

## Charge Delocalization and Photoinduced Charge Hopping in Aromatic Cluster Ions.

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Photodissociation spectroscopy is one of the most powerful methods to investigate electronic and vibrational structures, geometric structures, and excited state dynamics of cluster ions. In recent years, we have extensively studied aromatic cluster ions which contain benzene ( $C_6H_6$ , abbreviated to B), toluene ( $C_6H_5CH_3$ , T), phenol ( $C_6H_5OH$ , P), naphthalene ( $C_{10}H_8$ , N), and cyanobenzene ( $C_6H_5CN$ , C) in the region from infrared (IR) to ultraviolet (UV). In this study, two main topics on the charge distribution of the aromatic cluster ions are presented: static charge delocalization and dynamic photoinduced charge hopping. These fundamental investigations are thought to be indispensable for developing new conducting materials.

Photodissociation spectra in the region from near IR to UV provide information on the charge delocalization of the cluster ions. The spectra of  $B_2^+$ ,  $T_2^+$ , and  $N_2^+$  exhibit strong charge resonance (CR) bands at 920, 980, and 1180 nm, respectively. The existence of the CR bands implies that two molecules in the dimer ion are equivalent, and that the positive charge is delocalized between the two molecules. These homo-dimer ions are supposed to have a parallel configuration of the two phenyl rings. In the cases of  $P_2^+$  and  $C_2^+$ , however, no strong absorption is observed around 1000 nm. This result suggests that the positive charge is localized on a single molecule. Since the OH or CN group is prone to form intermolecular hydrogen bond, the parallel stacked structure is hindered and such a charge localization occurs in  $P_2^+$  and  $C_2^+$ . Although there is some difference in the ionization potentials, the positive charge is found to be delocalized in hetero-dimer ions. However, there exists some imbalanced probability of finding the charge on each constituent molecules. On the basis of the position of the CR-like bands, the probabilities of finding the charge in the hetero-dimer ions are determined as follows; 36 % (B) and 64 % (T) in  $BT^+$ , 9 % (B) and 91 % (N) in  $BN^+$ . In the cases of  $BP^+$  and  $BC^+$ , the positive charge is almost localized on P and B, respectively.

Photodissociation studies on  $B_3^+$  in the region of 400–1400 nm showed that the positive charge is localized on the two neighboring molecules (dimer ion core) and that the cluster ion has a triple parallel structure, like  $[BB]^+ \cdots B$ . Recently, we have measured IR photodissociation spectra of  $(C_6H_6)_3^+$ ,  $((C_6H_6)_2(C_6D_6))^+$ ,  $((C_6H_6)(C_6D_6)_2)^+$ , and  $(C_6D_6)_3^+$  in the region of 3.3  $\mu m$ . According to the contours of the C–H stretching bands emerging in this region and the branching ratios of the products, we conclude that the vibrationally excited trimer ion undergoes dissociation after experiencing the charge hoppings,  $[BB]^+ \cdots B \leftrightarrow B \cdots [BB]^+$ . The positive charge of  $B_3^+$  stays on the specific dimer in the ground state. However, once  $B_3^+$  is photoexcited, the positive charge begins to migrate along the intermolecular bond. If one can induce active molecular rotation in liquid benzene, it is possible to transfer the charge by the hopping mechanism. It may be also capable to initiate and control one-dimensional electric flow by using a pulsed laser excitation,

