Fermi resonance interaction in hetero-dimer and trimer ions containing aniline$^+$

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Abstract

Vibrational spectra of hetero-dimer and trimer ions containing aniline$^+$ are measured by infrared photodissociation spectroscopy. For the dimer ions, the NH_2 bending overtone band gains its intensity through Fermi resonance interaction with the hydrogen-bonded NH stretching fundamental. Unperturbed frequencies of the NH_2 bending overtone are calculated to be in the range of 3255–3276 cm^{-1}, suggesting that the frequency is almost intact upon cluster formation. For the trimer ions, Fermi resonance interaction occurs mainly between the NH_2 bending overtone and the stretching fundamental of the NH oscillator involved in the stronger hydrogen bond.

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1. Introduction

Infrared photodissociation spectroscopy is a powerful method for investigating vibrational and geometric structures of cluster ions in the gas phase [1, 2]. The aniline ion is one of the aromatic ions whose clusters have well been examined by the infrared spectroscopy. Nakanaga and co-workers have extensively studied a variety of aniline cluster ions [3]. In most of their researches, the infrared spectra were observed through a depletion of parent ions without the correction of depletion yields by laser intensities. Therefore, it was in principle difficult to compare the intensities of absorption bands. More recently, Solcà and Dopfer have reported the infrared spectra of aniline$^+$–Ar$_n$ (n = 1, 2) [4]. They discussed the detailed structures of aniline$^+$–Ar$_n$ with the aid of ab initio calculations. Our group has investigated intermolecular interactions, geometric structures and intermolecular proton transfers of aniline$^+$ cluster ions [5–8]. In the 2600–3600 cm^{-1} region of the infrared spectra of certain aniline$^+$ cluster ions, an extra band emerges in addition to two strong NH stretching bands. A weak band was observed at 3270 cm^{-1} in the spectra of aniline$^+$–M (M = N_2, CH_4, CHF_3, CO) [9]. The spectrum of aniline$^+$–Ar also shows a weak band at 3270 cm^{-1} [4]. In the spectrum of aniline$^+$–benzene, one band was observed at 3280 cm^{-1} with an intensity comparable to those of the NH stretching bands [5]. The emergence of these bands is likely to be due to vibrational mode mixing, although the details have not been clarified. A similar feature was seen for X^-•H_2O (X = Cl, Br, I) anion clusters [10]; Fermi resonance interaction occurs between the bending overtone of H_2O and a hydrogen-bonded OH stretching fundamental.

In this letter, we report Fermi resonance interaction in hetero-dimer and trimer ions containing aniline$^+$: aniline$^+$–M and aniline$^+$–benzene–M. Vibrational spectra in the 2700–3600 cm^{-1} region are measured by the infrared photodissociation spectroscopy. Figure 1 shows a schematic drawing of structures of the dimer (a) and trimer (b) ions. The use of a series of solvent molecules (benzene, toluene, thiophene, furan, water, methanol, ethanol) allows us to determine the quantitative details of Fermi resonance interaction as a function o f the hydrogen-bond strength. For the dimer ions, the NH_2 bending overtone gains its infrared intensity through the resonance interaction with a hydrogen-bonded NH stretching fundamental. From the band positions and relative intensities of these two bands, we obtain unperturbed frequencies of the NH_2 bending overtone. For the trimer ions, noticeable features of Fermi resonance interaction are discussed on the basis of the band intensities and widths.

2. Experimental

Infrared photodissociation spectra of the hetero-dimer and trimer ions are measured by an ion guide spectrometer with two quadrupole mass filters. Details of the experimental procedure have been described elsewhere [11]. Briefly, complex ions are produced in an electron-impact ion source. Parent ions are isolated by the first mass filter and introduced into the ion guide. The parent ions are photodissociated by an infrared laser (Continuum Mirage 3000). The resultant fragment ions are mass-analyzed by the second mass filter. For normalizing the yields of the fragment ions, the power of the infrared laser is monitored by a pyroelectric detector (Molectron P1-15H-CC). The infrared photodissociation spectra are obtained from the normalized yields of the fragment ions as a function of wavenumber of the infrared laser. The fragment ions detected are aniline$^+$ and aniline$^+$–M for aniline$^+$–M hetero-dimer and aniline$^+$–benzene–M hetero-trimer ions, respectively. Fully deuterated toluene (toluene-d_8) is used here, because the mass number of aniline and toluene-d_0 is close to each other.

3. Results and discussion

3.1. Dimer ions

Figure 2 shows the infrared photodissociation spectra (solid curves) of the aniline$^+$–M dimer ions (M = benzene (a), toluene-d_8 (b), thiophene (c), furan (d), water (e), methanol (f), ethanol (g)). Most of the spectra in Fig. 2 have been already reported independently in our previous papers [5, 7, 8, 12] except for the result of M = toluene-d_8. A sharp band emerges around 3445 cm^{-1} in all the spectra. In the spectra of the benzene, toluene-d_8 and thiophene complexes, two broad bands emerge at 3283 and 3202 (benzene), 3290 and 3198 (toluene-d_8) and 3291 and 3197 cm^{-1} (thiophene). In the case of the water, methanol and ethanol complexes, a very broad band is observed at 3109 (water), 2915 (methanol) and 2921 cm^{-1} (ethanol). In addition, a very weak and broad absorption is seen around 3300 cm^{-1}. The features in each spectrum can be adequately approximated by the sum of three Lorentzian functions (dotted curves); four functions are necessary only for the furan complex. Table 1 collects parameters obtained by fitting the band shape by Lorentzian functions.

All the dimers investigated here have two strong bands of the NH stretching fundamentals of aniline$^+$ in the 2700–3600 cm^{-1} region. The band around 3445 cm^{-1} is assigned to the stretching vibration of an uncoupled free NH bond, because the band is located in the middle of the symmetric and antisymmetric NH stretching bands of aniline$^+$ [4]. The appearance of this band confirms that all the dimer ions studied here have a free NH bond; the other one is involved in an N–H•••M hydrogen bond, as shown in Fig. 1a. The complexes with benzene, toluene-d_8 and thiophene possess an N–H•••π hydrogen bond; there is a σ-type hydrogen bond in the water, methanol and ethanol complexes [5, 7, 8, 12]. The stronger band centered at 3202 (benzene), 3198 (toluene-d_8), 3197 (thiophene), 3109 (water), 2915 (methanol) and 2921 cm^{-1} (ethanol) are assigned to the stretching vibration of the hydrogen-bonded NH oscillator.

The remaining absorption band is an overtone or a combination band. Schmid et al. ascribed the band at 3270 cm^{-1} in the spectra of aniline$^+$–M (M = N_2, CH_4, CHF_3, CO) either to the NH_2 bending overtone or to a ring stretching overtone [9]. Solcà and Dopfer a ssigned the 3270 cm^{-1} band in the spectrum of aniline$^+$–Ar to the NH_2 bending overtone, because the frequency is twice the frequency of the NH_2 bending fundamental of aniline$^+$–Ar (1635 cm^{-1}) [13]. The infrared spectra of aniline$^+$–$(\mathrm{N}_2)_{1-5}$ showed the NH_2 bending overtone band in the 3274–3283 cm^{-1} region [14]. From a similarity of the band position, we ascribe the bands at 3283 (benzene), 3290 (toluene-d_8) and 3291 cm^{-1} (thiophene) to the NH_2 bending overtone. The frequency of the NH_2 bending overtone of these dimers is higher than that of the aniline$^+$ monomer (3270 cm^{-1}) [4], suggesting an interaction with a vibration whose frequency is lower than 3270 cm^{-1}. The intensity of the NH_2 bending overtone is stronger than that of the free NH stretching band around 3445 cm^{-1}. In the case of aniline$^+$–Ar, in which the NH_2 bending overtone is scarcely perturbed by other vibrations, the integrated intensity of the overtone band seems to be less than 10 % of that of the NH stretching bands [4]. Finally, the width of the overtone band is almost the same as that of the hydrogen-bonded NH stretching band: 35 and 34 (benzene), 41 and 43 (toluene-d_8) and 49 and 47 cm^{-1} (thiophene), whereas the width of the free NH stretching band is approximately 20 cm^{-1} for all the dimer ions. These results suggest that Fermi resonance interaction occurs between the NH_2 bending overtone and the hydrogen-bonded NH stretching fundamental. For aniline$^+$–ethanol, a noticeable discrepancy between the observed and reproduced spectra is seen in the 3050–3200 cm^{-1} region. It can be assigned to the CH stretching vibrations of the aniline$^+$ ion [5].

In order to obtain unperturbed frequencies of the benzene, toluene-d_8 and thiophene complexes, we use the treatment reported by Wolff et al. [15, 16]. If the infrared intensity of the overtone itself is negligibly small, a coupling energy, W, and a difference between the unperturbed frequencies, $\Delta\nu^0$, are described as follows:

$$W = R^{1/2} \bullet \Delta\nu/(R+1), \tag{1}$$

$$\Delta\nu^0 = (R-1) \bullet \Delta\nu/(R+1), \tag{2}$$

where R and $\Delta\nu$ are the relative intensity and frequency difference of the two bands observed in the infrared spectra. The unperturbed frequencies, $\nu_2{}^0$ and $\nu_3{}^0$, are obtained by the equations,

$$\nu_2{}^0 = (\nu_2 + \nu_3 + \Delta\nu^0)/2, \tag{3}$$

$$\nu_3{}^0 = (\nu_2 + \nu_3 - \Delta\nu^0)/2, \tag{4}$$

where ν_2 and ν_3 are the perturbed frequencies. We obtain the following values for the unperturbed frequencies of the NH_2 bending overtone: 3256 (benzene), 3255 (toluene-d_8) and 3255 cm^{-1} (thiophene).

For the water, methanol and ethanol complexes, the existence of the broad absorption around 3300 cm^{-1} suggests the intensity borrowing of the NH_2 bending overtone transition from the hydrogen-bonded NH stretching fundamental one. The NH stretching band of each cluster is more red-shifted than that of the π-hydrogen-bonded complexes. Therefore, the intensity borrowing occurs less efficiently and the overtone band becomes weaker. The weakness makes it difficult to fit the spectrum by Lorentzian functions with fully adjustable parameters. We use the same width parameter for the ν_2 and ν_3 bands of each dimer; in addition, the position of the ν_2 band of the water complex is fixed to 3290 cm^{-1}. Thus the unperturbed frequencies of the NH_2 bending overtone are calculated to be 3276 (water), 3270 (methanol) and 3273 cm^{-1} (ethanol).

The spectrum of the aniline$^+$–furan ion is decomposed into four Lorentzian components centered at 3446, 3312, 3204 and 3119 cm^{-1}. Honkawa et al. reported that there are two structural isomers for aniline$^+$–furan [12]. One isomer is formed through a σ-type hydrogen bond (σ-isomer), where an NH bond is bound to the oxygen atom of the furan molecule. The other involves a π-hydrogen bond (π-isomer) between an NH bond and the π-electron cloud of furan. The components at 3119 and 3204 cm^{-1} are assigned to the hydrogen-bonded NH stretching bands of the σ- and π-isomers, respectively. The 3312 cm^{-1}

band is ascribed to the NH_2 bending overtone. The aniline$^+$–water ion shows the hydrogen-bonded NH stretching band at 3109 cm^{-1}; the position is almost the same as that of the σ-isomer (3119 cm^{-1}). The intensity of the NH_2 bending overtone of aniline$^+$–water is quite weak. For aniline$^+$–furan, therefore, most of the overtone intensity comes from the π-isomer. By using the values of the position and relative intensity of the π-isomer band at 3204 cm^{-1}, we obtain the unperturbed frequency of 3267 cm^{-1} for the NH_2 bending overtone.

All the values obtained here are listed in Table 1. The most unambiguous values for the unperturbed frequencies of the NH_2 bending overtone, $\nu_2{}^0$, are those of the benzene (3256 cm^{-1}), toluene-d_8 (3255 cm^{-1}) and thiophene (3255 cm^{-1}) complexes. These values are slightly lower than that of the aniline$^+$ monomer (3270 cm^{-1}) [4]. The furan complex has the $\nu_2{}^0$ value of 3267 cm^{-1}. The complexes of water, methanol and ethanol also show the reasonable $\nu_2{}^0$ values of 3276, 3270 and 3273 cm^{-1}, respectively. For all the dimers, the NH_2 bending overtone frequency is almost intact and the amount of the red-shift upon the complex formation falls within 15 cm^{-1}.

3.2. Trimer ions

Figure 3 displays the infrared photodissociation spectra of the aniline$^+$–benzene–M trimer ions (M = toluene-d_8 (a), thiophene (b), furan (c), water (d), methanol (e), ethanol (f)). These spectra can be approximated by the sum of an appropriate number of Lorentzian functions. We collect the values of the band positions, widths and relative intensities in Table 2. The spectrum of aniline$^+$–benzene–toluene-d_8 is decomposed into three Lorentzian components centered at 3197, 3282 and 3321 cm^{-1}. The aniline$^+$–benzene–toluene-d_8 ion probably has two N–H•••π hydrogen bonds [6]. We assign the bands at 3197 and 3321 cm^{-1} to the NH stretching vibrations of the N–H•••toluene-d_8 and N–H•••benzene parts, respectively. The NH stretching vibration of the N–H•••benzene part of aniline$^+$–benzene

–toluene-d_8 has the frequency (3321 cm^{-1}) higher than that of aniline^{+}–benzene (3202 cm^{-1}). Preliminary molecular orbital calculations confirm the increase of the frequency from aniline^{+}–benzene to aniline^{+}–benzene–toluene-d_8. The 3282 cm^{-1} band is attributed to the NH$_2$ bending overtone. Because the π-hydrogen bond with toluene-d_8 is similar to that with benzene in this trimer, the intensity of both NH stretching bands should be almost the same as each other. However, the intensity of the 3197 cm^{-1} band is weaker than that of the 3321 cm^{-1} band. The intensity reduction of the former band is explained by Fermi resonance interaction between the NH stretching fundamental of the N–H•••toluene-d_8 part and the NH$_2$ bending overtone. As listed in Table 2, the sum of the intensities of the 3197 and 3282 cm^{-1} bands is close to the intensity of the 3321 cm^{-1} band. This result suggests that the NH$_2$ bending overtone borrows most of the intensity from the NH stretching fundamental of the N–H•••toluene-d_8 part. This conclusion is consistent with that of the aniline^{+} hetero-dimer ions; Fermi resonance interaction occurs between the NH$_2$ bending overtone and the lower-frequency band of the two NH stretching vibrations. The spectrum of aniline^{+}–benzene–thiophene (Fig. 3b) can be decomposed into three Lorentzian functions in a similar manner as that of aniline^{+}–benzene–toluene-d_8. The components at 3203, 3296 and 3331 cm^{-1} are assigned to the NH stretching of the N–H•••thiophene part, NH$_2$ bending overtone and NH stretching of the N–H•••benzene part, respectively. There appears a difference in the band width of these components between aniline^{+}–benzene–toluene-d_8 and aniline^{+}–benzene–thiophene. The three components of aniline^{+}–benzene–toluene-d_8 have a band width almost the same as each other. For aniline^{+}–benzene–thiophene, on the other hand, the NH stretching band of the N–H•••thiophene part shows a band width of 53 cm^{-1}, while the overtone band displays a width of 37 cm^{-1}. These values are larger than that of the NH stretching band of the N–H•••benzene part (31 cm^{-1}). This result may imply that the NH$_2$ bending overtone borrows the intensity from the NH stretching fundamental of the N–H•••thiophene part.

In the infrared spectra of aniline$^+$–benzene–furan and aniline$^+$–benzene–water (Figs. 3c and 3d), two maxima appear in the 3000–3400 cm^{-1} region. We ascribe the lower- and higher-frequency bands to the NH stretching bands of the N–H•••M (M = furan and water) and N–H•••benzene parts, respectively. These spectra can be decomposed into two Lorentzian functions. The NH_2 bending overtone may exist around 3300 cm^{-1}, overlapping with the NH stretching band of the N–H•••benzene part. A sign of the overlap is manifested in the intensity and width of the high-frequency bands. As mentioned above, the NH stretching band at lower frequency efficiently gives its infrared intensity to the NH_2 bending overtone in the case of aniline$^+$–benzene–toluene-d_8 and aniline$^+$–benzene–thiophene. As seen in Figs. 3c and 3d, the NH stretching band of the N–H•••M part shows a red shift from furan (3161 cm^{-1}) to water (3117 cm^{-1}). We expect that the red shift causes the decrease in the intensity of the NH_2 bending overtone and the increase of the NH stretching fundamental as a result of decoupling. Actually, the relative intensity of the lower-frequency band to the higher-frequency one increases from the furan (0.51) to water (0.87) complexes. The width of the higher-frequency band decreases drastically from the furan (70 cm^{-1}) to water (43 cm^{-1}) complexes. The decrease suggests reduced coupling with the NH stretching band of the N–H•••M part at lower frequency, which should be broader than the N–H•••benzene part.

The same consideration can explain the spectral features of aniline$^+$–benzene–methanol and aniline$^+$–benzene–ethanol. As seen in Figs. 3e and 3f, the infrared spectra show only one band at 3295 (methanol) and 3298 cm^{-1} (ethanol). These bands are assigned to the NH stretching of the N–H•••benzene part. The NH stretching band of the N–H•••methanol and N–H•••ethanol part should exist below 3000 cm^{-1}. For both trimers, the band width is 30 cm^{-1}, which is narrower than that of aniline$^+$–benzene–water (43 cm^{-1}). The band position is similar to that of the NH_2 bending overtone observed for the toluene-d_8 and thiophene complexes. The absence of splitting and broadening implies negligibly small interaction between the NH_2 bending overtone and the NH stretching of the N–H•••benzene pa rt. Inspection of Fig. 3 shows that the infrared spectra (solid curves) deviate from the Lorentzian functions (dotted curves) to some extent in the 3100–3250 cm^{-1} region. This absorption may be ascribed to the NH_2 bending overtone that borrows the intensity from the NH stretching fundamental of the N–H•••methanol or N–H•••ethanol part, because the aniline$^+$–methanol and aniline$^+$–ethanol dimer ions display the broad spectral feature of the NH_2 bending overtone in the 3200–3400 cm^{-1} region. Consequently, in the aniline$^+$ hetero-trimer ions, the NH_2 bending overtone gains the infrared intensity through Fermi resonance interaction with the stretching fundamental of the NH oscillator involved in the stronger N–H•••M hydrogen bond.

4. Conclusion

We have investigated vibrational mode mixing in hetero-dimer and trimer ions containing aniline$^+$. For the dimer ions, the NH_2 bending overtone gains the intensity through Fermi resonance interaction with the hydrogen-bonded NH stretching fundamental. From the band position and relative intensity, the unperturbed vibrational frequencies are obtained. For all the dimers studied here, the unperturbed frequencies of the NH_2 bending overtone are almost the same as that of the aniline$^+$ monomer. For the trimer ions, the NH_2 bending overtone borrows the intensity mainly from the stretching fundamental of NH in the stronger hydrogen bond.

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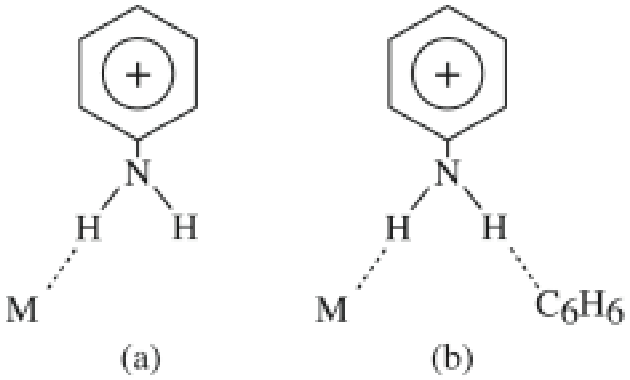

Figure 1. Inokuchi et al.

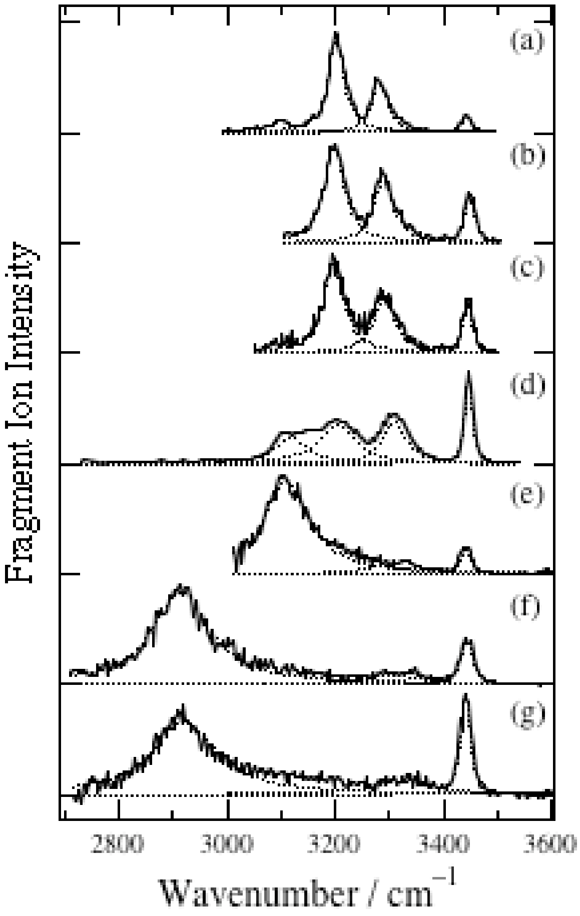

Figure 2. Inokuchi et al.

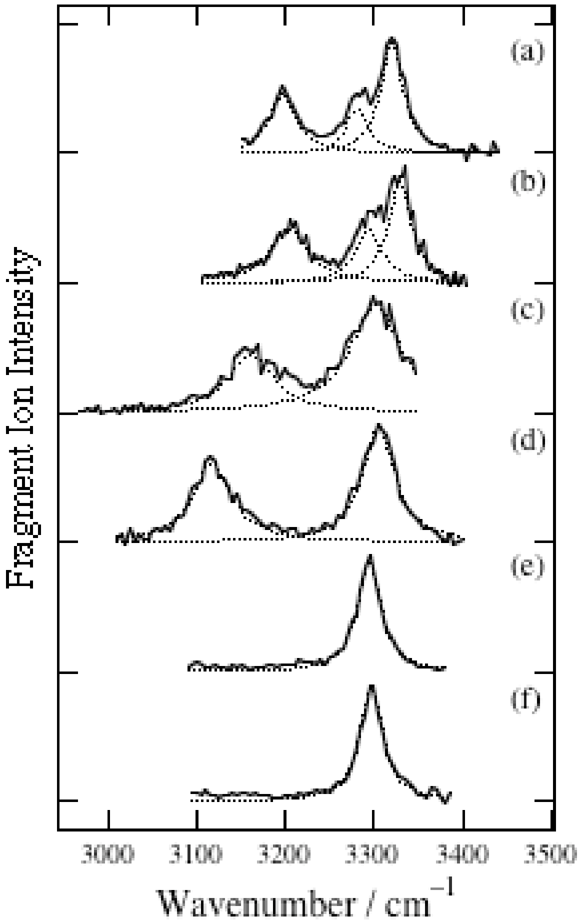

Figure 3. Inokuchi et al.

Figure captions

Figure 1. Schematic drawing of structures of dimer (a) and trimer (b) ions containing aniline$^+$ investigated in this work.

Figure 2. Infrared photodissociation spectra (solid curves) of aniline$^+$–M (M = benzene (a), toluene-d_8 (b), thiophene (c), furan (d), water (e), methanol (f), ethanol (g)). Dotted curves show Lorentzian functions used to decompose the spectra.

Figure 3. Infrared photodissociation spectra (solid curves) of aniline$^+$–benzene–M (M = toluene-d_8 (a), thiophene (b), furan (c), water (d), methanol (e), ethanol (f)). Dotted curves show Lorentzian functions used to decompose the spectra.