

**Vibrational and electronic spectra of (benzene–benzyl alcohol)⁺.
Predominance of charge resonance interaction
over hydrogen bonding interaction**

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Abstract

Vibrational and electronic spectra of the benzene–benzyl alcohol hetero-dimer ion are measured by photodissociation spectroscopy. The vibrational spectrum shows a prominent band at $3662\pm 3\text{ cm}^{-1}$, which is assigned to the stretching vibration of the OH group free from intermolecular perturbations. The electronic spectrum shows a broad band around 950 nm, which arises from a charge resonance interaction between the aromatic rings. These results suggest that the ion has a sandwich-like structure suitable for the resonance interaction, *without* the hydrogen bond between the OH group of benzyl alcohol and the π -electrons of benzene.

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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 an answer to the question whether hydrogen bonds are involved in cluster ions of these molecules. 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.

For homo-dimer ions of benzene, toluene and *p*-difluorobenzene, the transition energy of the CR band was found to be just twice the binding energy [4]. The result suggests that the dominant contribution to the binding energy is from the CR interaction between the π -electron systems belonging to the aromatic rings. Strong bands were also observed in the near-infrared region of the electronic spectrum of (benzene–toluene)⁺ [5], indicating that a near-resonance interaction is important in the hetero-dimer ion as well as the CR interaction in the homo-dimer ions. These dimer ions are expected to have a sandwich-like structure so that the mutual orientation of the component molecules is appropriate for the CR interaction. Alternatively, hydrogen bonding interactions seem to be dominant in hetero-dimer ions composed of benzene and other molecules with OH or NH bond. Fujii et al. observed the vibrational spectrum of (benzene–phenol)⁺ [6]. They found an extremely large red-shift and a substantial broadening of the band due to the OH stretching vibration. The result indicates that (benzene–phenol)⁺ has a structure with a hydrogen bond between the OH bond of phenol and the π -electrons of benzene. Nakanaga et al. proposed that (benzene–aniline)⁺ also has a hydrogen-bonded structure, where aniline is bound to benzene through a π -type hydrogen bond [7]. In these dimer ions, the hydrogen bonding interaction overwhelms the CR interaction.

The main purpose of this work is to characterize the intermolecular interaction in the benzene–benzyl alcohol hetero-dimer ion. The magnitude of the intermolecular resonance interaction decreases with increasing the difference in the ionization energies (Δ IE) of the component molecules [6]. The IE of benzene and benzyl alcohol is reported to be 9.243842

[8] and 8.963 eV [9], respectively. The resulting ΔIE of 0.281 eV is considered to be small enough for the near-resonance interaction. On the other hand, the OH group of benzyl alcohol has an ability to form a hydrogen bond with the π -electrons of benzene. We measure vibrational and electronic spectra of (benzene–benzyl alcohol)⁺ to explore the CR and hydrogen bonding interactions in this ion.

2. Experimental

We apply the photodissociation spectroscopy to the mass-selected ion in the gas phase. We use two different sets of experimental apparatus. Each apparatus consists of a tandem mass spectrometer and a molecular beam source for preparing neutral clusters.

Vibrational spectra in the infrared region (3100–3800 cm⁻¹) are recorded by using an apparatus with a quadrupole ion guide and two quadrupole mass filters [10,11]. The parent ions are produced by electron-impact ionization of neutral clusters and selected through a quadrupole mass filter. After the deflection by an ion bender, the ion beam of (benzene–benzyl alcohol)⁺ is decelerated and introduced into a quadrupole ion guide. An infrared laser beam (Continuum, Mirage 3000) merges with the ion beam in the ion guide. Vibrational excitation induces the predissociation of the parent ions. After the deflection by another ion bender, mass numbers of the resulting fragment ions are analyzed by another quadrupole filter. Only (benzyl alcohol)⁺ is detected as the fragment ion from (benzene–benzyl alcohol)⁺ excited in the infrared region. Therefore, the vibrational spectrum is obtained from the yield of (benzyl alcohol)⁺ as a function of wavenumber of the infrared laser.

Electronic spectra in the near-infrared region (750–1400 nm) are measured by using an apparatus with a reflectron-type time-of-flight (TOF) mass spectrometer [4,12]. The parent ions are produced by resonant 2-photon ionization of neutral clusters in an acceleration region of the mass spectrometer. A packet of the selected ions is intersected by a dissociation laser beam (Spectra-Physics, MOPO-730) while traveling in the acceleration region. After the secondary acceleration, both the remaining parent and fragment ions are introduced into a drift chamber of the mass spectrometer. The ions are then reflected by an ion reflector and detected by a microchannel plate detector. For measuring photodissociation cross sections of

(benzene–benzyl alcohol)⁺ relative to those of (benzene)₂⁺, the dissociation laser beam is adjusted to irradiate the packets of these two ions simultaneously. The relative cross sections are determined from the depletion of the parent ion signals in the following way [13,14].

Fig. 1 shows the TOF mass spectra of the dimer ions without the dissociation laser (a) and with the laser (b). Ion signals observed at 44.1 and 48.1 μs are due to (benzene)₂⁺ and (benzene–benzyl alcohol)⁺, respectively. In Fig. 1b, the packets of both ions are irradiated simultaneously. Approximately 50 % of the (benzene)₂⁺ signal is depleted by the introduction of the dissociation laser. The depletion of approximately 40 % is also seen for (benzene–benzyl alcohol)⁺. The relation between the photodissociation cross section, σ , and the observed signal intensities is given by

$$\sigma \propto \ln(I_{\text{off}} / I_{\text{on}}), \quad (1)$$

where I_{on} and I_{off} are the intensities of the ion signals detected with and without the dissociation laser, respectively. The relative cross sections are estimated from the values of $\ln(I_{\text{off}} / I_{\text{on}})$ for (benzene–benzyl alcohol)⁺ and (benzene)₂⁺. We can finally obtain the spectrum of (benzene–benzyl alcohol)⁺, since we have already determined the cross section of (benzene)₂⁺ as a function of wavelength [4].

3. Results and discussion

3.1. Infrared spectrum

Fig. 2 exhibits the photodissociation spectrum of (benzene–benzyl alcohol)⁺ in the region of 3100–3800 cm⁻¹. The spectrum shows a prominent band at 3662±3 cm⁻¹; no appreciable signal is seen in the lower frequency region. The band can be assigned to the OH stretching vibration of the benzyl alcohol ion, because the positive charge stays mainly on the benzyl alcohol molecule with lower IE. In order to compare the frequency of this band with that of the bare (benzyl alcohol)⁺ ion, we also measure the infrared spectrum of (benzyl alcohol–Ar)⁺ [15]. Since the perturbation of the Ar atom to (benzyl alcohol)⁺ is considered to be small [16], the spectrum of (benzyl alcohol–Ar)⁺ is essentially the same with that of (benzyl alcohol)⁺. The most intense band is located at 3662±3 cm⁻¹, although weaker signals are seen in the lower frequency region [15]. The spectra of both (benzene–benzyl alcohol)⁺ and

(benzyl alcohol–Ar)⁺ show the OH stretching band at the same position. The frequency is slightly higher than that of the neutral benzyl alcohol (3650 cm⁻¹ for the dominant isomer [17]). These results suggest that the band of (benzene–benzyl alcohol)⁺ observed at 3662±3 cm⁻¹ is attributed to the stretching vibration of the OH group which is not perturbed by the benzene molecule.

3.2. Near-infrared spectrum

Fig. 3 displays the photodepletion spectrum of (benzene–benzyl alcohol)⁺ in the region of 750–1400 nm. The closed circles represent the cross sections of (benzene–benzyl alcohol)⁺ obtained from the photodepletion efficiencies. The error bars indicate one standard deviation of statistical uncertainties determined from at least 10 sets of the measurement. 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. At the wavelengths where the cross sections of (benzene)₂⁺ are large, we should reduce the power of the dissociation laser to avoid saturation of the depletion efficiencies; the experimental uncertainties are large in the 850–1000 nm region. The spectrum of (benzene–benzyl alcohol)⁺ exhibits a maximum around 950 nm with a full width at half maximum of 160 nm. The maximum cross section of (benzene–benzyl alcohol)⁺ amounts to approximately 35 % of that of (benzene)₂⁺. The spectrum of (benzene–benzyl alcohol)⁺ is in marked contrast to those of (benzene–phenol)⁺ and (benzene–aniline)⁺; the maximum cross sections of these ions are at most 2 % of that of (benzene)₂⁺ [18]. The appearance of the moderately strong band in the near-infrared region suggests that the near-resonance interaction is important in (benzene–benzyl alcohol)⁺.

3.3. Structure of (benzene–benzyl alcohol)⁺

Now we discuss the structure of (benzene–benzyl alcohol)⁺ in comparison with those of (benzene–phenol)⁺ and other hetero-dimer ions. Fujii et al. found that the frequency of the OH stretching vibration of (benzene–phenol)⁺ is by 475 cm⁻¹ lower than that of the bare (phenol)⁺ ion [6]. They attributed the large frequency reduction to the formation of the π -type hydrogen bond between the OH group of the phenol ion and the π -electrons of the neutral

benzene. In contrast to the large frequency reduction observed for (benzene–phenol)⁺, the frequency of the OH stretching vibration of (benzene–benzyl alcohol)⁺ is found to be the same as that of the bare (benzyl alcohol)⁺ ion. The result strongly suggests that the OH group of the benzyl alcohol ion is not bound to the benzene molecule. Therefore, we conclude that (benzene–benzyl alcohol)⁺ has a structure without the hydrogen bond.

We demonstrated that the near-resonance interaction between the aromatic rings is insignificant in (benzene–phenol)⁺ by measuring the electronic spectrum in the near-infrared region [18]. The observation is consistent with the π -type hydrogen-bonded structure of (benzene–phenol)⁺, in which the aromatic rings cannot take a sandwich-like configuration. In contrast to the hydrogen-bonded structure of (benzene–phenol)⁺, we have proposed a structure without the hydrogen bond for (benzene–benzyl alcohol)⁺. In such a structure, the aromatic rings are able to take a sandwich-like configuration so that the near-resonance interaction is possible. Actually, the electronic spectrum of (benzene–benzyl alcohol)⁺ shows the absorption band arising from the near-resonance interaction between the aromatic rings. The magnitude of the near-resonance interaction is shown to increase with decreasing Δ IE between the component molecules [5]. It is not surprising, therefore, that the near-resonance interaction is observed in (benzene–benzyl alcohol)⁺ with Δ IE = 0.281 eV, because the similar interaction is still significant in (benzene–toluene)⁺ with Δ IE = 0.4162 eV [5]. On the other hand, the values of Δ IE are larger for the hydrogen-bonded dimer ions: 0.7350 eV for (benzene–phenol)⁺ and 1.5232 eV for (benzene–aniline)⁺. The absence of the hydrogen bond in (benzene–benzyl alcohol)⁺ does not necessarily imply that (benzyl alcohol)⁺ has the poor ability, compared with (phenol)⁺ and (aniline)⁺, to form the hydrogen bond with other molecules. Mainly because the magnitude of Δ IE is small in (benzene–benzyl alcohol)⁺, the sandwich-like structure stabilized by the near-resonance interaction is considered to be favorable rather than the hydrogen-bonded structure.

The presence of the near-resonance interaction in (benzene–benzyl alcohol)⁺ indicates that the positive charge stays on the benzene moiety with higher IE in some probability. We applied a simple perturbation theory to (benzene–naphthalene)⁺ and (benzene–toluene)⁺ for estimating the probability distribution of the charge in these ions [5,10]. The wave functions

of the hetero-dimer ions are written as a linear combination of the unperturbed wave functions for the separated molecules. Only near-resonance interaction is taken into account as the perturbing interaction. The perturbed wave functions are determined from the values of ΔIE and the transition energy of the near-resonance band. We treat (benzene–benzyl alcohol)⁺ in a similar way and obtain the following wave function for the ground state:

$$\begin{aligned} \Psi = & (0.39)^{1/2} \psi[(\text{benzene})^+] \psi[(\text{benzyl alcohol})] \\ & + (0.61)^{1/2} \psi[(\text{benzene})] \psi[(\text{benzyl alcohol})^+], \end{aligned} \quad (2)$$

where ψ is the electronic wave function of the component molecule. The probability of finding the charge on the benzene moiety is 0.39 and that on the benzyl alcohol moiety is 0.61 in the ground state. The result falls in line with the relation between the probability distribution and ΔIE observed for (benzene)₂⁺, (benzene–toluene)⁺, (benzene–*p*-xylene)⁺ and (benzene–naphthalene)⁺ [5].

4. Conclusions

The structure of a cluster ion is thought to be determined by a balance between different kinds of intermolecular interactions. In homo-dimer ions of (benzene)₂⁺, (toluene)₂⁺ and (*p*-difluorobenzene)₂⁺, the bulk of the intermolecular interaction is due to the CR interaction. In hetero-dimer ions of (benzene–phenol)⁺ and (benzene–aniline)⁺, on the other hand, the π -type hydrogen bond is the dominant intermolecular interaction. In this work, we have shown that (benzene–benzyl alcohol)⁺ are stabilized by the near-resonance interaction and that the ion takes a sandwich-like structure without the hydrogen bond, although the OH group in benzyl alcohol could form a hydrogen bond with the π -electrons of benzene. This system is the first example of the non-hydrogen-bonded dimer ion composed of benzene and another molecule with the OH or NH group. The magnitude of ΔIE is probably one of the main factors that determine the nature of the intermolecular interaction and the structure of these ions.

Acknowledgements

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Figure Captions

Fig. 1. TOF mass spectra showing photodepletion behavior of $(\text{benzene})_2^+$ at 44.1 μs and $(\text{benzene-benzyl alcohol})^+$ at 48.1 μs : (a) without the photodissociation laser and (b) with the laser at $\lambda_d = 1000$ nm. The values of $\ln(I_{\text{off}} / I_{\text{on}})$, which are proportional to the photodissociation cross sections (see text), are 0.75 and 0.55 for $(\text{benzene})_2^+$ and $(\text{benzene-benzyl alcohol})^+$, respectively.

Fig. 2. Vibrational spectrum of $(\text{benzene-benzyl alcohol})^+$ obtained by monitoring the yield of the $(\text{benzyl alcohol})^+$ fragment ion as a function of wavenumber of the infrared laser.

Fig. 3. Electronic spectrum of $(\text{benzene-benzyl alcohol})^+$ (closed circles) obtained from the photodepletion efficiency of $(\text{benzene-benzyl alcohol})^+$ relative to that of $(\text{benzene})_2^+$ as a function of wavelength of the dissociation laser. The ordinate stands for the cross section scaled to the maximum cross section of $(\text{benzene})_2^+$ at 920 nm. Broken curve is the spectrum of $(\text{benzene})_2^+$ for reference.

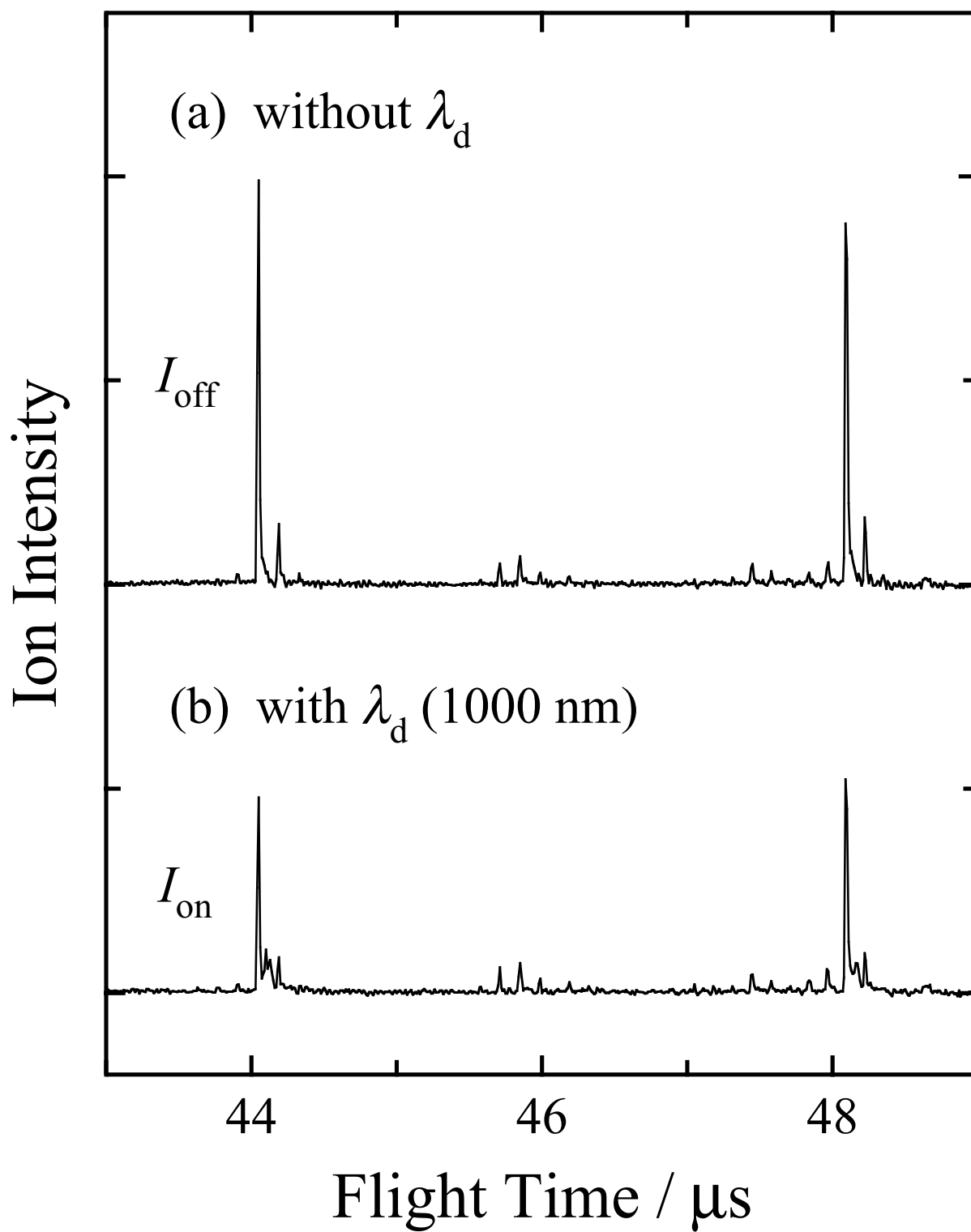


Fig. 1. Ohashi et al.

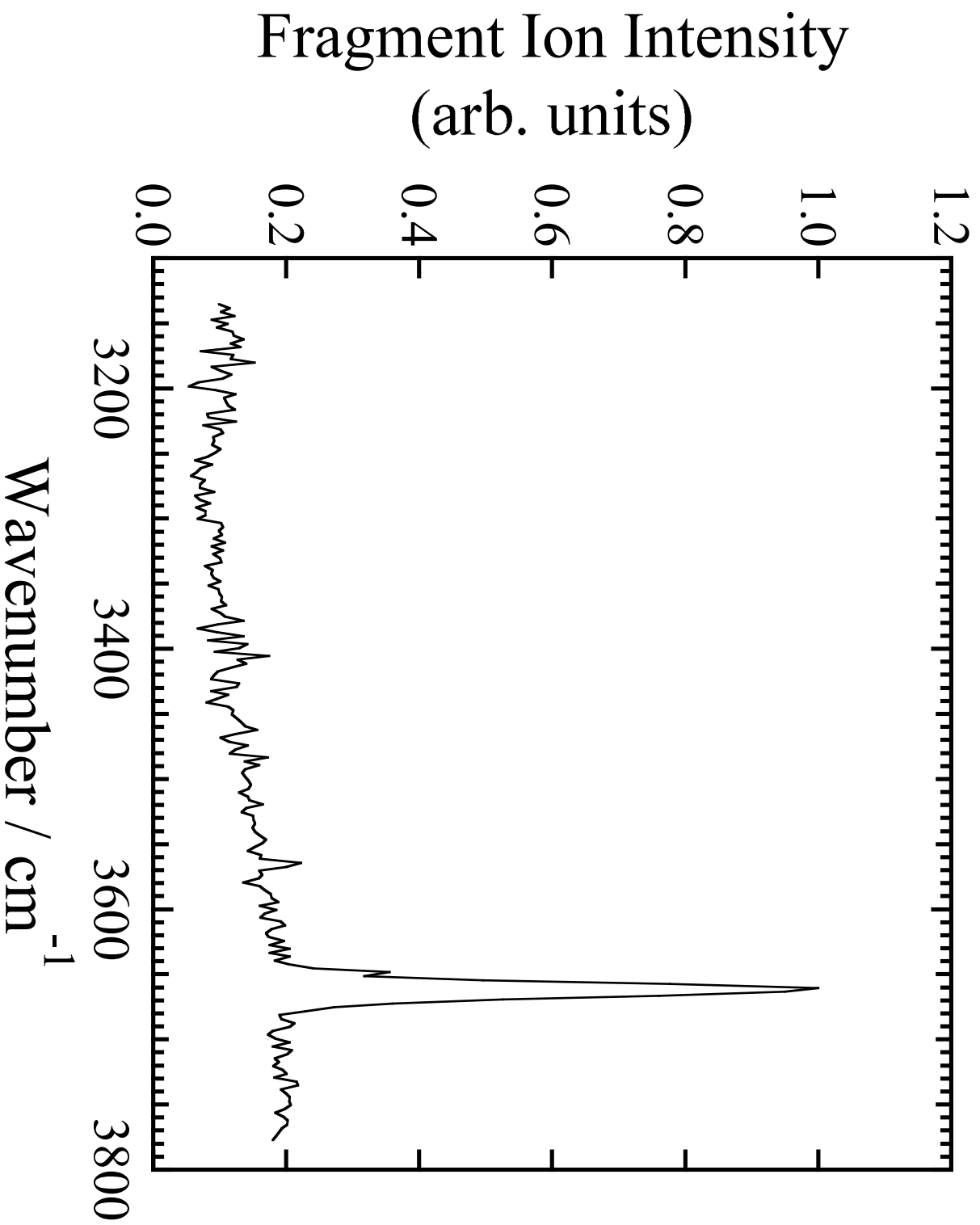


Fig. 2. Ohashi et al.

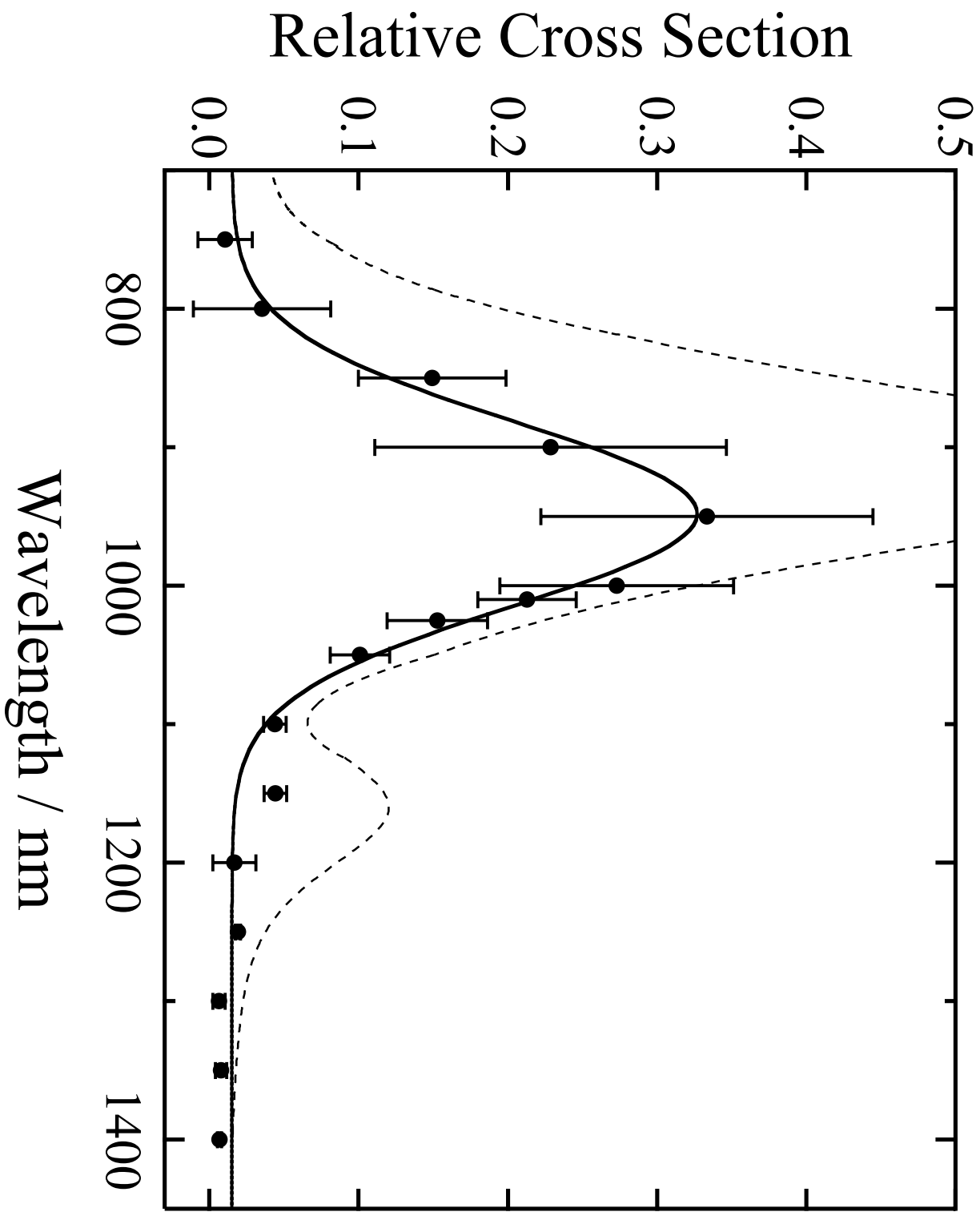


Fig. 3. Ohashi et al.