

Charge Resonance and Charge Transfer Interactions in Naphthalene Homo- and Hetero-Dimers

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Abstract Charge resonance interaction in naphthalene homo- and hetero-dimer cations is studied by photodissociation spectroscopy of the charge resonance and the local excitation transitions. The resonance interaction in naphthalene dimer cation is slightly weaker than that of a benzene dimer cation because of partial overlapping of the respective aromatic rings. A local excitation band of the benzene cation chromophore is observed in the spectrum of a naphthalene-benzene hetero-dimer cation at nearly the same position as that of the benzene dimer cation. This indicates that in spite of its higher ionization potential the positive charge stays on the benzene molecule in some probability. On the basis of the band position of the charge resonance transition as well as the intensity of the local excitation band, the probability is analyzed to be approximately 9%. This means 91% is localized on the naphthalene chromophore in this hetero-dimer.

CHARGE RESONANCE INTERACTION IN CLUSTERS

A cation molecule in contact with neutral molecule(s) has a significant effect on the electrons in higher occupied orbitals of the neutral species. In particular, aromatic molecules with low ionization potentials could show some specific behavior in molecular cluster cations. A model of charge delocalization over all molecules in a cluster has been proposed for benzene cation clusters, $(C_6H_6)_n^+$, on the basis of this situation.[1] However, not only the local excitation(LE) bands but also the charge resonance(CR) bands of $(C_6H_6)_n^+$ with $n=3-6$ showed the spectral positions and widths quite similar to those of the dimer cation, $(C_6H_6)_2^+$, although the trimer cation showed the largest spectral shift of the LE(π , σ) band.

[2,3] Interestingly the spectrum of the hexamer cation, $(C_6H_6)_6^+$, exhibited nearly the same pattern as that of the dimer. These results clearly demonstrate that the charge is localized on the dimer unit. This means that other neutral molecule(s) interact with the dimer cation rather weakly just like solvent molecule(s).

Similar ion core structures were found in $(CO_2)_n^+$ [4] and Ar_n^+ [5] clusters. Ionization potentials of benzene (9.2437 eV) and naphthalene (8.1442 eV) are, however, very much smaller than those of CO_2 (13.773 eV) and Ar (15.7596 eV), suggesting higher possibilities of electron hopping to the cation species induced by inter-molecular motions of neutral and cation molecules. The charge resonance interaction in a cation homo-dimer provides the ground state wavefunction:

$\Psi_+ = \sqrt{1/2} \psi(B_1^+) \psi(B_2) + \sqrt{1/2} \psi(B_1) \psi(B_2^+)$. This interaction produces also the

antisymmetric state: $\Psi_- = \sqrt{1/2} \psi(B_1^+) \psi(B_2) - \sqrt{1/2} \psi(B_1) \psi(B_2^+)$. The CR transition

takes place from the ground symmetric state to the antisymmetric one. The upper state is unstable because of the repulsive interaction. In both states of the homo-dimer, the B_1 and B_2 molecules have an equal probability of carrying a charge. $(C_6H_6)_2^+$ shows the CR band at 920 nm. The CR transition moves the charge from B_1 to B_2 and B_2 to B_1 with the frequency of a photon energy. The transition probability is fairly large compared to the local excitations in this case.

The resonance interaction is expected also in the hetero-dimers composed of molecules with similar ionization potentials. We have studied the photodissociation spectrum of the benzene-toluene hetero-dimer cation. [6] The spectrum revealed a strong CR band located at 1170 nm. This observation suggested that the probability of the charge residing in toluene is approximately 70 % and in benzene 30 %. The difference in the ionization potential is 0.42 eV. This energy is smaller than the stabilization energy (0.674 eV) of $(C_6H_6)_2^+$. Thus, the appearance of the CR band is reasonable.

The ionization potential of naphthalene is 8.144 eV, 1.10 eV lower than benzene. The difference in the ionization potentials is now much larger than the resonance interaction energy in $(C_6H_6)_2^+$. Therefore, the positive charge in the naphthalene-benzene dimer cation $(C_{10}H_8 - C_6H_6)^+$ is expected to be localized on the naphthalene chromophore. Saigusa and Lim [7] reported the photo-dissociation spectra of naphthalene cation clusters. Their band positions were not in agreement with our spectrum of the naphthalene dimer cation, $(C_{10}H_8)_2^+$. [8]

EXPERIMENTAL

The apparatus used in this work has been described elsewhere.[8] The experiment was carried out using an octopole ion trap with two quadrupole mass filters. The parent ions were prepared using the laser-induced plasma technique. Cation clusters were formed by accretion of neutral molecule(s) to the ionized one and were successively cooled in the expansion. Naphthalene or naphthalene-benzene dimer cations were selected by a quadrupole mass filter. After 90° deflection the ion beam was introduced into the octopole trap where the photodissociation laser beam was propagated coaxially, exciting the trapped ions. The photoexcitation induced the fragmentation of $(C_{10}H_8)_2^+$ or $(C_{10}H_8-C_6H_6)^+$ producing $C_{10}H_8^+$ fragments. Yields of the fragment ions were measured as a function of photon energy and laser output. The output of an optical parametric oscillator (Spectra-Physics MOPO-730) pumped with a Nd:YAG laser (Spectra-Physics GCR-250) was utilized in the regions of 460-680nm and 740-1200nm. A dye laser (Spectra Physics PDL-3) was used for the wavelength range 680-740nm.

PHOTODISSOCIATION SPECTRA

Figure 1 shows the photodissociation spectra of $(C_{10}H_8)_2^+$ (top) and $(C_{10}H_8-C_6H_6)^+$ (middle) as well as that of $(C_6H_6)_2^+$ (bottom). Relative intensities of the three spectra in Figure 1 are just arbitrary. They are adjusted for the comparison of the band positions. The charge resonance band of $(C_{10}H_8)_2^+$ appears at 1180 nm corresponding to a transition energy of 1.05 eV. On the basis of a simple interaction model[3], this value gives an interaction energy of 0.525 eV (cf. 0.674 eV for $(C_6H_6)_2^+$). Inokuchi et al. proposed a partial overlap structure for $(C_{10}H_8)_2^+$ based on the position of the LE band at 580 nm[8]. A partial overlap structure is in conformity with an interaction energy weaker than that of $(C_6H_6)_2^+$.

In a hetero-dimer cation, the position of the CR band is related to the difference in the ionization potentials. A larger difference locates the excited state at a higher energy, while the interaction energy decreases inversely proportional to

the square of the difference. The CR band of $(C_{10}H_8 - C_6H_6)^+$ appears at 920 nm, the same position as that of $(C_6H_6)_2^+$. There is no reason for the CR band positions to coincide.

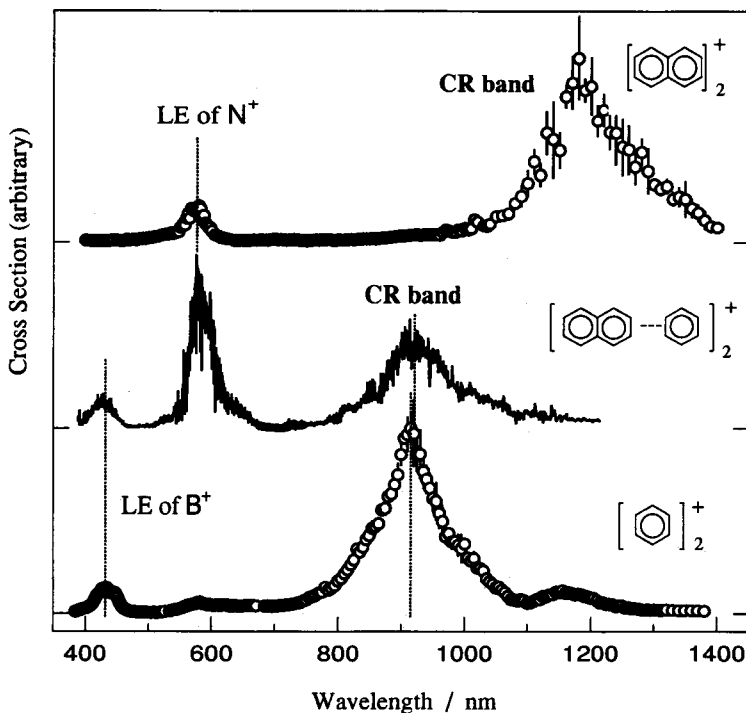


Figure 1. Photodissociation spectra of naphthalene dimer cation(top), naphthalene-benzene hetero-dimer cation(middle), and benzene dimer cation(bottom). The middle spectrum was taken through the naphthalene cation window of the mass spectrometer. The data were corrected for the laser intensity distribution.

The local excitation band at 580 nm in the spectrum of $(C_{10}H_8 - C_6H_6)^+$ appears stronger than the CR band. The relative cross sections of the 580 nm bands in the two spectra could be compared by measuring the photodepletion yields of the parent signals in a time-of-flight mass spectrum. It was found that the peak intensity of the LE band of $(C_{10}H_8 - C_6H_6)^+$ at 580 nm is $0.6 (\pm 0.2)$ times as strong as that of $(C_{10}H_8)_2^+$. Therefore the vertical intensity scale of the middle spectrum should be reduced to 14% of the scale of the top spectrum. The peak intensity of the CR band of the hetero-dimer is then only 7 % of that of the homo-dimer.

PRESENCE OF THE "LE" BAND OF $(C_6H_6^+)$ IN $(C_{10}H_8 - C_6H_6)^+$

In the spectrum of $(C_6H_6)_2^+$, the LE band of the monomer cation of $(C_6H_6)^+$ appeared at 430 nm. The hetero-dimer cation also weakly showed this band at the same position. In Figure 2, an expanded view of the LE bands of the two cation dimers is given on the same intensity scale. The vertical scale is a measure of intensities relative to the peak of the CR band of $(C_6H_6)_2^+$.

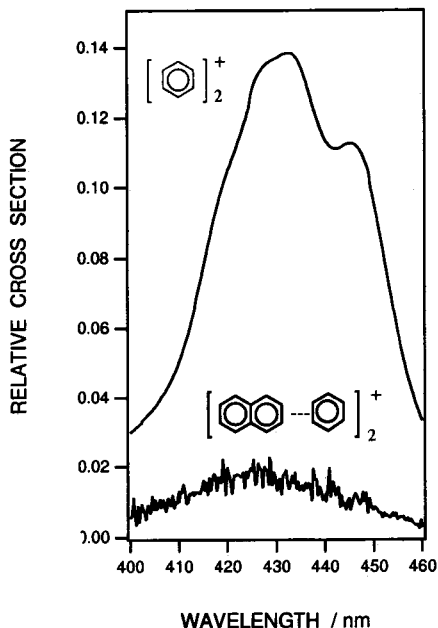


Figure 2. The second LE bands of $(C_6H_6)_2^+$ and $(C_{10}H_8 - C_6H_6)^+$.

Although the signal is rather noisy, the spectrum of the hetero-dimer shows a profile quite similar to that of the local transition of $(C_6H_6^+)$ in $(C_6H_6)_2^+$. Moreover, the peak positions also coincide. In this region, there exists a very broad band originating from $(C_{10}H_8)^+$. This background band is almost flat in this region contributing approximately 40% of the observed intensity. Therefore, the relative cross section of the LE transition of the hetero-dimer is estimated to be $8 (\pm 2)\%$ of that of $(C_6H_6)_2^+$. This fact strongly

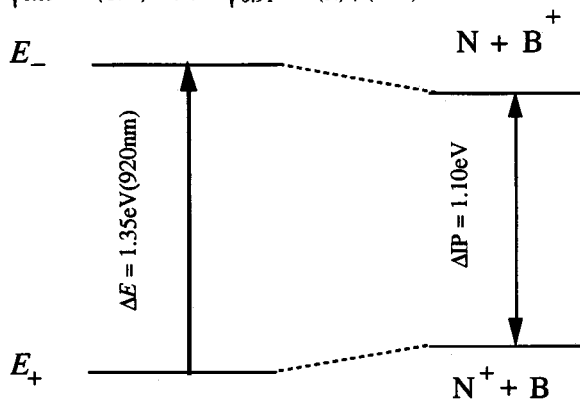
suggests that the charge is localized on the benzene with a probability of approximately 10%. This value has to be varied using a more reliable method.

NEAR RESONANCE INTERACTION IN HETERO-DIMERS

As demonstrated in the case of benzene-toluene cations[6], hetero-dimer cations can show intervalence transitions from the ground $(A^+ + B)$ state to the excited $(A + B^+)$ state, which is a charge transfer transition. The presence of this transition also demonstrates that the ground state is stabilized by the resonance interaction between the two states. The degree of stabilization is related to the

difference in the ionization potentials of A and B molecules. The CR transition of $(C_{10}H_8 - C_6H_6)^+$ was observed at 1.35 eV. The difference in the ionization potentials is 1.10 eV. Since locally excited states may not strongly couple with these local ground states, a simple perturbation theory can be applied to estimate the mixing coefficients based on these values. Figure 3 shows a result of the analysis. One numerical analysis results in a ground state wavefunction with an admixture of the $\psi(N) \psi(B^+)$ configuration of 9 %. This value is in accord with that obtained in the previous section.

$$\psi_- = \sqrt{0.09} \psi(N^+) \psi(B) - \sqrt{0.91} \psi(N) \psi(B^+)$$



$$\psi_+ = \sqrt{0.91} \psi(N^+) \psi(B) + \sqrt{0.09} \psi(N) \psi(B^+)$$

Figure 3. Interaction diagram for naphthalene(N)-benzene(B) dimer cation.

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