexes. Therefore, the perturbation to the proton-donating oscillator of the aniline ion is smaller than that of the phenol ion, resulting in the smaller amount of the frequency reduction and the broadening width of the band.

The infrared spectrum of aniline$^+$–$(H_2O)_2$ was reported by Nakanaga and Ito [12]. In their spectrum, five bands were observed at 3240, 3299, 3414, 3637 and 3723 cm^{-1}. The existence of two isomers was invoked to explain the spectral features. Figs. 1b and 1c depict the proposed structures for the two isomers of aniline$^+$–$(H_2O)_2$. In the 1-1 structure (Fig. 1b), each NH bond is bound to a water molecule. In the 2-0 structure (Fig. 1c), one NH bond is bound to the water dimer and the other is free from intermolecular bonds. With the aid of DFT calculations, they attributed the bands at 3240, 3637 and 3723 cm^{-1} to the hydrogen-bonded NH stretch of aniline$^+$, the symmetric and antisymmetric OH-stretching vibrations of H_2O of the 1-1 structure, respectively. The 3299- and 3414-cm^{-1} bands were ascribed to the hydrogen-bonded OH oscillator in the $(H_2O)_2$ unit and the free NH stretch of aniline$^+$ of the 2-0 structure, respectively. They also suggested that the 1-1 structure is the dominant isomer on the basis of absorption intensity of the free OH bands of the water part and the stabilization energy calculated at the B3LYP/6-31++G** level [12]. However, the intensity of the free OH bands is very small. Therefore, the observation of the intense NH bands of the aniline$^+$ part is desired for addressing the questions about the structure of aniline$^+$–$(H_2O)_2$ and the relative abundance of the isomers.

Fig. 2b displays the spectrum of aniline$^+$–$(H_2O)_2$ obtained in the present work. Four distinct bands emerge at 3105, 3225, 3635 and 3725 cm^{-1}. The region of the lowest-frequency transition was not scanned by Nakanaga and Ito [12]. The 3225-cm^{-1} band corresponds to the feature observed around 3240 cm^{-1} in the previous spectrum. No band is identified at 3414 cm^{-1}, where the free NH stretch of aniline$^+$ of the 2-0 structure was observed in the earlier work [12]. In addition, any indications of absorption are not recognized around 2800 cm^{-1}, where the hydrogen-bonded NH band of the 2-0 structure is expected from DFT calculations. Therefore, we can exclude the contribution of the 2-0 structure to the present spectrum; all the features are proved due to the 1-1 structure. Then we assign the bands at 3105 and 3225 cm^{-1} to the symmetric and antisymmetric stretching vibrations of the hydrogen-bonded NH_2 group. The 3635- and 3725-cm^{-1} bands are attributed to the symmetric and antisymmetric OH stretching vibrations of the water molecules. The position and intensity of these bands are in good agreement with those calculated for the 1-1 structure [12].

We have shown that the aniline$^+$–$(H_2O)_2$ ion produced in our experiment exclusively takes the 1-1 structure. On the other hand, Nakanaga and Ito suggested the presence of the 2-0 structure as a minor isomer [12]. The discrepancy is considered to originate in the different methods of preparing the ions. In the previous work, the cluster ions were produced via multiphoton ionization (MPI) of the neutral aniline/water clusters. In MPI processes, configurations of cluster ions that are similar to those of neutral precursors are mainly accessible [19]. 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, a part of the cluster ions remain at the local minima without isomerizing 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 the water molecules. In such a case, the cluster ions are produced predominantly in their lowest-energy form. The observation of the 1-1 structure in our experiment indicates that it is the most stable form of the aniline$^+$–$(H_2O)_2$ ion.

3.2. Aniline^{+}–(CH_3OH)$_{1,2}$

Fig. 3a exhibits the infrared photodissociation spectrum of aniline^{+}–$(CH_3OH)_1$. Two prominent bands are seen at 2915 and 3440 cm^{-1}. From the similarity of the spectral features to those of aniline^{+}–$(H_2O)_1$, the 2915- and 3440-cm^{-1} bands are assigned to the hydrogen-bonded and free NH oscillators of aniline^{+}, respectively. A weak band around 3675 cm^{-1} can be attributed to the free OH oscillator of the methanol molecule, because the frequency is almost the same as that of the bare methanol (3681 cm^{-1}) [20]. The overall spectral features are consistent with the structure including a hydrogen bond between one NH bond of aniline^{+} and the oxygen atom of CH_3OH. The N–H•••O-type hydrogen-bonded structure is similar to that of aniline^{+}–$(H_2O)_1$. One can characterize the NH bands of the aniline^{+} moiety by comparing the spectra of aniline^{+}–$(CH_3OH)_1$ and aniline^{+}–$(H_2O)_1$. The frequency of the free NH oscillator (3440 cm^{-1}) hardly shifts from aniline^{+}–$(H_2O)_1$ to aniline^{+}–$(CH_3OH)_1$. On the other hand, the hydrogen-bonded NH oscillator reveals a large red-shift from aniline^{+}–$(H_2O)_1$ (3105 cm^{-1}) to aniline^{+}–$(CH_3OH)_1$ (2915 cm^{-1}). The width of the bands also becomes broad from the former ion (85 cm^{-1}) to the latter one (110 cm^{-1}). These observations are reasonably explained by the magnitude of the proton affinity of the solvent molecules: 754 kJ/mol for methanol and 690 kJ/mol for water [16]. The solvent molecule with the larger proton affinity value is bound more tightly to the amino proton. As a result, the hydrogen-bonded NH band of aniline^{+}–$(CH_3OH)_1$ appears at the lower frequency with the broader width.

Fig. 3b displays the spectrum of aniline^{+}–$(CH_3OH)_2$. Two bands appear at 3015 and 3675 cm^{-1}. The latter band is assigned to the free OH oscillator of CH_3OH. The 3015-cm^{-1} band has a wing on the high-frequency side; this band can be deconvoluted into two transitions. Two Lorentzian functions are employed for reproducing the shape of the band. The result is demonstrated in the top panel of Fig.4. The two functions (dotted curves) have a maximum at 3009 and 3116 cm^{-1}, respectively. Three stable isomers are obtained from DFT calculations for aniline^{+}–$(CH_3OH)_2$ at the B3LYP/cc-pVDZ level. The structures and infrared spectra predicted for these isomers are represented in Fig. 4. The most stable isomer has the geometry depicted in Fig. 4a, which corresponds to the 1-1 structure of aniline^{+}–$(H_2O)_2$. The 2-0 structure (Fig. 4b) turns out to be less stable in our calculations. In addition, the third isomer with a cyclic form is obtained as shown in Fig. 4c. The contribution of the 2-0 structure to the infrared spectrum can be ruled out, because the experimental spectrum exhibits no absorption band attributable to the hydrogen-bonded NH oscillator of the 2-0 structure (2683 cm^{-1}, Fig. 4b). The contribution of the cyclic structure is probably excluded because of the smallest stabilization energy calculated and the absence of the band corresponding to the 3559-cm^{-1} transition of the theoretical spectrum (Fig. 4c). Only the spectrum calculated for the 1-1 structure predicts the two bands with comparable intensity in the 2900–3300 cm^{-1} region (Fig. 4a). The experimental spectrum can be reasonably explained by assuming the 1-1 structure. Then we assign the 3009- and 3116-cm^{-1} components to the symmetric and antisymmetric stretching vibrations of the hydrogen-bonded NH_2 group. The origin of a large difference in the width between the two bands has yet to be understood. The predominant contribution of the 1-1 structure to the present infrared spectrum indicates that it is the most stable arrangement of the aniline$^+$–$(CH_3OH)_2$ ion.

4. Conclusions

We have measured the infrared spectra of aniline$^+$–$(H_2O)_{1,2}$ and aniline$^+$–$(CH_3OH)_{1,2}$ in the regions of the NH and OH stretching vibrations. In the aniline$^+$–$(H_2O)_1$ and aniline$^+$–$(CH_3OH)_1$ complexes, the solvent molecule is bound to one of the two amino protons, forming the N–H•••O-type hydrogen bond. The frequency shift and the broadening width of the hydrogen-bonded NH transition are reasonably explained by the magnitude of the proton affinity of the constituent species. For aniline$^+$–$(H_2O)_2$, both of the two NH oscillators are subject to large perturbations, suggesting that each amino proton is bound to a water molecule (the 1-1 structure). The comparison between the observed and calculated spectra of aniline$^+$–$(CH_3OH)_2$ indicates that the lowest-energy form of the complex is also the 1-1 structure. In the primary stage of the solvation process of the aniline ion by water and methanol, the first solvent molecule binds to one NH bond and the second molecule to the other NH bond rather than the OH group of the first solvent.

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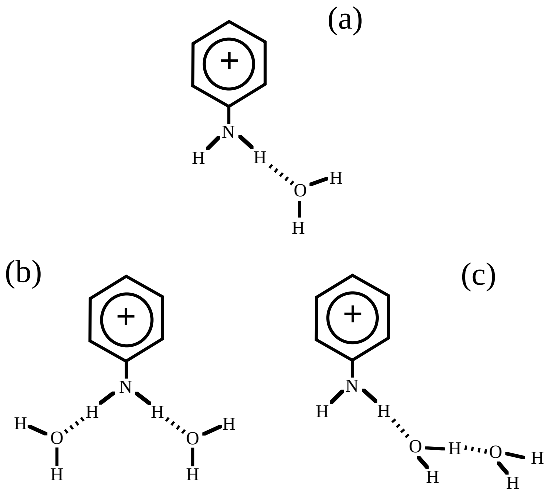
Figure Captions

Fig. 1. Schematic illustration of the structures of (a) aniline$^+$–$(H_2O)_1$ and (b, c) aniline$^+$–$(H_2O)_2$ proposed by Nakanaga et al. [11,12].

Fig. 2. Infrared photodissociation spectra of (a) aniline$^+$–$(H_2O)_1$ and (b) aniline$^+$–$(H_2O)_2$ produced via electron-impact ionization of the aniline monomer followed by three-body association with water molecule(s). The spectra are obtained from the yields of (a) aniline$^+$ and (b) aniline$^+$–$(H_2O)_1$.

Fig. 3. Infrared photodissociation spectra of (a) aniline$^+$–$(CH_3OH)_1$ and (b) aniline$^+$–$(CH_3OH)_2$ produced via electron-impact ionization of the aniline monomer followed by three-body association with methanol molecule(s). The spectra are obtained from the yields of (a) aniline$^+$ and (b) aniline$^+$–$(CH_3OH)_1$.

Fig. 4. Experimental infrared spectrum of aniline$^+$–$(CH_3OH)_2$ and theoretical spectra of three isomers obtained by DFT calculations at the B3LYP/cc-pVDZ level. The absorption band around 3015 cm^{-1} in the experimental spectrum (dots) is deconvoluted into two transitions represented by Lorentzian functions (dotted curves); sum of the two functions is drawn by solid curve. A factor of 0.9753 is used to scale the calculated spectra.



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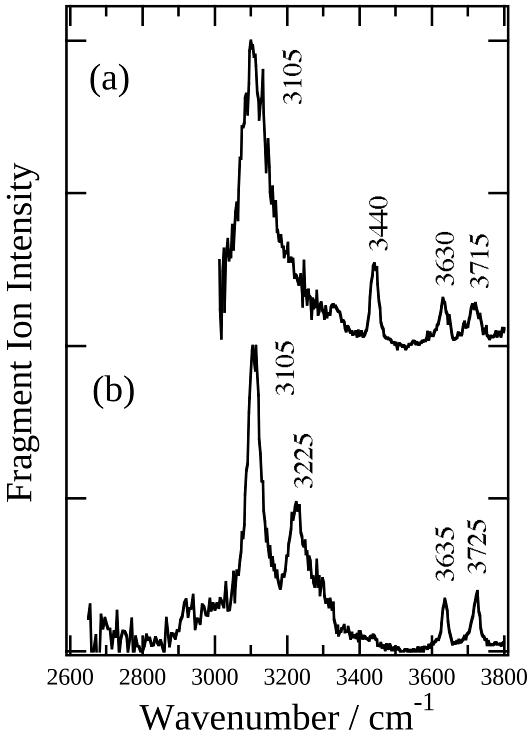

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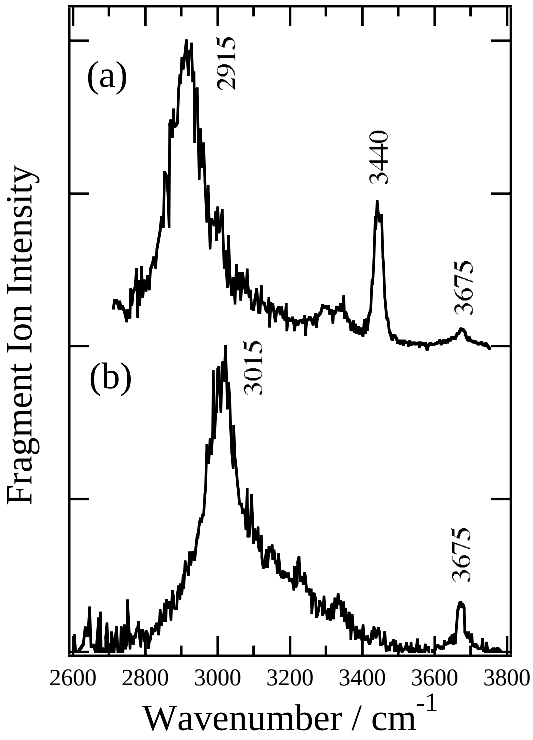

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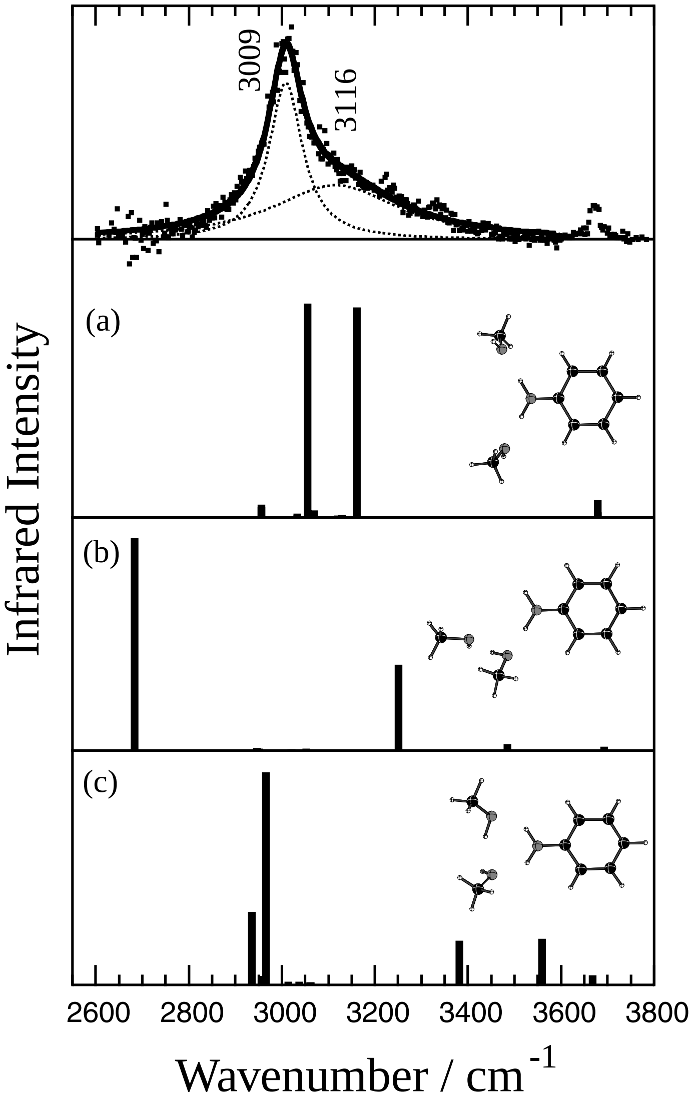

Fig. 4. Honkawa et al.