Electronic Structures of Aromatic Cluster Ions

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We have employed mass-selected photodissociation spectroscopy to obtain electronic spectra of cluster ions of several aromatic molecules including benzene, toluene, phenol, and naphthalene. The method employs tandem mass filter arrangements which isolate specific cluster ions for photodissociation and analyze the mass number of the resultant fragments. The electronic spectra (photodissociation spectra) are obtained by recording the yields of the fragment ions as functions of photodissociation wavelengths.

We have reported the photodissociation spectra of $(C_6H_6)_2^+$ and $(C_6H_6)_3^+$ [1]. The most intense band of $(C_6H_6)_2^+$ at 920 nm is assigned to a charge resonance (CR) band. One of the central issues for larger cluster ions is the degree of charge localization within them. The location of the CR band is a diagnostic of the charge localization. Although the CR bands of $(C_6H_6)_n^+$ with $n = 3$–6 gradually shift to the red with increasing size, the entire spectra exhibit essentially the same features with those of $(C_6H_6)_2^+$. The result suggests that the larger clusters have a charge-localized structure, $(C_6H_6)_2^+(C_6H_6)_{n-2}$, and that the $(C_6H_6)_2^+$ subunit is the chromophoric core for the CR transition.

The appearance of the intense CR band of homo-molecular dimer ions indicates that the two moieties should be equivalent to each other. Then we turn our attention to the structure of dimer ions in which the two moieties are expected to be inequivalent. One example of such species is the phenol dimer ion and the work on $(C_6H_5OH)_2^+$ is now in progress. A different class of such species is hetero-dimer ions composed of benzene and substituted benzene. In the photodissociation spectrum of benzene–toluene hetero-dimer ion, $[(C_6H_6)(C_6H_5CH_3)]^+$, an intense absorption band is observed at 1175 nm and a weaker one at 670 nm. Benzene–fluorobenzene dimer ion is also found to absorb a photon in near-infrared region. These observations indicate that the resonance-type interaction is important in the hetero-dimer ions as well as in the homo-dimer ions.

[1] T. Shibata, K. Ohashi, Y. Nakai, and N. Nishi, *Chem. Phys. Lett.*, **229**, 604 (1994).