



Charge Resonance Interaction and Positive Charge Distribution in Aromatic Cluster Ions

(芳香族分子クラスターイオンの
電荷共鳴相互作用とその正電荷分布)

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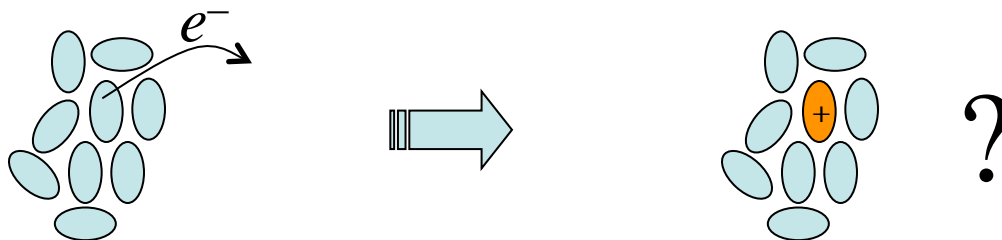
Molecular Cluster Ions

What we want to figure out is...

ion core structure, positive charge distribution
and its dynamic behavior.

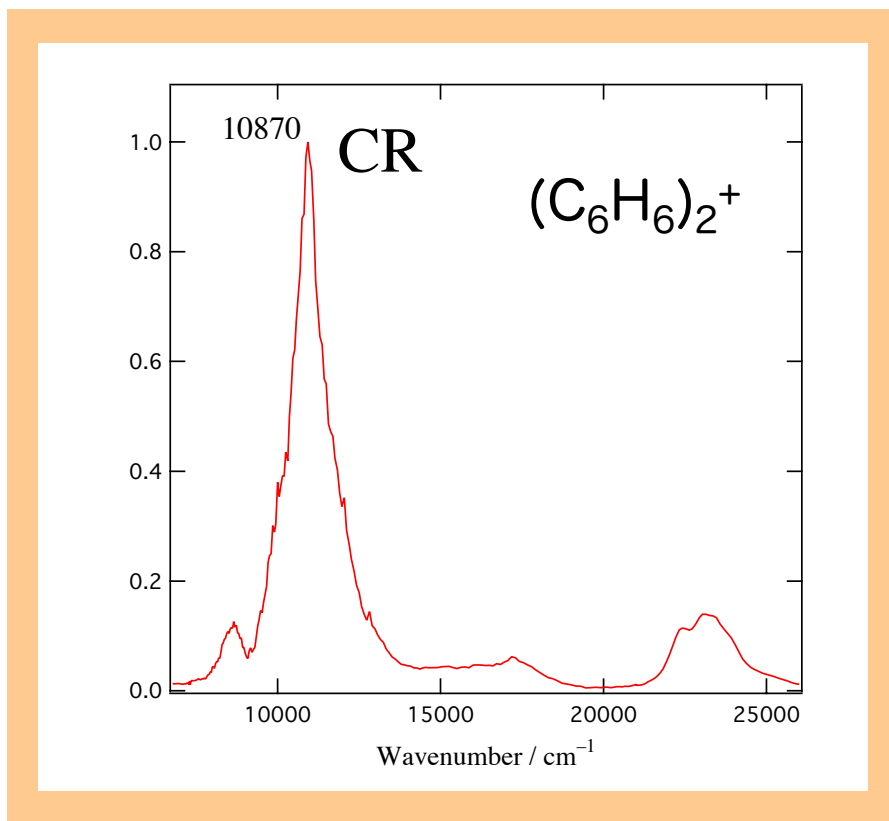
Is the positive charge localized on the original molecule?

→ **The answer is NO in a certain case.**



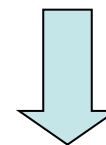


Near IR–Visible Spectrum of $(\text{C}_6\text{H}_6)_2^+$



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

(Benzene and its cation have no electronic band in the near IR region.)

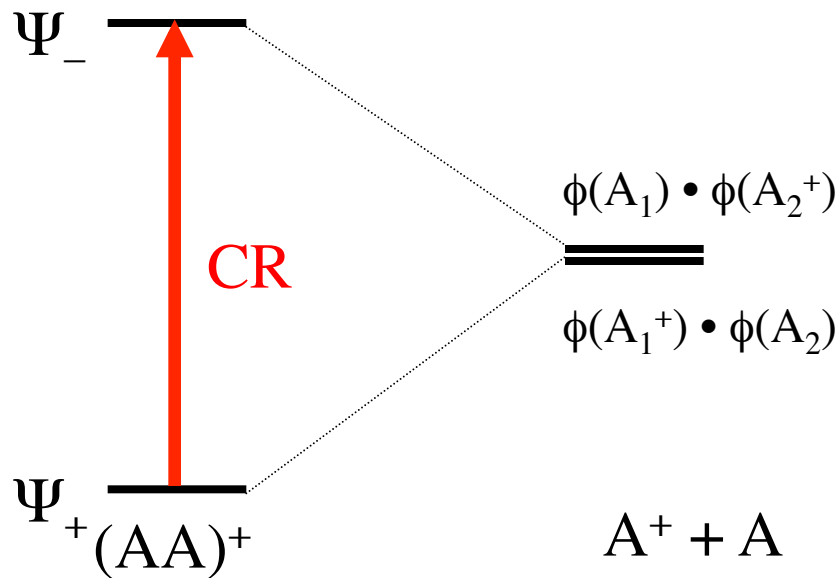


- This band is assigned to the **charge resonance band (CR)**.
- Appearance of this band implies that the positive charge is delocalized in the dimer.



Charge Resonance Interaction

- Two degenerate states, $\phi(A_1^+) \cdot \phi(A_2)$ and $\phi(A_1) \cdot \phi(A_2^+)$, are coupled, and the positive charge is delocalized in the dimer.
- An electronic transition between these charge resonance states is called **charge resonance band (CR)**.
- Appearance of the CR suggests the positive charge delocalization.



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

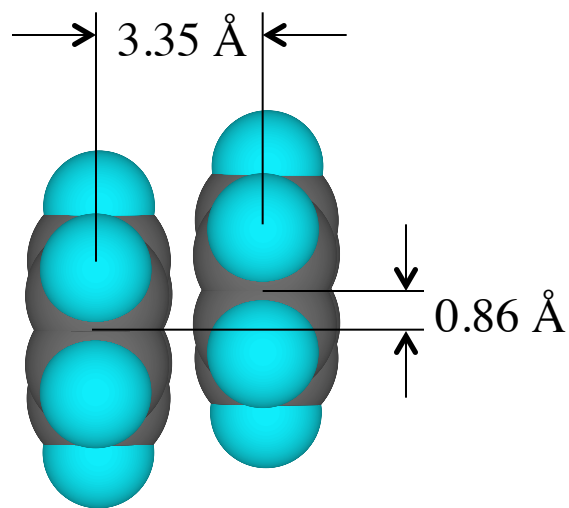
The positive charge distribution is

$$\begin{array}{ll} A_1 \text{ side} & 0.5 \\ A_2 \text{ side} & 0.5. \end{array}$$

Molecules A_1 and A_2 are identical to each other in the dimer.



Structure of $(C_6H_6)_2^+$



Miyoshi et al.
Chem. Phys. Lett. 275, 404 (1997).
ab initio MO calculation.



How is the charge distribution affected

by

increase in the number of molecules, or
contamination with another kind of molecules ?



In This Study,

- Aromatic cluster ions.
 1. Benzene trimer ion.
 2. Benzene–toluene mixed trimer ions.
- Positive charge distribution and its dynamic behavior.
- Mass-selected photodissociation spectroscopy.

We obtain photodissociation (\approx absorption) spectra.

Near IR region.
Appearance of the CR \rightarrow Charge delocalization.

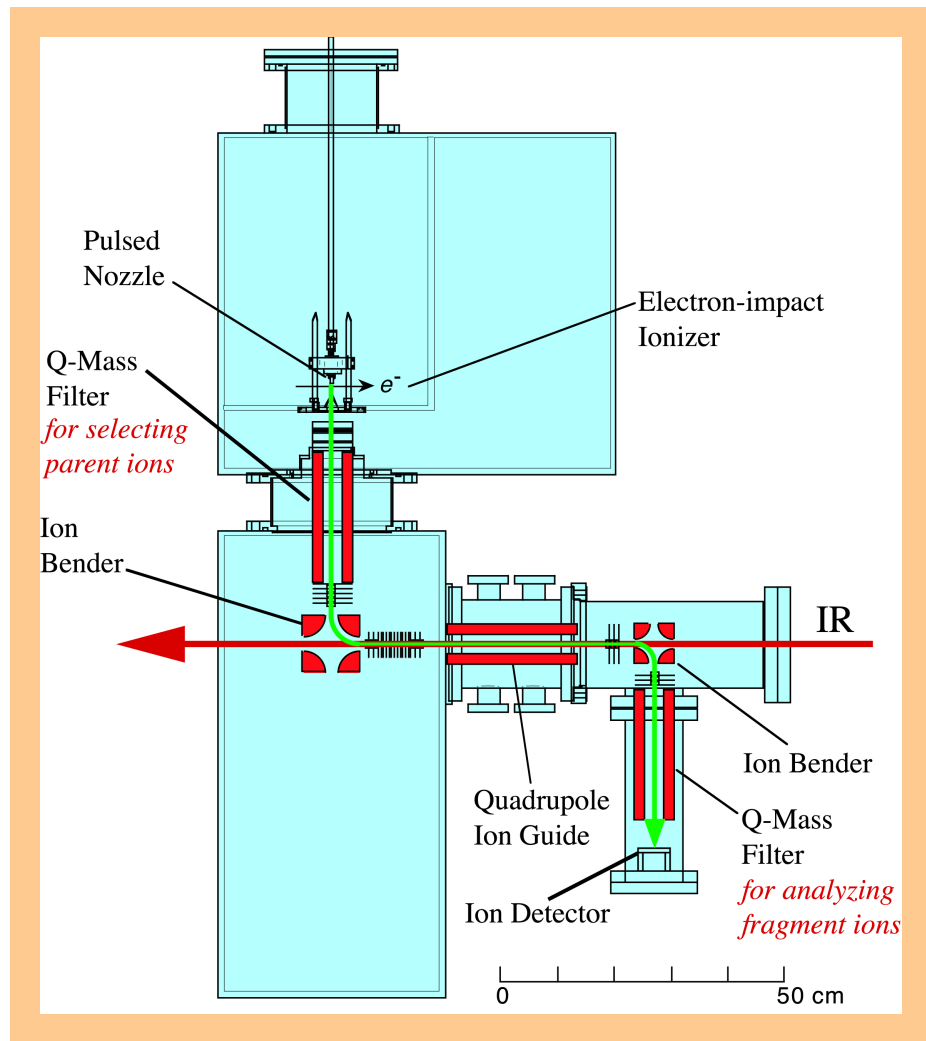
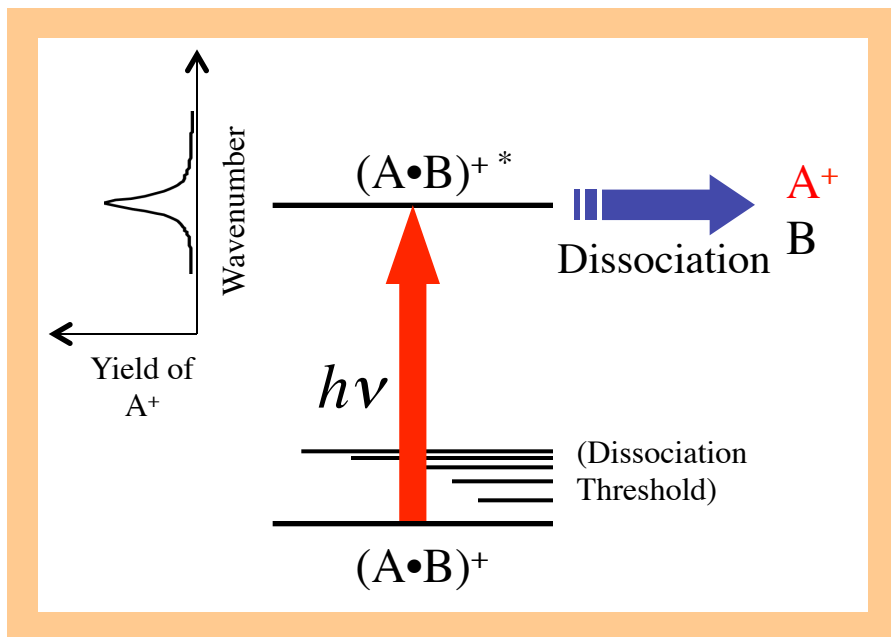
IR region.
Vibrational structures.



Positive Charge Distribution and
Charge Hopping
in
Benzene Trimer Ion

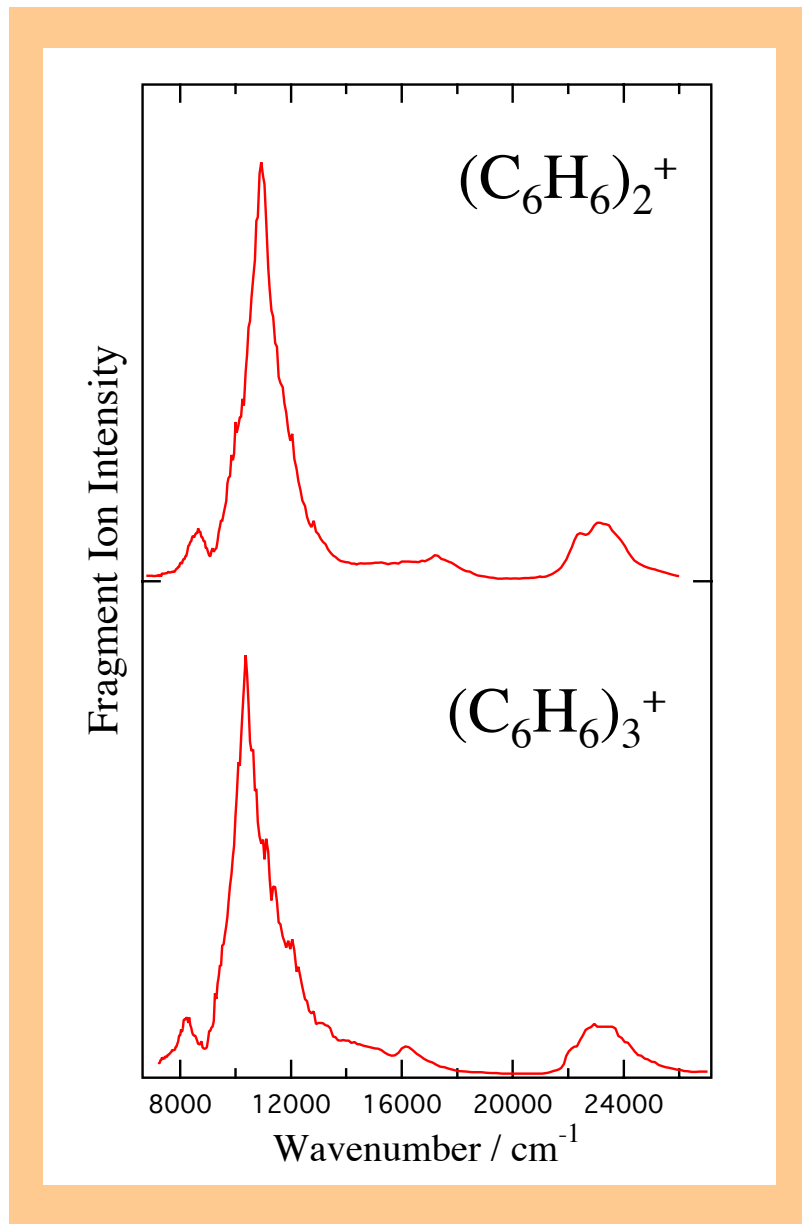


Photodissociation Spectroscopy

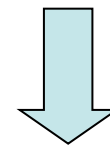




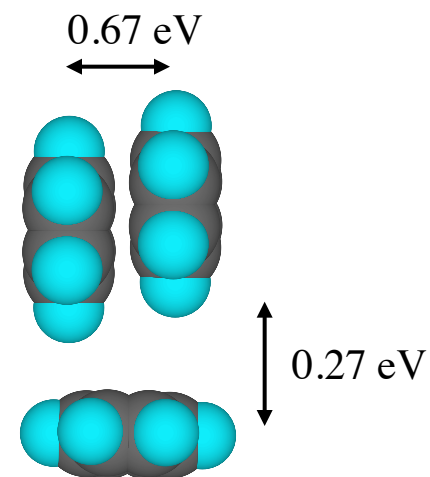
Near IR–Visible Spectrum of $(\text{C}_6\text{H}_6)_3^+$



The spectrum is quite similar to that of $(\text{C}_6\text{H}_6)_2^+$.

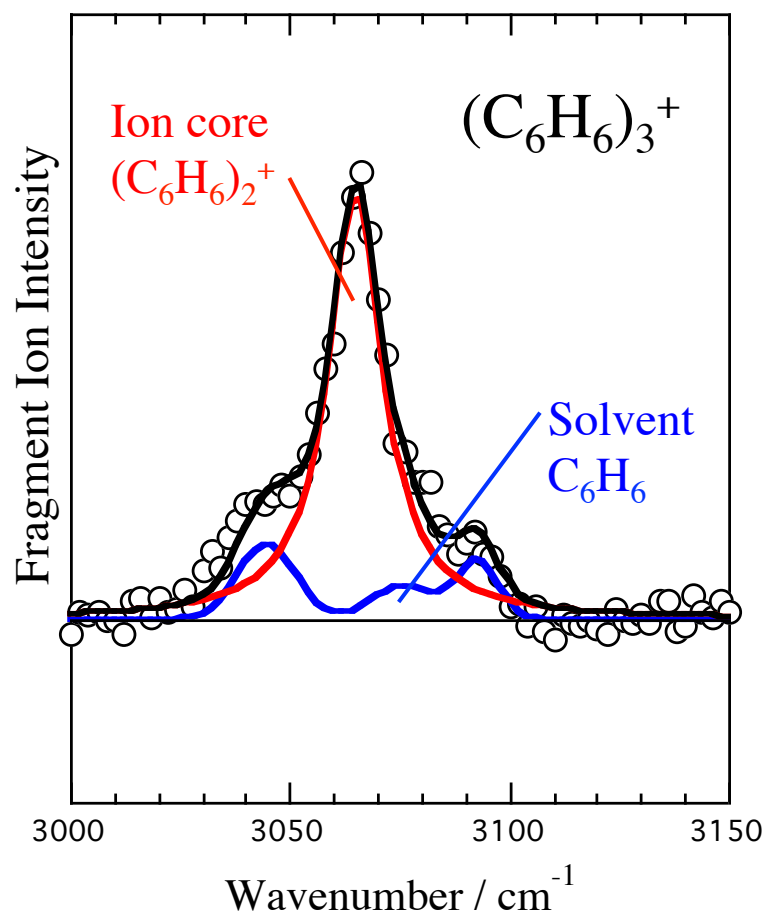


$(\text{C}_6\text{H}_6)_3^+$ has a dimer ion core.





IR Spectrum of $(\text{C}_6\text{H}_6)_3^+$



CH stretching region.

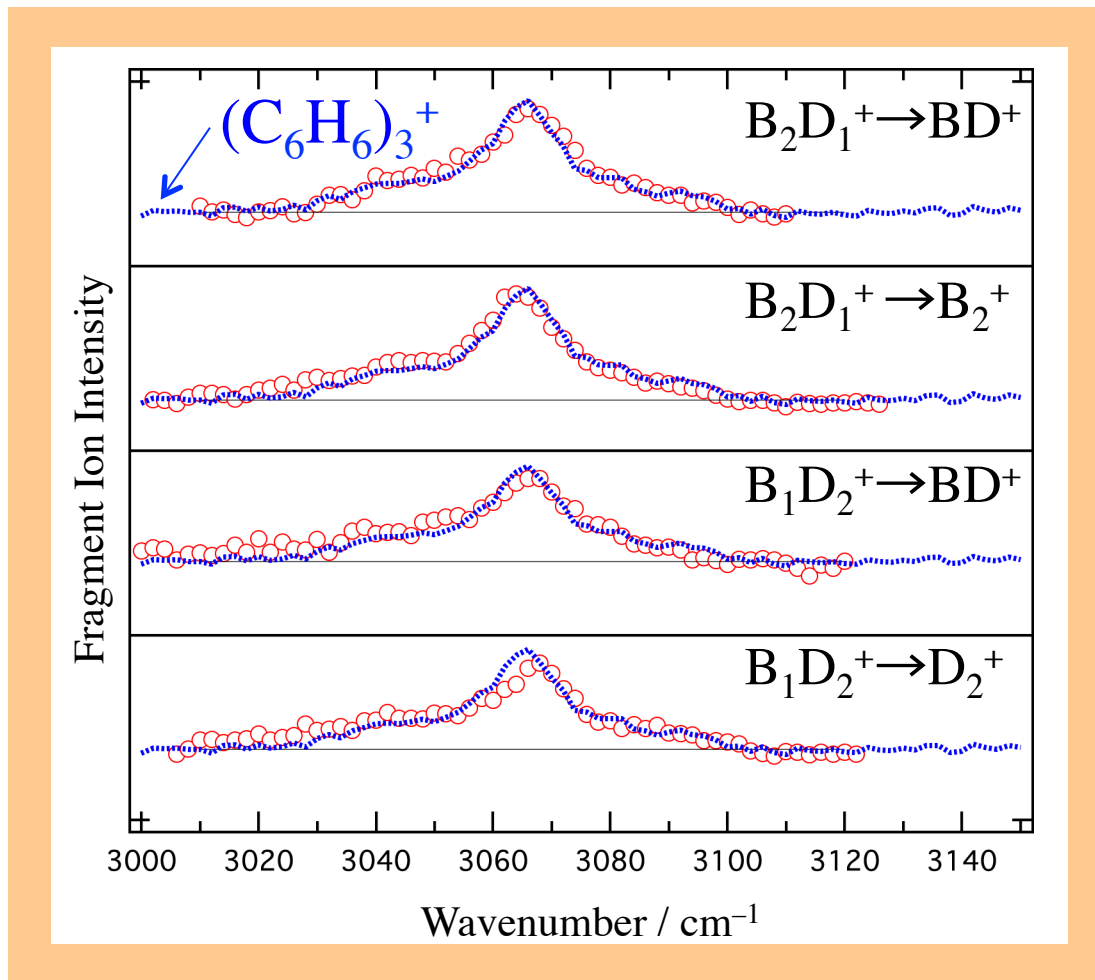
The spectrum can be reproduced by a strong Lorentzian band and absorption bands of neutral benzene.

On the basis of the dimer ion core structure of $(\text{C}_6\text{H}_6)_3^+$, we assign red component \rightarrow ion core $(\text{C}_6\text{H}_6)_2^+$ blue component \rightarrow solvent C_6H_6 .

(The solvent benzene in $(\text{C}_6\text{H}_6)_3^+$ has an absorption similar to that of neutral benzene.)



IR Spectra of Trimer Ions Containing C_6D_6

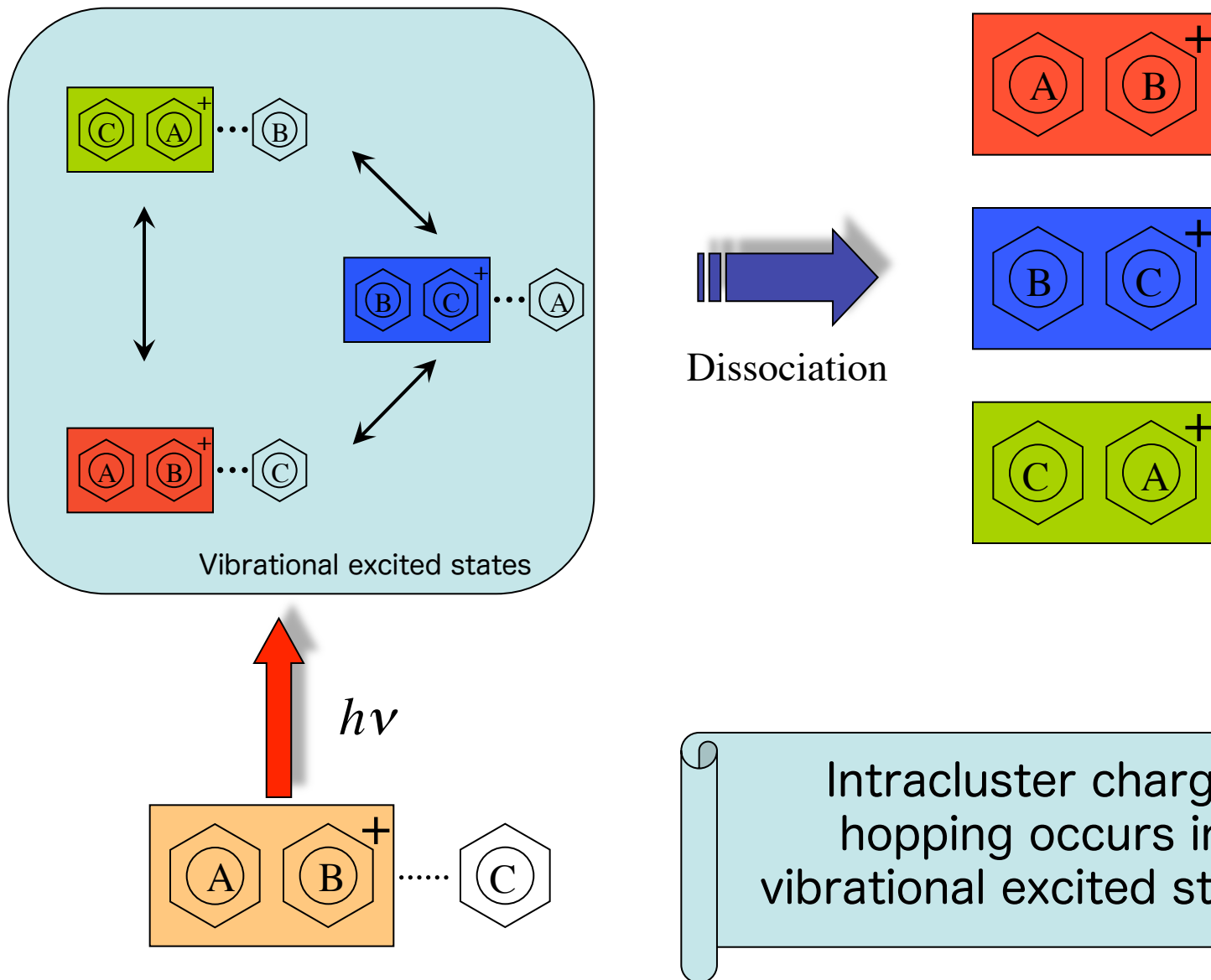


$B=C_6H_6$
 $D=C_6D_6$

All the spectra resemble that of $(C_6H_6)_3^+$.
 Spectral features are independent of fragment species monitored.

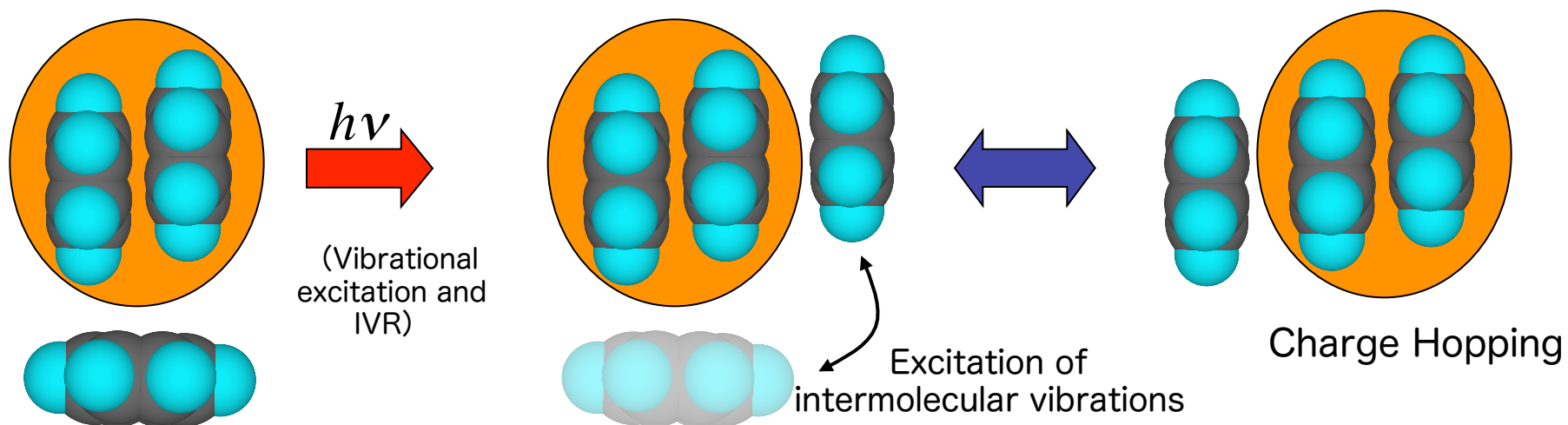


Intracluster Charge Hopping





Charge Hopping



The charge hopping is initiated by the light irradiation and assisted by intermolecular vibrations.

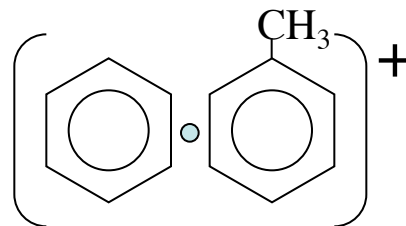


Positive Charge Distribution
in
Benzene–Toluene Mixed Trimer Ions



Mixed Dimer Ion

The positive charge exists also on benzene, although benzene has an ionization potential (IP) higher than that of toluene.

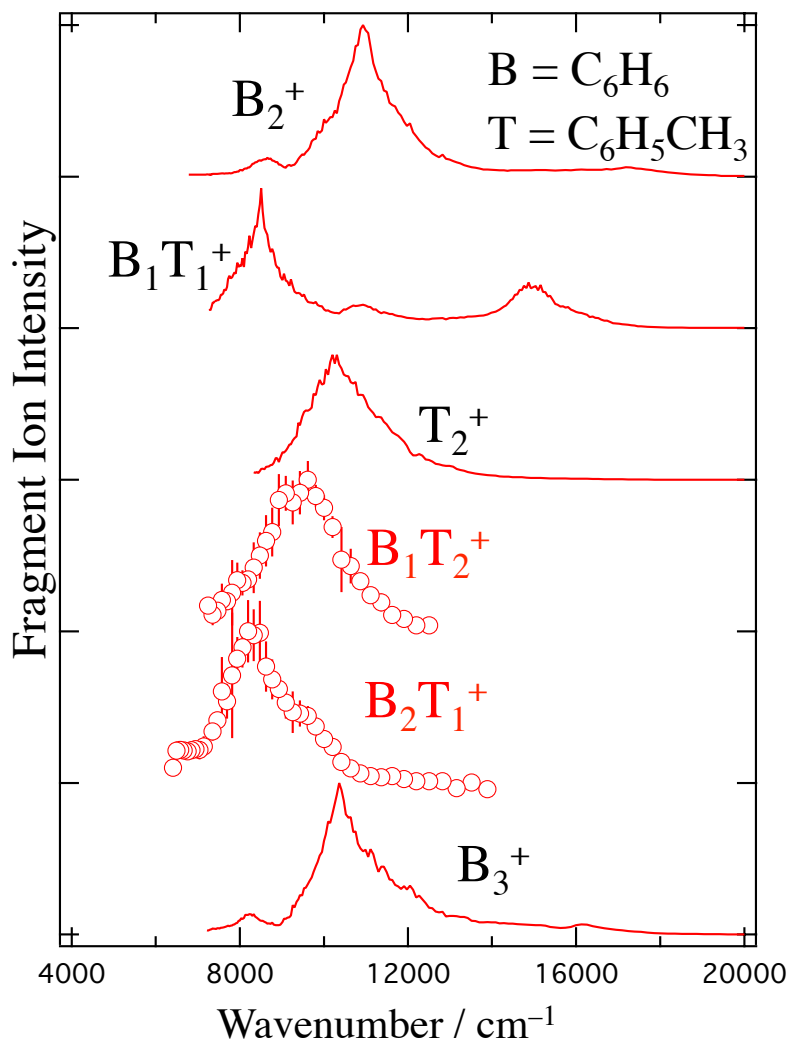


Benzene Toluene

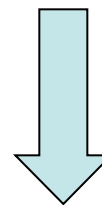
Charge Distribution (%)	36	64
IP (eV)	9.24	8.83



Near IR Spectra



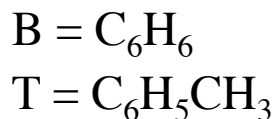
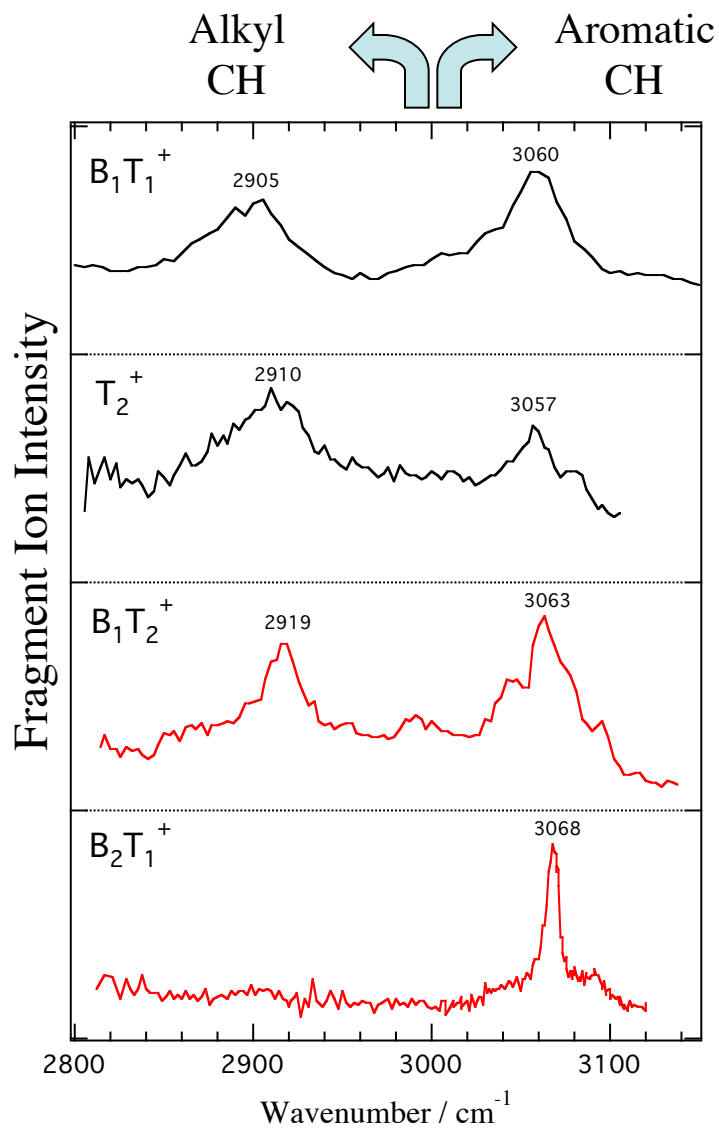
Both $B_1T_2^+$ and $B_2T_1^+$ have a broad and strong band in the near IR region.



- The charge resonance interaction occurs in these clusters.
- The positive charge is not localized in a single molecule.



IR Spectra

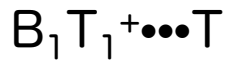
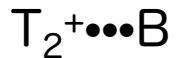


- CH stretching region
- Band features of $B_2T_1^+$ are fairly different from those of other ions.
 - ◆ No strong band is observed in the alkyl CH region.
 - ◆ The band in the aromatic CH region is quite narrower than those of other ions.



Positive Charge Distribution in $B_1T_2^+$

- Possible structures are



- Ionization potential

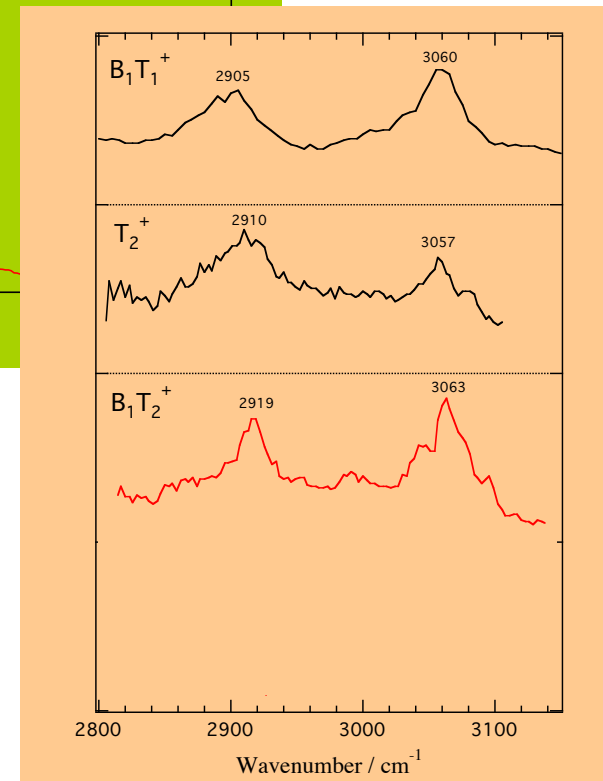
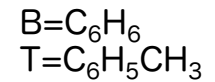
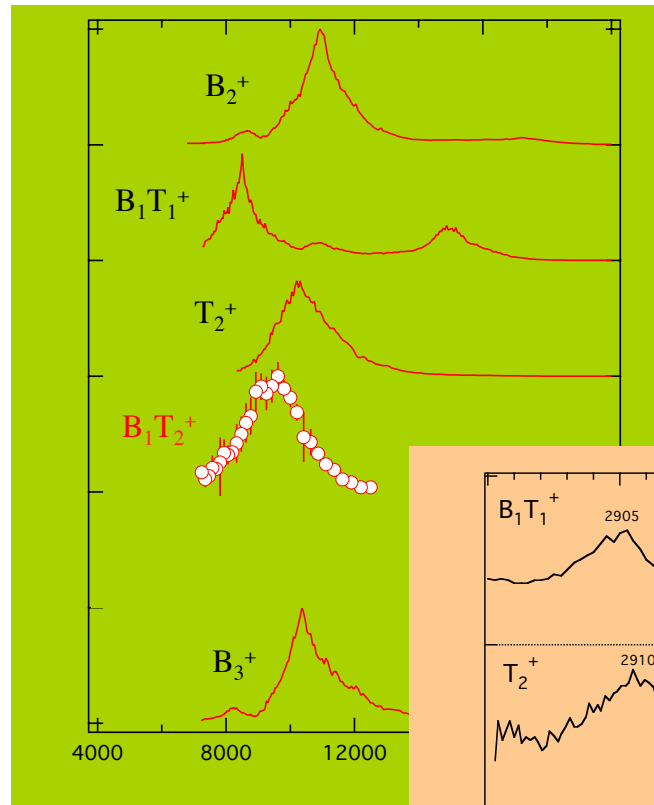


- It cannot be determined definitely from the near IR and IR spectra.

✓The maximum of the near IR band is located in the middle of those of $B_1T_1^+$ and T_2^+ .

✓The IR spectrum is similar to those of both $B_1T_1^+$ and T_2^+ .

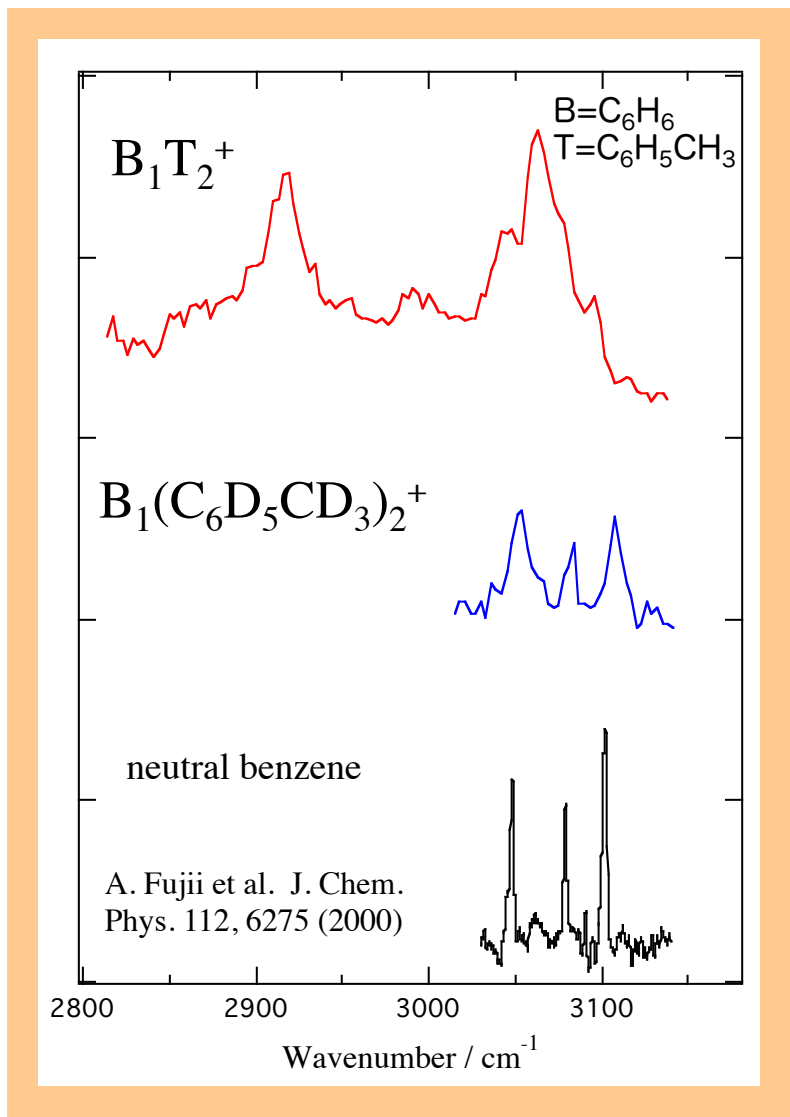
- Prediction of the spectra of $(B T T)^+$ is difficult.





IR Spectrum of $B_1(C_6D_5CD_3)_2^+$

We use $C_6D_5CD_3$ instead of $C_6H_5CH_3$, and measure an IR spectrum.



The spectrum of $B_1(C_6D_5CD_3)_2^+$ displays three bands, which are characteristic of neutral benzene.



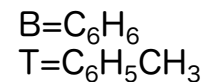
The benzene molecule in $B_1T_2^+$ is almost neutral.

Positive charge distribution of $B_1T_2^+$ is

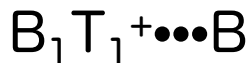
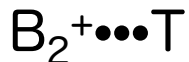




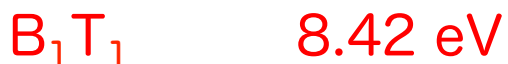
Positive Charge Distribution in $B_2T_1^+$



- Possible structures are



- Ionization potential

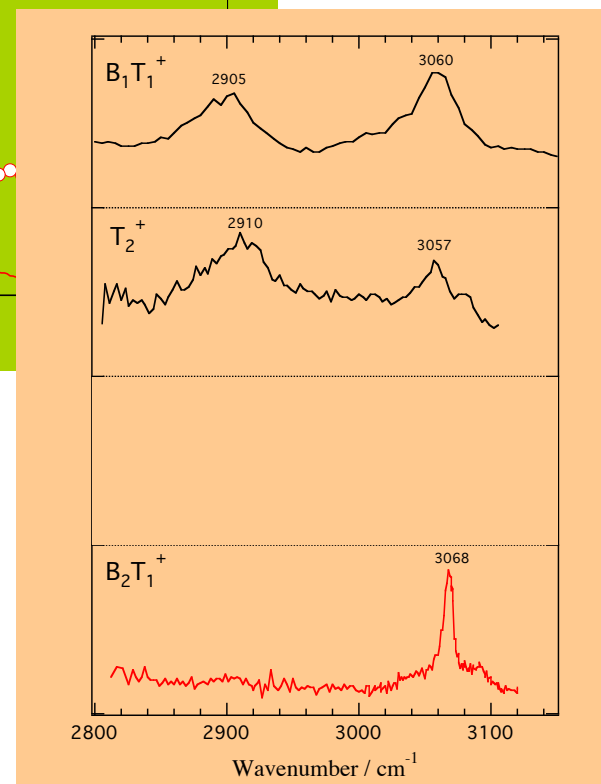
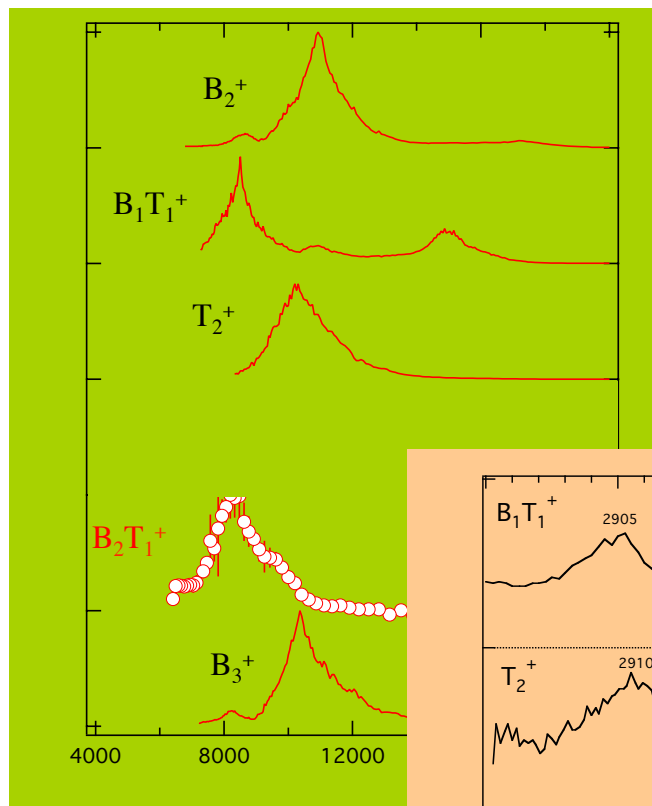


- It cannot be determined definitely from the near IR and IR spectra.

✓ The maximum of the near IR band is located near that of $B_1T_1^+$.

✓ The IR spectrum is similar to that of B_2^+ .

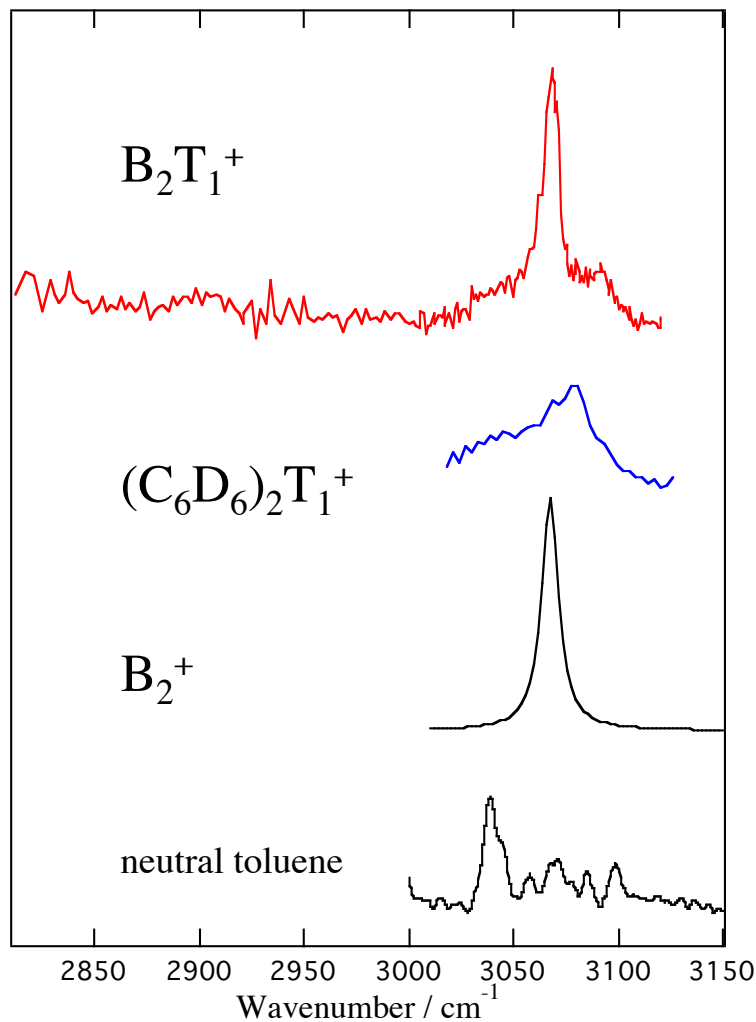
- Prediction of the spectra of $(B B T)^+$ is difficult.





IR Spectrum of $(C_6D_6)_2T_1^+$

We use C_6D_6 instead of C_6H_6 , and measure an IR spectrum.



- No sharp band is observed at 3068 cm⁻¹ in the spectrum of $(C_6D_6)_2T_1^+$.
- The sharp band in the spectrum of $B_2T_1^+$ is quite similar to that of B_2^+ .

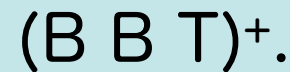


The structure is like $B_2^+ \cdots T_1$?

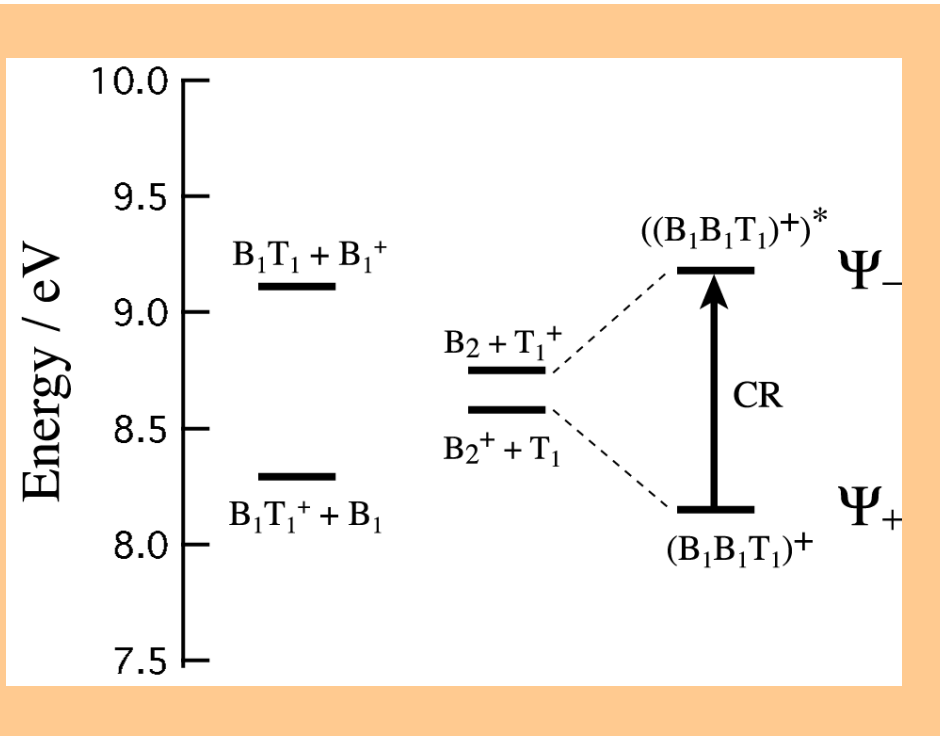


The spectrum of $(C_6D_6)_2T_1^+$ is different from that of neutral toluene. The toluene molecule in $B_2T_1^+$ is NOT neutral.

Positive charge distribution of $B_2T_1^+$ is



Energy Diagram of $B_2T_1^+$



- The energy difference between $(B_2^+ + T)$ and $(B_2 + T^+)$ is *accidentally* small (0.10 eV), inducing **the charge resonance interaction** between B_2 and T .
- The wave function of the electronic ground state is

$$\Psi_+ = (0.58)^{1/2} \cdot \phi(B_2^+) \cdot \phi(T) + (0.42)^{1/2} \cdot \phi(B_2) \cdot \phi(T^+).$$

The positive charge distribution of $B_2T_1^+$ is

B_2 58%

T 42%.



Summary

- Benzene trimer ion
 - ◆ Dimer ion core structure $(\text{C}_6\text{H}_6)_2^+\cdots\text{C}_6\text{H}_6$
 - ◆ Charge hopping in vibrational excited states

- Benzene–toluene mixed trimer ions
 - ◆ B_1T_2^+
 $\text{T}_2^+\cdots\text{B}$; the ion core is T_2^+ .
 - ◆ B_2T_1^+
 The charge is delocalized in the trimer; the distribution is B_2 (58%) and T (42%).