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

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Host Molecules

hold other ions and molecules inside

- Crown ether
- Calix[4]arene
- Porphyrin
- Cyclophane
- Cyclodextrin
Crown ethers (CEs) show ion selectivity.

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

DB18C6 captures $K^+$ selectively in water.

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

in water, 298 K

Our final goal is to reveal the origin of ion selectivity in terms of quantum chemistry.
$\Delta H$ for Complex Formation

Bare complexes cannot explain the ion selectivity in solution.

$$\text{M}^+ + \text{DB18C6} \xleftrightarrow{\Delta H} \text{M}^+ \cdot \text{DB18C6}$$

![Graph showing the change in enthalpy ($\Delta H$) for complex formation at 298 K with various cations.](image)

Solvated Complexes

Solvated complexes are used to examine the solvent effect at a molecular level.

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

- $\text{M}^+\cdot\text{DB18C6}$ ($\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$)
- $\text{M}^+\cdot\text{DB18C6}\cdot(\text{H}_2\text{O})_n$ ($n = 1–5$)

- UV and IR spectroscopy in a cold, 22-pole ion trap
- The number and structure of conformers are determined.
UV and IR spectra of ions are measured under cold (~10 K) conditions in the gas phase.
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.

IR-UV Double-Resonance
UV Spectra of $M^+ \cdot \text{DB18C6}$

All the complexes show sharp UV bands. Conformer-specific IR spectra can be measured.

Inokuchi et al., JACS, 2011, 133, 12256.
IR Spectra of $M^+ \cdot $DB18C6

Different IR features originate from different conformers.

Inokuchi et al., JACS, 2011, 133, 12256.
Structure of $M^+ \cdot DB18C6$

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.
Conformers of $\text{K}^+\cdot\text{DB18C6}\cdot(\text{H}_2\text{O})_3$

Two conformers for $\text{K}^+$.

Inokuchi et al., JACS, 2014, 136, 1815.
Conformers of $M^+\cdot$DB18C6•(H$_2$O)$_3$

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

$Rb3a$

$Cs3a$

Two conformers for $K^+$.

$K3a$

$K3g$

Inokuchi et al., *JACS*, 2014, 136, 1815.
The Number of Conformers

If the metal ion is completely surrounded by CE, multiple conformers can exist for solvated complexes.
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...*

- $M^+\cdot DB18C6$  ($M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+$)
- $M^+\cdot DB18C6\cdot(H_2O)_n$
- 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.
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Future Prospects

Quantum chemical approaches in host-guest chemistry

Gas phase

Diagram:
- Paul ion trap (R. M. Jordan), ~8 K (with He buffer gas injected)
- He cryostat (Sumitomo RD-408D2)
- Electrospray: 0.1 mL/h, ~3000 V, ~1 X 10^-4 mol/L
- Vaporization tube: ~100 °C
- Octopole ion guide: ~2 MHz, ~200 V p.p.
- UV laser
- MCP
- Reflectron
Future Prospects

Quantum chemical approaches in host-guest chemistry

On gold surface

SEIRA (Surface-enhanced IR absorption) spectroscopy with ATR configuration

Thank you for your attention!