

Positive charge distribution in (benzene)₁(toluene)₂⁺ and (benzene)₂(toluene)₁⁺ studied by photodissociation spectroscopy

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ABSTRACT

The positive charge distribution in benzene–toluene hetero-trimer ions is investigated by photodissociation spectroscopy in the near-infrared (6000–14000 cm⁻¹) and infrared (2800–3150 cm⁻¹) regions. The electronic spectra of (benzene)₁(toluene)₂⁺ and (benzene)₂(toluene)₁⁺ in the near-infrared region display a strong band at 9430 and 8330 cm⁻¹, respectively. These bands are ascribed to the charge resonance band; the positive charge is not localized on a single molecule. The vibrational spectrum of (benzene)₁(toluene-*d*₈)₂⁺ shows three distinct bands at 3054, 3084, and 3108 cm⁻¹; these bands are assigned to the CH stretching vibrations of the benzene moiety. The similarity of the spectral features to those of the neutral benzene monomer suggests that the benzene molecule in the (benzene)₁(toluene)₂⁺ ion has a neutral character. The positive charge is localized on the toluene dimer unit with a structure written as (toluene)₂⁺•••(benzene)₁. The vibrational spectrum of (benzene)₂(toluene)₁⁺ bears a resemblance to that of (benzene)₂⁺. The vibrational spectrum of (benzene-*d*₆)₂(toluene)₁⁺ shows dissimilar features to the spectrum of the neutral toluene monomer, suggesting that a certain amount of the positive charge is carried by the toluene moiety. These results are explained by the charge resonance interaction between (benzene)₂ and (toluene)₁. A simple perturbation theory is applied for determining the positive charge distribution in (benzene)₂(toluene)₁⁺.

The probability of finding the charge on the (benzene)₂ and (toluene)₁ moieties is analyzed to be 58 and 42 %, respectively.

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I. INTRODUCTION

Studies on the behavior of a positive charge in cluster ions are fairly important in connection with solvated ions and charge transportation in condensed matter.^{1, 2} Mass-selected photodissociation spectroscopy has proven to be a useful method for studying the structures, charge distributions, and excited-state dynamics of aromatic cluster ions.^{3, 4} In the last decade, we have performed the photodissociation studies of (benzene)₂⁺ and (benzene)₃⁺.^{5–6789} Figure 1 exhibits the photodissociation spectra of (a) (benzene)₂⁺ and (b) (benzene)₃⁺ in the 7000–28000 cm⁻¹ region, which were reported previously.^{7, 8} The spectrum of (benzene)₂⁺ shows a very strong band at 10930 cm⁻¹. This band is assigned to the charge resonance (CR) band, which is due to an electronic transition between two CR states correlating to benzene⁺ (X) + benzene (X). The appearance of the CR band indicates that the benzene molecules are equivalent to each other, and the positive charge is delocalized in the dimer. An analogous CR band is observed also for (toluene)₂⁺ and (naphthalene)₂⁺.^{10, 11} For these ions, the principal intermolecular interaction is the CR interaction between the π -electrons of the aromatic molecules. As seen in Fig. 1(b), the spectral features of (benzene)₃⁺ are similar to those of (benzene)₂⁺; this resemblance implies the dimer ion core structure of (benzene)₃⁺. Inokuchi and Nishi reported the vibrational spectrum of (benzene)₃⁺ in the 3000–3150 cm⁻¹ region; the spectrum can be decomposed into the absorption components of a dimer ion core and a neutral benzene molecule.¹² From these spectroscopic results, it was concluded that the (benzene)₃⁺ ion has a charge-localized structure, (benzene)₂⁺•••benzene, where (benzene)₂⁺ is the dimer ion core. A similar dimer ion core structure was proposed for (naphthalene)₃⁺.¹³

In the case of hetero-cluster ions, the difference in ionization energy (Δ IE) between the constituent molecules is an important factor in governing the behavior of the positive charge. Meot-Ner and co-workers measured binding energies of aromatic dimer ions by using high-pressure mass spectrometry.¹⁴ They suggested that the binding

energies are the largest in homo-dimer ions and decrease in hetero-dimer ions with increasing Δ IE between the constituent molecules. The binding energies of the homo- and hetero-dimer ions of benzene, toluene, and *p*-difluorobenzene were determined by Neusser et al.¹⁵ from the measurement of the IEs of the dimers and the appearance energies of the monomer ions that arise from the dissociation of the dimer ions. They demonstrated that the binding energies of the hetero-dimer ions are smaller than those of (benzene)₂⁺ and (toluene)₂⁺. More recently, we reported the photodissociation spectra of (benzene)₁(toluene)₁⁺ and (benzene)₁(naphthalene)₁⁺.^{10, 16} For both ions, a strong absorption band is observed in the near-infrared region; these results mean that the CR interaction occurs even in the hetero-dimer ions with a certain amount of Δ IE. Neusser et al. also presented an energetic scheme for predicting the dissociation pathways of (benzene)₁(toluene)₂⁺ and (benzene)₂(toluene)₁⁺; this scheme well explains the observed fragmentation patterns.¹⁵ However, they made no attempt to estimate the charge distribution in these trimer ions.

In this paper, we report the positive charge distribution in benzene (B)–toluene (T) hetero-trimer ions, B₁T₂⁺ and B₂T₁⁺. On the basis of our previous studies, two possible structures should be examined for the hetero-trimer ions. One is the structure with the charge localized on a single molecule, and the other is the structure with the charge delocalized over at least two molecules. In order to explore the existence of the CR interaction, we measure the photodissociation spectra of B₁T₂⁺ and B₂T₁⁺ in the near-infrared (6000–14000 cm⁻¹) region. The spectra in the infrared (2800–3150 cm⁻¹) region are observed for identifying the positive-charge carriers in the trimer ions. We also use benzene-*d*₆ and toluene-*d*₈ in the infrared spectroscopic measurement to provide unambiguous assignments. From these results, the positive charge distribution in B₁T₂⁺ and B₂T₁⁺ is discussed.

II. EXPERIMENTAL

The photodissociation spectra of benzene–toluene hetero-trimer ions are measured by using an ion guide spectrometer with two quadrupole mass filters.¹⁷ Argon gas is bubbled through liquid mixture of benzene and toluene at room temperature. The gas mixture of argon, benzene, and toluene is expanded into a vacuum chamber through a pulsed nozzle (General Valve Series 9) with a 0.80 mm orifice diameter. The total stagnation pressure is 2×10^5 Pa. Neutral clusters are ionized by an electron-impact ionizer situated near the exit of the nozzle. The electron kinetic energy is adjusted to 350 eV. After passing through a skimmer, the ionized clusters are introduced into the mass spectrometer. The parent ions are mass-selected by the first quadrupole mass filter. After deflection by 90° through an ion bender, the parent ions are led into a quadrupole ion guide and merged with a laser beam. The photoexcitation induces fragmentation of the parent ions. The resultant fragment ions are mass-analyzed by the second quadrupole mass filter and detected with a secondary electron multiplier tube. For normalizing the yields of the fragment ions, the power of the dissociation laser is monitored by a pyroelectric detector (Molelectron P1-15H-CC). The photodissociation spectra of the parent ions can be obtained by plotting the normalized yields of the fragment ions against the wavenumbers of the dissociation laser.

The idler output of an optical parametric oscillator (OPO) system (Spectra-Physics MOPO-730) pumped with a Nd:YAG laser (Spectra-Physics PRO-270) is used for the photodissociation spectra in the near-infrared ($6000\text{--}13000\text{ cm}^{-1}$) region. A tunable infrared source for the spectra in the $2800\text{--}3200\text{ cm}^{-1}$ region is another OPO system (Continuum Mirage 3000) pumped with a Nd:YAG laser (Continuum Powerlite 9010); the output energy is 1–2 mJ/pulse and the linewidth is approximately 1 cm^{-1} .

III. RESULTS AND DISCUSSION

A. Electronic spectra

Figure 2 shows the near-infrared photodissociation spectra of (a) B_2^+ , (b) $B_1T_1^+$, (c) T_2^+ , (d) $B_1T_2^+$, and (e) $B_2T_1^+$ in the 6000–14000 cm^{-1} region. The spectra of B_2^+ , $B_1T_1^+$, and T_2^+ have already been reported in our previous publications,^{7, 10} and are reproduced here for comparison. The fragment ions monitored for measuring these spectra are B^+ (for B_2^+), T^+ (for $B_1T_1^+$ and T_2^+), T_2^+ (for $B_1T_2^+$), and $B_1T_1^+$ (for $B_2T_1^+$); the benzene molecule is preferentially lost from the hetero-cluster ions.¹⁵ All the spectra display a strong band in this region. The band positions are 10930 (B_2^+), 8510 ($B_1T_1^+$), 10260 (T_2^+), 9430 ($B_1T_2^+$), and 8330 cm^{-1} ($B_2T_1^+$). These bands are characteristic of the cluster ions, because the neutral monomers and the monomer ions of benzene and toluene have no electronic transition in this region.¹⁸ For B_2^+ , the band at 10930 cm^{-1} is assigned to the CR band; the positive charge is delocalized in the dimer.⁷ Similarly, the 10260 cm^{-1} band in the spectrum of T_2^+ is attributed to the CR band; the charge delocalization takes place also in T_2^+ .¹⁰ For $B_1T_1^+$, there is one strong band at 8510 cm^{-1} , which can be ascribed to the CR band. On the basis of the overall features of the spectrum in the region from the visible to near-infrared, the probability of finding the charge on the toluene molecule is analyzed to be approximately 64 % for $B_1T_1^+$.¹⁰ The spectra of $B_1T_2^+$ and $B_2T_1^+$ show the strong band at 9430 and 8330 cm^{-1} , respectively; these bands are also due to the CR transition. The appearance of the CR band in these trimer ions indicates that the positive charge is delocalized over at least two constituent molecules.

B. Vibrational spectra

Figure 3 exhibits the infrared photodissociation spectra of (b) $B_1T_1^+$, (c) T_2^+ , (d) $B_1T_2^+$, and (e) $B_2T_1^+$ in the 2800–3150 cm^{-1} (CH stretching) region. The fragment ions monitored for the spectra are the same as those for the electronic spectra. It has been demonstrated that the CH stretching frequencies of aromatic cluster ions are insensitive to the cluster structures; the intensity of the CH stretching bands of the constituent species is additive in the vibrational spectra of aromatic cluster ions.¹² As an alternative to the vibrational spectrum of B_2^+ , the absorption band of the dimer ion core emerging in the vibrational spectrum of B_3^+ is shown in Fig. 3(a).¹² The CH stretching vibrations of neutral benzene are well studied by IR spectroscopy.^{19, 20} The CH stretching vibrations of the aromatic rings of benzene and toluene are thought to exist in the 3000–3200 cm^{-1} region.¹⁹ The methyl group of toluene has the CH stretching vibrations around 2900 cm^{-1} .¹⁹ Mikami and co-workers suggested that the infrared intensity of the CH stretching vibrations of the monomer ions of benzene and toluene is fairly lower than that of the corresponding neutral species.¹⁷ On the other hand, the cluster ions accompanied by the CR interaction have the infrared intensity stronger than that of the neutral species.¹² Therefore, one can suppose that the bands emerging in Fig. 3 are mainly due to the ionic molecules existing in the cluster ions. In the spectrum of B_2^+ , a sharp band is observed at 3068 cm^{-1} . This band can be assigned to the CH stretching vibration of the aromatic rings. The spectra of the $B_1T_1^+$, T_2^+ , and $B_1T_2^+$ ions exhibit similar features. In the spectrum of $B_1T_1^+$, there are two broad bands at 2905 and 3060 cm^{-1} . For T_2^+ , two bands emerge at 2910 and 3057 cm^{-1} . The spectrum of $B_1T_2^+$ has two bands at 2919 and 3063 cm^{-1} . The lower-frequency bands around 2910 cm^{-1} in the spectra of $B_1T_1^+$, T_2^+ , and $B_1T_2^+$ are attributed to the CH stretching vibrations of the methyl group; the higher-frequency bands around 3060 cm^{-1} are ascribed to the CH stretching vibrations of the aromatic rings. On the other hand, the spectrum of $B_2T_1^+$ displays spectral features similar to those of B_2^+ rather than the other ions containing toluene; there is only one sharp band at 3068 cm^{-1} .

We also measure the infrared photodissociation spectra of the trimer ions containing benzene- d_6 (B') and toluene- d_8 (T'). The IEs of benzene and benzene- d_6 are 9.243841 and 9.247181 eV, respectively.²¹ The Δ IE is less than 0.01 eV, which seems to hardly change the charge distribution between the normal and the deuterated species. The IE of the normal toluene is 8.8276 eV;²² there is no report on the IE of the toluene- d_8 molecule. However, it is probable that the Δ IE between toluene and toluene- d_8 is too small to change the charge distribution. Figure 4(b) depicts the infrared photodissociation spectrum of $B_1T_2^+$ with the spectrum of $B_1T_2^+$ (Fig. 4(a)) and the vibrational spectrum of the neutral benzene monomer (Fig. 4(c)).¹⁹ The spectrum of $B_1T_2^+$ shows three bands at 3054, 3084, and 3108 cm^{-1} . These bands can be attributed to the CH stretching vibrations of the benzene site, because the frequencies of the CD stretching vibrations are about 2300 cm^{-1} .²³ The neutral benzene monomer has three bands at 3048, 3079, and 3101 cm^{-1} .^{19, 20} The spectral features of $B_1T_2^+$ appear to be similar to those of the neutral benzene monomer. Figure 5 exhibits the infrared photodissociation spectra of (a) $B_2T_1^+$, (b) $B'_2T_1^+$, and (c) B_2^+ with the vibrational spectrum of the neutral toluene monomer (Fig. 5(d)).¹⁹ The spectrum of $B'_2T_1^+$ (Fig. 5(b)) has a band at 3078 cm^{-1} with an asymmetric band shape; the band is attributed to the CH stretching vibrations of the toluene site. However, the spectral features of $B'_2T_1^+$ turn out to be dissimilar to those of the neutral toluene monomer.

C. Positive charge distribution in (benzene)₁(toluene)₂⁺

In order to account for the appearance of the CR band, we consider three types of structures for $B_1T_2^+$: $(T_2)^+\bullet\bullet B_1$, $(B_1T_1)^+\bullet\bullet T_1$, and $(B_1T_2)^+$. The vibrational spectrum of $B_1T_2^+$ (Fig. 3(d)) displays two bands at 2919 and 3063 cm^{-1} . Since the overall features are similar to those of both $B_1T_1^+$ (Fig. 3(b)) and T_2^+ (Fig. 3(c)), we cannot distinguish the positive-charge carrier in $B_1T_2^+$ from these spectra. The vibrational spectrum of $B_1T_2^+$ (Fig. 4(b)) shows three distinct bands; the spectral features

are similar to those of the neutral benzene monomer (Fig. 4(c)). This result clearly indicates that the benzene moiety has a neutral character in $B_1T_2^+$. Figure 6 represents an energy level diagram of the species related to $B_1T_2^+$. The vertical axis represents the energy relative to $(B_1+T_1+T_1)$, in which all the molecules are in the neutral ground state and free from intermolecular interactions. Neusser and co-workers reported the energetics of benzene–toluene hetero-clusters.¹⁵ The energies of the $(B_1T_1^++T_1)$ and $(T_2^++B_1)$ systems ($E(B_1T_1^++T_1)$ and $E(T_2^++B_1)$, respectively) are obtained from the following equations:

$$E(B_1T_1^++T_1) = -D_0(B_1T_1) + IE(B_1T_1) \quad (1a)$$

$$E(T_2^++B_1) = -D_0(T_2) + IE(T_2) \quad (1b)$$

where D_0 stands for the intermolecular binding energy of the neutral dimer. The energies of $E(B_1T_1^++T_1) = 8.29$ eV and $E(T_2^++B_1) = 8.19$ eV are obtained from the following data: $D_0(B_1T_1) = 0.130$ eV, $IE(B_1T_1) = 8.42$ eV, $D_0(T_2) = 0.150$ eV, and $IE(T_2) = 8.34$ eV.¹⁵ Because $E(T_2^++B_1)$ is lower than $E(B_1T_1^++T_1)$, it is reasonable that the main fragment ion is not $B_1T_1^+$ but T_2^+ . For the same reason, it is probable that the positive charge is located on T_2 in $B_1T_2^+$. The CR band of T_2^+ is observed at 10260 cm^{-1} . The CR transition of $B_1T_2^+$ has an energy of 9430 cm^{-1} , which is lower than that of T_2^+ . The reduction of the CR transition energy upon solvation is analogous to the case of B_2^+ and B_3^+ ; the solvation of one benzene molecule to the dimer ion unit shifts the CR band from 10930 cm^{-1} (B_2^+) to 10360 cm^{-1} (B_3^+).^{7, 8} Thus we come to a conclusion that the positive charge in $B_1T_2^+$ is localized on the T_2 moiety, which is solvated by the benzene molecule. In the present stage, the binding energy between T_2^+ and B_1 is unknown; the value between B_2^+ and B_1 (0.27 eV) in the $B_2^+\cdots B_1$ ion is tentatively used for the diagram shown in Fig. 6.²⁴ The structure can be described as $T_2^+\cdots B_1$; the probability of finding the charge on the T_2 moiety is close to unity in $B_1T_2^+$.

D. Positive charge distribution in (benzene)₂(toluene)₁⁺

The electronic spectrum of B₂T₁⁺ (Fig. 2(e)) displays the CR band at 8330 cm⁻¹; this result manifests the charge delocalization in B₂T₁⁺. As seen in Fig. 3(e), the vibrational spectrum of B₂T₁⁺ shows the features similar to those of B₂⁺; one prominent band appears at 3068 cm⁻¹ with a width sharper than those of the corresponding bands of B₁T₁⁺ and T₂⁺; no band assignable to the CH stretching vibration of the methyl group is observed around 2900 cm⁻¹. This result implies the existence of the B₂⁺ subunit in B₂T₁⁺. On the other hand, the vibrational spectrum of B'₂T₁⁺ (Fig. 5(b)) looks dissimilar to that of the neutral toluene monomer (Fig. 5(d)); a certain amount of the positive charge may be carried by the toluene moiety. We ascribe the charge delocalization in B₂T₁⁺ to the CR interaction between B₂ and T₁. A simple perturbation theory for a nondegenerate system has been used for analyzing hetero-dimer ions.^{10, 16} We apply the same procedure for B₂T₁⁺. Figure 7 depicts an energy level diagram of the species related to B₂T₁⁺. The wave function of B₂T₁⁺ can be written as

$$\Psi = \alpha \cdot \psi(B_2^+) \cdot \psi(T_1) + \beta \cdot \psi(B_2) \cdot \psi(T_1^+) \quad (2)$$

where α^2 and β^2 stand for the probability of finding the charge on B₂ and T, respectively.

The perturbed energies are given by

$$E_+ = (1/2) \cdot (H_{BB-BB} + H_{T-T}) - (1/2) \cdot [(H_{BB-BB} - H_{T-T})^2 + 4 \cdot H_{BB-T}^2]^{1/2} \quad (3a)$$

$$E_- = (1/2) \cdot (H_{BB-BB} + H_{T-T}) + (1/2) \cdot [(H_{BB-BB} - H_{T-T})^2 + 4 \cdot H_{BB-T}^2]^{1/2} \quad (3b)$$

for the ground and excited states, respectively, where $H_{BB-BB} =$

$\langle \psi(B_2^+) \cdot \psi(T_1) | H | \psi(B_2^+) \cdot \psi(T_1) \rangle$, $H_{T-T} = \langle \psi(B_2) \cdot \psi(T_1^+) | H | \psi(B_2) \cdot \psi(T_1^+) \rangle$, and $H_{BB-T} = \langle \psi(B_2^+) \cdot \psi(T_1) | H | \psi(B_2) \cdot \psi(T_1^+) \rangle$. The overlap integral, $S_{BB-T} =$

$\langle \psi(B_2^+) \cdot \psi(T_1) | \psi(B_2) \cdot \psi(T_1^+) \rangle$, is omitted here, because the quantity should be negligibly small for the lowest pair states composed of the ground electronic configuration of the ion and the neutral species.⁷ Then the energy difference between the ground and the excited states, ΔE , is given by

$$\Delta E = E_- - E_+ = [(H_{BB-BB} - H_{T-T})^2 + 4 \cdot H_{BB-T}^2]^{1/2}. \quad (4)$$

The observed CR transition energy of $B_2T_1^+$ is 1.03 eV (8330 cm^{-1}). We evaluate H_{BB-BB} and H_{T-T} from the following equations,

$$H_{BB-BB} = E(B_2^+ + T_1) = -D_0(B_2) + IE(B_2) \quad (5a)$$

$$H_{T-T} = E(B_2 + T_1^+) = -D_0(B_2) + IE(T_1), \quad (5b)$$

with the values of $D_0(B_2) = 0.070$ eV, $IE(B_2) = 8.65$ eV,¹⁵ and $IE(T_1) = 8.8276$ eV.²²

Substitution of $\Delta E = 1.03$ eV, $H_{BB-BB} = 8.58$ eV, and $H_{T-T} = 8.76$ eV into Eq. 4 yields $H_{BB-T} = 0.51$ eV. Using these values, we finally obtain the following wave functions

$$\Psi_+ = (0.58)^{1/2} \cdot \psi(B_2^+) \cdot \psi(T_1) + (0.42)^{1/2} \cdot \psi(B_2) \cdot \psi(T_1^+) \quad (6a)$$

$$\Psi_- = (0.42)^{1/2} \cdot \psi(B_2^+) \cdot \psi(T_1) - (0.58)^{1/2} \cdot \psi(B_2) \cdot \psi(T_1^+) \quad (6b)$$

for the ground and excited states, respectively. In the ground state, the probability of finding the charge on the B_2 and T_1 moieties is 58 and 42 %, respectively. The off-diagonal matrix element, H_{BB-T} , represents the CR interaction energy. For the dimers of B_2^+ and $B_1T_1^+$, the CR interaction energies are 0.67 and 0.69 eV, respectively.^{7, 10} The interaction energy of $B_2T_1^+$ ($H_{BB-T} = 0.51$ eV) is smaller than that of $B_1T_1^+$, although the ΔE value for $B_2T_1^+$ (0.18 eV) is smaller than that for $B_1T_1^+$ (0.42 eV). This result may

be originated in a diffuse nature of the molecular orbitals of B_2 , which spreads over the two benzene molecules.⁷

The energies of the $(B_1T_1^++B_1)$ and $(B_1T_1+B_1^+)$ systems, $E(B_1T_1^++B_1)$ and $E(B_1T_1+B_1^+)$, respectively, are calculated from the following equations:

$$E(B_1T_1^++B_1) = -D_0(B_1T_1) + IE(B_1T_1) \quad (7a)$$

$$E(B_1T_1+B_1^+) = -D_0(B_1T_1) + IE(B). \quad (7b)$$

The energies of $E(B_1T_1^++B_1) = 8.29$ eV and $E(B_1T_1+B_1^+) = 9.11$ eV are obtained from the values of $D_0(B_1T_1) = 0.130$ eV, $IE(B_1T_1) = 8.42$ eV,¹⁵ and $IE(B) = 9.243841$ eV.²¹ The $(B_2^++T_1)$ system is higher in energy than the $(B_1T_1^++B_1)$ system by 0.29 eV. This is the reason why the main fragment ion from $B_2T_1^+$ is $B_1T_1^+$. On the other hand, the difference between $E(B_2^++T_1)$ and $E(B_2+T_1^+)$ is smaller than that between $E(B_1T_1^++B_1)$ and $E(B_1T_1+B_1^+)$; the $(B_2^++T_1)$ system is more favorable for the CR interaction among the three molecules than the $(B_1T_1^++B_1)$ system. The B_2^+ ion is stabilized by the CR interaction between the two benzene molecules. The energy levels of $(B_2^++T_1)$ and $(B_2+T_1^+)$ become accidentally close. As a result, the CR interaction occurs between B_2 and T_1 , and the positive charge is delocalized over the trimer.

IV. CONCLUSION

The electronic and vibrational spectra of the benzene–toluene hetero-trimer ions, $B_1T_2^+$ and $B_2T_1^+$, have been observed using the tunable near-infrared and infrared lasers and the tandem mass spectrometer. The electronic spectra of both ions display the CR band, demonstrating that the positive charge is not localized on one molecule. The vibrational spectrum of $B_1T_2^+$ in the CH stretching region shows band features quite similar to those of the neutral benzene monomer. This result represents that the positive

charge is localized in toluene dimer, which is solvated by the benzene molecule; the structure is described as $T_2^+ \cdots B_1$. For $B_2T_1^+$, the vibrational spectrum resembles that of B_2^+ . However, there is a noticeable difference between the vibrational spectra of $B_2T_1^+$ and the neutral toluene monomer, implying that a certain amount of the positive charge resides on the toluene site. We explain these results by the CR interaction between B_2 and T. By applying the simple perturbation theory, the probability of finding the charge on the B_2 and T_1 moieties is analyzed to be 58 and 42 %, respectively.

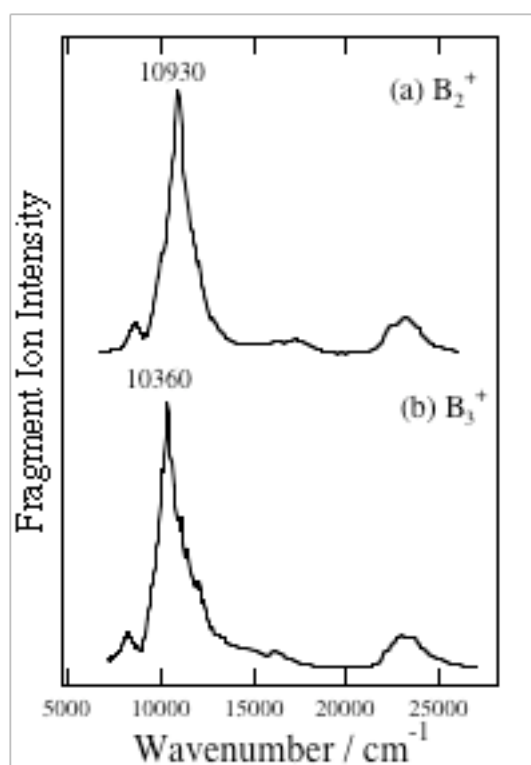


Figure 1. Inokuchi et al.

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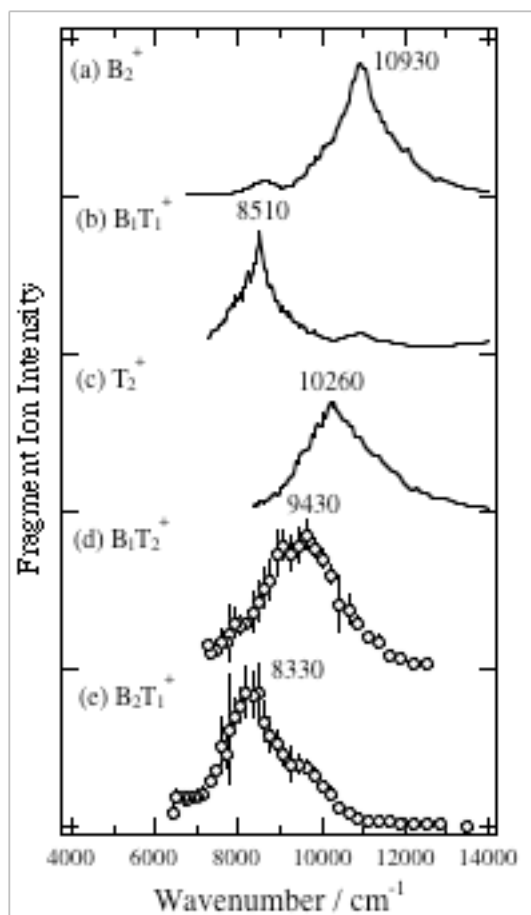


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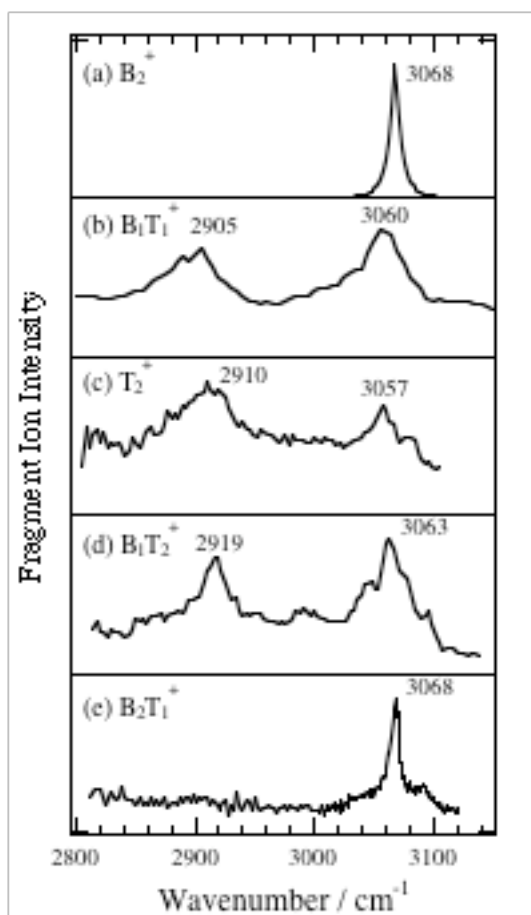


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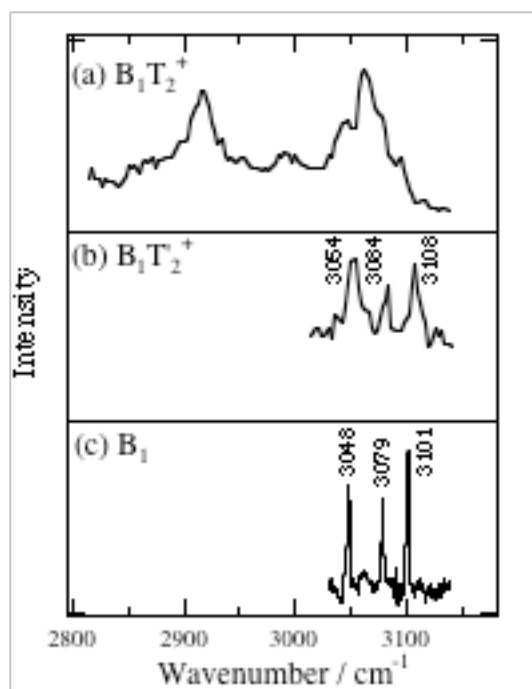


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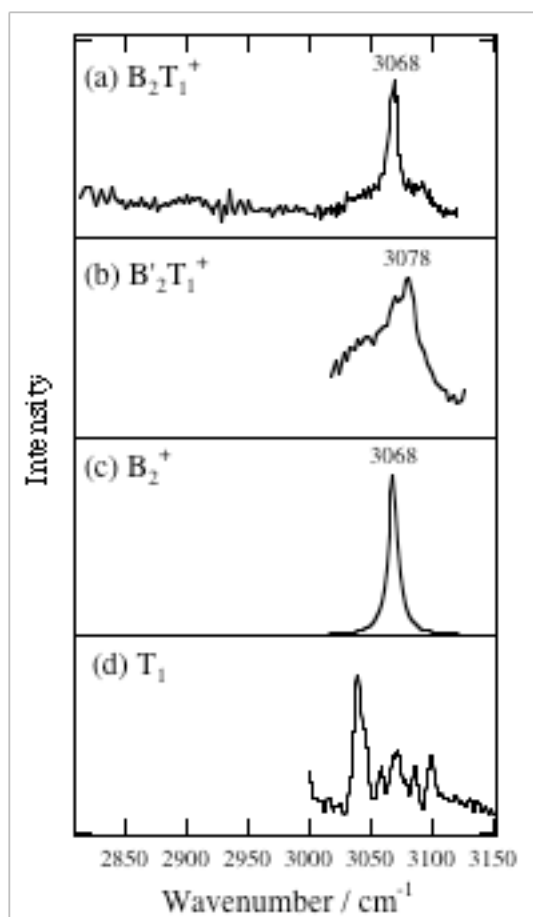


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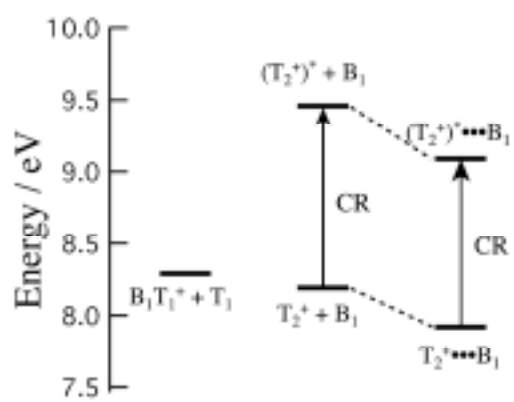


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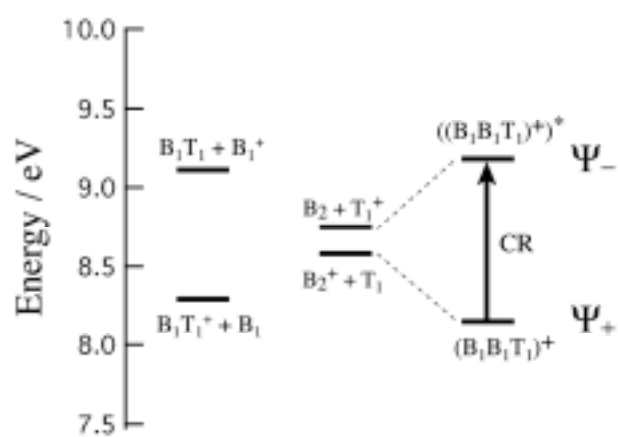


Figure 7. Inokuchi et al.
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FIGURE CAPTIONS

Figure 1. Electronic spectra of (a) B_2^+ and (b) B_3^+ in the 7000–28000 cm^{-1} region.

Figure 2. Electronic spectra of (a) B_2^+ , (b) $B_1T_1^+$, (c) T_2^+ , (d) $B_1T_2^+$, and (e) $B_2T_1^+$ in the 6000–14000 cm^{-1} region. The spectra of B_2^+ , $B_1T_1^+$, and T_2^+ are reproduced from refs. 7 and 10. The error bars indicate one standard deviation of statistical uncertainties determined from repeated laser scans.

Figure 3. Vibrational spectra of (a) B_2^+ , (b) $B_1T_1^+$, (c) T_2^+ , (d) $B_1T_2^+$, and (e) $B_2T_1^+$ in the 2800–3150 cm^{-1} region. The absorption band in spectrum (a) is taken from the absorption component of the B_2^+ core in B_3^+ .

Figure 4. Photodissociation spectra of (a) $B_1T_2^+$ and (b) $B_1T'_2^+$, and infrared spectrum of the neutral benzene monomer (c), where T' indicates a toluene- d_8 molecule.

Figure 5. Photodissociation spectra of (a) $B_2T_1^+$ and (b) $B'_2T_1^+$ with infrared spectra of B_2^+ (c) and the neutral toluene monomer (d), where B' indicates a benzene- d_6 molecule.

Figure 6. Energy level diagram of the $B_1T_2^+$ system (see text).

Figure 7. Energy level diagram of the $B_2T_1^+$ system (see text).