# Spectroscopic Studies on Host-Guest Complexes in the Gas Phase and on Gold Surface

**Yoshiya INOKUCHI**

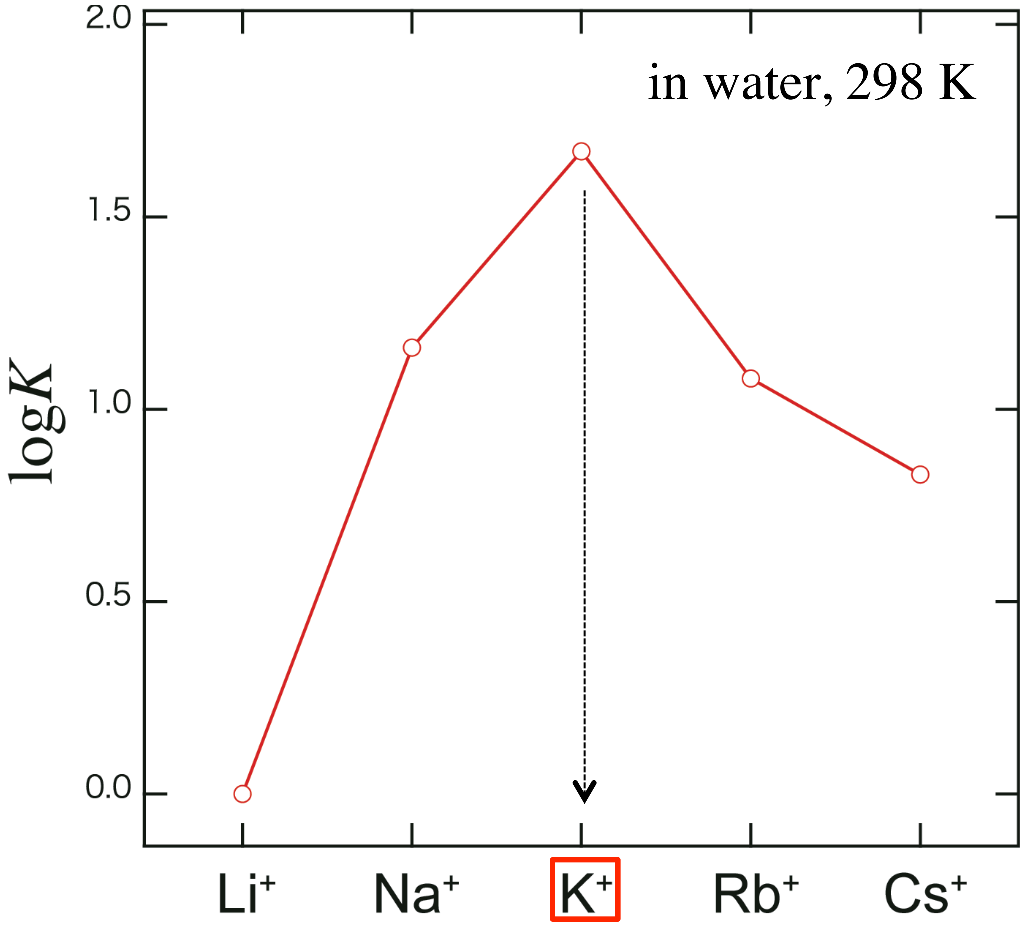
***Hiroshima University***

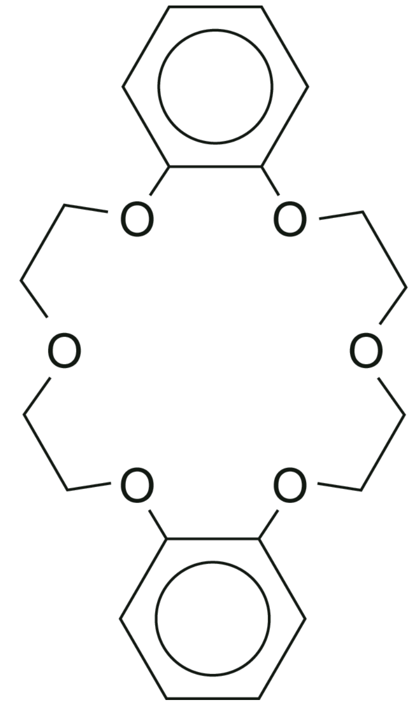
PACIFICHEM 2015, "Developments in Spectroscopic Investigation of Intermolecular Interactions and Dynamics of Molecular Clusters" (#438)
16/12/2015

# Ion Selectivity of CE

*DB18C6 captures $K^+$ selectively in water.*

$$M^+ + DB18C6 \underset{}{\overset{K}{\rightleftarrows}} M^+\bullet DB18C6$$



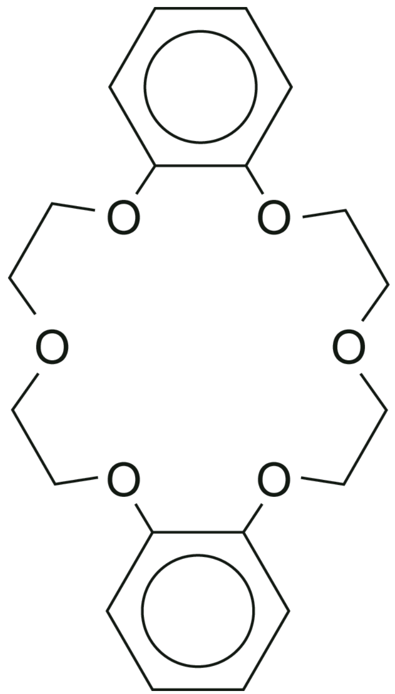




DB18C6

Izatt et al., *Chem. Rev.*, **1985**, *85*, 271.

# Our Final Goal

*Our final goal is*
*to reveal the origin of ion selectivity*
*with spectroscopic methods.*

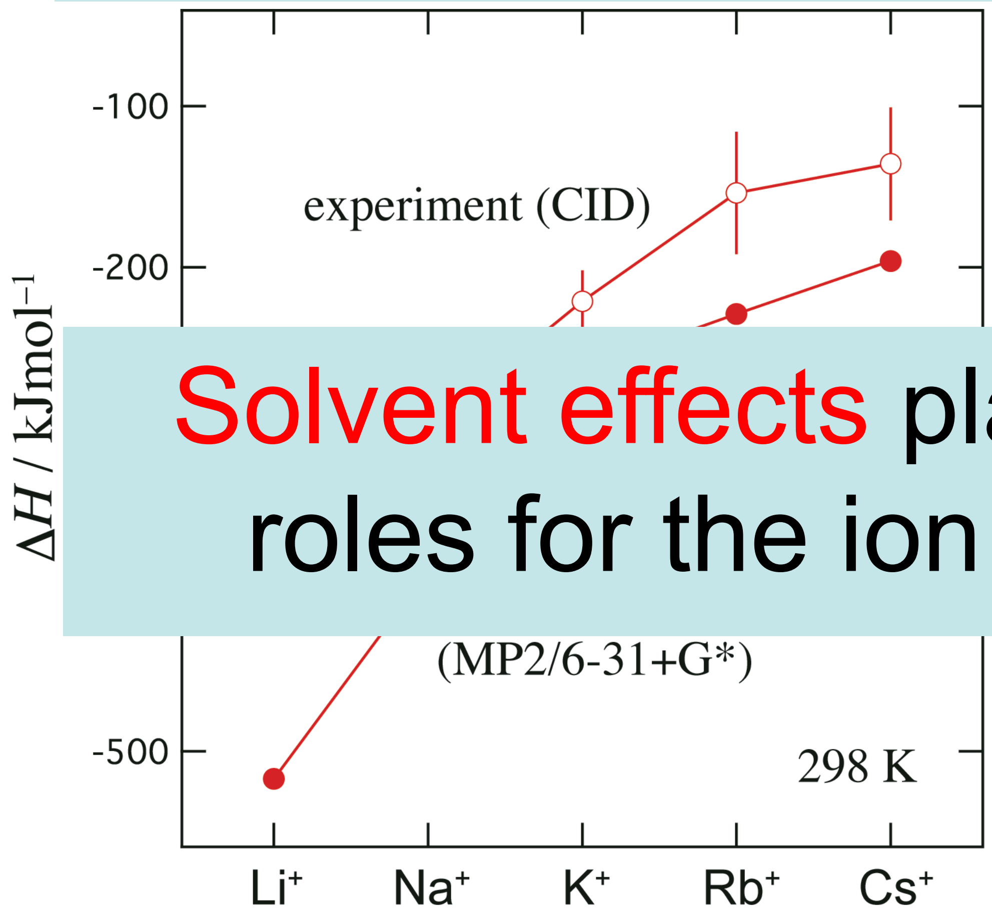


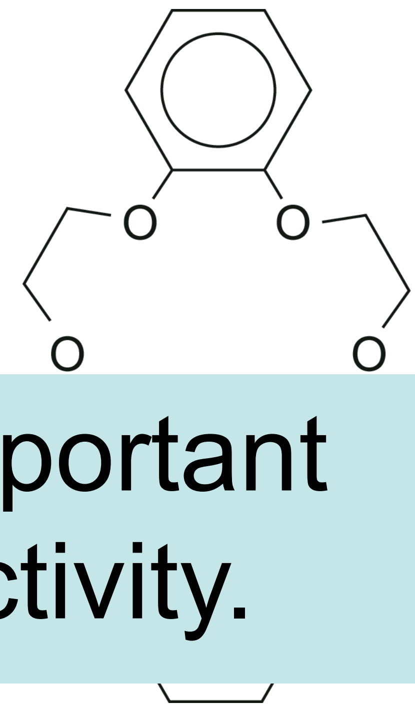

Dibenzo-18-crown-6
(DB18C6)

# $\Delta$*H* for Complex Formation

*Bare complexes cannot explain the ion selectivity in solution.*

$$M^+ + DB18C6 \underset{}{\overset{\Delta H}{\rightleftharpoons}} M^+ \bullet DB18C6$$



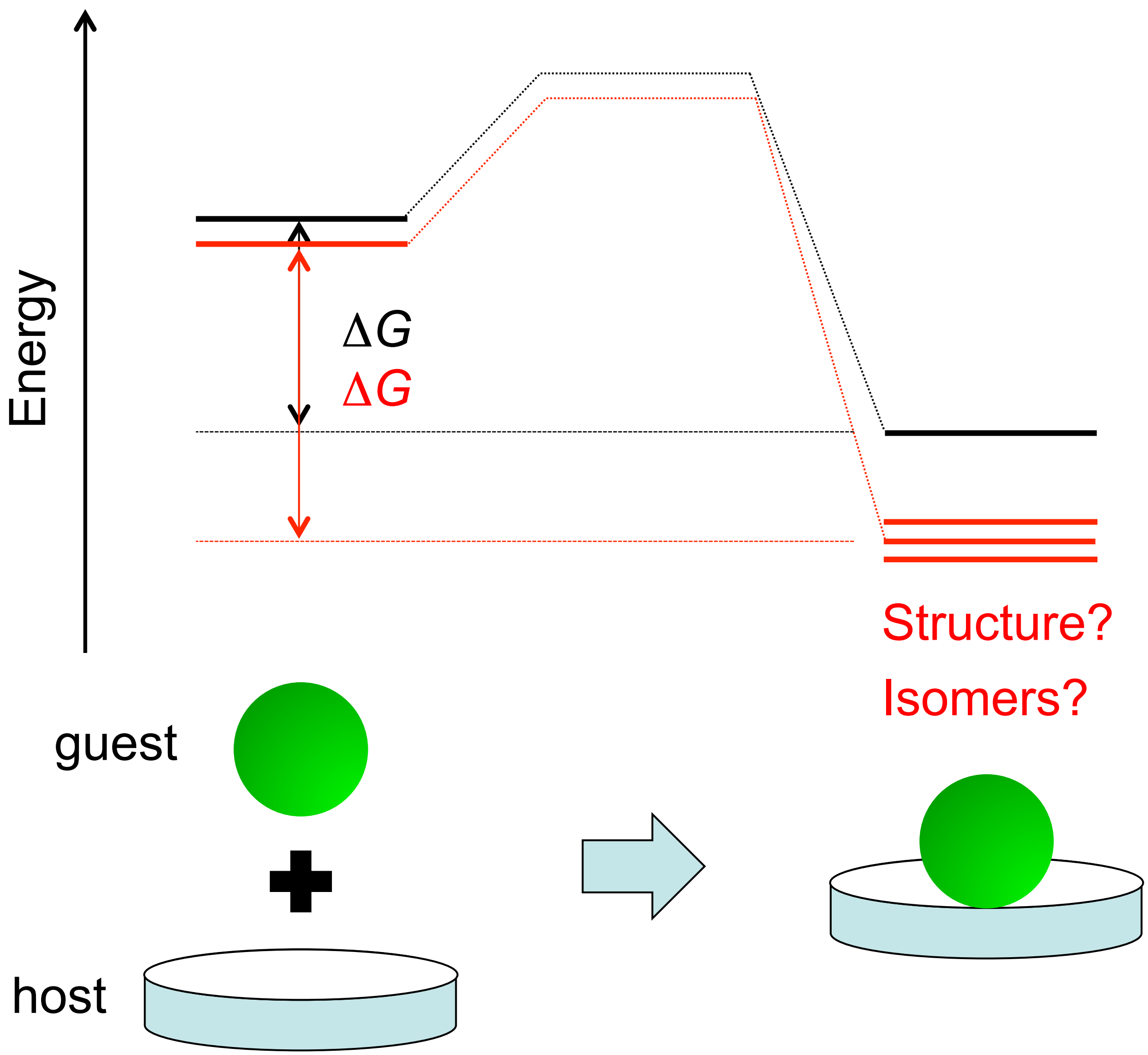




DB18C6

**Solvent effects play important roles for the ion selectivity.**

Anderson et al., *Int. J. Mass Spectrom.*, **2003**, *227*, 63.

# Properties of complexes reflect selectivity?

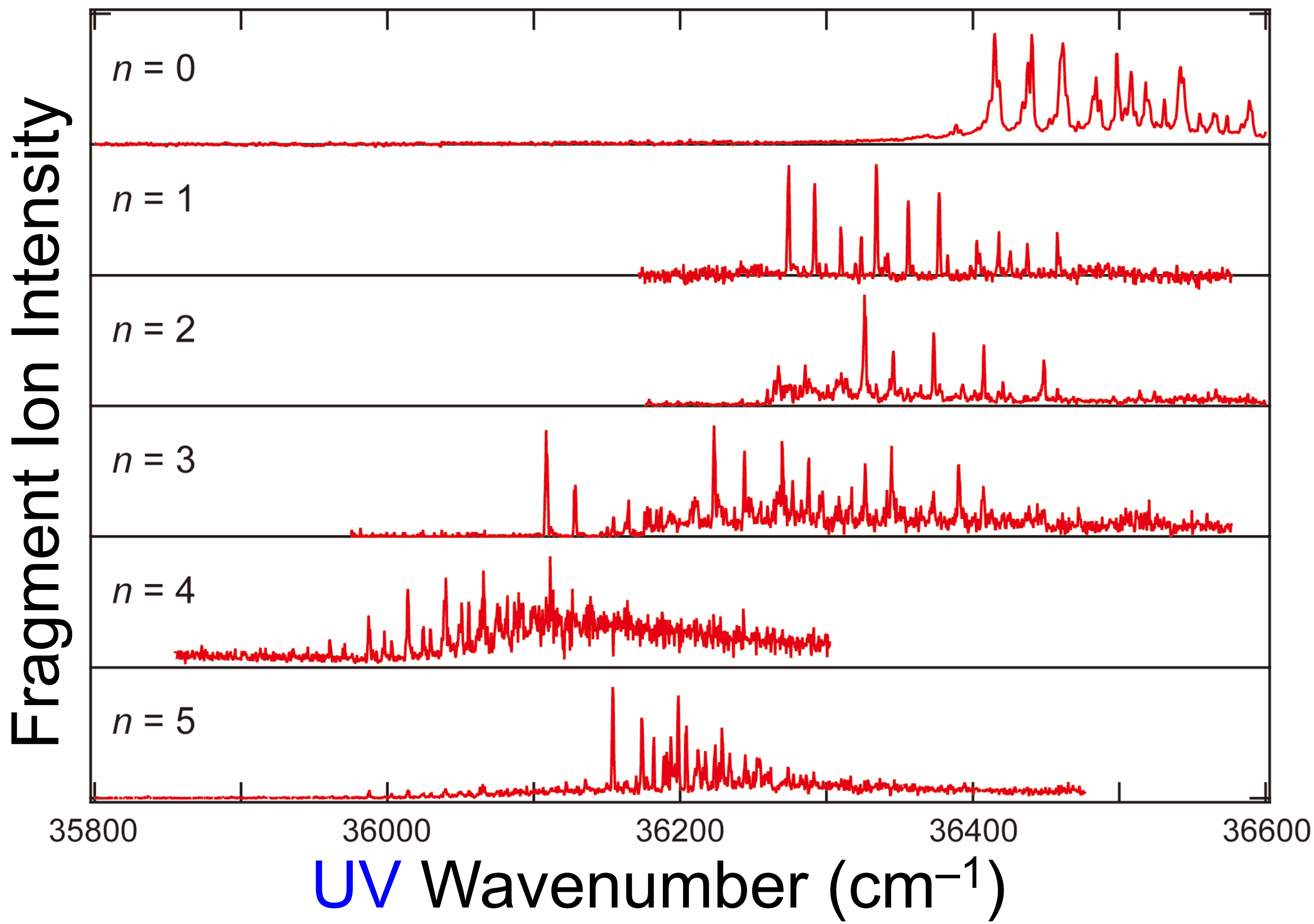


# Our Studies on Host-Guest Complexes

“Solvated” Host-Guest Complexes

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

# UV Spectra of $K^+$•DB18C6•$(H_2O)_n$




Inokuchi et al., *J. Am. Chem. Soc.*, **2014**, *136*, 1815.

# Our Studies on Host-Guest Complexes

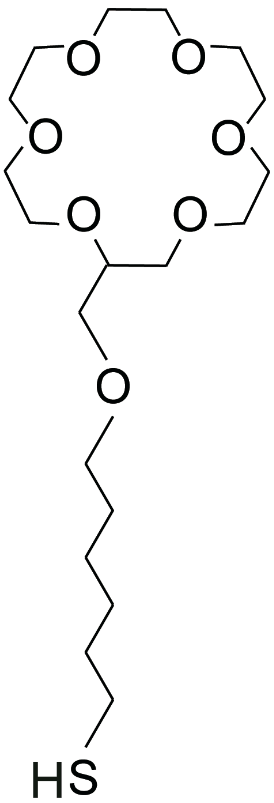
- "Solvated" Host-Guest Complexes
  - "Cold" Spectroscopy in the Gas Phase
  - IR Spectroscopy on Gold Surface

# Surface-Enhanced IR Absorption Spectroscopy (SEIRAS) on Gold Surface

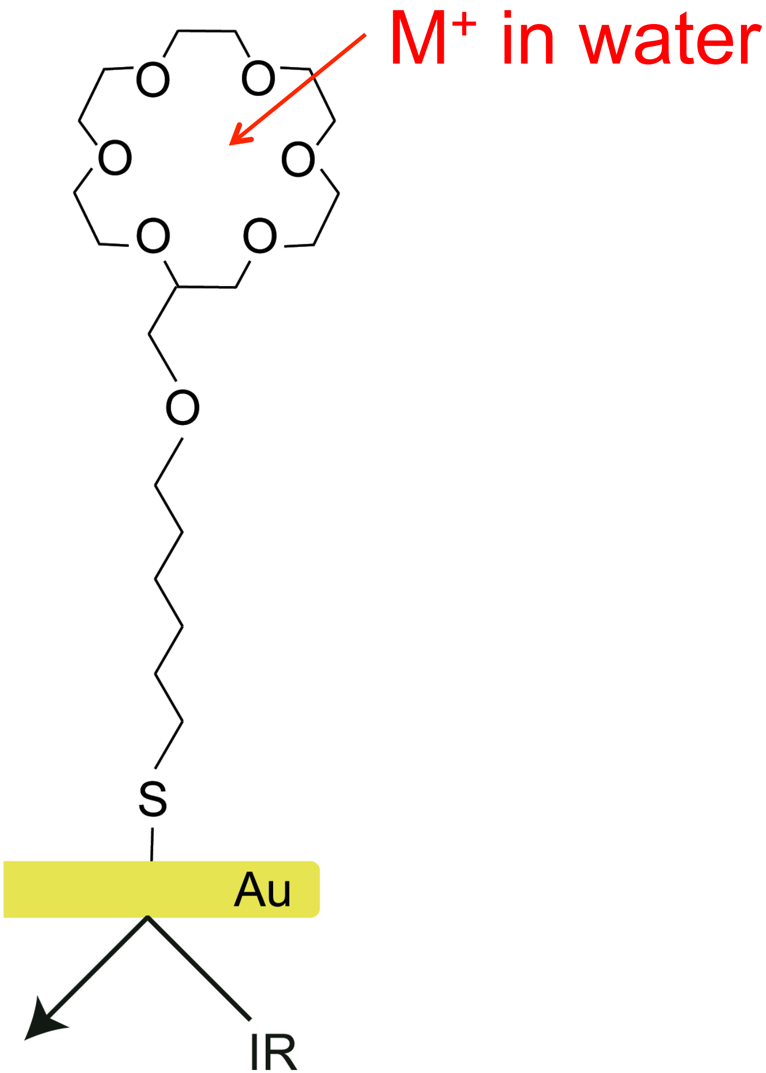
Furutani and co-workers, *Chem. Phys.*, **2013**, *419*, 8.

Inokuchi et al., *Chem. Phys. Lett.*, **2014**, *592*, 90.
Inokuchi et al., *New J. Chem.*, **2015**, *39*, 8673.

# Host-Guest Complexes on Au




$18C6\text{-}C_1OC_6\text{-}SH$

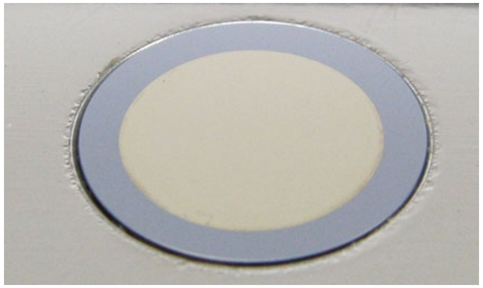



$M^+ \bullet 18C6\text{-}C_1OC_6$

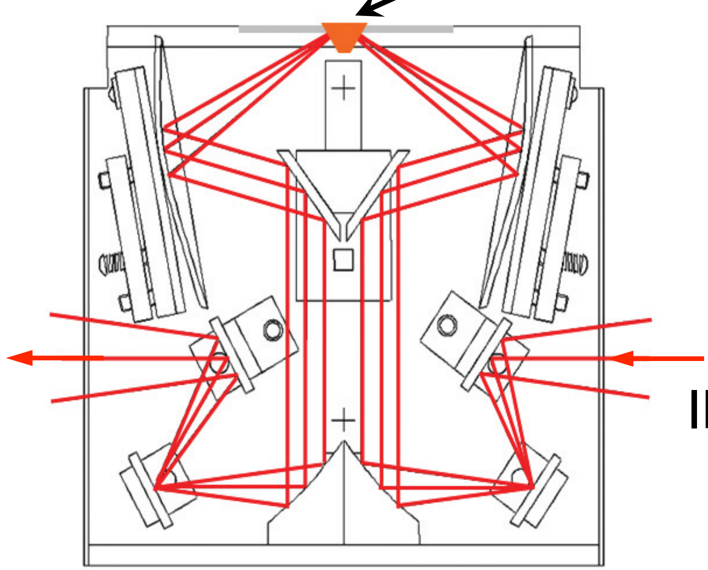
# SEIRA with ATR Configuration

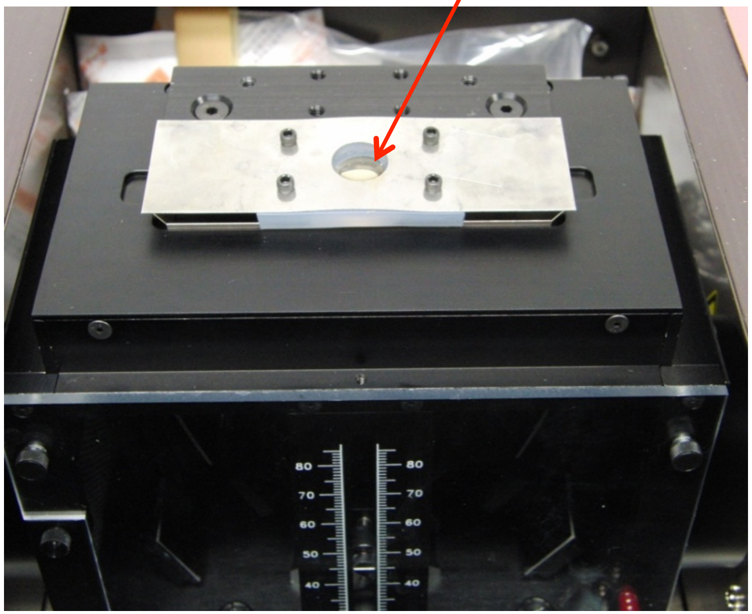
SEIRA (Surface-Enhanced IR Absorption) spectroscopy

(1) Au surface (~8 nm) is formed on an ATR element (Si prism) 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.



Au surface on Si prism



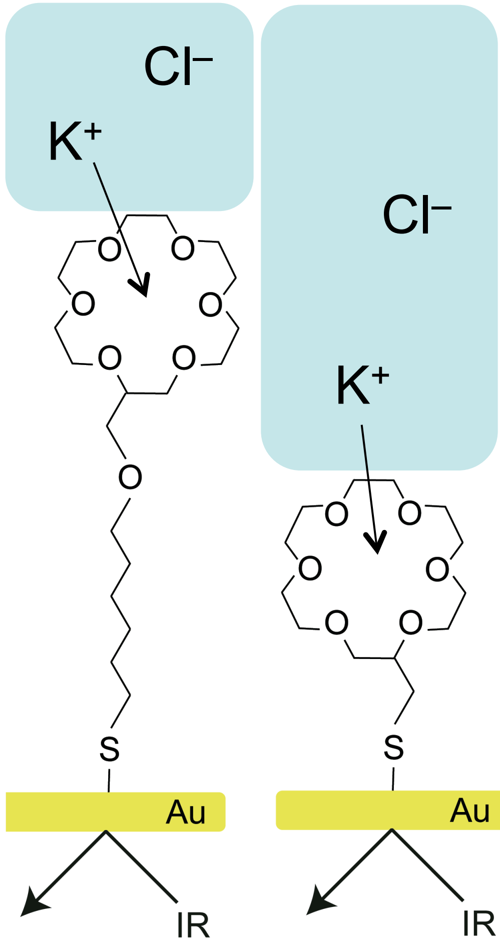
(Furutani's group at IMS)

# Advantages and Disadvantages

- High sensitivity due to Au surface
- Reusable (washable)
- Small quantity
- Not need to care about solubility of hosts
- Applications

  ion filters, sensing devices

- Necessary to synthesize thiol derivatives
- Effects of Au surface on encapsulation



# Host-Guest Complexes on Au

(1) Long chain ⟺ Short chain

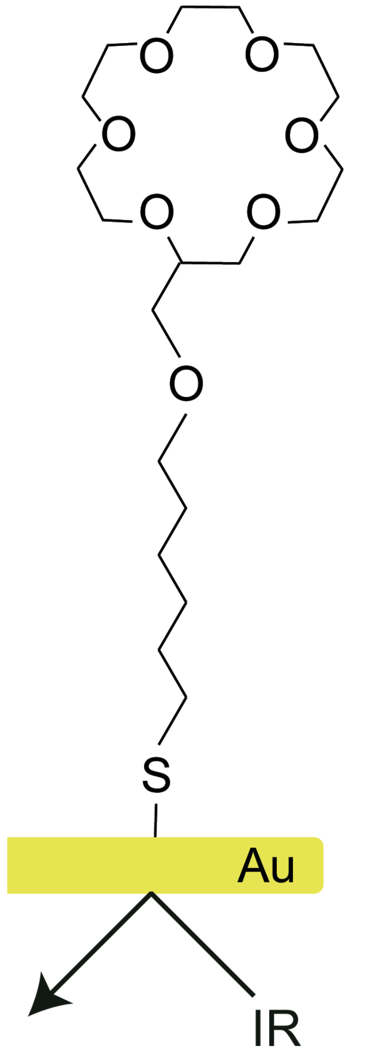
(2) 18-crown-6 ⟺ 15-crown-5

(3) Water ⟺ Methanol

Inokuchi et al., *Chem. Phys. Lett.*, **2014**, *592*, 90.
Inokuchi et al., *New J. Chem.*, **2015**, *39*, 8673.

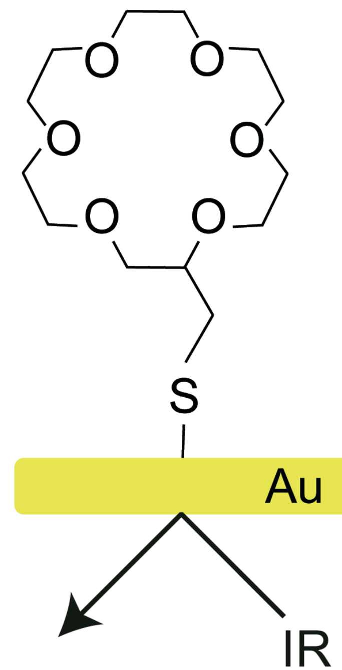
# (1) Long Chain vs. Short Chain

in water




18C6-$C_1OC_6$

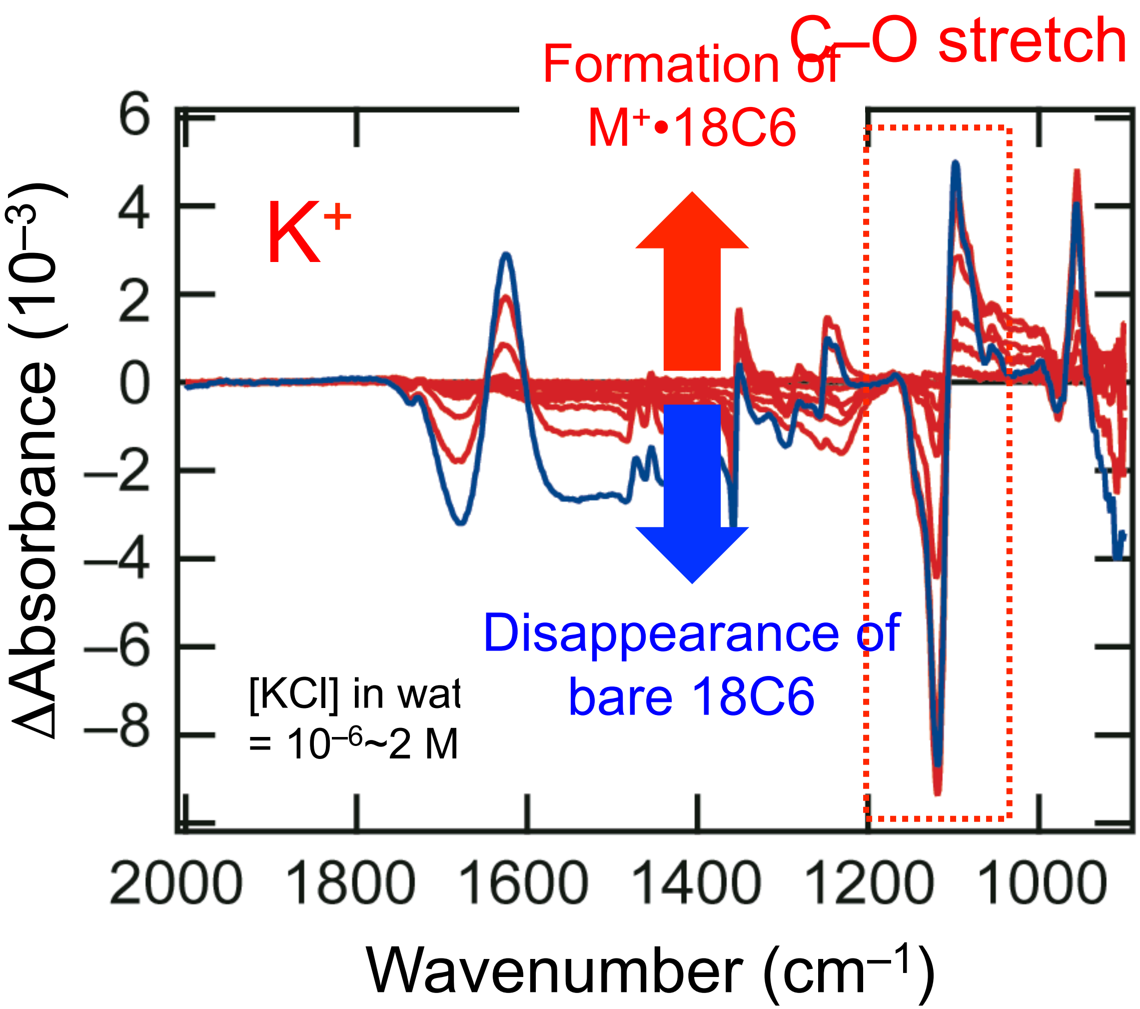
"Long"

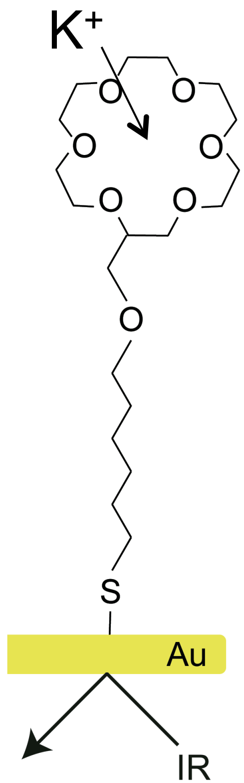



18C6-$C_1$

"Short"

# IR Difference Spectra of $K^+$•18C6-$C_1OC_6$

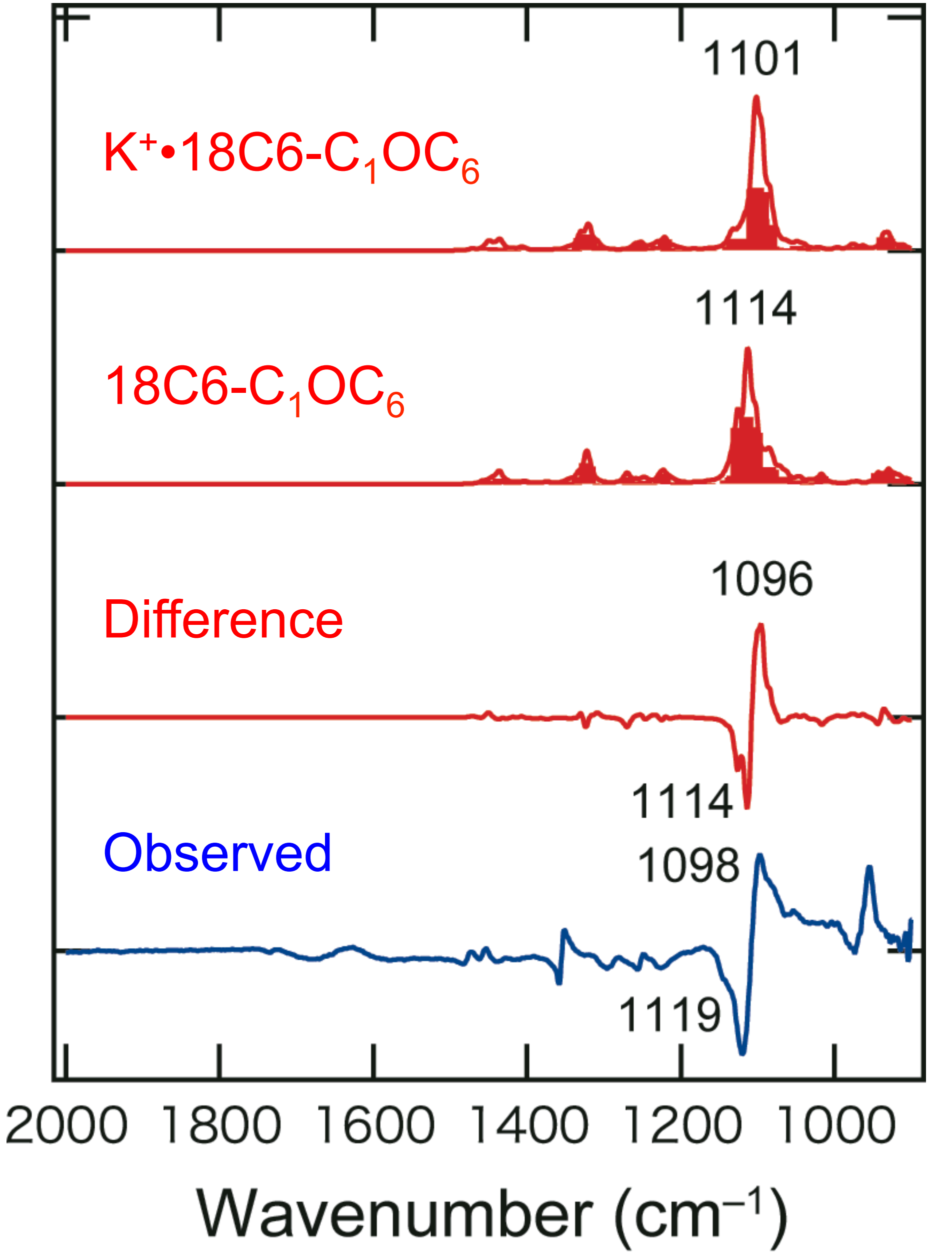


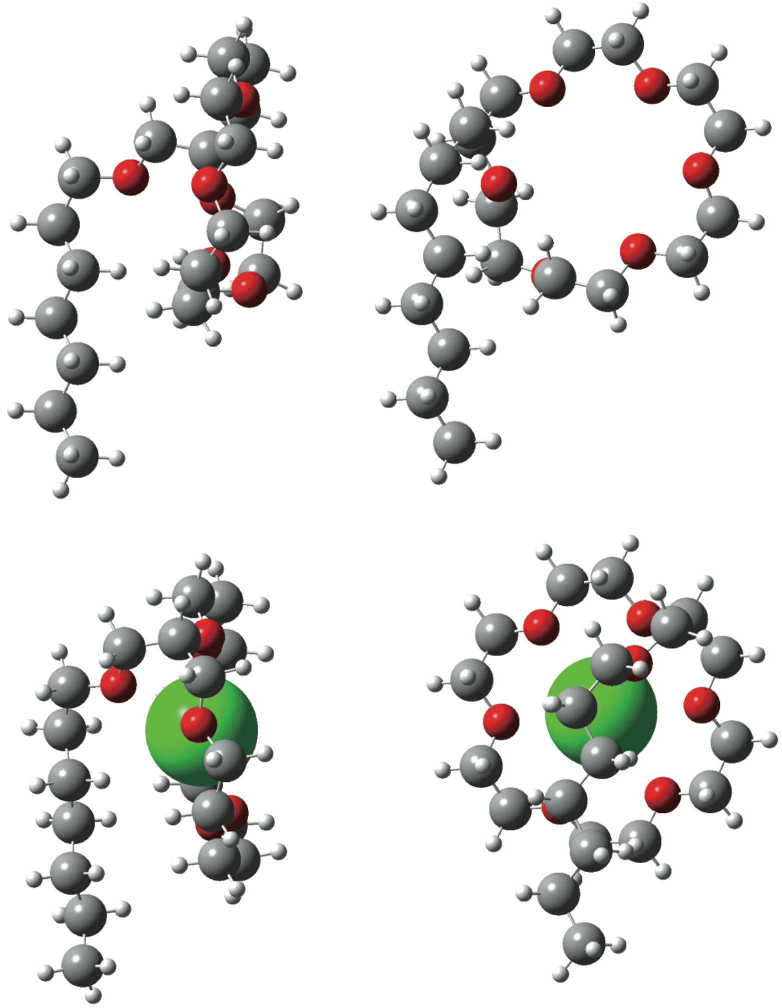




$K^+$•18C6-$C_1OC_6$

"Long"

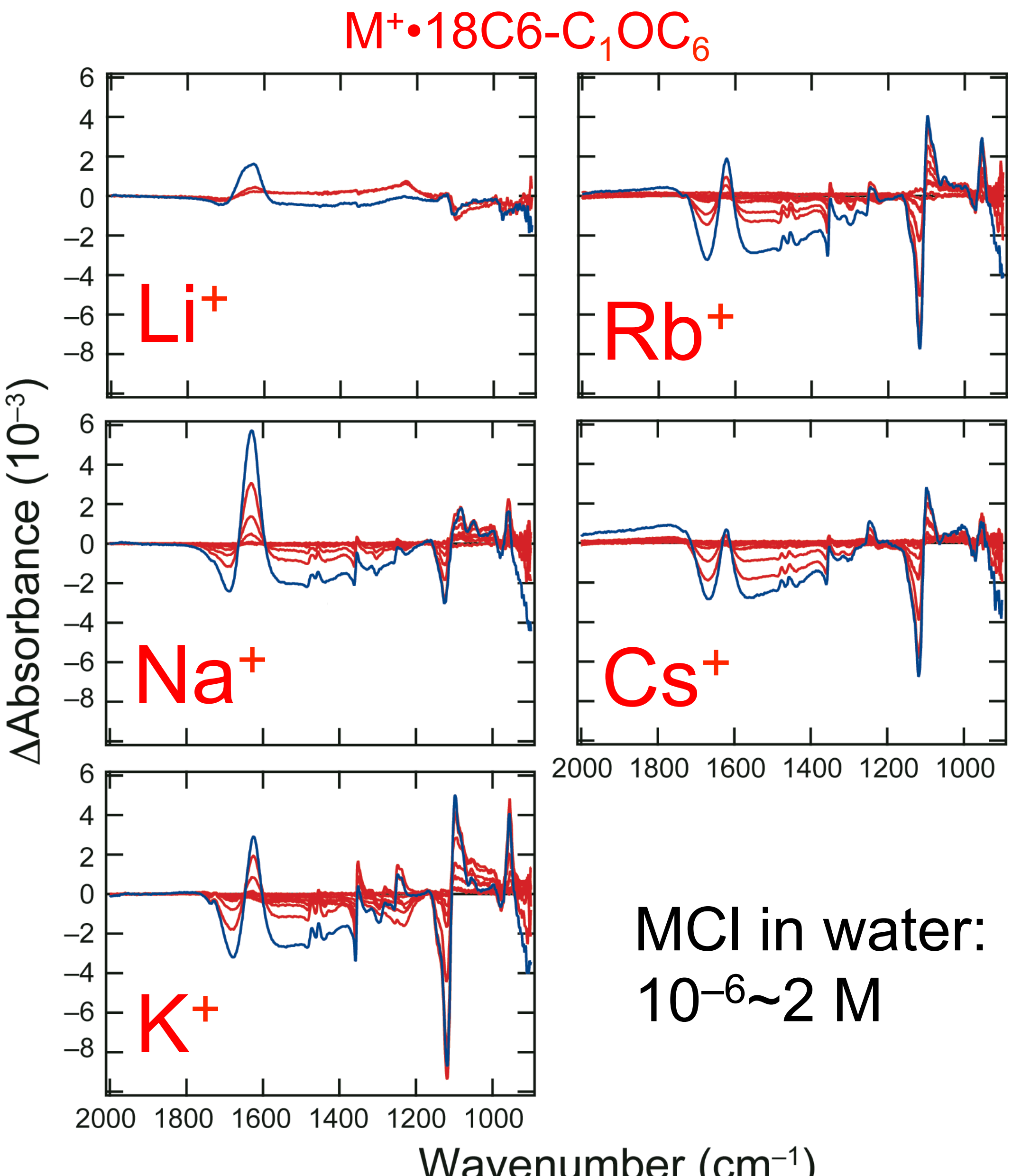
# Simulation of IR Spectra



Calculated in water with PCM
M05-2X/6-31+G(d)

# IR Difference Spectra of $M^+$•18C6-$C_1OC_6$

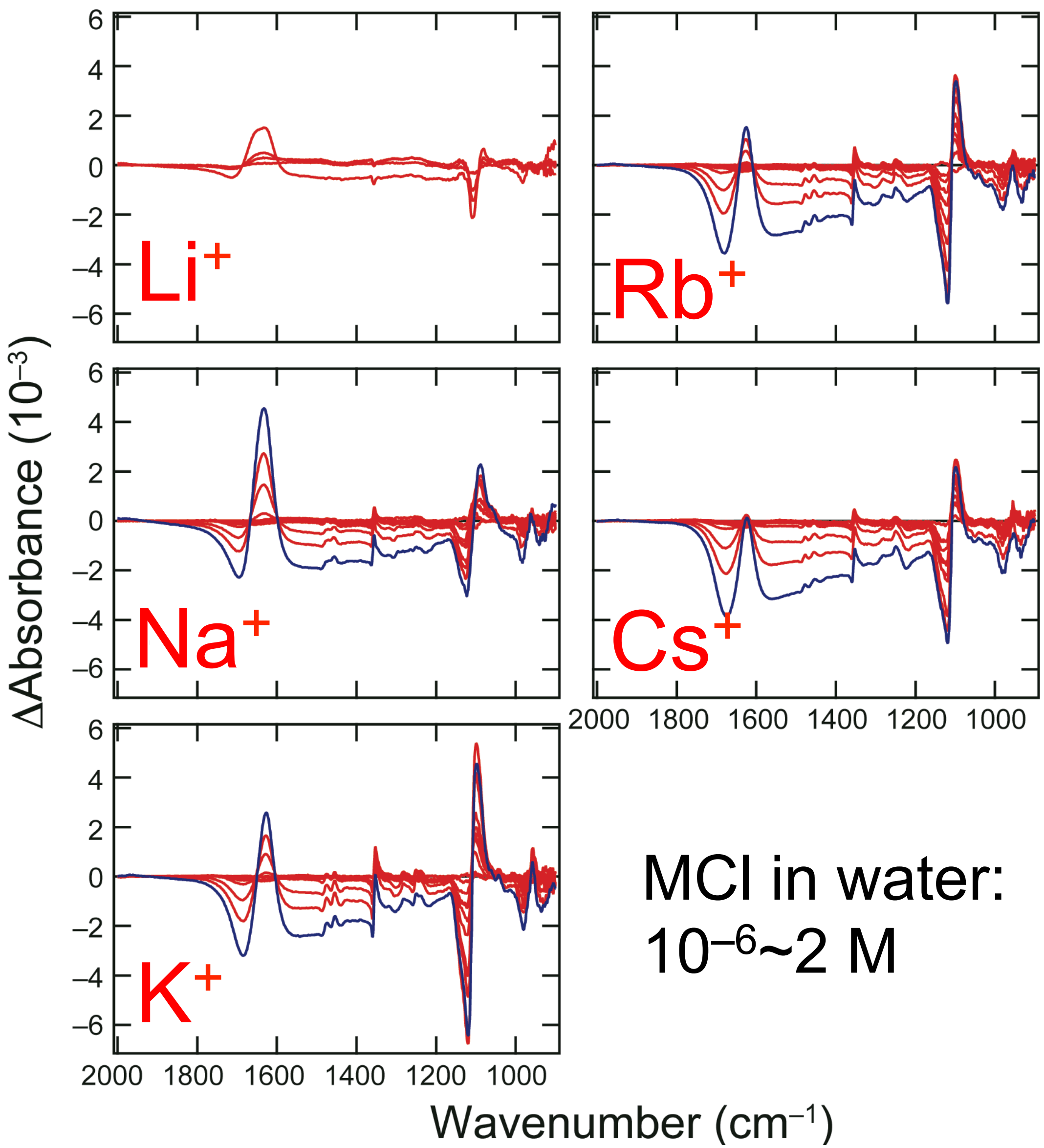



Strong signals of the C–O stretching vibrations are found for $Na^+$ to $Cs^+$.

Intermol. interactions of $M^+$•••18C6 are similar for $Na^+$ to $Cs^+$ in water.

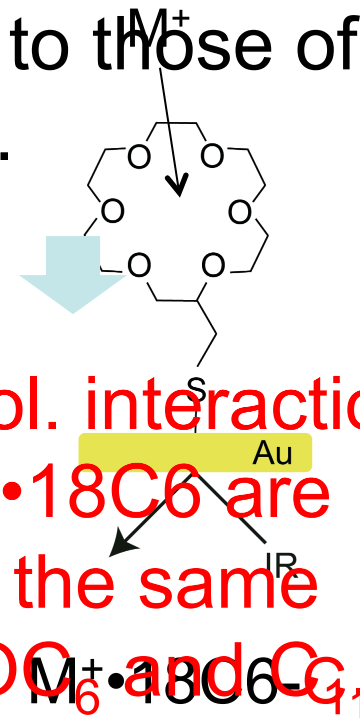
# IR Difference Spectra of $M^+$•18C6-$C_1$

$M^+$•18C6-$C_1$




MCl in water: $10^{-6}$~2 M

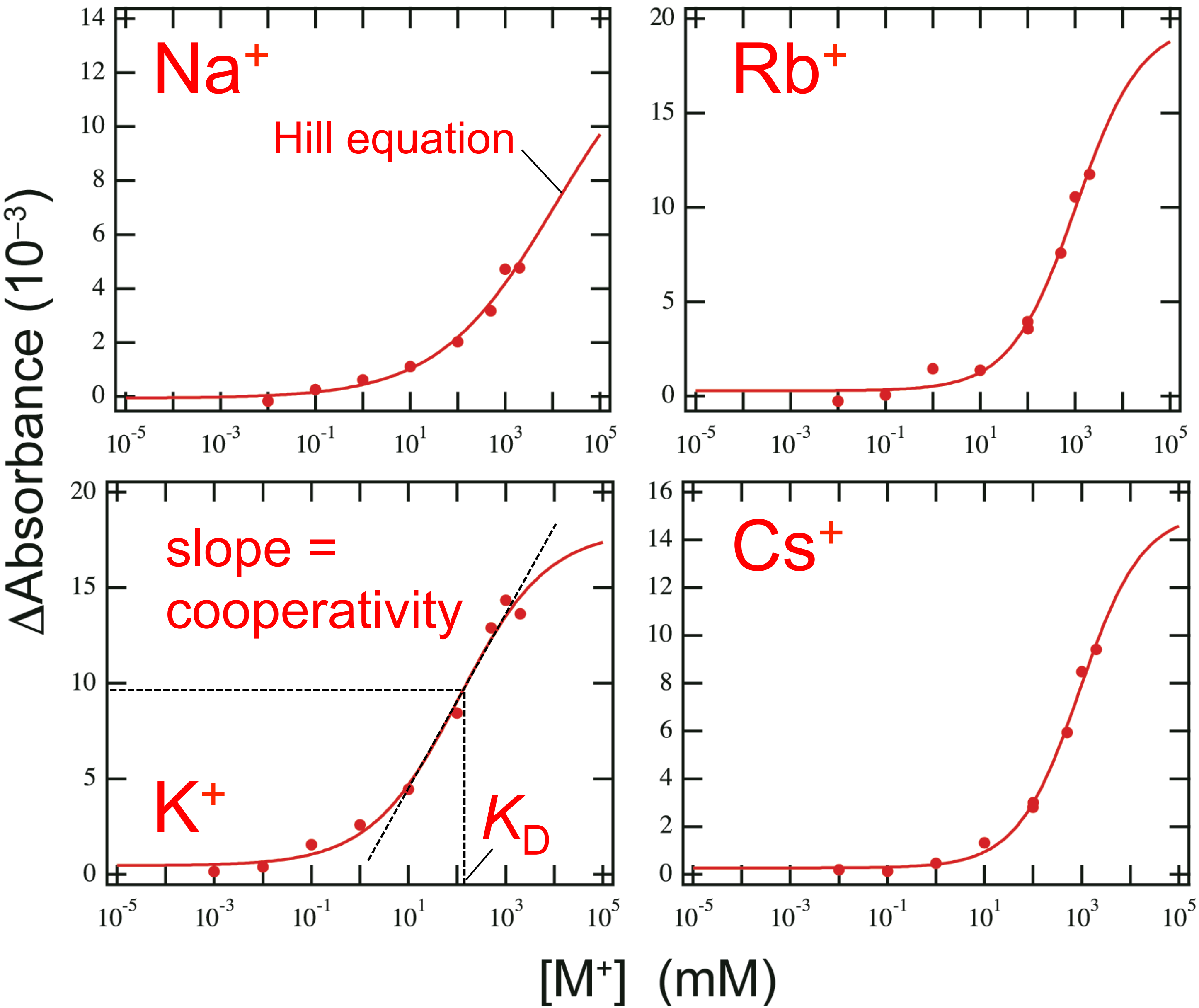
The spectra are similar to those of $C_1OC_6$.



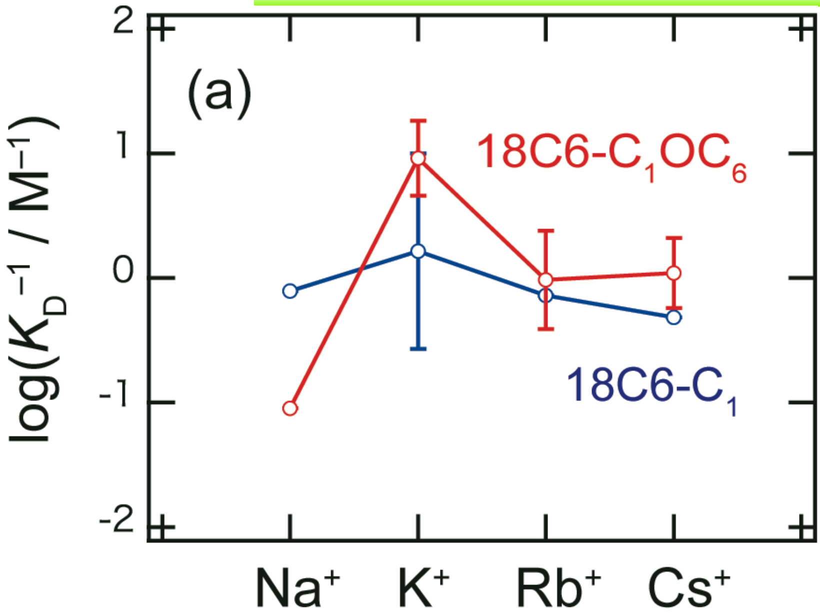

Intermol. interactions of $M^+$•••18C6 are almost the same for $C_1OC_6$ and $C_1$

"Short"

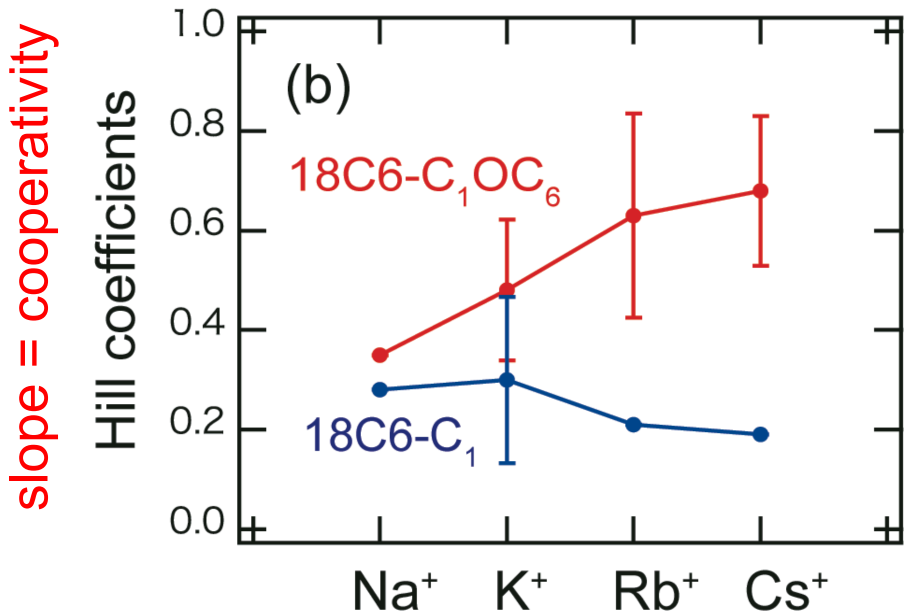
# Titration Curves for $M^+ \bullet$18C6-$C_1OC_6$



# $K_D$ and Hill Coefficients



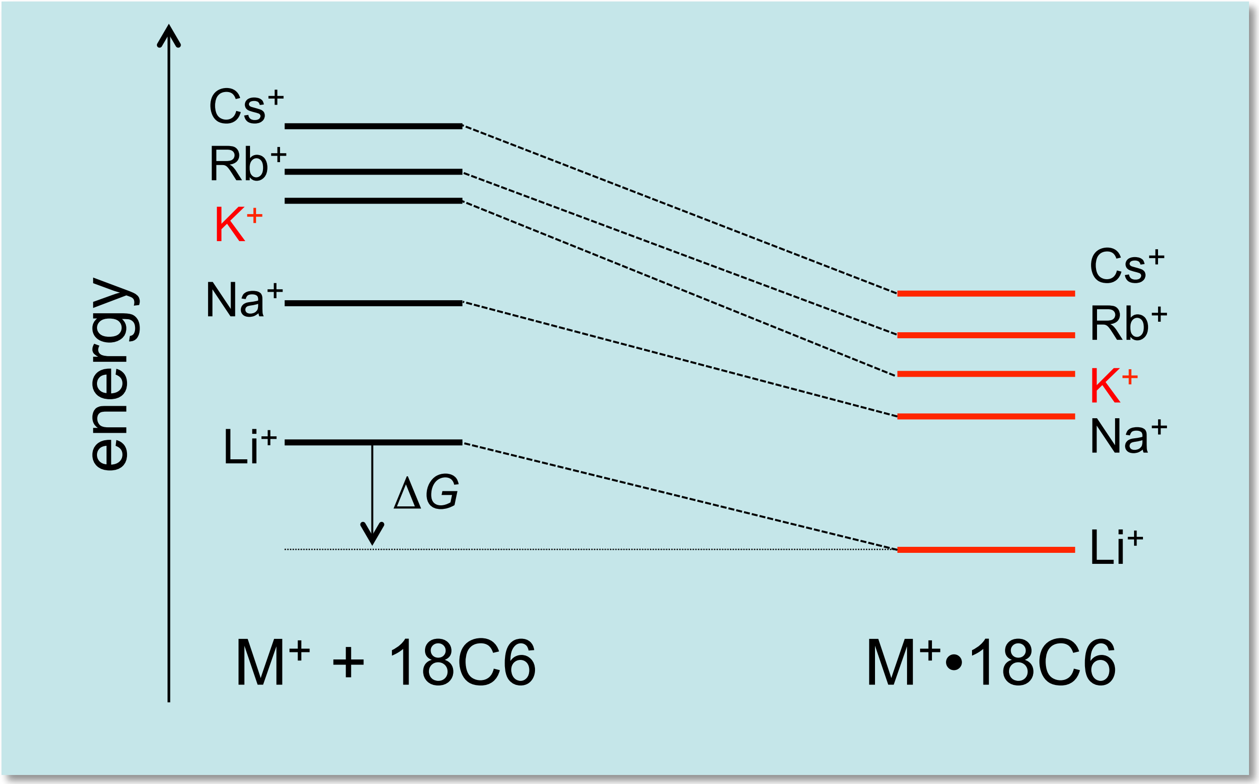

Ion selectivity for $K^+$ can be seen, though it is not so obvious for 18C6-$C_1$.




18C6-$C_1$ shows smaller cooperativity.

$M^+$•18C6-$C_1$ at interface inhibits successive encapsulation.

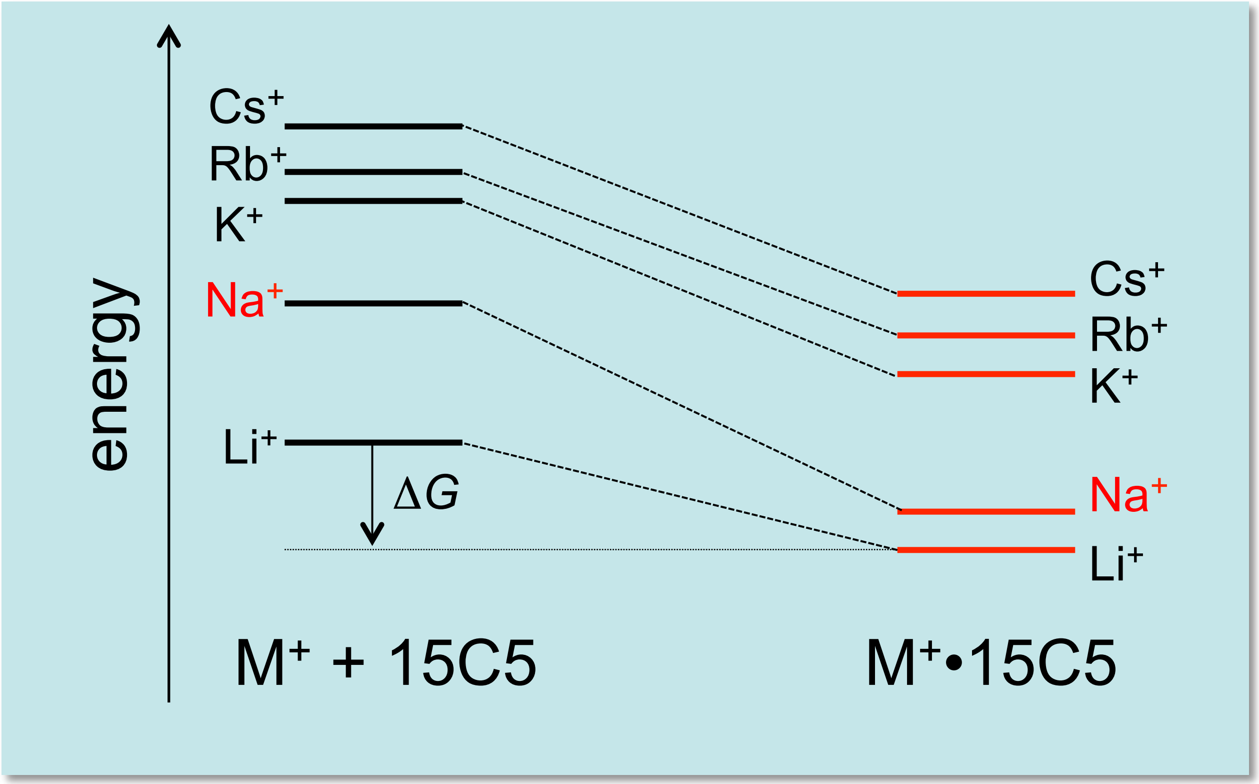
# Conclusion (1) Ion Selectivity of 18C6




Intermol. interactions are similar for $Na^+$, $K^+$, $Rb^+$, and $Cs^+$.
18C6 shows preference for $K^+$.

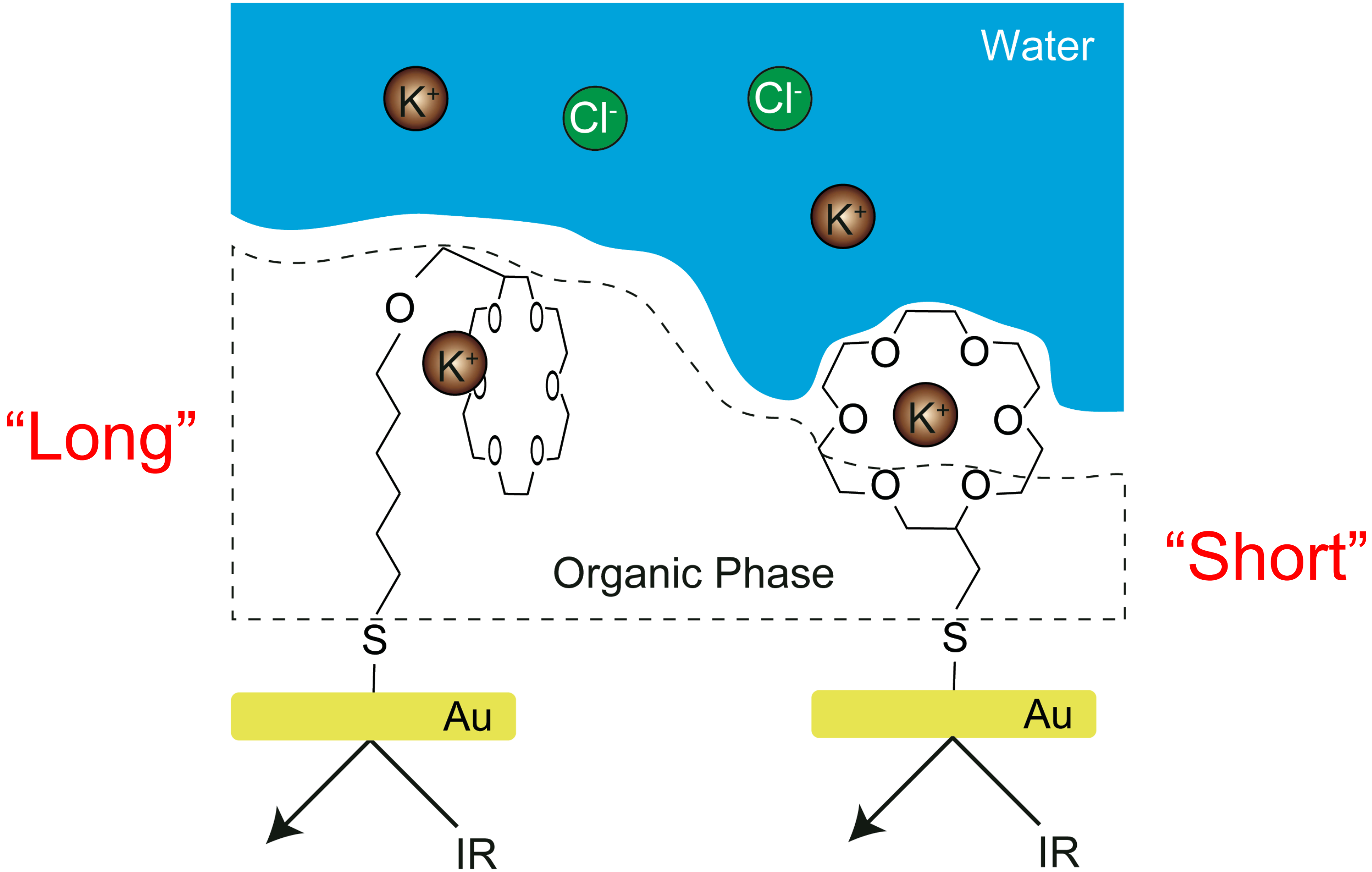
Solvation energy of free $M^+$ controls the ion preference for $K^+$.

# Ion Selectivity of 15C5




Intermol. interactions are similar for $Li^+$ and $Na^+$, and for $K^+$, $Rb^+$, and $Cs^+$.
15C5 shows preference for $Na^+$.

# Conclusion (2)  Structure at Interface




Ion complexes are **isolated** from water

Ion complexes **face** water phase

# Summary and Prospects

- $M^+$•18C6
- $M^+$•15C5
- in water and methanol
- SEIRA Spectroscopy
- IR spectra give information on the intermolecular interaction between $M^+$ and CEs and the origin of ion selectivity.

■ Relation between IR spectra and structure in condensed phase?
■ Density and orientation of host species on Au?
■ Lengths of hydrocarbon chains?
■ Theoretical studies
■ Application to actinide and lanthanide ions

# Acknowledgment

- École Polytechnique Fédérale de Lausanne (EPFL)

Prof. Thomas R. Rizzo　　Dr. Oleg V. Boyarkin　　LCPM members

- Hiroshima University

Prof. Takayuki Ebata　　Dr. Ryoji Kusaka

# Acknowledgment

■Hiroshima University

Prof. Takeharu Haino

■Institute for Molecular Science (Okazaki, Japan)

Prof. Yuji Furutani

¥¥¥ The Japan Society for the Promotion of Science (JSPS)
The Mitsubishi Chemical Foundation
The Sumitomo Foundation
The Kurata Memorial Hitachi Science and Technology Foundation