UV and IR Spectroscopic Studies of Cold Alkali Metal Ion-Benzo Crown Ether Complexes in the Gas Phase

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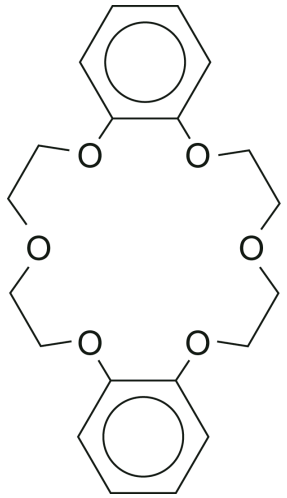
T. Ebata and T. R. Rizzo

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

Crown Ethers

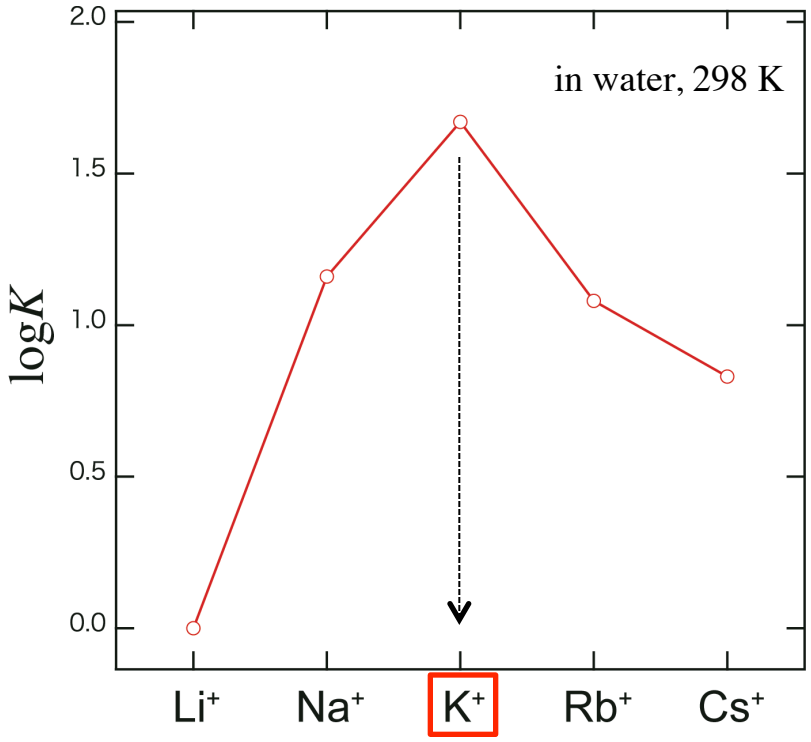
- Ionophores
- Used as phase-transfer catalyses
- *Ion selectivity*



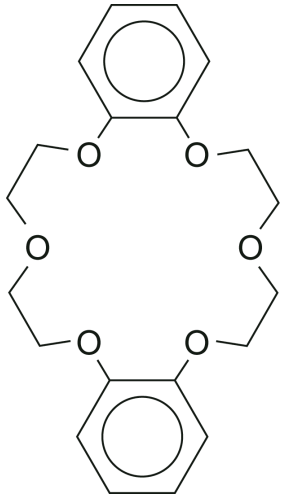
Dibenzo-18-crown-6
(DB18C6)

Ion Selectivity

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



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



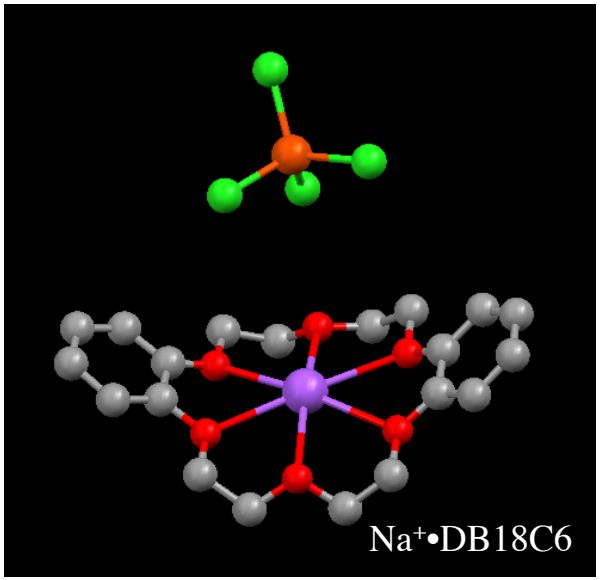
DB18C6

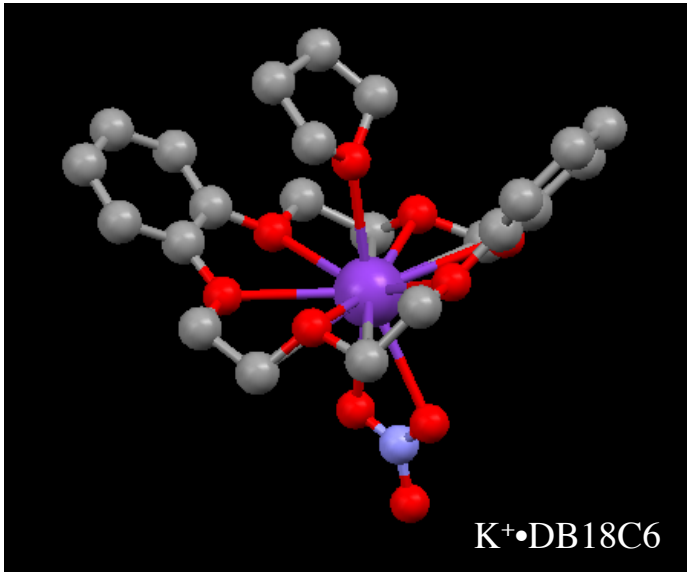
DB18C6 captures K^+ selectively

Optimum matching in size

Structure?

Crystal Structure





(Cambridge Structural Database)

Few reports for Li^+, Rb^+, and Cs^+

Conformations similar for Na^+ and K^+

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

Necessary to study in the gas phase

Crown Ethers in the Gas Phase

- Mass spectrometric studies of metal ion-CE complexes

  Dearden (1991), Brodbelt (1992), Bowers (1995), Armentrout (1996), Brutschy (1997)

- IR spectroscopy of metal ion-CE complexes

  Lisy (2009), Martinez-Haya (2009)

- UV spectroscopy of metal ion-CE complexes

  Kim (2009)

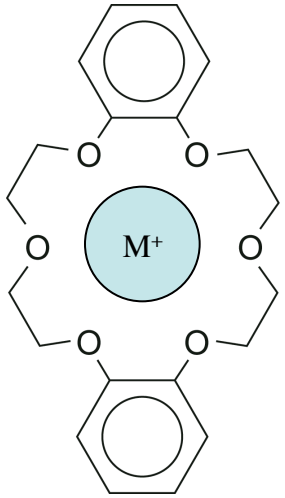
- UV and IR spectroscopy of jet-cooled CE and neutral complexes

  Zwier (2009), Ebata (2007)

This Study

- DB18C6 with $M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+$

  1:1 complexes

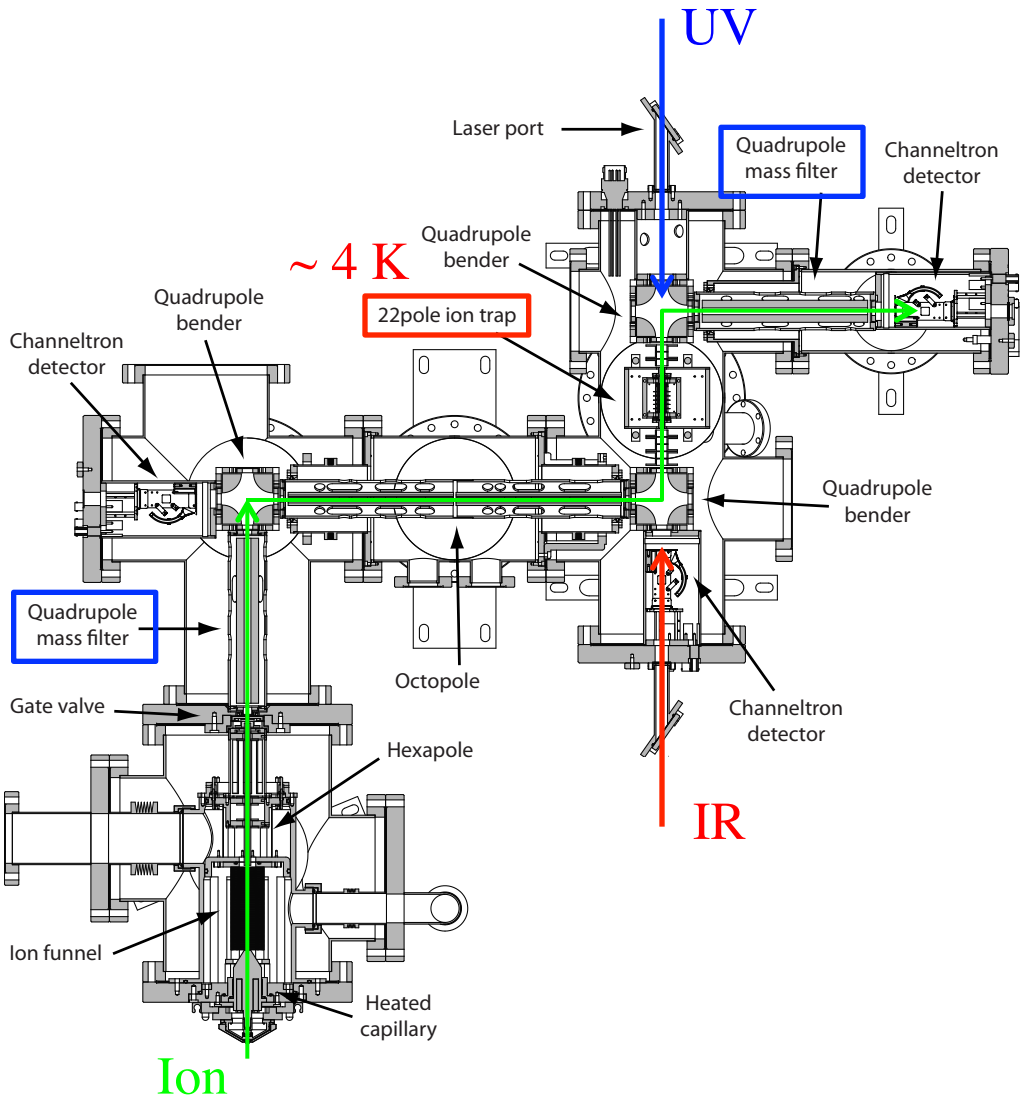


- UV and IR spectroscopy in a cold, 22-pole ion trap

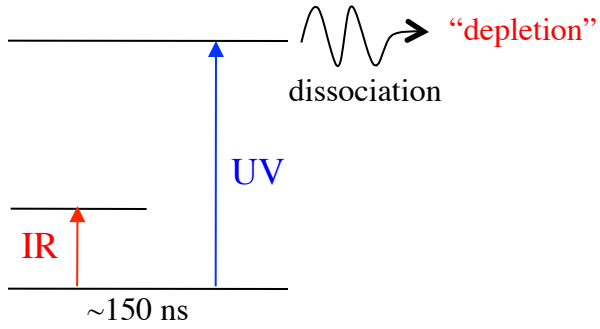
  DFT, TD-DFT
- The number and structure of conformers

  Relation between ion selectivity and structure

Experimental

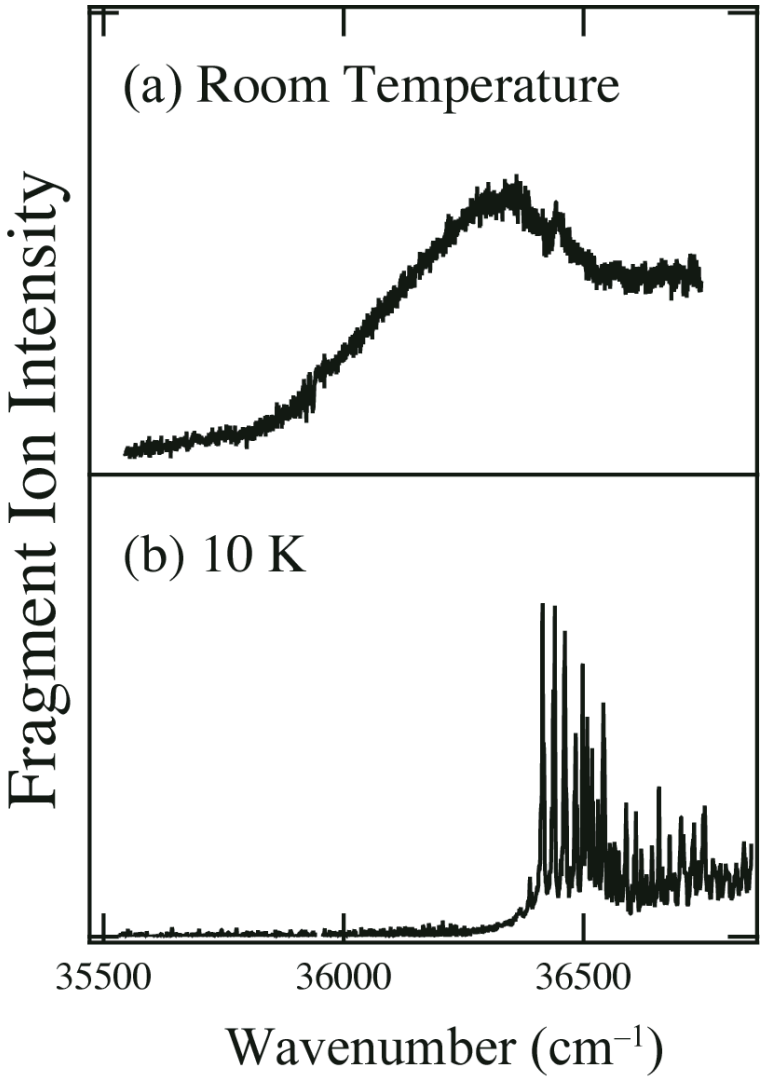


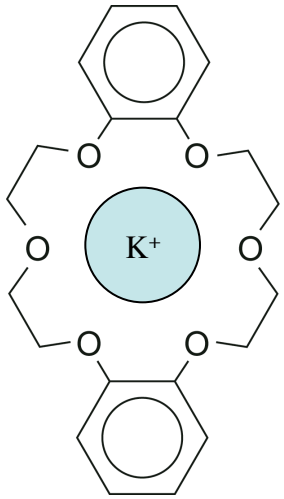
- nanoelectrospray
  - DB18C6
  - LiCl, NaCl, KCl, RbCl, CsCl
  - in Methanol
  - 20–200 μM
- UV photodissociation spectroscopy
- IR-UV double-resonance
  - UV power 1–1.5 mJ/pulse
  - IR power 4–5 mJ/pulse



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

UV Spectra of K^+•DB18C6

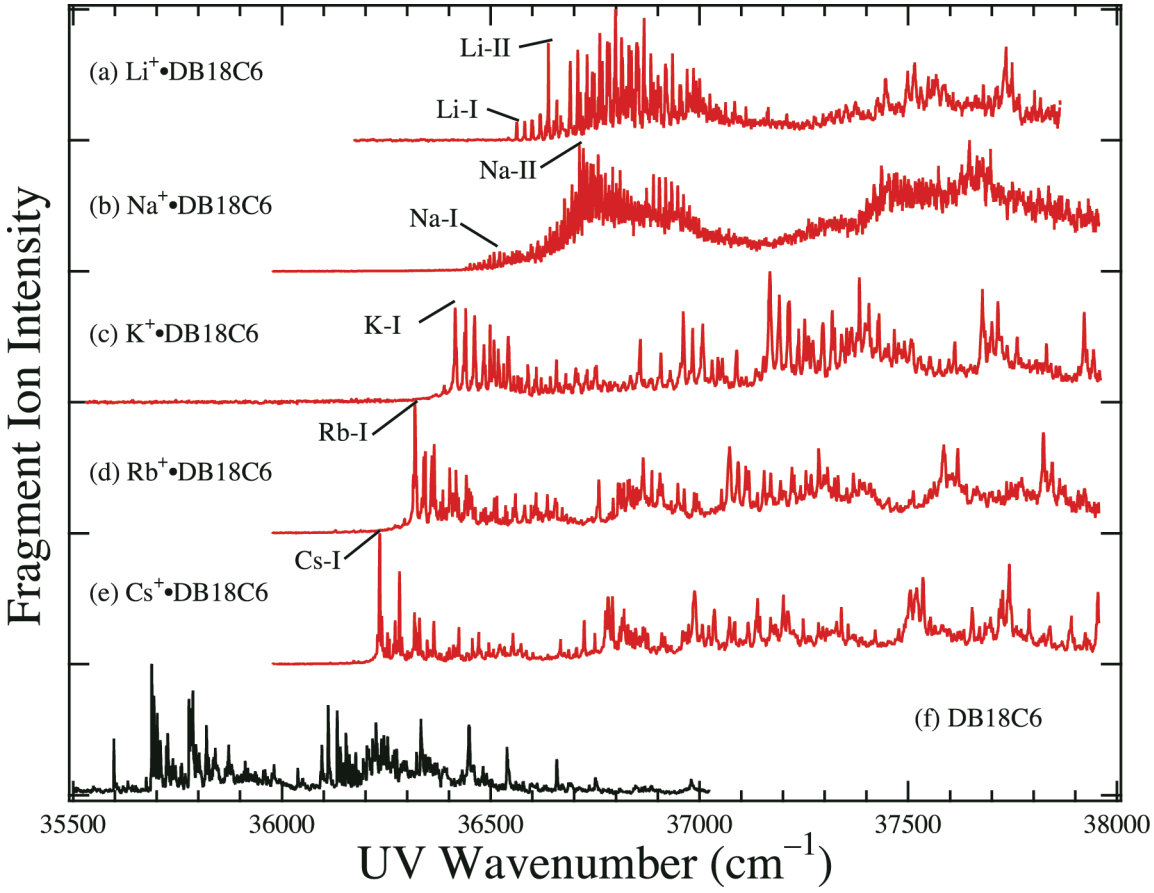


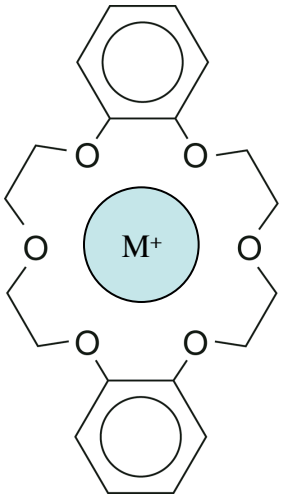


K^+•DB18C6

Sharp vibronic bands observed under cold condition

UV Spectra of M^+•DB18C6



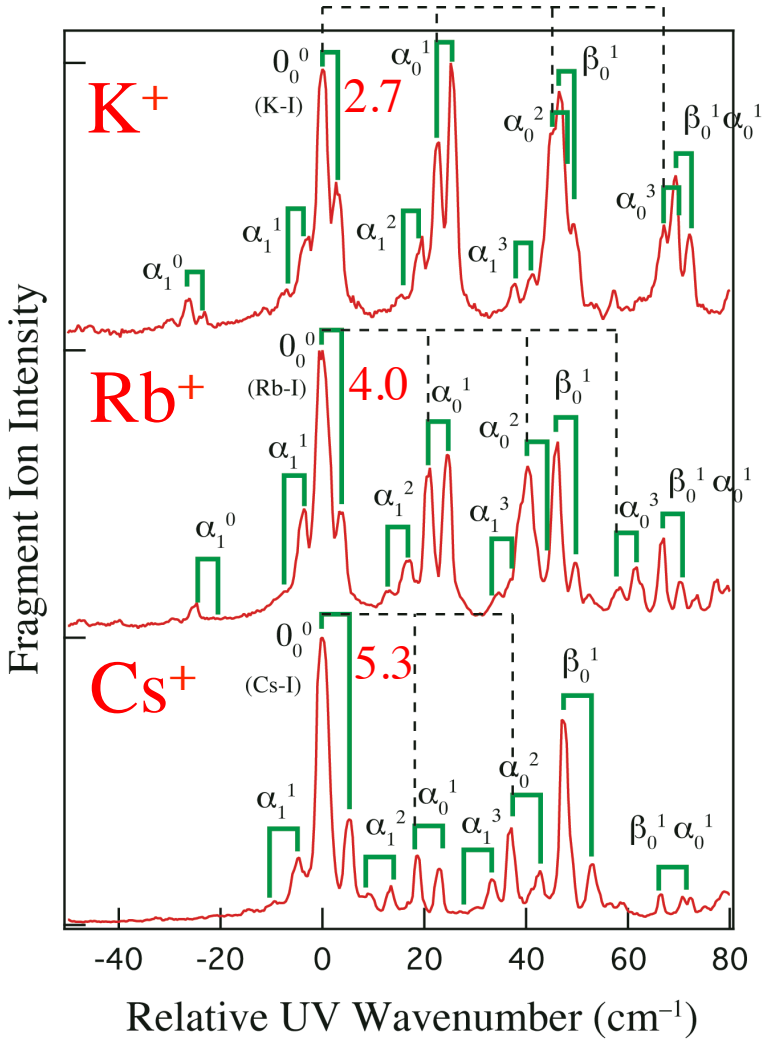


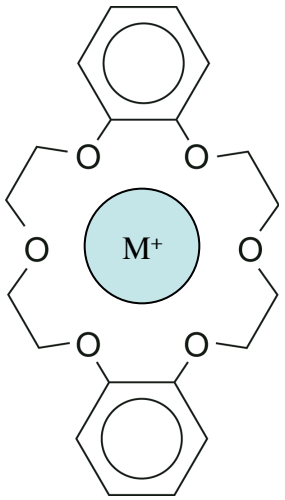
M⁺•DB18C6

Low freq. progressions extensive for Li^+ and Na^+

The origin band strong for K^+~Cs^+

Exciton Splitting

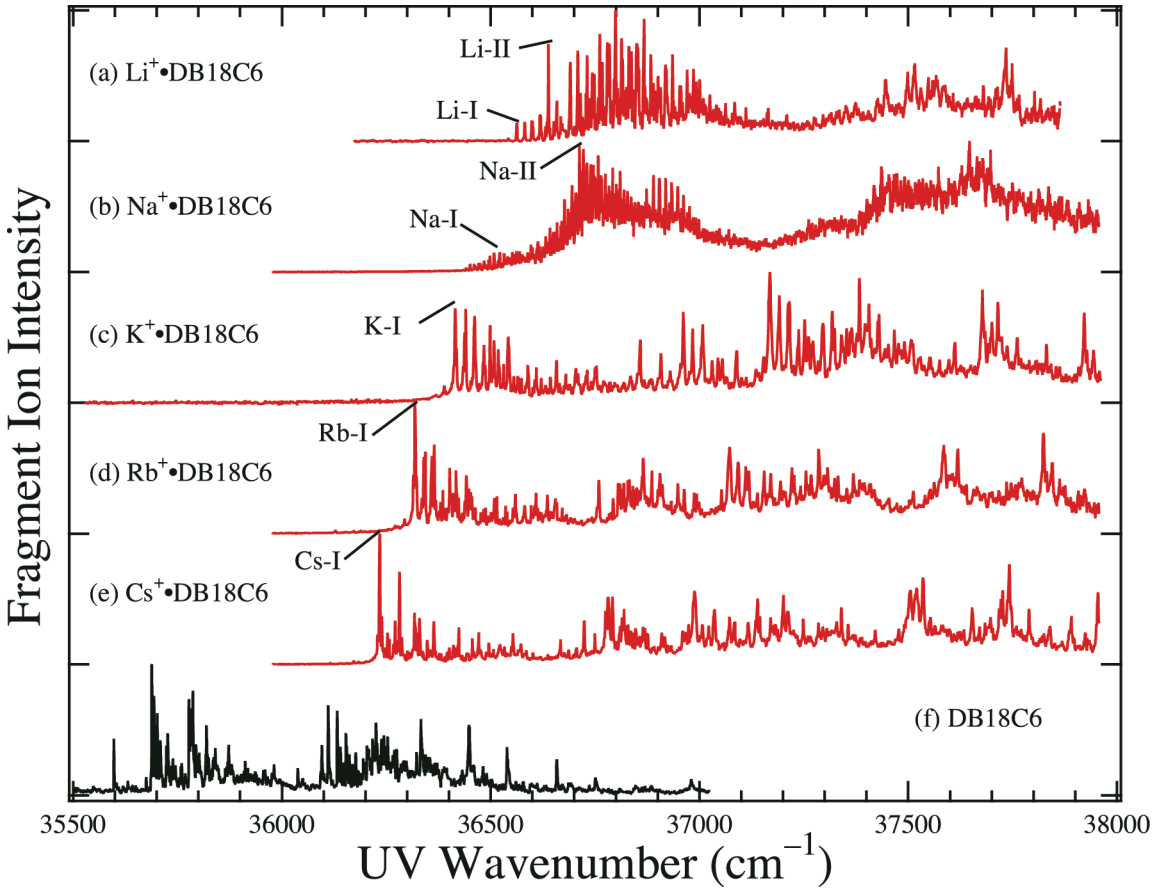


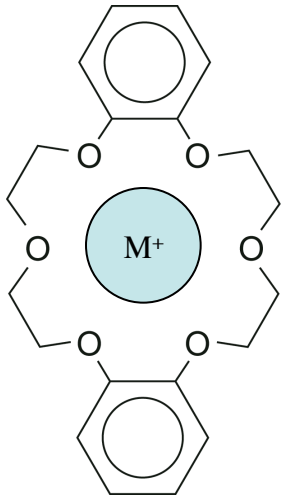


M⁺•DB18C6

Exciton splitting is seen for K^+~Cs^+.

UV Spectra of M^+•DB18C6



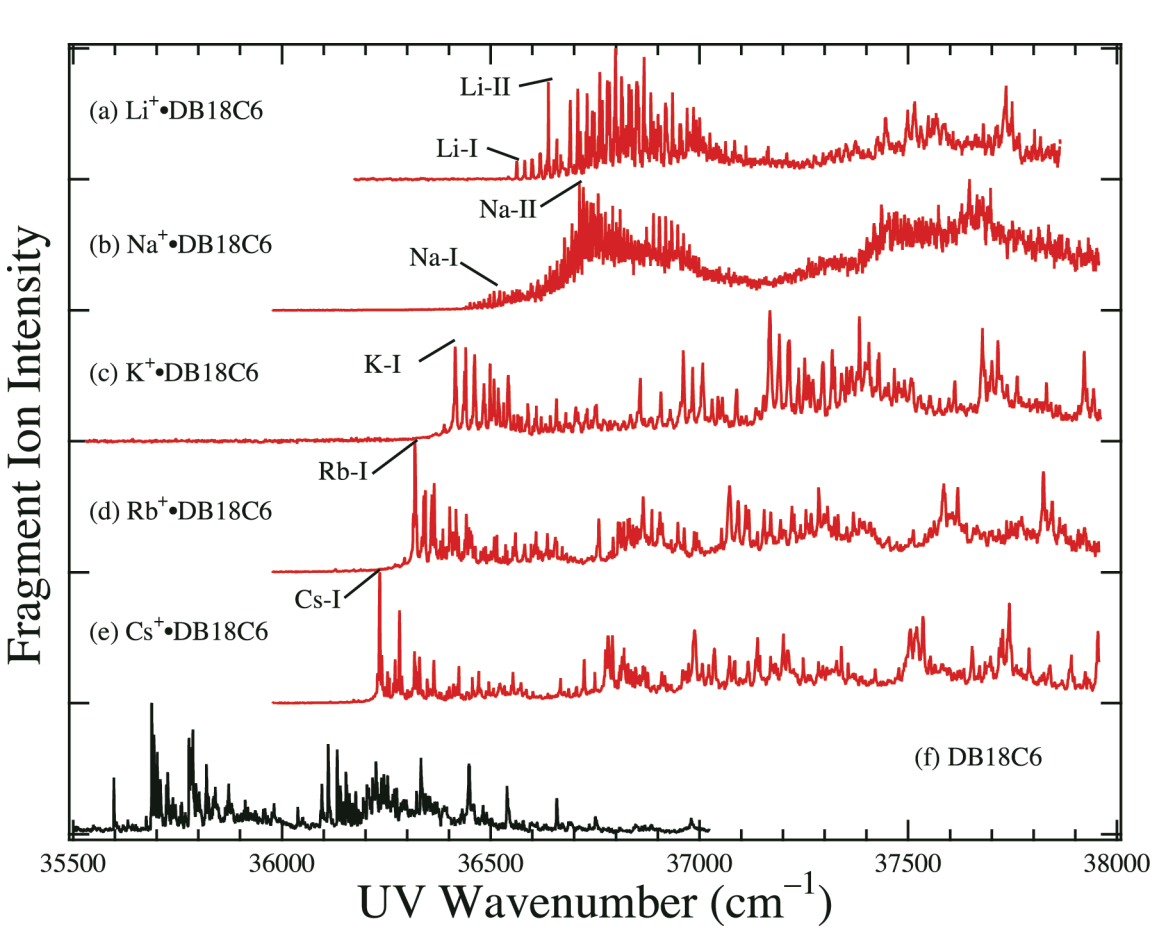


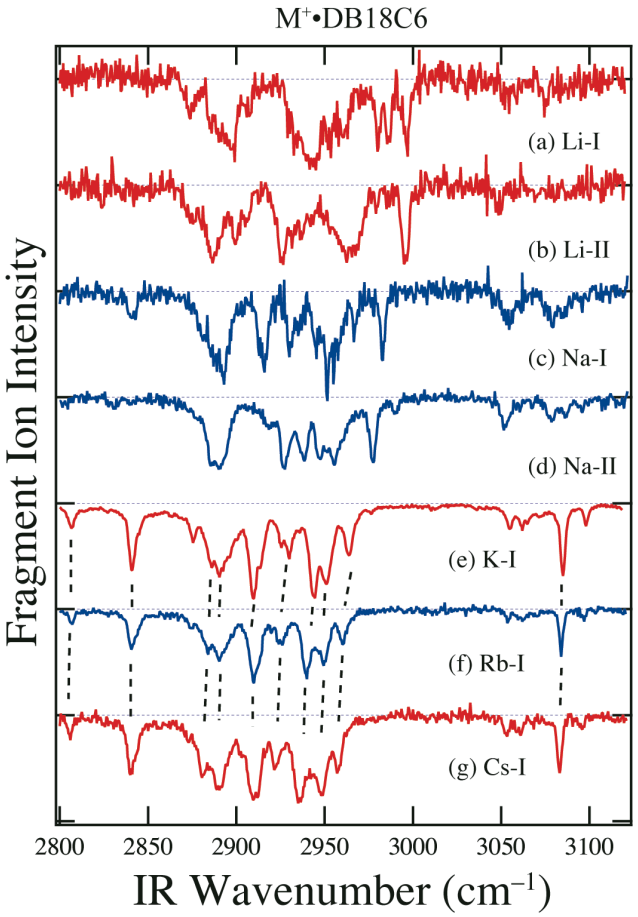
M^+•DB18C6

Structure largely different for Li^+~K^+

Similar structure for K^+~Cs^+

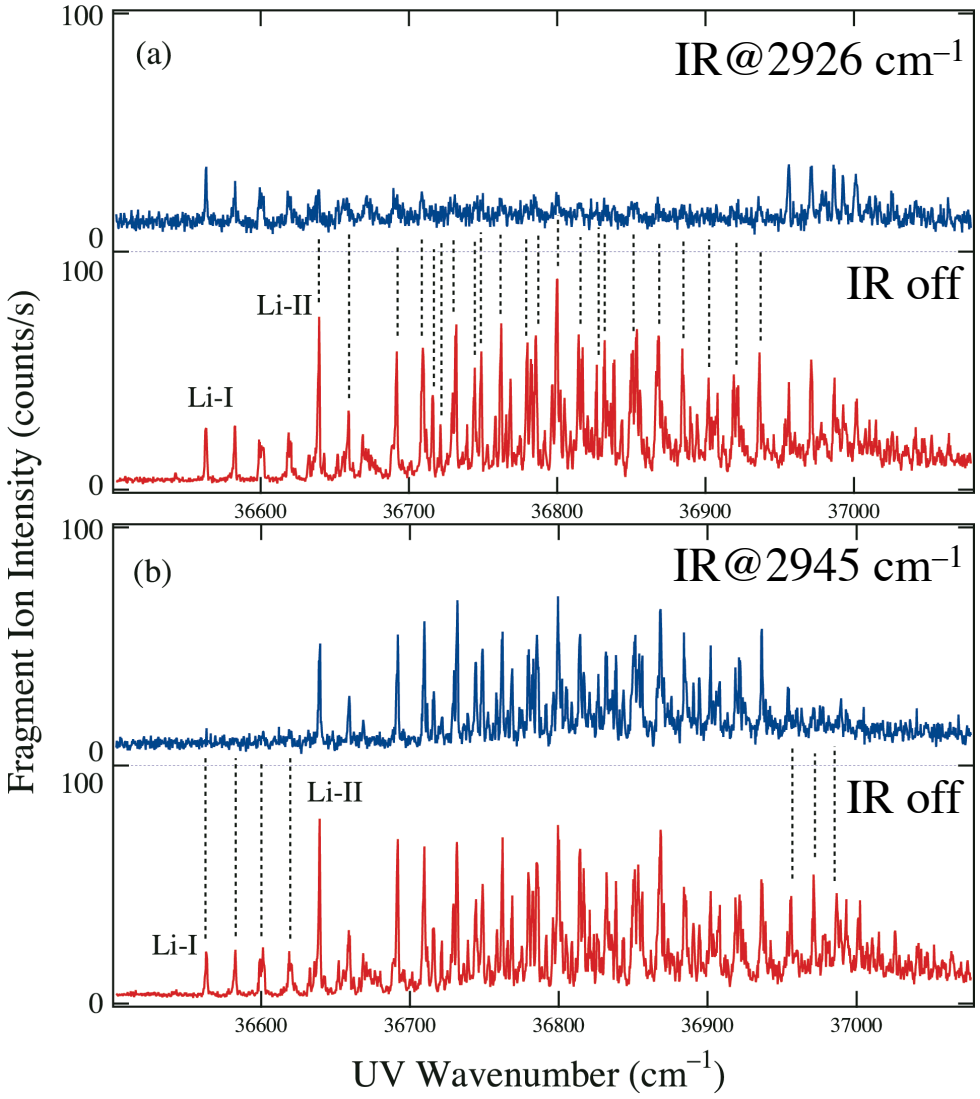
IR Spectra of M^+•DB18C6

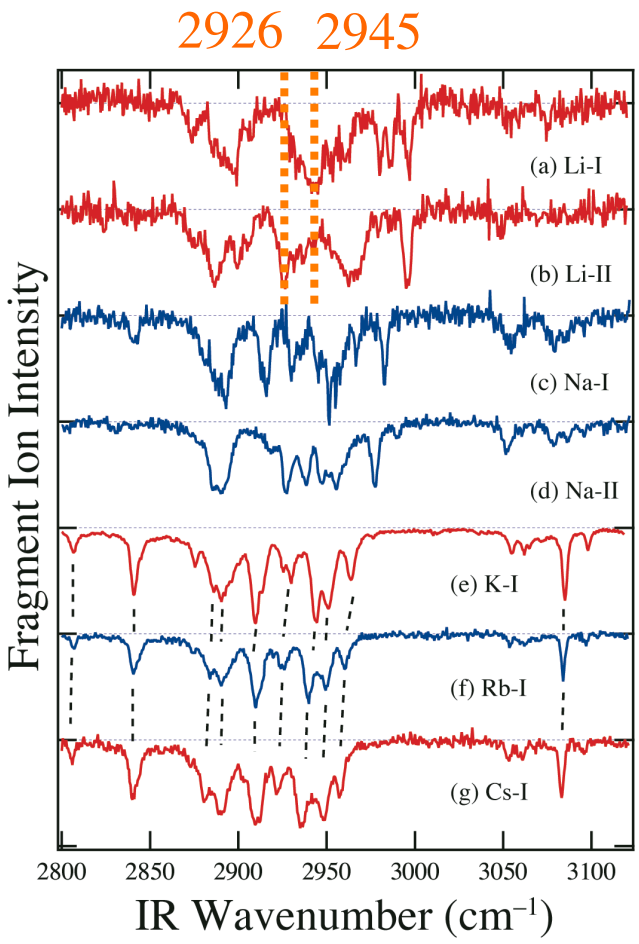




IR spectra similar for K^+~Cs^+ ⇨ Similar structure

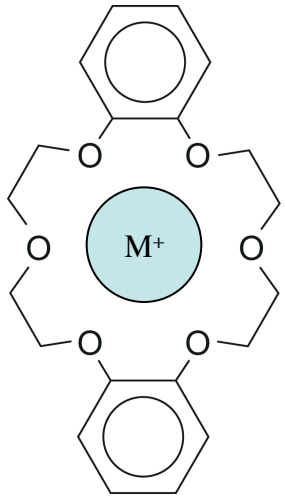
IR-UV HB Spectra of Li^+•DB18C6





The Number of Conformers

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



M^+•DB18C6

The Number of Conformers

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

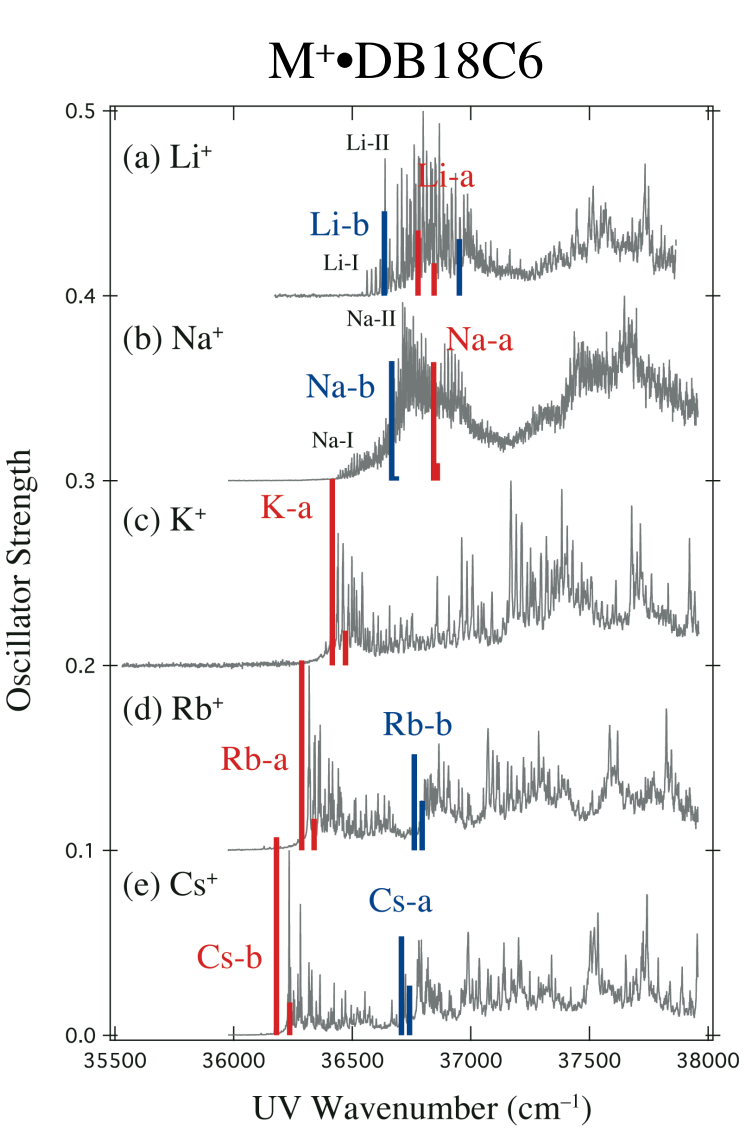
- Molecular mechanics calculations

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

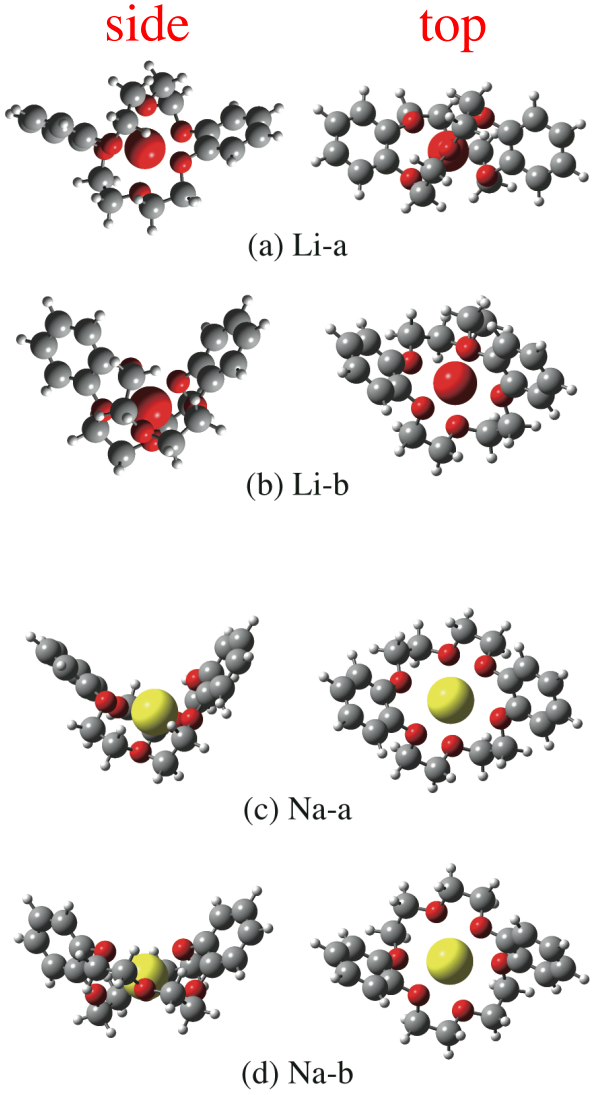
- TD-DFT
  electronic spectra

UVPD spectra

Structure of M^+•DB18C6 (M = Li, Na)

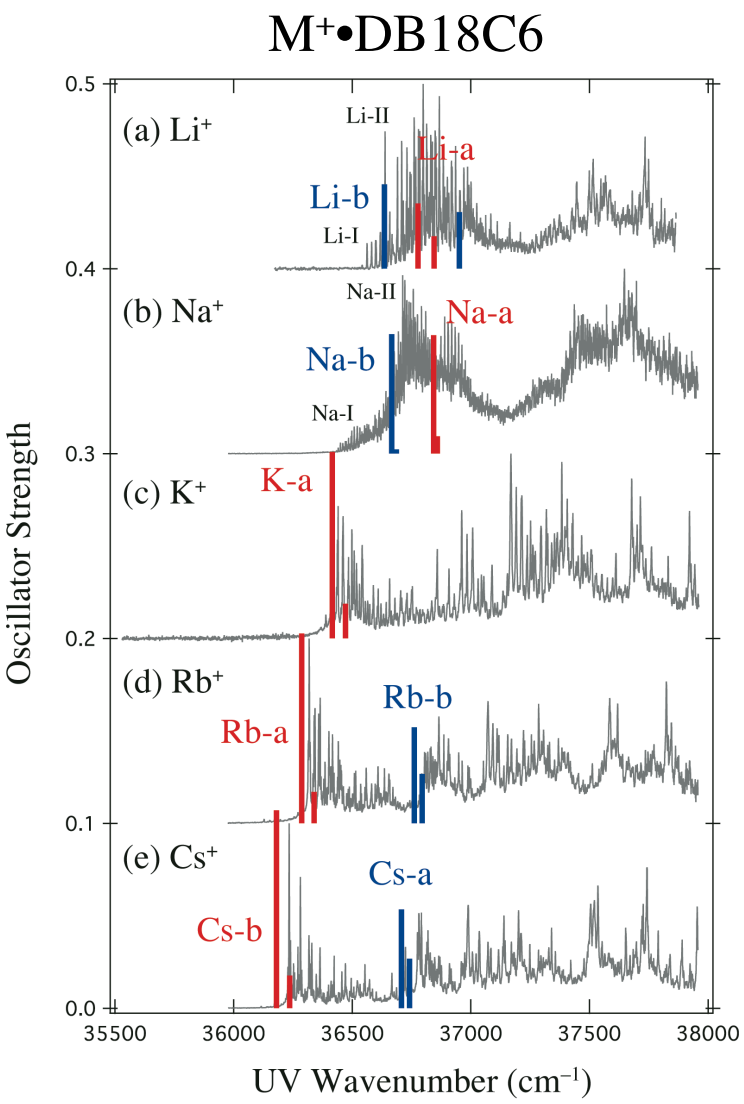


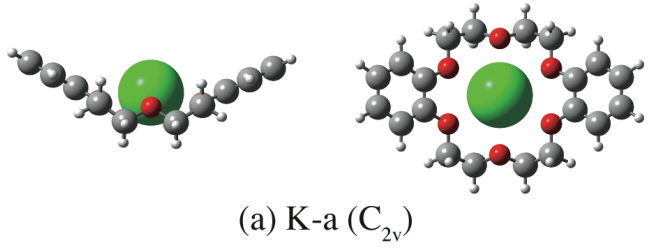
M05-2X/6-31+G(d) with Stuttgart RLC ECP
A scaling factor of 0.8340 is used.



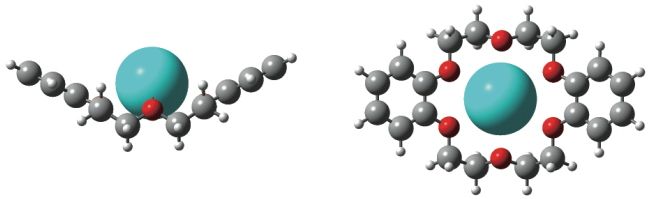
Ether rings distorted for Li^+ and Na^+

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

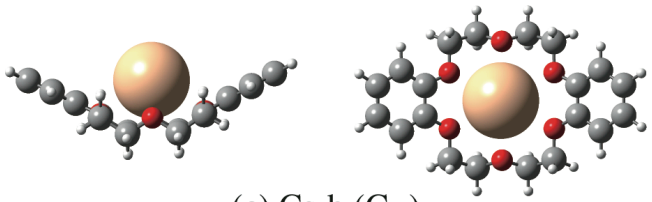




(a) K-a (C_{2v})



(b) Rb-a (C_{2v})



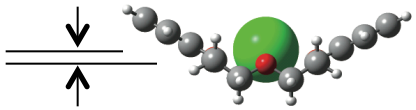
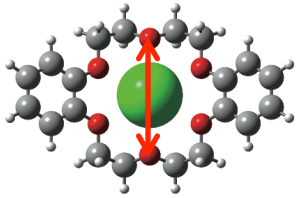
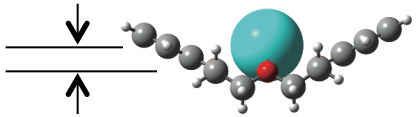
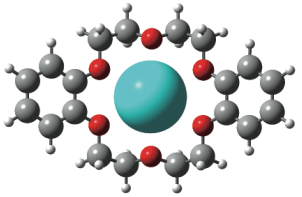
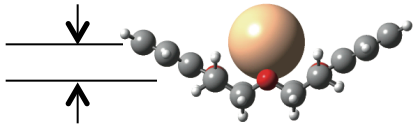
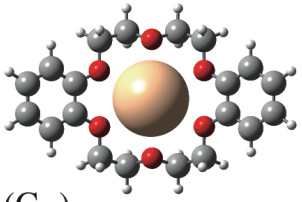
(c) Cs-b (C_{2v})

Ether rings largely open

K^+ in the ring

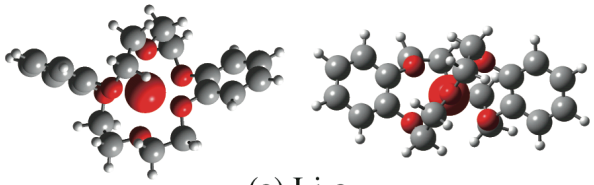
Rb^+, Cs^+ on the ring

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

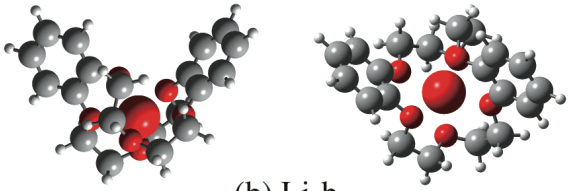
	Ion radii/Å			
K^+	1.52	0.51		 5.41
			(a) K-a (C_{2v})	
Rb^+	1.66	1.00		
			(b) Rb-a (C_{2v})	
Cs^+	1.81	1.36		
			(c) Cs-b (C_{2v})	

cf. Li^+ (0.90 Å), Na^+ (1.16 Å)

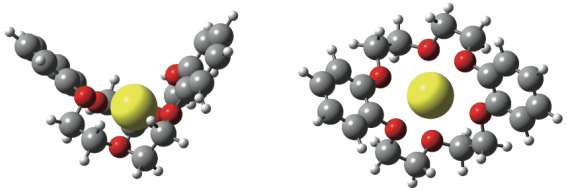
Structure of M^+•DB18C6



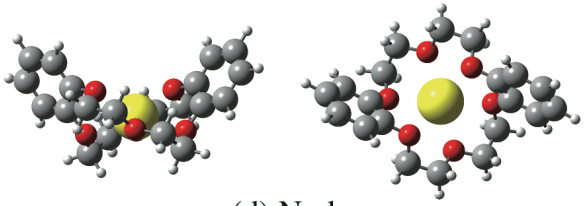
(a) Li-a



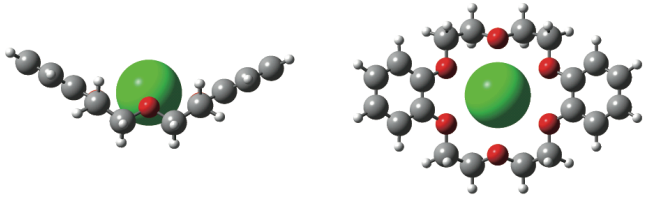
(b) Li-b



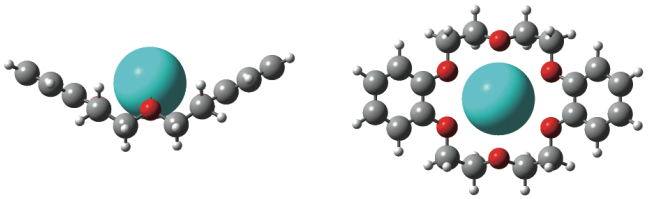
(c) Na-a



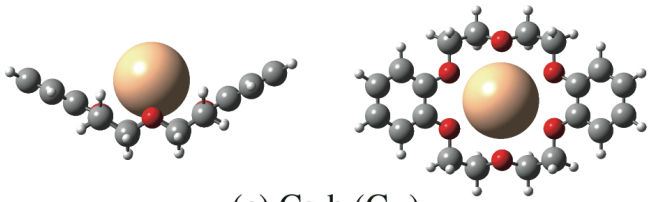
(d) Na-b



(a) K-a (C_{2v})



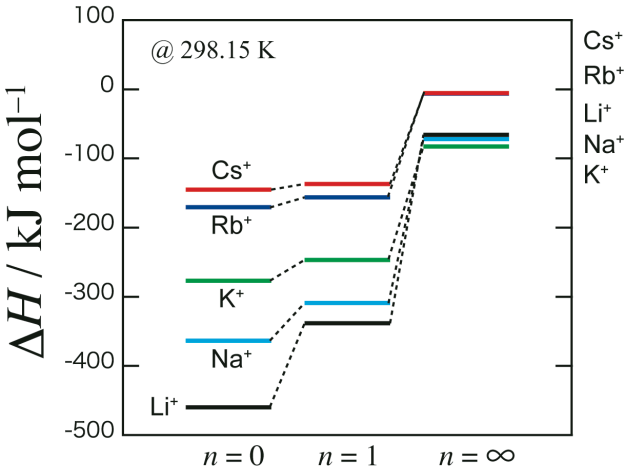
(b) Rb-a (C_{2v})

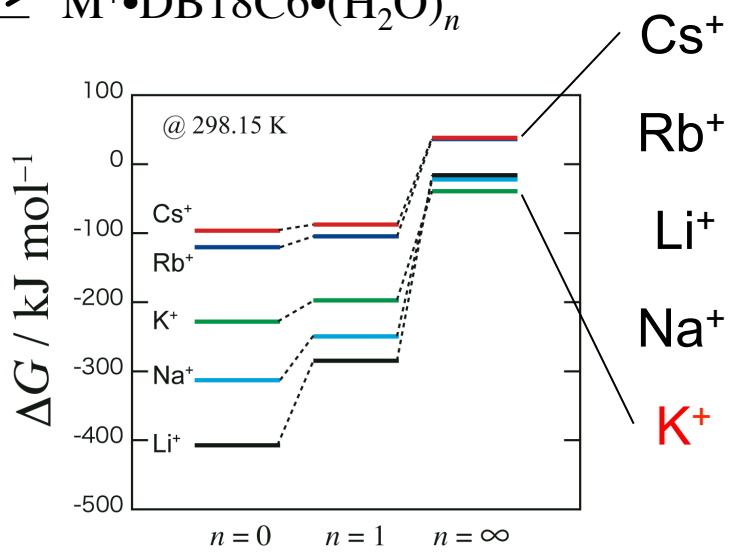


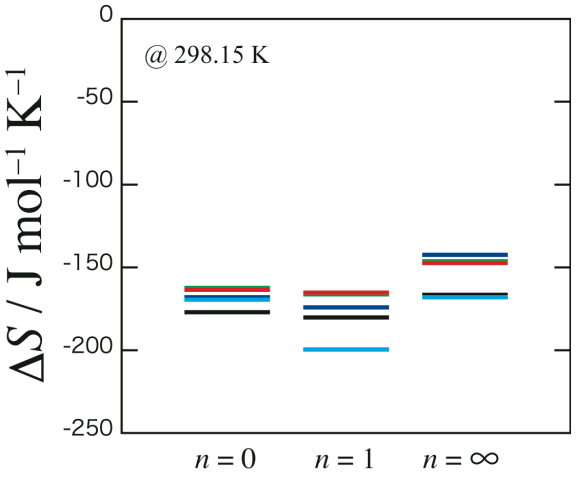
(c) Cs-b (C_{2v})

ΔH, ΔS, and ΔG for DB18C6

$$M^+\bullet(H_2O)_n + DB18C6 \rightleftharpoons M^+\bullet DB18C6\bullet(H_2O)_n$$







ΔH changes largely with increasing n

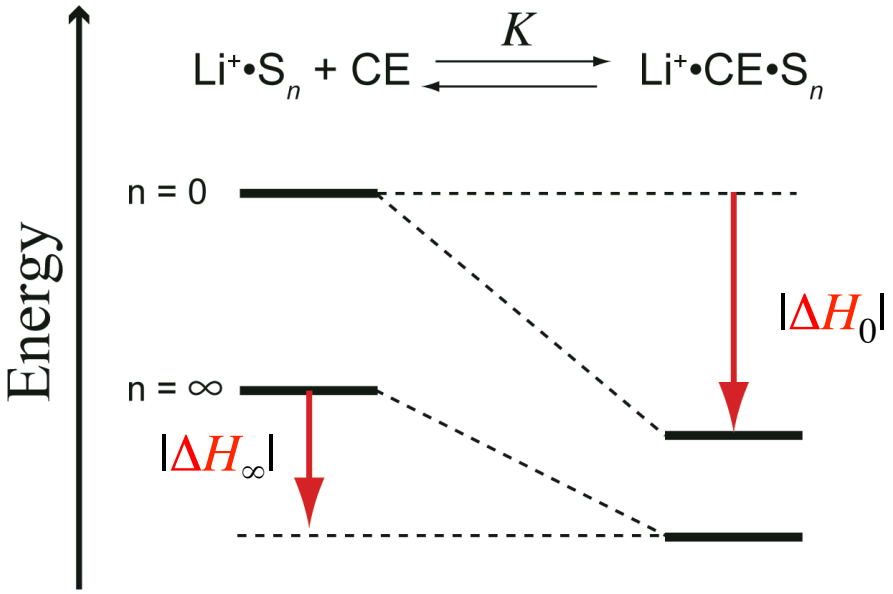
ΔS similar for $n = 0$, 1, and ∞

ΔG smallest for K^+ in water

Ion selectivity driven by ΔH

(For $n = \infty$, the Polarizable Continuum Model is used.)

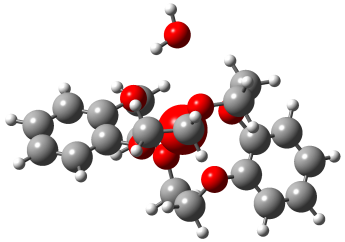
Complex Structure and Selectivity

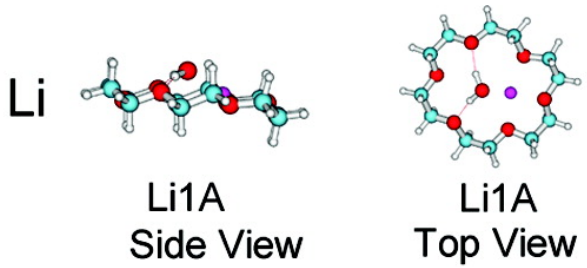


Li$^+$ surrounded by CE
Interaction between Li$^+$ and H_2O small

$$|\Delta H_\infty| << |\Delta H_0|$$

K becomes small





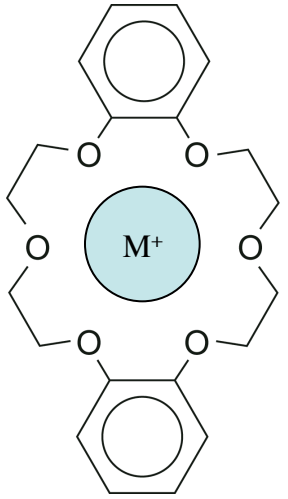
Rodriguez and Lisy, JACS (2011)

Where are solvent molecules?

Summary

- DB18C6 with $M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+$

  1:1 complexes
- UV and IR spectroscopy in a cold, 22-pole ion trap



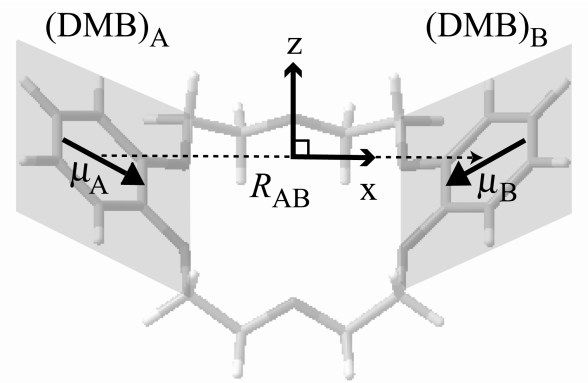
- The number and structure determined
- Ion selectivity mainly driven by ΔH
- Future work

  Solvent effect

  Temperature effect

  Structure in condensed phase

Exciton Splitting



$$\Delta E = 2 \bullet V_{AB} \bullet F$$

$$V_{AB} = \frac{\mu_A \cdot \mu_B}{4\pi\varepsilon_0} \cdot \frac{\left(2\cos\theta_A \cos\theta_B - \sin\theta_A \sin\theta_B \cos\varphi\right)}{R_{AB}^3}$$

Part 1 Part 2

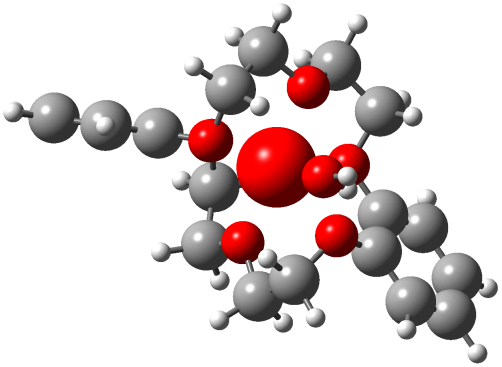
F: Franck-Condon part

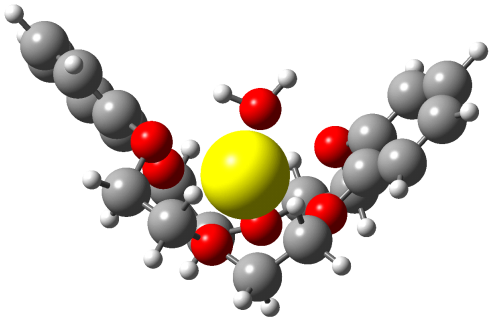
	K^+•DB18C6	Rb^+•DB18C6	Cs^+•DB18C6
Exciton Splitting (cm^{-1})	2.7	4.0	5.3
$\mu_{M+\bullet DMB}$ (10^{-30} Cm)	4.11	4.55	4.67
R_{AB} (Å)	9.09	9.24	9.25
θ_A (degree)	28	25	25
Part 1 (dipole part)	1.52×10^{-49}	1.86×10^{-49}	1.96×10^{-49}
Part 2 (structure part)	2.37×10^{27}	2.31×10^{27}	2.30×10^{27}
$2 \bullet V_{AB}$ (cm^{-1})	36	43	46
$\Delta(S_1-S_2)_{TD\text{-}DFT}$ (cm^{-1})	66	63	66

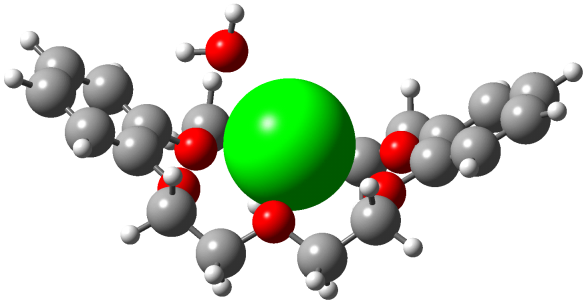
Charge on M with NBO

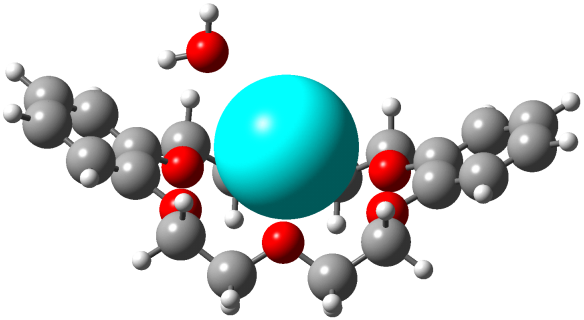
M	M^+•DB18C6
Li	0.56347 (Li-a) 0.56637 (Li-b)
Na	0.74949 (Na-a) 0.75049 (Na-b)
K	0.84249 (K-a)

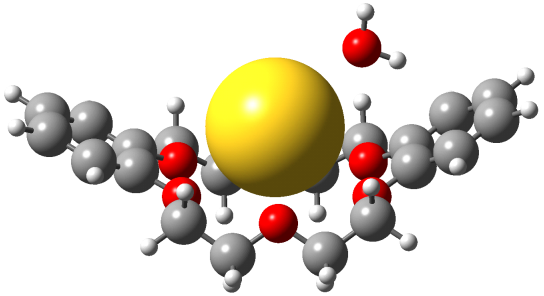
Structure of $M^+ \cdot DB18C6 \cdot H_2O$



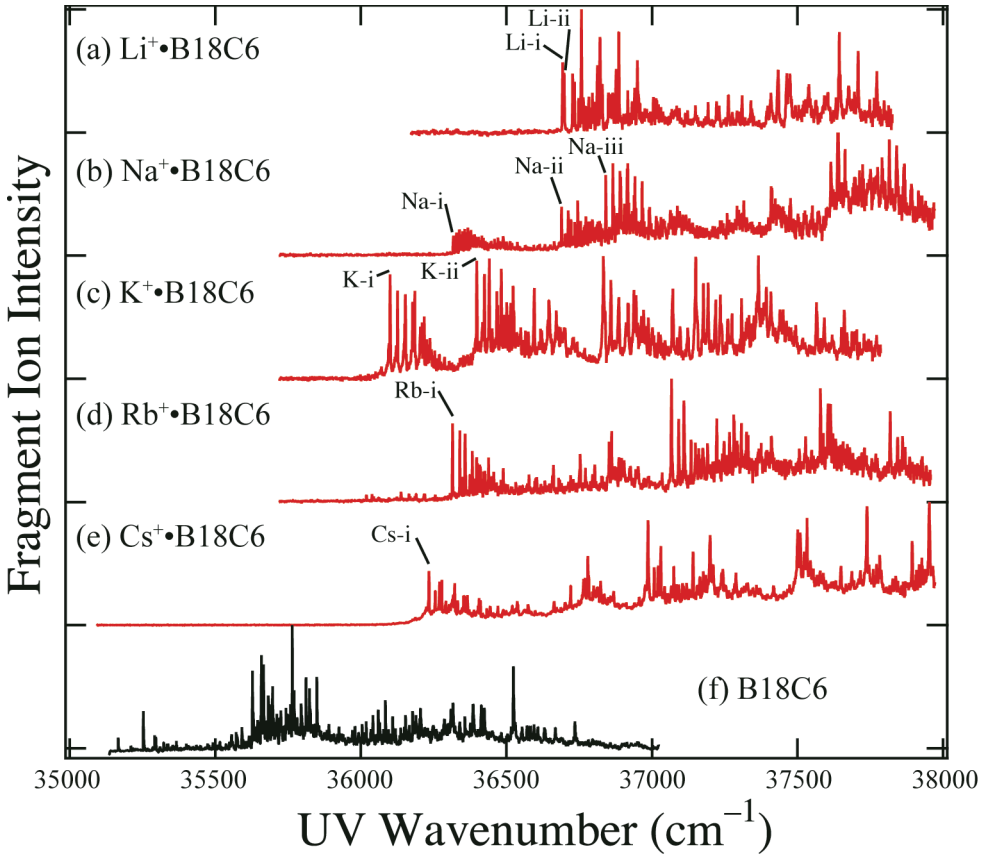


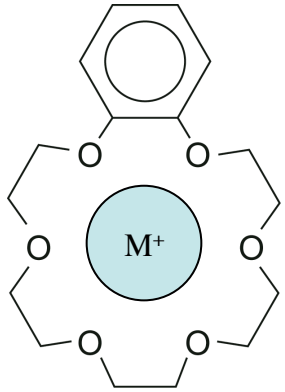






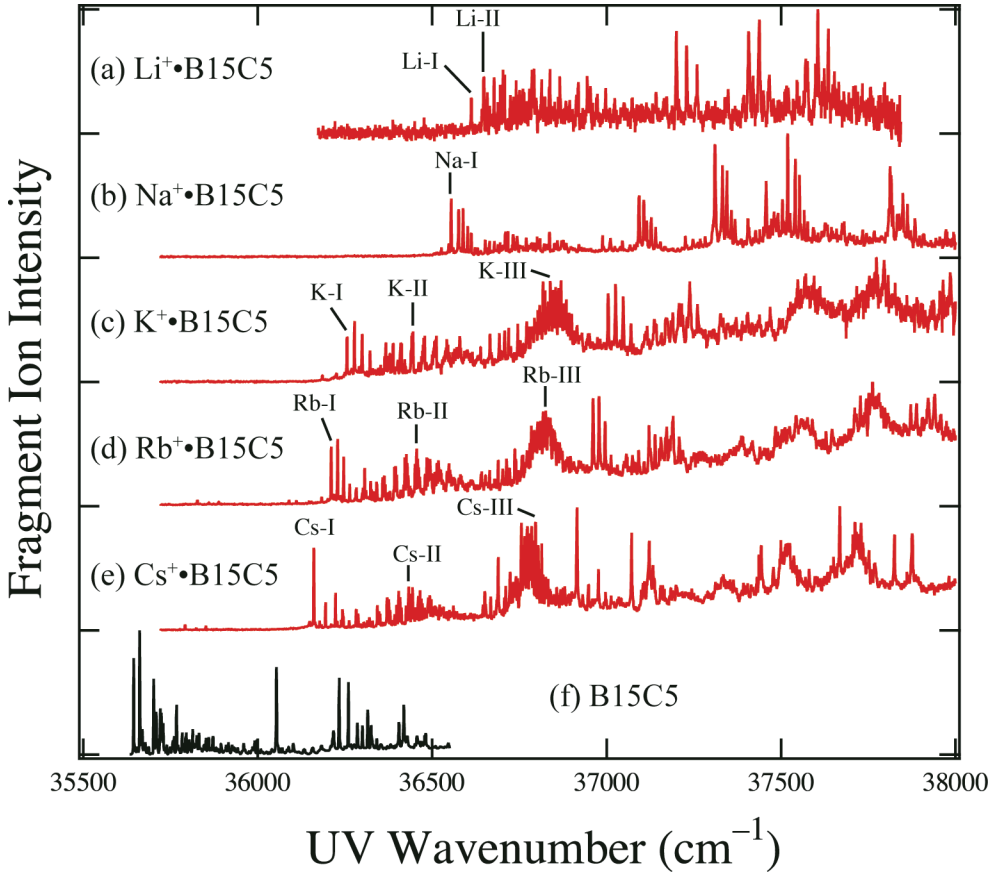
UV Spectra of $M^+ \bullet B18C6$

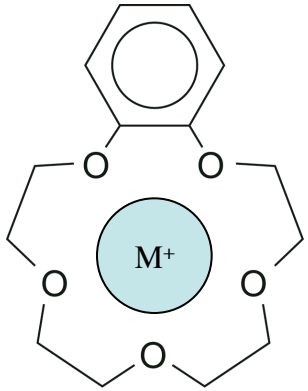




$M^+ \bullet B18C6$

UV Spectra of $M^+ \bullet B15C5$



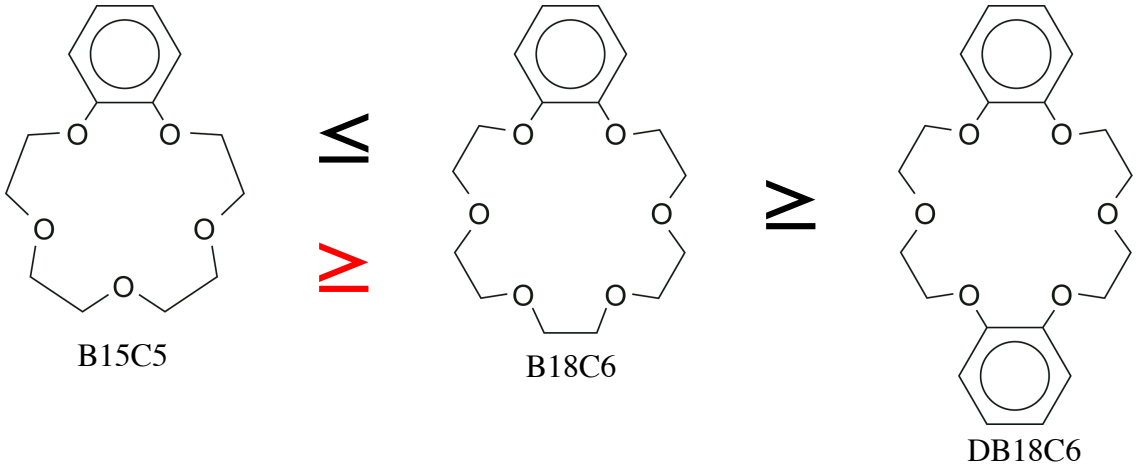


$M^+ \bullet B15C5$

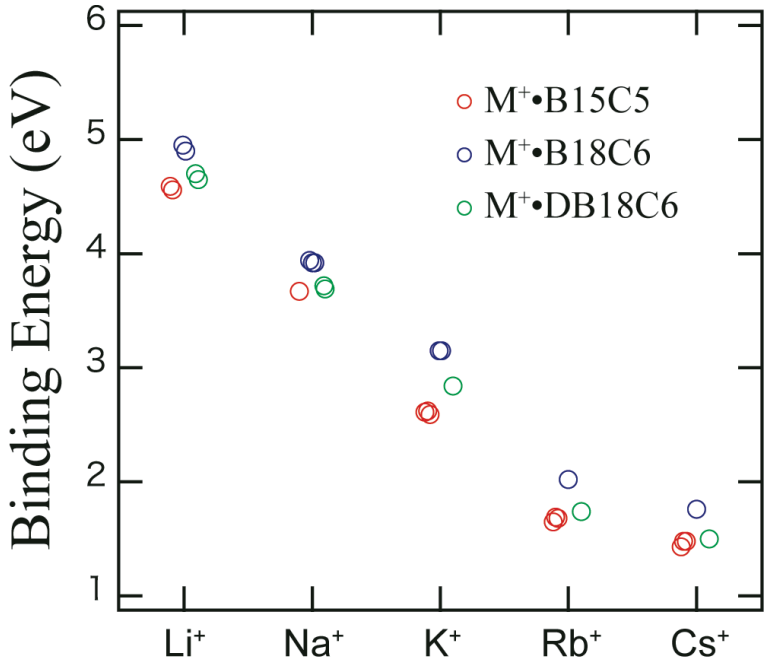
The Number of Conformers

M^+	M^+•B15C5	M^+•B18C6	M^+•DB18C6
Li^+	2	2	2
Na^+	1	3	2
K^+	3	2	1
Rb^+	3	1	1
Cs^+	3	1	1
(monomer)	3[a]	4[b]	2[b]

[a]Zwier and co-workers, *J. Phys. Chem. A*, **2009**, *113*, 8055.
[b]Ebata and co-workers, *Sensors*, **2010**, *10*, 3519.



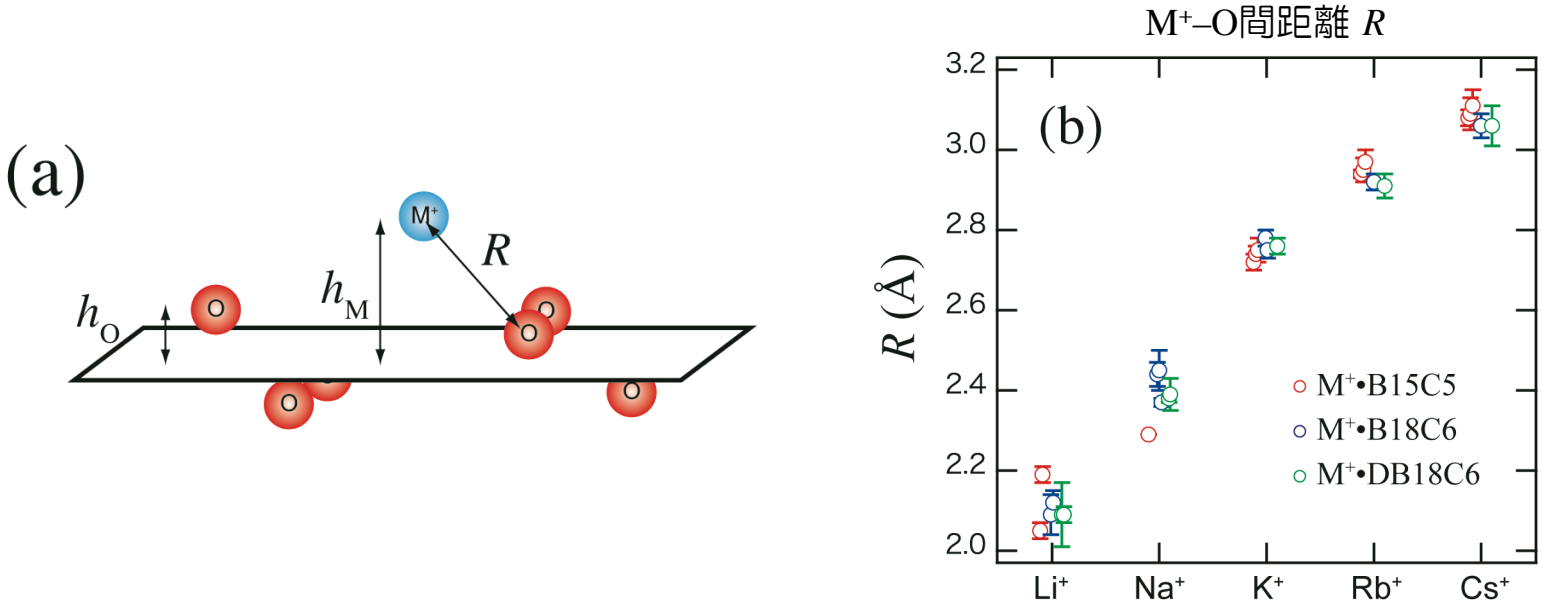
Calculated Binding Energy



M05-2X/6-31+G(d)

B.E. decreases monotonously

Structural Parameters

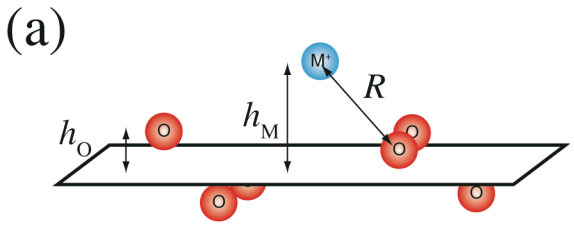


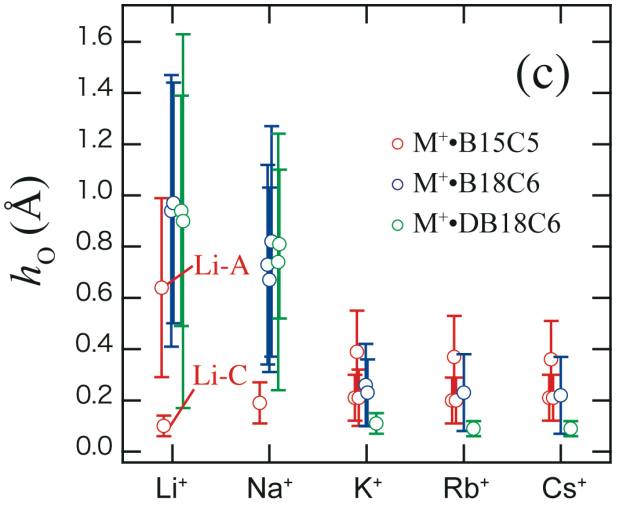
R independent of the ether size and the number of benzene ring

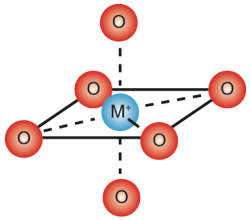
Deviation of *R* small

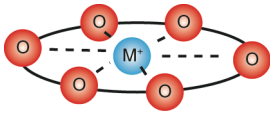
M^+ equally bonded to all O atoms

Structural Parameters









Structural Parameters