Charge Resonance Interaction and Positive Charge Distribution in Aromatic Cluster Ions

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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

- $A_1$ side: 0.5
- $A_2$ side: 0.5.

Molecules $A_1$ and $A_2$ are identical to each other in the dimer.
Structure of \((\text{C}_6\text{H}_6)_2^+\)

Miyoshi et al.
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 (≈ absorption) spectra.
  - Near IR region.
    - Appearance of the CR → Charge delocalization.
  - IR region.
    - Vibrational structures.
Positive Charge Distribution and Charge Hopping in Benzene Trimer Ion
Photodissociation Spectroscopy

\[(A\cdot B)^+ \rightarrow (A^+ + B)\]

\[h\nu \text{ (Dissociation Threshold)}\]

Yield of \(A^+\)

Electron-impact Ionizer

Pulsed Nozzle

Q-Mass Filter

for selecting parent ions

Ion Bender

Quadrupole Ion Guide

Ion Detector

for analyzing fragment ions

0 10 20 30 40 50 cm

IR
Near IR–Visible Spectrum of \((C_6H_6)_3^+\)

The spectrum is quite similar to that of \((C_6H_6)_2^+\).

\((C_6H_6)_3^+\) has a dimer ion core.

- 0.67 eV
- 0.27 eV
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 → ion core \((\text{C}_6\text{H}_6)_2^+\)
blue component → solvent \(\text{C}_6\text{H}_6\).

(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 $\text{C}_6\text{D}_6$

All the spectra resemble that of $(\text{C}_6\text{H}_6)_3^+$. Spectral features are independent of fragment species monitored.
Spectrum Interpretation for $[(\text{C}_6\text{H}_6)_2 \cdot \text{C}_6\text{D}_6]^+$

<table>
<thead>
<tr>
<th>Structures</th>
<th>$((\text{C}_6\text{H}_6)_2 \cdot \text{C}_6\text{D}_6)$</th>
<th>$((\text{C}_6\text{H}_6 \cdot \text{C}_6\text{D}_6))_1 \cdot \text{C}_6\text{H}_6$</th>
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(If fragment dimer ions are the same as ion core species,)
Band features predicted.

The spectral features are independent of fragment dimer species monitored, and are similar to those of $(\text{C}_6\text{H}_6)_3^+$. The trimer ions lose information on the ion core in the course of photodissociation.
Intracluster Charge Hopping

Dissociation

Vibrational excited states

Intracluster charge hopping occurs in vibrational excited states.
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.

\[
\text{Benzene} \quad \text{Toluene}
\]

<table>
<thead>
<tr>
<th></th>
<th>Benzene</th>
<th>Toluene</th>
</tr>
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<tbody>
<tr>
<td>Charge Distribution (%)</td>
<td>36</td>
<td>64</td>
</tr>
<tr>
<td>IP (eV)</td>
<td>9.24</td>
<td>8.83</td>
</tr>
</tbody>
</table>

Ohashi et al.  
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

\[ B = C_6H_6 \]
\[ T = C_6H_5CH_3 \]

- 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
  
  $T_2^+\cdots B$
  $B_1T_1^+\cdots T$
  $(B\ T\ T)^+$.

- Ionization potential
  
  $T_2 \quad 8.34$ eV
  $B_1T_1 \quad 8.42$ eV

- 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 $T_2^+\cdots\cdots B$. 

Positive Charge Distribution in $B_2T_1^+$

- Possible structures are $B_2^+\cdots T$, $B_1T_1^+\cdots B$, $(B B T)^+$. 

- Ionization potential
  - $B_2$ 8.65 eV
  - $B_1T_1$ 8.42 eV

- 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 \((\text{C}_6\text{D}_6)_2\text{T}_1^+\)

We use \(\text{C}_6\text{D}_6\) instead of \(\text{C}_6\text{H}_6\), and measure an IR spectrum.

- No sharp band is observed at 3068 cm\(^{-1}\) in the spectrum of \((\text{C}_6\text{D}_6)_2\text{T}_1^+\).
- The sharp band in the spectrum of \(\text{B}_2\text{T}_1^+\) is quite similar to that of \(\text{B}_2^+\).

The structure is like \(\text{B}_2^+\cdots\text{T}_1\)?

The spectrum of \((\text{C}_6\text{D}_6)_2\text{T}_1^+\) is different from that of neutral toluene. The toluene molecule in \(\text{B}_2\text{T}_1^+\) is NOT neutral.

Positive charge distribution of \(\text{B}_2\text{T}_1^+\) is

\((\text{B B T})^+\).
Energy Diagram of B$_2$T$_1^+$

- 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

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

The positive charge distribution of B$_2$T$_1^+$ is

- B$_2$ 58%
- T 42%.
Summary

• Benzene trimer ion
  ◆ Dimer ion core structure \((C_6H_6)_2^+\cdots C_6H_6\)
  ◆ Charge hopping in vibrational excited states

• Benzene–toluene mixed trimer ions
  ◆ \(B_1T_2^+\)
    \(T_2^+\cdots B\); 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%).