UV and IR Spectroscopy of Metal Ion-Crown Ether Complexes

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Acknowledgment

■ Gas-Phase Spectroscopy

Takayuki Ebata (Hiroshima Univ.)
LCPM members (EPFL)
Oleg V. Boyarkin (EPFL)
Thomas R. Rizzo (EPFL)

■ Surface-Enhanced Infrared Absorption Spectroscopy

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Takeharu Haino (Hiroshima Univ.)

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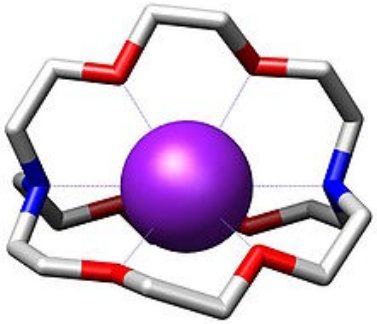
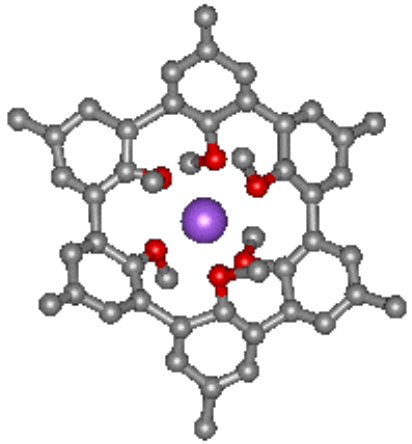
(1) Gas-Phase Spectroscopy

Inokuchi et al., *J. Am. Chem. Soc.*, **2011**, *133*, 12256
Phys. Chem. Chem. Phys., **2012**, *14*,4457
J. Phys. Chem. A, **2012**, *116*, 4057
ChemPhysChem, **2013**, *14*, 649
Submitted for publication

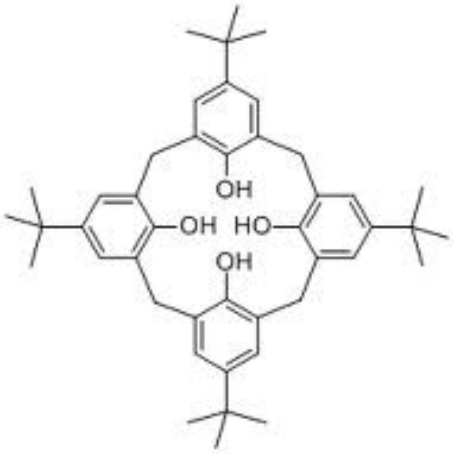
Ionophores



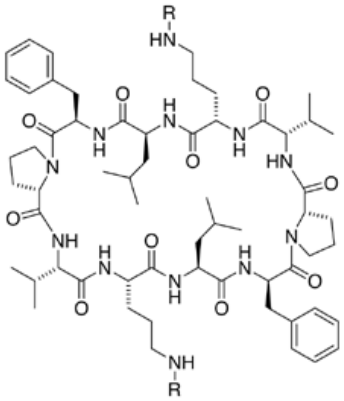
Cryptand



Spherand

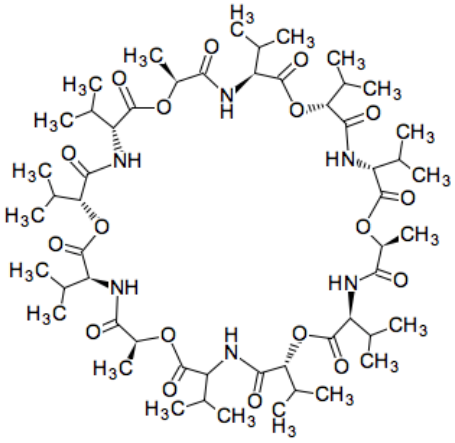


Calixarene



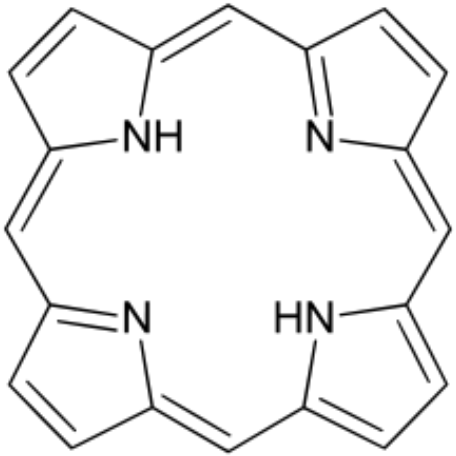
GS: R=H-
AcGS: R=CH_3CO-
TcGS: R=CCl_3CO-
BrGS: R=*m*-Br(C_6H_4)CO-

Gramicidin



C06684

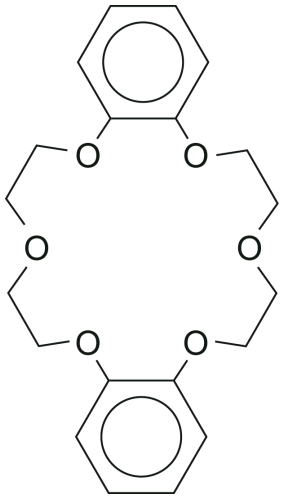
Valinomycin



Porphyrin

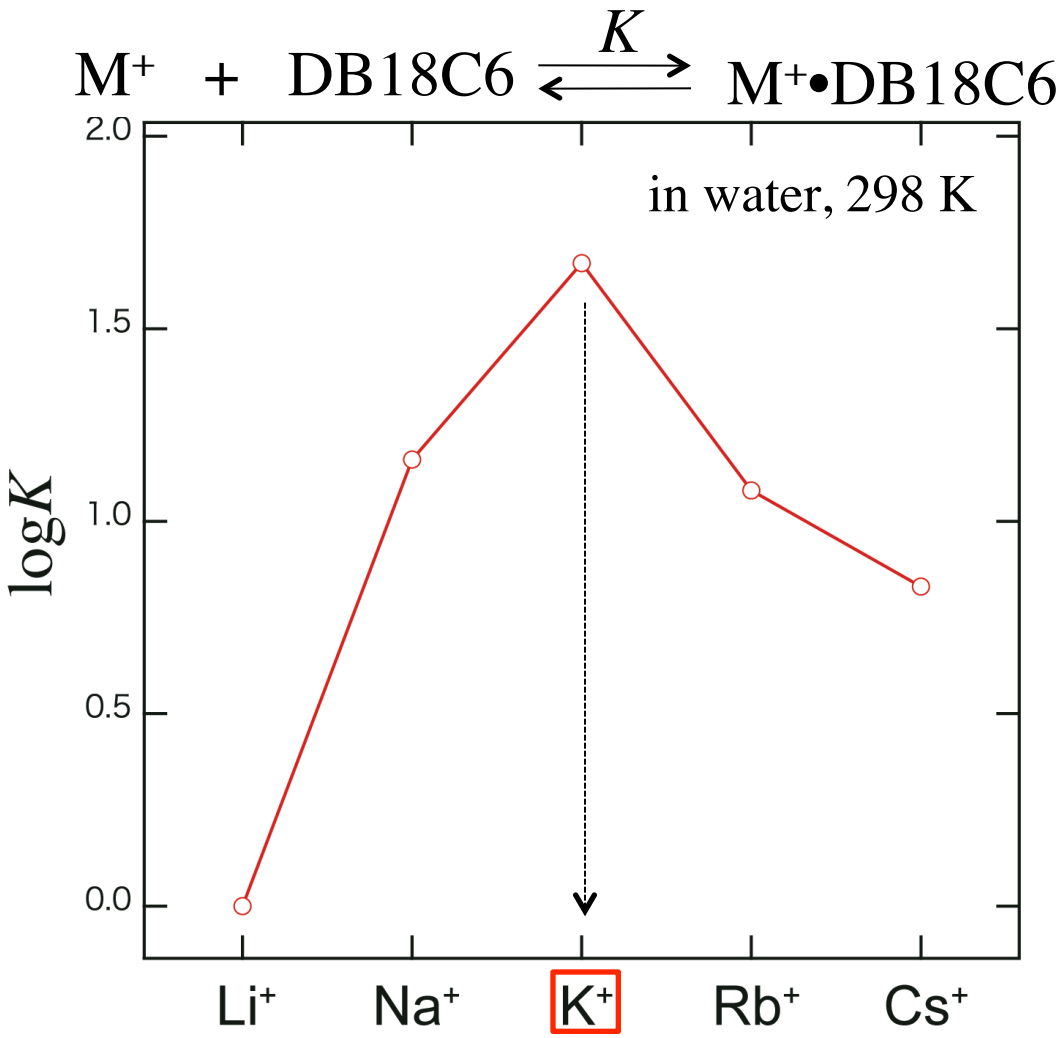
Crown Ethers

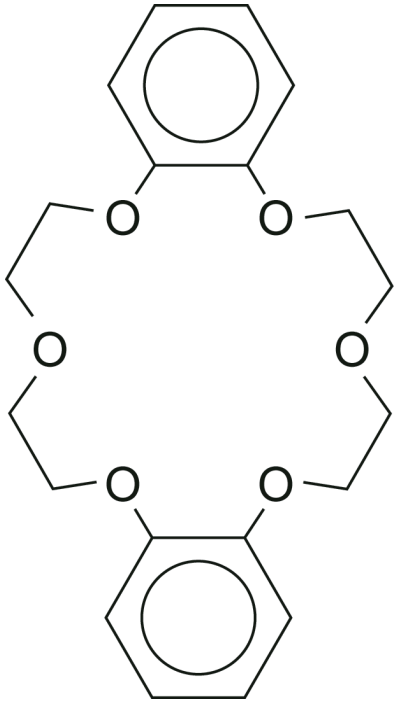
- Ionophores
- Used as phase-transfer catalysts
- Ion selectivity



Dibenzo-18-crown-6
(DB18C6)

Ion Selectivity





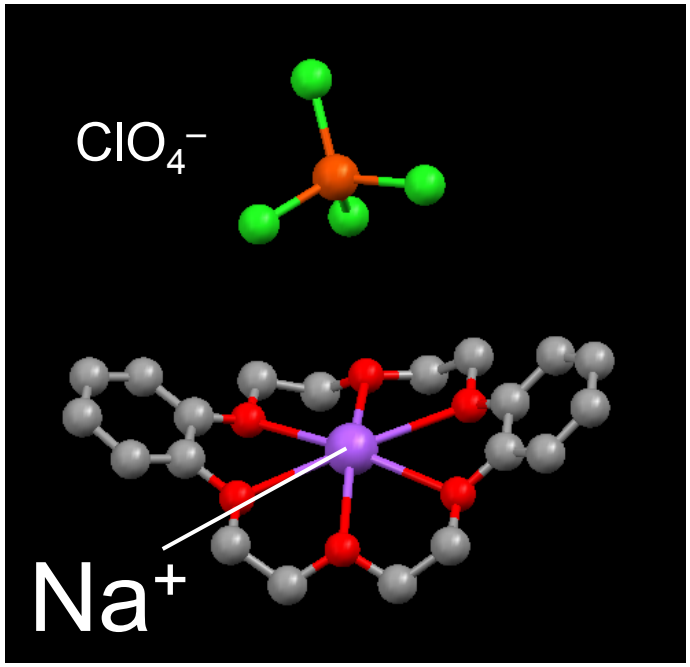
DB18C6

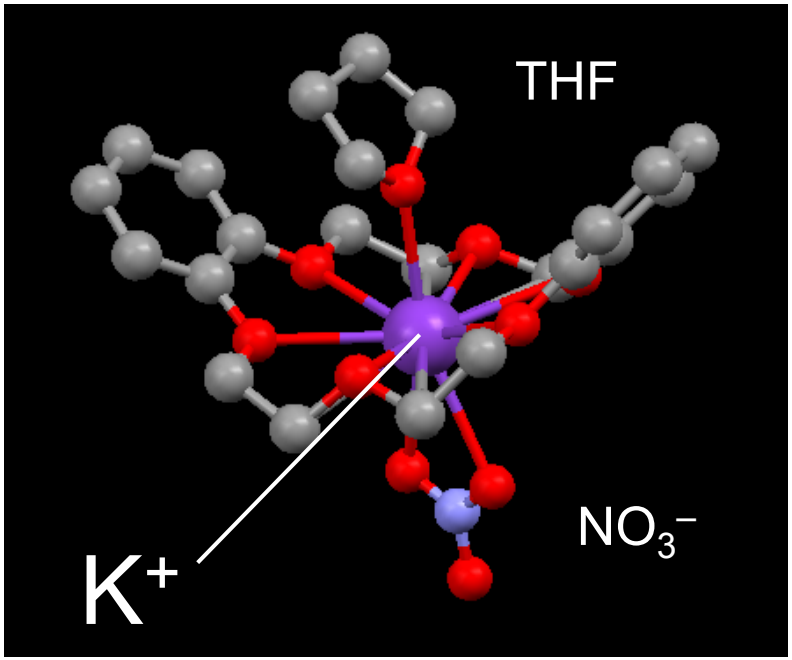
Izatt et al., *Chem. Rev.*, **1985**, *85*, 271.

DB18C6 captures K^+ selectively

Due to optimum matching in size?

Crystal Structure of M^+•DB18C6





(Cambridge Structural Database)

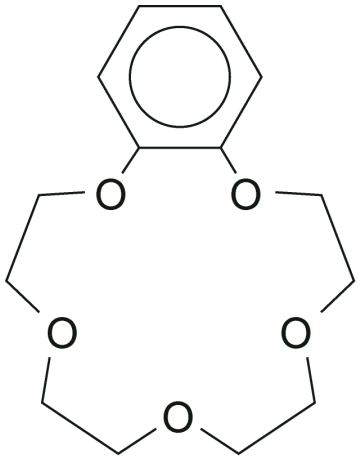
Conformations similar for Na^+ and K^+

Counter anions also bonded to M^+, affecting the structure

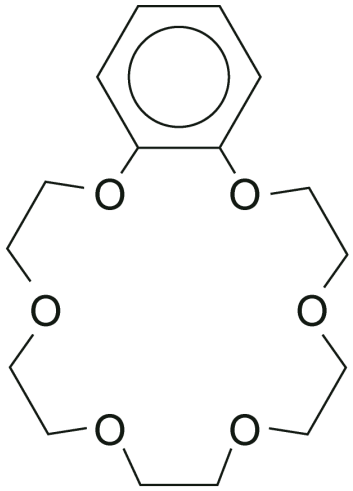
Necessary to study in liquid phase, but spectra are broad…

We study complexes in the gas phase under cold conditions

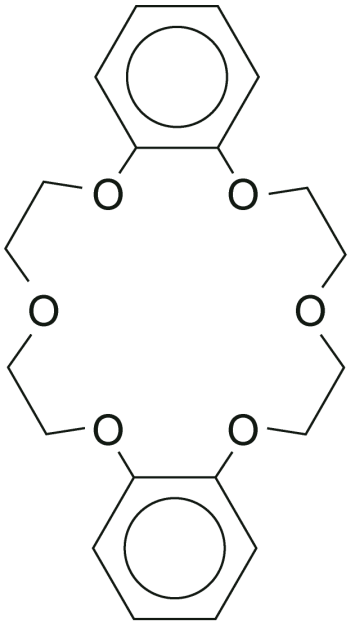
Crown Ethers in This Study



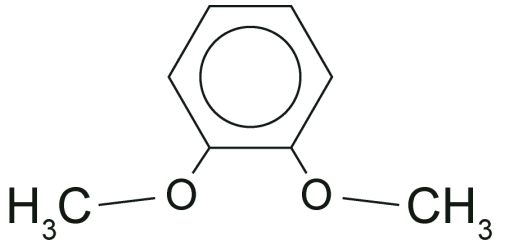
B15C5



B18C6



DB18C6

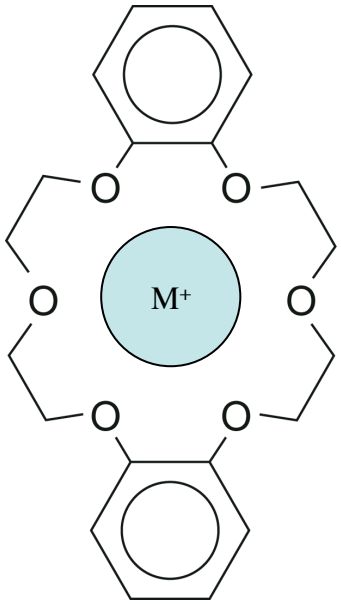


1,2-Dimethoxybenzene

(DMB)

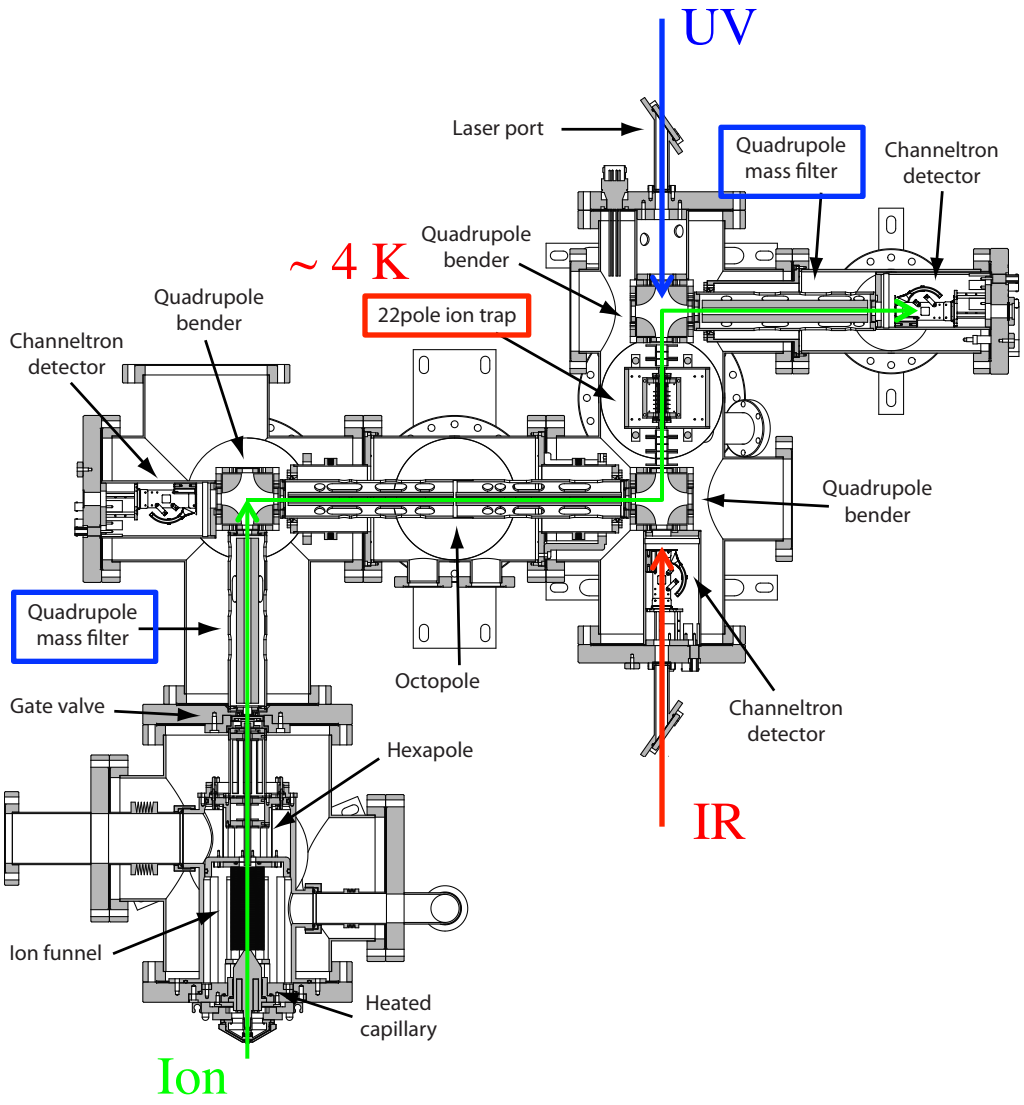
This Study

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

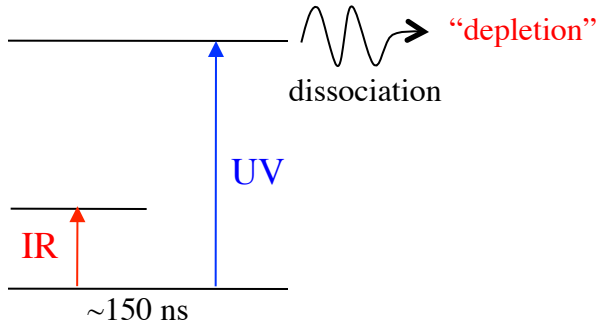


- UV and IR spectroscopy in a cold, 22-pole ion trap
  DFT, TD-DFT
- The number and structure of conformers determined

Experimental

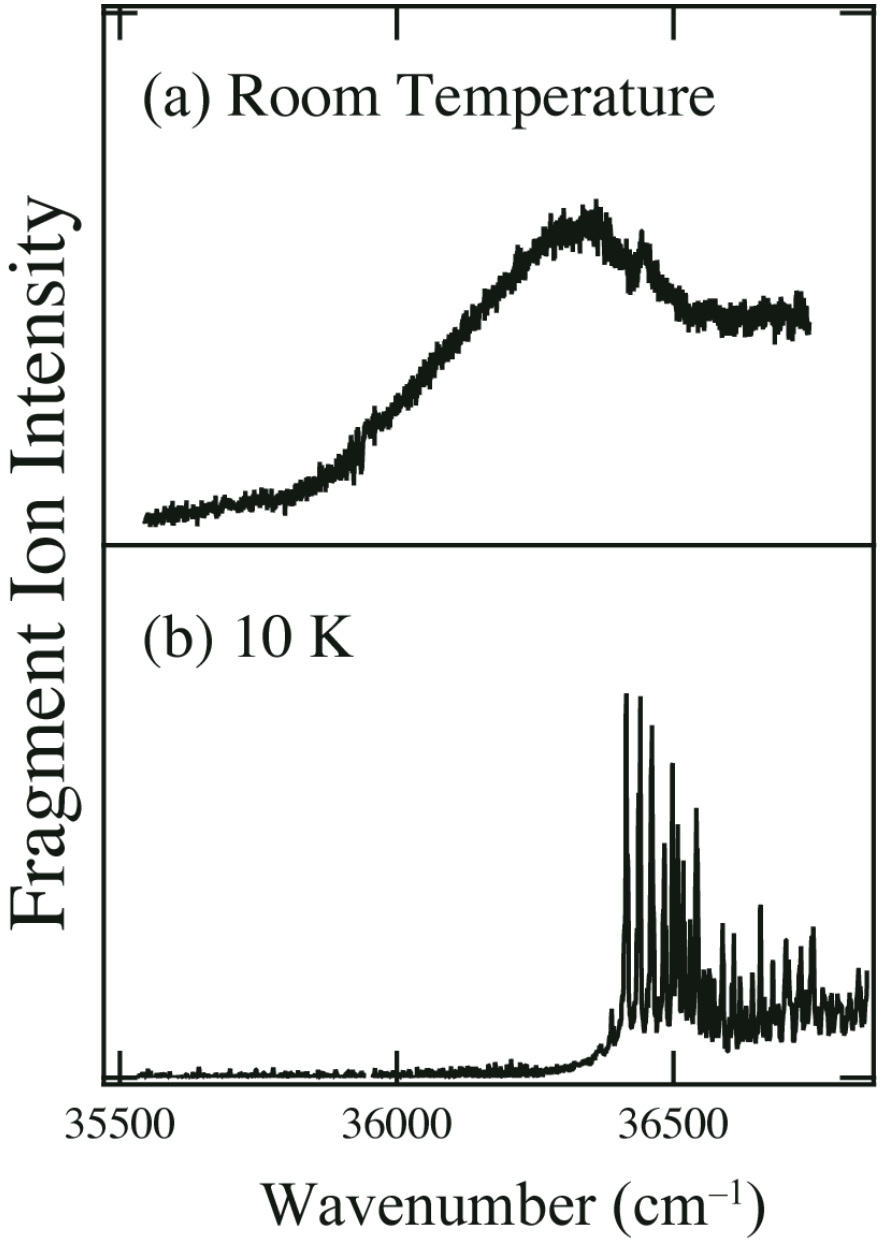


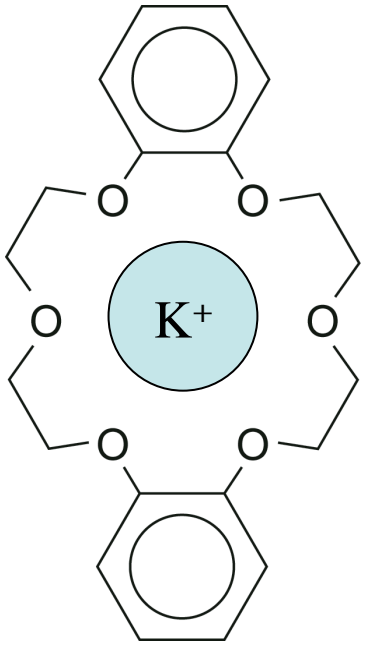
- nanoelectrospray
  - DB18C6
  - LiCl, NaCl, KCl, RbCl, CsCl
  - in Methanol
  - 20–200 μM
- UV photodissociation spectroscopy
- IR-UV double-resonance
  - UV power 1–1.5 mJ/pulse
  - IR power 4–5 mJ/pulse



Svendsen, Lorenz, Boyarkin, and Rizzo,
Rev. Sci. Instrum., **2010**, *81*, 073107.

UVPD Spectra of K^+•DB18C6

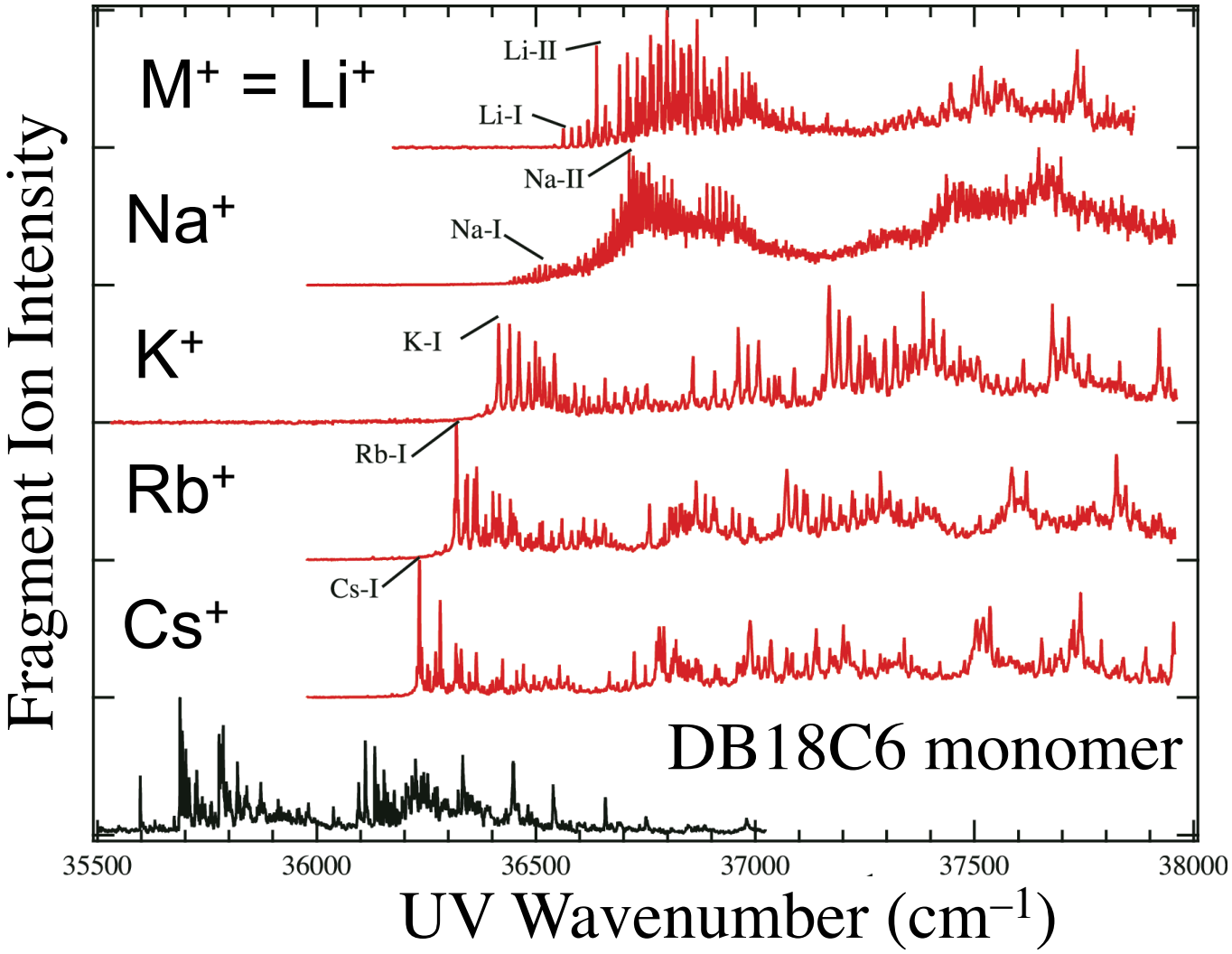


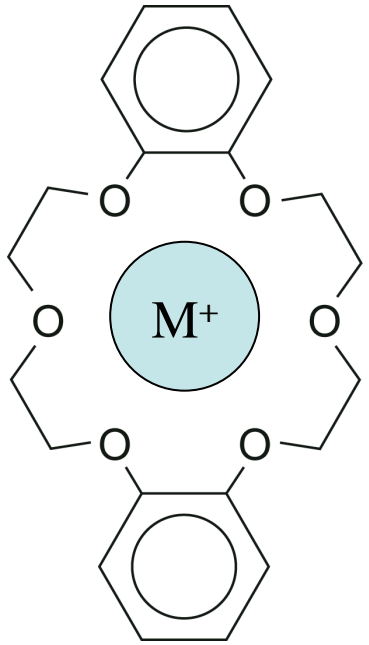


K^+•DB18C6

Sharp vibronic bands
are observed
under cold condition

UVPD Spectra of M^+•DB18C6

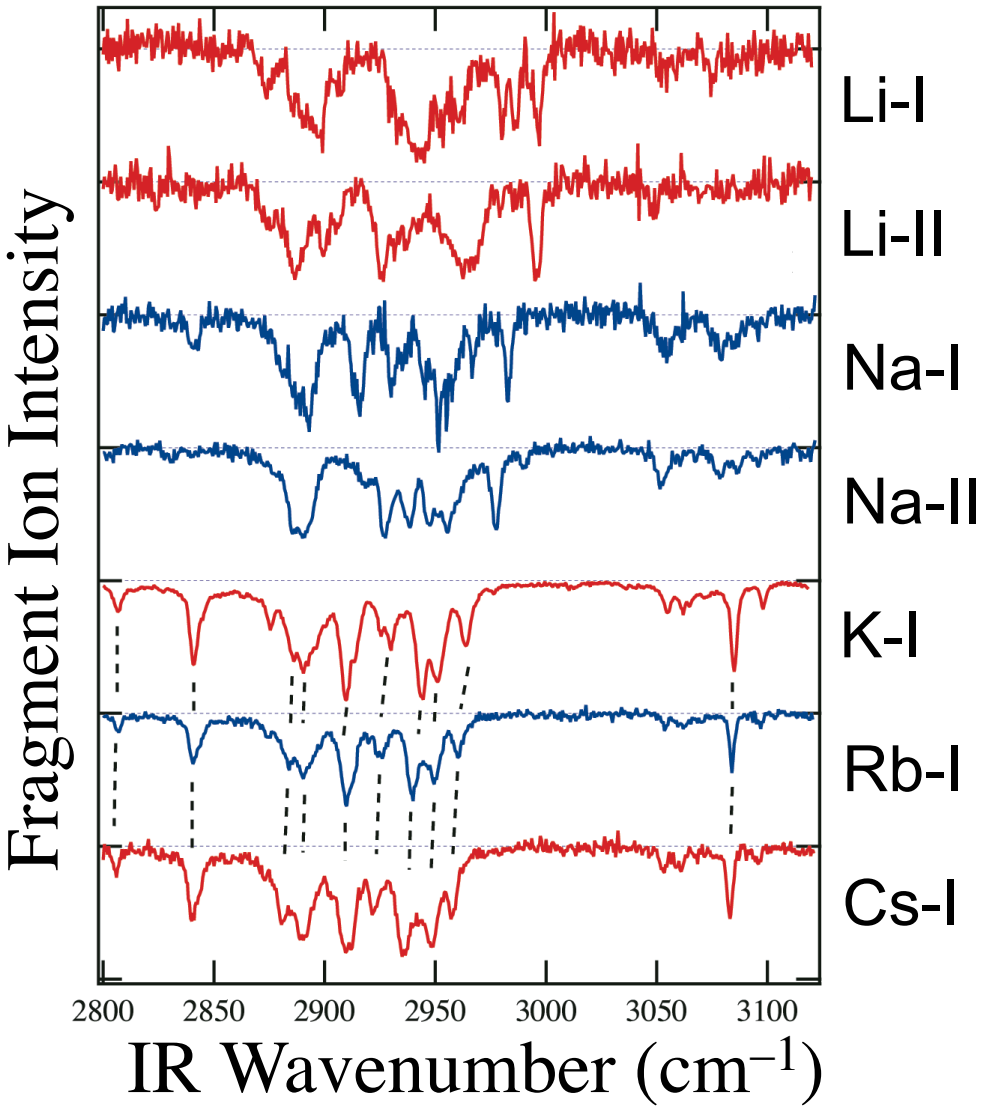


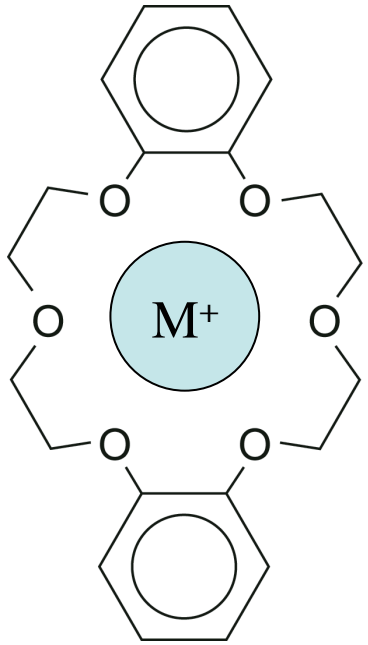


M^+•DB18C6

Sharp vibronic bands;
conformer-specific IR spectra can be measured.

IR-UV Spectra of M^+•DB18C6





M^+•DB18C6

IR spectra similar for K^+~Cs^+ ➡ Similar structure

The Number of Conformers

M^+	M^+•DB18C6
Li^+	2
Na^+	2
K^+	1
Rb^+	1
Cs^+	1
(monomer)	2

- Molecular mechanics calculations

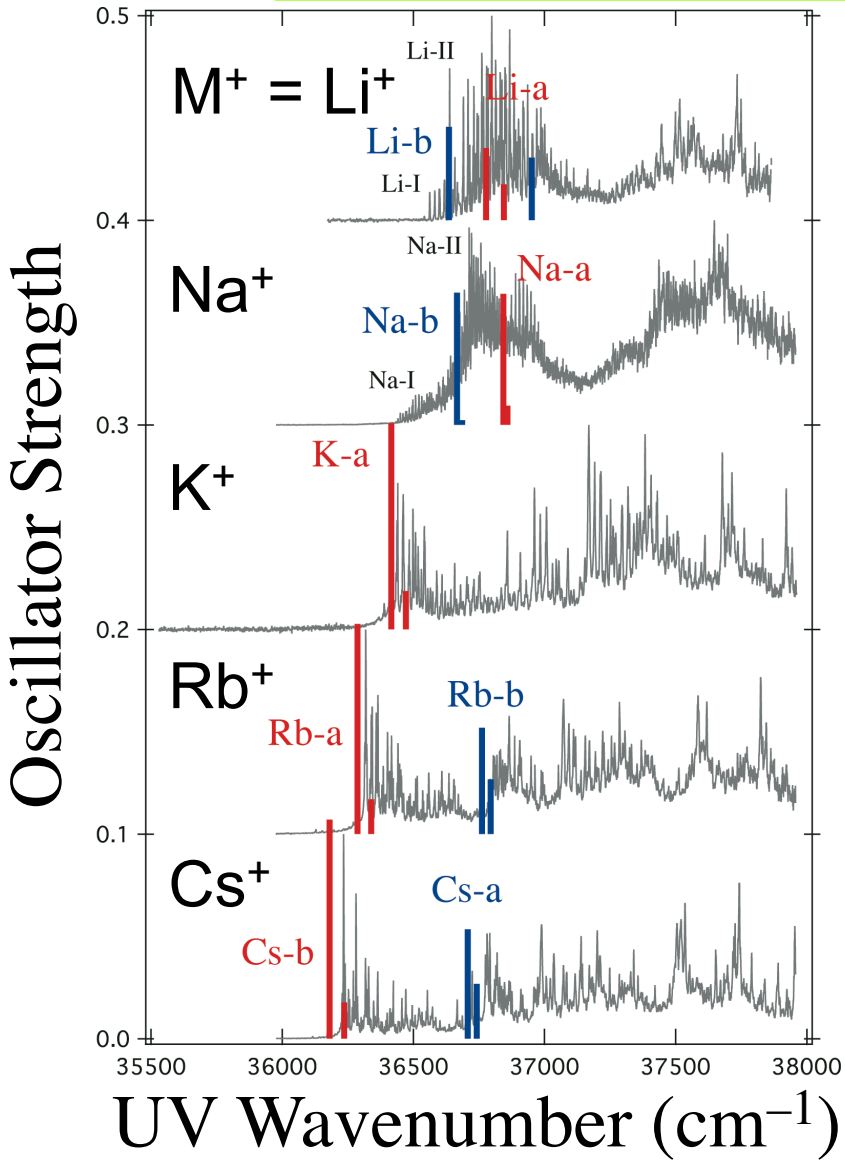
- DFT (M05-2X/6-31+G(d))
  geometry optimization
  vibrational analysis

- TD-DFT
  electronic spectra

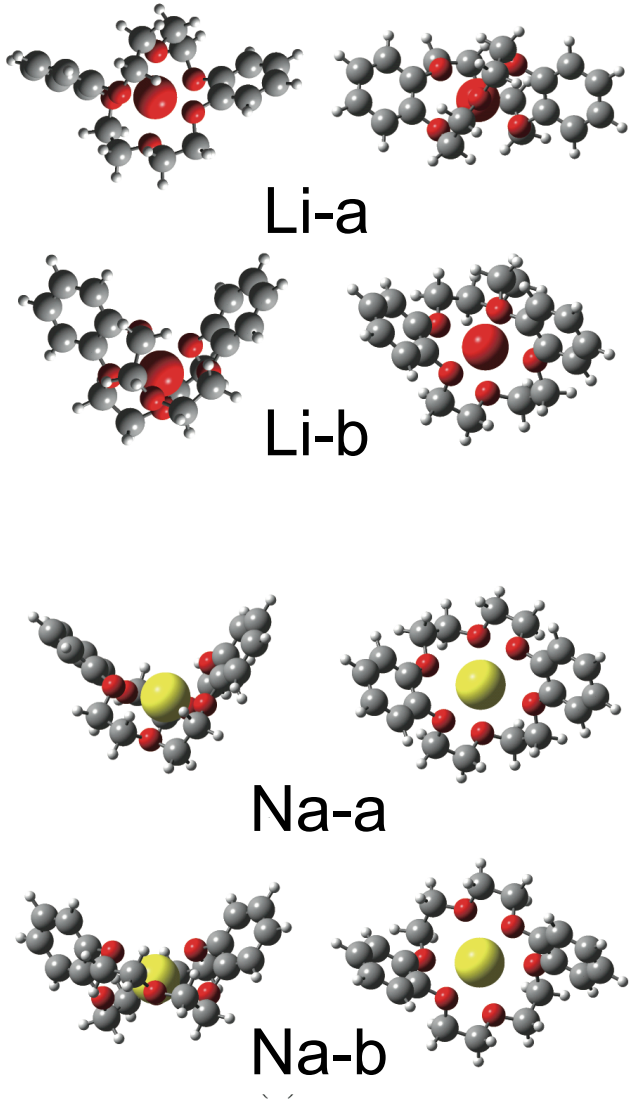
  ↕

  UVPD spectra

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

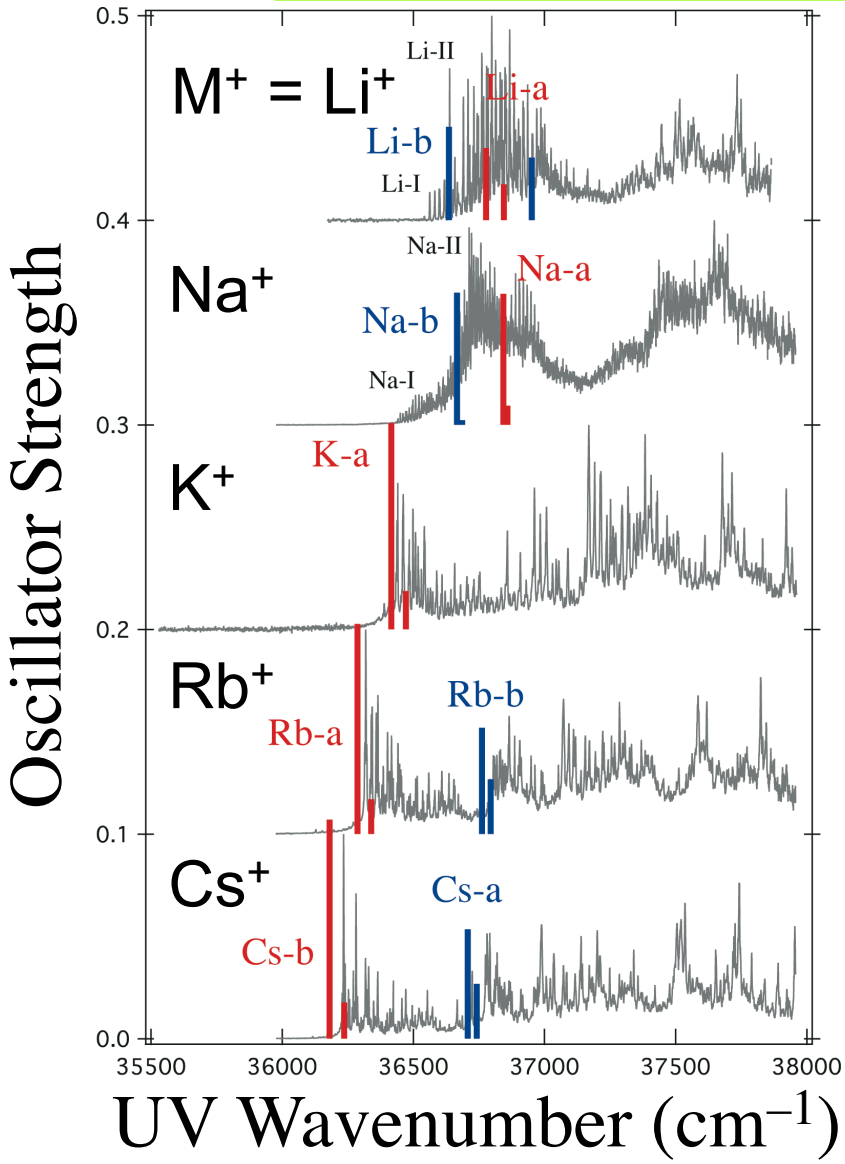


M05-2X/6-31+G(d) with Stuttgart RLC ECP
A scaling factor of 0.8340 is used.

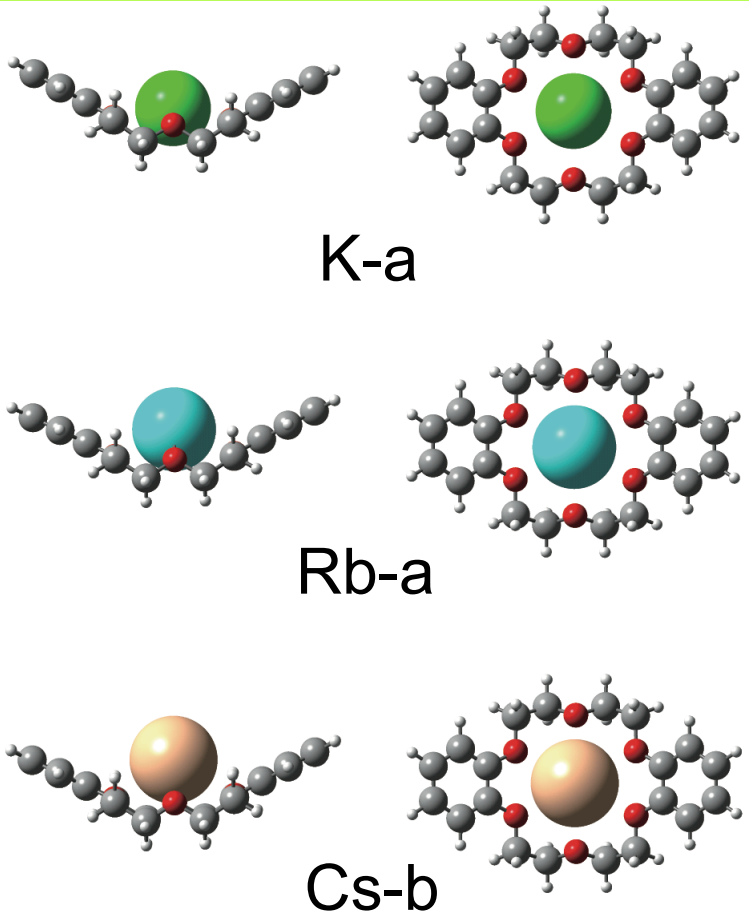


Ether rings distorted for Li^+ and Na^+

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.

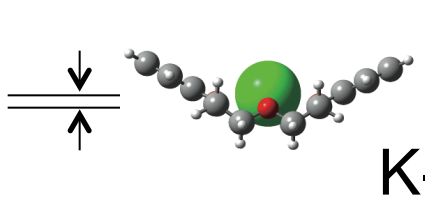
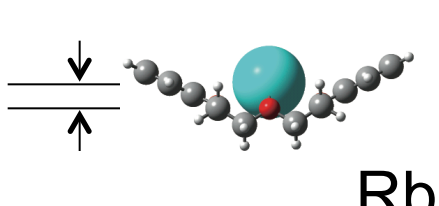
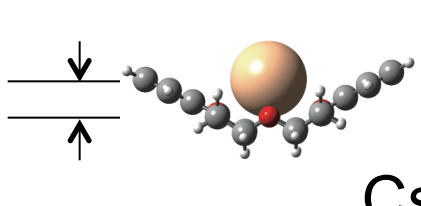


Ether rings largely open

K^+ in the ring

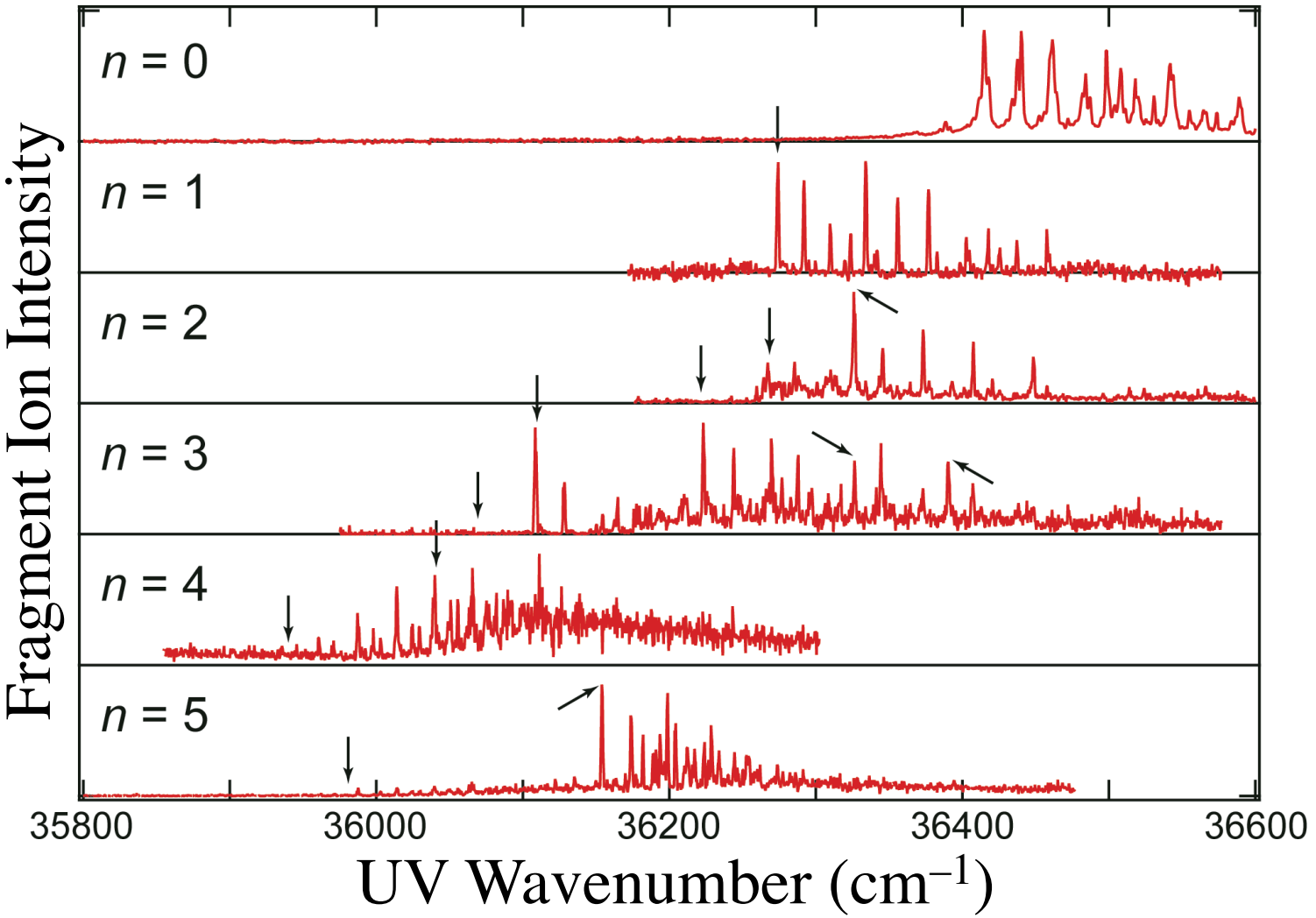
Rb^+, Cs^+ on the ring

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)

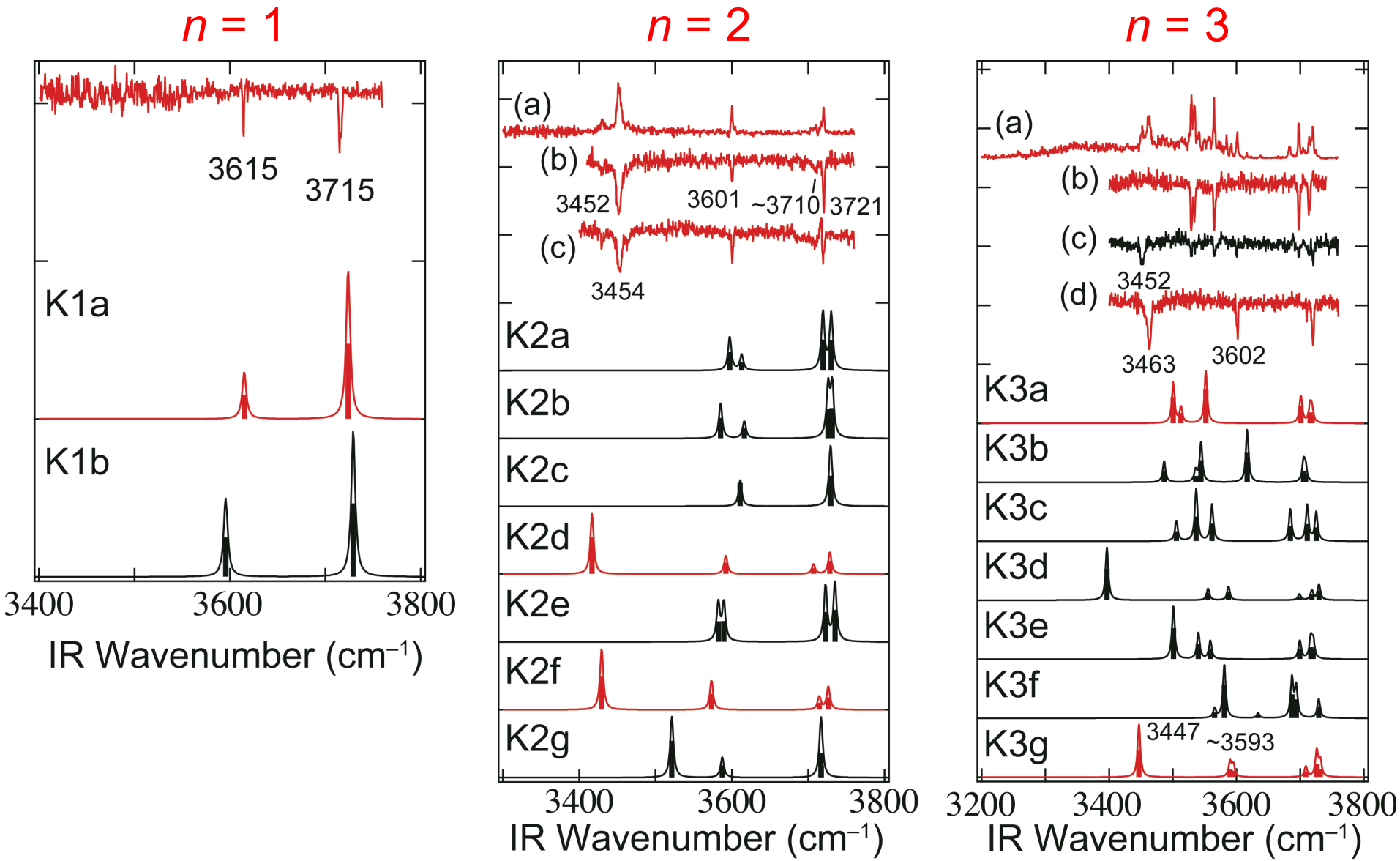
UVPD Spectra of $K^+ \cdot DB18C6 \cdot (H_2O)_n$



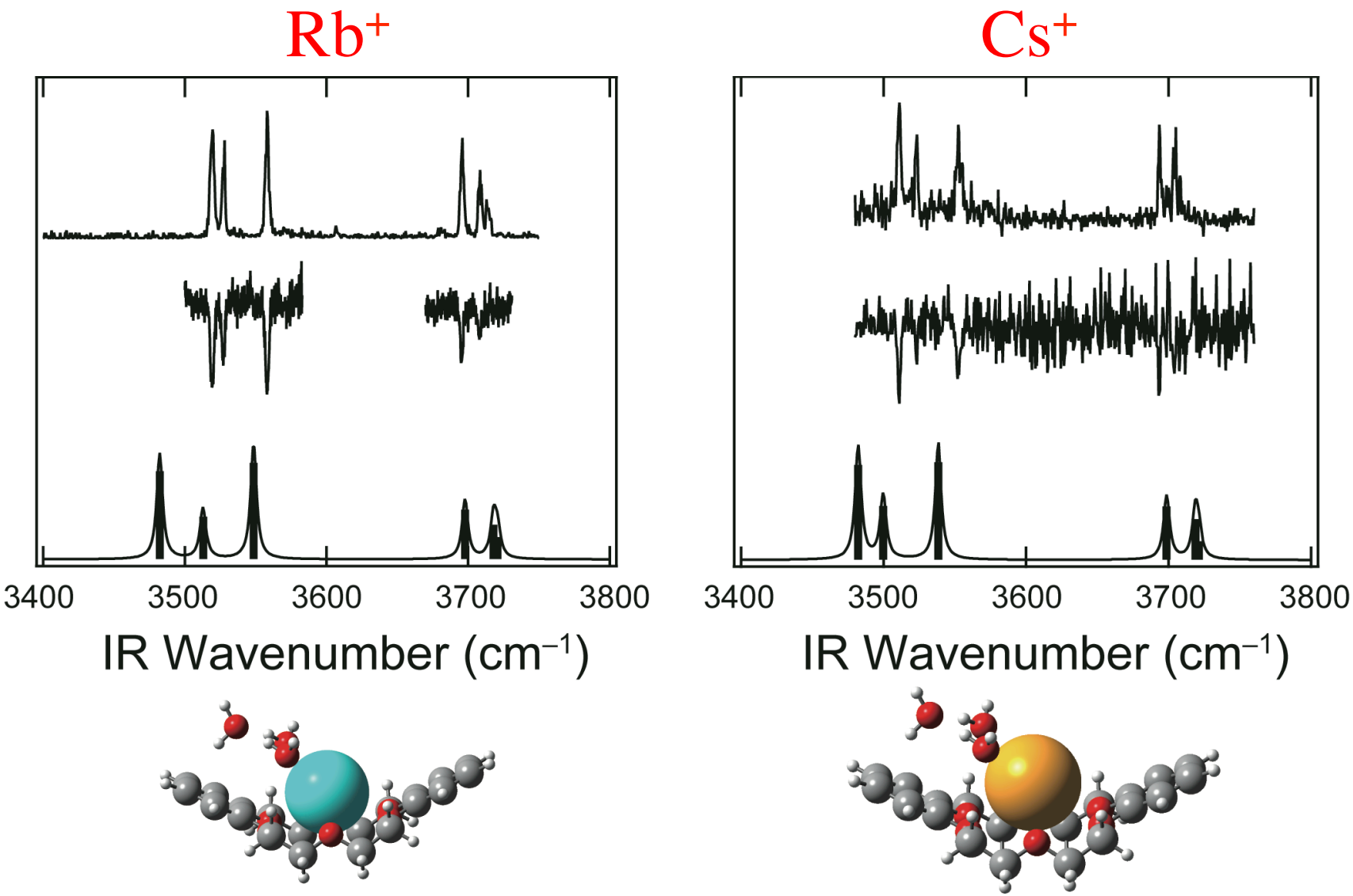
UV spectra also show sharp bands.

→ Conformer-specific IR spectra can be measured.

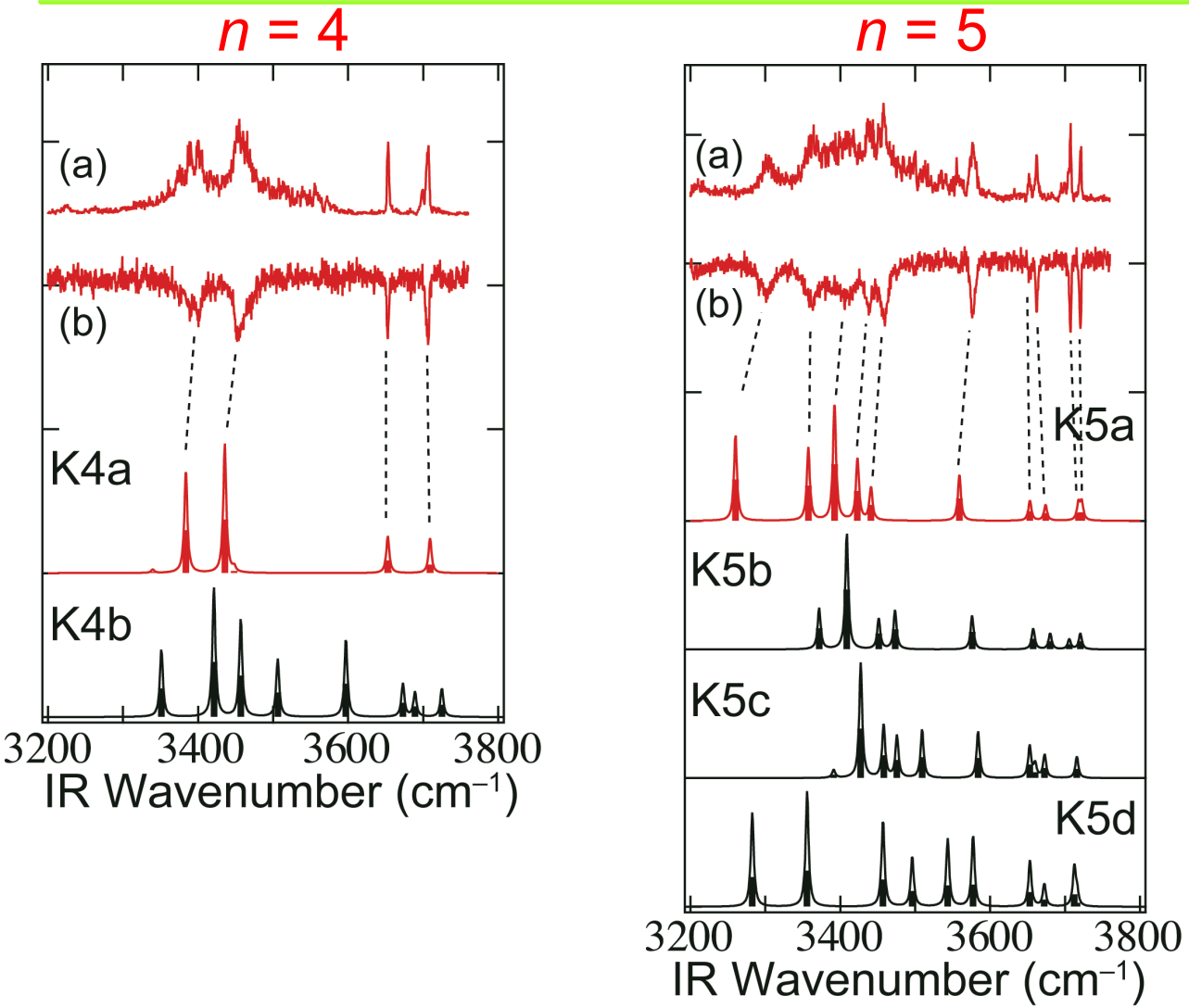
IR-UV Spectra of $K^+ \cdot DB18C6 \cdot (H_2O)_n$



IR-UV Spectra of $M^+ \cdot DB18C6 \cdot (H_2O)_3$

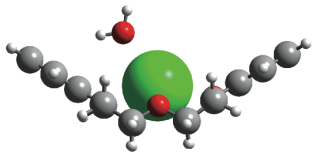


IR-UV Spectra of $K^+ \cdot DB18C6 \cdot (H_2O)_n$

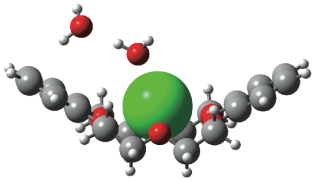


IR spectra in the OH stretch region give clear pictures of hydration structure.

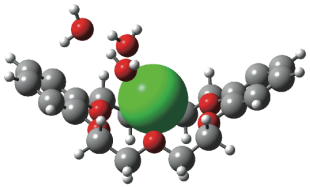
Structure of $K^+ \cdot DB18C6 \cdot (H_2O)_n$



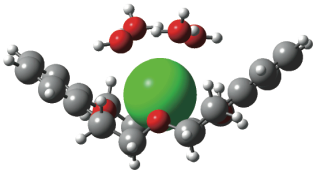
K1a



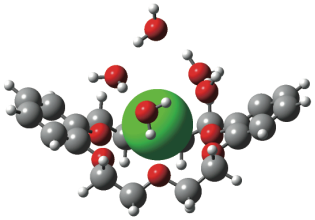
K2d



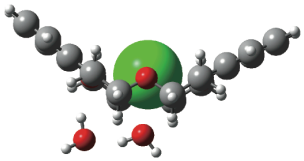
K3a



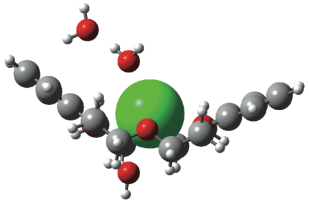
K4a



K5a



K2f

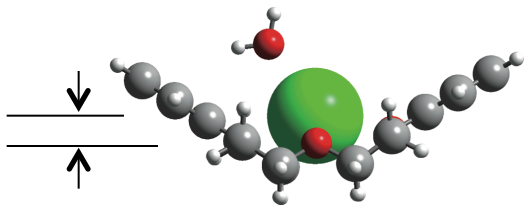


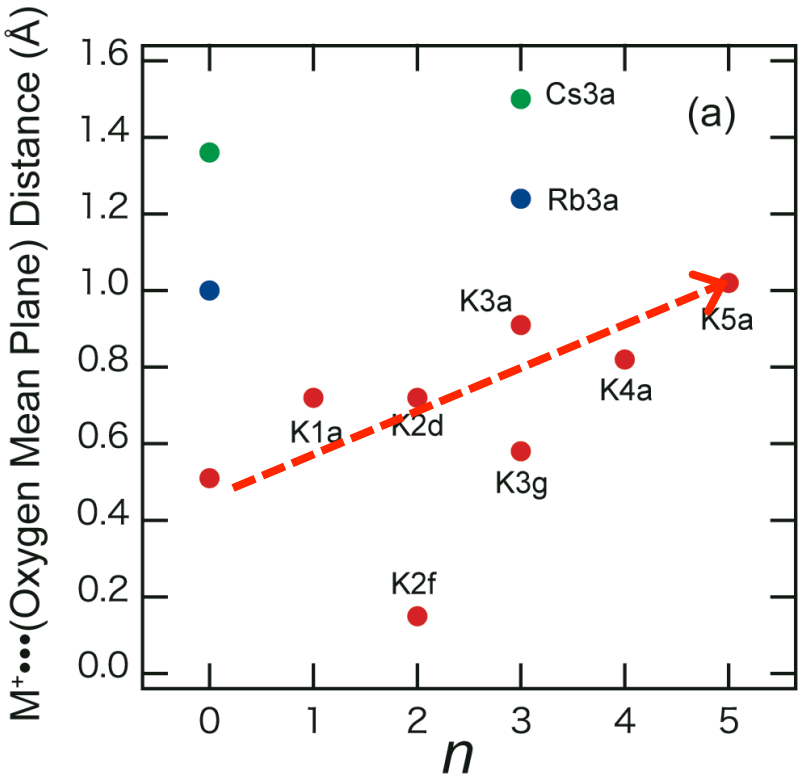
K3g

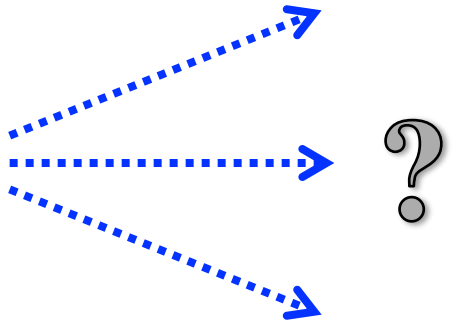
n = 1 *n* = 2 *n* = 3 *n* = 4 *n* = 5

Hydration occurs on one side.
→ Cooperativity

Structure of $K^+ \cdot DB18C6 \cdot (H_2O)_n$



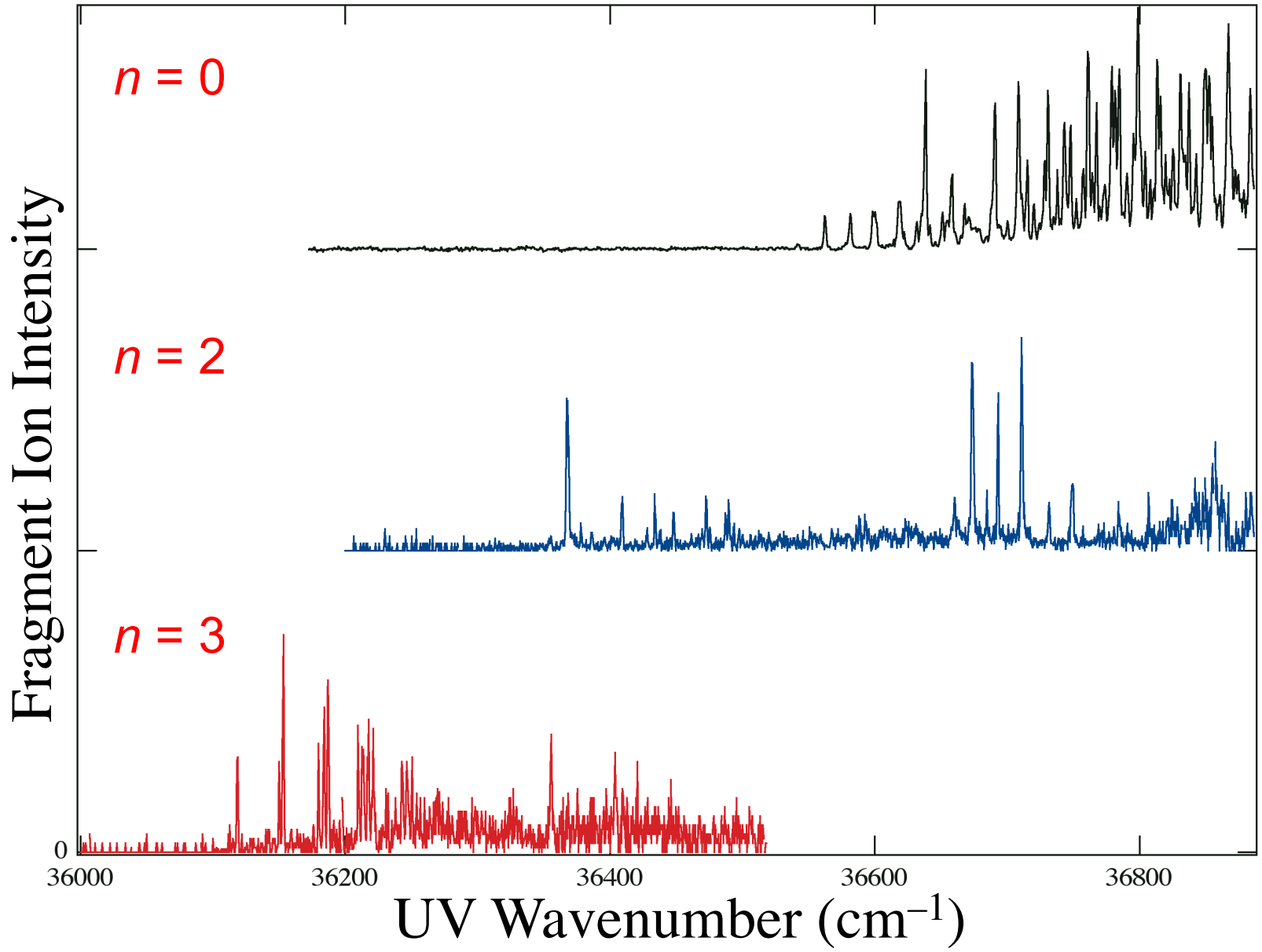




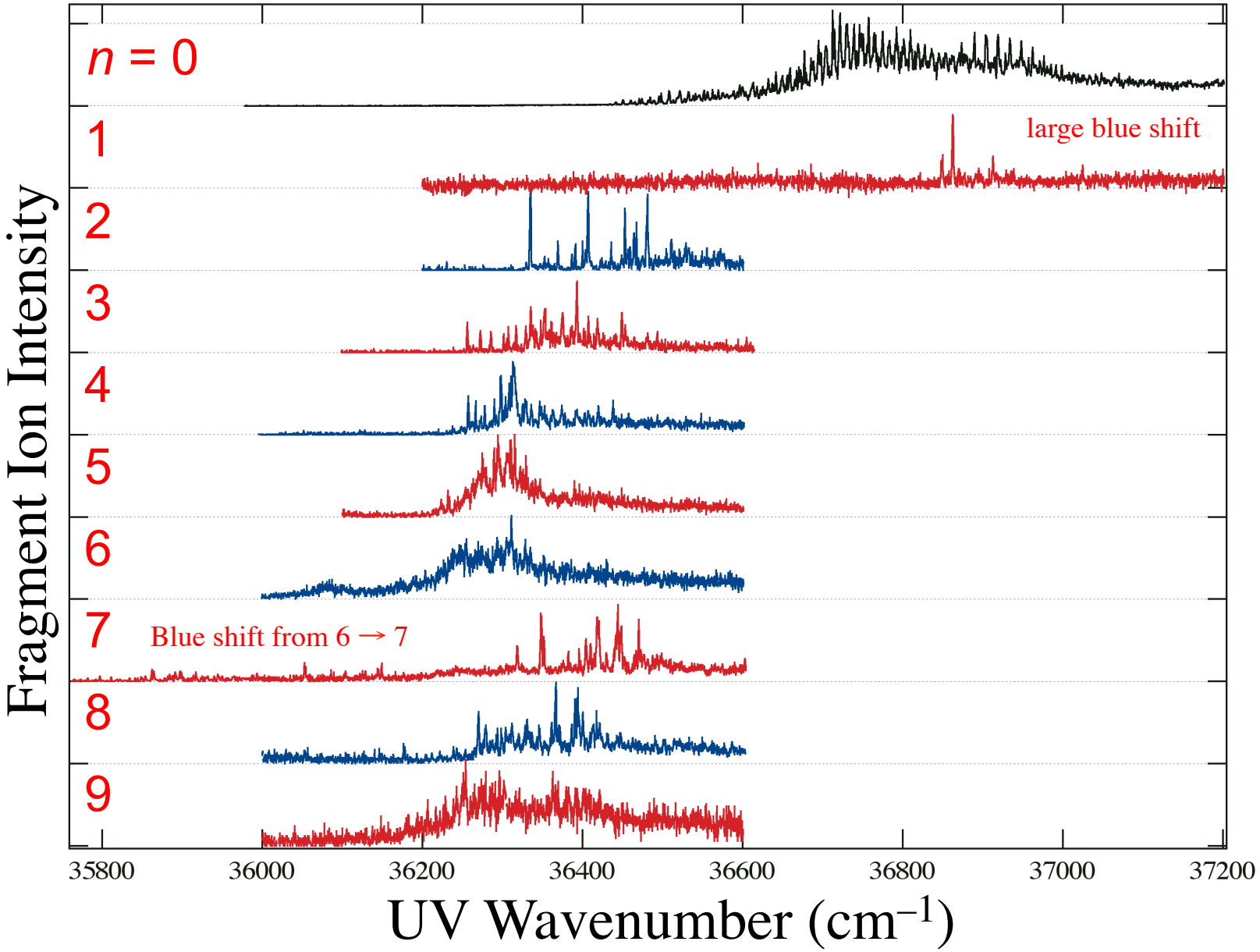
Distance increases with increasing n.

It continues for $n > 5$?

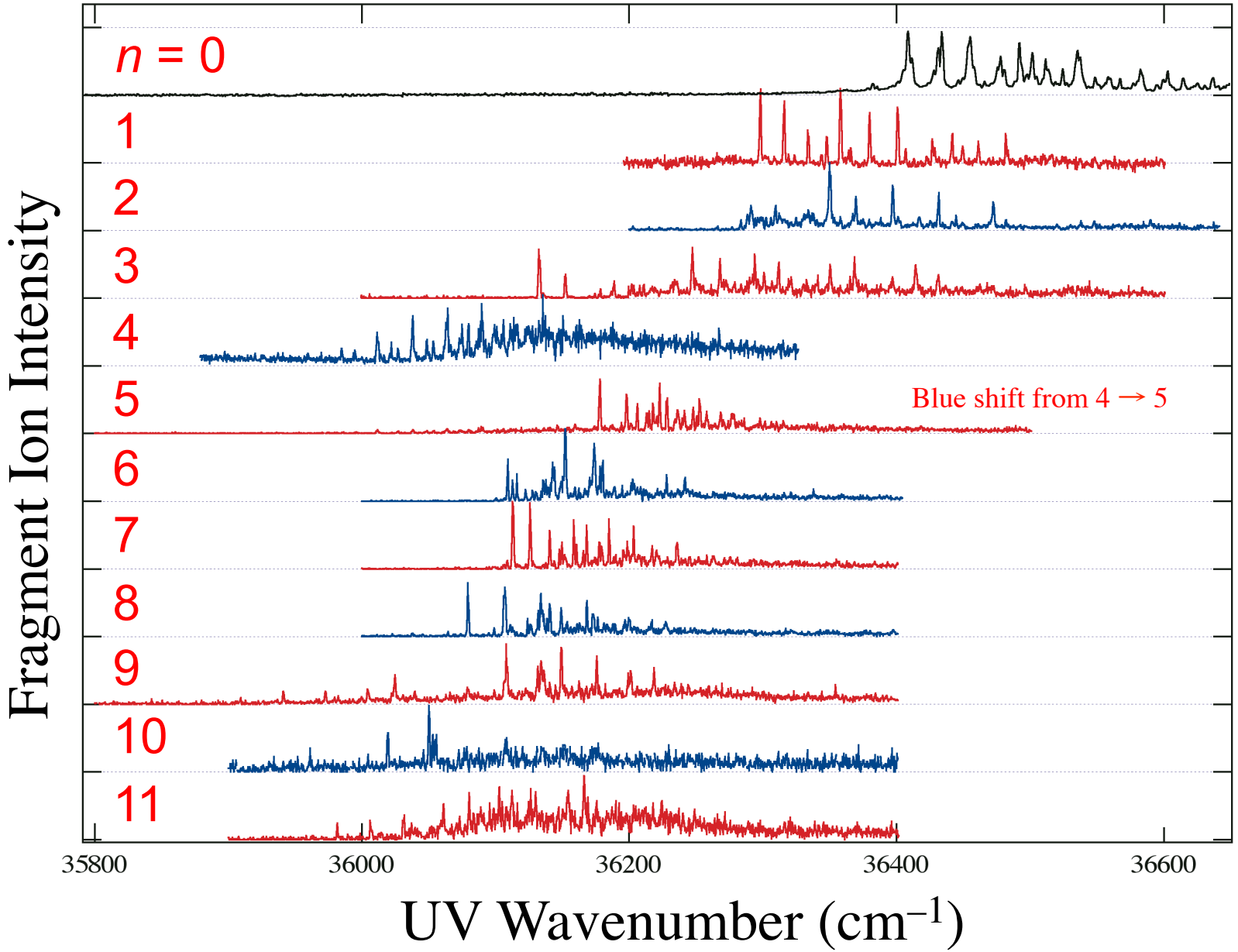
UVPD Spectra of $Li^+ \cdot DB18C6 \cdot (H_2O)_n$



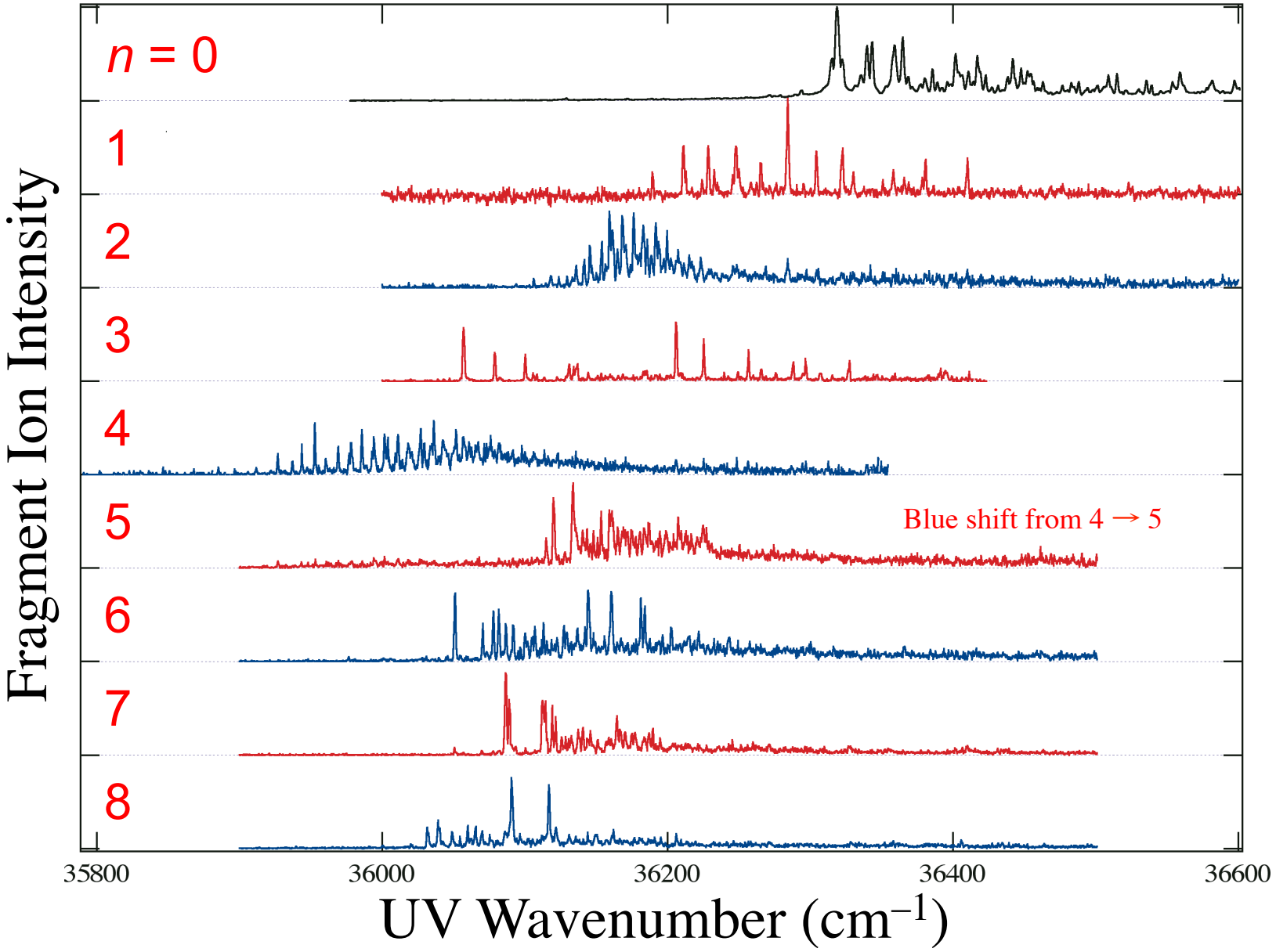
UVPD Spectra of $Na^+ \cdot DB18C6 \cdot (H_2O)_n$



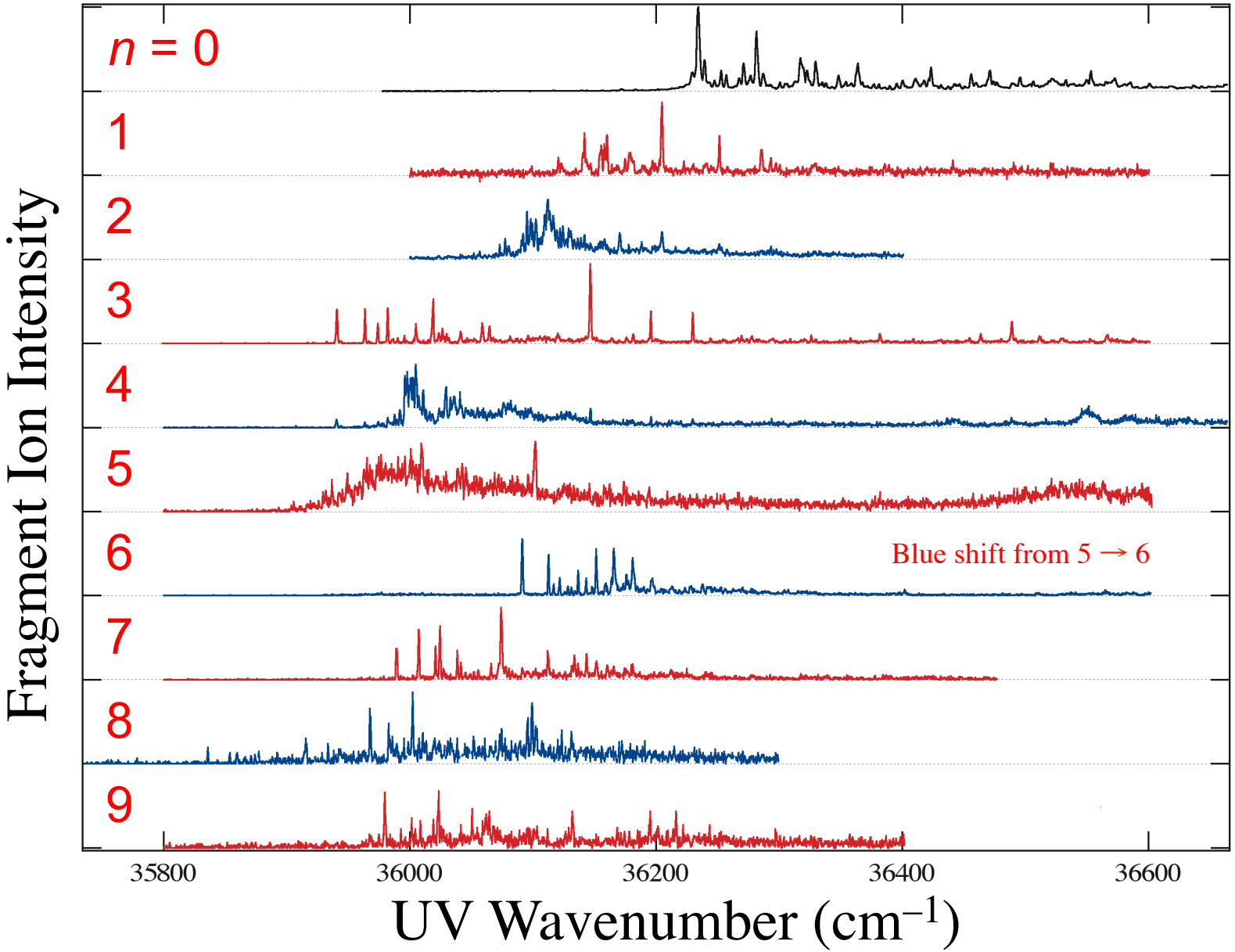
UVPD Spectra of $K^+ \cdot DB18C6 \cdot (H_2O)_n$



UVPD Spectra of $Rb^+ \cdot DB18C6 \cdot (H_2O)_n$

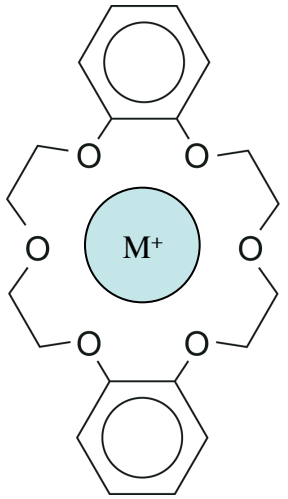


UVPD Spectra of $Cs^+ \cdot DB18C6 \cdot (H_2O)_n$



Summary

- M^+•DB18C6 ($M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+$)
- K^+•DB18C6•$(H_2O)_n$
- UV and IR spectroscopy in a cold, 22-pole ion trap

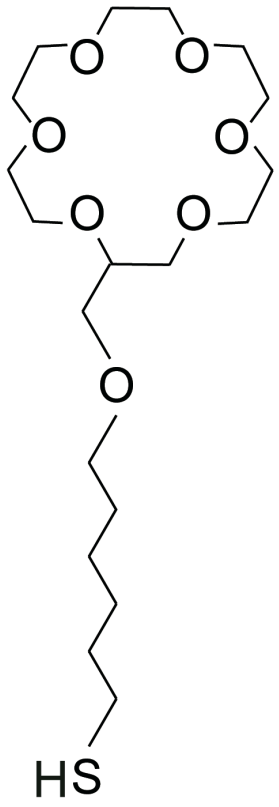


- The number and structure of conformers are determined thanks to the cooling, giving well resolved UV and IR spectra.
- This technique will provide molecular-level insights into "huge" systems in supramolecular chemistry.
- We have to extend this to larger solvated systems...
- We need spectroscopy in liquid phase…

(2) Surface-Enhanced Infrared Absorption (SEIRA) Spectroscopy

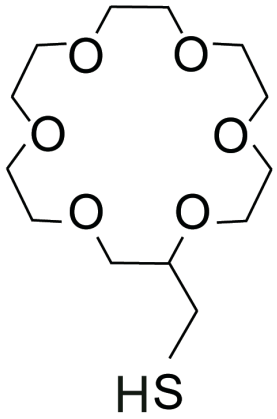
Inokuchi et al., submitted for publication

Crown Ethers Chemisorbed on Au Surface



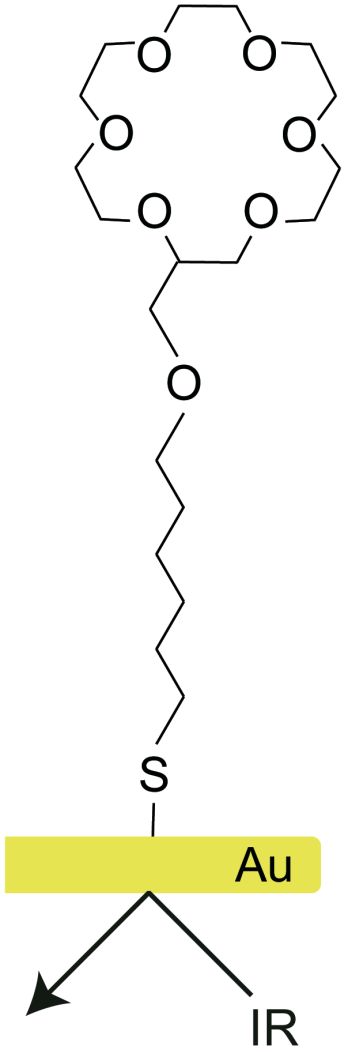
1

(a) 18C6-C_1OC_6-SH

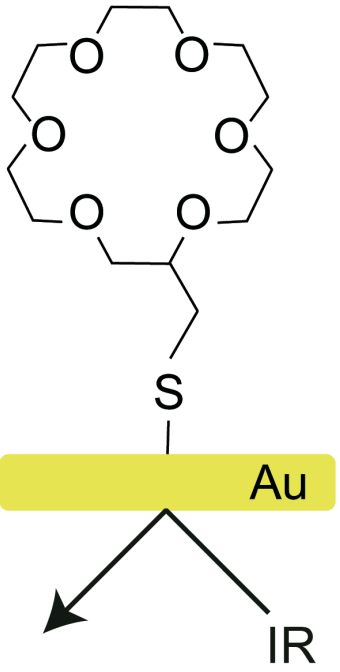


2

(b) 18C6-C_1-SH



(c) 18C6-C_1OC_6

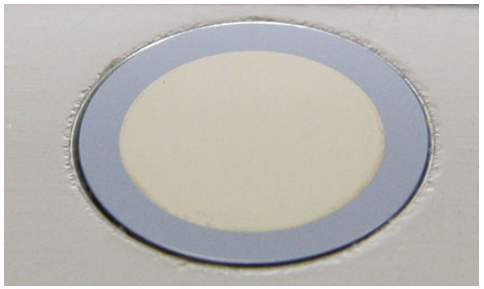


(d) 18C6-C_1

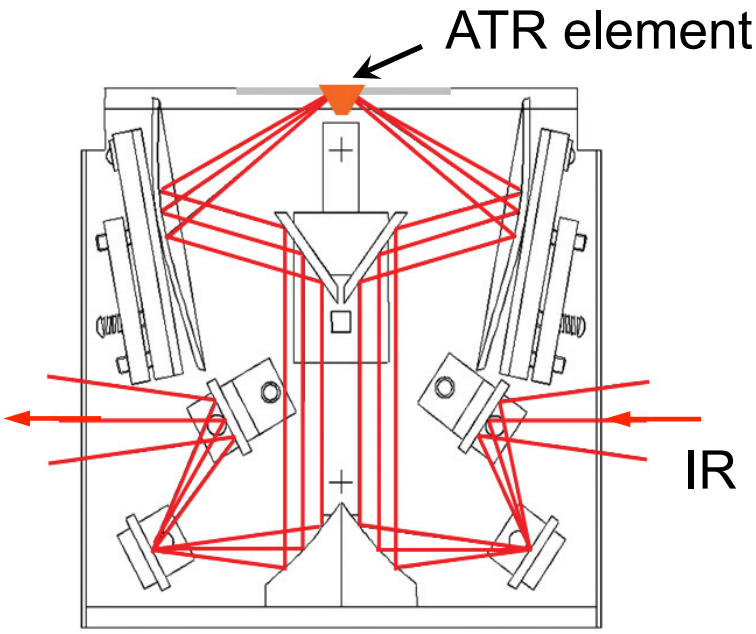
SEIRA with ATR Configuration

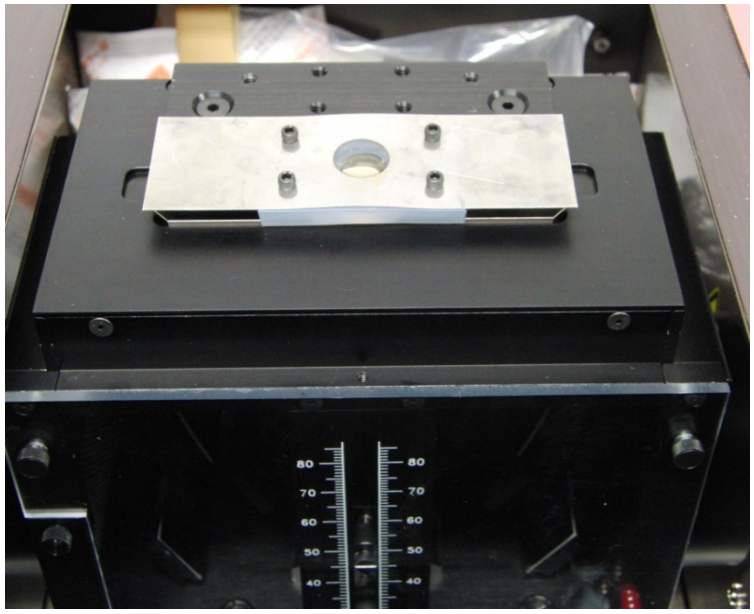
SEIRA (Surface-Enhanced IR Absorption) spectroscopy

(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.



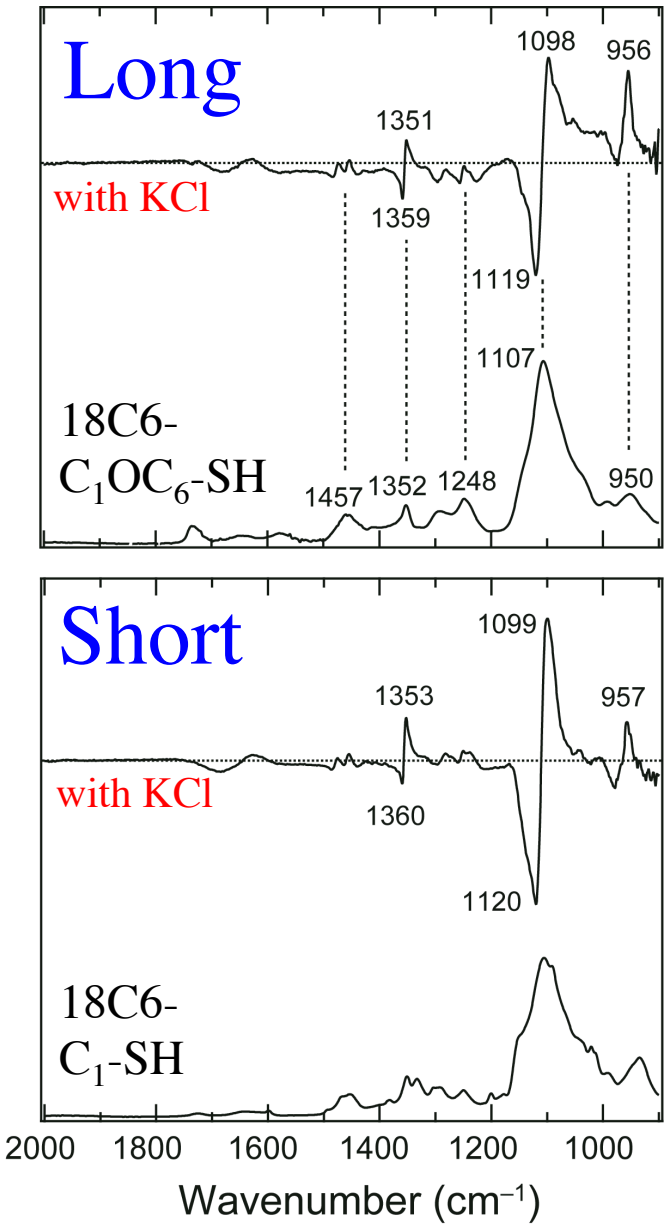
Au surface on Si prism of ATR
~ 8 nm thickness

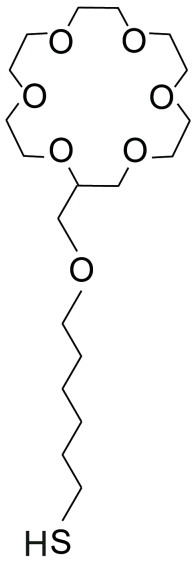




Attenuated total reflection setup

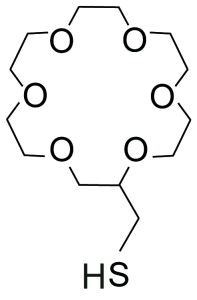
IR Spectra of K^+•18C6 on Au





1

(a) 18C6-C_1OC_6-SH



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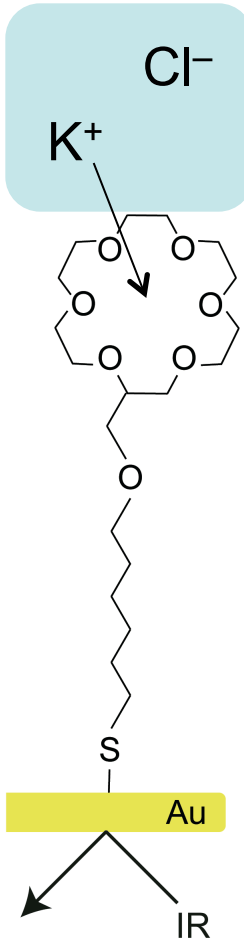
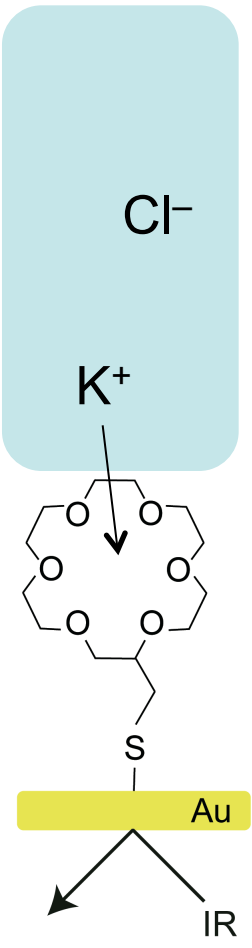
(b) 18C6-C_1-SH



(c) 18C6-C_1OC_6

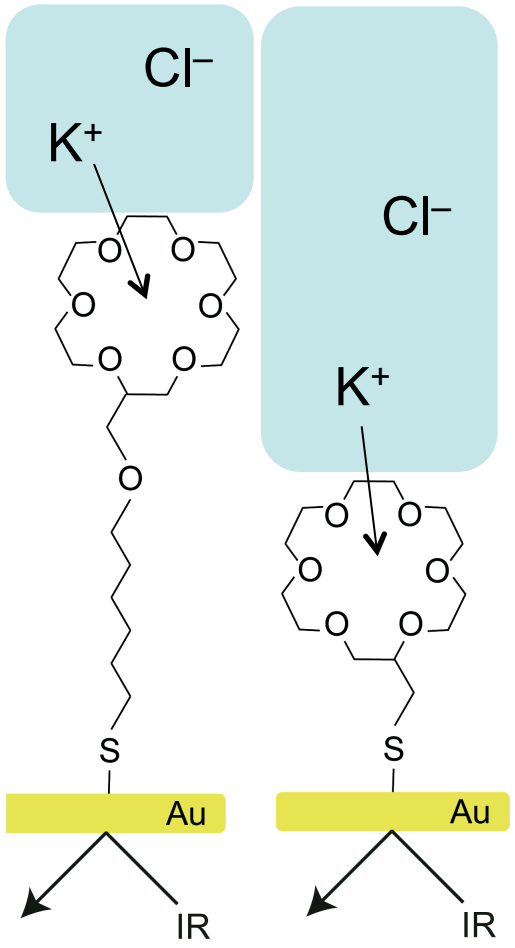


(d) 18C6-C_1

Long Short

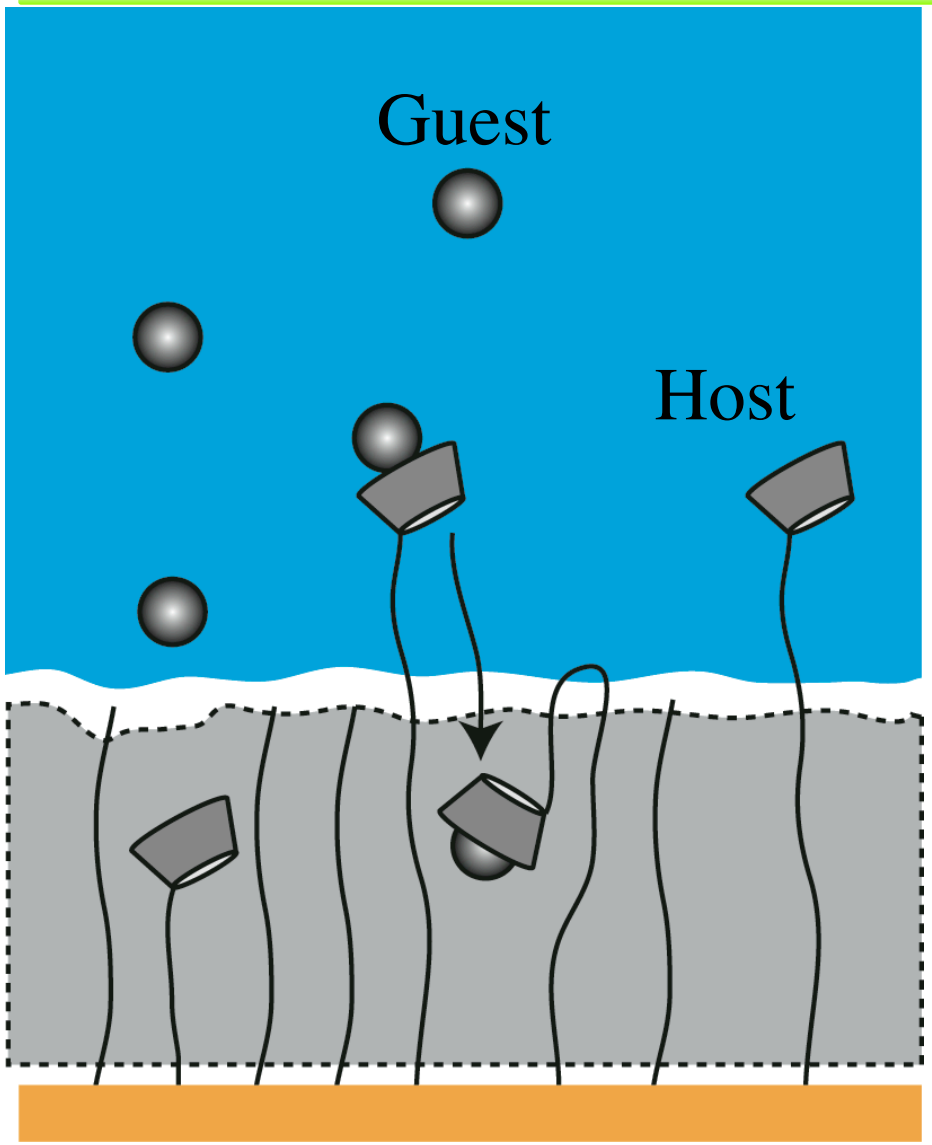
Advantages and Disadvantages

- 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

Condensed Phase, Interface



Aqueous phase

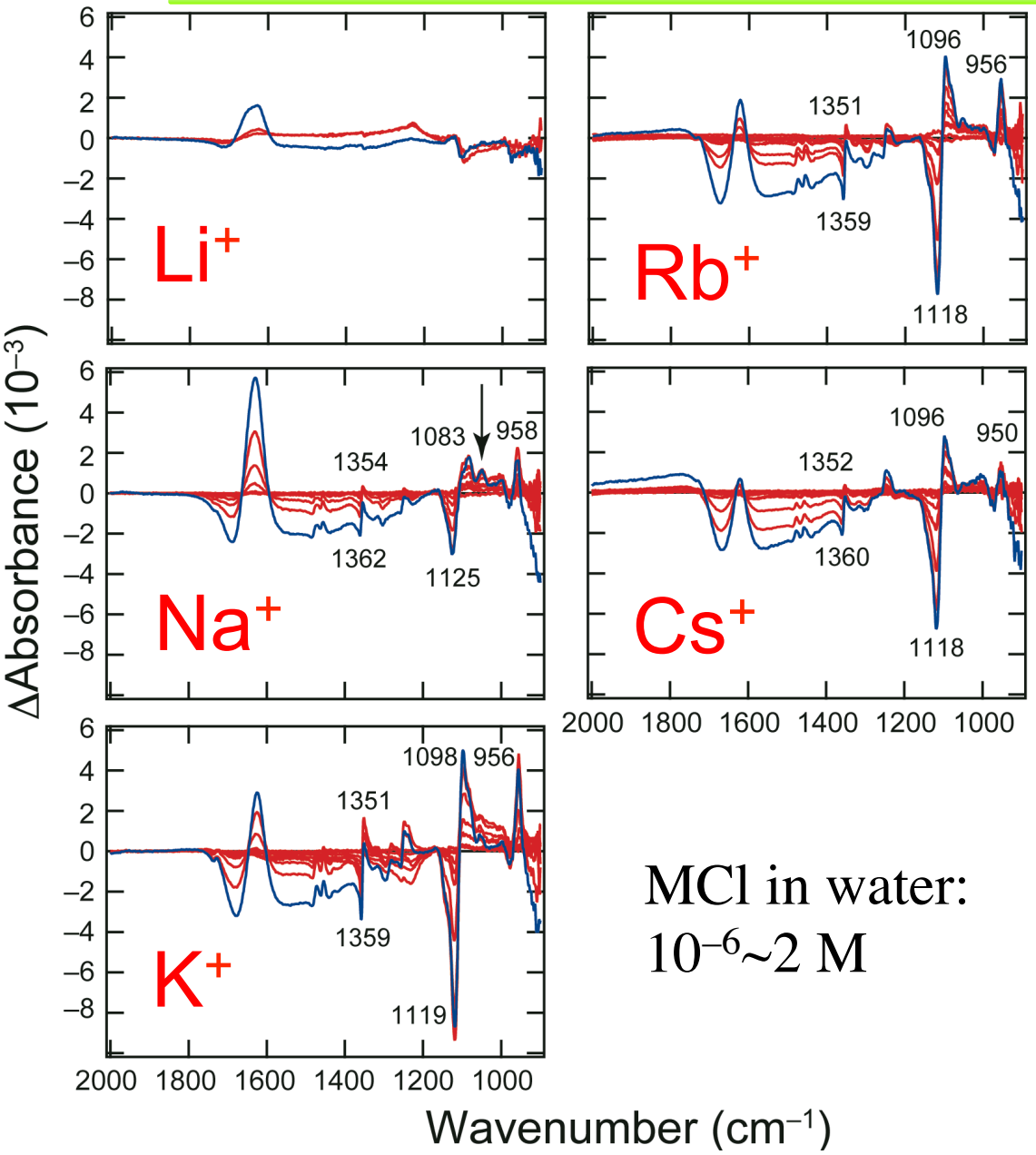
Interface

Organic phase

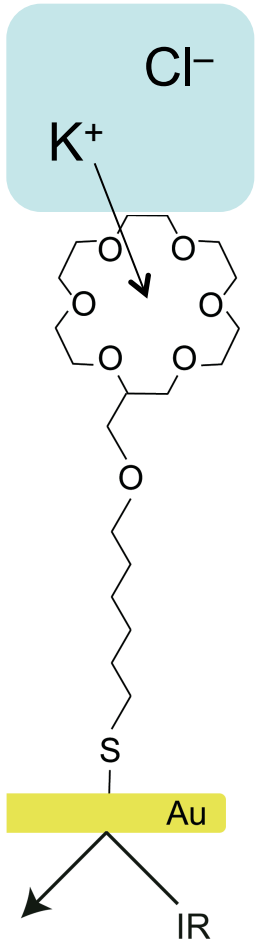
Au surface

Position of complexes is controllable.

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

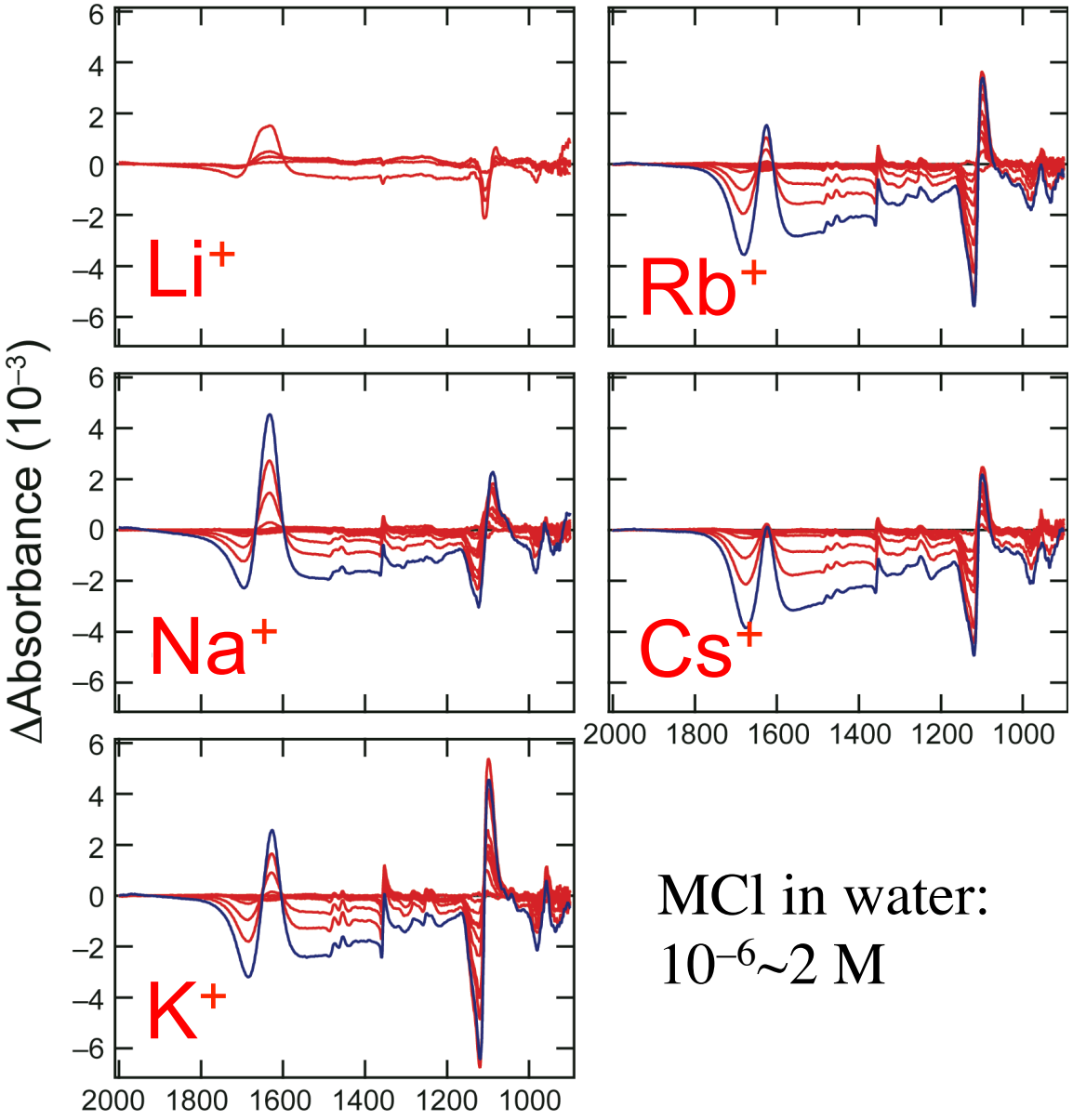


MCl in water:
10^{-6}~2 M

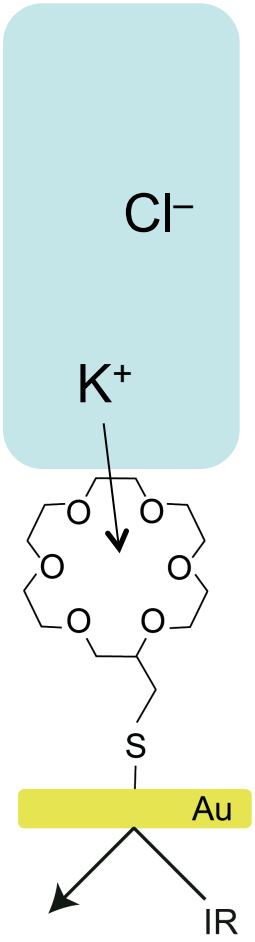


18C6-C_1OC_6

IR Difference Spectra of M^+•18C6-C_1

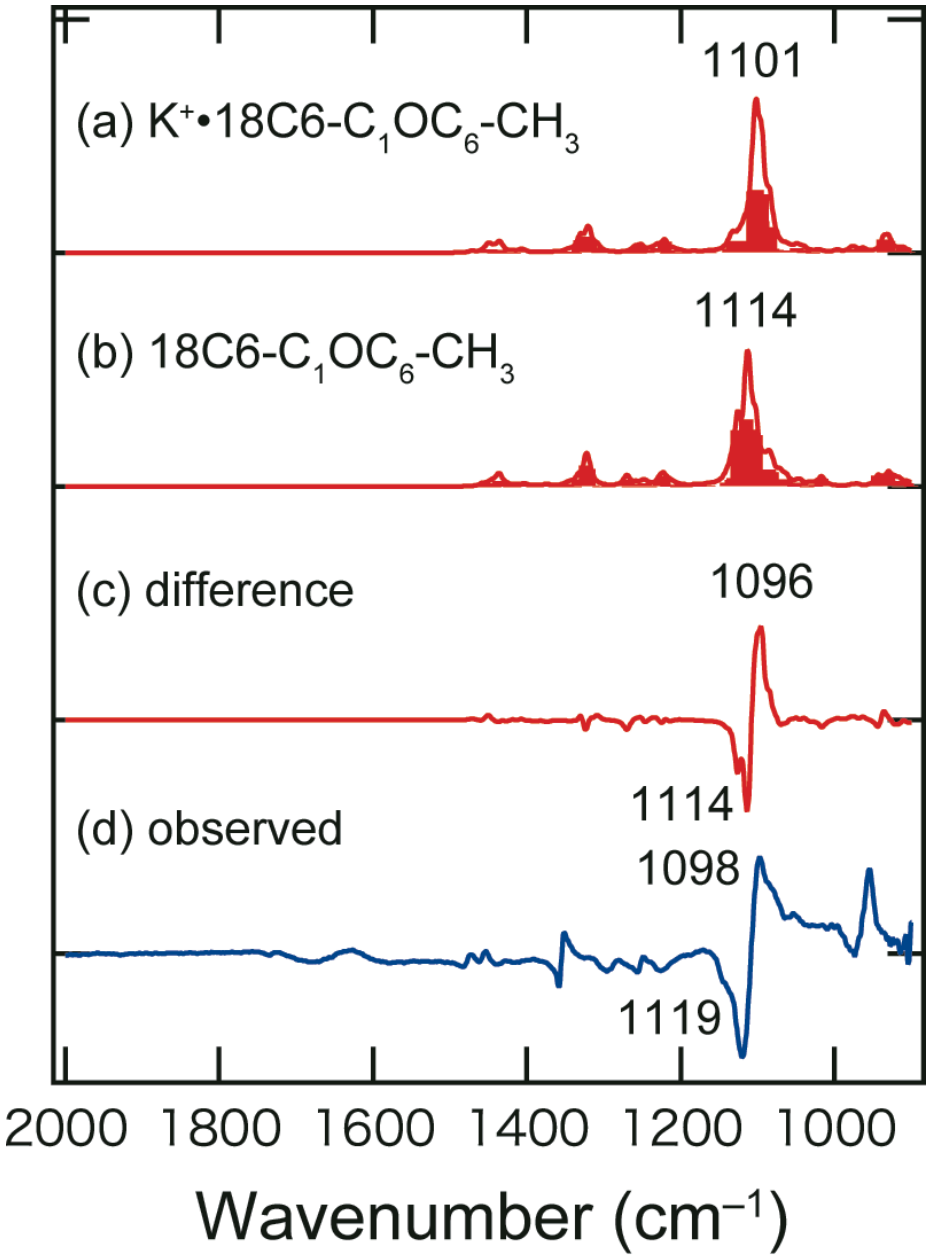


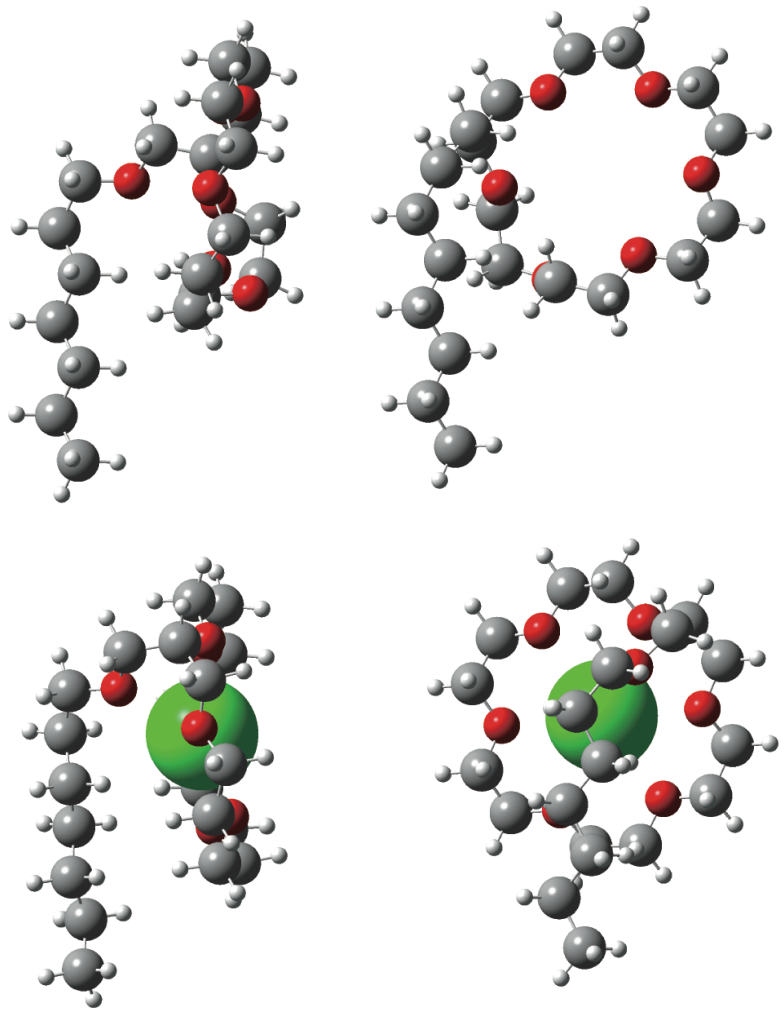
MCl in water:
10^{-6}~2 M



18C6-C_1

Comparison of IR Spectra

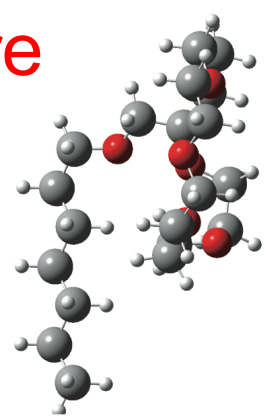


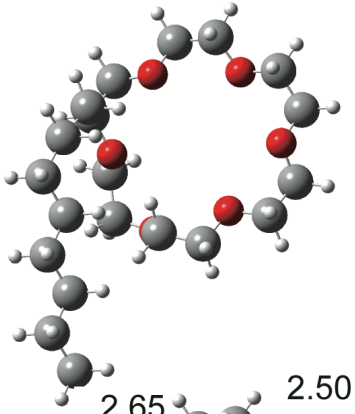


Calculated in water with PCM
(polarizable continuum model)

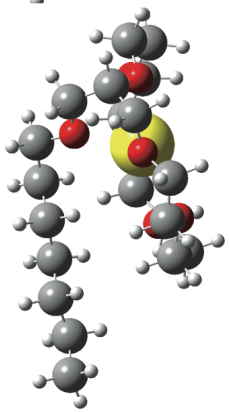
Structure of M^+•18C6-C_1OC_6-CH_3

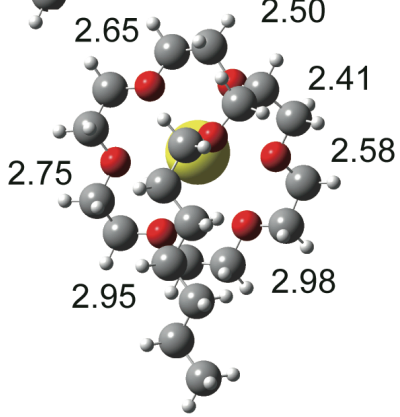
bare



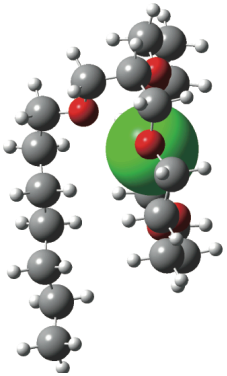


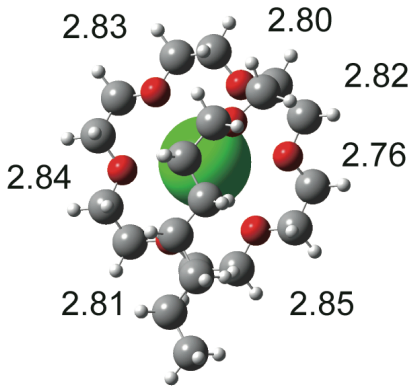
Na^+



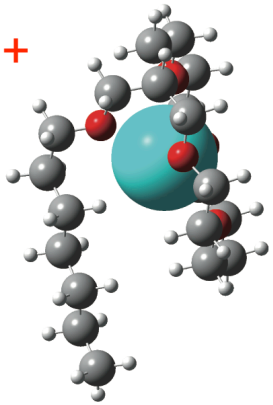


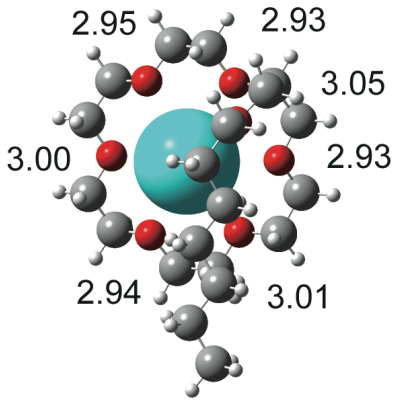
K^+



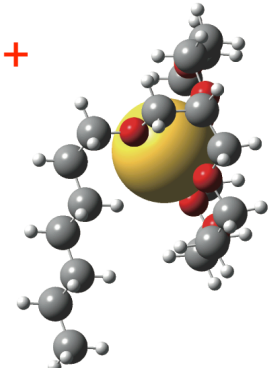


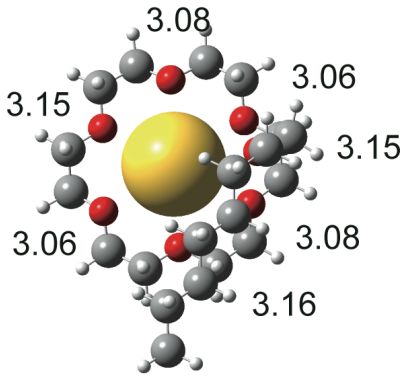
Rb^+





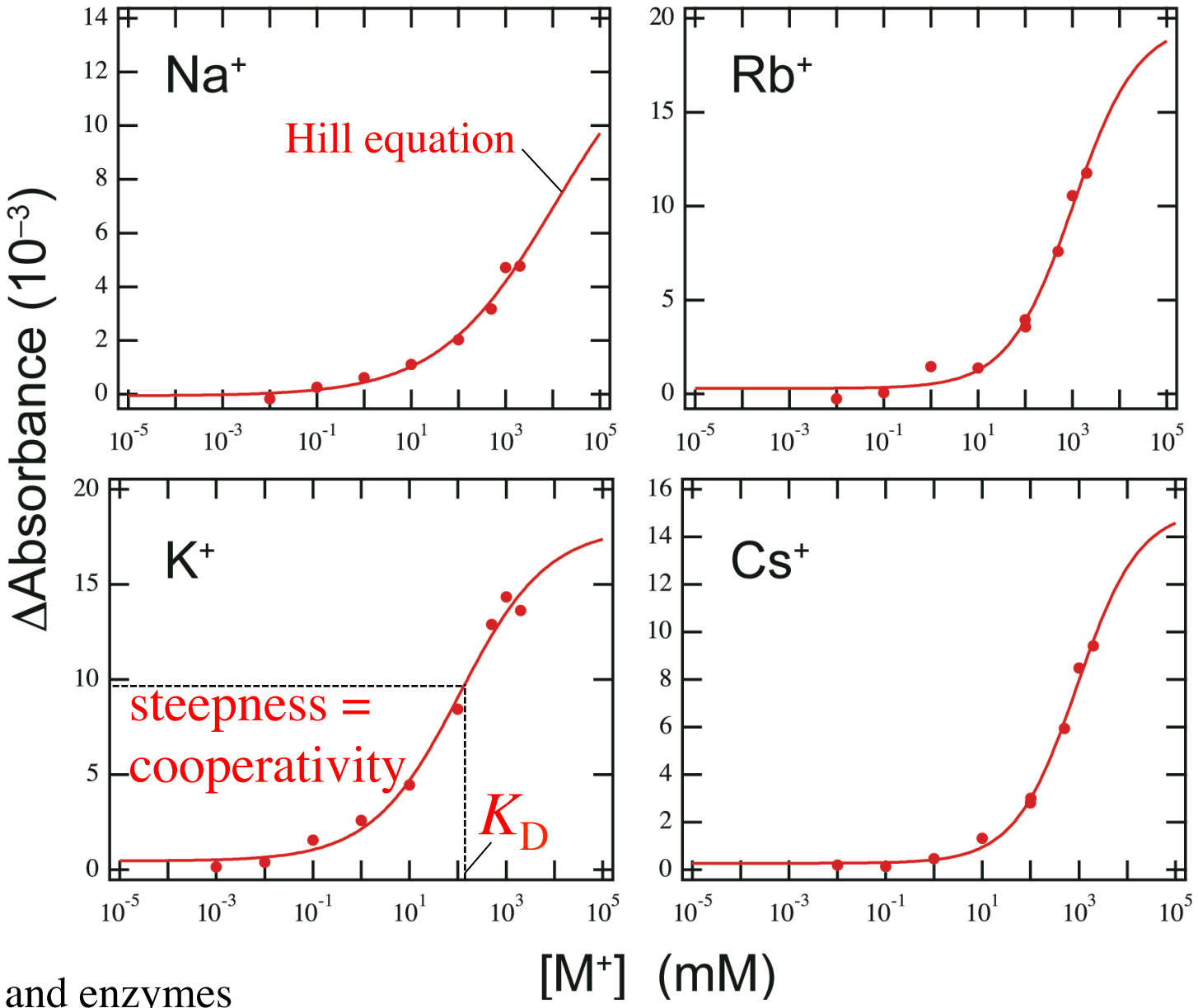
Cs^+





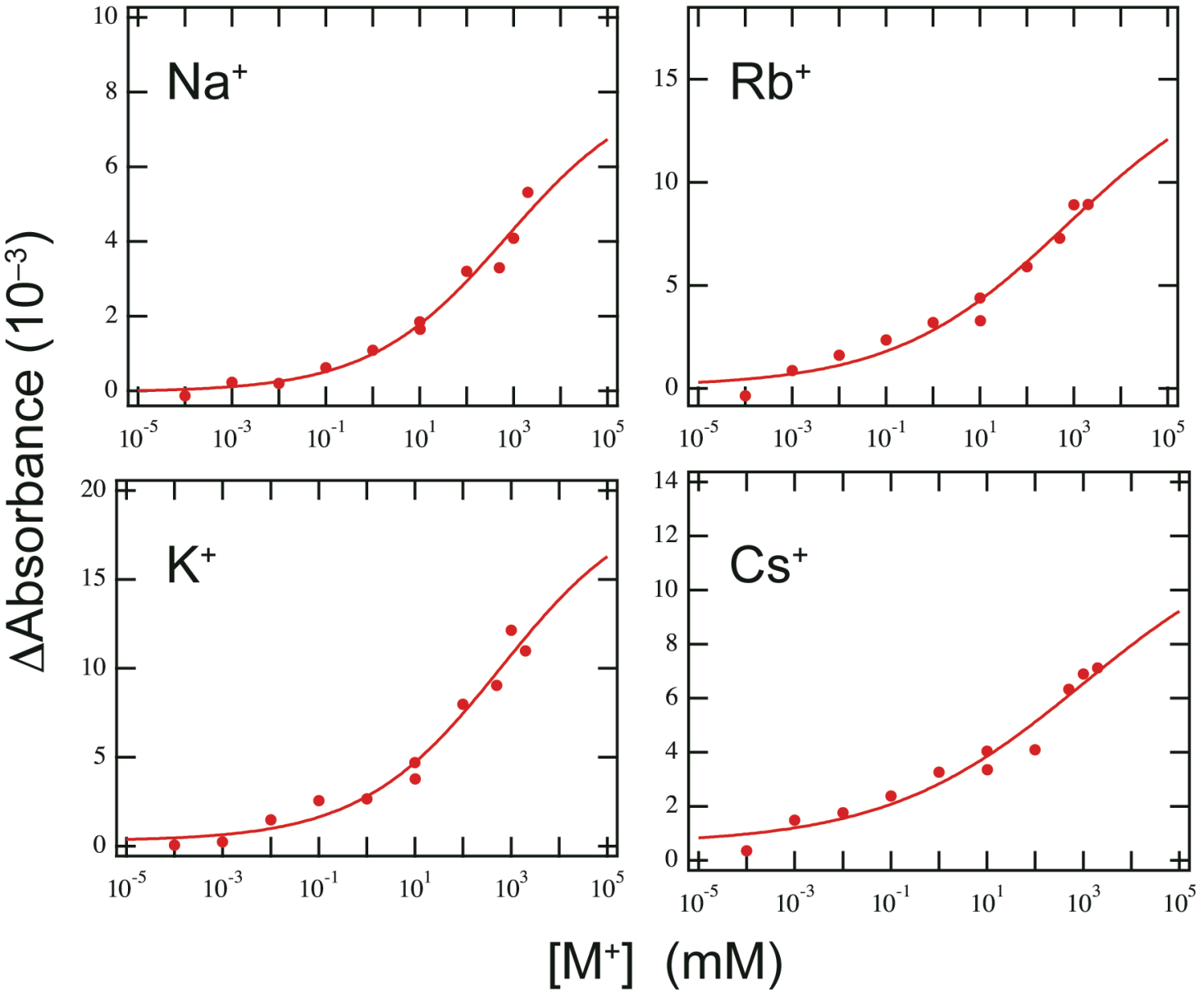
Molecules act as a lariat and complexes are folded

Titration Curves for M^+•18C6-C_1OC_6

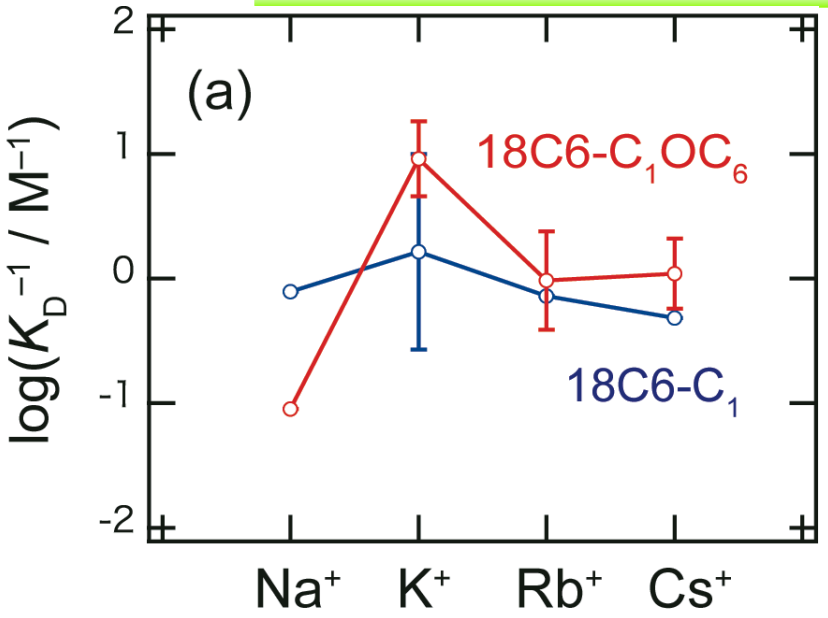


substrates and enzymes

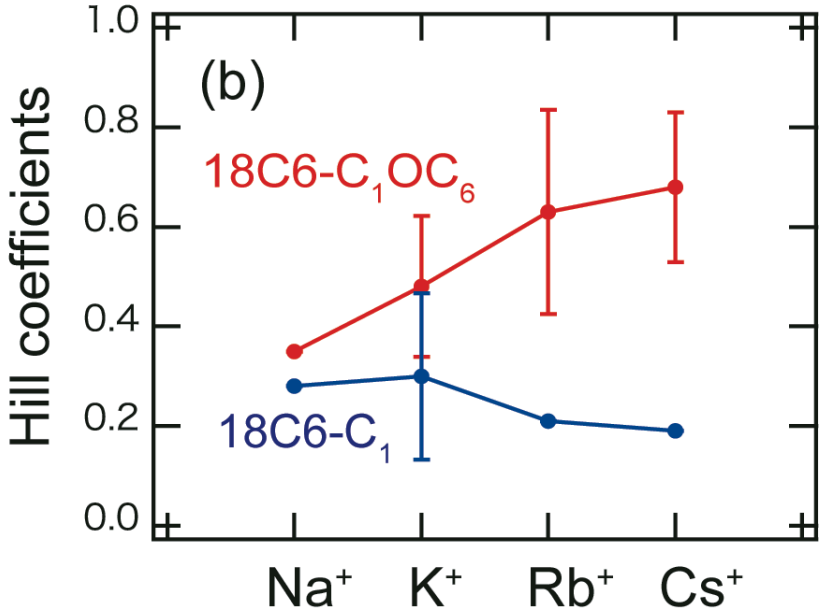
Titration Curves for M^+•18C6-C_1



K_D and Hill Coefficients



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

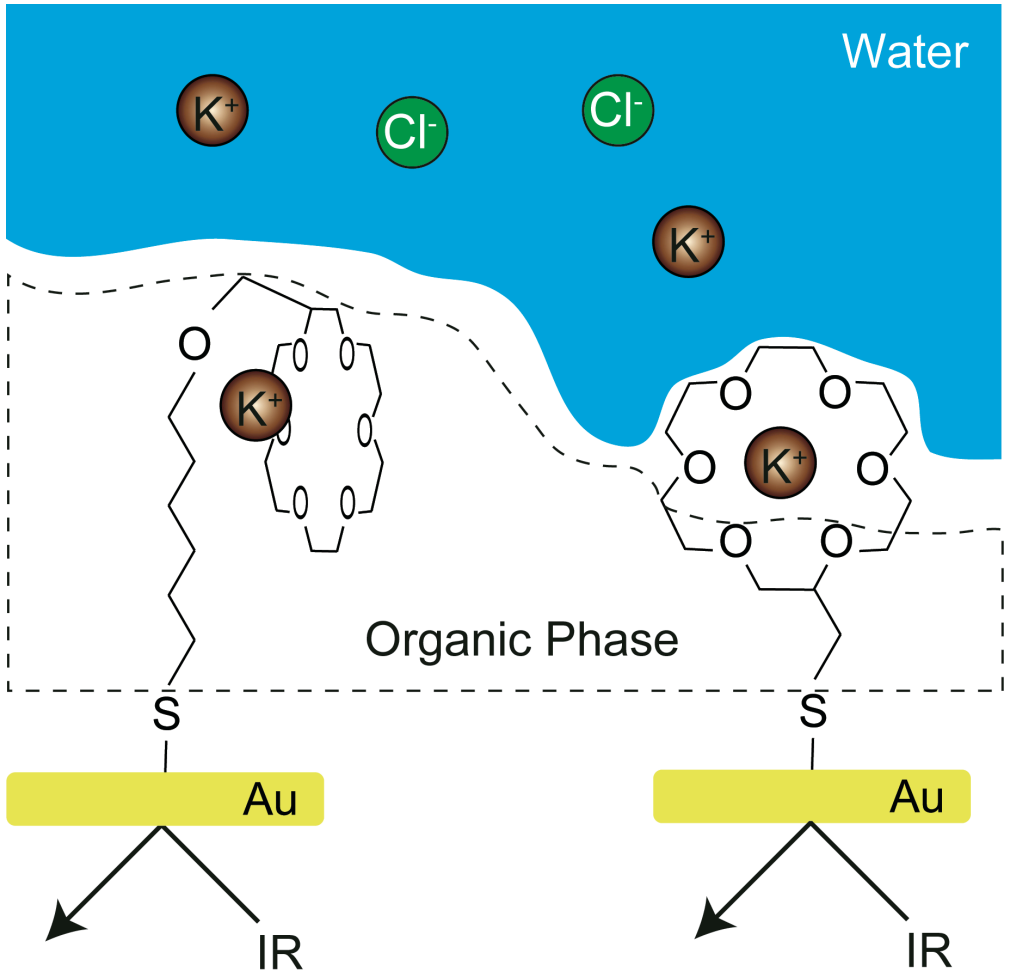


steepness

18C6-C_1 shows more
negative 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

- 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