

Infrared photodissociation spectroscopy of benzene trimer ions. Switching of the dimer ion core in vibrationally excited states

Yoshiya Inokuchi^{a,b}, Kazuhiko Ohashi^a, Nobuyuki Nishi^a

^a*Institute for Molecular Science, Myodaiji, Okazaki 444, Japan*

^b*Department of Chemistry, Faculty of Science, Kyushu University,
Hakozaki, Fukuoka 812-81, Japan*

Abstract

A vibrational spectrum of benzene trimer ion, $(\text{C}_6\text{H}_6)_3^+$, was measured in the 2900–3100 cm^{-1} region by infrared photodissociation spectroscopy. An intense band at 2986 cm^{-1} was attributed to a C–H stretching vibration of the dimer ion core in $(\text{C}_6\text{H}_6)_3^+$. The spectra of isotopically mixed benzene trimer ions with benzene- d_6 molecules were also obtained. From the analysis of asymmetric band shape, a switching of the dimer ion core is proposed to occur in the vibrationally excited state prior to the vibrational predissociation.

Introduction

In the last decade studies on spectroscopy and photodissociation dynamics of benzene cluster ions, $(\text{C}_6\text{H}_6)_n^+$, have been carried out extensively [1–5]. Recently, we have reported the mass-selected photodepletion spectra of $(\text{C}_6\text{H}_6)_n^+$ in the range of 800–1100 nm [6]. The most important finding is that the absorption bands of $(\text{C}_6\text{H}_6)_n^+$ with $n = 3$ –6 exhibit essentially the same features with that of $(\text{C}_6\text{H}_6)_2^+$, indicating the presence of a dimer ion core in the clusters. The translational energies of neutral molecules ejected following photoexcitation of $(\text{C}_6\text{H}_6)_n^+$ have been measured in the photon energy range of 0.5–3.0 eV [6]. The fraction of the translational energies of the products in the excess energies has been estimated to be $\approx 15\%$ for $n = 3$ and $\approx 25\%$ for $n = 8$. Since the resultant internal energies of the products are much larger than the binding energies of the product cluster ions [7], the intramolecular vibrations of the ejected monomers are thought to play a significant role in the energy disposal particularly for small $(\text{C}_6\text{H}_6)_n^+$. Excitation of the intramolecular vibrations of the monomer product is possible when the equilibrium geometry of the molecule changes in the course of dissociation. The dimer ion core acts as a chromophore for the photoabsorption. In the photoexcited state, the positive charge is initially localized on the same pair of benzene molecules as in the ground state. If the charge continually hops from one pair to another pair in the cluster, all the molecules in the cluster have chances to be neutral for a moment and ionic for the other. In such a case, the molecules are vibrationally excited along the directions of the change in the equilibrium geometries between the neutral and the ion. However, we have not obtained any direct evidence yet for the hopping of the positive charge within $(\text{C}_6\text{H}_6)_n^+$.

In this letter, we show the infrared (IR) photodissociation spectra of benzene trimer ions in the 2920–3040 cm^{-1} region. The features of the spectra can be explained by considering a switching of the dimer ion core, or in other words, a hopping of the positive charge in the cluster.

Experimental Procedure

The experiment was carried out by using a tandem mass spectrometer with an octopole ion guide. The mixture of benzene, benzene- d_6 and argon was expanded into the vacuum chamber through a pulsed valve. The total stagnation pressure was 1.0×10^5 Pa. After passing through a skimmer, neutral benzene clusters were ionized by electron-impact with an electron energy of 50 eV. The trimer ions of interest were selected by a quadrupole mass filter. Then, the ion beam was deflected 90° by a quadrupole ion bender and introduced into an octopole ion guide. An IR laser beam in the energy region of $2900\text{--}3100\text{ cm}^{-1}$ propagated coaxially along the octopole and irradiated the trapped ions. IR excitation in this energy region induces intramolecular vibrational transition of benzene molecules. The vibrational energy is redistributed to intermolecular modes of the trimer ions. The energy is large enough to break an intermolecular bond of $(\text{C}_6\text{H}_6)_3^+$; a dimer ion is produced as a result of vibrational predissociation. After deflected 90° by another quadrupole ion bender, the fragment dimer ions were mass-analyzed by the last quadrupole mass filter and detected by a secondary electron multiplier. We obtained the IR photodissociation spectra of the trimer ions by plotting the yields of the fragment dimer ions against the frequencies of the IR laser. The tunable light source was a commercial optical parametric oscillator (OPO) system (Continuum Mirage 3000) pumped with an injection-seeded Nd:YAG laser (Continuum Powerlite 9000). The resolution of the OPO was less than 0.02 cm^{-1} . Benzene (nacalai tesque, 99.5 %) and benzene- d_6 (Aldrich, 99.6 atom % D) were used without further purification. In the following sections, benzene and benzene- d_6 molecules are abbreviated as H and D, respectively; H \equiv C_6H_6 and D \equiv C_6D_6 .

Results

Figure 1 shows the IR photodissociation spectrum of H_3^+ . Two distinct maxima are seen at 2986 cm^{-1} and 3047 cm^{-1} . The shape of the 2986-cm^{-1} band is asymmetric; the intensity is reduced more slowly on the low-frequency side. The 3047-cm^{-1} band has the intensity of only 13 % of the main band. Its position almost coincides with a band observed in the vibrational spectrum of neutral benzene (3048 cm^{-1}) [8].

Figure 2 displays the IR photodissociation spectra of (a) H_3^+ (the same spectrum as shown in Fig.1), (b, c) HD_2^+ , and (d) D_3^+ . The spectra of HD_2^+ were obtained by monitoring the yields of either the fragment HD^+ (b) or D_2^+ (c). These spectra are called the HD^+ -yield spectrum and the D_2^+ -yield spectrum, respectively. Open circles in Figs. 2(b) and 2(c) are the experimental points with error bars showing one standard deviation of statistical uncertainties determined from repeated laser scans. While the HD^+ -yield spectrum has a shoulder on the low-frequency side, the D_2^+ -yield spectrum shows almost symmetrical band shape. The D_2^+ -yield spectrum is reproduced by a single Lorentzian (solid curve). The HD^+ -yield spectrum is decomposed into two bands by fitting the experimental points with two Lorentzians (dotted curves); the sum of the two functions is indicated by the solid curve. The spectrum of H_3^+ is also decomposed into two bands. The spectrum of D_3^+ shows no absorption band in this region.

Figs. 3(a) and 3(b) are the HD^+ - and H_2^+ -yield spectra of H_2D^+ , respectively. Both spectra show pronounced shoulders on the low-frequency side. The solid curves in Fig. 3 indicate the sum of three Lorentzian components (dotted curves). The reason for the use of three Lorentzians is given in a later section.

Discussion

Electronic spectra of H_2^+ and H_3^+ were measured in the near IR region [9, 10]. In the spectrum of H_2^+ , one main band and another subband emerge at 920 and 1160 nm, respectively. These bands were attributed to the charge resonance (CR) bands, that are characteristic of H_2^+ . The existence of the CR band suggests that H_2^+ has a parallel structure. The spectrum of H_3^+ shows the main band at 960 nm and a relatively weak one at 1220 nm. Because of the similarity of the spectrum of H_3^+ with that of H_2^+ , the charge is considered to be localized on a dimer subunit in H_3^+ . The electronic spectra of H_2^+ and H_3^+ were recorded also in the visible region [11]. Two local excitation bands are observed for both H_2^+ and H_3^+ ; one is a π - π band and the other is a σ - π band. The position of the σ - π band moves to the red with increasing cluster size; 550 nm for H^+ , 580 nm for H_2^+ , and 620 nm for H_3^+ , while the π - π band shows little shift with increasing size. These spectral shifts can be explained reasonably by the stabilization of π orbitals due to the parallel stacking of neutral molecule(s) on the ion. These observations suggest that H_3^+ has a triply parallel structure with the charge localized on the dimer core.

A vibrational spectrum of neutral benzene was measured in a supersonic beam by IR-UV double resonance spectroscopy [8]. The frequency of an IR-active C-H stretching vibration of neutral benzene is 3065 cm^{-1} (ν_{20} in Wilson's numbering, deperturbed value from Fermi resonance interaction). Unfortunately, the corresponding frequency of the benzene cation is not reported to our best knowledge. The frequency of the stretching vibration of the C-H group adjacent to a triple bond is typically $\approx 3300\text{ cm}^{-1}$; the frequency decreases to ≈ 3020 and $\approx 2960\text{ cm}^{-1}$ for a double and a single bond system, respectively [12]. This tendency implies that the frequency of the C-H stretching vibration becomes higher as the bond order of the carbon atom becomes larger. Since the bond order of the carbon atoms of the benzene cation is lower than that of the neutral benzene, the C-H stretching frequency of the benzene cation must be lower than that of

the neutral benzene. In the IR photodissociation spectrum of H_3^+ shown in Fig.1, two maxima are seen at 2986 and 3047 cm^{-1} . From the reasons mentioned above, we attribute the main band at 2986 cm^{-1} to the C–H stretching vibration of the charged benzene molecules in the dimer ion core, and the minor band at 3047 cm^{-1} to that of the third benzene molecule of neutral character.

No information is available about electronic spectra, structures, and binding energies of H_2D^+ and HD_2^+ . Ionization potential (IP) of benzene- d_6 is slightly higher than that of benzene; $\text{IP}(\text{benzene}) = 9.243841 \text{ eV}$ and $\text{IP}(\text{benzene-}d_6) = 9.247181 \text{ eV}$ from the results of high n Rydberg spectroscopy [13]. The difference in the IP's (ΔIP) might be thought to prevent the CR interaction between benzene and benzene- d_6 . However, we observed that the CR band of HD^+ is as intense as that of H_2^+ [14]. Since ΔIP is less than 0.01 eV between benzene and benzene- d_6 , the interaction between them is essentially the same as the CR interaction between two benzenes. Therefore, the mixed trimer ions, H_2D^+ and HD_2^+ , probably have electronic and geometric structures similar to H_3^+ without distinction between benzene and benzene- d_6 . In addition, H_2D^+ has three isomers of $[\text{HH}]^+\cdots\text{D}$, $[\text{HD}]^+\cdots\text{H}$, and $[\text{DH}]^+\cdots\text{H}$, and HD_2^+ has the isomers of $[\text{DD}]^+\cdots\text{H}$, $[\text{DH}]^+\cdots\text{D}$, and $[\text{HD}]^+\cdots\text{D}$. These isomers are thought to be produced equally in the beam independent of the mixing ratio of H and D.

The fragment D_2^+ was produced from HD_2^+ following the excitation of the C–H stretching vibration of H in the dimer ion core, $[\text{HD}]^+$; H is a component of the dimer ion core in the ground state, but the fragment dimer ion contains no H. The observation suggests switching of the charge-carrying unit from $[\text{HD}]$ to $[\text{DD}]$, i.e., hopping of the charge from the $[\text{HD}]$ pair to the $[\text{DD}]$ pair, in the vibrationally excited state. If the trimer ion dissociates after the switching of the ion core, the fragment dimer ion can be composed of a different pair of molecules from the pair in the ground state. Figure 4 illustrates a schematic diagram of the predissociation mechanism for HD_2^+ . Two isomers are possible for HD_2^+ with H in the dimer core. One isomer is $[\text{DH}]^+\cdots\text{D}$ where H stays

in the center of the triple sandwich (isomer (a) in Fig. 4). Another isomer is $[\text{HD}]^+\cdots\text{D}$ where H stays at the end position (isomer (b) in Fig. 4). We assume that the positional order of the three molecules in parallel stacking does not change upon the photoexcitation and that the two molecules at both ends cannot form a pair as the fragment dimer ion. When the C–H stretching vibration of isomer (a) of $[\text{DH}]^+\cdots\text{D}$ is photoexcited, only HD^+ is produced as a fragment ion. When the C–H stretching vibration of isomer (b) of $[\text{HD}]^+\cdots\text{D}$ is excited, two different fragment ions, HD^+ and D_2^+ , can be observed. The fragment HD^+ is produced from both isomers (a) and (b). The fragment D_2^+ , on the other hand, is created only from isomer (b). The HD^+ -yield spectrum (Fig. 2(b)) is found to be reproduced by the sum of two Lorentzians. In contrast to this, the D_2^+ -yield spectrum (Fig. 2(c)) can be reproduced by a single Lorentzian. Therefore, we attribute the absorption band seen in Fig. 2(c) to the C–H stretching vibration of H in isomer (b). Since the position of the high-frequency component in Fig. 2(b) coincides with that of the band in Fig. 2(c), we ascribe this component to H of isomer (b). The low-frequency component in Fig. 2(b) is assigned to H of isomer (a). The spectrum of H_3^+ in Fig. 2(a) also can be reproduced by two functions. The low- and high-frequency components in Fig. 2(a) are attributed to the center-H and the end-H, respectively, because of the similarity to Fig. 2(b).

As indicated in Fig. 4, x stands for the probability that the vibrationally excited isomer (b) dissociates into the fragment HD^+ . Then, the probability of the dissociation into the fragment D_2^+ is $1-x$. If the time scale of the dissociation is faster than the period of the core switching, the dimer core in the ground state remains intact, and x should be ≈ 1 . If the dissociation is much slower than the period of the core switching, the trimer ion experiences a large number of the core switching processes, and x should be ≈ 0.5 . Isomer (a) produces the fragment HD^+ with the probability of 1, as far as our assumptions are correct. We suppose that the oscillator strength of the C–H vibrational transition of the center-H is approximately the same as that of the end-H. Then, in the IR photodissociation spectrum, the ratio of abundance of the low-frequency component to

that of the high-frequency component is $1:x$. From Fig. 2(b), we estimate the ratio to be $1:0.51$, yielding $x = 0.51$. This result suggests that the dissociation is much slower than the period of the core switching. In the case of H_3^+ , the vibrationally excited H_3^+ dissociates into H_2^+ , whether or not the core switching occurs. Although we cannot get information on the relationship between the time scales of the dissociation and the core switching in this case, one can estimate an upper bound of 350 fs for the core switching in H_3^+ from the band widths. The ratio of the low-frequency component to the high-frequency one in Fig. 2(a) reflects only the relative oscillator strength between the end-H and the center-H. Since we get the ratio of 1:1.1 from Fig. 2(a), we can confirm the assumption that the oscillator strength of the center-H is approximately the same as that of the end-H.

In Figs. 2(a)–2(c), the high-frequency components show the peaks at 2984, 2978, and 2979 cm^{-1} . These values are almost the same with each other within 7 cm^{-1} . The position of the low-frequency component, however, shows much larger difference for H_3^+ (2968 cm^{-1}) and HD_2^+ (2954 cm^{-1}). This may suggest that the frequency changes dependent on the core isomers. Therefore, we use three Lorentzians to decompose the spectra of H_2D^+ as shown in Fig. 3. As mentioned previously, H_2D^+ has three possible isomers: $[\text{HH}]^+\cdots\text{D}$, $[\text{HD}]^+\cdots\text{H}$, and $[\text{DH}]^+\cdots\text{H}$. The highest-frequency component is due to the end-H sites of the ion cores in $[\text{HH}]^+\cdots\text{D}$ and $[\text{HD}]^+\cdots\text{H}$. The intermediate-frequency component is due to the center-H in $[\text{HH}]^+\cdots\text{D}$. The lowest-frequency component is due to the center-H in $[\text{DH}]^+\cdots\text{H}$. For analyzing each of Figs. 3(a) and 3(b), we assume that the lowest-frequency component has the same width and the same peak height with those of the intermediate-frequency component; only the peak positions are treated as independent parameters. The experimental spectra in Fig. 3 can be reproduced by the sum of the three Lorentzian components.

We then consider the relative abundance of the lowest-, intermediate-, and highest-frequency components in the spectra. If the dissociation occurs more slowly than

the core switching, the fragment HD^+ is produced from the excitation of the center-H in $[\text{DH}]^+\cdots\text{H}$ and $[\text{HH}]^+\cdots\text{D}$ with a probability of 0.5 for each, contributing to the lowest- and intermediate-frequency components, respectively. The end-H excitation in $[\text{HH}]^+\cdots\text{D}$ produces HD^+ with a probability of 0.5, contributing to the highest-frequency component. The excitation of the end-H in $[\text{HD}]^+\cdots\text{H}$ produces HD^+ with a probability of unity, contributing to the highest-frequency component as well. Thus the relative abundance of the three components becomes 1:1:3 ($= 0.5:0.5:(0.5+1)$). In the same way, the relative abundance of the three components in the H_2^+ -yield spectrum is estimated to be 1:1:1. The experimental results show 1:1:3.1 and 1:1:1.1 for the HD^+ - and H_2^+ -yield spectra, respectively. These values nicely coincide with the predicted values, indicating that the predissociation mechanism of H_2D^+ has no differences from that of HD_2^+ , and that the core switching occurs sufficiently faster than the predissociation.

Conclusion

We have measured the IR photodissociation spectra of isotopically mixed benzene trimer ions. HD_2^+ shows remarkable differences in the band shape dependent on the monitored fragment ions. Asymmetric band shapes can be decomposed into a few components, which are due to the benzene molecules in the different sites of the trimer ions. We can reasonably explain the relative abundance of the components in the spectra by considering the core switching in advance of the dissociation. Now the evidence of the core switching is obtained for the trimer ions in the vibrational excited state of the ground electronic state. The core switching is more likely to occur in the electronically excited states, inducing the intramolecular vibrations of benzene molecules. Thus, a large amount of the excess energy is partitioned into the internal energies of the neutral monomers, following the electronic excitation of the dimer ion core [6].

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Figure Captions

Figure 1 IR photodissociation spectrum of H_3^+ . The ordinate stands for the yields of H_2^+ . Two maxima emerge at 2986 and 3047 cm^{-1} .

Figure 2 IR photodissociation spectra of (a) H_3^+ (the same spectrum as Fig. 1), (b, c) HD_2^+ , and (d) D_3^+ in the region of the main band. The ordinates stand for the yields of (a) H_2^+ , (b) HD^+ , (c) D_2^+ , and (d) D_2^+ .

Figure 3 IR photodissociation spectra of H_2D^+ . The ordinates stand for the yields of (a) HD^+ and (b) H_2^+ , respectively.

Figure 4 Schematic diagram of the photodissociation mechanism for HD_2^+ . In isomer (a), benzene stays in between two benzene- d_6 molecules and forms the dimer ion core with one benzene- d_6 . In isomer (b), benzene is also a component of the dimer ion core, but stays at the end position. Solid arrows and dotted arrows indicate the photoexcitation and the vibrational predissociation, respectively. The quantities below the dotted arrows are the fractions of branching along the directions of the arrows (see text).