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Charge Delocalization in Benzene−Naphthalene Hetero-Dimer Cation

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The electronic spectrum of the benzene−naphthalene hetero-dimer cation is measured in the 400−1200 nm region by photodissociation spectroscopy. The most intense band at 580 nm is assigned to a local excitation (LE) band of the naphthalene cation chromophore. In addition to this band, an LE band of the benzene cation chromophore of the hetero-dimer is observed at nearly the same position (430 nm) as that of the benzene homo-dimer cation. The observation indicates that the positive charge stays on the benzene molecule in some probability, although the ionization potential of benzene is by 1.10 eV higher than that of naphthalene. The spectrum of the hetero-dimer cation also shows an intermolecular charge transfer (CT) band around 920 nm. On the basis of the position of the CT band as well as the intensity of the LE band relative to that of the homo-dimer, the probability of finding the charge on the benzene molecule is analyzed to be approximately 9%.

I. Introduction

Spectroscopic studies of dimer ions have provided insights into the nature of charge resonance interactions between the component molecules. Traditionally, conventional absorption spectroscopy was applied to dimer ions of aromatic molecules produced in condensed phases.[1−6] Recently, we have measured electronic spectra of dimer ions of benzene,[7,8] toluene,[9] and naphthalene[10] by mass-selected photodissociation spectroscopy in the gas phase. Two types of absorption bands are commonly seen on the spectra in the visible to near-infrared wavelength region. One is a charge resonance (CR) band. In a dimer ion composed of molecules X and Y, *i.e.*, $(XY)^+$, the attractive CR interaction provides the ground state described by the wave function: $\Psi_+ = \alpha\psi(X^+)\psi(Y) + \beta\psi(X)\psi(Y^+)$, where $\alpha^2 + \beta^2 = 1$. The repulsive interaction produces the excited state: $\Psi_- = \beta\psi(X^+)\psi(Y) - \alpha\psi(X)\psi(Y^+)$. The CR band is due to the transition between the two CR states. We can determine the degree of the resonance interaction from the position of the CR band, as far as configuration interactions of the CR states with other electronically excited states are negligibly small.[8] The other type is a local excitation (LE) band, in which an electronic transition of a monomer ion unit within the dimer (X^+ or Y^+) is locally excited. For each homo-dimer ion ($X = Y$) studied,[7−10] the CR band is much stronger than the LE band. The observation indicates that the charge is equally shared with the two component molecules as a result of strong CR interaction. In a hetero-dimer ion comprised of dissimilar partners ($X \neq Y$), on the other hand, the positive charge may reside principally on the molecule 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.

Meot-Ner and co-workers measured dissociation energies for homo- and hetero-dimer ions of aromatic molecules by high-pressure mass spectrometry.[11,12] The dissociation energy was found to decrease with increasing the difference in the IP's (ΔIP) of the component molecules. Neusser and co-workers determined the dissociation energies of several aromatic dimer ions from the ionization potentials of neutral dimers and the appearance potentials for the dissociation of dimer ions (breakdown measurement).[13−15] The binding energies of hetero-dimer ions of benzene with other molecules were found to be smaller than that of the benzene homo-dimer ion. Both groups assigned the decreased bonding energy in hetero-dimer ions to the reduced resonance interaction.[11−15] Kira and co-workers first presented spectroscopic evidence for the formation of the *intermolecular* naphthalene−pyrene hetero-dimer ion in a low-temperature matrix.[16] However, it was difficult to unambiguously identify the species responsible for the photoabsorption in the CR band region. Yamamoto and co-workers used bichromophoric compounds linked by a methylene chain as precursors of the dimer ions and studied *intramolecular* dimer ions by laser photolysis at room temperature.[17,18] They observed the CR band of the intramolecular naphthalene−phenanthrene hetero-dimer ion, $(NpPh)^+$, but failed to observe the naphthalene−pyrene dimer ion, $(NpPy)^+$, at 298 K.[19] They considered that the large ΔIP between Np and Py (0.55 eV) resulted in a small stabilization energy for $(NpPy)^+$ and that it could be observed only at a low temperature. They concluded therefore that the IP's of both moieties should be similar to each other for the formation of a stable hetero-dimer ion.

Dimer ions with small binding energies may hardly be observed in solutions at room temperature, as pointed out by Yamamoto and co-workers. In the gas phase, however, the dimer ions can be cooled in a supersonic expansion. Moreover, we can determine the position of the CR band without any solvent effect. We plan to study hetero-dimer ions of benzene with a series of other aromatic molecules as a function of ΔIP. In this article, we report the results on the benzene−naphthalene hetero-dimer ion, $(BzNp)^+$. The IP's of benzene and naphthalene are reported to be 9.243 842[20] and 8.1442 eV,[21] respectively, resulting in a large ΔIP of 1.10 eV.

II. Experimental Section

The photodissociation spectrum of $(BzNp)^+$ was measured by using an apparatus with an octopole ion guide and two quadrupole mass filters.[10] Argon gas was bubbled through liquid benzene at room temperature and then passed through a heated cell (80 °C) filled with naphthalene. The mixture was expanded through a pulsed nozzle. A rotating disk (stainless

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steel) was situated parallel to the expansion axis beyond the nozzle exit. The fundamental output of a Nd:YAG laser (Spectra-Physics GCR-14S) was focused onto the disk to induce plasma in the expansion for the ionization.[22] Several cluster ions were formed by accretion of neutral molecules to the ionized one and were successively cooled in the expansion. The $(BzNp)^+$ ion was isolated by a quadrupole mass filter (Extrel Model 4-270-9). After deflection through 90° by a quadrupole bender,[23] the ion beam was decelerated and introduced into an octopole ion guide.[24] The photodissociation laser beam propagated coaxially along the octopole and merged with the ion beam. The output of an optical parametric oscillator (Spectra-Physics MOPO-730) pumped with a Nd:YAG laser (Spectra-Physics GCR-250) was used in the regions of 460−680 and 740−1200 nm. The output of a dye laser (Spectra-Physics PDL-3) pumped with a Nd:YAG laser (Spectra-Physics GCR-18S) was used in the 680−740 nm region, where MOPO-730 has a gap in the gain curve. A dye laser (Lumonics HyperDYE-300) pumped with an excimer laser (Lumonics EXCIMER-600) was used in the 400−460 nm region. The resulting photofragment ions were mass-analyzed by another quadrupole filter (ANELVA AGA-360) and detected by a secondary electron multiplier. The power of the photodissociation laser was monitored with either a PIN photodiode (Hamamatsu Photonics S1722-02, 400−1000 nm) or an InGaAs photodiode (Hamamatsu Photonics G3476-05, 900−1200 nm). Both the ion signals received by the detector and the signals from the photodiode were fed into a digital storage oscilloscope (LeCroy 9314M) coupled with a microcomputer. A digital delay-pulse generator (Stanford Research Systems DG-535) was used to control the opening of the pulsed nozzle and also to trigger the lasers with variable delay time.

The mass spectra of the photofragment ions and the photodissociation cross sections of $(BzNp)^+$ relative to those of homodimer ions were measured by using a reflectron-type time-of-flight mass spectrometer. The apparatus and the experimental procedure were described in our previous publications.[25,26]

III. Results and Discussion

A. Dissociation Channels. Upon photoexcitation in the visible to near-infrared region, the $(BzNp)^+$ hetero-dimer ion may dissociate in two different ways as follows:

$$(BzNp)^+ + h\nu \rightarrow Bz^+ + Np \qquad (1a)$$

$$(BzNp)^+ + h\nu \rightarrow Bz + Np^+ \qquad (1b)$$

The dissociation channels of $(BzNp)^+$ were examined by using the time-of-flight mass spectrometer. Figure 1 shows typical mass spectra of the fragment ions produced from $(BzNp)^+$. The ion signals were accumulated with the dissociation laser, and then the background signals due to metastable decay processes were accumulated without the laser. The mass spectra of the photofragment ions were obtained by subtracting the laser-off spectra from the laser-on spectra. At all wavelengths studied, the dissociation of $(BzNp)^+$ yields preferentially $Bz + Np^+$ (eq 1b). Therefore, the photodissociation spectrum of $(BzNp)^+$ can be obtained by monitoring the yield of only the Np^+ product.

B. Photodissociation Spectra. Figure 2 exhibits the photodissociation spectra of $(Np)_2^+$, $(BzNp)^+$, and $(Bz)_2^+$. These spectra are arranged for comparison of the band positions; relative intensities of them are just arbitrary to one another. The spectra of $(Np)_2^+$ and $(Bz)_2^+$ were already reported in our previous publications;[8,10] the assignments of the bands are as follows. The 430 and 580 nm bands of $(Bz)_2^+$ are the local excitation (LE) bands, in which the $\pi(e_{1g}) \leftarrow \pi(a_{2u})$ and the $\pi(e_{1g}) \leftarrow \sigma(e_{2g})$ transitions are locally excited in a Bz^+ unit, respectively.[8,25] The 580 nm band of $(Np)_2^+$ is due to the local excitation of the $\pi(a_u) \leftarrow \pi(b_{3g})$ transition in a Np^+ unit.[10] The position of this band accidentally coincides with that of the $\pi \leftarrow \sigma$ band of $(Bz)_2^+$. The 920 nm band of $(Bz)_2^+$ and the 1180 nm band of $(Np)_2^+$ are the CR bands.[7,8,10] The spectrum of $(BzNp)^+$ was measured in this work. The intensities of the Np^+ fragment ions were normalized according to the dissociation laser power, and the results were plotted against the wavelengths of the laser. Three distinct absorption bands are seen in the 400−1200 nm region. Two bands at 430 and 580 nm can be attributed to LE bands. The 920 nm band may arise from near resonance interaction in the hetero-dimer ion.

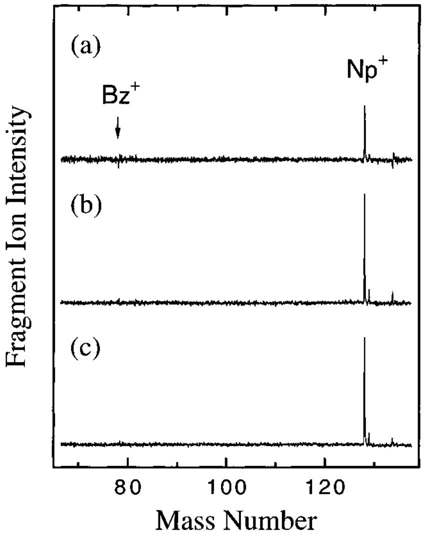

Figure 1. TOF mass spectra of photofragment ions produced from $(BzNp)^+$. The wavelength of the photodissociation laser is (a) 430, (b) 580, and (c) 920 nm. The spectra are obtained by subtracting the laser-off spectra from the laser-on spectra in order to eliminate the background signals due to metastable decay processes.

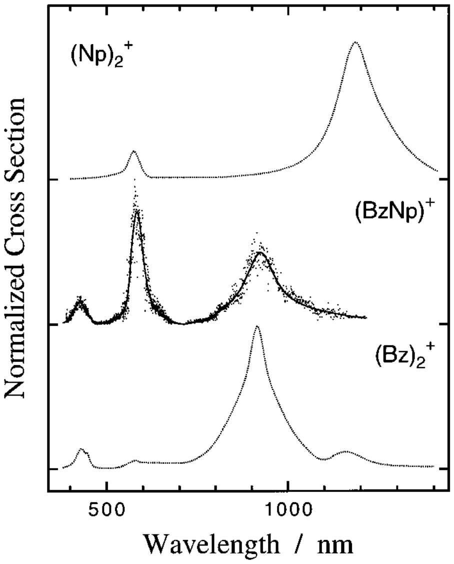

Figure 2. Photodissociation spectra of $(Np)_2^+$ (top), $(BzNp)^+$ (middle), and $(Bz)_2^+$ (bottom). Solid curve is drawn through the raw data points of $(BzNp)^+$. The spectra of $(Np)_2^+$ and $(Bz)_2^+$ have already been reported in our previous publications[8,10] and are reproduced by broken curves for comparison of the band positions. Amplitudes of three spectra are normalized independently; relative intensities of them are just arbitrary to one another.

(a) Local Excitation Band. First we make assignment of the 580 nm band of $(BzNp)^+$. Both the Np^+ unit in $(Np)_2^+$ and

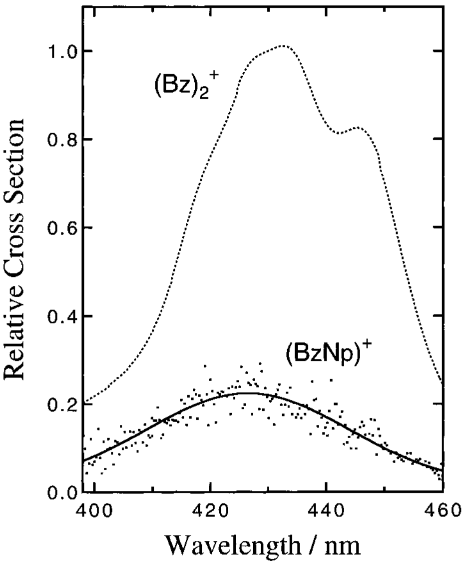

Figure 3. Photodissociation spectra of $(Bz)_2^+$ and $(BzNp)^+$ in the LE band region of the Bz^+ unit. Amplitudes of the spectra are scaled to each other according to the relative cross sections measured at 430 nm. The vertical scale is normalized to the cross section of $(Bz)_2^+$ at 430 nm.

the Bz^+ unit in $(Bz)_2^+$ show absorption bands at 580 nm. In the ground state of $(BzNp)^+$, the positive charge is likely to reside on the Np moiety because of its lower IP; the probability of finding the $(BzNp)^+$ ion in the Bz···Np^+ form is much higher than that in the Bz^+···Np form. This point is confirmed in section III.B.b by quantitative estimation of the probability. Therefore, the main contribution to the 580 nm band of $(BzNp)^+$ is from the local excitation of the Np^+ unit.

Figure 3 shows an expanded view of the spectra of $(Bz)_2^+$ and $(BzNp)^+$ in the 430 nm band region. We determined the relative cross sections by measuring the photodepletion yields of these ions in the time-of-flight spectra. In Figure 3, amplitudes of the spectra are scaled to each other according to the relative cross sections measured at 430 nm; $\sigma[(Bz)_2^+]:\sigma[(BzNp)^+]:\sigma[(Np)_2^+] = 1:0.21:0.10$. The vertical scale is normalized to $\sigma[(Bz)_2^+]$ at 430 nm. The spectrum of $(Bz)_2^+$ shows the main hump at 430 nm and the second hump at 445 nm. We tentatively assign these humps to vibrational structure of the $\pi(e_{1g}) \leftarrow \pi(a_{2u})$ transition. The position of the absorption maximum of $(BzNp)^+$ almost coincides with the main hump of $(Bz)_2^+$, although the second hump is not clearly seen due to large fluctuation in the $(BzNp)^+$ signals. Therefore, we can attribute the hump of $(BzNp)^+$ at 430 nm to the local excitation of the Bz^+ unit in $(BzNp)^+$. The presence of this LE band suggests that the charge is also carried by the Bz moiety, although the IP of Bz is by 1.10 eV higher than that of Np. The spectrum of $(Np)_2^+$ in this region is almost flat, showing no distinct maxima. Since the charge stays mainly, though not exclusively, on the Np moiety in $(BzNp)^+$, it also exhibits flat background band in this region.[27] The spectrum of $(BzNp)^+$ is composed of the hump due to the Bz^+ unit and the flat background due to the Np^+ unit. According to the relative cross sections measured at 430 nm, the contribution of the Np^+ unit is approximately a half of the apparent intensity. Therefore, the intensity of the LE band due to the Bz^+ unit in $(BzNp)^+$ is estimated to be 10% of that of $(Bz)_2^+$. This fact suggests that the probability of finding the charge on the Bz moiety is approximately 10%.[28] This value is subject to the approval by another way of more reliable estimation.

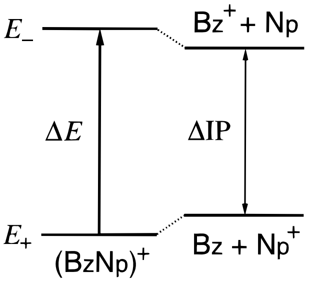

Figure 4. Energy level diagram for the analysis of near-resonance interaction in $(BzNp)^+$. The energies for the ground state (E_+) and the excited state (E_-) of $(BzNp)^+$ are given by eq 4. The observed transition energy (ΔE) is 1.35 eV. The $Bz^+ + Np$ asymptote is located above the $Bz + Np^+$ asymptote by ΔIP (1.10 eV).

(b) "Charge Transfer" Band. In contrast to the CR bands of the homo-dimer ions, the 920 nm band of $(BzNp)^+$ is weaker than the LE band at 580 nm. According to the measurement of the photodepletion yields, the maximum cross section of $(BzNp)^+$ at the 920 nm band is only 7% of that of $(Np)_2^+$ at the CR band. The transition energy of this band ($\Delta E = 1.35$ eV) is by only 0.25 eV larger than ΔIP between Bz and Np. Duncan and co-workers studied the photodissociation processes of a variety of Bz−metal complex ions.[29−31] In essentially every system studied, the metal atom in the complex has an IP much lower than that of Bz. Therefore, the charge is expected to be localized on the metal atom in the ground electronic state of these complexes. For many of these complexes, "dissociative charge transfer" is a prominent photoprocess at energies in the neighborhood of ΔIP,

$$\text{Bz}\cdots\text{metal}^+ + h\nu \rightarrow \text{Bz}^+\cdots\text{metal} \rightarrow \text{Bz}^+ + \text{metal} \qquad (2)$$

which produces Bz^+ as the fragment ion. Similarly, the 920 nm band of $(BzNp)^+$ is possibly due to an intermolecular "charge transfer" (CT) transition, although the dissociation products are not $Bz^+ + Np$ but $Bz + Np^+$ in this case. The photodissociation mechanism for the formation of $Bz + Np^+$ following the CT transition is discussed in section III.C.

The transition energy of the CT band is larger than ΔIP, indicating that the ground state of $(BzNp)^+$ is more stable than the $Bz + Np^+$ asymptote and the excited state is less stable than the $Bz^+ + Np$ asymptote due to intermolecular interactions. The energy level diagram is shown in Figure 4. A simple perturbation theory for a nondegenerate system can be applied here, because locally excited states may not seriously couple with the charge-transfer excited state or the ground state. The wave function of $(BzNp)^+$ can be written as

$$\Psi = \alpha\psi(\text{Bz}^+)\,\psi(\text{Np}) + \beta\psi(\text{Bz})\,\psi(\text{Np}^+) \qquad (3)$$

where α^2 and β^2 stand for the probabilities of finding the charge on Bz and Np, respectively. The perturbed energies are given by

$$E_+ = (1/2)(H_{BB} + H_{NN}) - (1/2)[(H_{BB} - H_{NN})^2 + 4H_{BN}^{\ 2}]^{1/2} \qquad (4a)$$

$$E_- = (1/2)(H_{BB} + H_{NN}) + (1/2)[(H_{BB} - H_{NN})^2 + 4H_{BN}^{\ 2}]^{1/2} \qquad (4b)$$

for the ground and the excited states, respectively, where $H_{BB} = \langle\psi(\text{Bz}^+)\psi(\text{Np})|H|\psi(\text{Bz}^+)\psi(\text{Np})\rangle$, $H_{NN} = \langle\psi(\text{Bz})\psi(\text{Np}^+)|H|\psi(\text{Bz})\psi(\text{Np}^+)\rangle$, and $H_{BN} = \langle\psi(\text{Bz}^+)\psi(\text{Np})|H|\psi(\text{Bz})\psi(\text{Np}^+)\rangle$. We omit the intermolecular overlap integral, $S_{BN} = \langle\psi(\text{Bz}^+)\psi(\text{Np})|\psi(\text{Bz})\psi(\text{Np}^+)\rangle$, in the derivation of eqs 4a and 4b, because the quantity was shown to be negligibly small for the lowest pair states composed of the ground electronic configuration of the ion and the neutral species.[8] Then the transition energy between the two states is given by

$$\Delta E = E_- - E_+ = [(H_{BB} - H_{NN})^2 + 4H_{BN}{}^2]^{1/2} \quad (5)$$

The observed transition energy for the CT band is 1.35 eV. Substitution of this value for ΔE and the difference in the IP's between Bz and Np (1.10 eV) for $(H_{BB} - H_{NN})$ in eq 5 yields $H_{BN} = 0.38$ eV. Using these values, we finally obtain the following wave functions

$$\Psi_+ = (0.09)^{1/2}\psi(\mathrm{Bz}^+)\,\psi(\mathrm{Np}) + (0.91)^{1/2}\psi(\mathrm{Bz})\,\psi(\mathrm{Np}^+) \quad (6a)$$

$$\Psi_- = (0.91)^{1/2}\psi(\mathrm{Bz}^+)\,\psi(\mathrm{Np}) - (0.09)^{1/2}\psi(\mathrm{Bz})\,\psi(\mathrm{Np}^+) \quad (6b)$$

for the ground and the excited states, respectively. In the ground state, the probability of finding the charge on the Np moiety is 91% and that on the Bz moiety is 9%. This value is in accord with that obtained from the analysis of the relative intensities of the LE band in the previous section.

(c) Resonance Interaction Energies. Meot-Ner and co-workers estimated the resonance energies by subtracting the dissociation energies of the protonated dimers, X···XH$^+$, from that of the nonprotonated dimer ions, (X···X)$^+$, because they considered that the charge resonance was not possible in the protonated dimers.[11,12] Thus, the resonance energies contributing to the total binding energies were determined to be 0.26 eV for $(\mathrm{Bz})_2^+$ and 0.16 eV for $(\mathrm{Np})_2^+$.[12] Neusser and co-workers measured the binding energies of $(\mathrm{Bz})_2^+$ (0.66 eV) and the Bz−cyclohexane hetero-dimer ion (0.20 eV).[13−15] They supposed that no CR interaction contributes to the bonding in (Bz−cyclohexane)$^+$, because any π-electron system is missing in cyclohexane. By comparing the data of $(\mathrm{Bz})_2^+$ with CR interaction and (Bz−cyclohexane)$^+$ without CR interaction, they concluded that the contribution of the resonance energy to the binding energy is 0.46 eV.[14,15] We employed another method of estimating the CR energy. For $(\mathrm{Bz})_2^+$ and $(\mathrm{toluene})_2^+$, we compared the CR transition energies measured by our group[7−9] and the binding energies reported by Neusser and co-workers.[13−15] The CR transition energy was found to be just twice of the binding energy for each homo-dimer ion.[8] In accordance with the conclusion by Neusser and co-workers, the result suggests that the dominant contribution to the binding energy of $(\mathrm{Bz})_2^+$ and $(\mathrm{toluene})_2^+$ is from the resonance interaction. In this case, the resonance interaction energy is given as a half of the CR transition energy: 0.67 eV for $(\mathrm{Bz})_2^+$. Yamamoto and co-workers estimated the degree of resonance interaction in the same way with ours.[17−19] They regarded a half of the transition energy as its stabilization energy even for the (Np−phenanthrene)$^+$ hetero-dimer ion.[19] However, we insist on the use of eq 5 for estimating the degree of resonance interaction in hetero-dimer ions. In the following discussion, we consider halves of the CR transition energies to be the resonance energies of homo-dimer ions, because these values can be directly compared with those of hetero-dimer ions (H_{BN} in eq 5).

The interaction energy of (BzNp)$^+$ (H_{BN}) is 0.38 eV, which is smaller than that of $(\mathrm{Bz})_2^+$ (0.67 eV) and $(\mathrm{Np})_2^+$ (0.53 eV). The strength of the CR interaction is reduced when ΔIP is increased, as pointed out by Meot-Ner and co-workers[11,12] and by Neusser and co-workers.[13−15] However, the reduction is not so rapid; the value of H_{BN} amounts to approximately 70% of that of $(\mathrm{Np})_2^+$, despite the large value of ΔIP between Bz and Np. The measurement of the spectra of (Bz−toluene)$^+$ (ΔIP = 0.42 eV) and (Bz−*p*-xylene)$^+$ (ΔIP = 0.76 eV) is in progress in order to bridge the gap between the $(\mathrm{Bz})_2^+$ homo-dimer (ΔIP = 0) and the (BzNp)$^+$ hetero-dimer (ΔIP = 1.10 eV). The results of the Bz−toluene system will be of interest, because the binding energy of (Bz−toluene)$^+$ has already been reported by Neusser and co-workers.[13−15]

C. Photodissociation Mechanisms. On the basis of the diagram shown in Figure 4, the threshold energies for the two dissociation channels are 1.22 eV for eq 1a and 0.12 eV for eq 1b. The formation of Np$^+$ (eq 1b) is found to be the dominant dissociation channel from each of the three excited states with distinct characters, although the formation of Bz$^+$ (eq 1a) is energetically possible even from the lowest (CT) excited state.

The dissociation mechanism seems to be most simple after the excitation of the Np$^+$ chromophore. In the ground state of (BzNp)$^+$, the charge stays on the Np moiety with 91% probability. The photoexcitation at the 580 nm band promotes the electronic transition of the Np$^+$ chromophore; the excited state should correlate to the Bz + (Np$^+$)* asymptote. As we showed for the local excitation of $(\mathrm{Bz})_2^+$,[32] the (BzNp)$^+$ ion in the locally excited state undergoes an internal conversion to vibrationally excited levels of the ground state with the charge remaining on the Np moiety. Then the hot (BzNp)$^+$ dissociates to the lowest-energy channel, yielding Bz + Np$^+$.

The local excitation of the Bz$^+$ chromophore also produces Np$^+$. The Bz$^+$ chromophore in (BzNp)$^+$ can be excited only when the charge stays on the Bz moiety. The excited state should correlate to the (Bz$^+$)* + Np asymptote. If the dissociation occurred directly from this state, the products should be Bz$^+$ and Np. As shown in Figure 1, however, we observed only Np$^+$ as the product ion. We can explain the observation by considering an internal conversion to the ground state similar to the one mentioned above. This process is accompanied by charge transfer from the Bz moiety to the Np moiety. After the internal conversion, the resulting vibrationally excited (BzNp)$^+$ dissociates to Bz + Np$^+$.

After the CT transition, the charge stays on the Bz moiety with 91% probability as indicated by eq 6b. The excited state is higher in energy than the Bz$^+$ + Np asymptote. Direct dissociation out of this state produces Bz$^+$ and Np. Actually, the products are Bz$^+$ and neutral metal atom in the dissociative charge transfer of Bz−metal complex ions (eq 2).[29−31] In the case of (BzNp)$^+$, however, Bz and Np$^+$ are produced upon the CT band excitation. For the CR transition of $(\mathrm{Bz})_2^+$,[28] we demonstrated that the time of dissociation is comparable to or longer than a rotational period of $(\mathrm{Bz})_2^+$ (subnanosecond). Similarly, the time of dissociation in the (BzNp)$^+$ system is expected to be quite long compared to the time scale for the direct dissociation from the dissociative excited state (subpicosecond). The dissociation occurs via a process analogous to internal conversion, with reversal of the charge transfer.

IV. Conclusion

The photodissociation spectrum of (BzNp)$^+$ in the gas phase exhibits three bands at 430, 580, and 920 nm. The positions of the first two bands are consistent with those of the LE bands of $(\mathrm{Bz})_2^+$ and $(\mathrm{Np})_2^+$, respectively. The 430 nm band is assigned to the LE band of the Bz$^+$ chromophore, while the 580 nm band to that of the Np$^+$ chromophore. The 920 nm band is attributed to the intermolecular CT band. On the basis of the position of the CT band as well as the intensity of the LE band relative to that of $(\mathrm{Bz})_2^+$, the probability of finding the charge on the Bz moiety is analyzed to be approximately 9%. We can see the near-resonance interaction in the (BzNp)$^+$ hetero-dimer ion, although the IP of Bz is by 1.10 eV higher than that of Np.

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(27) Strictly, the intensity of the background band of $(BzNp)^+$ is not the same as but slightly weaker than that of $(Np)_2{}^+$, because the probability of finding the charge on the Np moiety is 100% for $(Np)_2{}^+$ but is slightly smaller than 100% for $(BzNp)^+$.

(28) We assume that the intensity of the LE band is essentially independent of the partner molecule; *i.e.*, both Bz in $(Bz^+\cdots Bz)$ and Np in $(Bz^+\cdots Np)$ exert a similar solvent effect on the Bz^+ chromophores.

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