UV and IR Spectroscopy of Metal Ion-Crown Ether Complexes in the Gas Phase

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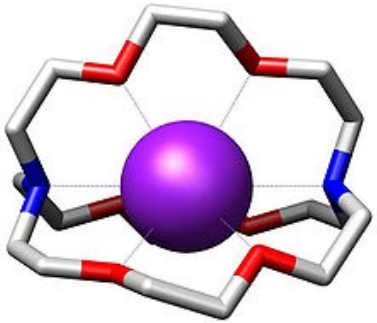
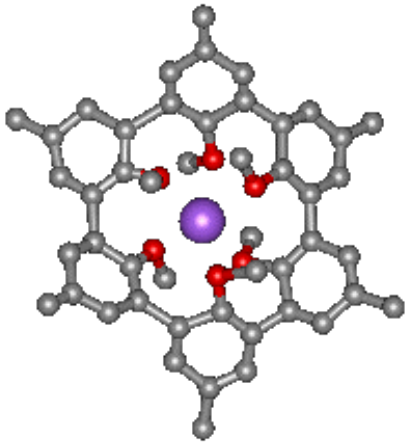
¥¥¥ Japan Society for the Promotion of Science (JSPS)

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

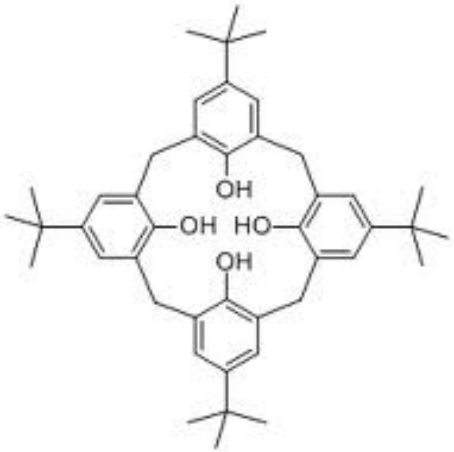
Ionophores



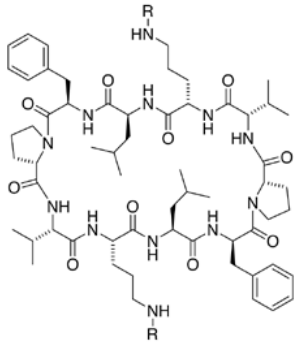
Cryptand



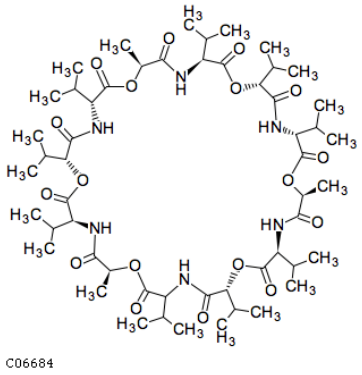
Spherand



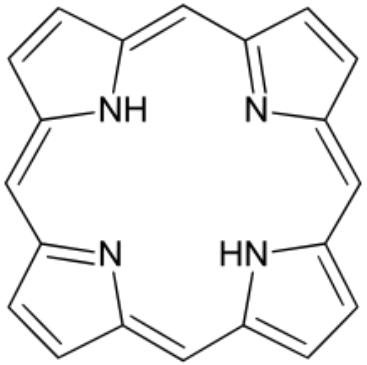
Calixarene



Gramicidine



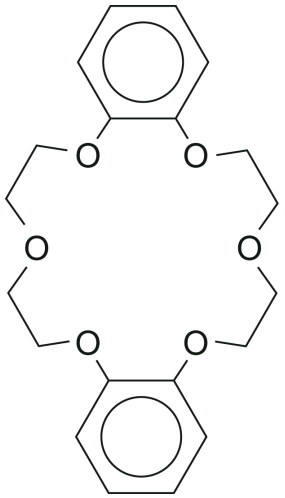
Valinomycin



Porphyrin

Crown Ethers

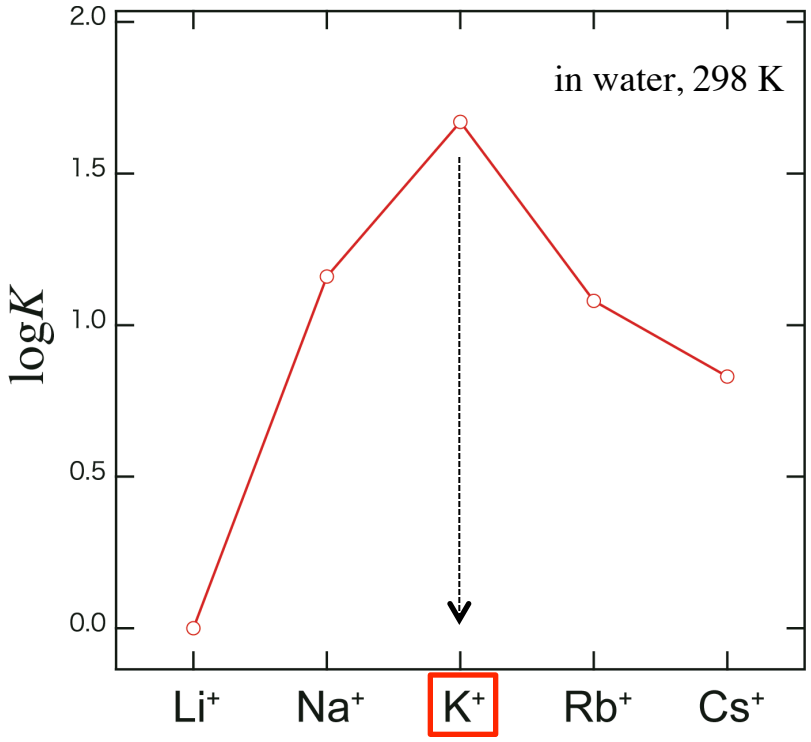
- Ionophores
- Used as phase-transfer catalysts
- *Ion selectivity*



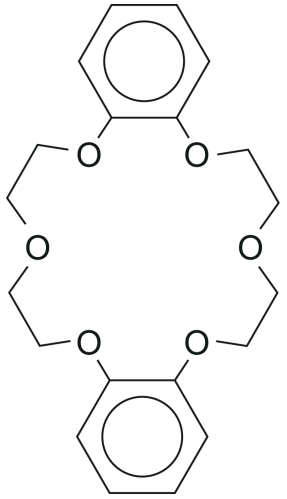
Dibenzo-18-crown-6
(DB18C6)

Ion Selectivity

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



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

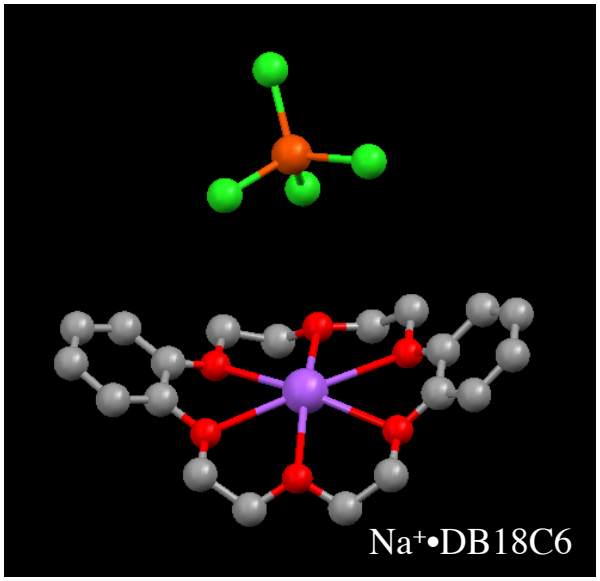


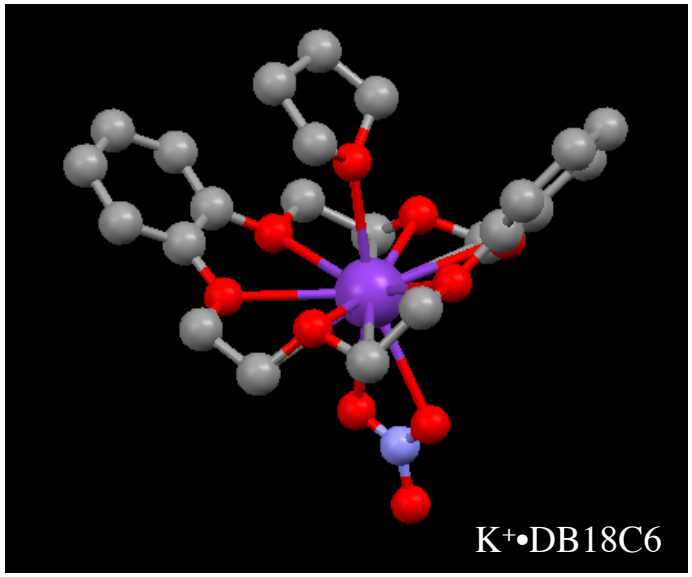
DB18C6

DB18C6 captures K^+ selectively

Due to optimum matching in size?

Crystal Structure





(Cambridge Structural Database)

Conformations similar for Na^+ and K^+

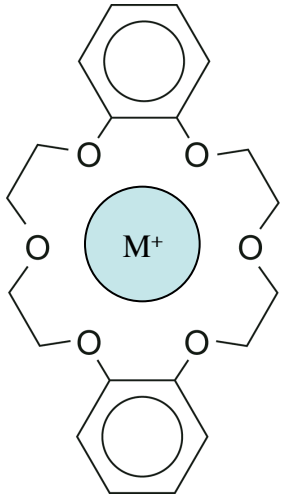
Counter anions also bonded to M^+ , affecting the structure

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

We study complexes in the gas phase under cold conditions

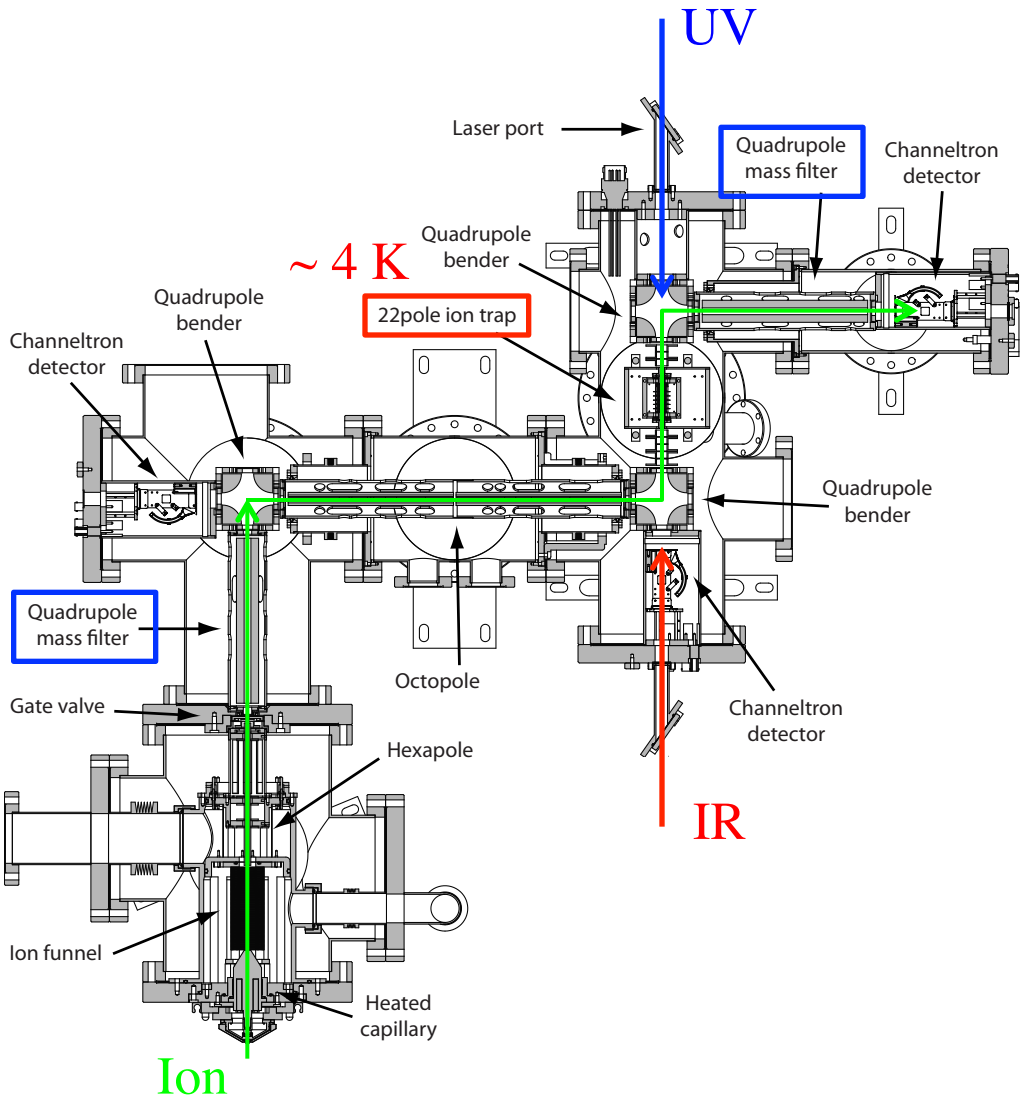
This Study

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

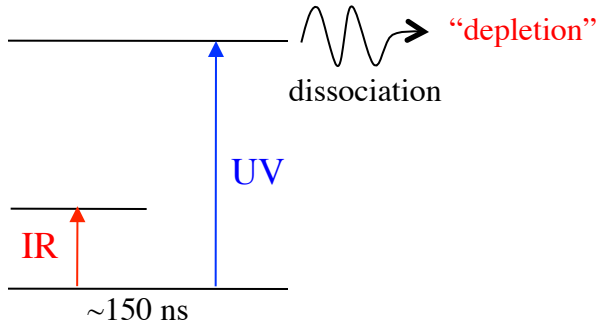


- UV and IR spectroscopy in a cold, 22-pole ion trap
  DFT, TD-DFT
- The number and structure of conformers determined

Experimental

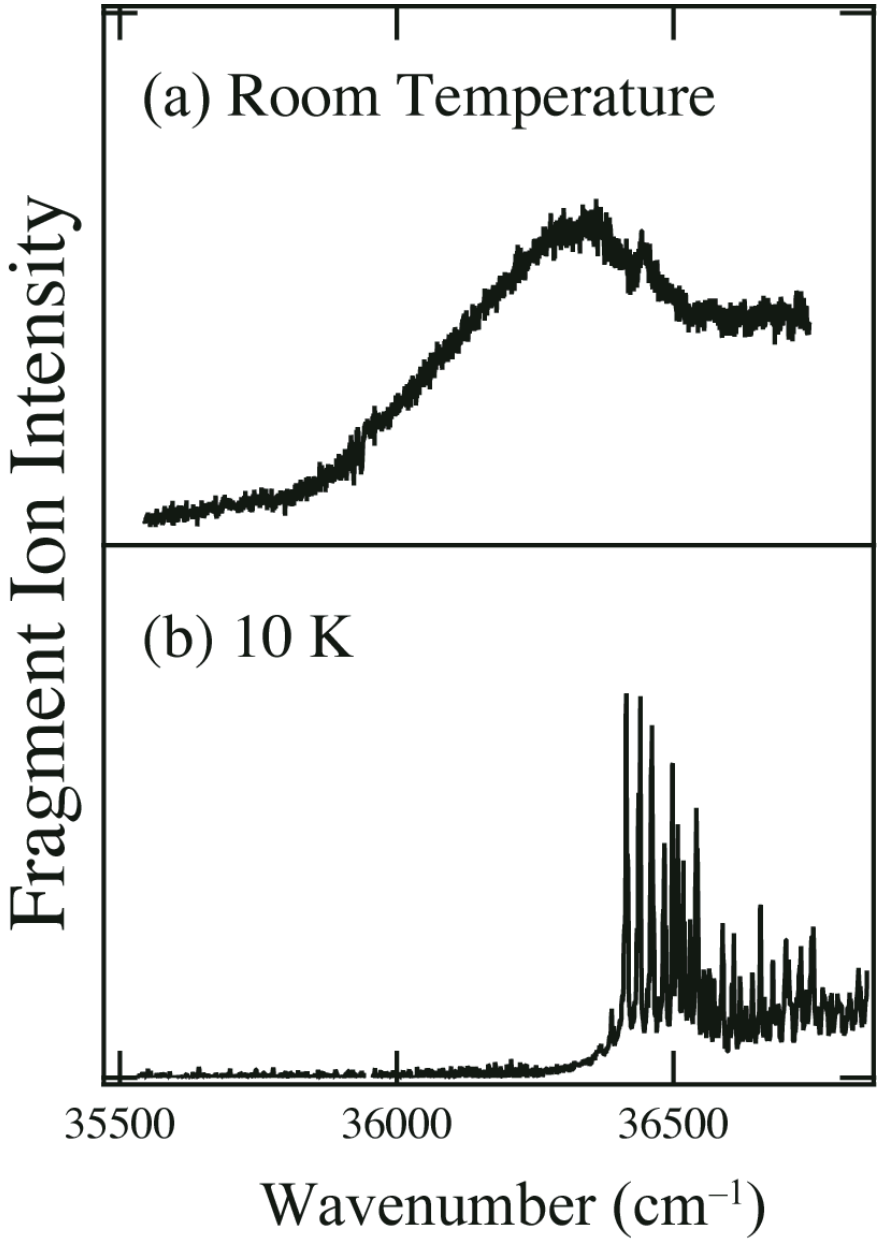


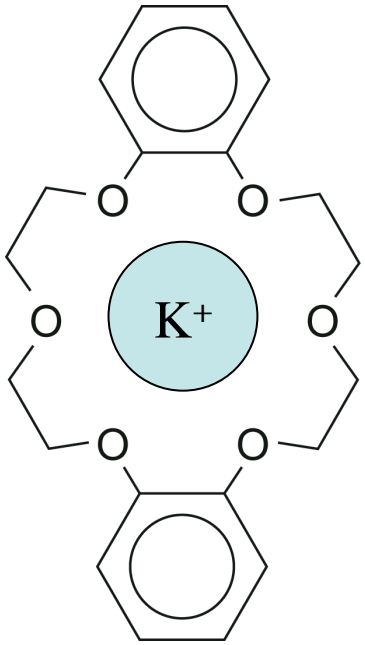
- nanoelectrospray
  - DB18C6
  - LiCl, NaCl, KCl, RbCl, CsCl
  - in Methanol
  - 20–200 μM
- UV photodissociation spectroscopy
- IR-UV double-resonance
  - UV power 1–1.5 mJ/pulse
  - IR power 4–5 mJ/pulse



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

UV Spectra of K^+•DB18C6

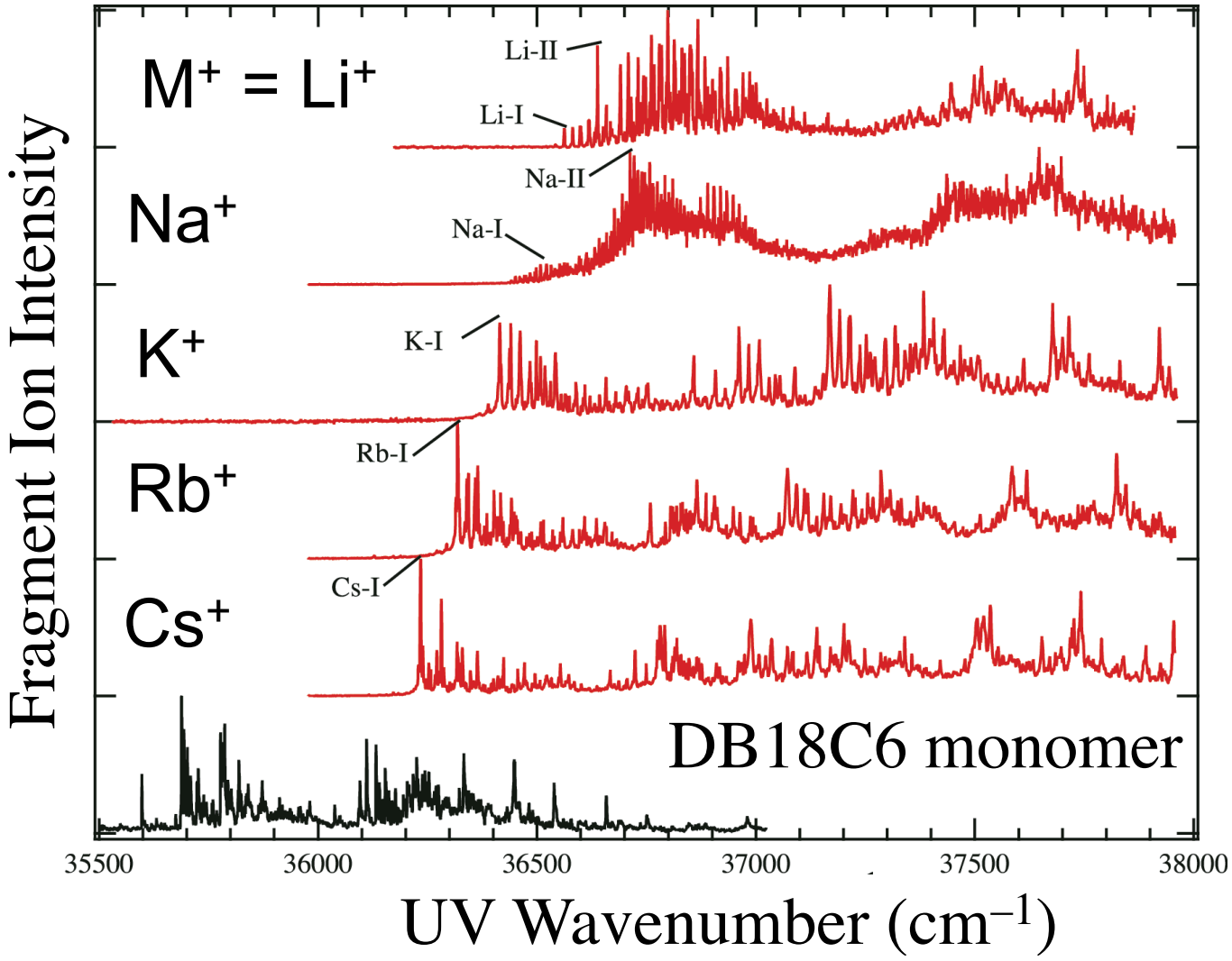


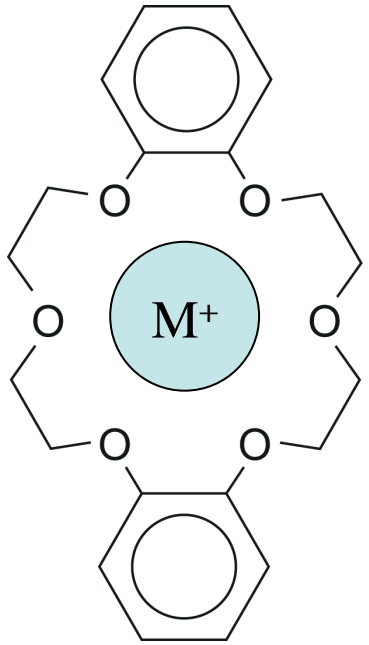


K^+•DB18C6

Sharp vibronic bands
are observed
under cold condition

UV Spectra of M^+•DB18C6

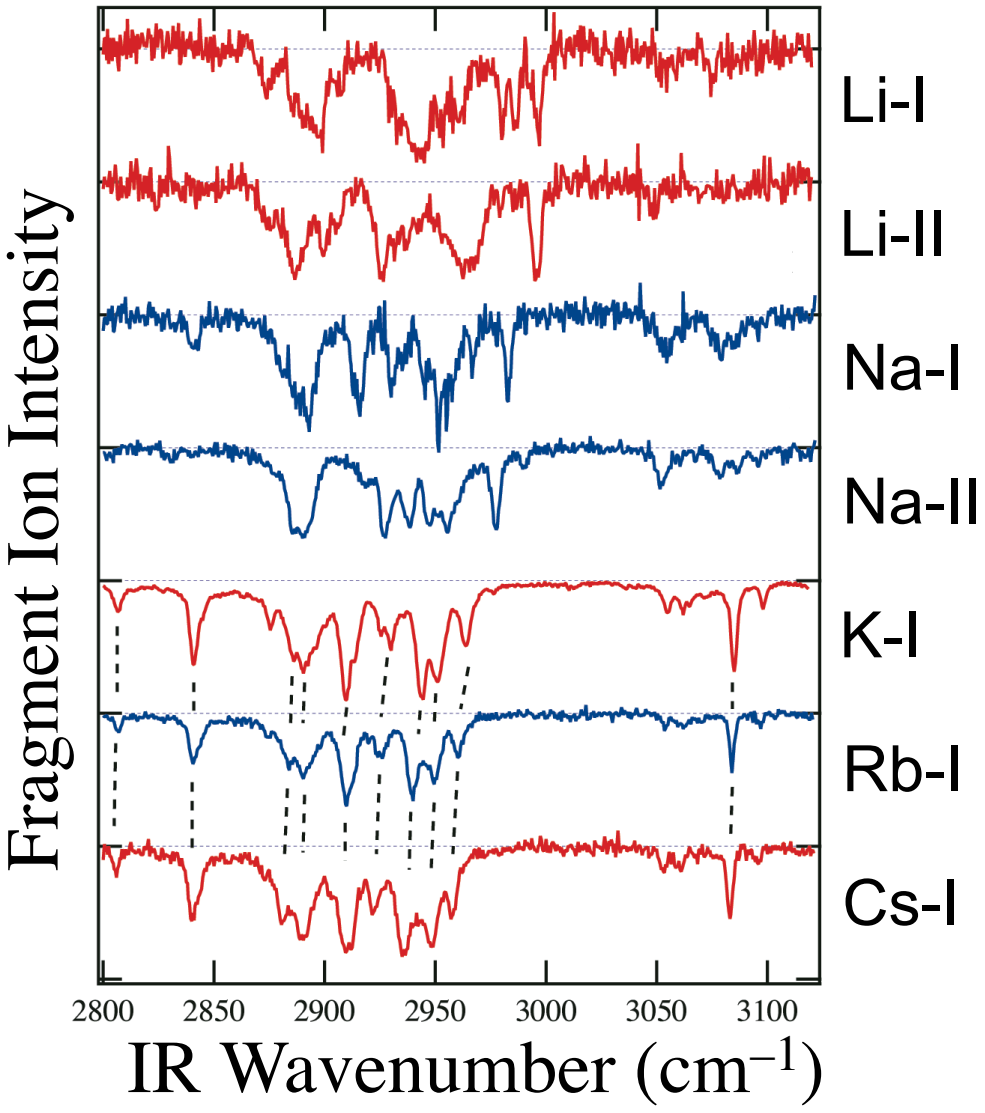


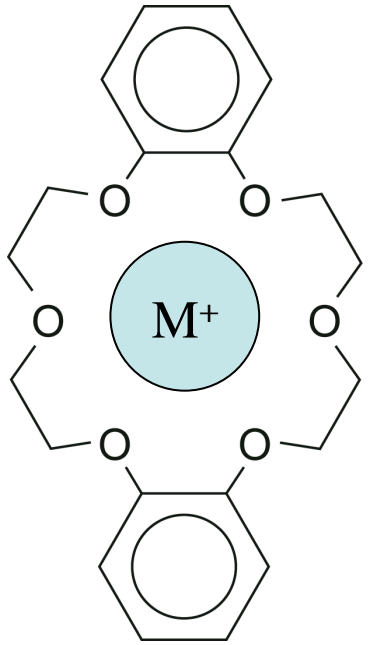


M^+•DB18C6

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

IR Spectra of M^+•DB18C6

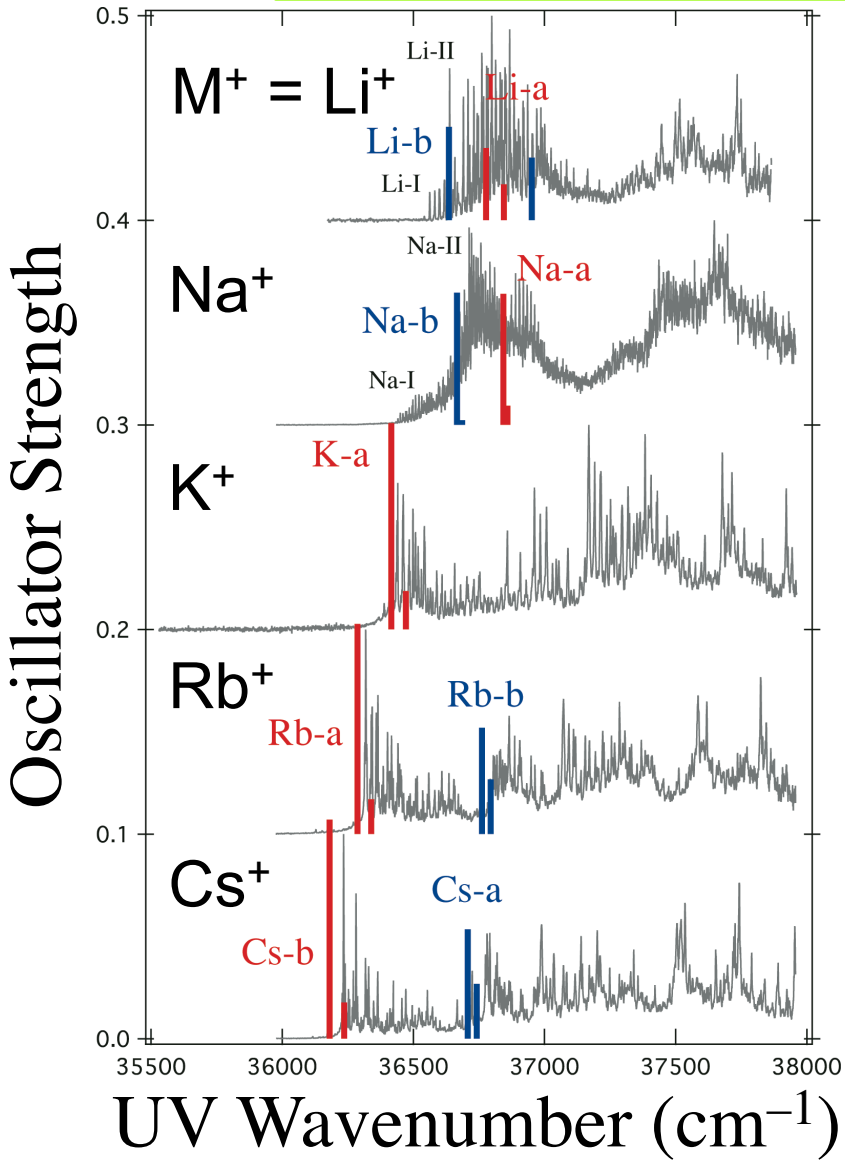




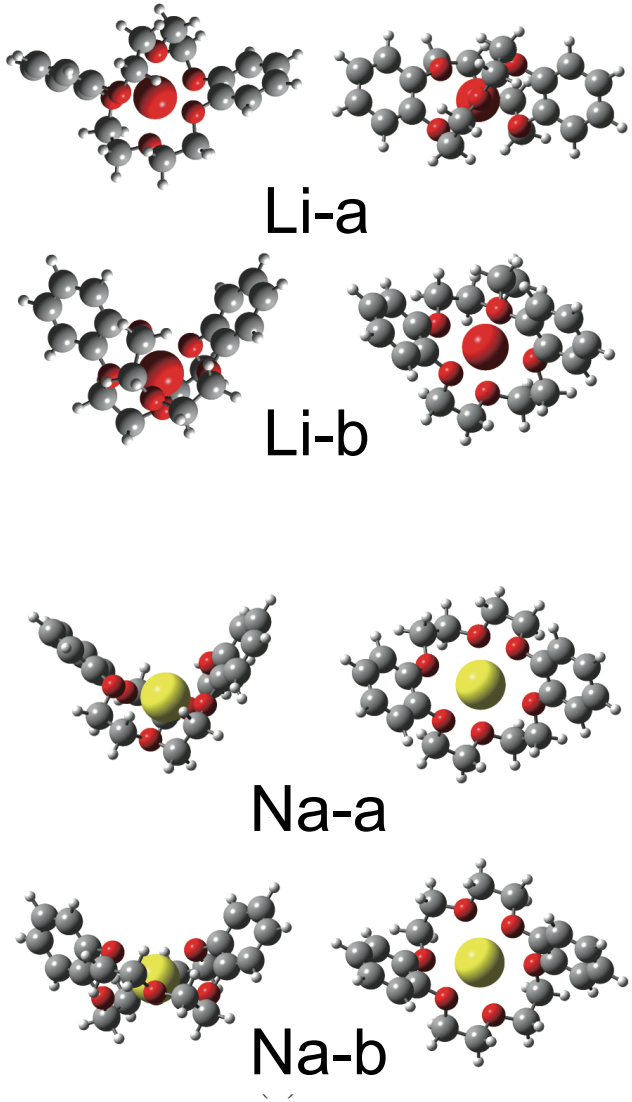
M^+•DB18C6

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

Structure of $M^+ \bullet DB18C6$ (M = Li, Na)

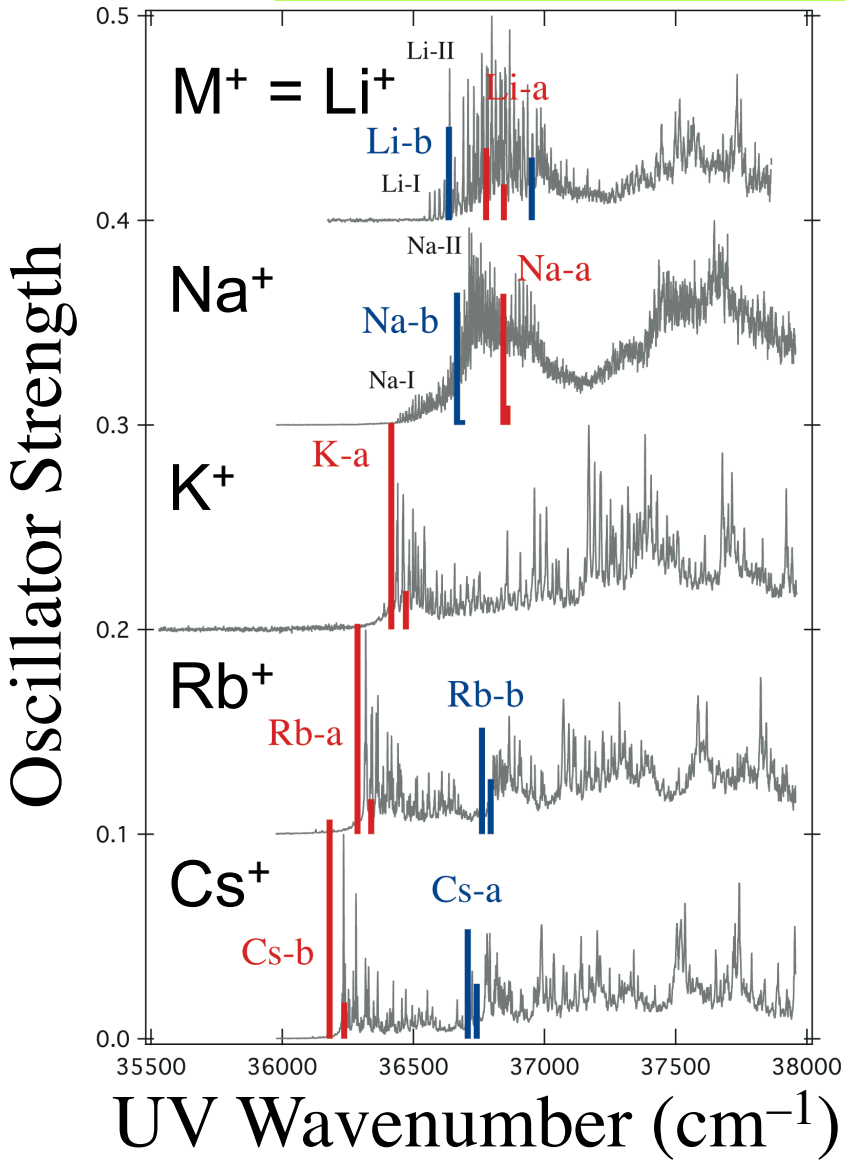


M05-2X/6-31+G(d) with Stuttgart RLC ECP
A scaling factor of 0.8340 is used.

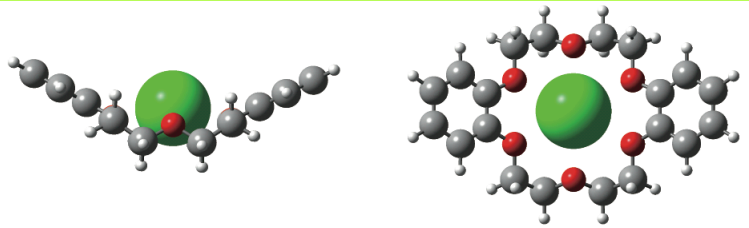


Ether rings distorted for Li^+ and Na^+

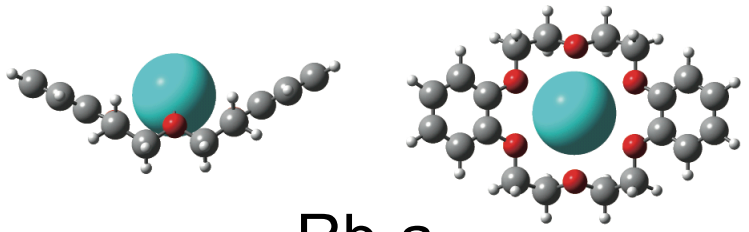
Structure of M^+•DB18C6 (M = Li, Na)



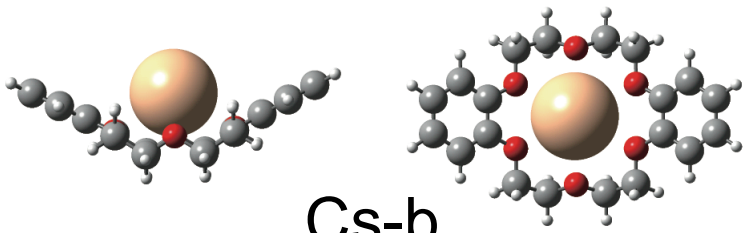
M05-2X/6-31+G(d) with Stuttgart RLC ECP
A scaling factor of 0.8340 is used.



K-a



Rb-a



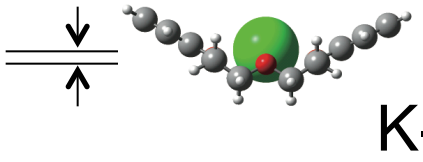
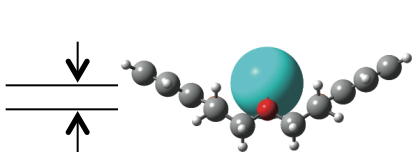
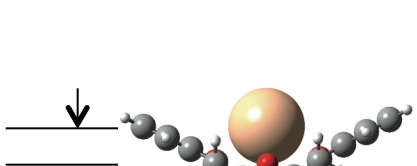
Cs-b

Ether rings largely open

K^+ in the ring

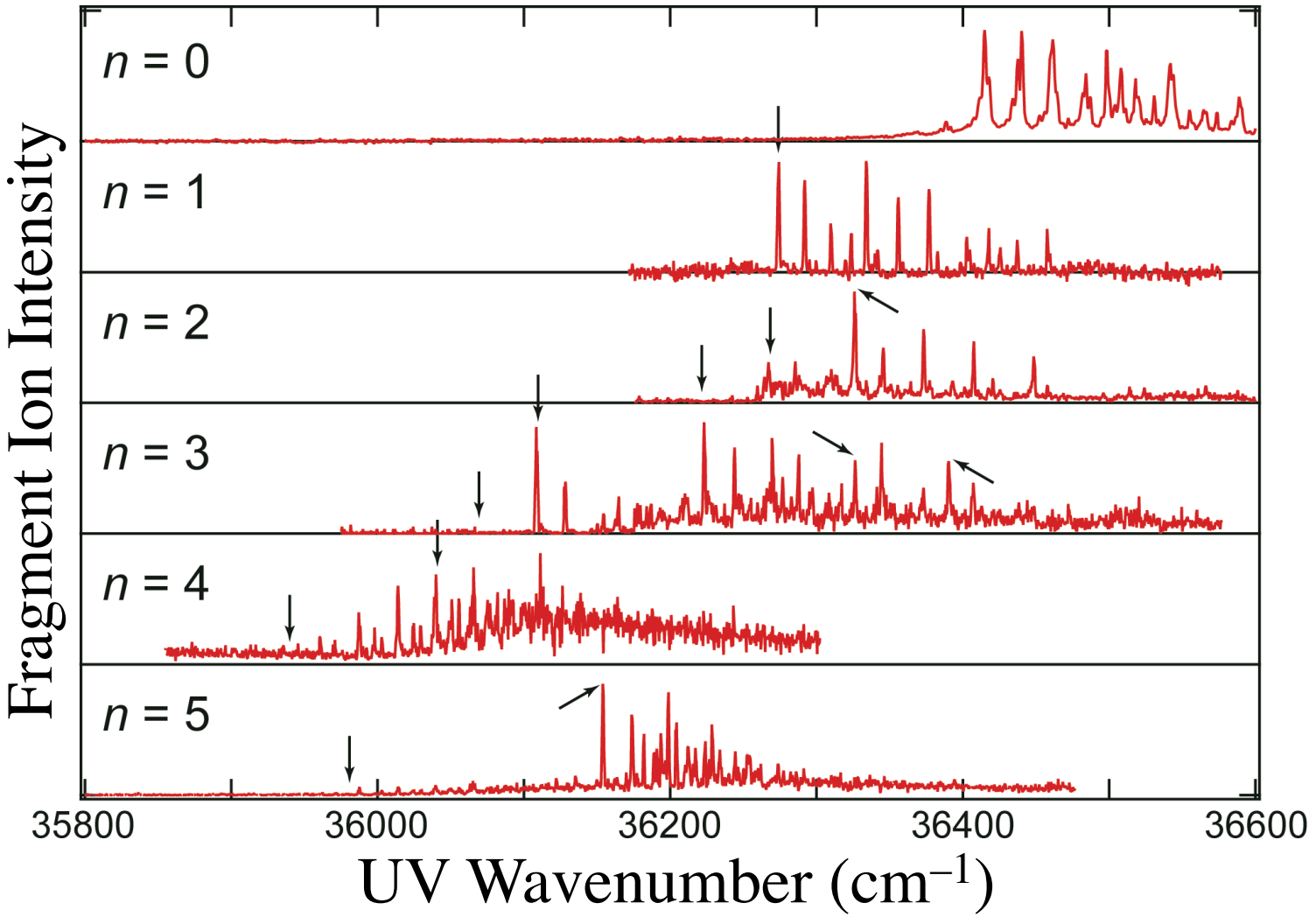
Rb^+, Cs^+ on the ring

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

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

cf. Li^+ (0.90 Å), Na^+ (1.16 Å)

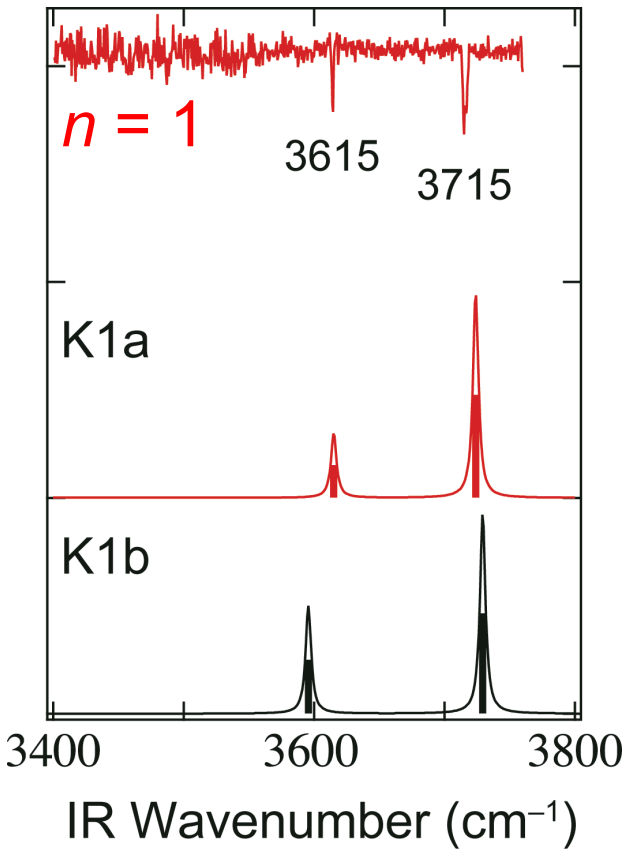
UV Spectra of $K^+ \cdot DB18C6 \cdot (H_2O)_n$

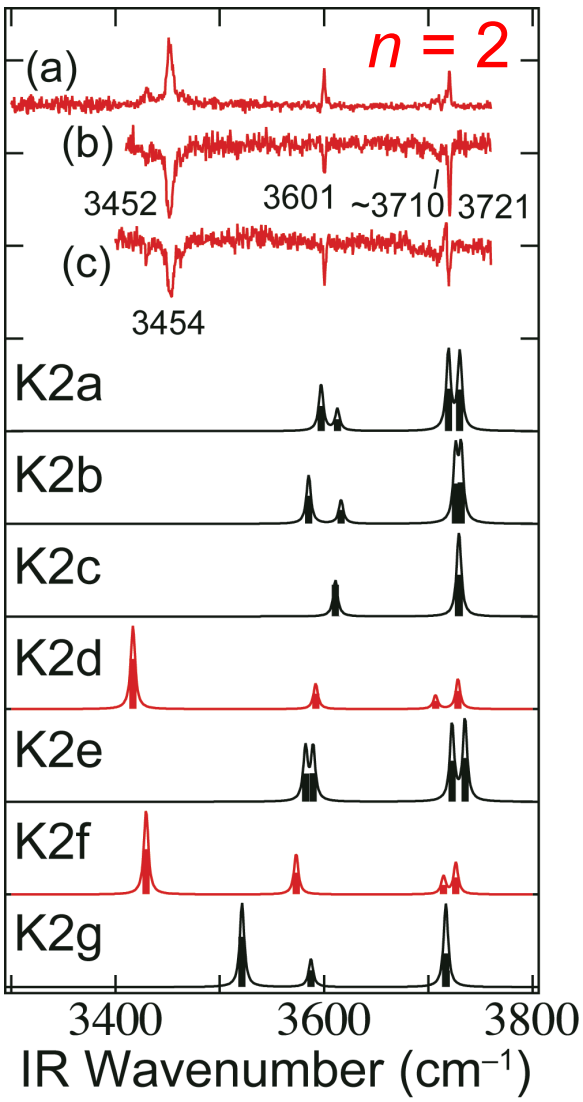


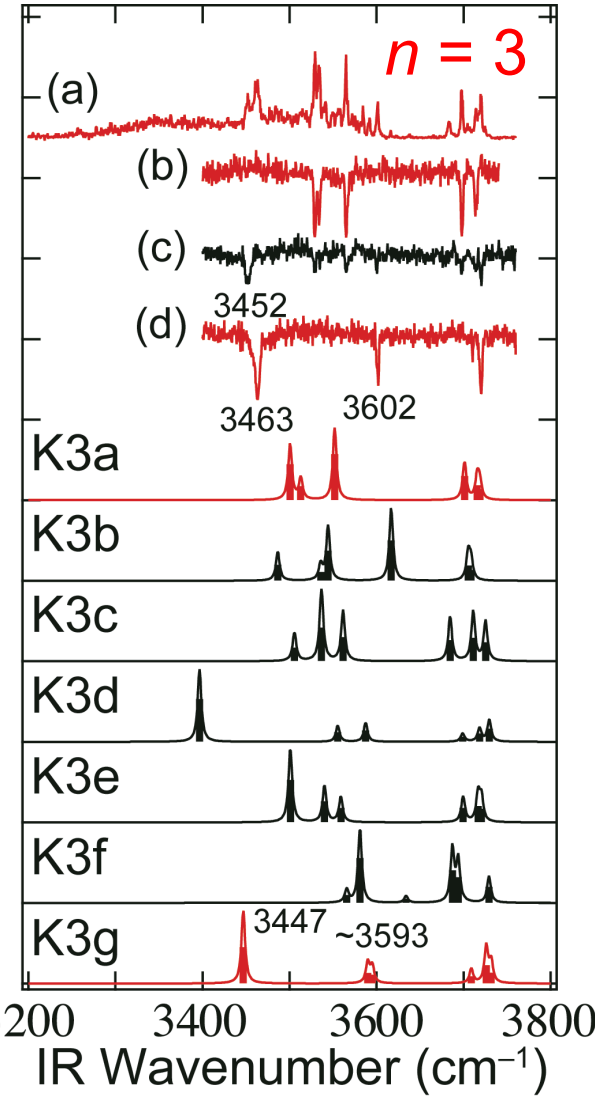
UV spectra also show sharp bands.

→ Conformer-specific IR spectra can be measured.

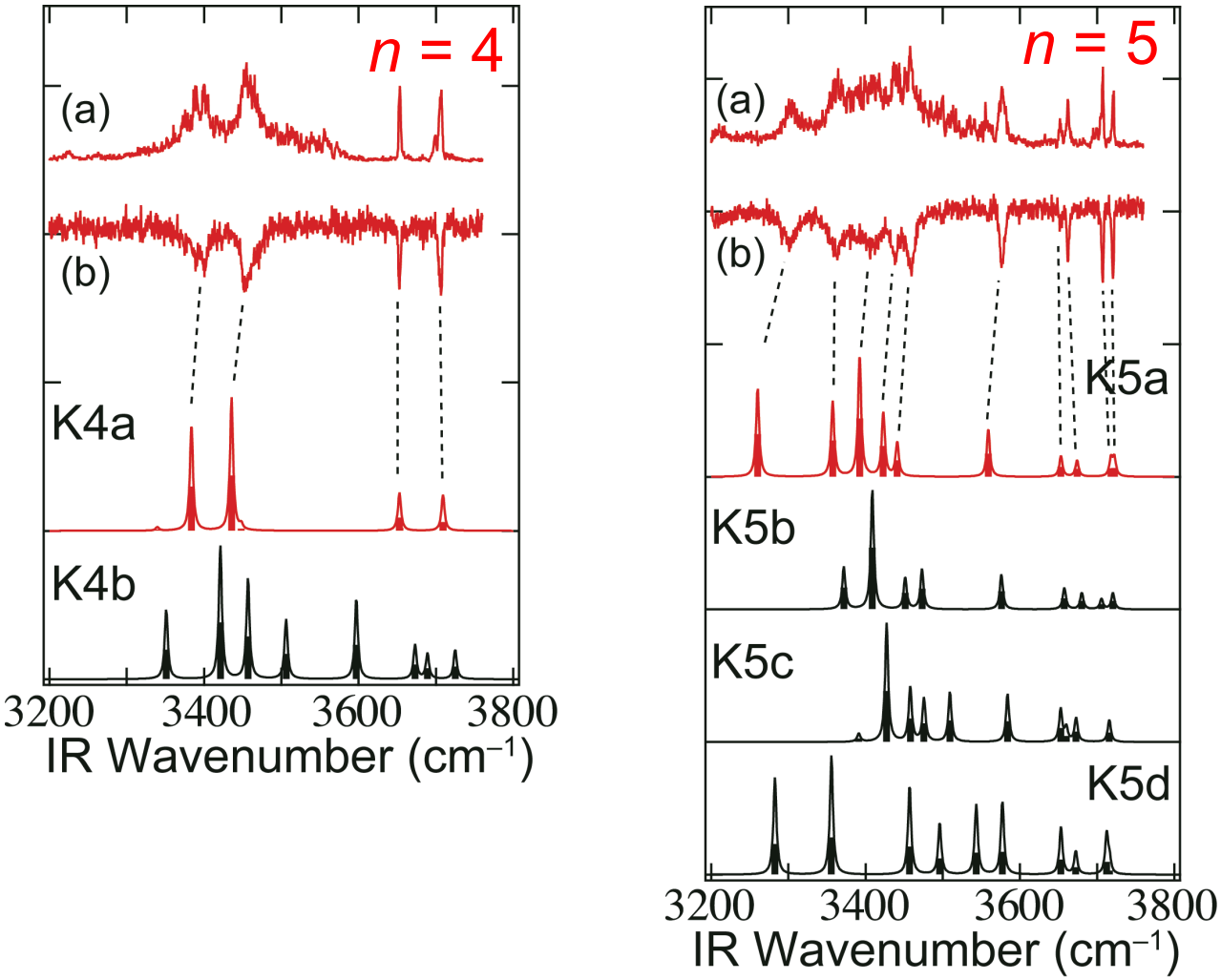
IR Spectra of $K^+ \cdot DB18C6 \cdot (H_2O)_n$





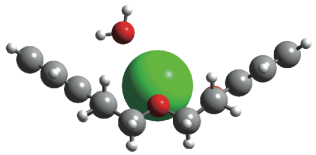


IR Spectra of $K^+ \cdot DB18C6 \cdot (H_2O)_n$

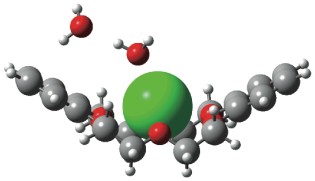


IR spectra in the OH stretch region give clear pictures of hydration structure.

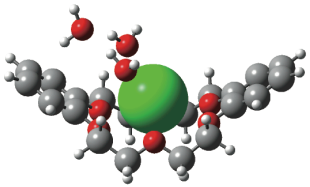
Structure of $K^+ \cdot DB18C6 \cdot (H_2O)_n$



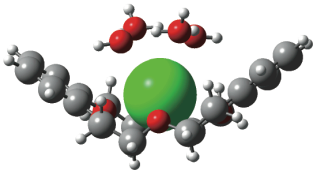
K1a



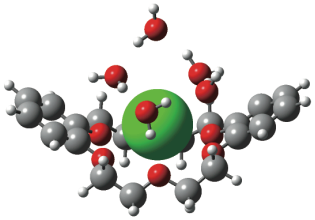
K2d



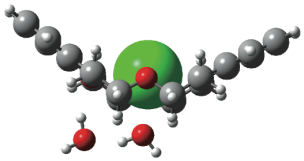
K3a



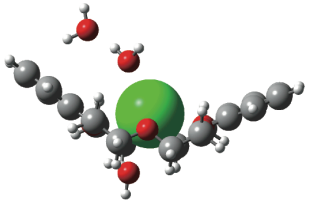
K4a



K5a



K2f

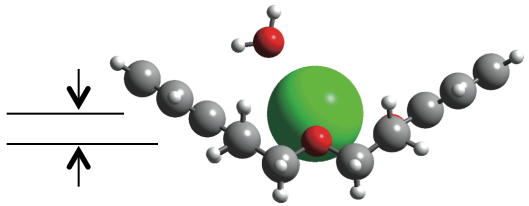


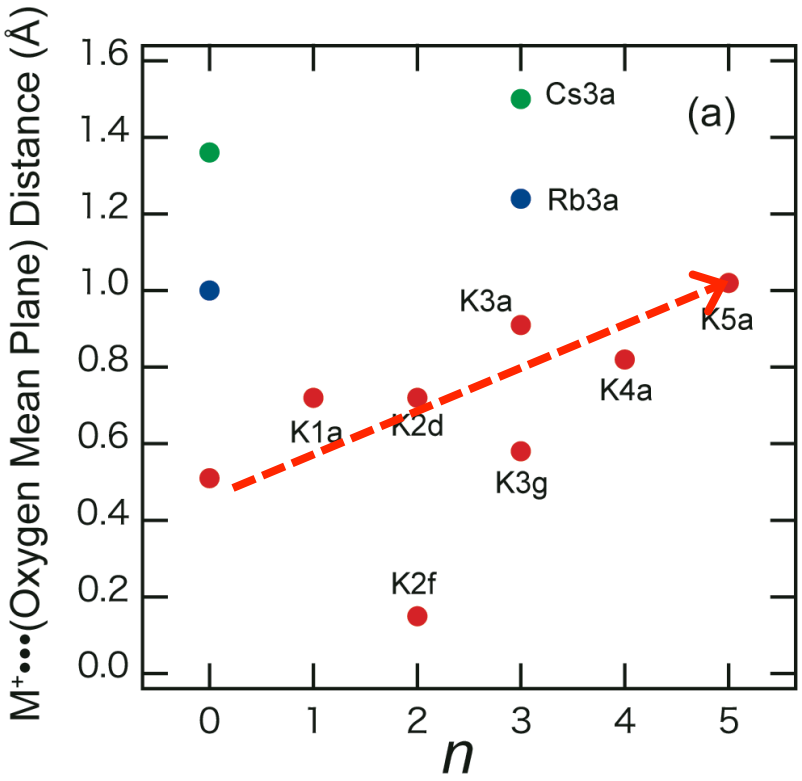
K3g

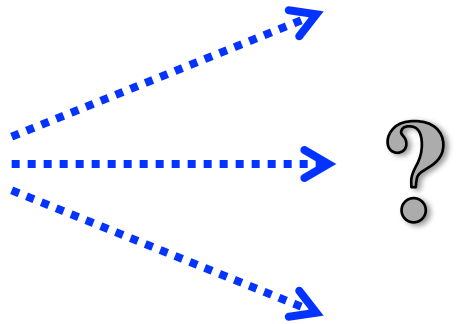
n = 1 *n* = 2 *n* = 3 *n* = 4 *n* = 5

Hydration occurs on one side.

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





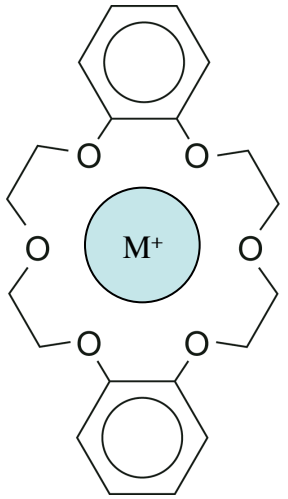


Distance increases for larger n.

continues increasing for $n > 5$?

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, in biology, etc…
- We may have to extend this to larger solvated systems, $n > 1000$?...
- We need spectroscopy in liquid phase…