

Infrared Photodissociation Spectra of Benzene Trimer Ions. Switching
of Dimer Ion Core in Vibrationally Excited States.

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In recent years there have been extensive studies on the photodissociation of benzene cluster ions, $(C_6H_6)_n^+$. We have found that the intramolecular vibrations of the ejected monomers are highly excited following the photoexcitation of $(C_6H_6)_n^+$.¹ We have proposed that a switching of the dimer ion core is responsible for the excitation of the intramolecular vibrations. However, there have been no direct evidence of the core switching. In this study, we measure IR photodissociation spectra of isotopically mixed benzene trimer ions in the 2900–3100 cm^{-1} region. The feature of the spectra can be explained by considering the switching of the dimer ion core.

The experiment was carried out by using a tandem mass spectrometer with an octopole ion guide.² We obtained the IR photodissociation spectra of the trimer ions by plotting the yields of the fragment dimer ions against the frequencies of the IR laser. Hereafter, C_6H_6 and C_6D_6 molecules are abbreviated as H and D, respectively.

In the spectrum of H_3^+ , two distinct maxima are seen at 2986 cm^{-1} and 3047 cm^{-1} . We attribute the main 2986- cm^{-1} band to a C–H stretching band of the benzene molecules in the dimer ion core. We also measure the spectrum of the HD_2^+ mixed trimer in the region of the C–H stretching of the dimer ion core. Both HD^+ and D_2^+ are detected as the fragment ion. The D_2^+ fragment is produced from HD_2^+ following the vibrational excitation of H in the dimer ion core; H is a component of the dimer ion core in the ground state, but the fragment dimer ion contains no H. This observation suggests the switching of the charge-carrying unit from [HD] to [DD] in the vibrationally excited state. If HD_2^+ has a triply parallel structure with H in the dimer ion core, HD_2^+ has two isomers, (a) $[HD]^+\cdots D$ and (b) $[DH]^+\cdots D$. We assume that the two molecules at both ends cannot form a pair as the fragment dimer ion. According to this model, the fragment HD^+ is produced from both isomers (a) and (b). The fragment D_2^+ , however, is created only from isomer (a). The band shape of the HD^+ -yield spectrum is asymmetric and can be decomposed into two Lorentzians. However, the D_2^+ -yield spectrum shows an almost symmetric band, which is reproduced by a single Lorentzian. Therefore, the band in the D_2^+ -yield spectrum of HD_2^+ is attributed to the C–H stretching vibration of isomer (a), and two components in the HD^+ -yield spectrum are attributed to that of isomers (a) and (b).

References

1. Y. Nakai, K. Ohashi, and N. Nishi, *J. Phys. Chem.*, **101**, 472 (1997).
2. Y. Inokuchi, K. Ohashi, M. Matsumoto, and N. Nishi, *J. Phys. Chem.*, **99**, 3416 (1995).