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

Yoshiya INOKUCHI

Hiroshima University

10th Symposium on Gas-Phase Laser Spectroscopy and Reaction Dynamics
Muju Resort, Republic of Korea
12/02/2015

Outline

Host-Guest Complexes

1. Motivation

2. Cold Spectroscopy in the Gas Phase

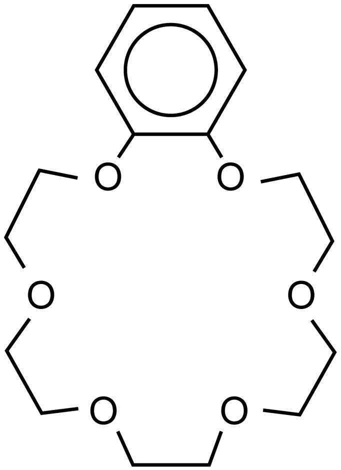
3. Surface-Enhanced IR Absorption Spectroscopy (SEIRAS) on Gold Surface

4. Future Prospects

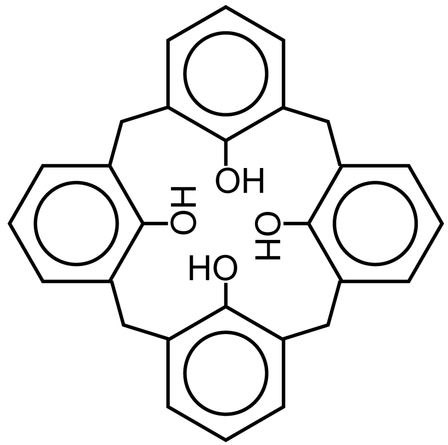
1. Motivation

Host Molecules

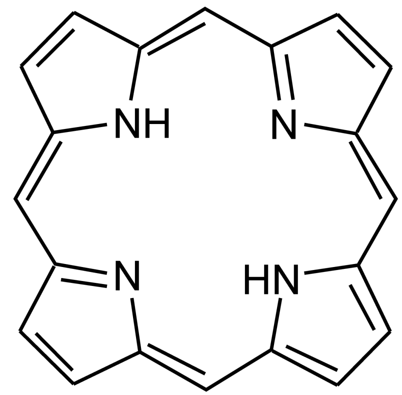
can hold other ions and molecules inside



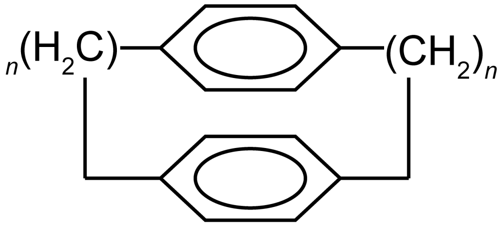
Crown ether



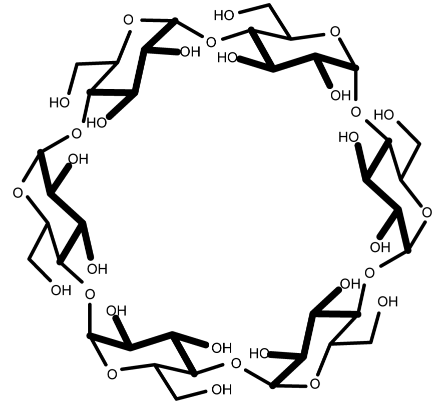
Calix[4]arene



Porphyrin



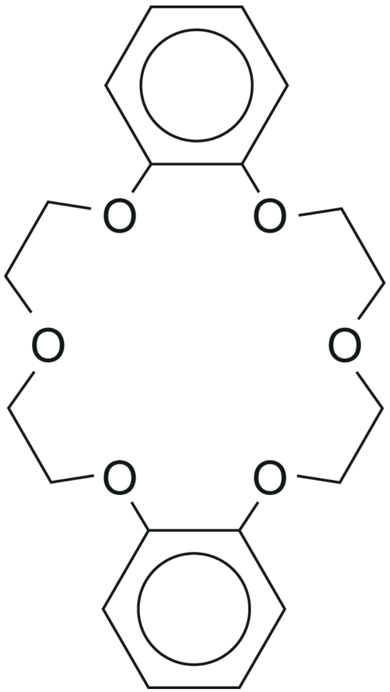
Cyclophane



Cyclodextrin

Crown Ethers (CEs)

Crown ethers (CEs) show ion selectivity.

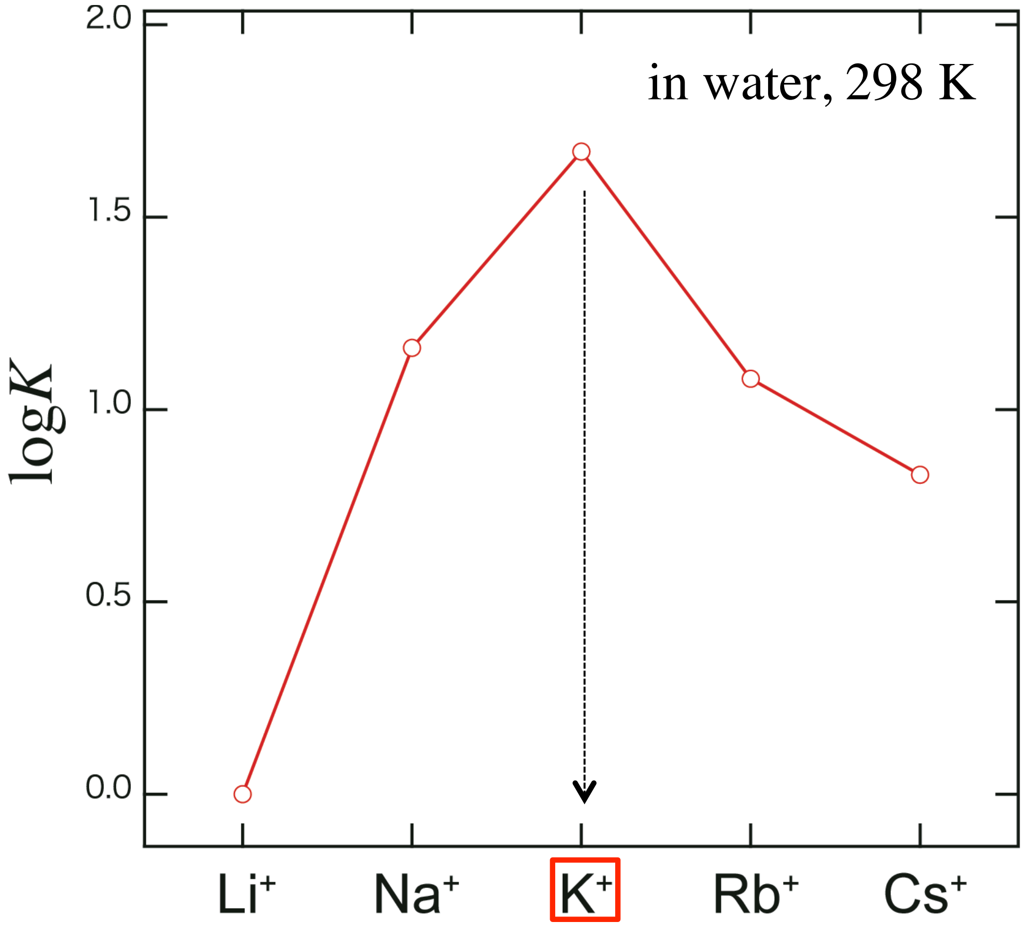


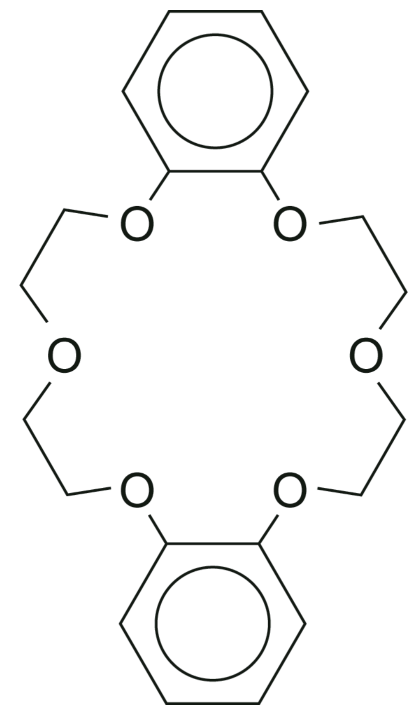
Dibenzo-18-crown-6
(DB18C6)

Ion Selectivity of CE

DB18C6 captures K^+ selectively in water.

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



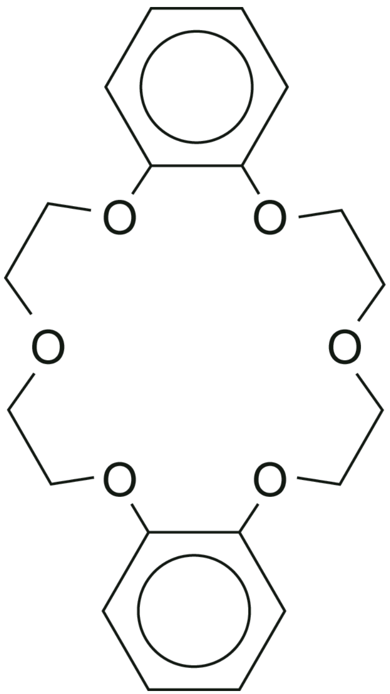


DB18C6

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

Our Final Goal

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



Dibenzo-18-crown-6
(DB18C6)

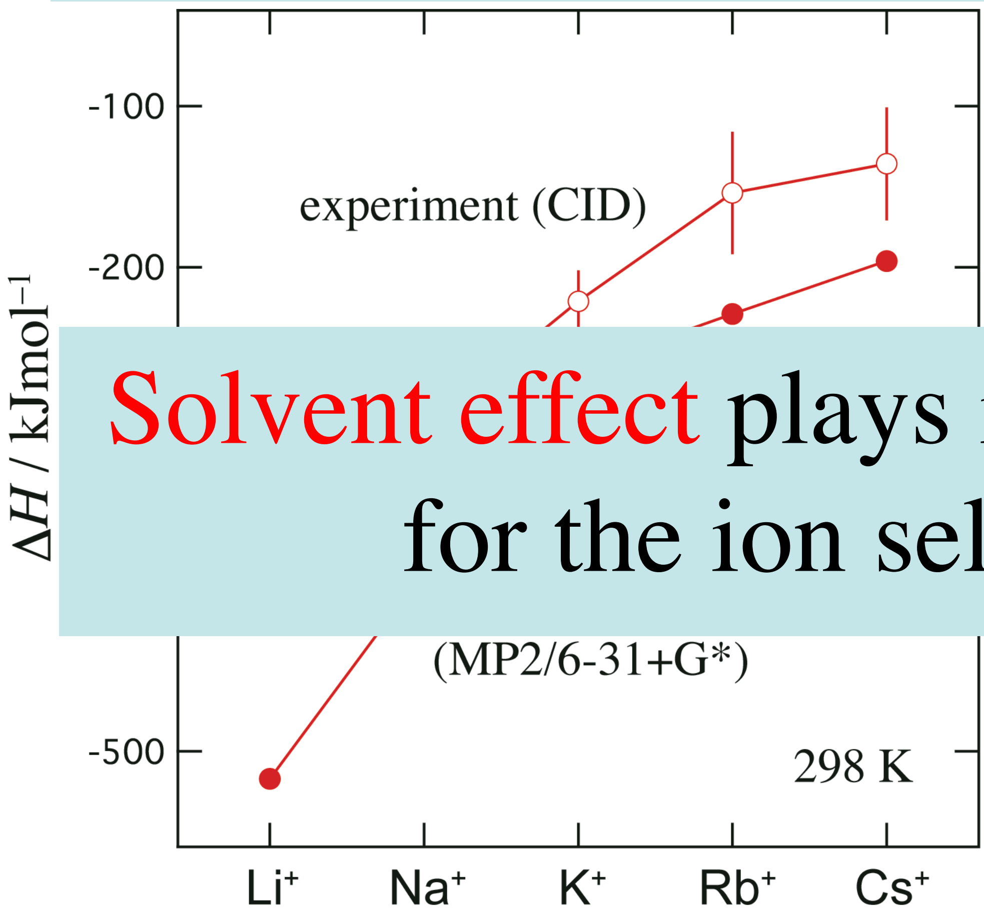
Crown Ethers in the Gas Phase

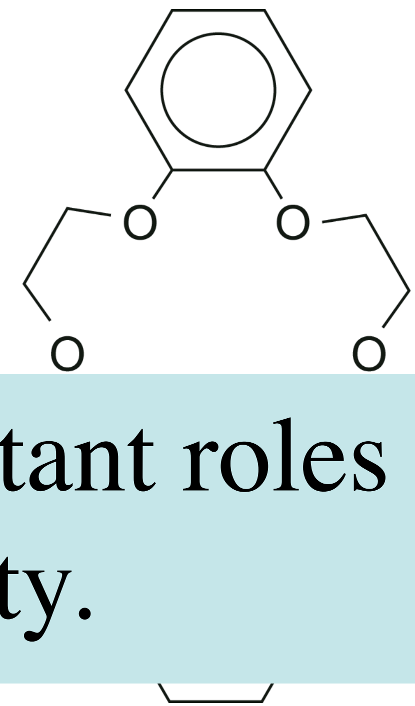
- Mass spectrometric studies of metal ion-CE complexes
  - Dearden (1991), Brodbelt (1992), Armentrout (1996), Brutschy (1997)
- UV and IR spectroscopy of jet-cooled CE
  - Ebata, Inokuchi (2007~), Zwier (2009)
- IR photodissociation spectroscopy of metal ion-CE complexes
  - Lisy (2009), Martinez-Haya (2009)
- UV photodissociation spectroscopy of metal ion-benzo-CE complexes
  - N. J. Kim, J. Heo (2008~)

ΔH for Complex Formation

Bare complexes cannot explain the ion selectivity in solution.

$$M^+ + DB18C6 \xrightleftharpoons{\Delta H} M^+\bullet DB18C6$$





DB18C6

Solvent effect plays important roles for the ion selectivity.

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

Our Studies on Host-Guest Complexes

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

What is the Origin of Ion Selectivity?

Complex structure

Number and sort of solvent molecules

Number of conformers

↕

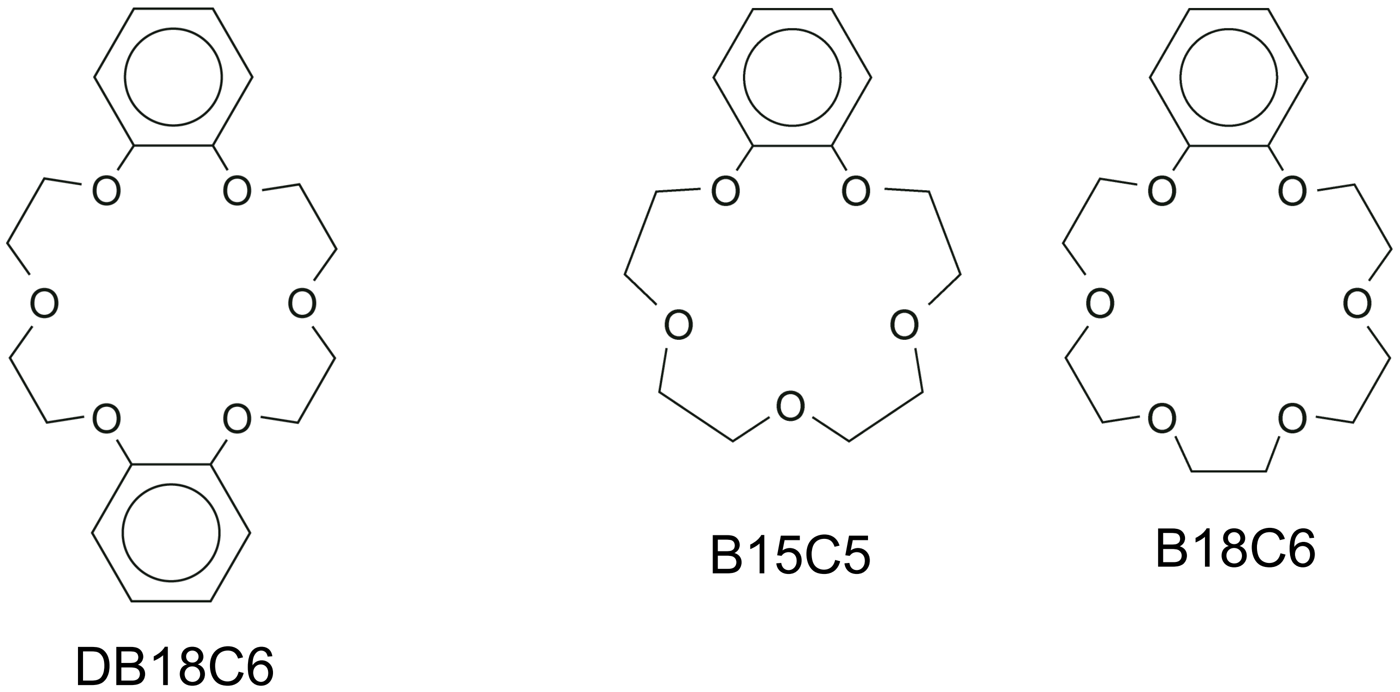
Ion selectivity

2. Cold Spectroscopy in the Gas Phase

J. Am. Chem. Soc., **2014**, 136, 1815.
ChemPhysChem, **2013**, *14*, 649.
Phys. Chem. Chem. Phys., **2012**, *14*, 4457.
J. Phys. Chem. A, **2012**, *116*, 4057.
J. Am. Chem. Soc., **2011**, *133*, 12256.

This Study

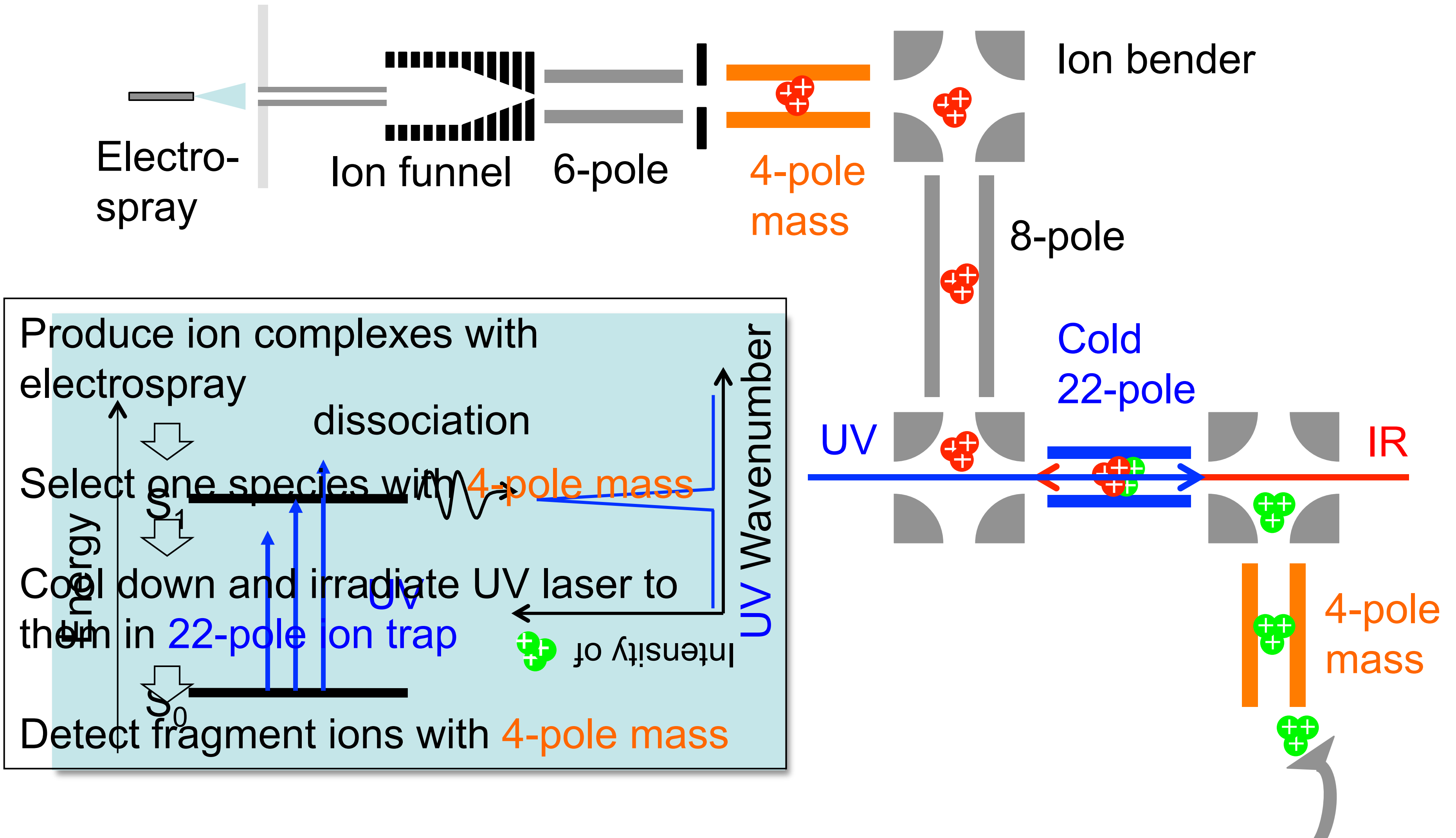
- M^+•DB18C6•L_n (M = Li, Na, K, Rb, Cs)
- M^{2+}•B15C5•L and M^{2+}•B18C6•L (M = Ca, Sr, Ba, Mn)



- UV and IR spectroscopy in a cold, 22-pole ion trap
- Relation between ion selectivity and the number of conformers.

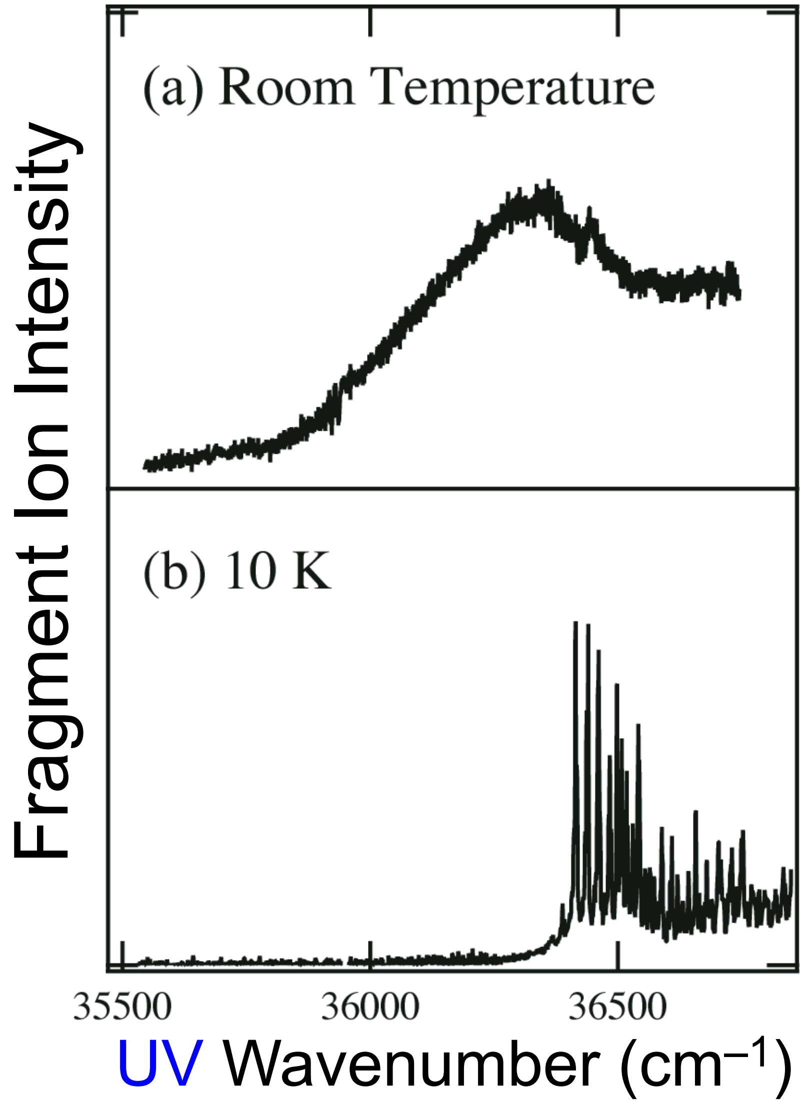
Experimental

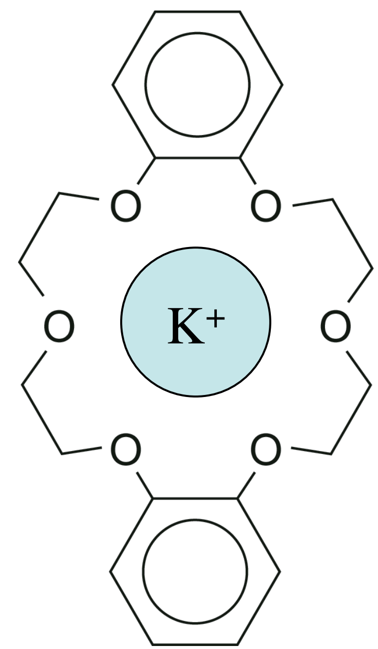
UV and IR spectra of ions are measured under cold (~10 K) conditions in the gas phase.



Effect of the Cooling on UV Spectra

Sharp UV bands are observed thanks to the cooling.



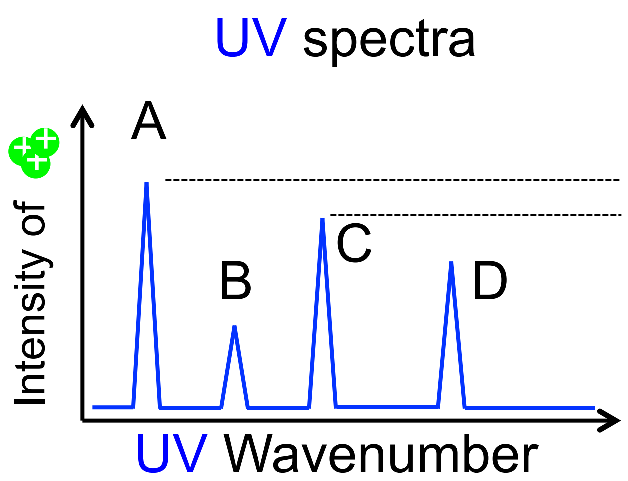


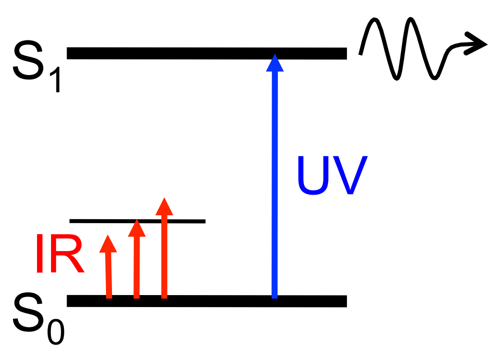
K+•DB18C6

Inokuchi et al., *JACS*, **2011**, *133*, 12256.

IR-UV Double-Resonance

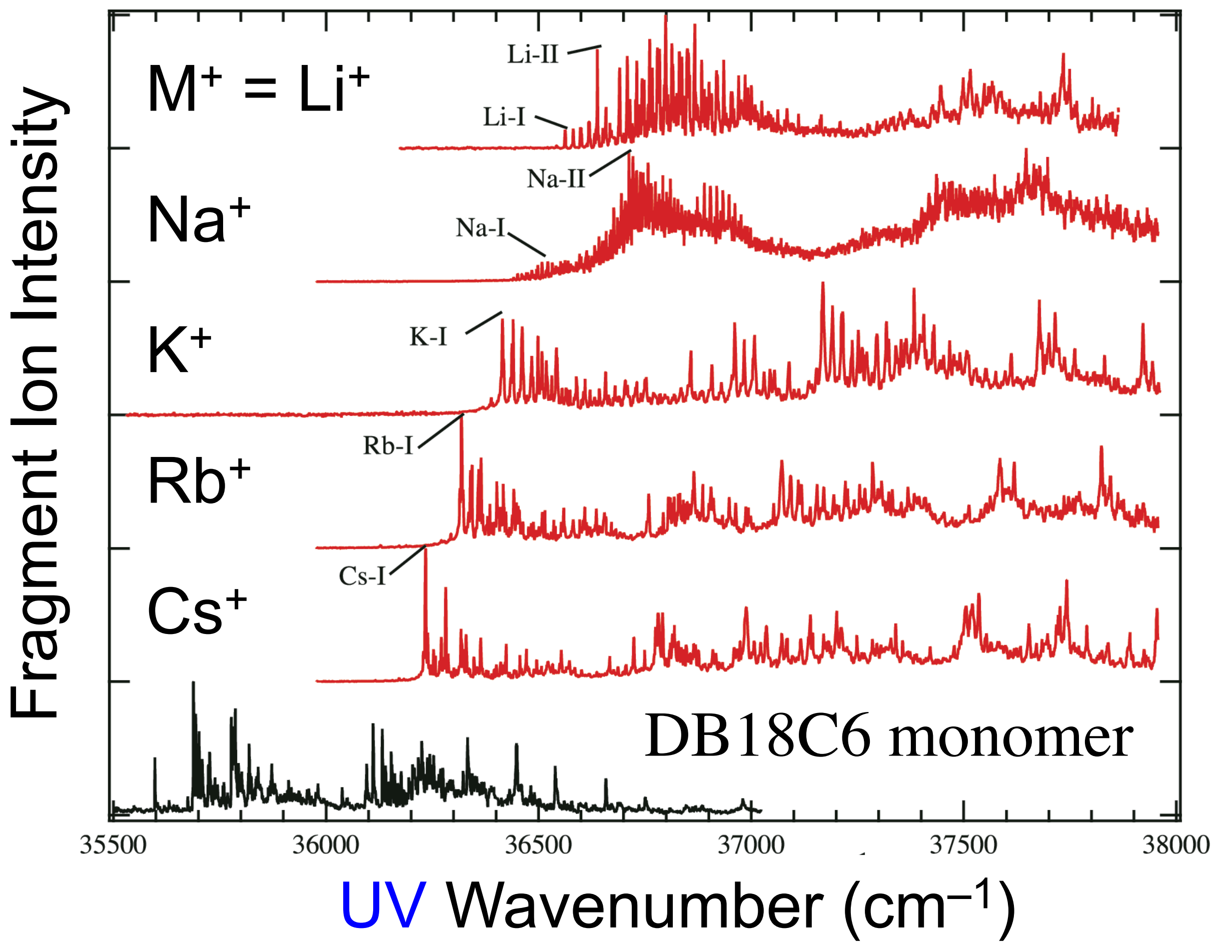
Conformer-specific IR spectra can be measured by IR-UV double-resonance.

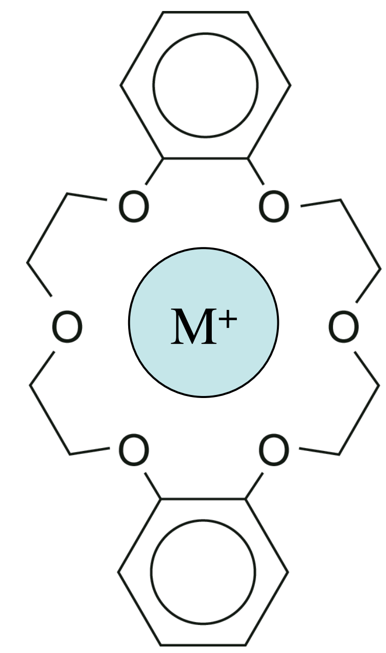




UV Spectra of M^+•DB18C6

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



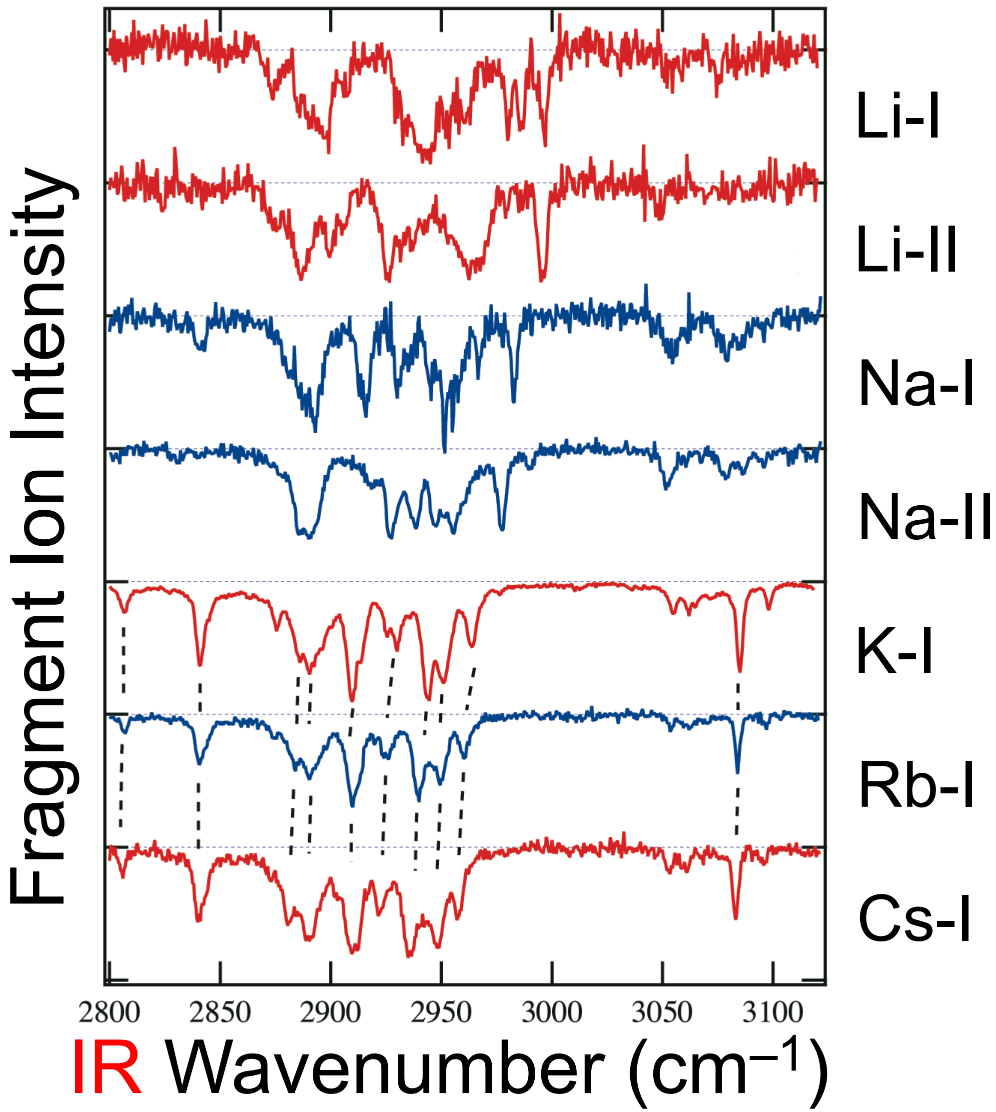


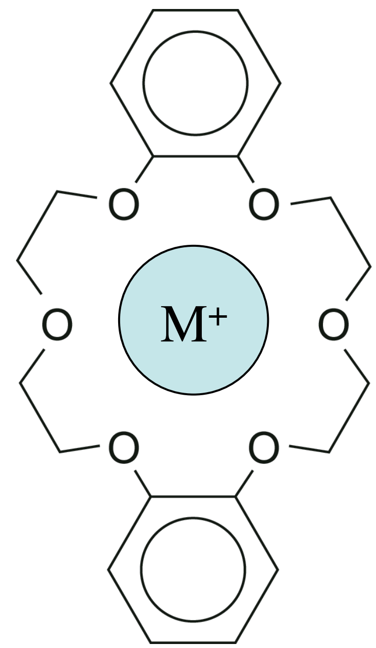
M^+•DB18C6

Inokuchi et al., *JACS*, **2011**, *133*, 12256.

IR Spectra of M^+•DB18C6

Different IR features originate from different conformers.

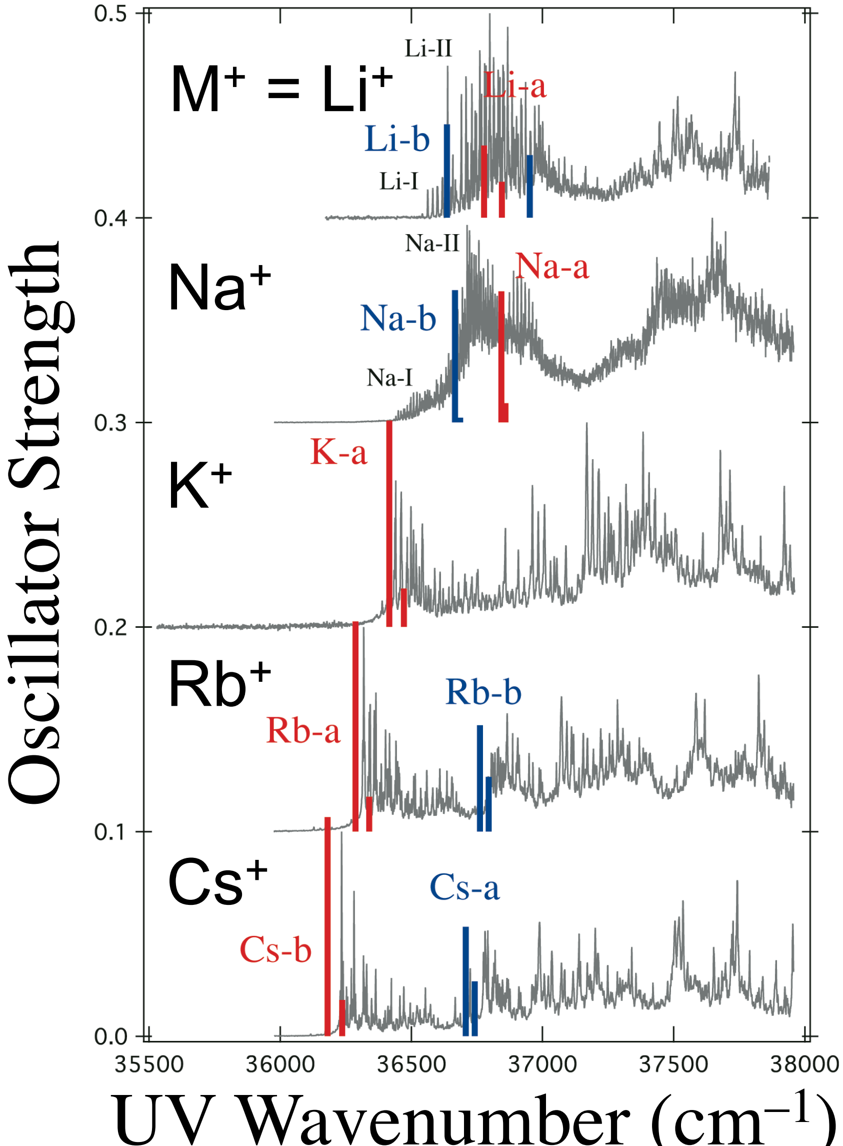




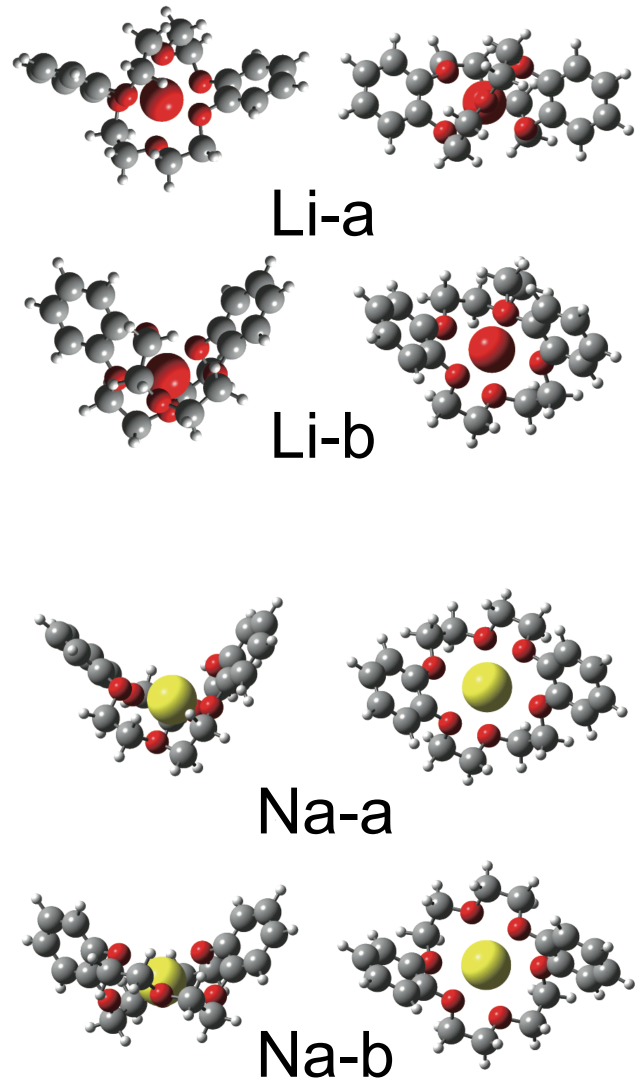
M^+•DB18C6

Inokuchi et al., *JACS*, **2011**, *133*, 12256.

Structure of M⁺•DB18C6 (M⁺ = Li⁺, Na⁺)

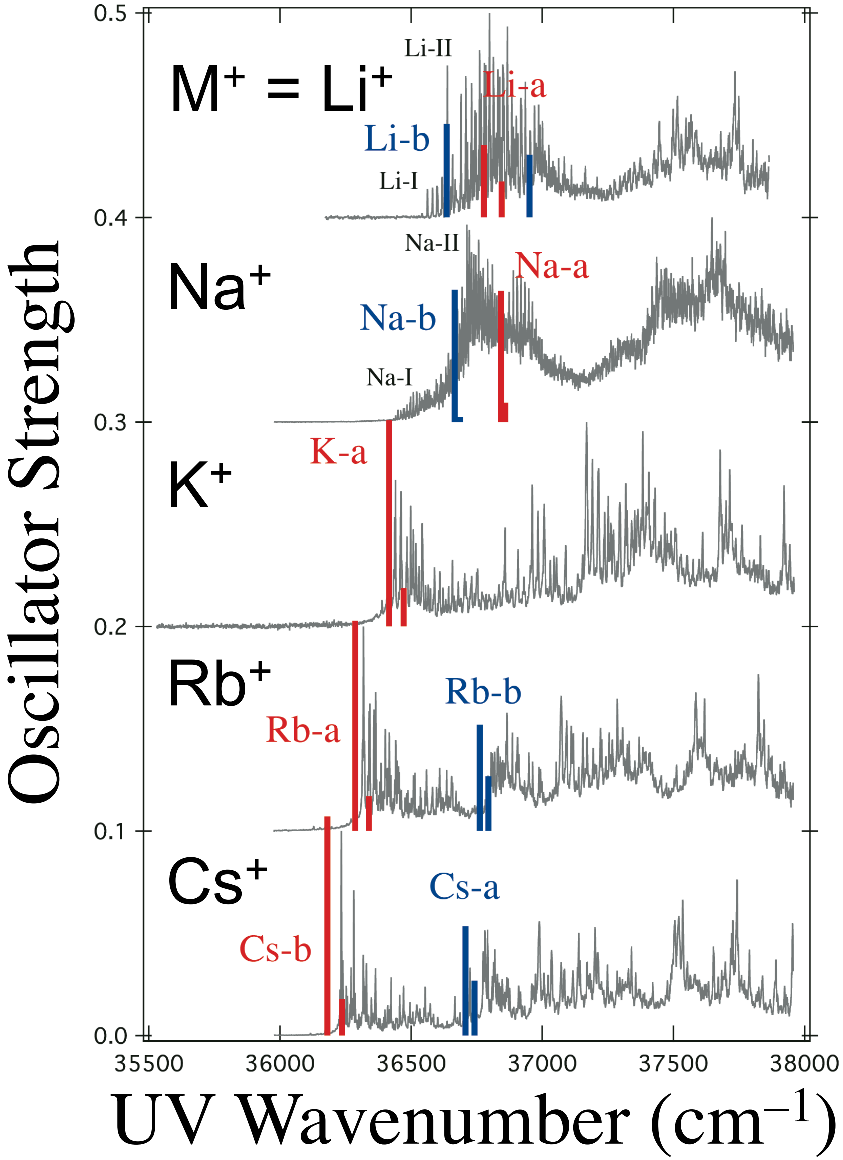


M05-2X/6-31+G(d) with Stuttgart RLC ECP
A scaling factor of 0.8340 is used.

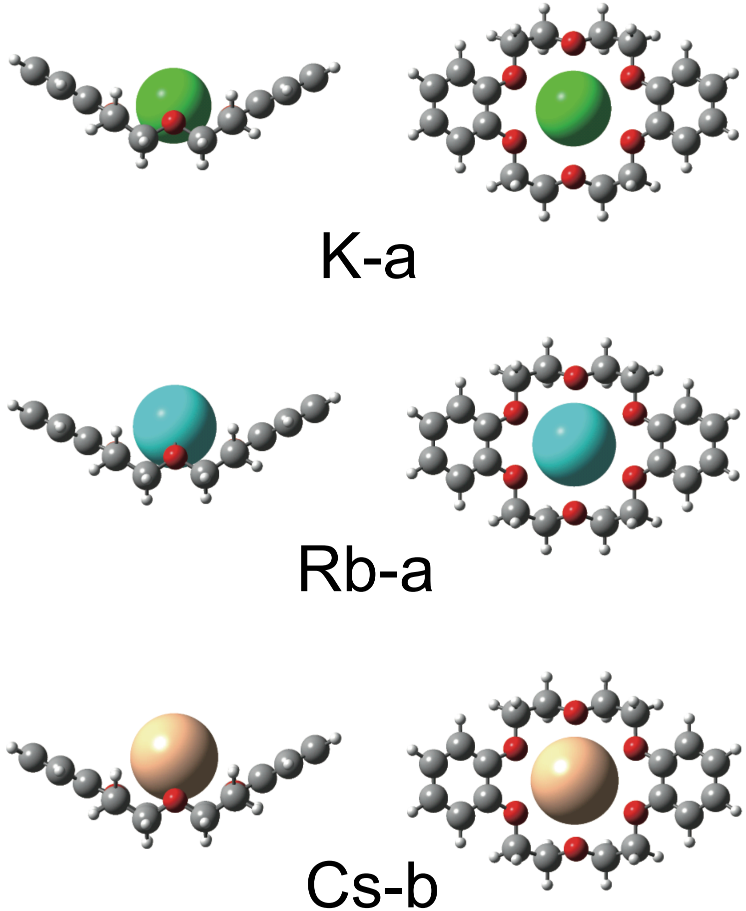


Ether rings distorted for Li⁺ and Na⁺

Structure of M⁺•DB18C6 (M⁺ = K⁺, Rb⁺, Cs⁺)



M05-2X/6-31+G(d) with Stuttgart RLC ECP
A scaling factor of 0.8340 is used.

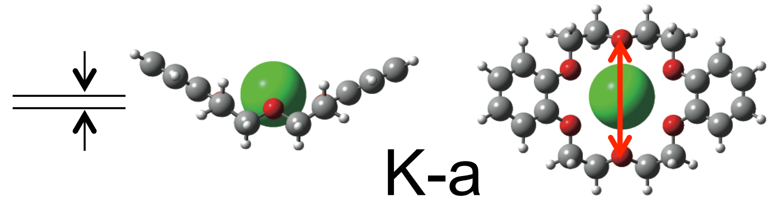
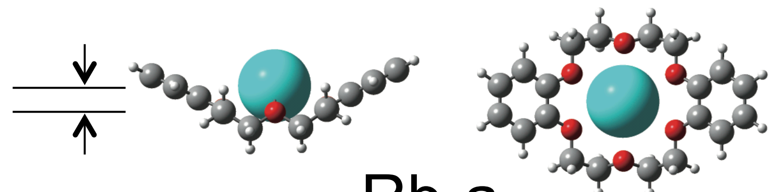
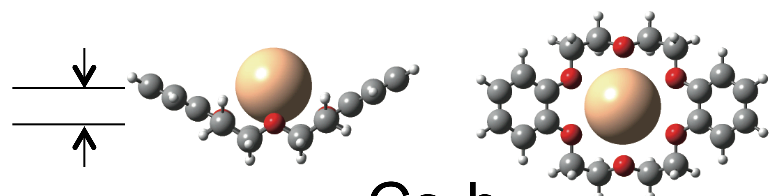


Ether rings largely open

K^+ in the ring

Rb^+, Cs^+ on the ring

Structure of M^+•DB18C6 (M^+ = K^+, Rb^+, Cs^+)

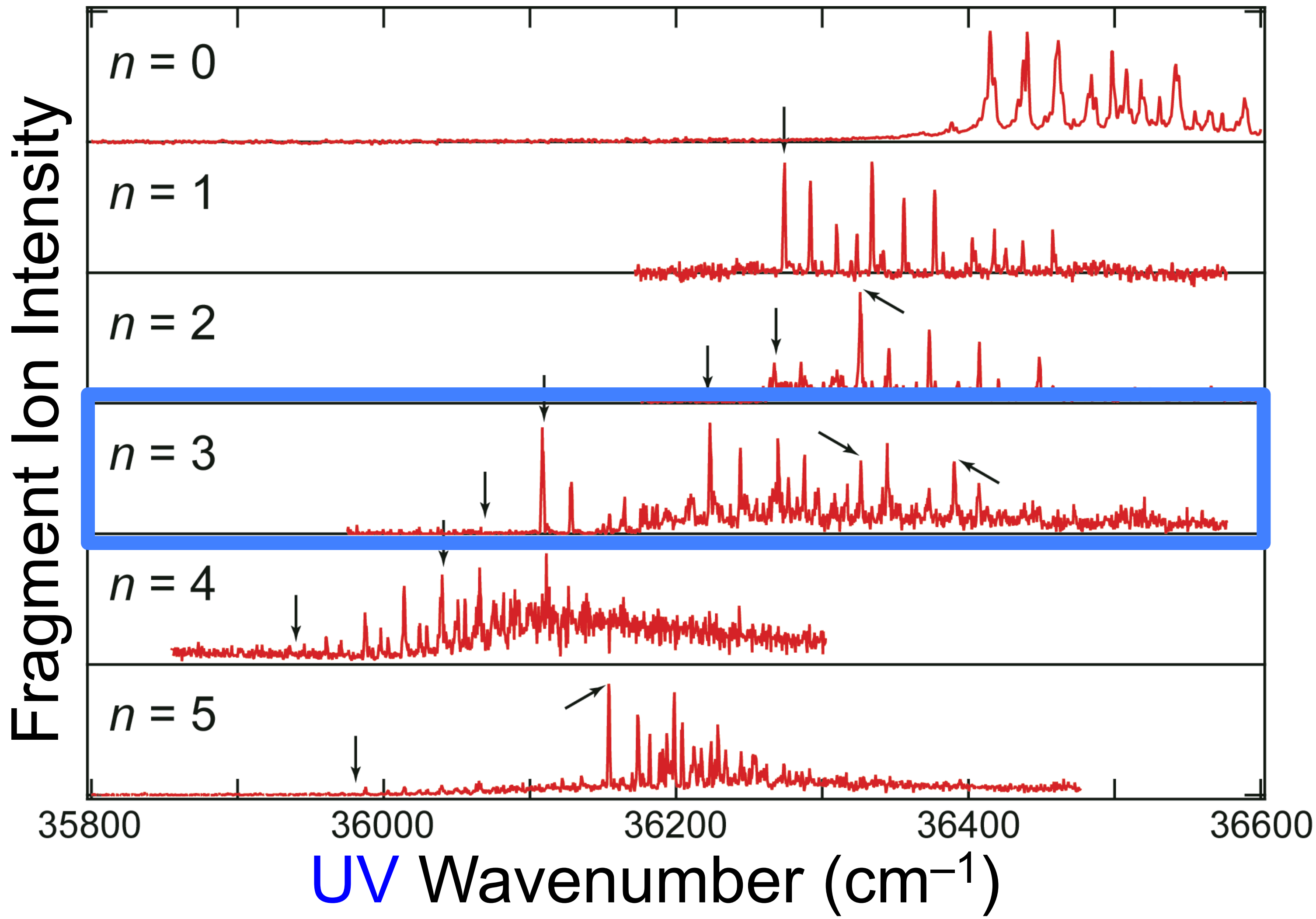
	Ion radii/Å			
K^+	1.52	0.51	 K-a	5.41
Rb^+	1.66	1.00	 Rb-a	
Cs^+	1.81	1.36	 Cs-b	

cf. Li^+ (0.90 Å), Na^+ (1.16 Å)

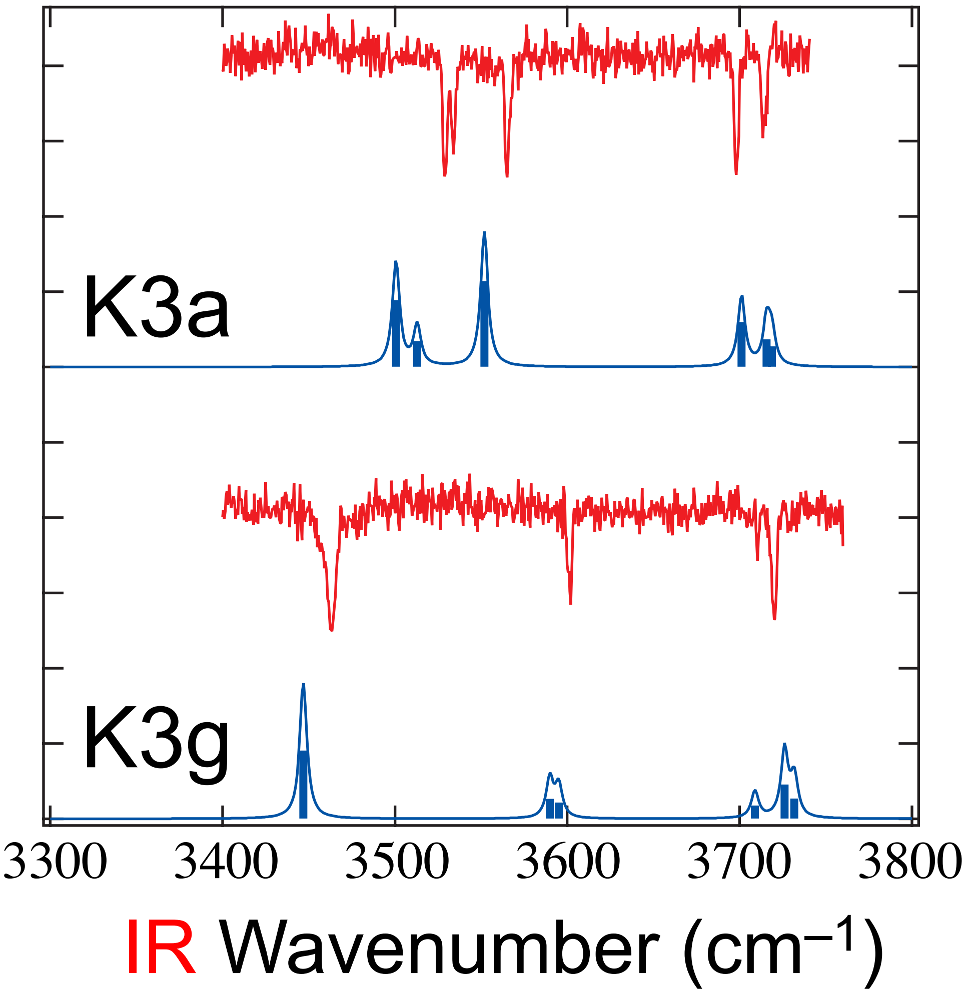
UV Spectra of K^{+}•DB18C6•$(H_2O)_n$

UV spectra also show sharp bands.

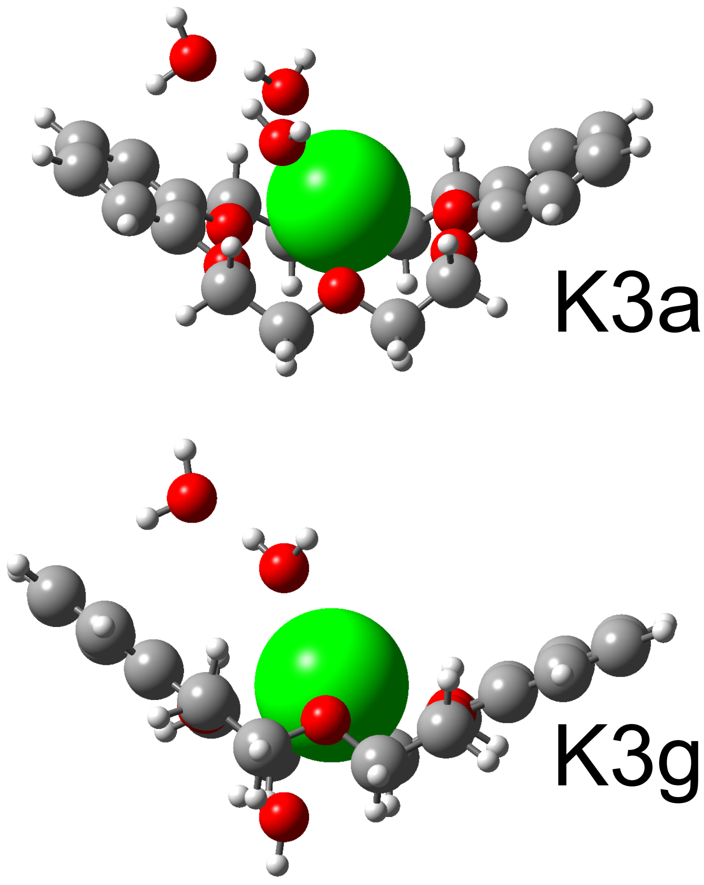
Conformer-specific IR spectra can be measured.



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



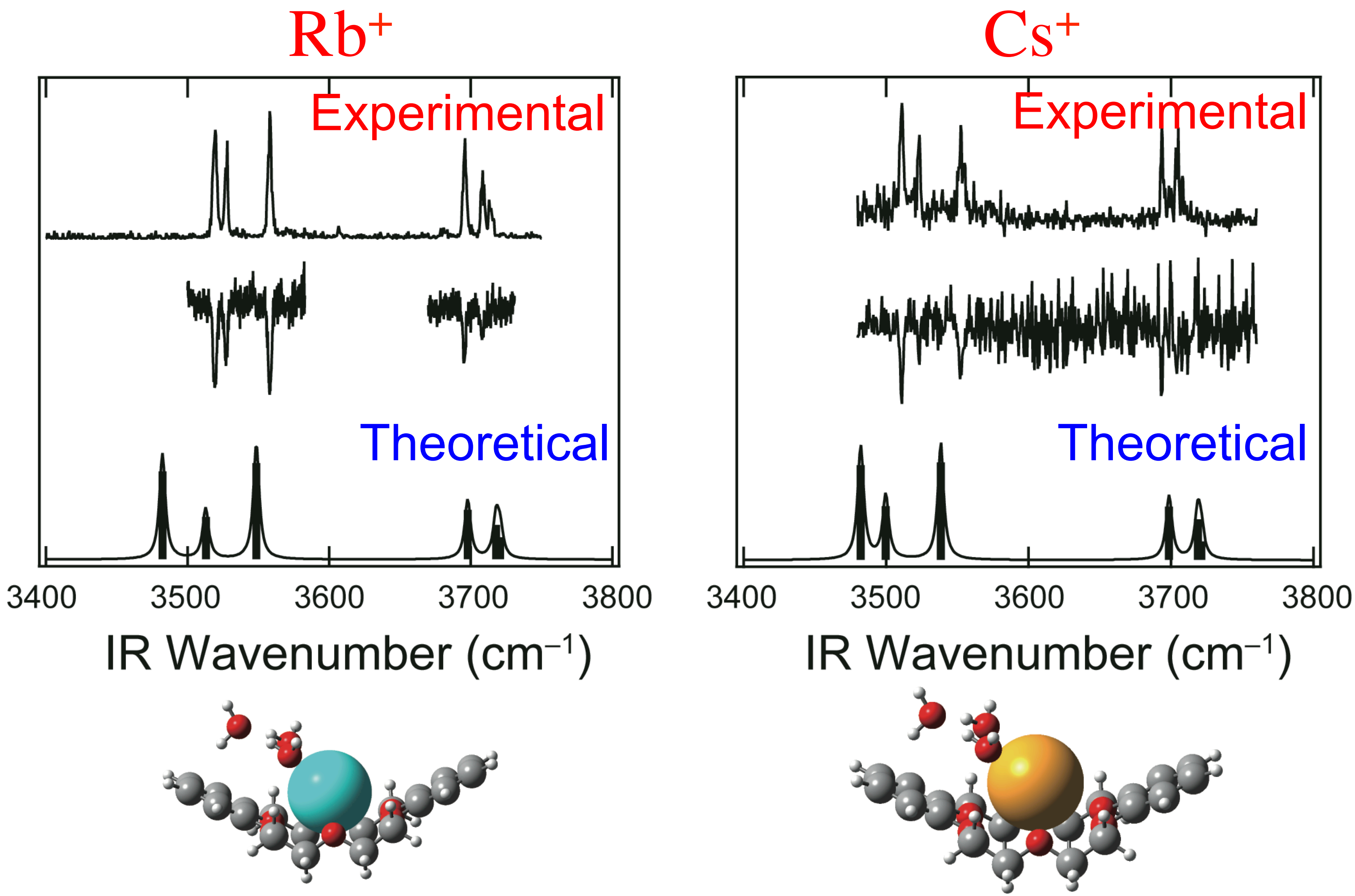
Two conformers for K^+.



Inokuchi et al., *JACS*, **2014**, *136*, 1815.

IR Spectra of M^+•DB18C6•$(H_2O)_3$

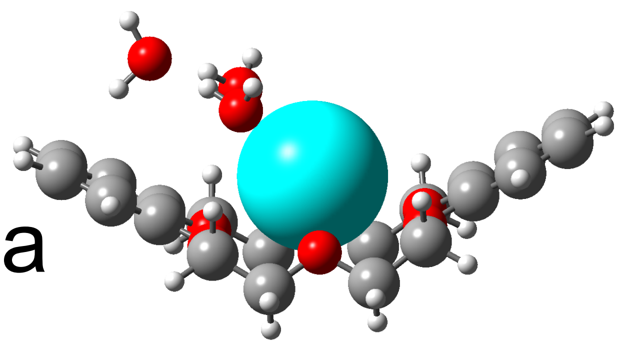
There is only one conformer for Rb^+ and Cs^+ complexes.



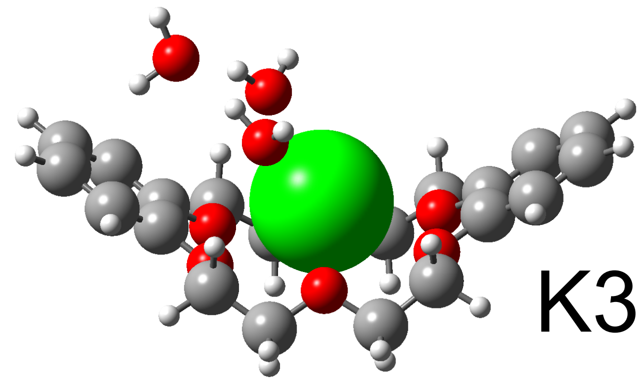
Conformers of M^+•DB18C6•$(H_2O)_3$

One conformer for Rb^+ and Cs^+.

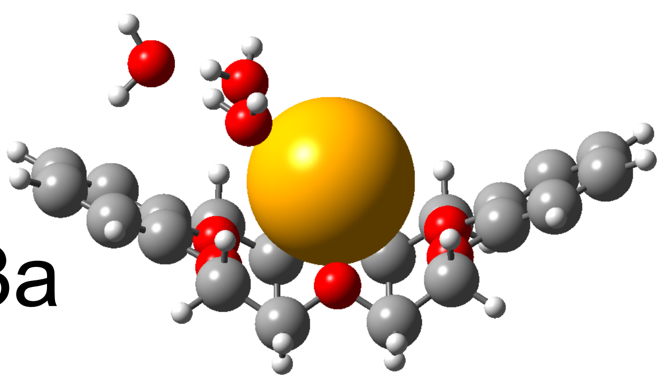
Two conformers for K^+.



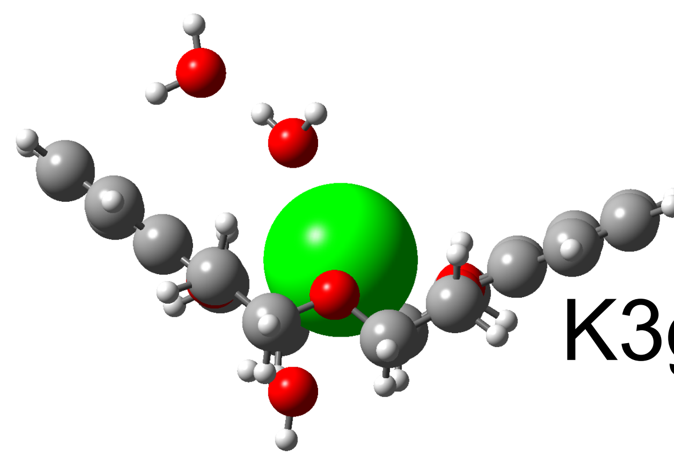
Rb3a



K3a



Cs3a

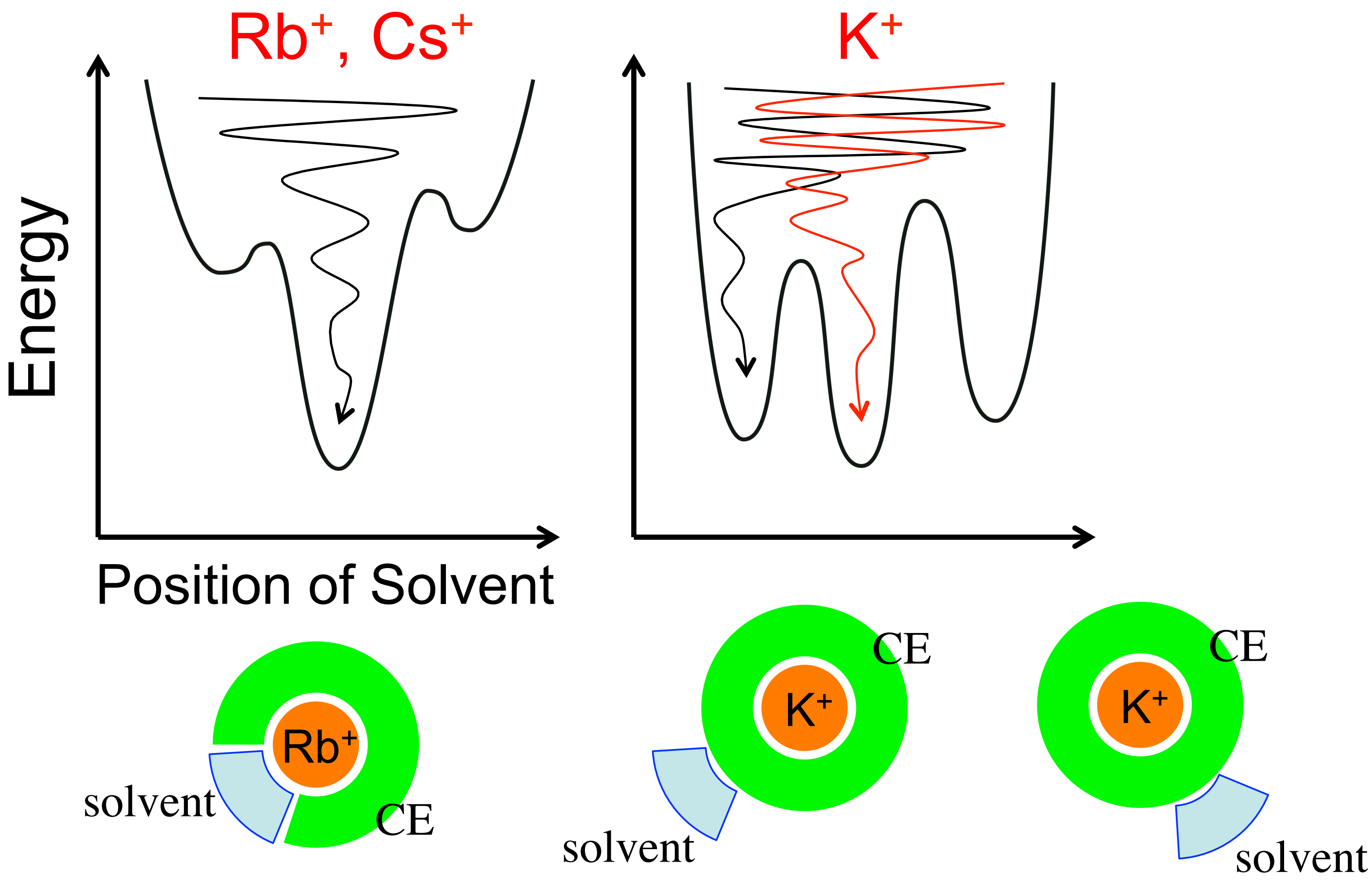


K3g

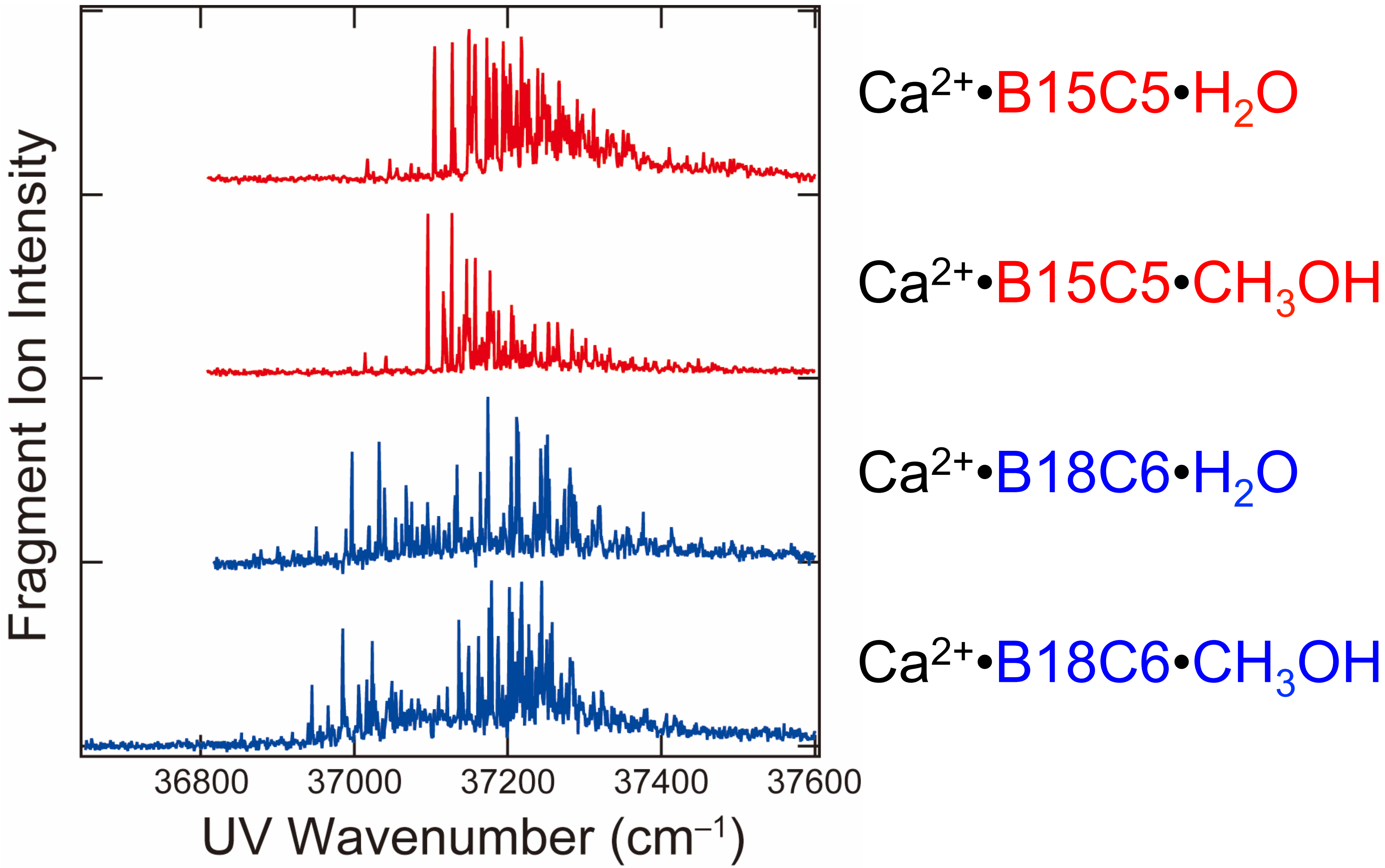
Inokuchi et al., *JACS*, **2014**, *136*, 1815.

The Number of Conformers

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



The Number of Conformers of M^{2+}•CE•L



Inokuchi et al., in preparation.

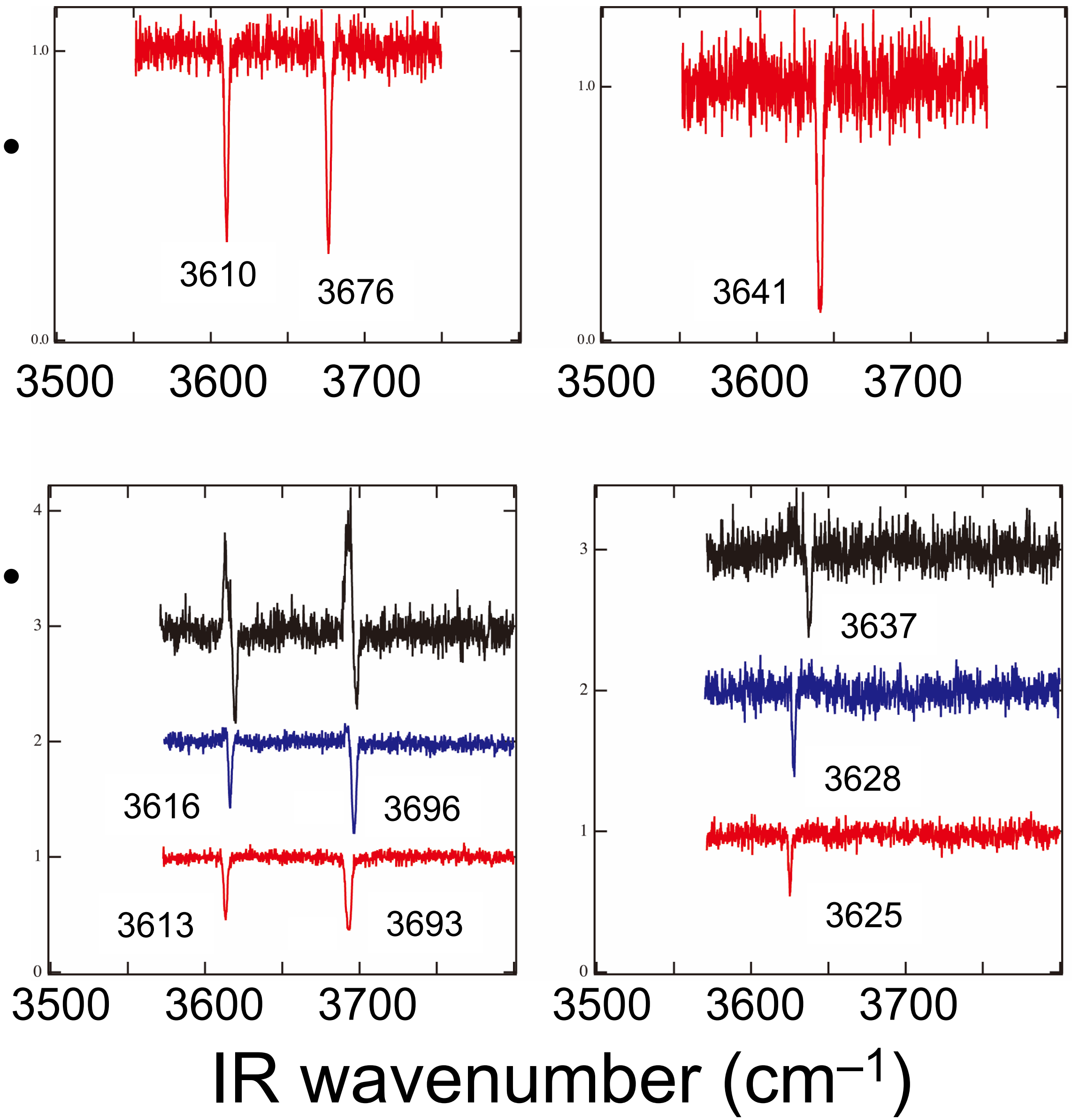
The Number of Conformers of M^{2+}•CE•L

Ca^{2+}•B15C5•H_2O

Ca^{2+}•B15C5•CH_3OH

Ca^{2+}•B18C6•H_2O

Ca^{2+}•B18C6•CH_3OH



The Number of Conformers of M^{2+}•CE•L

M^{2+}•CE•H_2O

	B15C5	B18C6
Ca^{2+}	1	3
Sr^{2+}	2	3
Ba^{2+}	2	1
Mn^{2+}	1	2

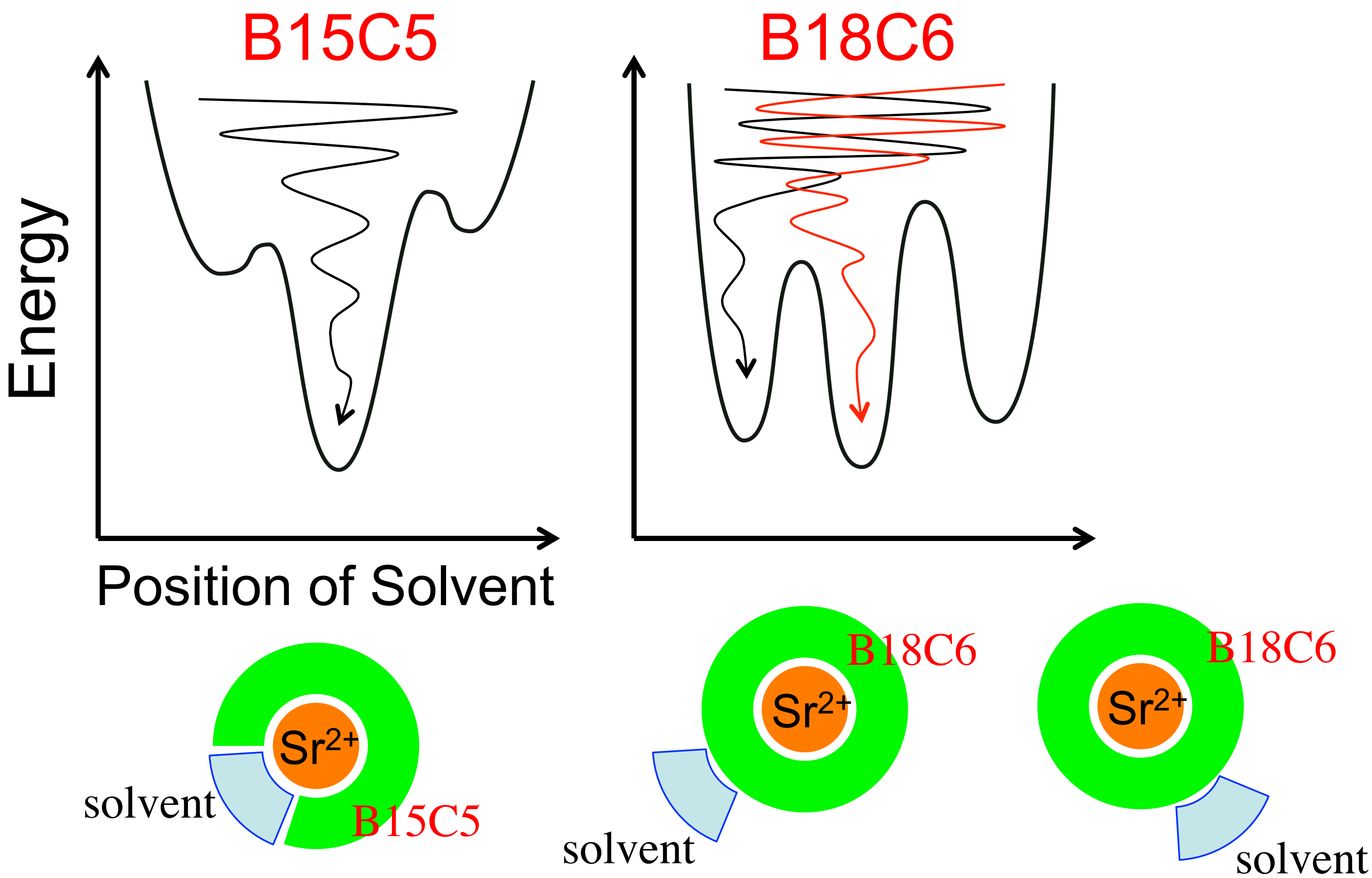
M^{2+}•CE•CH_3OH

	B15C5	B18C6
Ca^{2+}	1	3
Sr^{2+}	2	5
Ba^{2+}	1	2
Mn^{2+}	1	3

$n_{B15C5} < n_{B18C6}$, but

$n_{B15C5} \approx n_{B18C6}$ for Ba^{2+}

The Number of Conformers of M^{2+}•CE•L



Summary ~in the Gas Phase~

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

- M^+•DB18C6
- M^+•DB18C6•$(H_2O)_n$
- M^{2+}•B15C5•L and M^{2+}•B18C6•L
- UV and IR spectroscopy in a cold, 22-pole ion trap

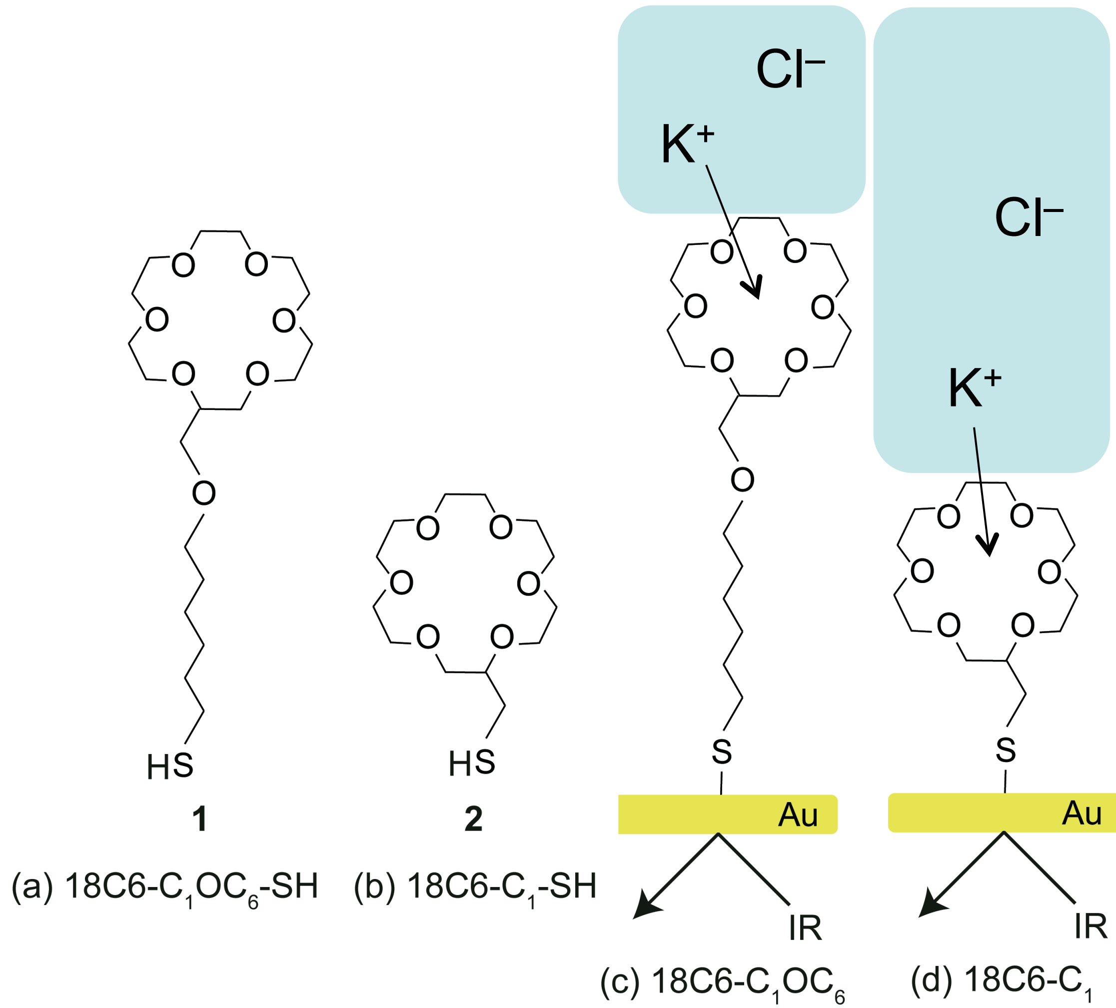
■ The structure and number of conformers are determined.

■ Host-guest complexes with an optimum matching in size tend to give multiple conformers with solvent molecules, resulting in entopic advantages.

3. Surface-Enhanced IR Absorption Spectroscopy (SEIRAS) on Gold Surface

Chem. Phys. Lett., **2014**, *592*, 90.

Host-Guest Complexes on Au

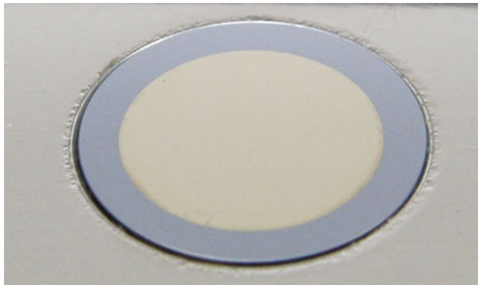


Long Short

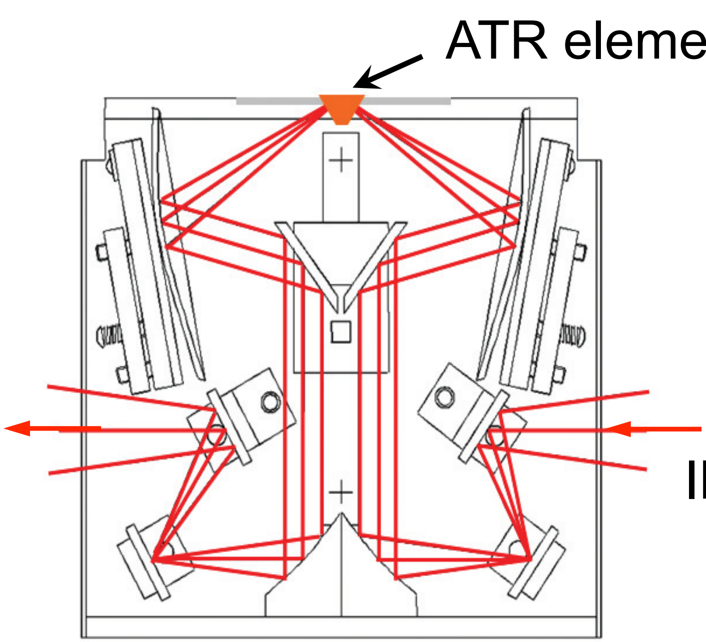
SEIRA with ATR Configuration

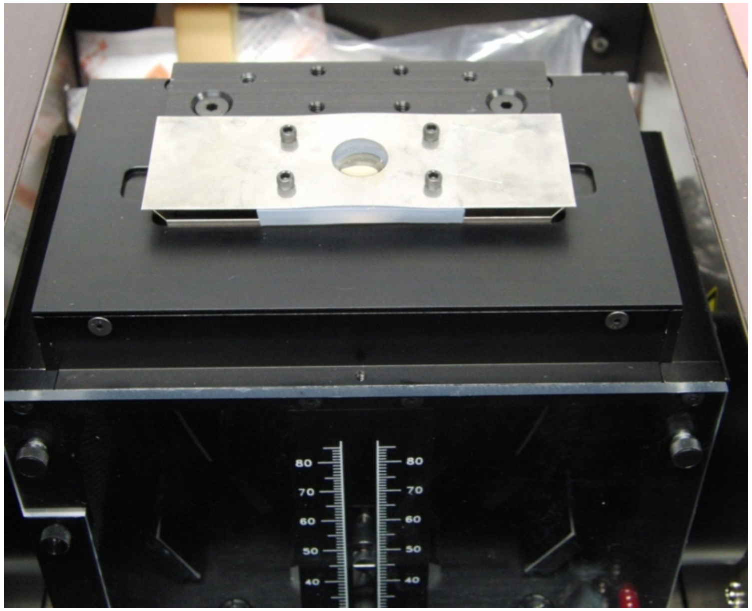
SEIRA (Surface-Enhanced IR Absorption) spectroscopy

(1) Au surface (~8 nm) is formed on an ATR (Attenuated total reflection) 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 of ATR
~ 8 nm thickness



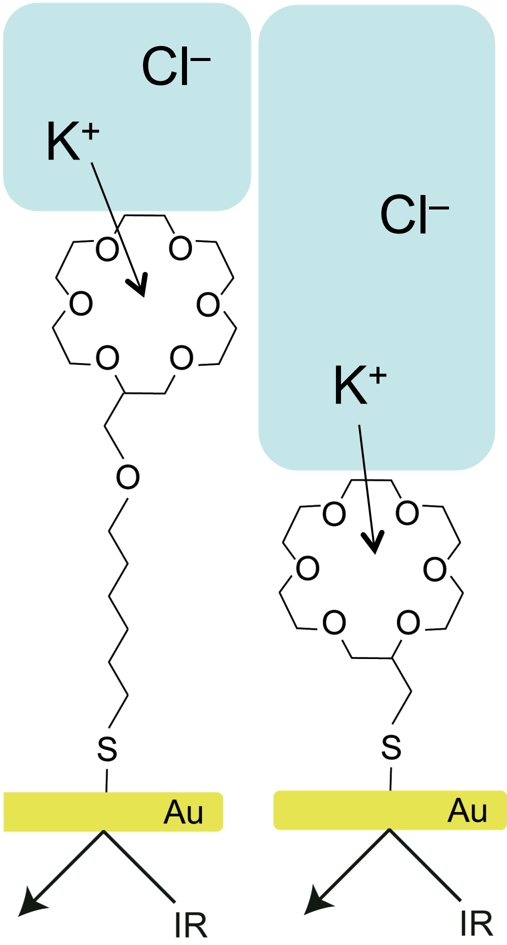


Attenuated total reflection setup

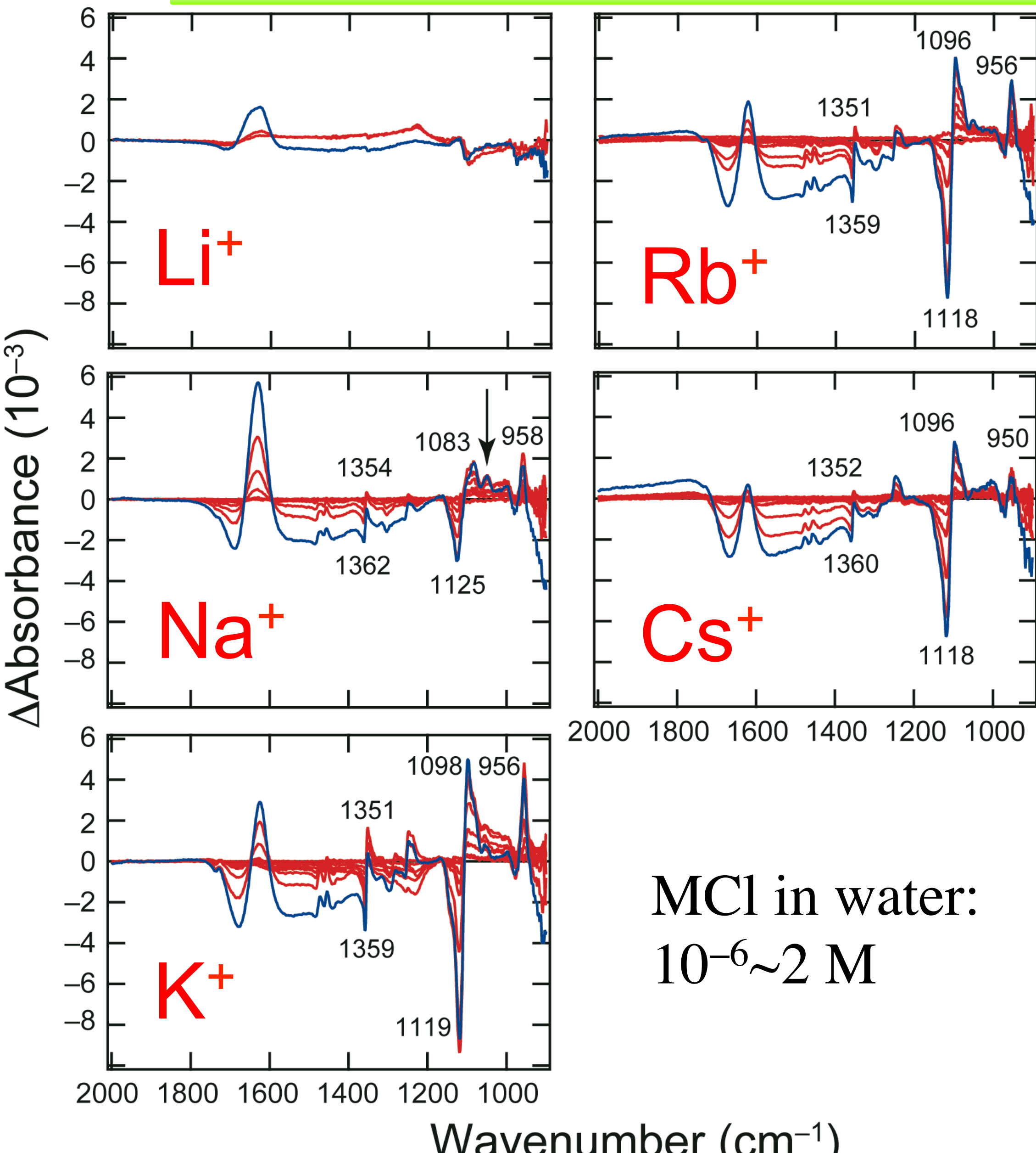
Advantages and Disadvantages

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

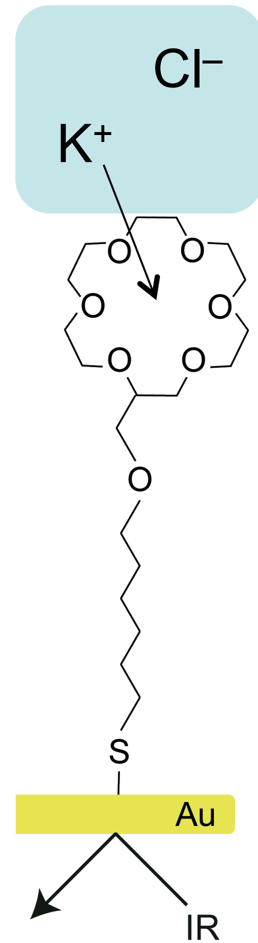
- □ Necessary to synthesize thiol derivatives
- □ Effects of Au surface on encapsulation



IR Difference Spectra of $M^{+} \cdot$18C6-C_1OC_6

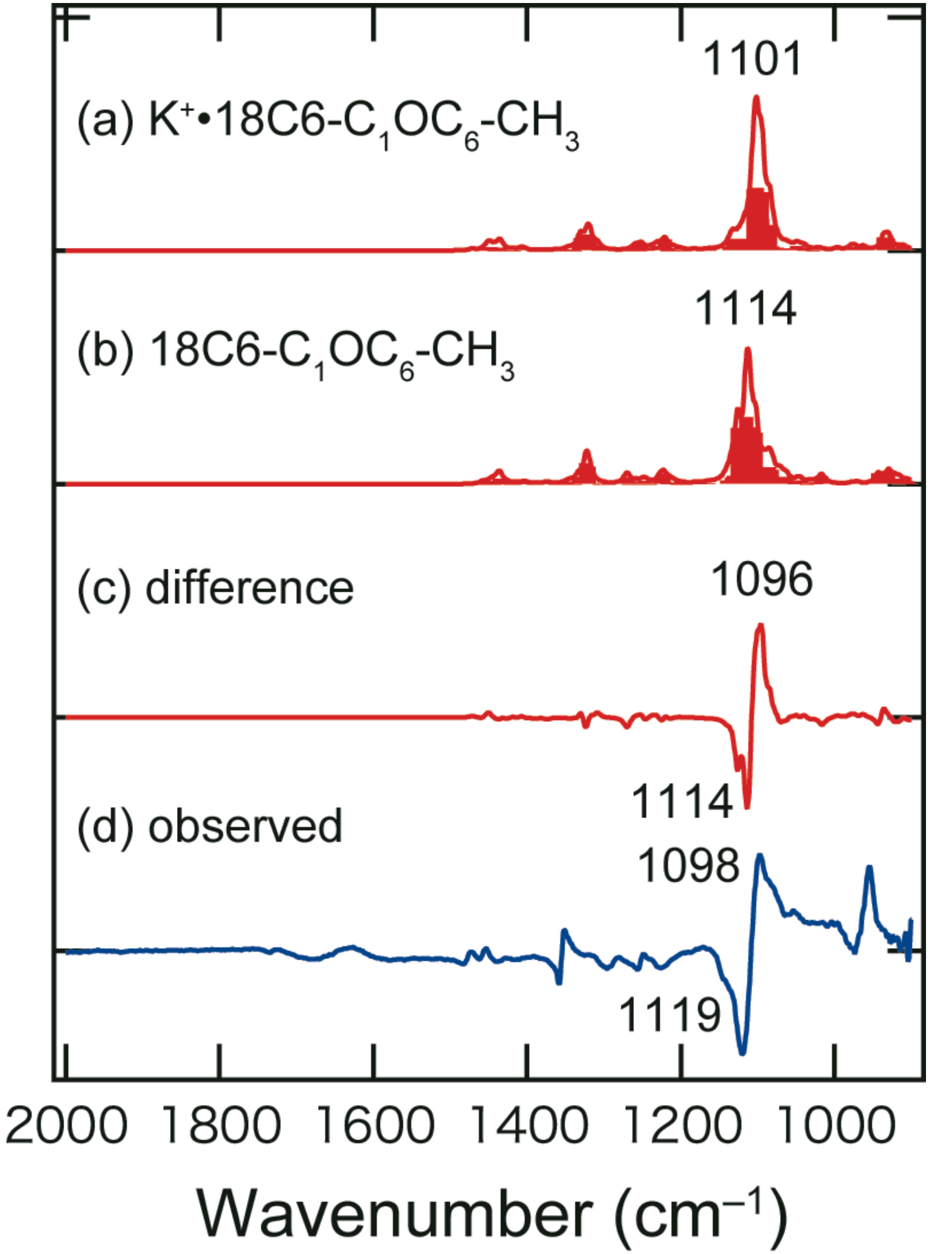


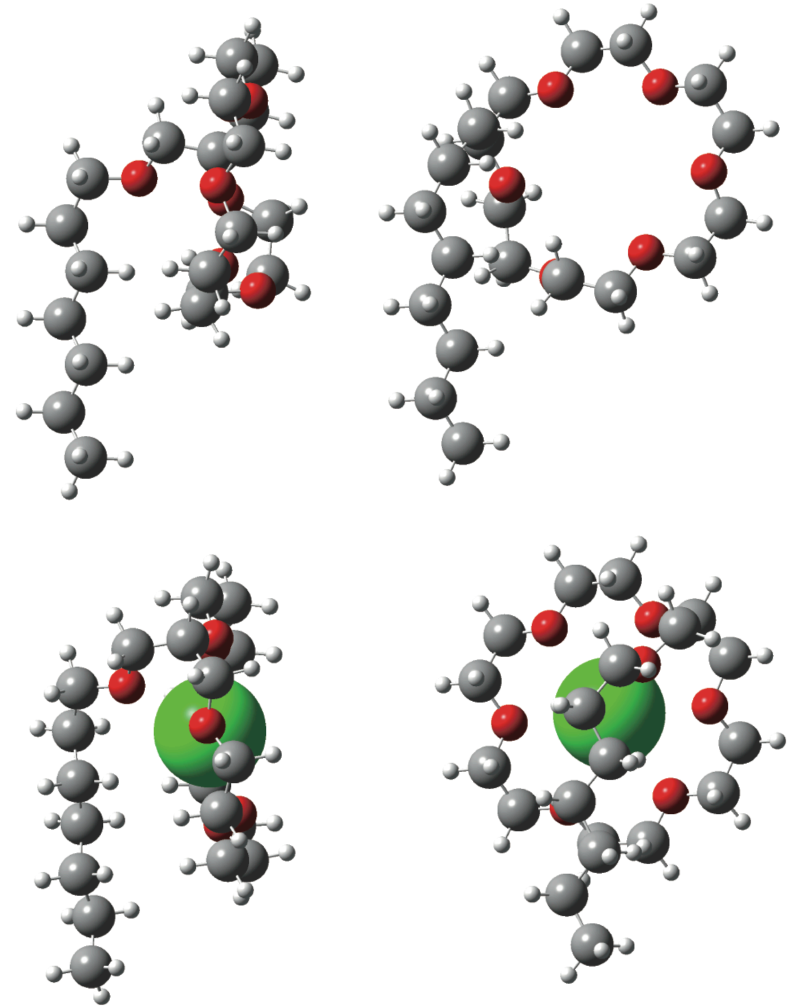
MCl in water:
10^{-6}~2 M



18C6-C_1OC_6

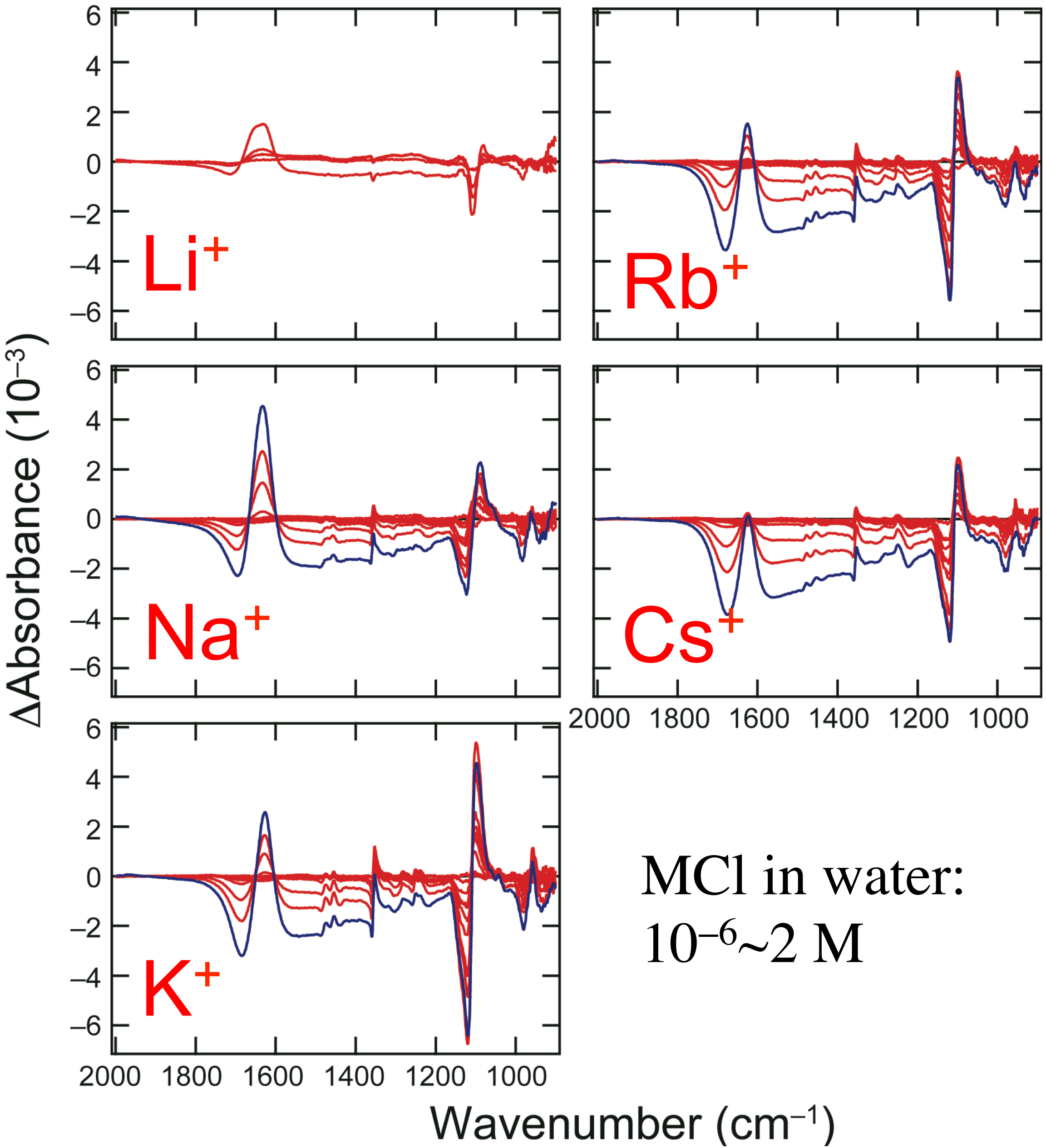
Comparison of IR Spectra



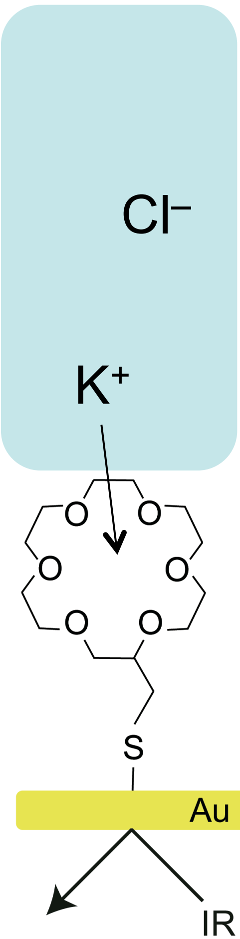


Calculated in water with PCM
(polarizable continuum model)

IR Difference Spectra of $M^+ \cdot 18C6\text{-}c_1$

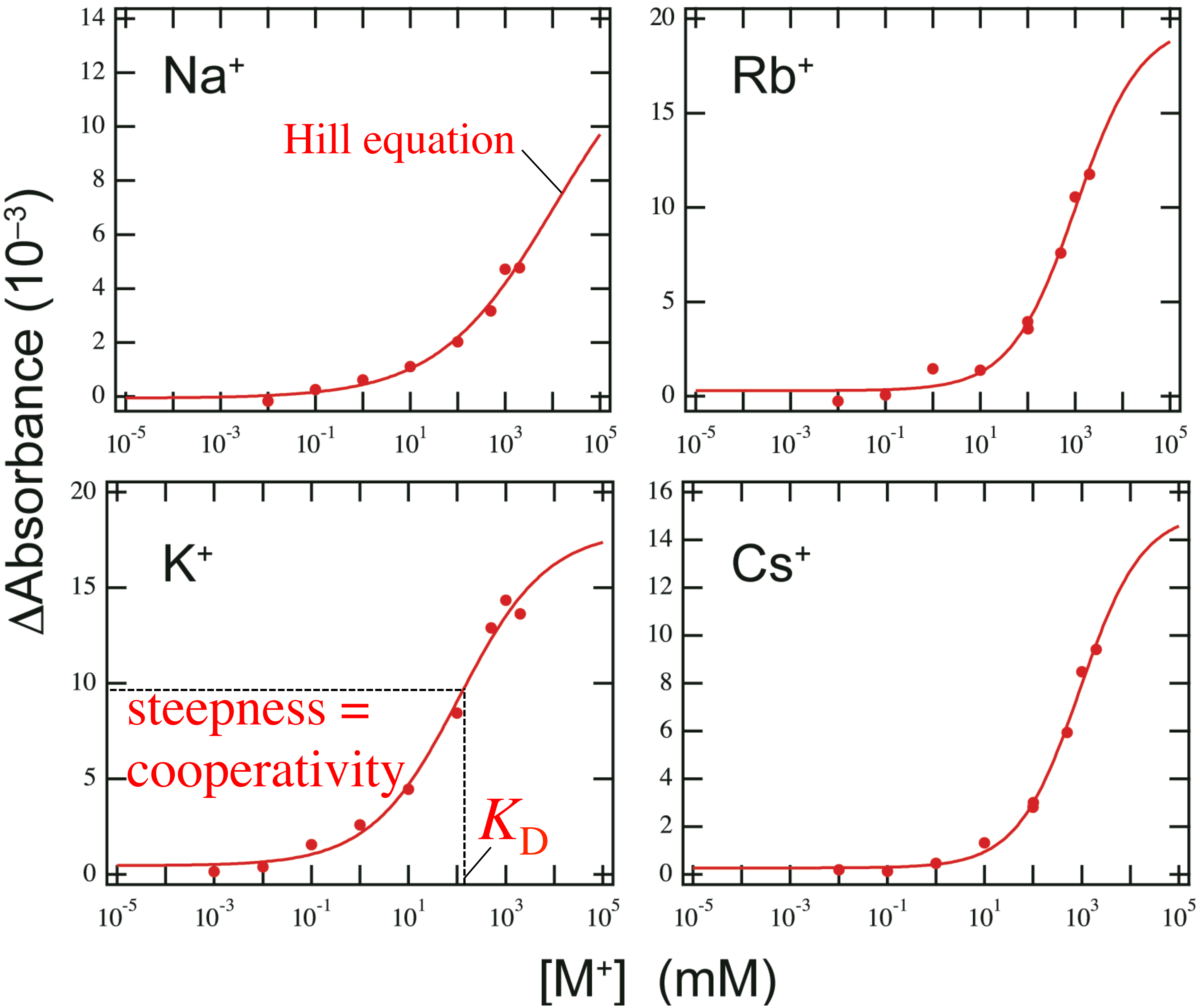


MCl in water:
10^{-6}~2 M

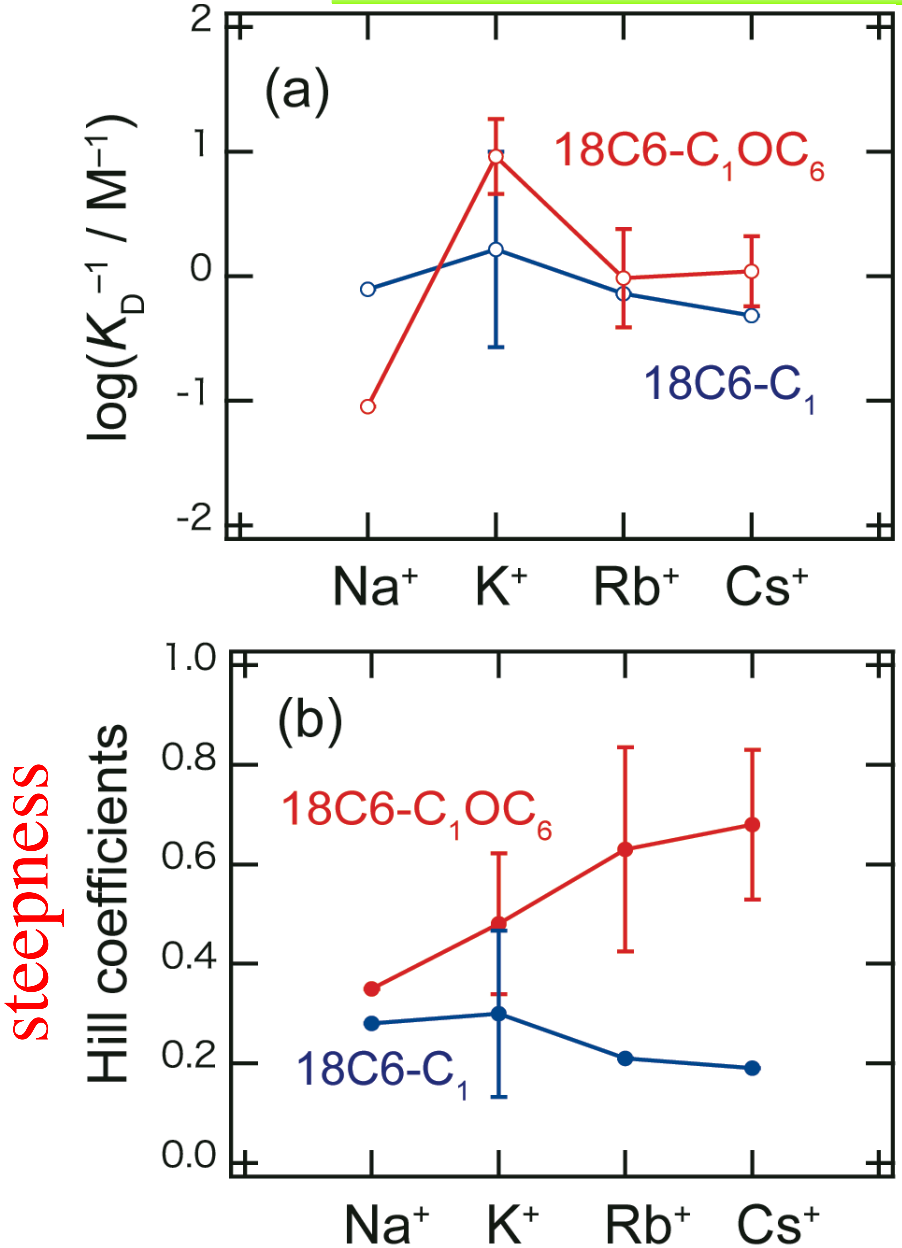


$18C6\text{-}C_1$

Titration Curves for M^+•18C6-C_1OC_6



K_D and Hill Coefficients

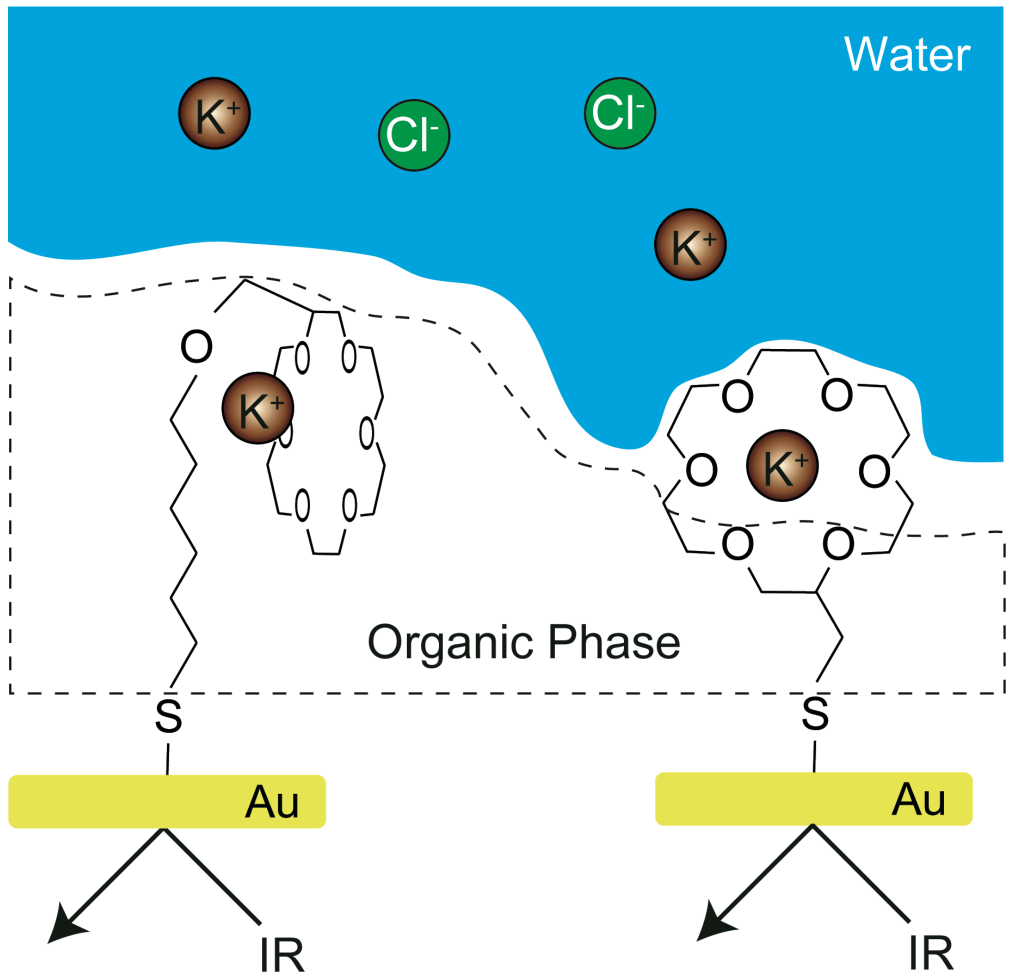


Ion selectivity for K^+
not so obvious for 18C6-C_1

18C6-C_1 shows
smaller cooperativity

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

Proposed Structure at Interface



18C6-C_1OC_6

18C6-C_1

Ion complexes are isolated from water

Ion complexes face water phase

Summary ~on Gold Surface~

- M^+•18C6 ($M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+$) in water
- Surface-Enhanced Infrared Absorption (SEIRA) Spectroscopy

■ Relation between IR spectra and structure in condensed phase?

■ Density of host species on Au, lengths of hydrocarbon chains?

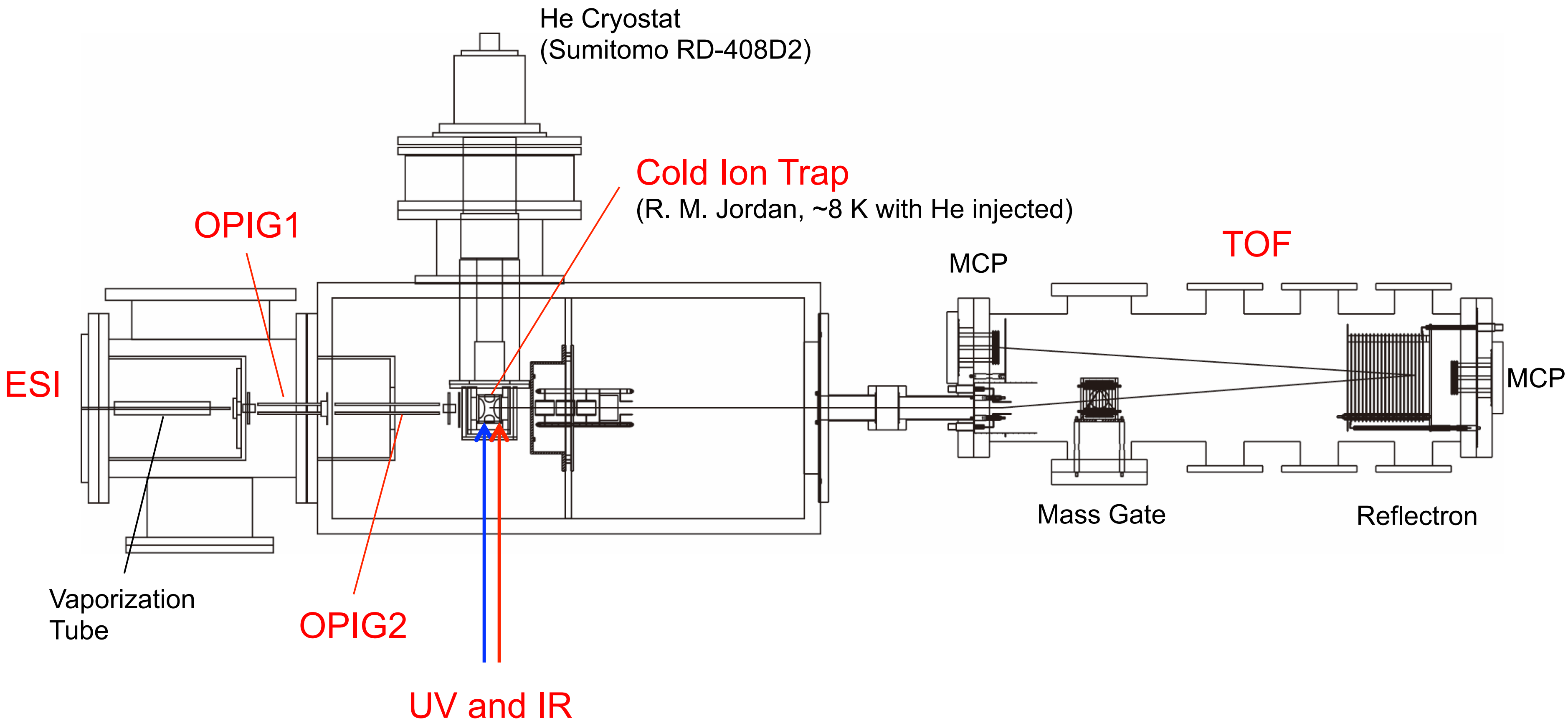
■ Theoretical studies

4. Future Prospects

Future Prospects

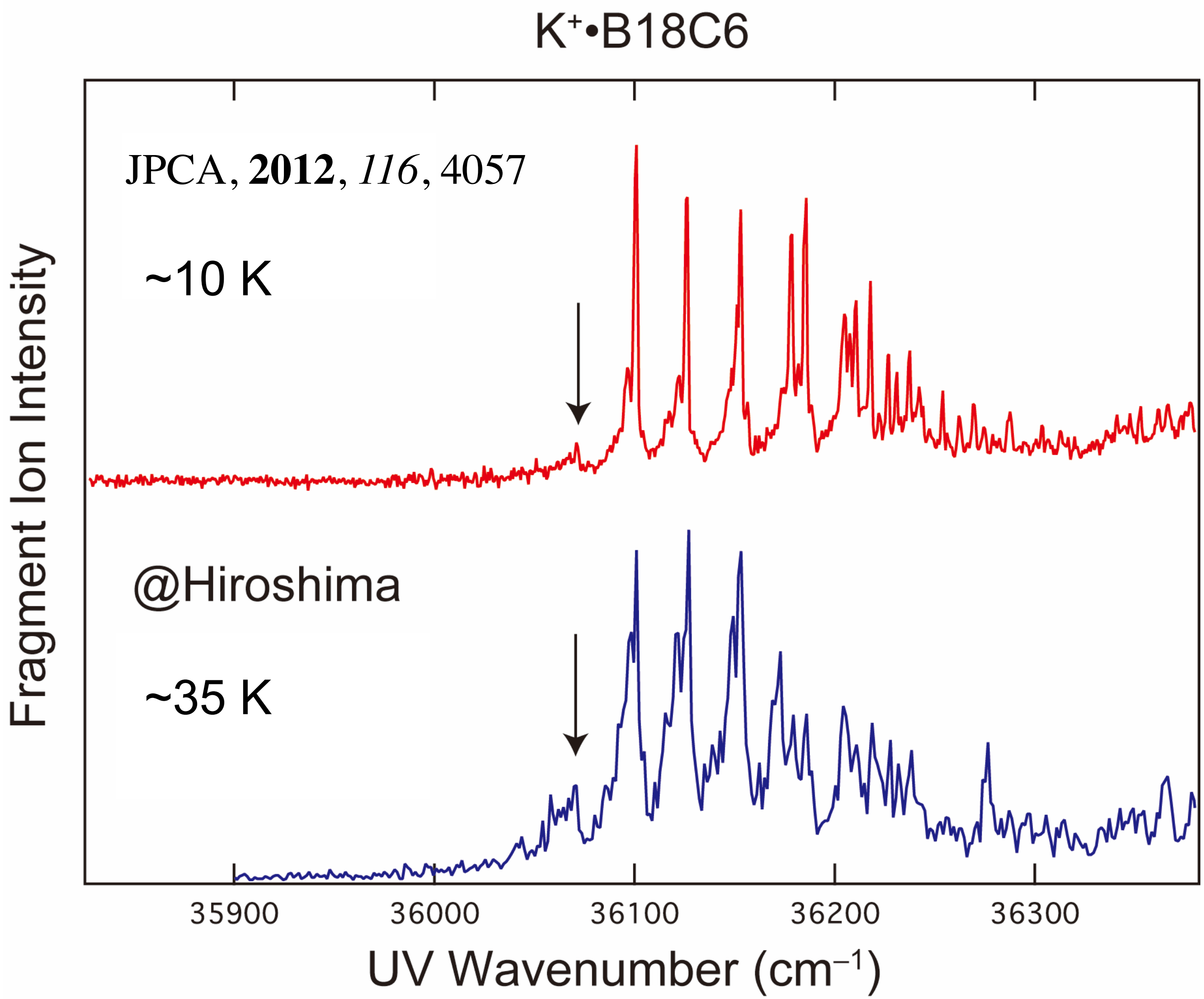
Quantum chemical approaches in host-guest chemistry

Gas phase



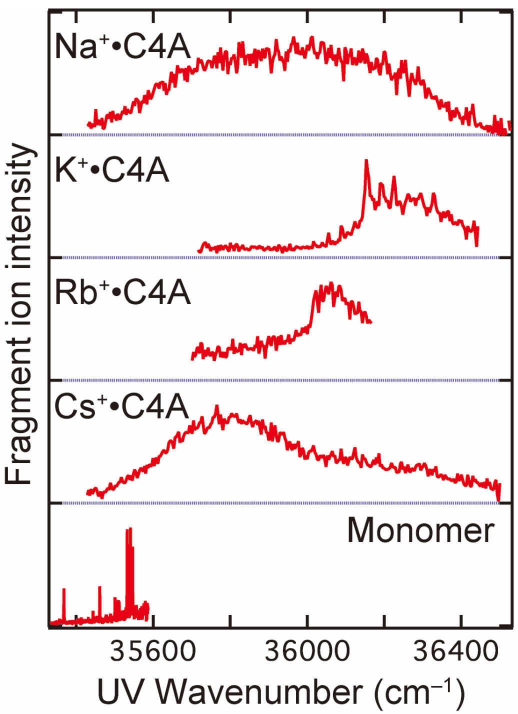
Future Prospects

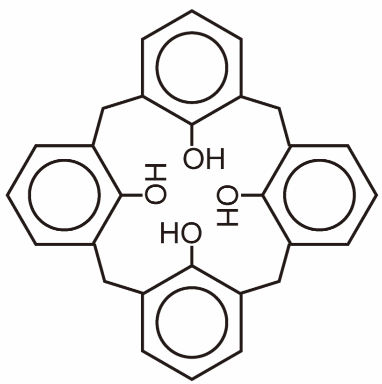
Quantum chemical approaches in host-guest chemistry



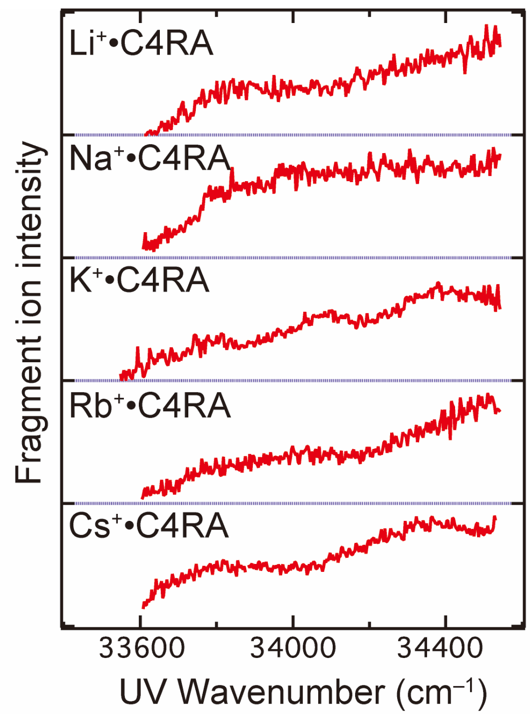
Future Prospects

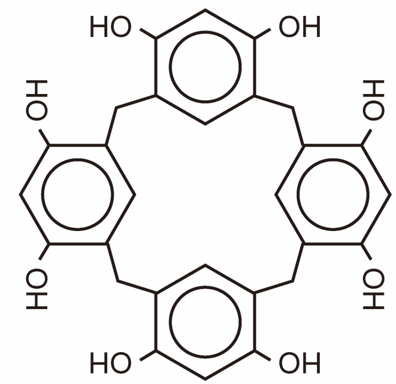
Quantum chemical approaches in host-guest chemistry





Calix[4]arene (C4A)





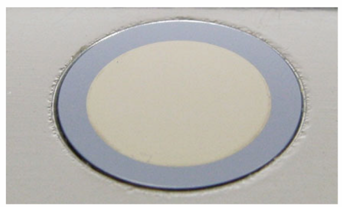
Calix[4]resorcinarene (C4RA)

Need colder conditions?

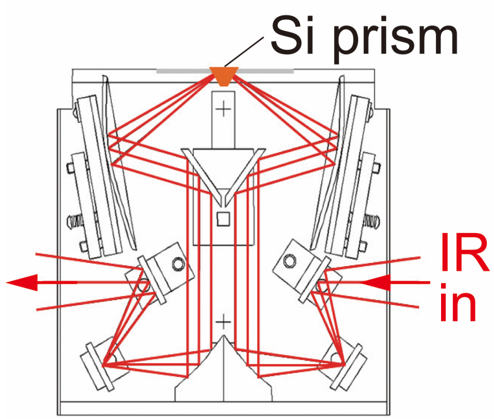
Future Prospects

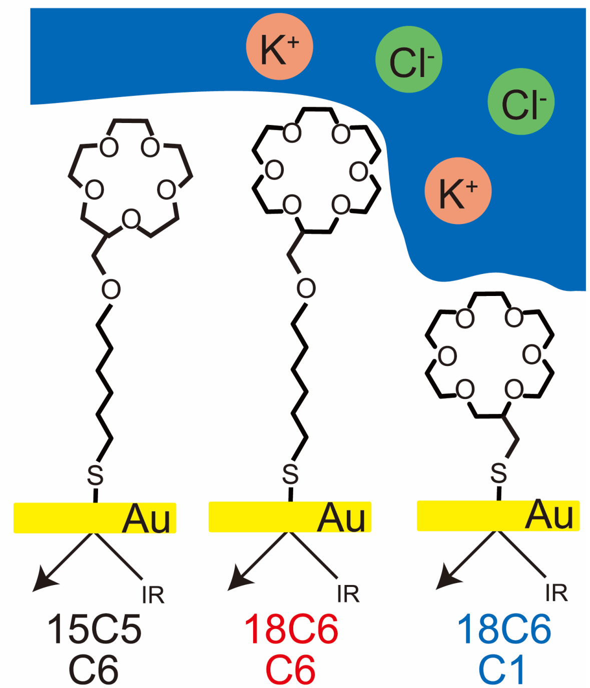
Quantum chemical approaches in host-guest chemistry

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



Au surface on Si prism of ATR (~8 nm thickness)





Acknowledgment

■École Polytechnique Fédérale de Lausanne (EPFL)

Prof. Thomas R. Rizzo

Dr. Oleg V. Boyarkin

LCPM members

■Hiroshima University

Prof. Takayuki Ebata

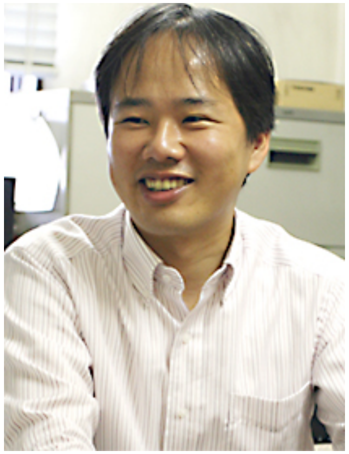
Dr. Ryoji Kusaka

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

Thank You

Thank you
for your attention!