In the last decade, we have studied the photodissociation spectroscopy and dynamics of benzene cluster ions, \((\text{C}_6\text{H}_6)_n^+\).

1. Charge Distribution of \((\text{C}_6\text{H}_6)_n^+\)
   - \((\text{C}_6\text{H}_6)_2^+\)  
     The positive charge is delocalized in the dimer.
   - \((\text{C}_6\text{H}_6)_n^+ \ (n = 3–5)\)  
     \((\text{C}_6\text{H}_6)_n^+\) has a dimer ion core structure.

2. Charge Hopping in the Excited States
   Intramolecular vibrations of the ejected neutral monomers are highly excited in the energy disposal occurring in the photodissociation of \((\text{C}_6\text{H}_6)_n^+\).

The ejected molecules should be vibrationally excited along the directions of the change in the equilibrium geometries between the neutral and the ion, if the charge continually hops in the cluster after the photoexcitation.
The charge resonance (CR) band is due to the transition from the ground state to the repulsive state of the wave functions,

\[
\psi_+ = \psi_1^+ \psi_2 + \psi_1 \psi_2^+
\]

\[
\psi_- = \psi_1^+ \psi_2 - \psi_1 \psi_2^+
\]

- The presence of the CR band implies that the two moieties should be equivalent.

The positive charge is delocalized in the dimer.

Photodissociation spectra of \((\text{C}_6\text{H}_6)_n^+\) \((n = 2–5)\)

- The absorption bands exhibit essentially the same features as that of \((\text{C}_6\text{H}_6)_2^+\).

These cluster ions have similar dimer ion core structures.
In this study, we want to make clear whether the charge hopping really occurs or not in the vibrational excited states of the benzene cluster ions.

- IR photodissociation spectroscopy is applied to the benzene cluster ions.

- We present vibrational spectra and the assignment of

\[
\begin{align*}
(C_6H_6)_n^+ & \quad (n=2-5), \\
(C_6H_6\cdot C_6D_6)^+ & \\
[(C_6H_6)_m\cdot(C_6D_6)_l]^+ & \quad (m+l=3).
\end{align*}
\]

- According to the relationship between the vibrational spectra and the photofragment species, we demonstrate that the frequent charge hopping really occurs in the vibrational excited states prior to the predissociation.
We used a tandem mass spectrometer with a quadrupole ion guide.

Photodissociation spectra of the parent ions are obtained by plotting the yields of the fragment ions against the wavenumbers of the IR laser.
The CR band has essentially a broad feature because this transition is from the bound state to the repulsive state.

The cross section is not zero up to 2500 cm\(^{-1}\).
The spectra of $n = 3–5$ exhibit sharp and well-resolved bands at 3066 cm$^{-1}$.

In the spectra of $n = 4$ and 5, we can find two maxima at 3045 and 3093 cm$^{-1}$. The intensity ratios of these bands relative to the central band at 3066 cm$^{-1}$ increase more and more with increasing cluster size from $n = 3$ to 5.
We conclude that vibrational structures of \((C_6H_6)_n^+\) \((n = 3–5)\) are composed of the C–H stretching vibration bands of the dimer ion core and the solvent benzene molecules.

Because ...

- the electronic spectra of \((C_6H_6)_n^+\) show that there is a dimer ion core in the cluster.
- neutral benzene has three C–H stretching bands in this region (we call them "triad") .
- we can reproduce the band shapes by decomposing into three components:
  
<table>
<thead>
<tr>
<th>component</th>
<th>triad (solvent benzene molecules)</th>
<th>Lorentzian curve (dimer ion core)</th>
<th>plateau</th>
</tr>
</thead>
<tbody>
<tr>
<td>component 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>component 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>component 3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- the ratios of the integrated intensity of the triad component to that of the Lorentzian component increase proportional to the number of the solvent benzene molecules.

<table>
<thead>
<tr>
<th>(n)</th>
<th>Integrated Intensity of component 1(^a)</th>
<th>the number of solvent benzene molecules (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.3</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>0.6</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>0.9</td>
<td>3</td>
</tr>
</tbody>
</table>

\(^a\) Relative intensity to that of component 2.

\(^b\) This is based on the fact that these have dimer ion core structures.
What is the origin of the plateau (component 3) in the IR spectra?

- In the case of of (\(
\text{C}_6\text{H}_6\)\(_2^+\)), the tail of the charge resonance (CR) band extends down to 2500 cm\(^{-1}\) over the threshold of the binding energy of 5400 cm\(^{-1}\) (0.67 eV).

- (\(\text{C}_6\text{H}_6\)\(_2^+\)) dissociates through one photon process even though the photon energy is lower than the binding energy.

Consequently, the hot bands of the CR transition may mainly contribute to the plateau component of the IR spectra.
Difference in ionization potential between C₆H₆ and C₆D₆ is only 0.003 eV. It is probable that the positive charge is delocalized in \((\text{C}_6\text{H}_6 \cdot \text{C}_6\text{D}_6)^+\) because of the charge resonance interaction.

\[
\begin{align*}
(\text{C}_6\text{H}_6 \cdot \text{C}_6\text{D}_6)^+ \xrightarrow{\text{hv}} & \quad \text{C}_6\text{H}_6^+ + \text{C}_6\text{D}_6 \\
& \quad \text{C}_6\text{D}_6^+ + \text{C}_6\text{H}_6
\end{align*}
\]

The spectra show the same feature as that of \((\text{C}_6\text{H}_6)_2^+\). The C–H stretching frequency of C₆H₆ in the dimer ion core is independent of the partner (C₆H₆ or C₆D₆).
All the spectra of the mixed benzene trimer ions show almost the same spectral feature as that of \((C_6H_6)_3^+\).
The mixed benzene trimer ions may also have the dimer ion core structure because of small difference in ionization potentials of C₆H₆ and C₆D₆ (0.003 eV).

There are two possible isomers for each trimer species.

If the photoexcitation induces the cleavage of the weakest intermolecular bond after the intracluster vibrational energy redistribution without changing the position of the charge, expected spectral feature is as follows,

However, photodissociation spectra detected with the respective fragment ions are nearly the same with each other.

If we construct the two spectra of these isomers with the statistical abundance ratio, we obtain overall photoabsorption spectra of each species with the same feature as that of (C₆H₆)₃⁺.

The dimer ion core switching, in other words, the charge hopping occurs in the photoexcited vibrational states of benzene trimer ions prior to the dissociation.
Overall absorption spectrum of \[ [(\text{C}_6\text{H}_6)_2\bullet\text{C}_6\text{D}_6]^+ \] is

\[ + (2 \times \text{expected band feature}) = 2 \times \text{expected band feature} \]

This is the same with the band shape of \((\text{C}_6\text{H}_6)_3^+\).
Photodissociation spectra of benzene cluster ions are measured in the IR region.

In particular we pay our attention to the trimer ions.

We can reasonably explain the IR spectrum of \((C_6H_6)_3^+\) by the dimer ion core model; the C–H stretching band of \((C_6H_6)_3^+\) is composed of the C–H stretching bands of the dimer ion core and the solvent benzene.

The IR spectra of the isotopically mixed benzene trimer ions show that the positive charge frequently hops from one dimer pair to another pair in the photoexcited vibrational states in the course of the dissociation.
• Vibrational temperature of \((C_6H_6)_n^+\) becomes lower and lower with increasing the cluster size from \(n = 3\) to 5.


• The intensity of the plateau (component 3) becomes lower and lower with increasing the cluster size.

These results also support the assignment of the plateau to the CR transitions from the vibrational excited states.