UV and IR Spectroscopy of Host-Guest Complexes in the Gas Phase and on Gold Surface

Yoshiya INOKUCHI

Hiroshima University
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)
DB18C6 captures $K^+$ selectively in water.

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

in water, 298 K

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

Dibenzo-18-crown-6 (DB18C6)
Our Studies

Host-Guest Complexes

- IR Spectroscopy on Gold Surface
- “Cold” Spectroscopy in the Gas Phase
“Cold” Spectroscopy in the Gas Phase

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

Inokuchi et al., JACS, 2011, 133, 12256.
SEIRA Spectroscopy on Gold Surface

Crown Ethers Chemisorbed on Au Surface

(a) 18C6-C_{1}OC_{6}-SH  (b) 18C6-C_{1}-SH

(c) 18C6-C_{1}OC_{6}  (d) 18C6-C_{1}
SEIRA (Surface-Enhanced IR Absorption) spectroscopy

(1) Au surface (~8 nm) is formed on an ATR (Attenuated total reflection) element by vacuum deposition.
(2) Thiol derivatives of crown ethers are chemisorbed on the Au surface with S–Au bonds.
(3) Solutions of metal salts are put on it to form complexes.
IR Spectra of K$^+$•18C6 on Au

Long
with KCl
18C6-C$_1$OC$_6$-SH

Short
with KCl
18C6-C$_1$-SH

Wavenumber (cm$^{-1}$)

(a) 18C6-C$_1$OC$_6$-SH
(b) 18C6-C$_1$-SH
(c) 18C6-C$_1$OC$_6$
(d) 18C6-C$_1$
Advantages and Disadvantages

- High sensitivity and selectivity due to Au surface
- Quantitative
- Reusable (washable)
- Condensed phase, interface
- Applications: ion filters, sensing devices

- Necessary to synthesize thiol derivatives
- Effects of Au surface on encapsulation
IR Difference Spectra of $\text{M}^+\cdot\text{18C6-}^\text{18C6-C}_1\text{OC}_6$ in water: $10^{-6}$~2 M

- $\text{Li}^+$
- $\text{Na}^+$
- $\text{K}^+$
- $\text{Rb}^+$
- $\text{Cs}^+$

18C6-\text{C}_1\text{OC}_6
Titration Curves for $M^+\cdot18C6-C_1OC_6$

Hill equation

steepness = cooperativity

substrates and enzymes
Ion selectivity for $K^+$ not so obvious for $18C6-C_1$

$18C6-C_1$ shows more negative cooperativity

$M^+ \cdot 18C6-C_1$ at interface inhibits successive encapsulation