“Cold” Ion Spectroscopy of Host-Guest Complexes in the Gas Phase

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Crown Ethers (CEs)

Crown ethers (CEs) show ion selectivity.

Dibenzo-18-crown-6
(DB18C6)
Ion Selectivity of CE

DB18C6 captures $K^+$ selectively in water.

$$M^+ + DB18C6 \rightleftharpoons M^+\cdot DB18C6$$

in water, 298 K

Our final goal is to reveal the origin of ion selectivity in terms of quantum chemistry.

Dibenzo-18-crown-6 (DB18C6)
Crystal Structure of $\text{M}^+ \cdot \text{DB18C6}$

X-ray analysis of crystal tells us the relation in size, but…
no information on the origin of ion selectivity in solution.
$\Delta H$ for Complex Formation

Bare complexes cannot explain the ion selectivity in solution.

$$\text{M}^+ + \text{DB18C6} \rightleftharpoons \text{M}^+ \cdot \text{DB18C6}$$


![DB18C6](image-url)
Solvated complexes are used to examine the solvent effect at a molecular level.

\[
\begin{align*}
M^+_{aq} + CE_{aq} & \xrightleftharpoons[K]{\ } (M^+\cdot CE)_{aq} \\
M^+\cdot(H_2O)_m + CE\cdot(H_2O)_n & \xrightleftharpoons[K]{\ } (M^+\cdot CE)\cdot(H_2O)_k
\end{align*}
\]
Relation between $K$, $\Delta G$, $\Delta H$, and $\Delta S$

We have to determine the structure and the number of conformers to evaluate the ion selectivity.

$$K = \exp\left(-\frac{\Delta G}{RT}\right)$$

$$\Delta G = \Delta H - T\Delta S$$

- $H$ and $S$ depend on the structure.
- The more conformations a complex takes, the more stable it is.
This Study

- $M^+\cdot DB18C6$ ($M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+$)
- $M^+\cdot DB18C6\cdot (H_2O)_n$ ($n = 1–5$)

- UV and IR spectroscopy in a cold, 22-pole ion trap
- The number and structure of conformers are determined.
**Experimental (simple ver.)**

**UV and IR spectra of ions are measured under cold (~10 K) conditions in the gas phase.**

- **Electrospray**
- **Ion funnel**
- **6-pole mass**
- **4-pole mass**
- **8-pole mass**
- **Ion bender**
- **Cold 22-pole ion trap**
- **UV**
- **IR**

1. Produce ion complexes with electrospray
2. Select one species with 4-pole mass
3. Cool down and irradiate UV laser to them in 22-pole ion trap
4. Detect fragment ions with 4-pole mass
Effect of the Cooling on UV Spectra

Sharp UV bands are observed thanks to the cooling.

Inokuchi et al., *JACS*, 2011, 133, 12256.
Conformer-specific IR spectra can be measured by IR-UV double-resonance.
All the complexes show sharp UV bands. Conformer-specific IR spectra can be measured.

UV Spectra of $M^+ \cdot DB18C6$

Inokuchi et al., JACS, 2011, 133, 12256.
Different IR features originate from different conformers.

Inokuchi et al., JACS, 2011, 133, 12256.
The conformer structure is determined with the aid of quantum chemical calculations.

Inokuchi et al., *JACS, 2011, 133, 12256.*
UV Spectra of K⁺•DB18C6•(H₂O)ₙ

UV spectra also show sharp bands.
Conformer-specific IR spectra can be measured.

<table>
<thead>
<tr>
<th>Fragment Ion Intensity</th>
<th>UV Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 0</td>
<td>35800 - 36600</td>
</tr>
<tr>
<td>n = 1</td>
<td>35800 - 36600</td>
</tr>
<tr>
<td>n = 2</td>
<td>35800 - 36600</td>
</tr>
<tr>
<td>n = 3</td>
<td>35800 - 36600</td>
</tr>
<tr>
<td>n = 4</td>
<td>35800 - 36600</td>
</tr>
<tr>
<td>n = 5</td>
<td>35800 - 36600</td>
</tr>
</tbody>
</table>
Conformers of $K^+\cdot DB18C6\cdot (H_2O)_3$

Two conformers for $K^+$. 

IR Wavenumber (cm$^{-1}$)

K3a

K3g
Conformers of $M^+\cdot DB18C6\cdot(H_2O)_3$

**One conformer** for $Rb^+$ and $Cs^+$.  

Rb3a  

Cs3a

**Two conformers** for $K^+$.  

K3a  

K3g
The Number of Conformers

If the metal ion is completely surrounded by CE, multiple conformers can exist for solvated complexes.
The Number of Conformers of $\text{Mn}^{2+}\cdot\text{CE}$

B18C6 occupies all the coordination sites, resulting in multiple conformers with $\text{CH}_3\text{OH}$.

<table>
<thead>
<tr>
<th>CE</th>
<th>$\text{Mn}^{2+}\cdot\text{CE}\cdot\text{CH}_3\text{OH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B15C5</td>
<td>1</td>
</tr>
<tr>
<td>B18C6</td>
<td>3</td>
</tr>
</tbody>
</table>

Diagram:
- B15C5
- B18C6
What’s happening in encapsulation?

We have just started understanding the relation between encapsulation and solvation.

\[ M^+ \cdot (H_2O)_m + CE \cdot (H_2O)_n \rightleftharpoons (M^+ \cdot CE) \cdot (H_2O)_k \]

We can determine the structure and the number of conformers at the same time.
Summary

We are still on a way to revealing the whole picture of the ion selectivity at a molecular level, but...

- $\text{M}^+\cdot\text{DB18C6}$ ($\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$)
- $\text{M}^+\cdot\text{DB18C6}\cdot(\text{H}_2\text{O})_n$
- UV and IR spectroscopy in a cold, 22-pole ion trap

- The structure and number of conformers are determined.
- Host-guest complexes with an optimum matching in size tend to give multiple conformers with solvent molecules, resulting in entropic advantages.
Acknowledgment

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