

Electronic and vibrational spectra of aniline–benzene hetero-dimer and aniline homo-dimer ions

Kazuhiko Ohashi^{a,*}, Yoshiya Inokuchi^b, Hironobu Izutsu^a,
Kazuyuki Hino^a, Norifumi Yamamoto^a, Nobuyuki Nishi^b, Hiroshi Sekiya^{a,#}

^a *Department of Molecular Chemistry, Graduate School of Science, Kyushu University,
Hakozaki, Fukuoka 812-8581, Japan*

^b *Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan*

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Abstract

Structures of (aniline–benzene)⁺ and (aniline)₂⁺ are re-investigated by electronic spectroscopy in the near-infrared region and vibrational spectroscopy in the NH stretching region. The spectra of (aniline–benzene)⁺ indicate a structure including a hydrogen bond between an NH bond of the ionic aniline and the π -electrons of the neutral benzene. Two isomers are suggested for (aniline)₂⁺ in which an NH bond of the ionic aniline forms different types of hydrogen bond with the neutral aniline: one with the π -electrons of the aromatic ring and the other with the lone pair of the nitrogen atom.

* Corresponding author. Fax: +81 92 642 2607; e-mail: kazu.scc@mbox.nc.kyushu-u.ac.jp

Corresponding author. Fax: +81 92 642 2607; e-mail: hsekiscc@mbox.nc.kyushu-u.ac.jp

1. Introduction

Spectroscopic methods offer the most direct approach to structural investigations of cluster ions [1]. Vibrational spectroscopy is particularly useful for probing intermolecular interactions [2,3], because certain vibrational modes are quite sensitive to intermolecular perturbations. For the molecules with OH and NH bonds, vibrational spectra in the OH and NH stretching regions provide information on the type of hydrogen bonds involved in cluster ions. For the molecules with aromatic rings, in addition, electronic spectra in the near-infrared wavelength region can be used to gauge the magnitude of charge resonance (CR) interactions among component molecules in cluster ions.

The principal intermolecular interaction is the CR interaction between the π -electrons of the aromatic rings for dimer ions such as (benzene) $_2^+$, (toluene) $_2^+$ and (*p*-difluorobenzene) $_2^+$ [4]. On the other hand, the hydrogen bonding interaction is expected to be significant in dimer ions of the molecules with OH and NH bonds. We measured the electronic spectra of (phenol) $_2^+$ and (phenol–benzene) $^+$ and showed that the CR interaction is not significant in these ions [5,6]. Fujii et al. observed the vibrational spectra of these dimer ions in the OH stretching region [7,8]. The spectra indicate that (phenol) $_2^+$ contains a single hydrogen bond between the OH bond of one phenol and the oxygen atom of the other, and that (benzene–phenol) $^+$ includes a hydrogen bond between the OH bond of phenol and the π -electrons of benzene. Nakanaga et al. reported the vibrational spectra of (aniline–benzene) $^+$ and (aniline) $_2^+$ [9]. They proposed that (aniline–benzene) $^+$ contains a hydrogen bond between one of the NH bonds of aniline and the π -electrons of benzene (Fig. 1a). On the basis of ab initio molecular orbital (MO) calculations for (aniline) $_2^+$, they showed that the NH bond of the ionic aniline is able to interact with two different sites of the neutral aniline: the π -electrons of the aromatic ring (NH– π -type structure, Fig. 1b) and the lone pair of the nitrogen atom (NH–N-type structure, Fig. 1c). However, the vibrational spectrum of (aniline) $_2^+$ measured by Nakanaga et al. was indicative of only the NH–N-type structure [9].

In this Letter, we re-investigate the structures of (aniline–benzene) $^+$ and (aniline) $_2^+$. We record the electronic spectra of these ions in the near-infrared region for the first time. The spectra indicate that the CR interaction between the component molecules is not

significant in (aniline–benzene)⁺ and (aniline)₂⁺. Next, we re-examine the vibrational spectra of these ions, extending the measurement to the frequency region lower than the earlier work [9]. The spectrum of (aniline–benzene)⁺ is consistent with the π -type hydrogen-bonded structure proposed before [9], but we need to revise the assignment of the hydrogen-bonded NH band. The spectrum of (aniline)₂⁺ gives an indication of the NH– π -type structure, in addition to the NH–N-type structure deduced previously [9].

2. Experimental

We apply the photodissociation spectroscopy to the mass-selected ions in the gas phase. Electronic spectra in the near-infrared region are measured by using an apparatus with a reflectron-type time-of-flight (TOF) mass spectrometer [4,10]. The photodissociation cross sections are determined from the intensity of the parent ions measured with and without the dissociation laser; details of the procedure have been described elsewhere [5,11]. Vibrational spectra in the infrared region are recorded by using an apparatus with a quadrupole ion guide and two quadrupole mass filters [12,13]. The spectra are obtained from the yields of (aniline)⁺ as functions of wavenumber of the infrared laser, because only (aniline)⁺ is detected as the fragment ion of both (aniline–benzene)⁺ and (aniline)₂⁺.

3. Results and discussion

3.1. Electronic spectra

Fig. 2 displays the photodepletion spectra of (a) (aniline–benzene)⁺ and (b) (aniline)₂⁺ in the near-infrared region. The closed circles represent the cross sections of (aniline–benzene)⁺ and (aniline)₂⁺ obtained from the photodepletion efficiency of the parent ions. As indicated by the broken curve, the spectrum of (benzene)₂⁺ shows the strong CR band around 920 nm and the weaker one around 1160 nm. The experimental uncertainties are large at wavelengths where the cross sections of (benzene)₂⁺ are enormous, because we should reduce the intensity of the dissociation laser to avoid saturation of the photodepletion efficiency. The (aniline–benzene)⁺ ion shows no appreciable band in this region. The cross sections of (aniline)₂⁺ are at most 3 % of the maximum cross section of (benzene)₂⁺.

3.2. Vibrational spectra

Fig. 3 shows the infrared photodissociation spectra of (a) (aniline–benzene)⁺ and (b) (aniline)₂⁺. Four distinct bands are seen around 3100, 3200, 3280 and 3440 cm⁻¹ in the spectrum of (aniline–benzene)⁺. The first two bands were not observed previously [9]. The 3280-cm⁻¹ band may correspond to the band observed at 3305 cm⁻¹ by Nakanaga et al. [9]. These discrepancies must be due to a drop in the intensity of their laser; the intensity decreased rapidly with decreasing the wavenumber below 3300 cm⁻¹ in the previous study, whereas the intensity is almost constant over the region of 3000–3500 cm⁻¹ in the present study. The spectrum of (aniline)₂⁺ exhibits two small humps around 3050 and 3100 cm⁻¹ and three prominent bands around 3180, 3270 and 3415 cm⁻¹. An extremely broad feature underlying the humps and bands extends from 2600 to 3500 cm⁻¹. Nakanaga et al. detected only the 3415-cm⁻¹ band [9]. The width of the 3415-cm⁻¹ band in Fig. 3b (approximately 35 cm⁻¹) is narrower than that observed previously (more than 50 cm⁻¹), suggesting that the parent ions prepared in this work are colder than those in the experiment made by Nakanaga et al. [9]. It is improbable, therefore, that the new bands in our spectrum originate from vibrationally hot ions.

3.3. Structure of (aniline–benzene)⁺

The electronic spectrum displayed in Fig. 2a indicates that the CR interaction is absent in (aniline–benzene)⁺. The observation suggests that the two aromatic rings do not take a sandwich-like form and that the positive charge is localized on the aniline molecule with lower ionization energy. Nakanaga et al. optimized the structure of (aniline–benzene)⁺ by ab initio MO calculations at the UHF/6-31G** level [9]. Fig. 1a depicts the optimized structure with a hydrogen bond between one of the NH bonds of the ionic aniline and the π -electrons of the neutral benzene.

Nakanaga et al. observed two absorption bands at 3440 and 3305 cm⁻¹ in the infrared spectrum, while they estimated the frequencies of 3474 and 3329 cm⁻¹ for the NH stretching vibrations by ab initio MO calculations [9]. Since the agreement between the observed and calculated frequencies was fairly good, they assigned the observed bands to the stretching

vibrations of the two NH bonds of aniline. Additional bands are newly observed in the present spectrum exhibited in Fig. 3a. The weak bands in the 3000–3100-cm⁻¹ region can be attributed to the CH stretching vibrations of the neutral benzene [14] and the ionic aniline [15]. The most intense band is observed at 3200 cm⁻¹ besides the two bands reported previously [9]. The appearance of three bands above 3100 cm⁻¹ is puzzling, because we expect the observation of only two bands due to the stretching vibrations of the two NH bonds. One explanation is that the extra band arises from a structural isomer of (aniline–benzene)⁺. However, the structure optimization indicates that only one structure is stable [9,16]. Another explanation is that the extra band is due to a vibrational mode other than the NH stretching modes. Schmid et al. observed two additional bands around 3270 and 3240 cm⁻¹ in the infrared spectra of (aniline–X)⁺ with X being N₂, CH₄, CHF₃ and CO [17]. They assigned these bands to the overtone of the NH₂-bending vibration or to the overtone of the ring stretching vibration. We tentatively attribute the 3280-cm⁻¹ band in Fig. 3a to such a vibration, rather than the NH stretching vibration as proposed initially [9]. Then we assign the 3200-cm⁻¹ band, instead of the 3280-cm⁻¹ band, to the stretching vibration of the NH bond connected with benzene through the hydrogen bond. The 3440-cm⁻¹ band is attributed unambiguously to the stretching vibration of the NH bond free from the hydrogen bond. The hydrogen-bonded NH band is more than five times as strong as the free NH band; the observation is consistent with the infrared absorption intensity calculated by Nakanaga et al. [9]. The frequency shifts of these bands from the symmetric and anti-symmetric stretching bands of the bare aniline ion are 195 and 48 cm⁻¹, respectively. The large differences in the intensity and the frequency shift between the two bands indicate that one of the NH bonds of the aniline ion interacts with the π -electrons of the neutral benzene. The results of the electronic and vibrational spectroscopy are totally consistent with the π -type hydrogen-bonded structure of (aniline–benzene)⁺ (Fig. 1a) proposed earlier [9].

3.4. Structure of (aniline)₂⁺

The electronic spectrum displayed in Fig. 2b indicates that the CR interaction is insignificant in (aniline)₂⁺. The observation suggests that the positive charge is localized on

one of the two aniline molecules. The charged aniline molecule acts as a proton donor in hydrogen bonds, because the acidity of the ionic aniline is stronger than that of the neutral aniline [17]. Nakanaga et al. proposed two possible structures for $(\text{aniline})_2^+$ from ab initio MO calculations [9]. One includes a hydrogen bond between the NH bond of the ionic aniline and the aromatic ring of the neutral aniline (Fig. 1b), and the other includes a hydrogen bond between the NH bond of the ionic aniline and the nitrogen atom of the neutral aniline (Fig. 1c).

The prominent bands observed in the infrared spectrum of $(\text{aniline})_2^+$ can be attributed to the NH stretching vibrations of the ionic moiety, because the infrared absorption intensity of the neutral moiety was evaluated to be much smaller than that of the ionic moiety [9]. The vibrational frequencies of the ionic moiety were calculated to be 3470 and 3327 cm^{-1} for the NH- π -type structure, and 3438 and 3051 cm^{-1} for the NH-N-type structure [9]. The position of the lower-frequency band can be used to discriminate the two structures. The infrared spectrum reported by Nakanaga et al. showed no band in the region from 3200 to 3350 cm^{-1} [9], where the lower-frequency band of the NH- π -type structure (3327 cm^{-1}) was expected to appear. Accordingly, they ruled out the NH- π -type structure and adopted the NH-N-type structure. As exhibited in Fig. 3b, however, new bands are observed around 3180 and 3270 cm^{-1} . These bands are too weak to be attributed to the hydrogen-bonded NH band of the NH-N-type structure. A convincing explanation is that the NH- π -type isomer exists in addition to the NH-N-type structure. We ascribe the 3180- and 3270- cm^{-1} bands to the NH- π -type isomer of $(\text{aniline})_2^+$ by analogy with the 3200- and 3280- cm^{-1} bands of $(\text{aniline-benzene})^+$. The contribution of the NH- π -type isomer to the intensity of the 3415- cm^{-1} band may be small, because the free NH band is expected to be much weaker than the hydrogen-bonded NH band at 3180 cm^{-1} . The NH-N-type isomer should be the dominant isomer and responsible for a large part of the 3415- cm^{-1} band.

Finally, we direct our attention to the hydrogen-bonded NH band of the NH-N-type isomer. Ab initio MO calculations at the UHF/6-31G** level estimated a frequency of 3051 cm^{-1} [9]. A lower frequency of 2789 cm^{-1} was calculated at the MP2/6-31G** level for the hydrogen-bonded NH band of the ionic aniline in $(\text{aniline-NH}_3)^+$, where the NH bond

interacts with the nitrogen atom of NH_3 [18]. Since the proton affinities of aniline and NH_3 are close to each other [19], $(\text{aniline-NH}_3)^+$ and the NH–N-type isomer of $(\text{aniline})_2^+$ are expected to show the hydrogen-bonded NH band at a similar position. The infrared spectrum of $(\text{aniline})_2^+$ exhibits no prominent band in the region below 3100 cm^{-1} except for the small humps around 3050 and 3100 cm^{-1} . The position of the former hump coincides with the frequency of 3051 cm^{-1} calculated for the hydrogen-bonded NH band of the NH–N-type isomer, but the hump is too small to be assigned to the hydrogen-bonded NH band. We prefer to assign the humps around 3050 and 3100 cm^{-1} to the CH stretching vibrations of the neutral and ionic molecules [15,20] in $(\text{aniline})_2^+$, respectively. The cluster ions of $(\text{phenol})_n^+$, $[\text{phenol-(H}_2\text{O)}_n]^+$ and $(\text{phenol-methanol})^+$ display no prominent band in the region of $2900\text{--}3600\text{ cm}^{-1}$ except for an extremely broad feature [7,8], which can be regarded as the hydrogen-bonded OH band. Similarly, we propose that the broad feature observed in the $2600\text{--}3500\text{ cm}^{-1}$ region of the spectrum of $(\text{aniline})_2^+$ is due to the hydrogen-bonded NH band of the NH–N-type isomer.

4. Conclusions

We have investigated the electronic spectra of $(\text{aniline-benzene})^+$ and $(\text{aniline})_2^+$ in the near-infrared region for the first time. The spectra indicate that the CR interaction is absent in $(\text{aniline-benzene})^+$ and insignificant in $(\text{aniline})_2^+$. We have re-examined the infrared spectra of these ions in the region of the NH stretching vibrations. The spectrum of $(\text{aniline-benzene})^+$ is consistent with the structure including a π -type hydrogen bond proposed previously [9], but we have revised the assignment of the hydrogen-bonded NH band. The previous study concluded that $(\text{aniline})_2^+$ had a single structure including an NH–N-type hydrogen bond [9]. However, the present spectrum of $(\text{aniline})_2^+$ suggests the existence of the NH– π -type hydrogen-bonded structure, in addition to the NH–N-type structure. Theoretical calculations at reliably high levels are desired for discussing the structure of these ions in further detail.

Acknowledgements

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Figure Captions

Fig. 1. Schematic illustration of (a) π -type hydrogen-bonded structure of (aniline–benzene)⁺, (b) NH– π -type and (c) NH–N-type hydrogen-bonded structures of (aniline)₂⁺ reported by Nakanaga et al. [9].

Fig. 2. Electronic spectra of (a) (aniline–benzene)⁺ and (b) (aniline)₂⁺. Closed circles represent the cross sections of (aniline–benzene)⁺ and (aniline)₂⁺ scaled to the maximum cross section of (benzene)₂⁺ at 920 nm. Error bars indicate one standard deviation of statistical uncertainties determined from at least 10 sets of the measurement. Broken curve in each panel is the spectrum of (benzene)₂⁺ for reference.

Fig. 3. Vibrational spectra of (a) (aniline–benzene)⁺ and (b) (aniline)₂⁺ obtained by monitoring the yields of (aniline)⁺ as functions of wavenumber of the infrared laser.

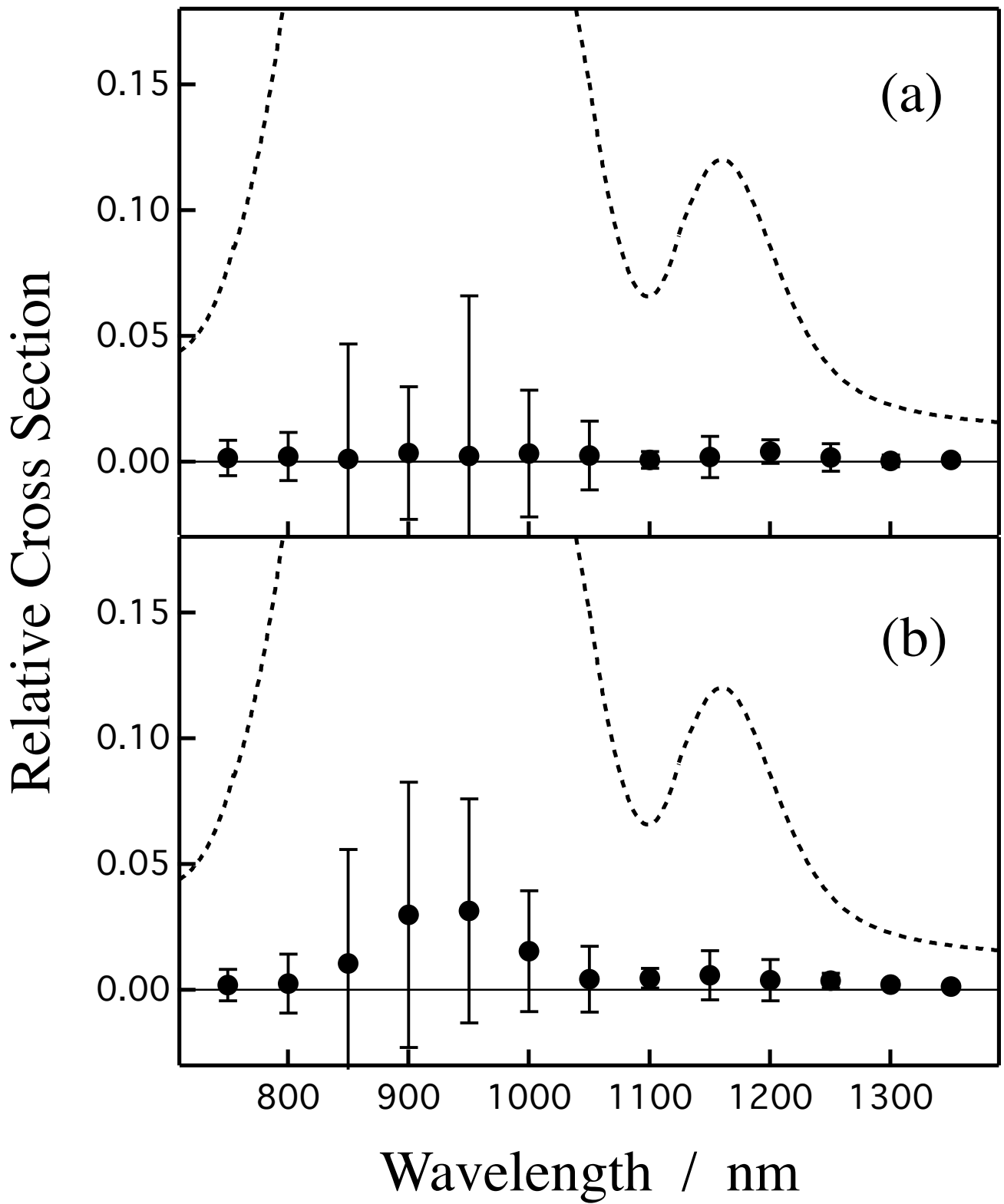


Fig. 2. Ohashi et al.

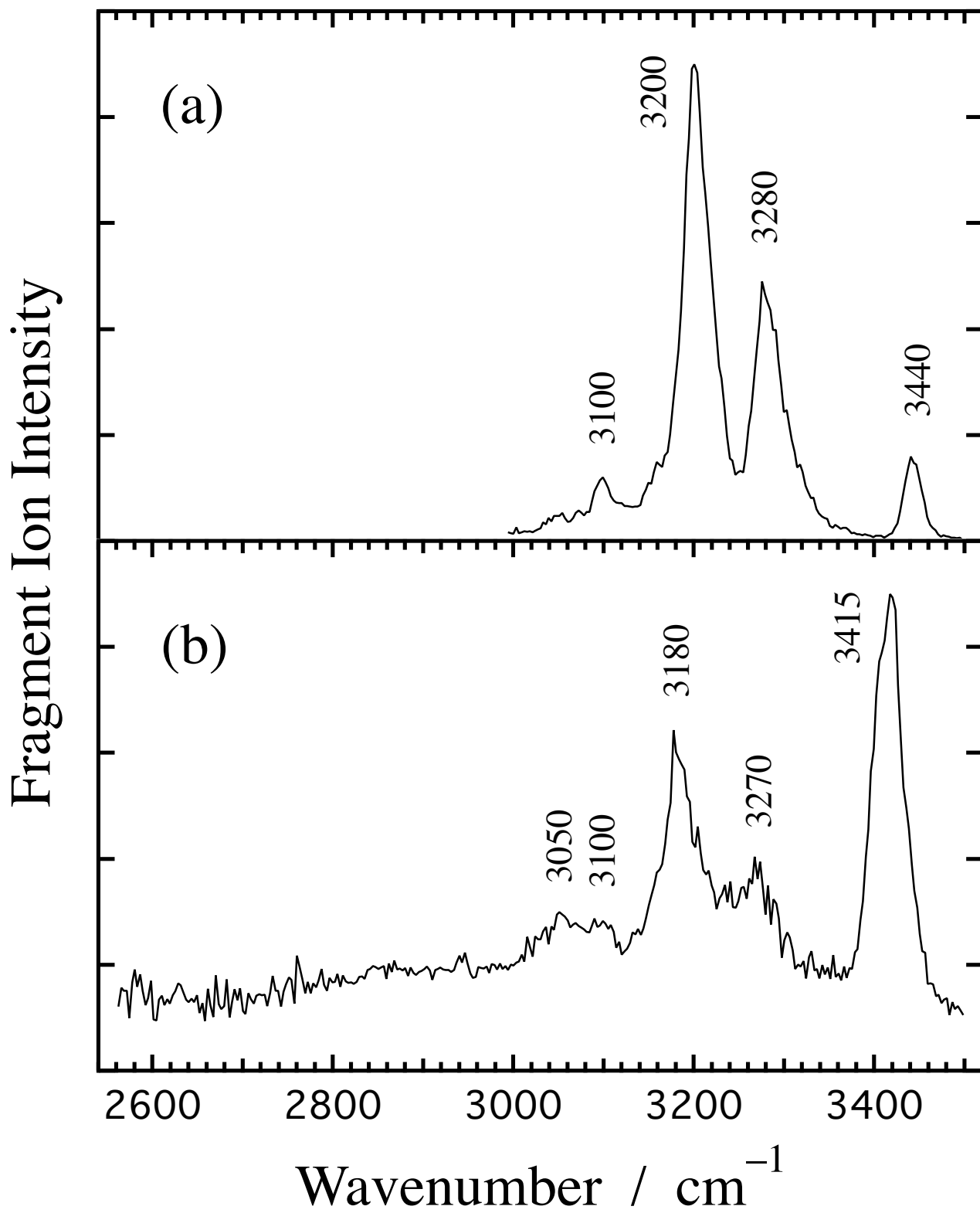


Fig. 3. Ohashi et al.