Structures, Charge Distribution, and Reactions of Molecular Cluster Ions

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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

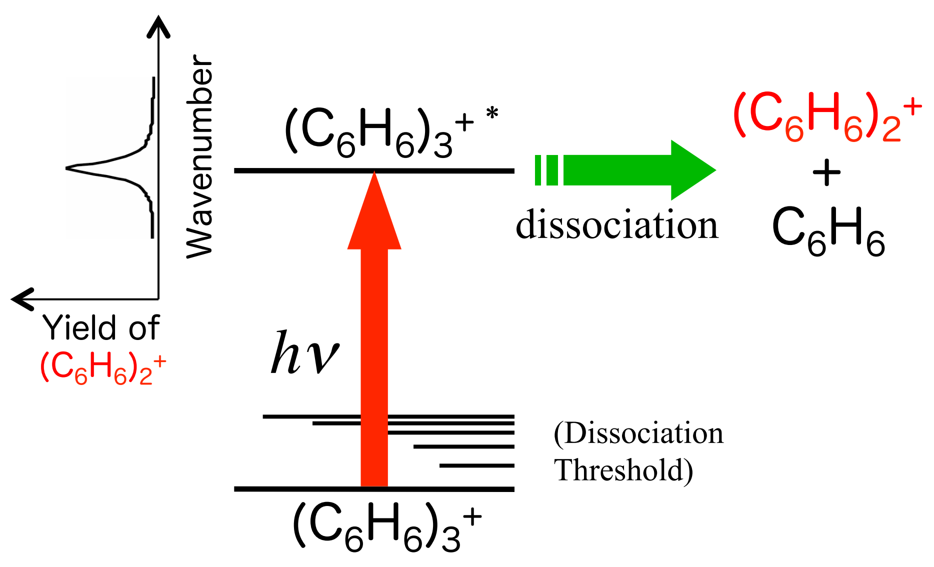
Necessary to select one specific cluster size and apply spectroscopic techniques to it

Spectroscopy coupled with the mass spectrometry

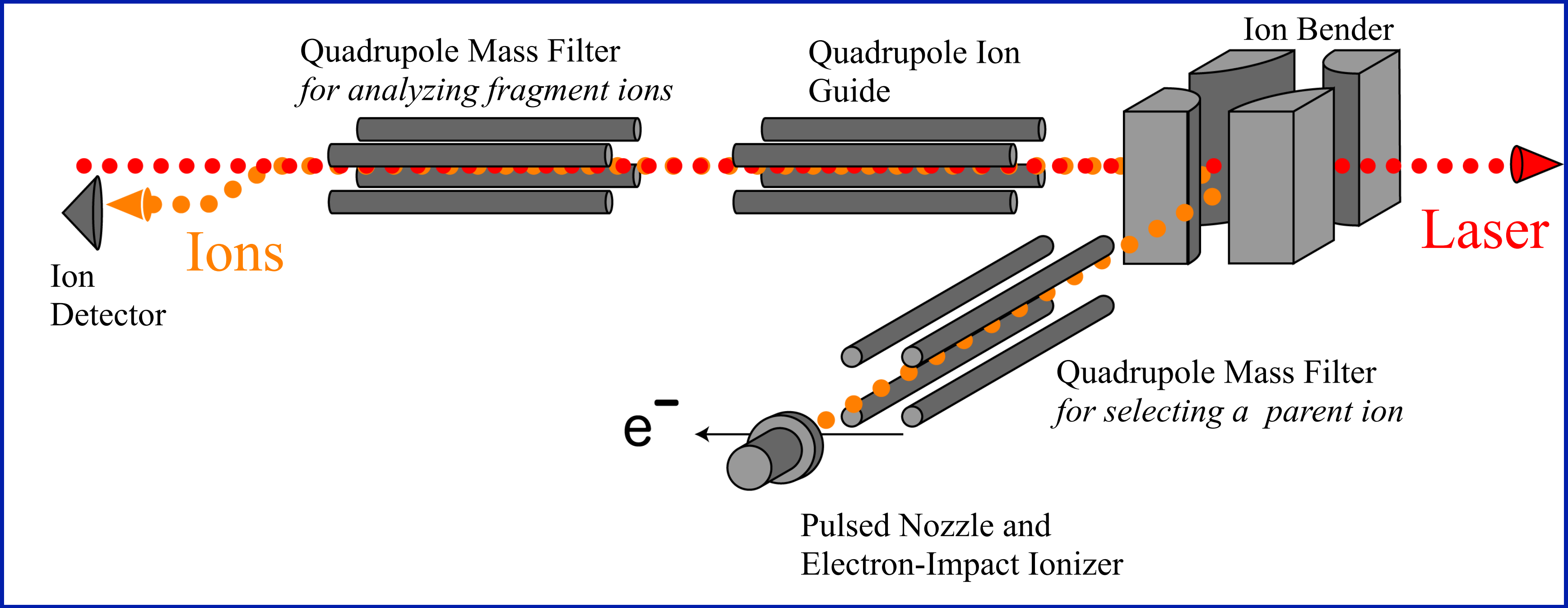
Number density of mass-selected ions is very small!

1 cm^3 of 10^{-4} mol/l solution → 6 x 10^{17} ions
Number of mass-selected ions → ~ 10^5 ions

Mass-Selected Photodissociation Spectroscopy



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, $(C_6H_6)_n^+$.
- Solvation features and reactions of aqueous metal ions.
- Electronic and geometric structures and photochemistry of carbon disulfide dimer anion, $(CS_2)_2^-$.

Static and Dynamic Features of the Positive Charge in Benzene Cluster Cations

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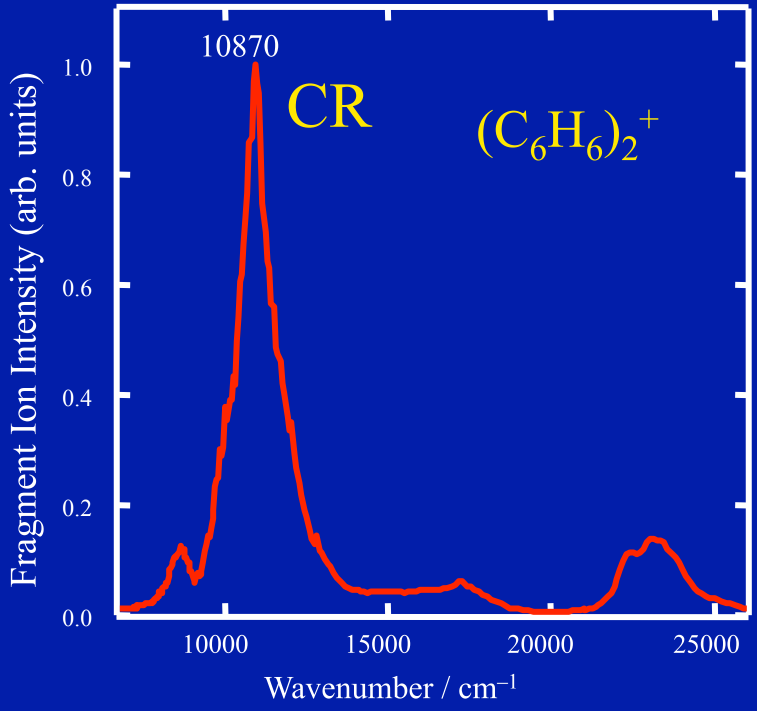
Aromatic Cluster Ions

- 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.)

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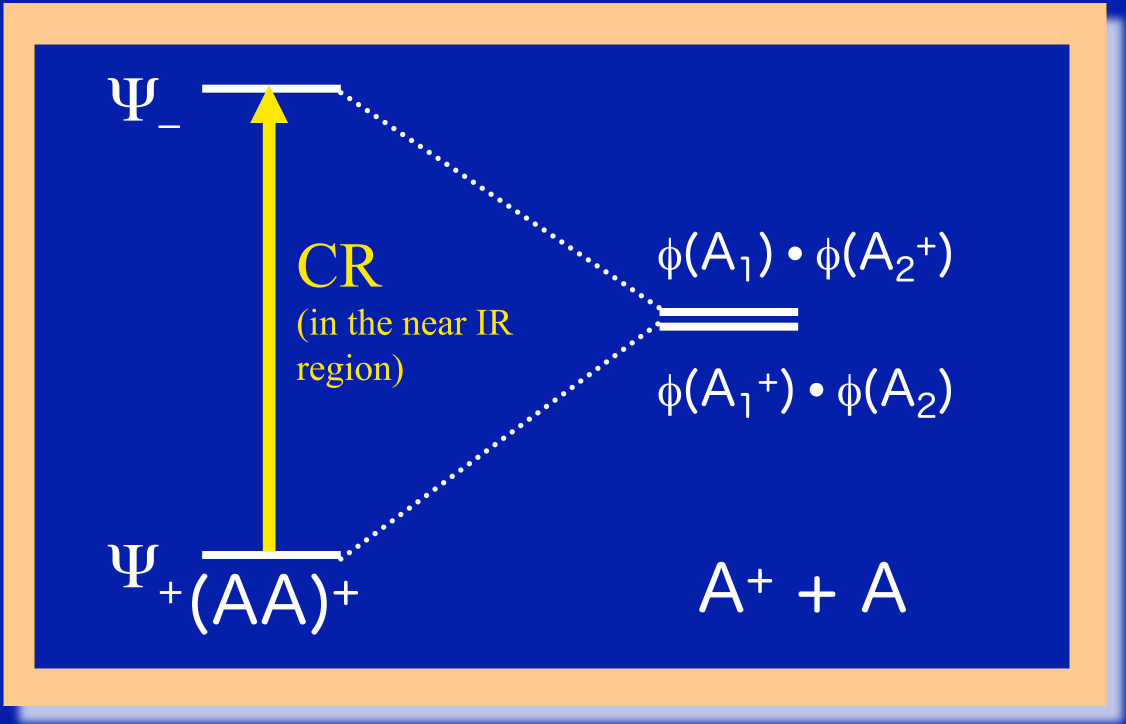
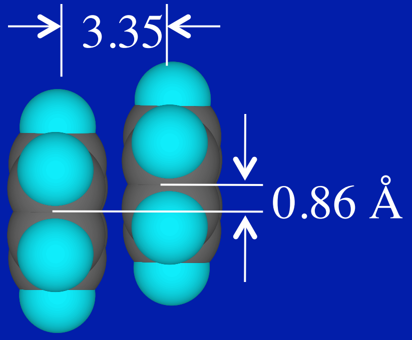
Charge resonance (CR) band, characteristic of $(C_6H_6)_2^+$

Charge Resonance Interaction
Charge Resonance Band

- Two degenerate states, $\phi(A_1^+)\bullet\phi(A_2)$ and $\phi(A_1)\bullet\phi(A_2^+)$, 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.



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



Miyoshi et al.
Chem. Phys. Lett. 275, 404 (1997).

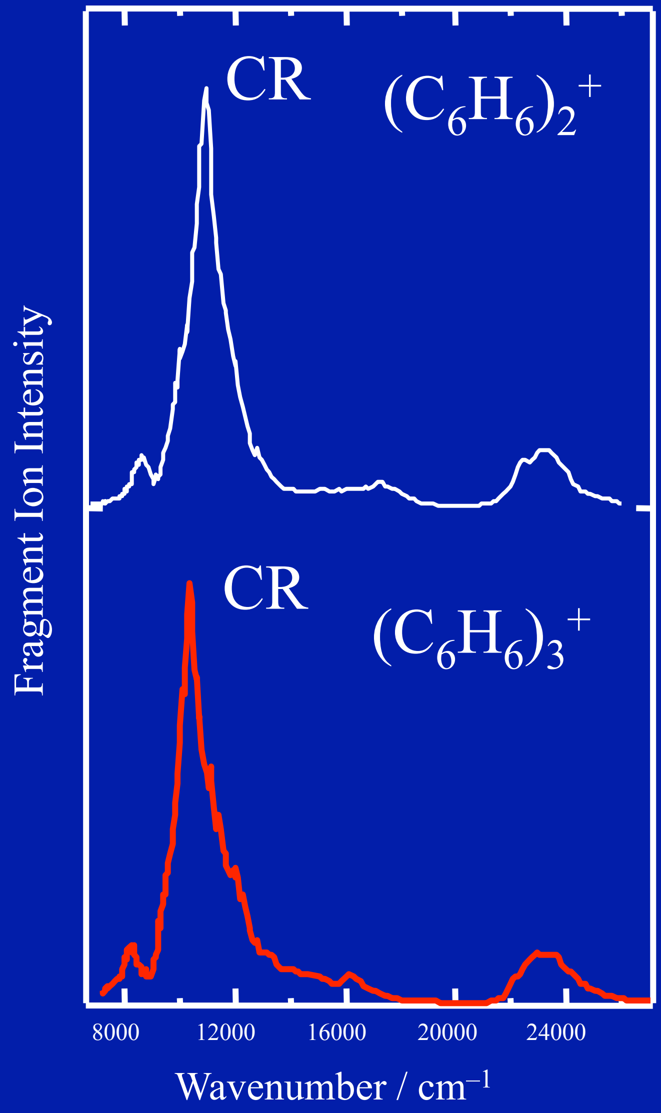
The question that arises now for this system is …

How is the charge distribution affected

by

increase of the number of molecules

Photodissociation Spectrum of $(C_6H_6)_3^+$



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

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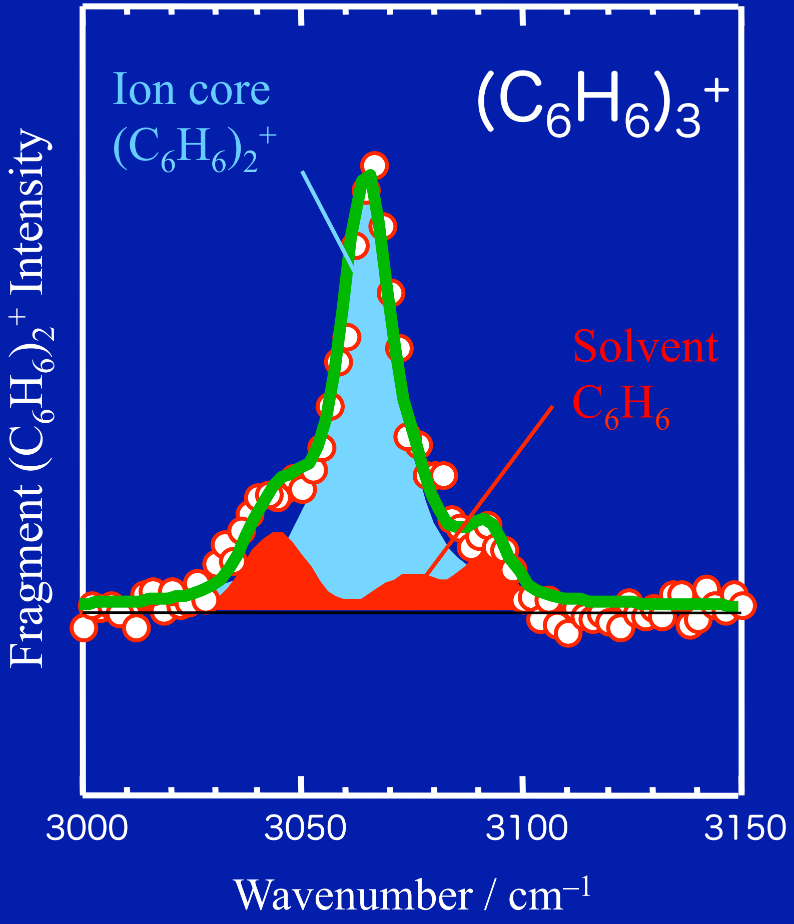
$(C_6H_6)_3^+$ has a dimer ion core structure

IR Photodissociation Spectrum of $(C_6H_6)_3^+$



CH stretching region.

The spectrum can be reproduced by
a strong Lorentzian band and
absorption bands similar to those of neutral benzene.

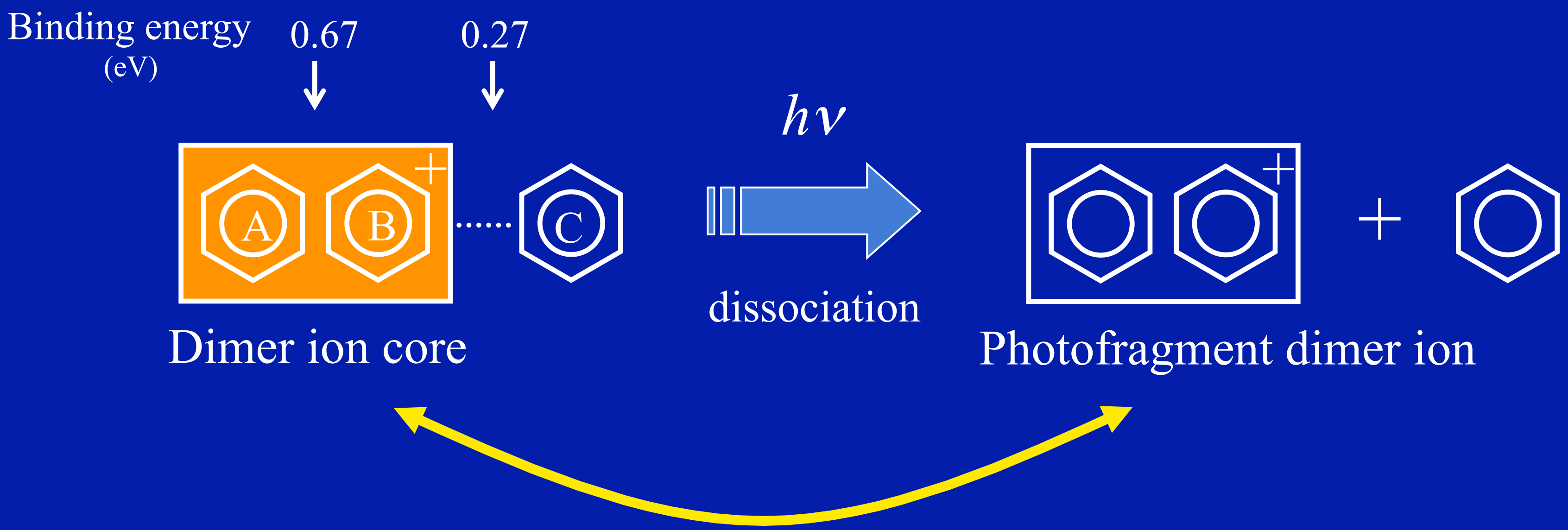
On the basis of the dimer ion core structure of $(C_6H_6)_3^+$, we assign

Lorentzian component → $(C_6H_6)_2^+$ ion core

red component → C_6H_6 solvent.

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

What occurs for the positive charge in the course of photodissociation ?



Binding energy (eV) 0.67 0.27

Dimer ion core

$h\nu$

dissociation

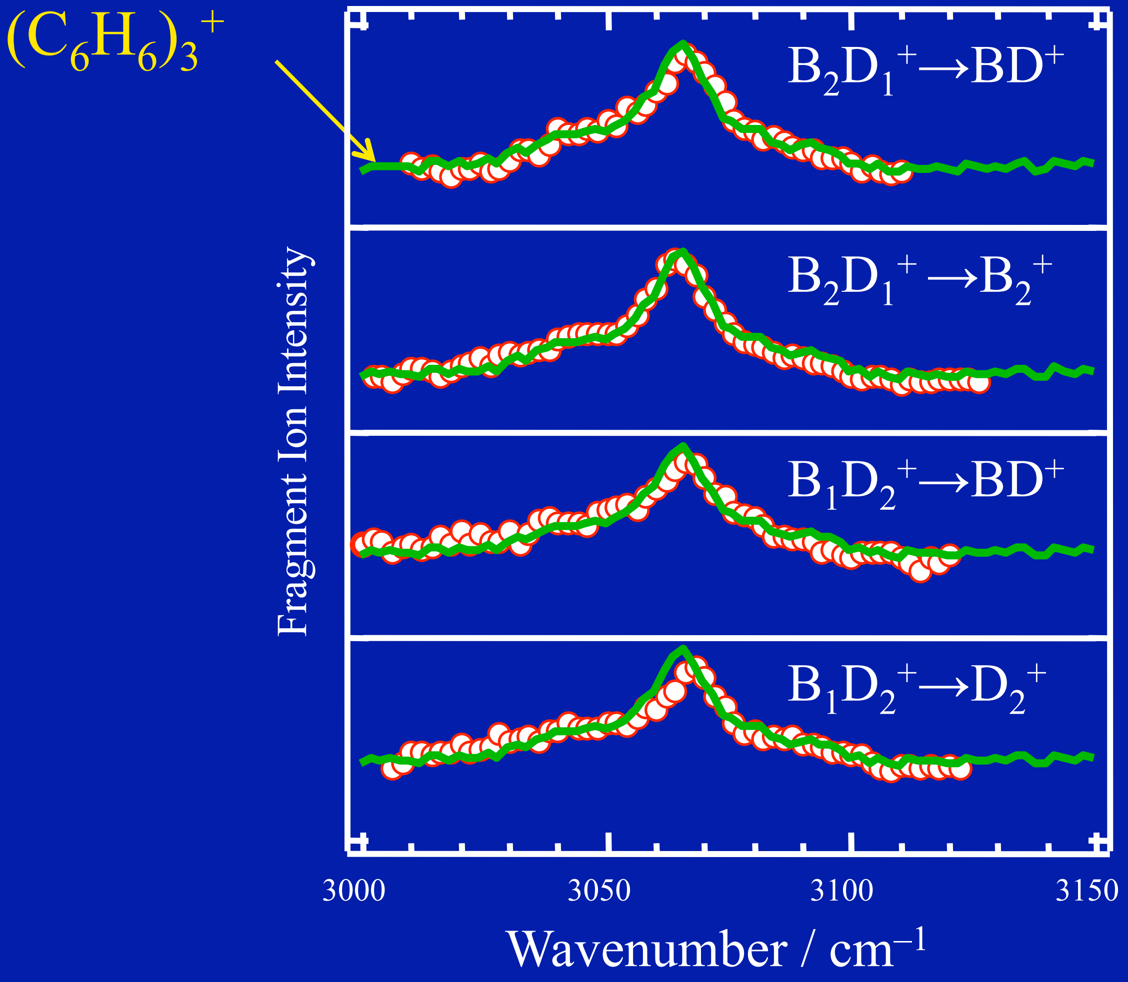
Photofragment dimer ion

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 C_6D_6 molecule.

IR Photodissociation Spectra of Benzene Trimer Ions Having One or Two C_6D_6

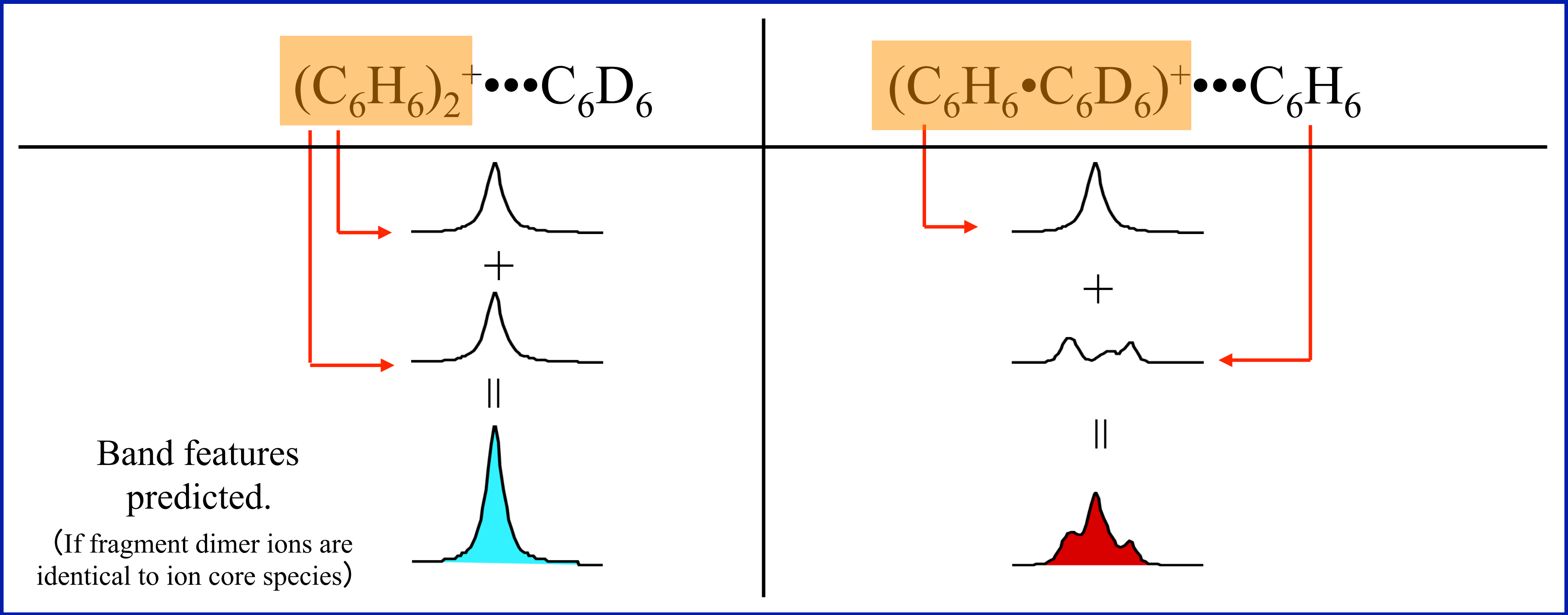


$B = C_6H_6$
$D = C_6D_6$

(CD stretching ~2300 cm^{-1})

Similar to that of $(C_6H_6)_3^+$
Independent of fragment species monitored.

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



Band features predicted.

(If fragment dimer ions are identical to ion core species)

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.

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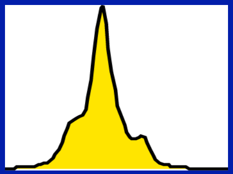
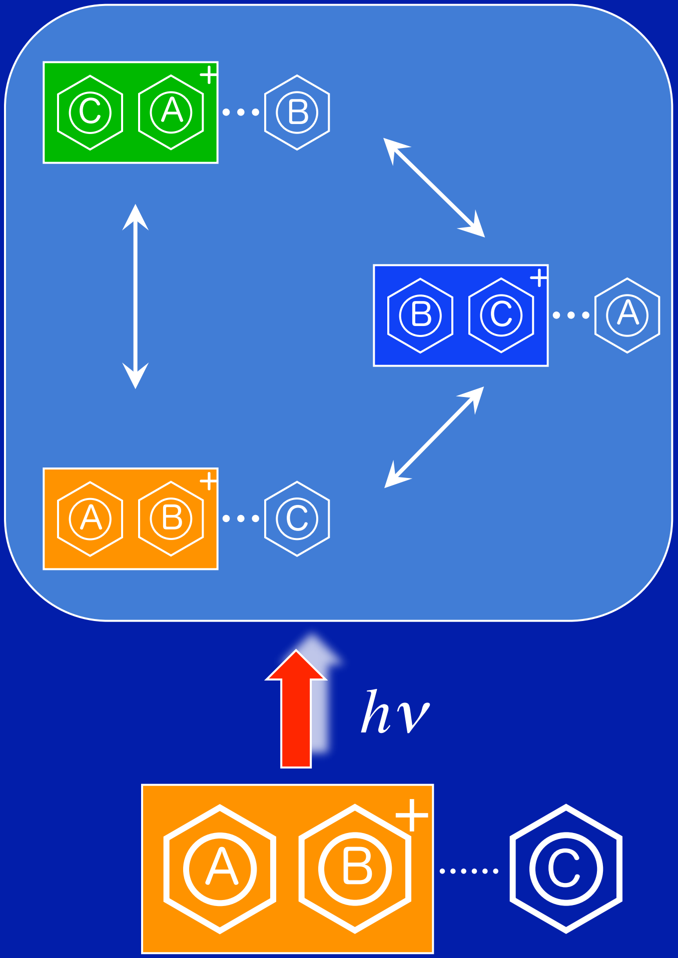
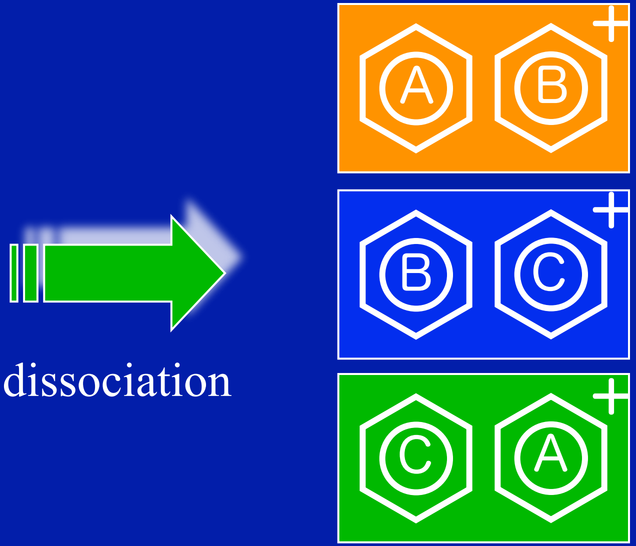
Resemblance of the spectra suggests that
the trimer ion loses the information of the ion core pair in the
course of the photodissociation.



$(C_6H_6)_3^+$

Positive Charge Hopping in the Trimer





Positive charge hopping occurs in the excited states.

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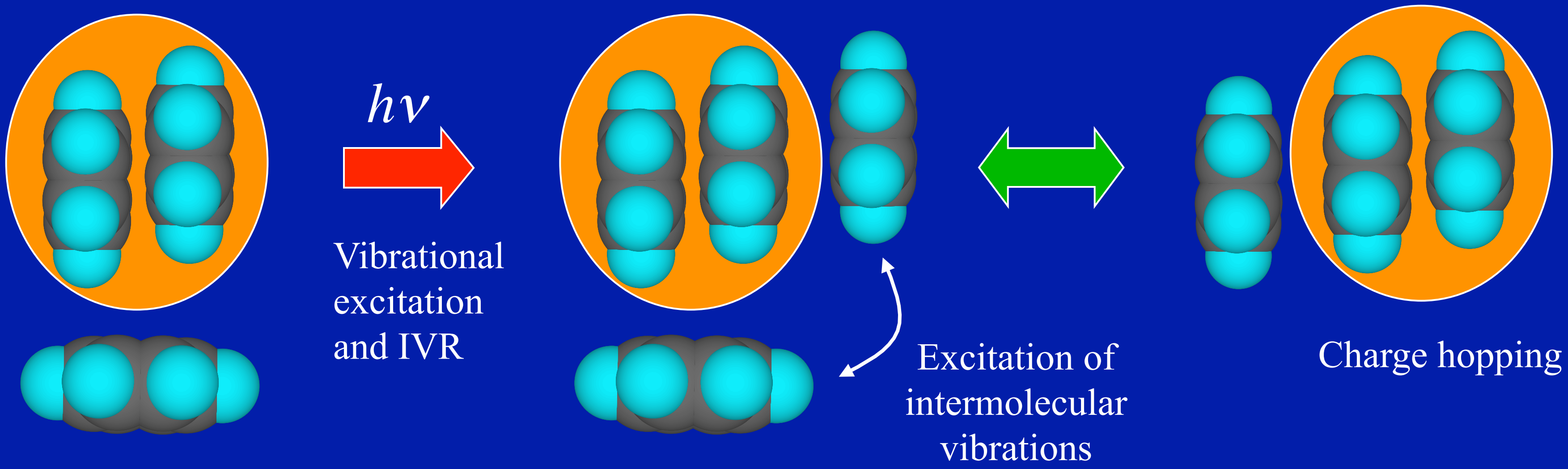
Three types of fragments are equally produced.

Proposed Mechanism of Positive Charge Hopping



$h\nu$

Vibrational
excitation
and IVR

Excitation of
intermolecular
vibrations

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 $(C_6H_6)_2^+ \bullet\bullet\bullet C_6H_6$
  - Positive charge hopping occurs in vibrationally excited states.