

## Electronic Structures of Aromatic Cluster Ions

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### Abstract

The photodissociation spectra are observed for cluster ions of several aromatic molecules including benzene, toluene, and phenol. Benzene cluster ions,  $(C_6H_6)_n^+$  with  $n=3-6$ , retain spectroscopic features characteristic of  $(C_6H_6)_2^+$ , suggesting that the positive charge is carried by a dimer subunit in  $(C_6H_6)_n^+$ . The spectrum of (benzene-toluene)<sup>+</sup> shows charge resonance bands, which are commonly seen in homo-dimer ions. The resonance interaction is also important in the hetero-dimer ion, despite the difference in the ionization potentials between the two components. Phenol dimer ion exhibits no strong charge resonance band, although it is a homo-dimer ion. Owing to the geometrical constraint of an O-H...O hydrogen bond, the two aromatic rings cannot be in a parallel configuration suitable for the resonance interaction.

### 1. Introduction

The study of molecular van der Waals clusters and cluster ions has provided insight into the nature of intermolecular interactions. Photodissociation of mass-selected cluster ions has been a useful technique in cluster ion spectroscopy [1]. The method employs tandem mass filter arrangements which isolate specific cluster ions for photodissociation and analyze the mass number of the resultant fragments [2]. We first investigated benzene dimer ion,  $(C_6H_6)_2^+$ , as a simple prototype system. A strong absorption band centered at 920 nm was assigned to a charge resonance (CR) band [3]. The CR band is common to most homo-molecular dimer ions and arises from the transition between the bound ground state and its sister repulsive excited state. The CR transition energy was found to be just twice of the binding energy, suggesting that the main contribution to the binding energy of  $(C_6H_6)_2^+$  is from the resonance interaction [4].

One of the central issues for larger cluster ions is the degree of charge localization within them. The location of the CR band is known to be a sensitive measure of the charge localization [5]. The idea of *core ion* has been documented for cluster ions of rare-gas atoms and small molecules. In the  $(CO_2)_n^+$  system, the presence of the transition characteristic of  $(CO_2)_2^+$  in the higher clusters ( $n \leq 10$ ) provides evidence that a  $(CO_2)_2^+$  subunit forms a core ion in the higher clusters [6].

In the  $Ar_n^+$  system, on the other hand, an  $Ar_3^+$  unit remains as a core ion in  $Ar_n^+$  with  $n \leq 14$  [7,8]. Here we investigate the CR bands of  $(C_6H_6)_n^+$  with  $n = 3-6$  to obtain information on the core structure of these ions.

The existence of the intense CR absorption by homo-dimer ions indicates that the charge is shared with the two component molecules in the ground state and that the two moieties should be equivalent to each other. In a hetero-dimer ion with dissimilar partners, on the other hand, the charge may reside principally on the component with the lower ionization potential (IP). Then a question arises whether the resonance interaction found in homo-dimer ions can be also seen in hetero-dimer ions. Here we present an answer for this question through the results of the photodissociation spectroscopy on benzene-toluene hetero-dimer ion and phenol dimer ion.

## 2. Experimental

The experiment was carried out by using a cluster beam apparatus with a reflectron-type time-of-flight mass spectrometer [4,9]. Neutral clusters were formed by expanding the mixture of sample and argon gas through a pulsed valve. After passing through a skimmer and a collimator, the cluster beam entered the acceleration region of the mass spectrometer. A pulsed ionization laser (210 nm) intersected the cluster beam, where the parent ions were produced by 2-photon ionization of the neutral clusters. While traveling in the acceleration region, the prepared ions were excited by a pulsed dissociation laser (370–1400 nm). The packet of specific ions was selectively excited by adjusting the delay time between the two laser pulses. After secondary acceleration, both the remaining parent ions and the photofragment ions were introduced into an ion-drift tube of the mass spectrometer. The ions were then reflected and separated by a two-stage ion reflector situated at the end of the drift tube. The reflected ions were detected by dual microchannel plates. The photodissociation spectra were obtained by recording the normalized yields of the fragment ions as functions of photodissociation wavelengths.

## 3. Results and Discussion

### 3.1. Photodissociation spectrum of $(C_6H_6)_2^+$

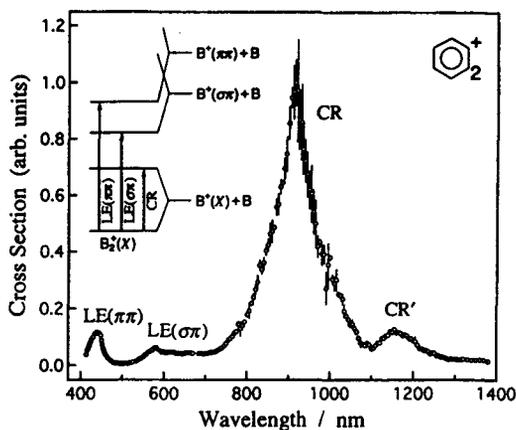


Fig. 1. Photodissociation spectrum of  $(C_6H_6)_2^+$ . Two local excitation (LE) bands correspond to the  $\pi \leftarrow \pi$  and  $\pi \leftarrow \sigma$  transitions of a monomer ion unit in  $(C_6H_6)_2^+$ . A strong charge resonance (CR) band is located at 920 nm. (inset) energy diagram indicating the respective transitions. "B" stands for a benzene molecule. "X" denotes the electronic ground state.

The photodissociation spectrum of  $(C_6H_6)_2^+$  is displayed in Fig. 1 as a reference spectrum to establish the identity of a chromophore in the larger cluster ions and other dimer ions. Two bands at 440 and 580 nm are due to local excitation (LE) of a monomer ion unit within  $(C_6H_6)_2^+$  [9]. An intense CR band is seen at 920 nm [3], suggesting that the two moieties should be equivalent to each other. The cross section at the CR band is almost one order of magnitude larger than those of the LE bands. A parallel sandwich structure was suggested or supposed for  $(C_6H_6)_2^+$  in most of traditional condensed-phase studies. Recently, Yamabe *et al.* determined the structure of  $(C_6H_6)_2^+$  by *ab initio* molecular orbital calculations [10]. Two isomers, T-shape and parallel ones, were found to be located at the potential-energy minima. However, the T-shape structure is in conflict with the observation of the intense CR band. A side band at 1160 nm is tentatively assigned to another CR band, which can appear when  $(C_6H_6)_2^+$  has a *displaced* sandwich structure [4].

### 3.2. Larger benzene cluster ions: $(C_6H_6)_n^+$ with $n=3-6$

A charge-localized (dimer core) structure is proposed in the photofragmentation studies of  $(C_6H_6)_n^+$  by Beck and Hecht [11] and by our group [12]. On the contrary, Krause *et al.* suggest the delocalization of the charge in  $(C_6H_6)_3^+$  and  $(C_6H_6)_4^+$  [13]. These arguments are based on the determination of the binding energies of  $(C_6H_6)_n^+$ . The electronic spectra of  $(C_6H_6)_n^+$  can provide direct information on this issue, where the position of the CR band is a diagnostic of the localization of the charge.

More than one dissociation channels were found in the photodissociation of  $(C_6H_6)_n^+$  with  $n > 2$  [12]. For these ions, the photodissociation spectroscopy requires accurate data on the branching ratio of the products at each wavelength in order to convert the fragment yield into the total cross section. Photodepletion spectroscopy [3] is an alternative approach, although the measurement of depletion of the parent ion signals is more difficult and less sensitive than the measurement of the photofragment yield. Figure 2 shows the photodepletion spectra of  $(C_6H_6)_n^+$  with  $n=3-6$  in the CR band region of  $(C_6H_6)_2^+$ . Although small shifts are found from the trimer (940 nm) to the hexamer ( $\approx 960$  nm), the absorption bands of  $(C_6H_6)_n^+$  with  $n=3-6$  exhibit essentially the same features with that of  $(C_6H_6)_2^+$ . The observation of the CR band of  $(C_6H_6)_3^+$  at 940 nm is not what would be expected for the case of the charge delocalization; the Hückel-type calculation for the charge-delocalized  $(C_6H_6)_3^+$  [14] predicts the main CR band at  $\approx 1320$  nm with the intensity  $\sqrt{2}$  times larger than that of  $(C_6H_6)_2^+$ . We confirmed here that the maximum cross sections of  $(C_6H_6)_n^+$  with  $n=2-6$  are similar to each other.

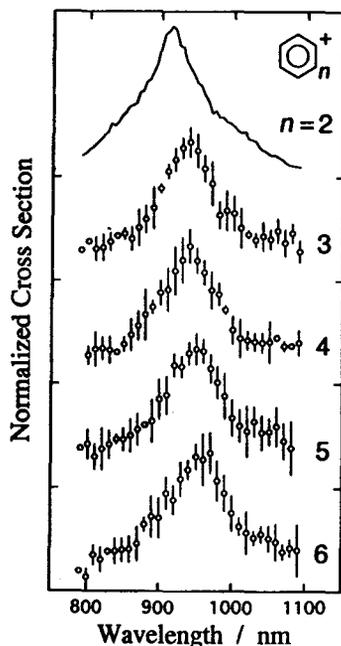


Fig. 2. Photodepletion spectra of  $(C_6H_6)_n^+$  with  $n=3-6$ . All the spectra are normalized to have the same amplitude at their maxima.

The CR band characteristic of  $(C_6H_6)_2^+$  remains essentially intact in  $(C_6H_6)_3^+$  as well as in the larger  $(C_6H_6)_n^+$  upon further clustering. The result suggests that the charge is localized on a dimer subunit, which acts as a chromophoric core for the CR transition in  $(C_6H_6)_n^+$ .

### 3.3. Benzene-toluene hetero-dimer ion: $[(C_6H_6)(C_6H_5CH_3)]^+$

Next we turn our attention to the structure of dimer ions in which the two moieties are inequivalent to each other. One class of such species is hetero-dimer ions composed of a benzene and a substituted benzene. These hetero-dimer ions are likely to be less stable than the homo-dimer ions because stabilization energy due to the charge delocalization is expected to decrease with increasing difference in the IPs between the two component molecules [15]. For benzene-toluene hetero-dimer ion (abbreviated as  $BT^+$  hereafter), the difference is 0.415 eV.

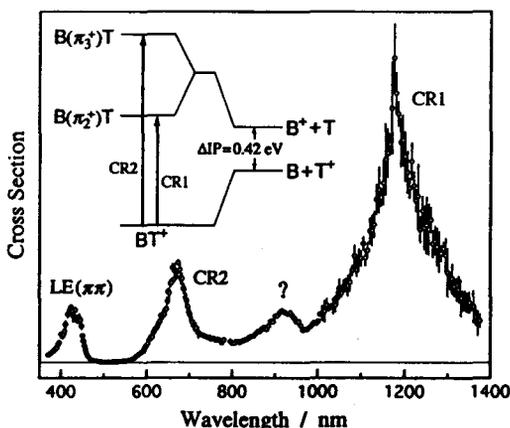


Fig. 3. Photodissociation spectrum of benzene(B)-toluene(T) hetero-dimer ion. Two bands at 670 and 1175 nm are assigned to charge resonance bands. (inset) energy diagram explaining the appearance of the two CR bands. Approximate molecular orbital configurations are shown at the most left part.

The predominant dissociation channel of  $BT^+$  was found to be the formation of B and  $T^+$  in the wavelength range studied here. Figure 3 shows the photodissociation spectrum of  $BT^+$  obtained by monitoring the yield of  $T^+$ . The 1175-nm band is approximately 5 times as strong as the LE band, although the photodissociation of  $BT^+$  at this band is less efficient than that of  $(C_6H_6)_2^+$  at the CR band. Both the 1175- and 670-nm bands seem to have characters of the CR bands of homo-dimer ions. In the zero-th order approximation, these two bands are interpreted to arise from the promotion of an electron from the  $\pi_2$  or  $\pi_3$  orbital of B to the  $\pi_3$  orbital of T. However, the observed transition energies disagree with the predicted one based on this simple charge transfer picture. Actually, stabilization and de-stabilization of the energy levels due to resonance-type interactions should be taken into consideration. Because the  $\pi_3$  orbital of T has the same character with the  $\pi_3$  orbital of B, the interaction between these two orbitals is stronger than that between the  $\pi_3$  orbital of T and the  $\pi_2$  orbital of B. Therefore the CR band of  $BT^+$  splits into CR1 and CR2, as indicated in the inset of the figure.

Benzene-fluorobenzene hetero-dimer ion is also found to efficiently dissociate by absorbing a photon in the near-infrared region. The resonance-type interaction is important in the hetero-dimer ions composed of a benzene and a substituted benzene, despite the difference in the properties of the two components.

### 3.4. Phenol dimer ion: $(C_6H_5OH)_2^+$

A different example of inequivalent dimer is phenol dimer ion. The multi-photon ionization spectroscopy of *neutral* phenol dimer suggested that the species has an O—H...O hydrogen bond, where one phenol molecule is a proton donor and the other is a proton acceptor [16]. Felker *et al.* proposed a nonplanar geometry with the two aromatic rings interacting in a way that maximizes the atom-atom contact between them subject to the geometrical constraint of the H bond [17]. The zero-kinetic-energy photoelectron spectroscopy suggested a significant strengthening of the H bond (shortening the bond length) on ionization [18]. From these observations we infer that the two phenol molecules are also inequivalent in  $(C_6H_5OH)_2^+$  and that the two rings are not in a parallel configuration.

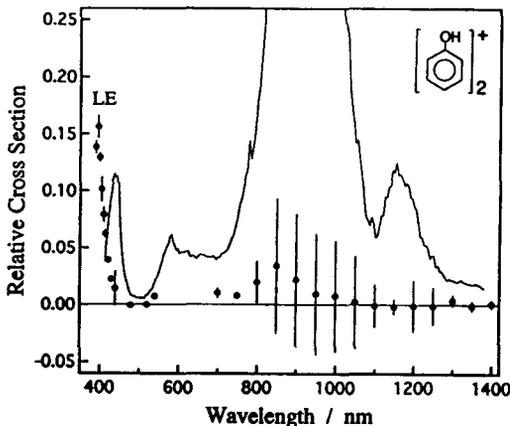


Fig. 4. Photodissociation spectrum of phenol dimer ion (closed circles). The ordinate stands for the cross section relative to the maximum of  $(C_6H_6)_2^+$  at 920 nm. The data points in 440–1400 nm region are obtained from the depletion yield relative to  $(C_6H_6)_2^+$ . The spectrum of  $(C_6H_6)_2^+$  is drawn by the solid line for reference.

Figure 4 shows the photodissociation spectrum of  $(C_6H_5OH)_2^+$ . An LE band is observed at 390 nm, where the cross section is comparable with that of  $(C_6H_6)_2^+$  at the LE( $\pi\pi$ ) band. However, no intense band is observed in 500–1400 nm region. A weak feature is seen at  $\approx 850$  nm, but the cross section is at most 4% of the maximum cross section of  $(C_6H_6)_2^+$ . The difference in the IP's between the proton-donating and proton-accepting phenols may reduce the resonance interaction. However, the difference is reported to be 0.08 eV [18], which is much smaller than the value for  $BT^+$  (0.415 eV). Another factor should be responsible for the lack of the CR band. For  $(C_6H_6)_2^+$  and probably for  $BT^+$ , we favor a parallel structure which allows  $\pi$  overlap between the two rings to explain the strong CR interaction. In  $(C_6H_5OH)_2^+$ , however, the O—H...O hydrogen bond probably prevents the two rings from taking a parallel configuration. Therefore the resonance interaction is expected to be less significant in  $(C_6H_5OH)_2^+$  and the CR band (if any) is much weaker than that of  $(C_6H_6)_2^+$ . On the other hand, the relative orientation of the rings is considered to have little influence on the intensity of the LE band. The description is in line with the observed spectrum of  $(C_6H_5OH)_2^+$  shown in Fig. 4.

Although  $(C_6H_5OH)_2^+$  is a homo-dimer ion, it shows no strong CR band. This is probably because the two aromatic rings cannot be in a parallel configuration suitable for the resonance interaction owing to the geometrical constraint of the hydrogen bond.

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## References

- [1] E. J. Bieske and J. P. Maier, *Chem. Rev.* **93**, 2603 (1993).
- [2] J. M. Farrar, in *Cluster Ions*, ed by C. Y. Ng, T. Baer, and I. Powis, (John Wiley & Sons, Chichester, 1993), p. 243.
- [3] K. Ohashi and N. Nishi, *J. Phys. Chem.* **96**, 2931 (1992).
- [4] K. Ohashi, Y. Nakai, T. Shibata, and N. Nishi, *Laser Chem.* **14**, 3 (1994).
- [5] A. Kira and M. Imamura, *J. Phys. Chem.* **83**, 2267 (1979).
- [6] M. A. Johnson, M. L. Alexander, and W. C. Lineberger, *Chem. Phys. Lett.* **112**, 285 (1984).
- [7] N. E. Levinger, D. Ray, M. L. Alexander, and W. C. Lineberger, *J. Chem. Phys.* **89**, 5654 (1988).
- [8] H. Haberland, B. von Issendorf, T. Kolar, H. Kornmeier, C. Ludewigt, and A. Risch, *Phys. Rev. Lett.* **67**, 3290 (1991).
- [9] K. Ohashi and N. Nishi, *J. Chem. Phys.* **95**, 4002 (1991).
- [10] K. Hiraoka, S. Fujimaki, K. Aruga, and S. Yamabe, *J. Chem. Phys.* **95**, 8413 (1991).
- [11] S. M. Beck and J. H. Hecht, *J. Chem. Phys.* **96**, 1975 (1992).
- [12] Y. Nakai, K. Ohashi, and N. Nishi, *J. Phys. Chem.* **96**, 7873 (1992).
- [13] H. Krause, B. Ernstberger, and H. J. Neusser, *Chem. Phys. Lett.* **184**, 411 (1991).
- [14] T. Shibata, K. Ohashi, Y. Nakai, and N. Nishi, *Chem. Phys. Lett.* **229**, 604 (1994).
- [15] M. S. El-Shall and M. Meot-Ner (Mautner), *J. Phys. Chem.* **91**, 1088 (1987).
- [16] K. Fuke and K. Kaya, *Chem. Phys. Lett.* **94**, 97 (1983).
- [17] L. L. Connell, S. M. Ohline, P. W. Joireman, T. C. Corcoran, and P. M. Felker, *J. Chem. Phys.* **96**, 2585 (1992).
- [18] O. Dopfer, G. Lembach, T. G. Wright, and K. Müller-Dethlefs, *J. Chem. Phys.* **98**, 1933 (1993).