Structures, Charge Distribution, and Reactions of Molecular Cluster Ions

(Nagata’s Group, Univ. of Tokyo)
Yoshiya INOKUCHI
Molecular Cluster Ions

- Microscopic model of ions in the condensed phase
- One of the best systems for investigating functions that ions achieve in the bulk system

Charge distribution, solvation features, intracluster reactions
Cluster-size dependence of them

Necessary to select one specific cluster size and apply spectroscopic techniques to it

Spectroscopy coupled with the mass spectrometry

Number density of mass-selected ions is very small!

1 cm$^3$ of $10^{-4}$ mol/l solution $\rightarrow$ $6 \times 10^{17}$ ions
Number of mass-selected ions $\rightarrow$ $\sim 10^5$ ions
Photodissociation spectra of cluster ions can be obtained as a function of cluster size. The spectra are almost identical to absorption spectra.
Today’s Topics

- Static and dynamic features of the positive charge in benzene cluster cations, \((\text{C}_6\text{H}_6)_n^+\).

- Solvation features and reactions of aqueous metal ions.

- Electronic and geometric structures and photochemistry of carbon disulfide dimer anion, \((\text{CS}_2)_2^-\).
Static and Dynamic Features of the Positive Charge in Benzene Cluster Cations

(Univ. of Tokyo,\textsuperscript{1} Kyushu Univ.,\textsuperscript{2} Institute for Molecular Science\textsuperscript{3})

Y. Inokuchi, \textsuperscript{1} K. Ohashi, \textsuperscript{2} and N. Nishi\textsuperscript{3}
Aromatic Cluster Ions

What we want to figure out for the clusters is …

ion core structure, positive-charge distribution, and their dynamic behavior

Is the positive charge localized in one molecule?

Not always so. It is delocalized in some cluster ions

A strong band is observed at 10870 cm$^{-1}$ (920 nm).

(This is not a transition originating from the neutral benzene or the benzene monomer ion.)

Charge resonance (CR) band, characteristic of (C$_6$H$_6$)$_2^+$
Two degenerate states, $\phi(A_1^+)\cdot\phi(A_2)$ and $\phi(A_1)\cdot\phi(A_2^+)$, are coupled through the charge resonance (CR) interaction.

An electronic transition between the CR states is called a CR band.

Appearance of the CR band suggests that $A_1$ and $A_2$ are identical to each other, and that the positive charge is delocalized in the dimer.

$$\Psi_+ = (0.5)^{1/2}\cdot\phi(A_1^+)\cdot\phi(A_2) + (0.5)^{1/2}\cdot\phi(A_1)\cdot\phi(A_2^+)$$

Miyoshi et al.  
The question that arises now for this system is ...

How is the charge distribution affected by

increase of the number of molecules
Photodissociation Spectrum of \((C_6H_6)_3^+\)

Similar to that of \((C_6H_6)_2^+\)

\((C_6H_6)_3^+\) has a dimer ion core structure
IR Photodissociation Spectrum of \((C_6H_6)_3^+\)

![Graph showing IR spectrum](image)

- **Ion core** \((C_6H_6)_2^+\)
- **Solvent** \(C_6H_6\)

**Wavenumber / cm\(^{-1}\):**

3000 3050 3100 3150

On the basis of the dimer ion core structure of \((C_6H_6)_3^+\), we assign:
- Lorentzian component \(\rightarrow (C_6H_6)_2^+\) ion core red component \(\rightarrow C_6H_6\) solvent.

(The solvent benzene in \((C_6H_6)_3^+\) has an absorption similar to that of neutral benzene.)

The spectrum can be reproduced by a strong Lorentzian band and absorption bands similar to those of neutral benzene.
What occurs for the positive charge in the course of photodissociation?

Are these dimer ions identical to each other? Does the positive charge stay in the same pair?

We investigate relationship between the dimer ion core and the fragment dimer ion by using C₆D₆ molecule.
IR Photodissociation Spectra of Benzene Trimer Ions Having One or Two $C_6D_6$

$(C_6H_6)_3^+$

- $B_2D_1^+ \rightarrow BD^+$
- $B_2D_1^+ \rightarrow B_2^+$
- $B_1D_2^+ \rightarrow BD^+$
- $B_1D_2^+ \rightarrow D_2^+$

$B=C_6H_6$
$D=C_6D_6$

(CD stretching $\sim 2300 \text{ cm}^{-1}$)

Similar to that of $(C_6H_6)_3^+$
Independent of fragment species monitored.
Resemblance of the spectra suggests that the trimer ion loses the information of the ion core pair in the course of the photodissociation.

If fragment dimer ions are identical to ion core species, the photodissociation spectra observed by monitoring \((C_6H_6)_2^+\) and \((C_6H_6\cdot C_6D_6)^+\) should be different from each other.

Interpretation of \([((C_6H_6)_2\cdot C_6D_6)^+]\) Spectra

Band features predicted.
(If fragment dimer ions are identical to ion core species)
Positive charge hopping occurs in the excited states.

Three types of fragments are equally produced.
Proposed Mechanism of Positive Charge Hopping

Intracluster vibrations are initiated by the IR excitation.

When the solvent molecule accidentally gets to the side position of the sandwich-type ion core, the positive charge hops to the new pair.
Conclusion (1)

Benzene Trimer Ion

- **Dimer ion core structure** \((C_6H_6)_2^+ \cdots C_6H_6\)
- Positive charge hopping occurs in vibrationally excited states.