A Cold Spectroscopic Study on Metal Ion–Benzo-Crown Ether Complexes in the Gas Phase

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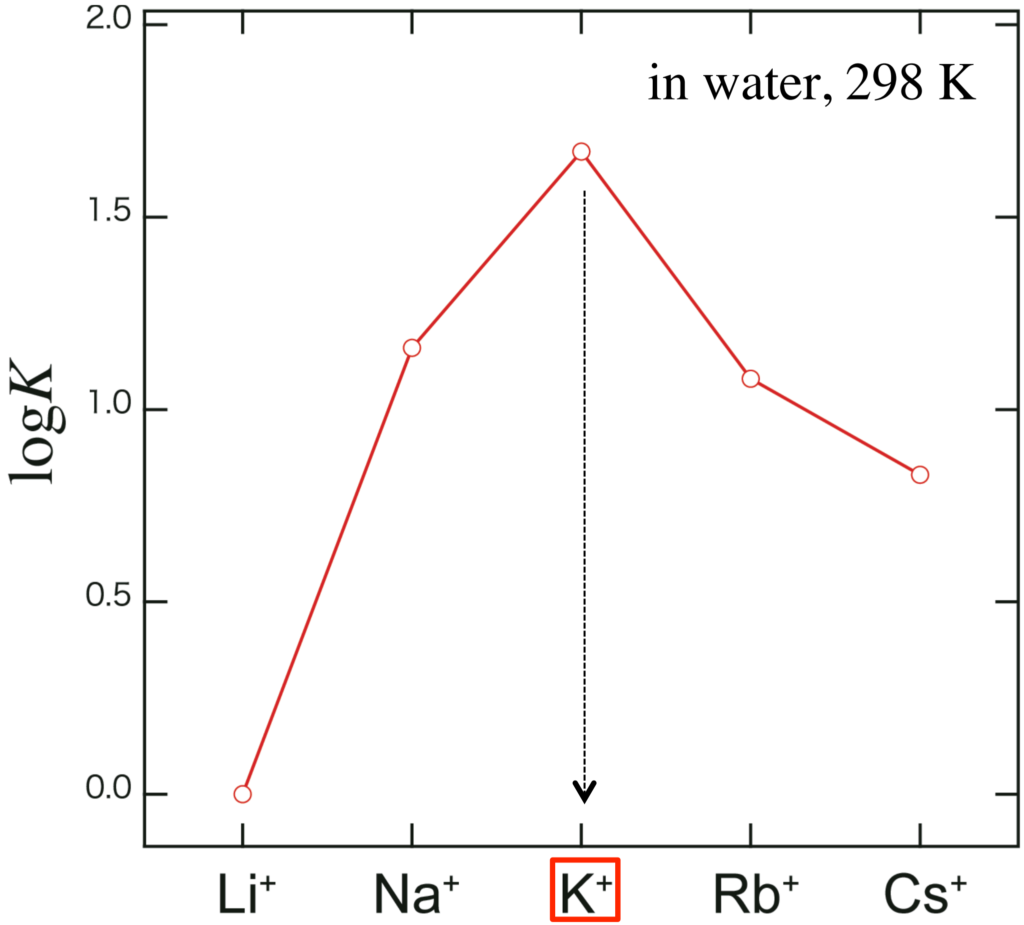
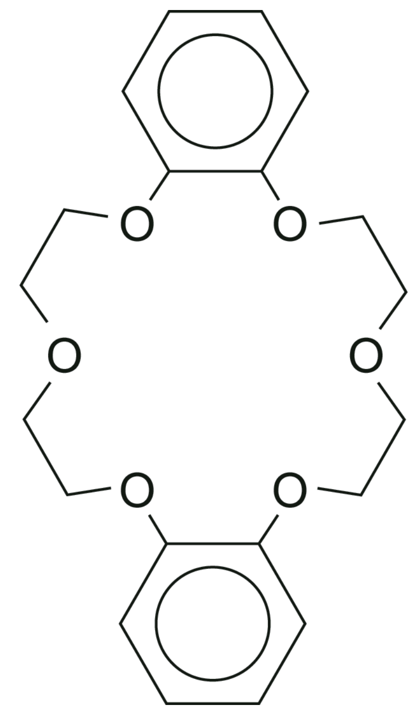
Ion Selectivity of CE

DB18C6 captures K^+ selectively in water.

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



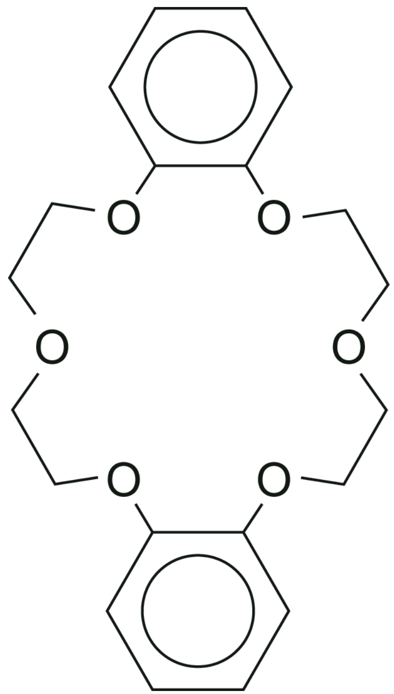


DB18C6

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

Our Final Goal

Our final goal is to reveal the origin of ion selectivity spectroscopically.

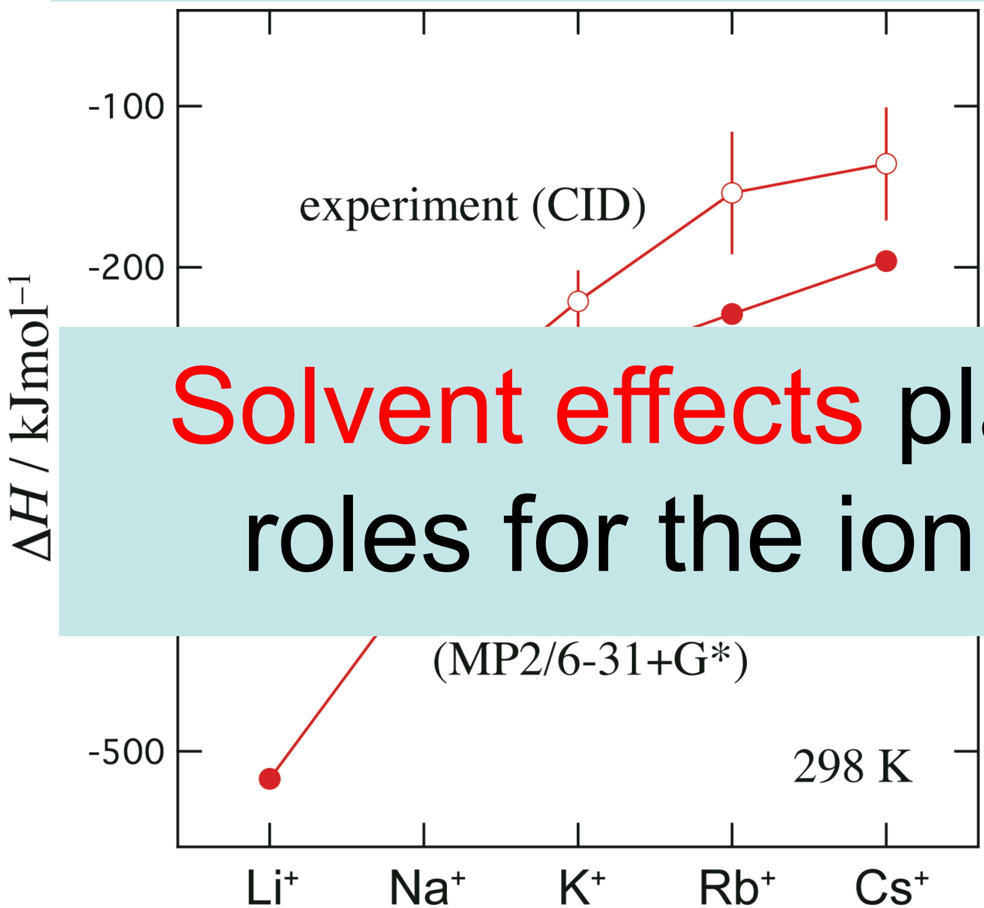


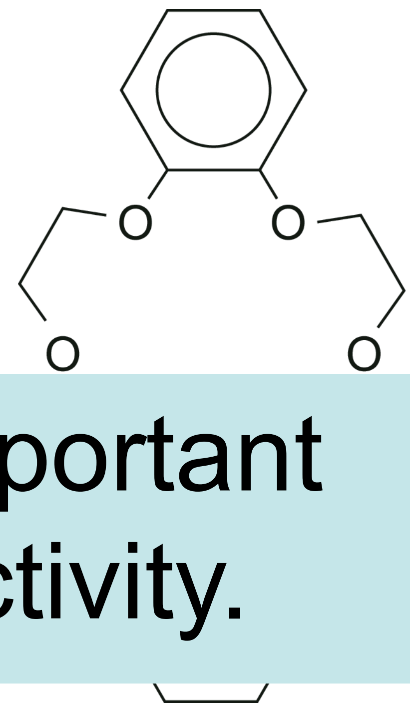
Dibenzo-18-crown-6 (DB18C6)

Δ*H* for Complex Formation

Bare complexes cannot explain the ion selectivity in solution.

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



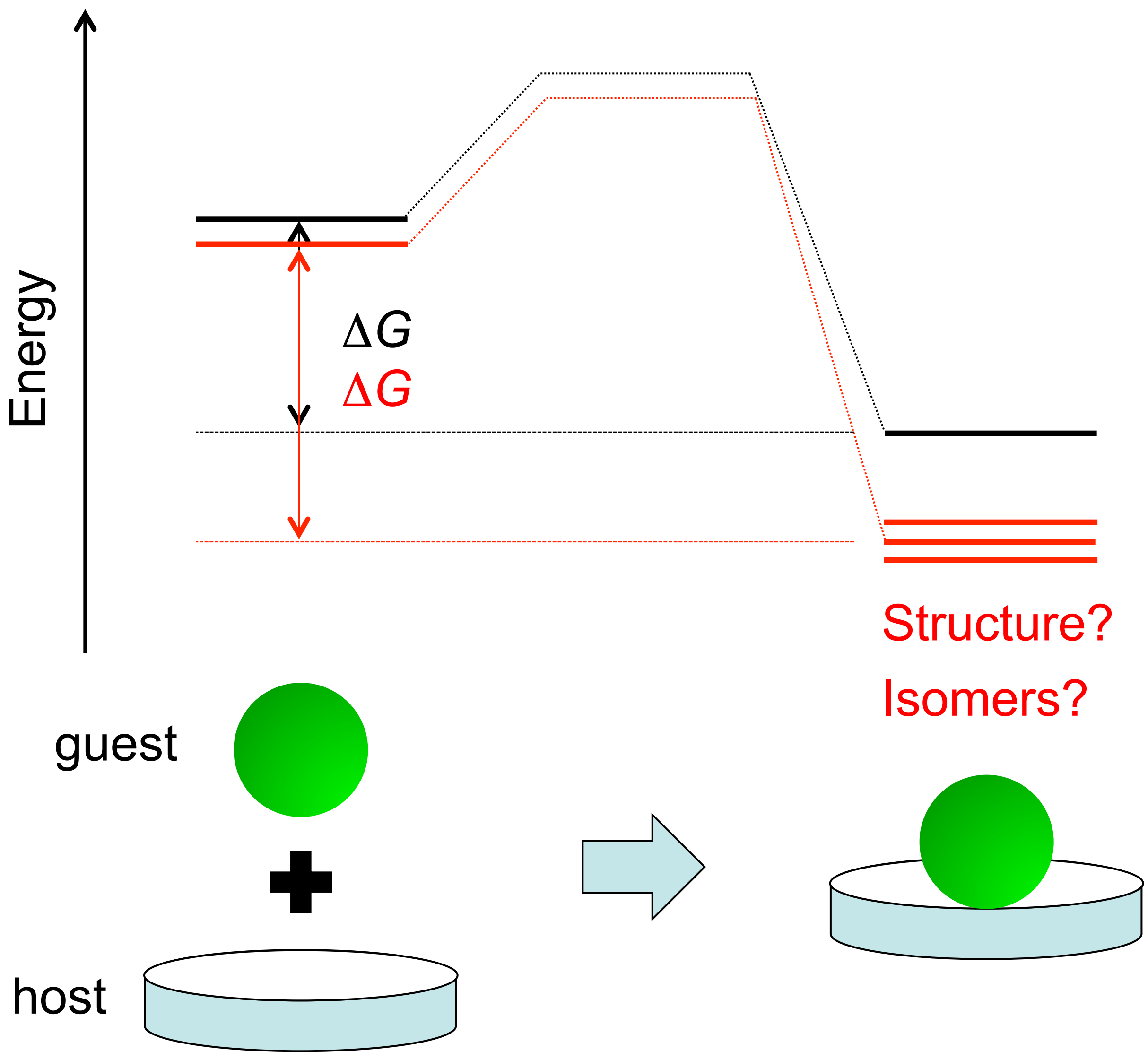


DB18C6

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

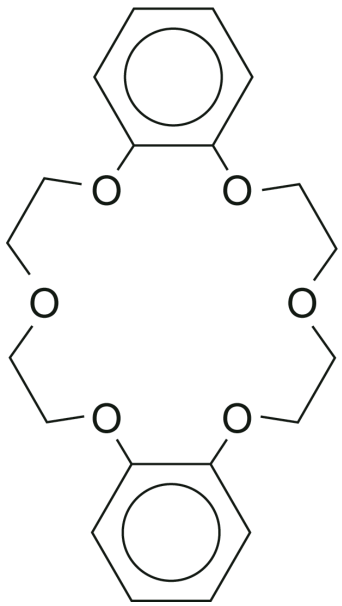
- “Cold” Spectroscopy in the Gas Phase
- IR Spectroscopy on Gold Surface

Cold Spectroscopy in the Gas Phase

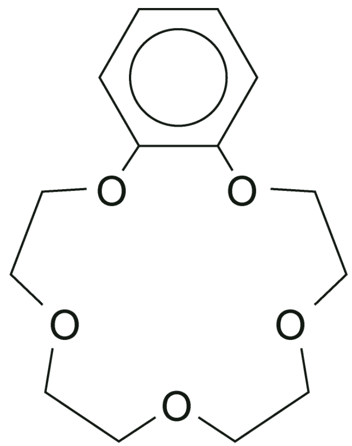
J. Phys. Chem. A, **2015**, *119*, 8097.
J. Am. Chem. Soc., **2014**, 136, 1815.
ChemPhysChem, **2013**, *14*, 649.
Phys. Chem. Chem. Phys., **2012**, *14*, 4457.
J. Phys. Chem. A, **2012**, *116*, 4057.
J. Am. Chem. Soc., **2011**, *133*, 12256.

This Study

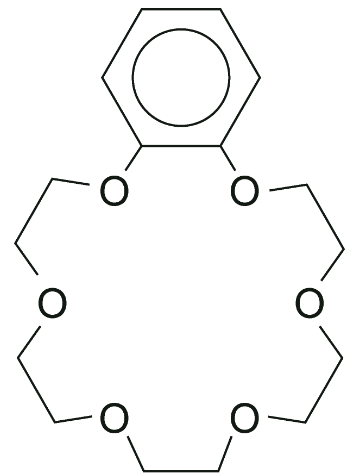
- M^{+}•DB18C6•$(H_2O)_n$
- M^{2+}•B15C5•L, M^{2+}•B18C6•L   (L = H_2O, CH_3OH)



DB18C6



B15C5

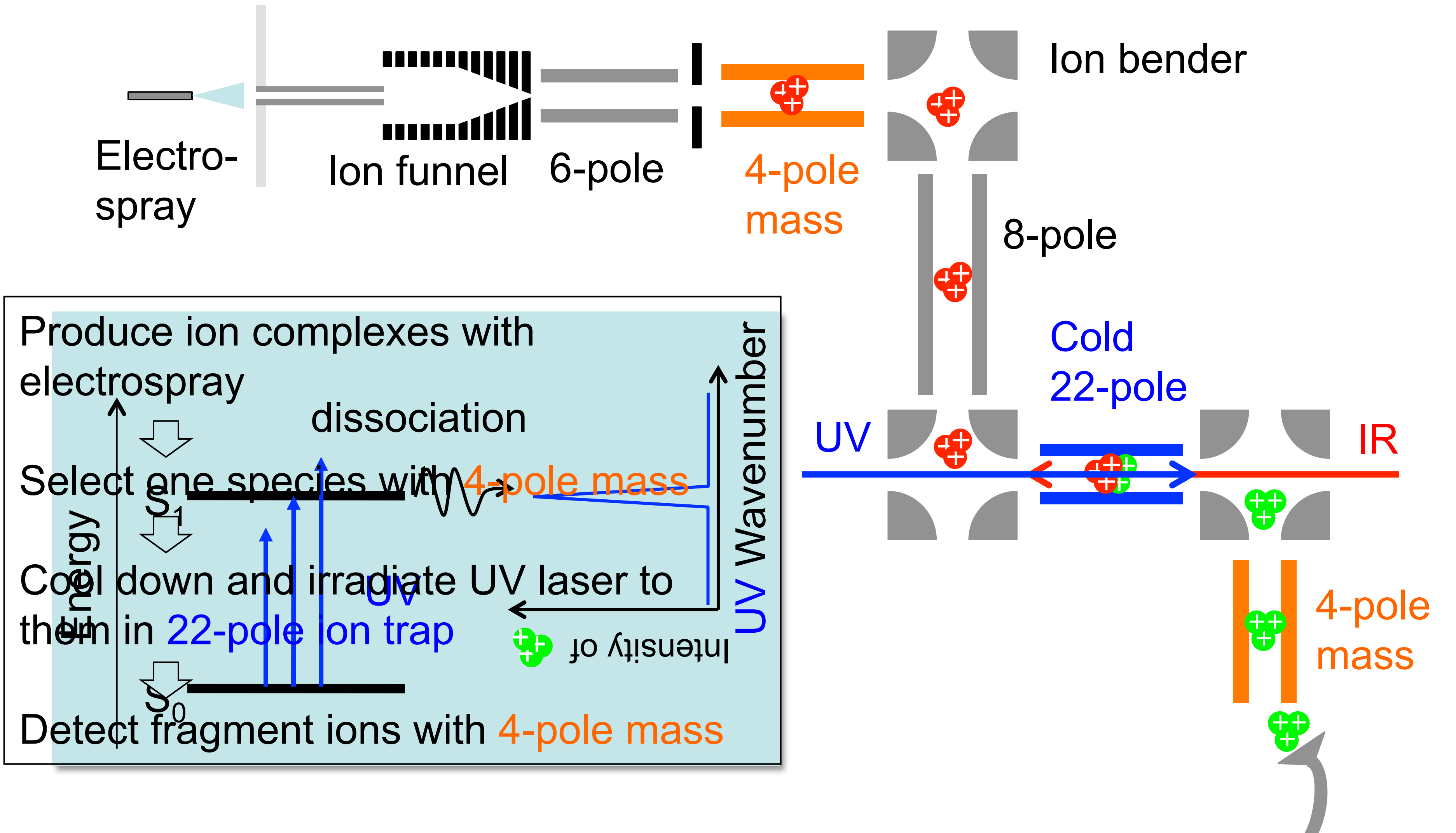


B18C6

- UV and IR spectroscopy in a cold, 22-pole ion trap
- Relation between ion selectivity and properties of ion complexes.

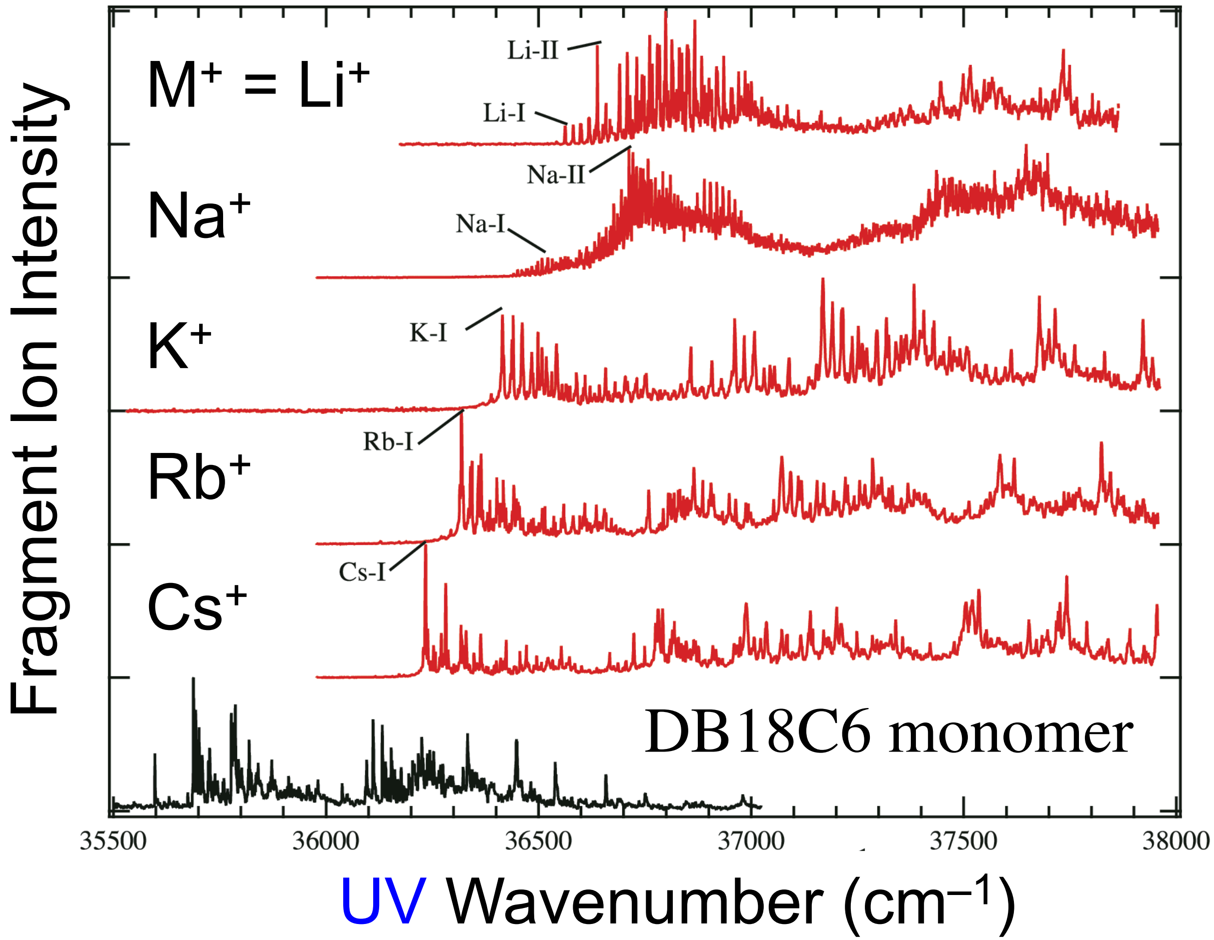
Experimental

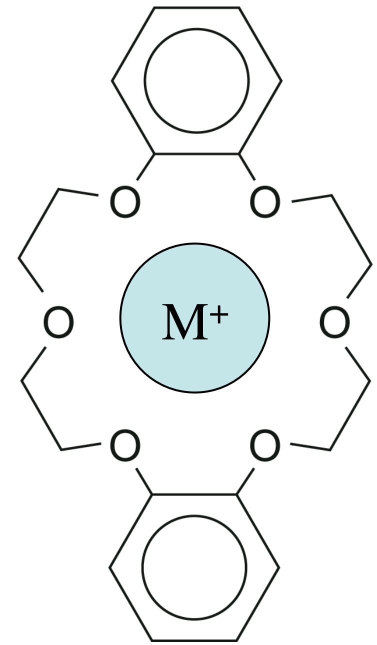
UV and IR spectra of ions are measured under cold (~10 K) conditions in the gas phase.



UV Spectra of M+•DB18C6

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



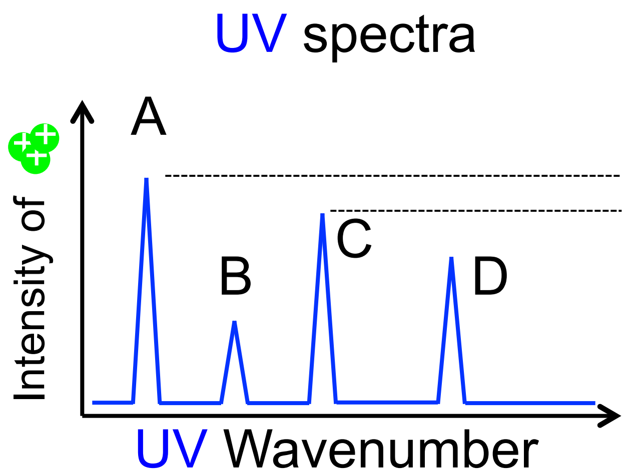


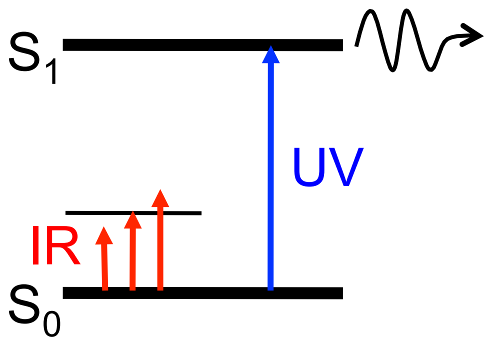
M+•DB18C6

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

IR-UV Double-Resonance

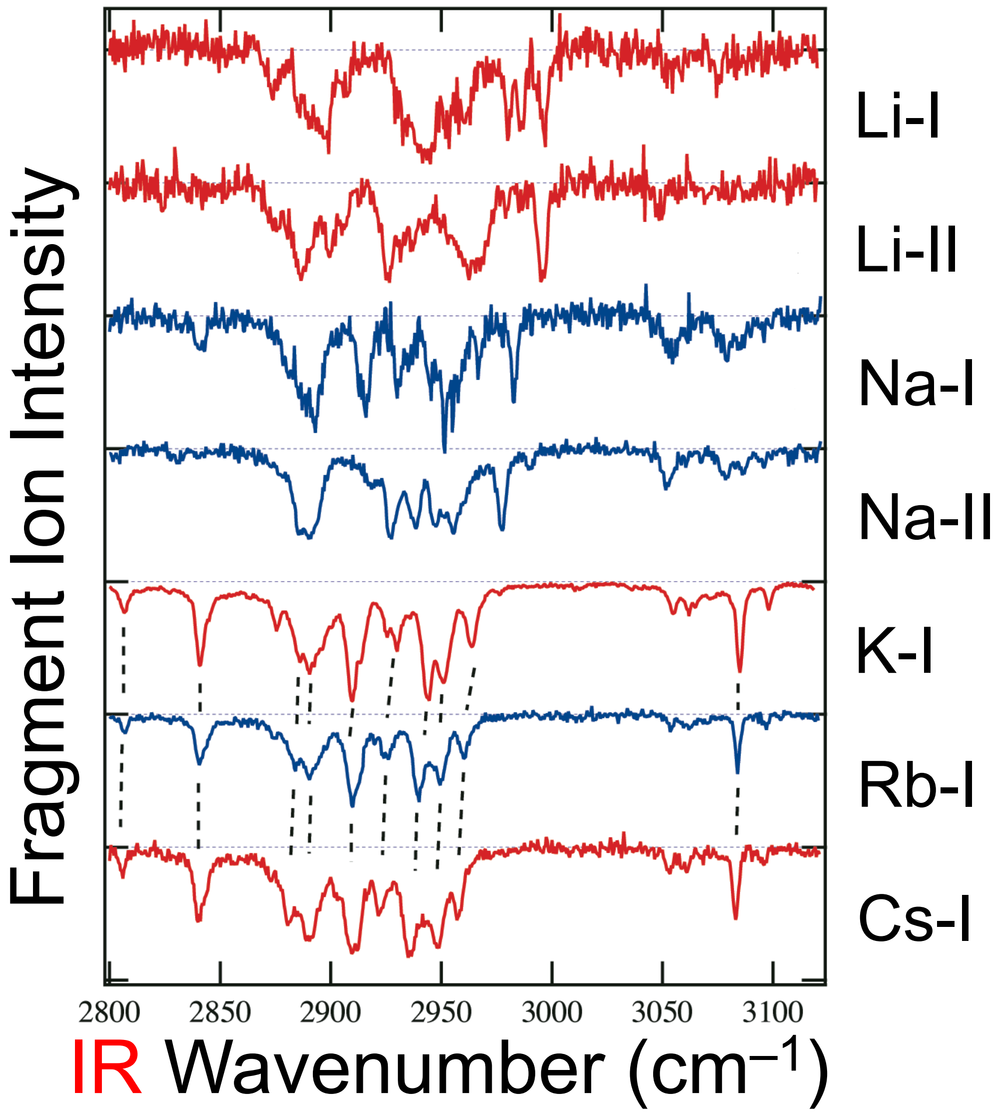
Conformer-specific IR spectra can be measured by IR-UV double-resonance.

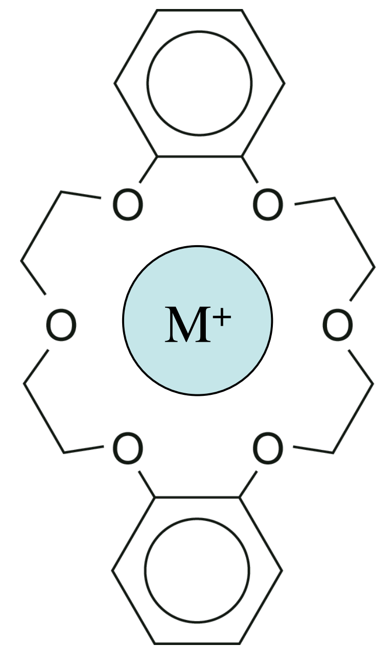




IR Spectra of M^+•DB18C6

Different IR features originate from different conformers.

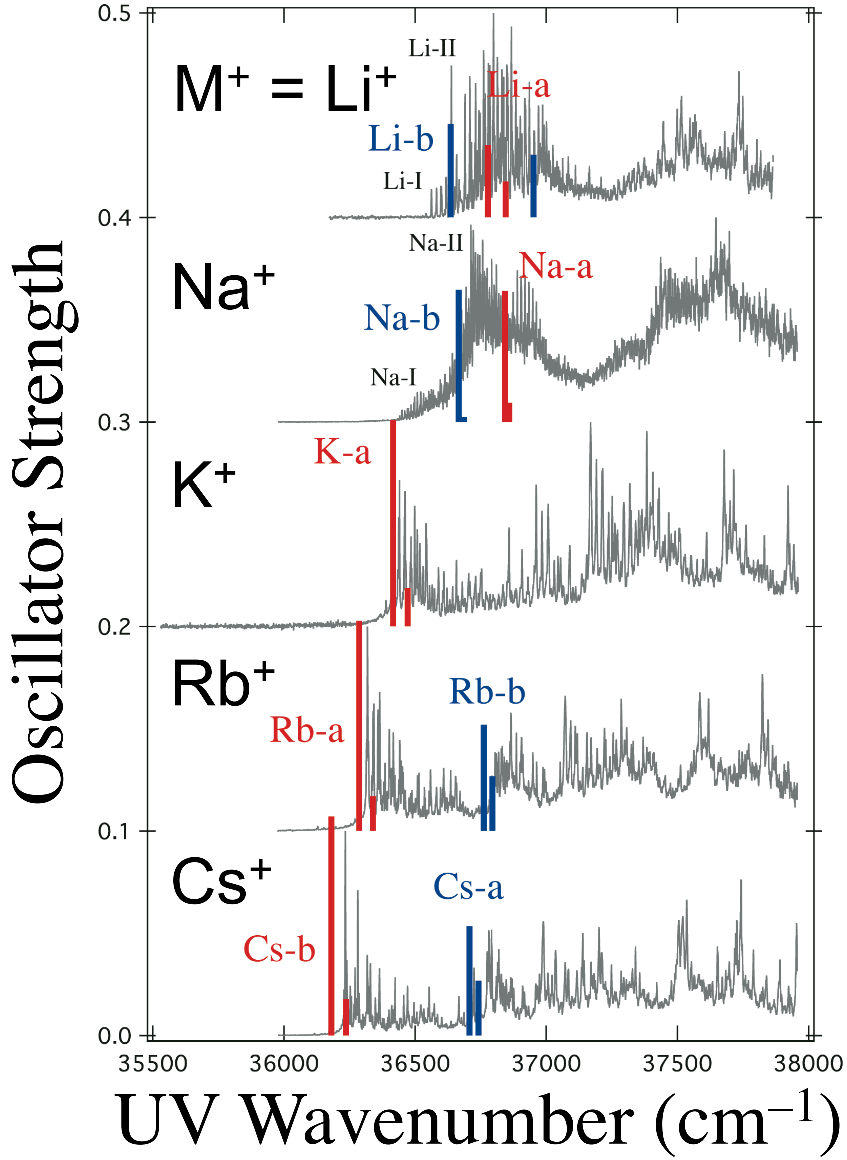




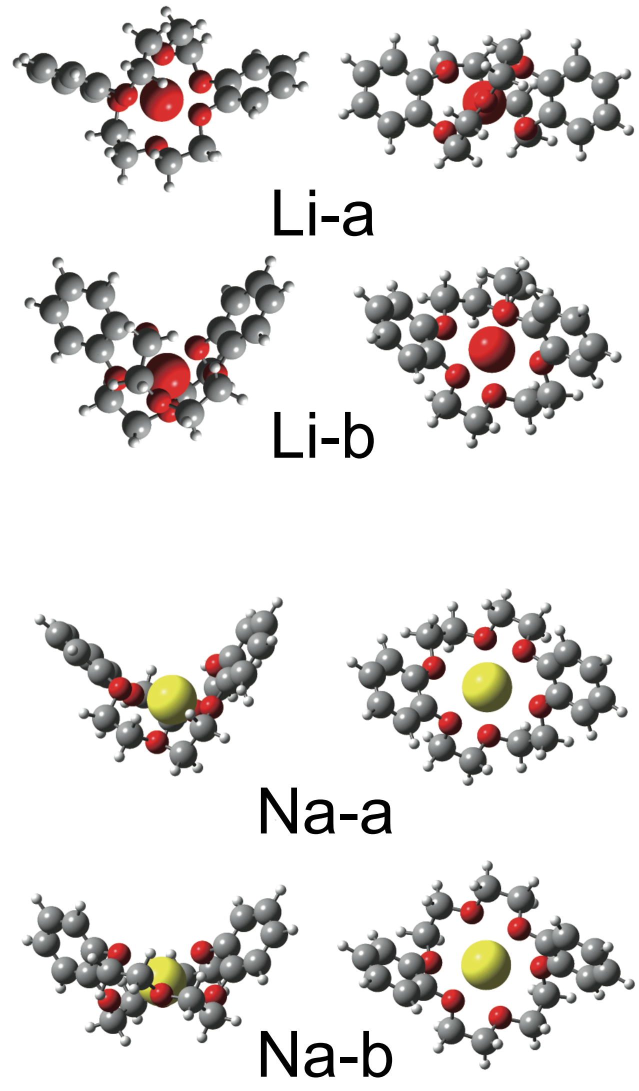
M^+•DB18C6

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

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

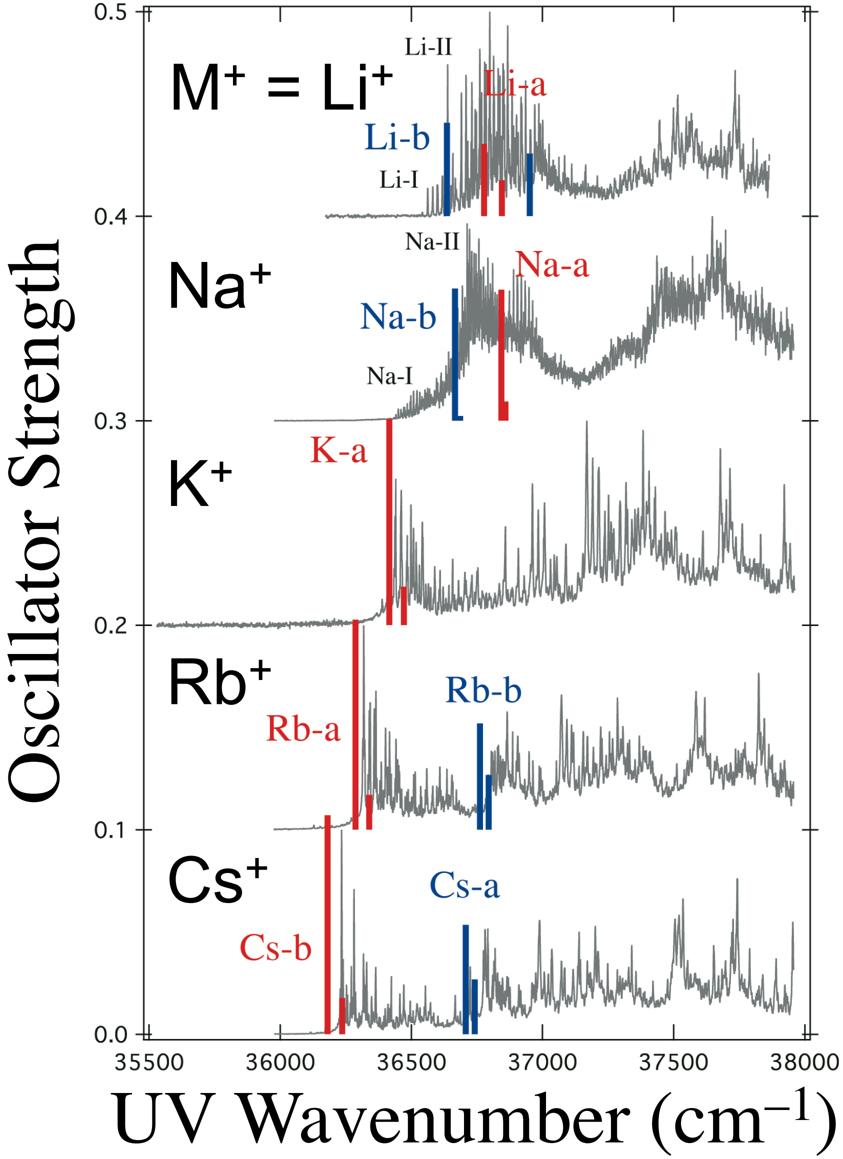


M05-2X/6-31+G(d) with Stuttgart RLC ECP
A scaling factor of 0.8340 is used.

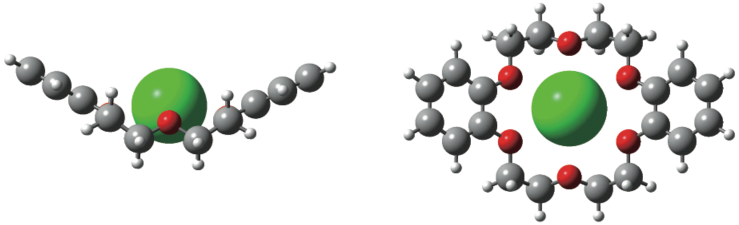


Ether rings distorted for Li^+ and Na^+

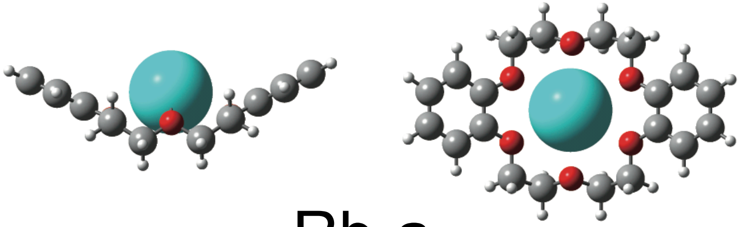
Structure of M⁺•DB18C6 (M⁺ = K⁺, Rb⁺, Cs⁺)



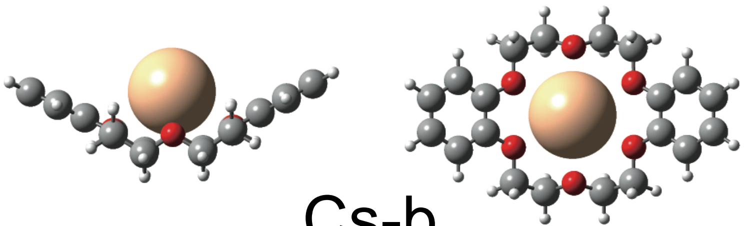
M05-2X/6-31+G(d) with Stuttgart RLC ECP
A scaling factor of 0.8340 is used.



K-a



Rb-a



Cs-b

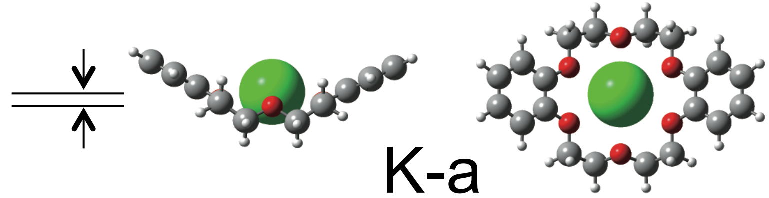
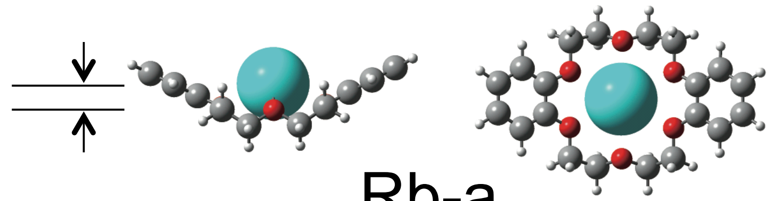
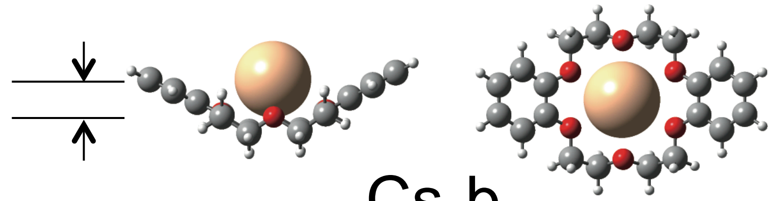
Ether rings largely open

K^+ in the ring

Rb^+, Cs^+ on the ring

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

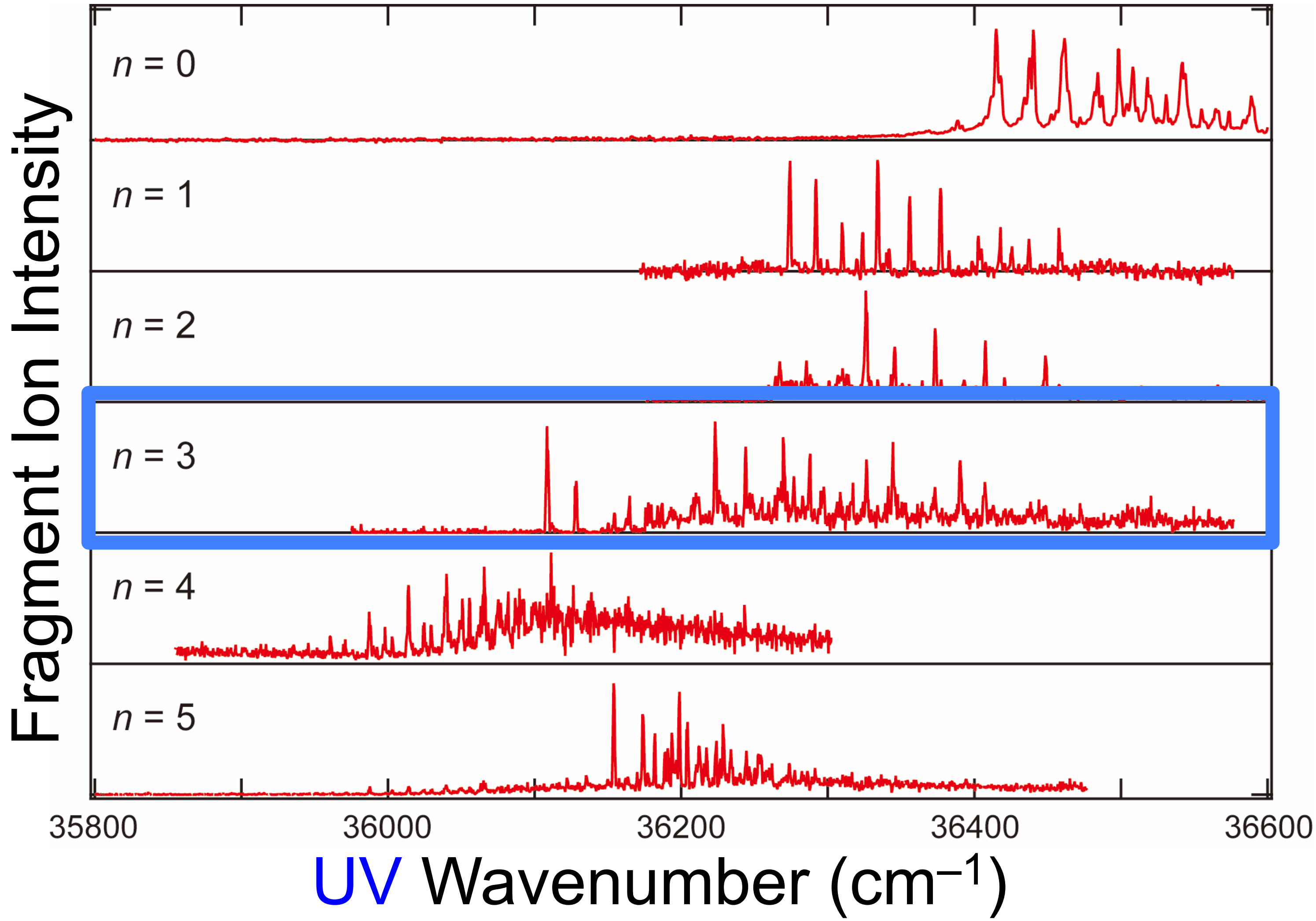
Distance between M^+ and DB18C6 becomes longer with increasing ion size.

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

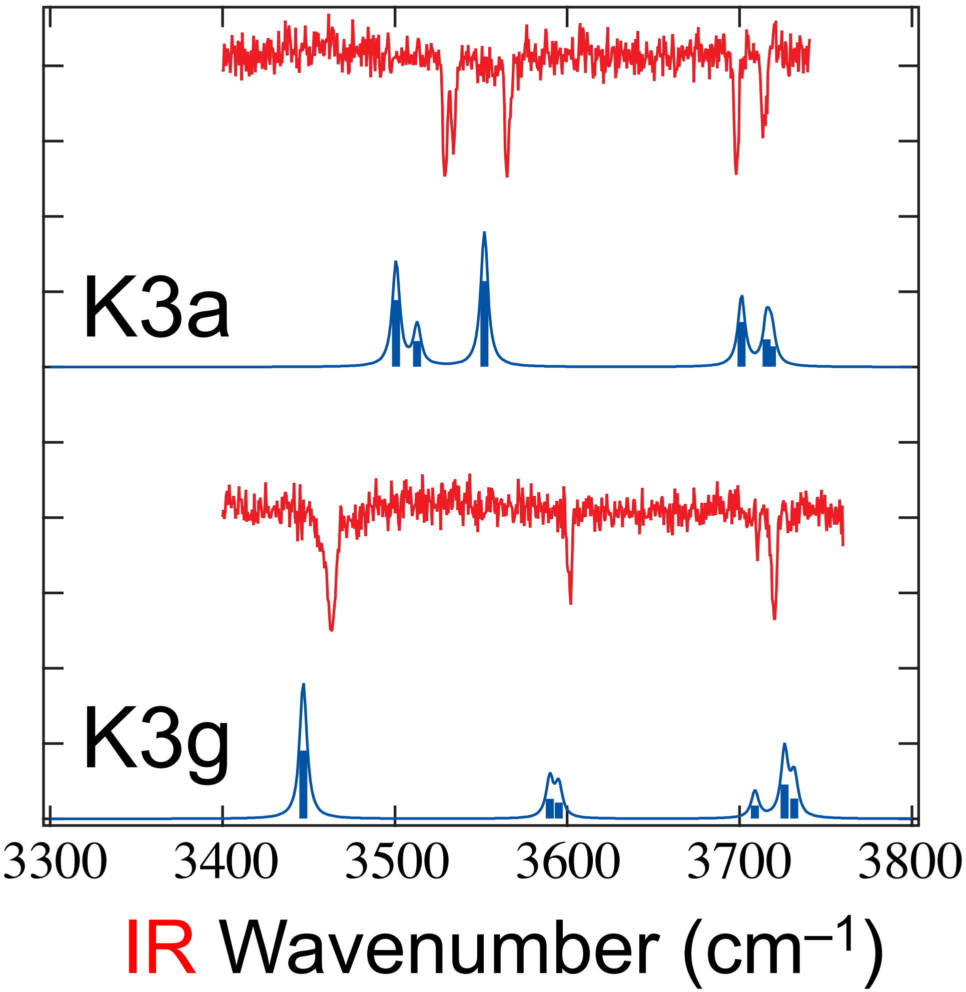
UV Spectra of $K^+ \cdot DB18C6 \cdot (H_2O)_n$

UV spectra also show sharp bands.

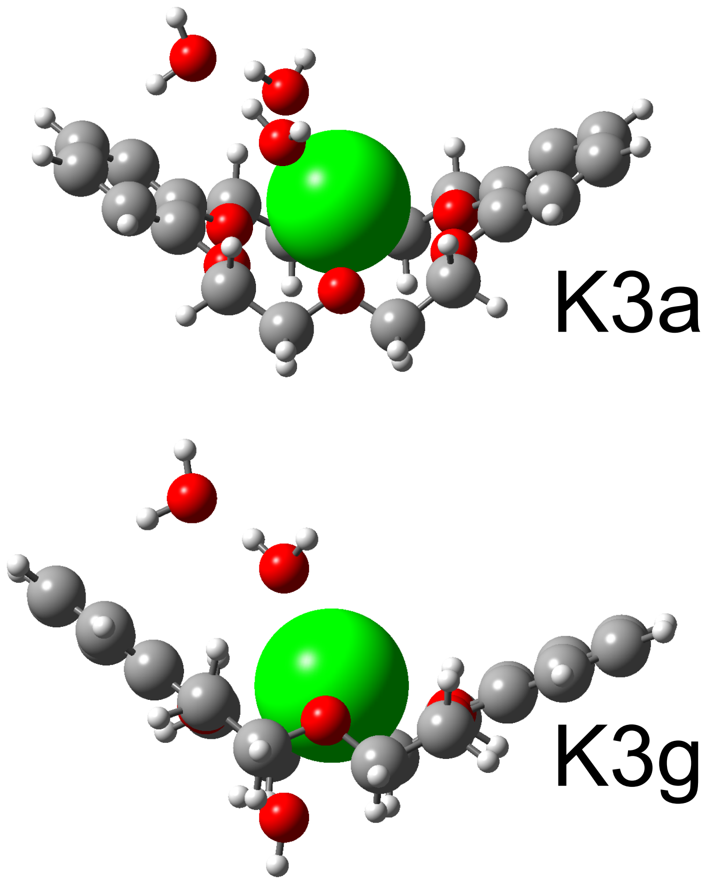
Conformer-specific IR spectra can be measured.



Conformers of K^+•DB18C6•$(H_2O)_3$



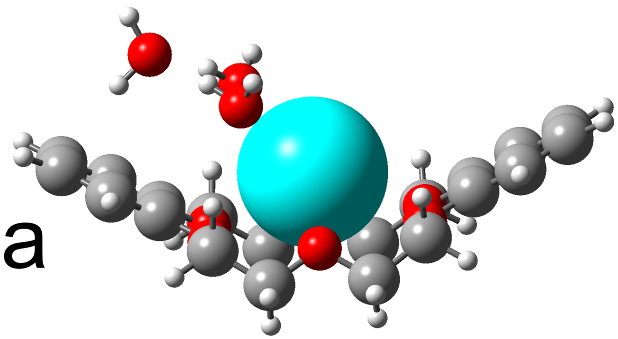
Two conformers for K^+.



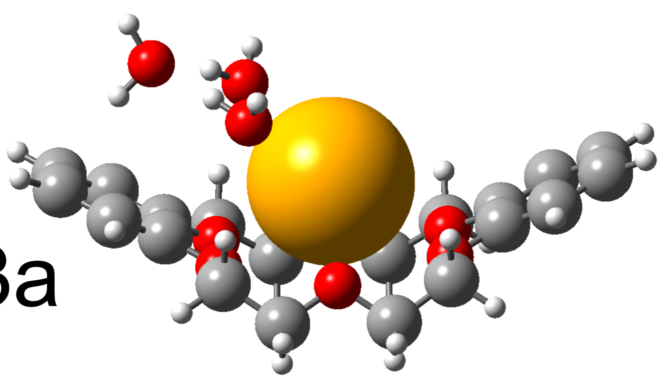
Inokuchi et al., *JACS*, **2014**, *136*, 1815.

Conformers of $M^+\bullet DB18C6\bullet(H_2O)_3$

One conformer for Rb^+ and Cs^+.

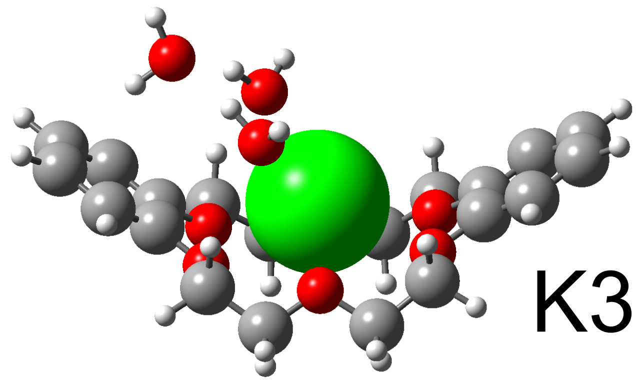


Rb3a

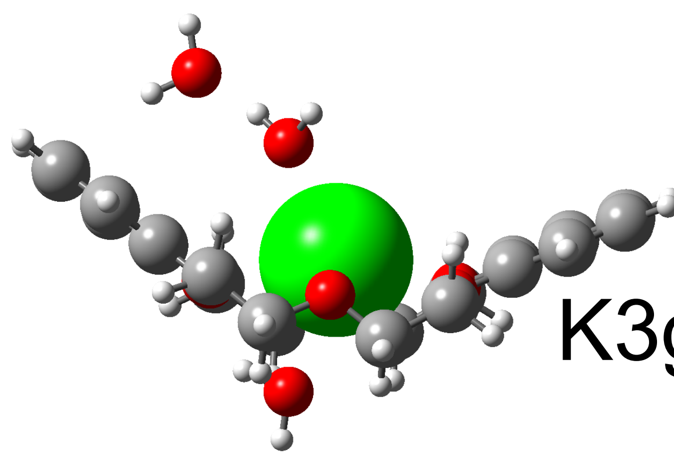


Cs3a

Two conformers for K^+.



K3a

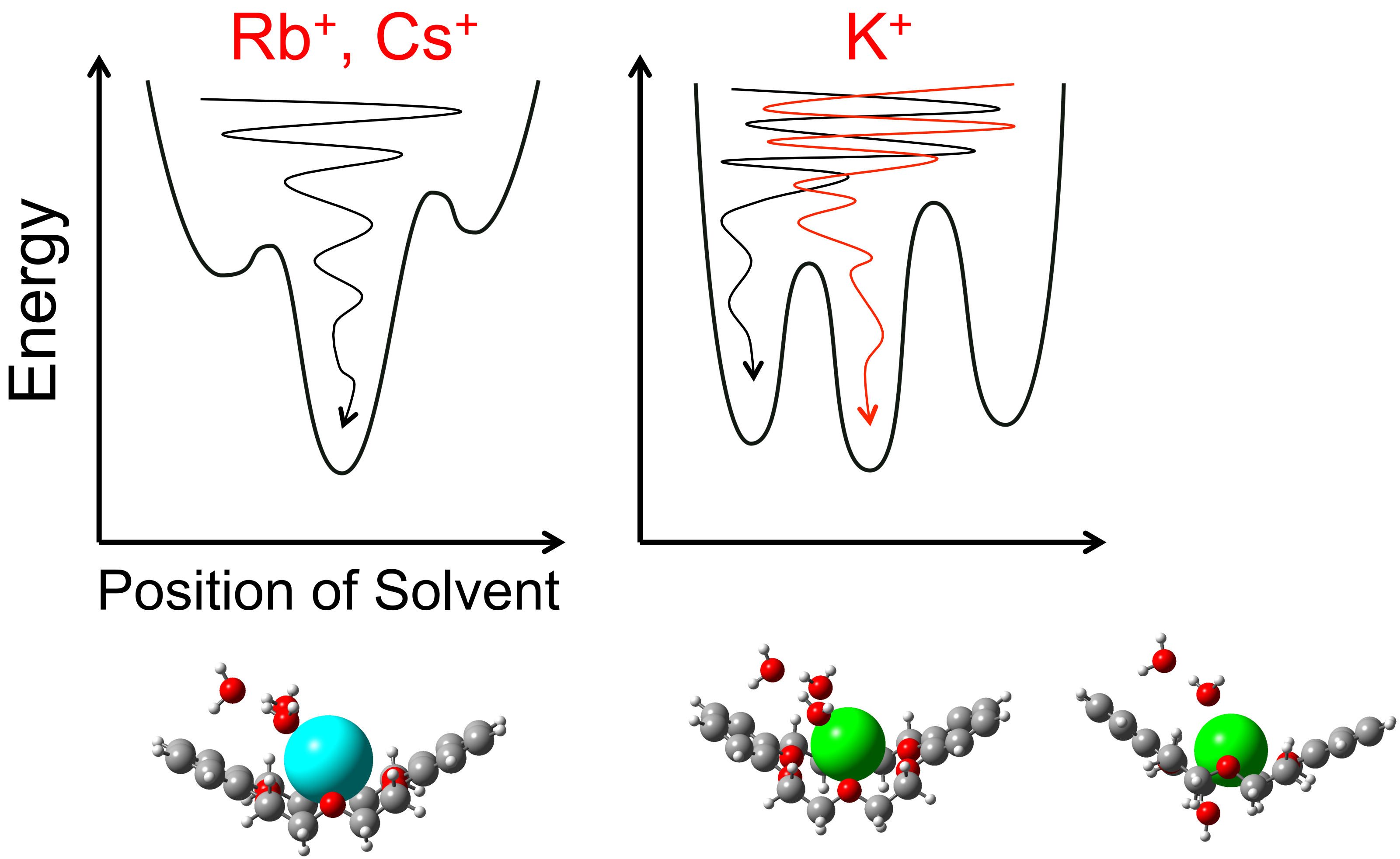


K3g

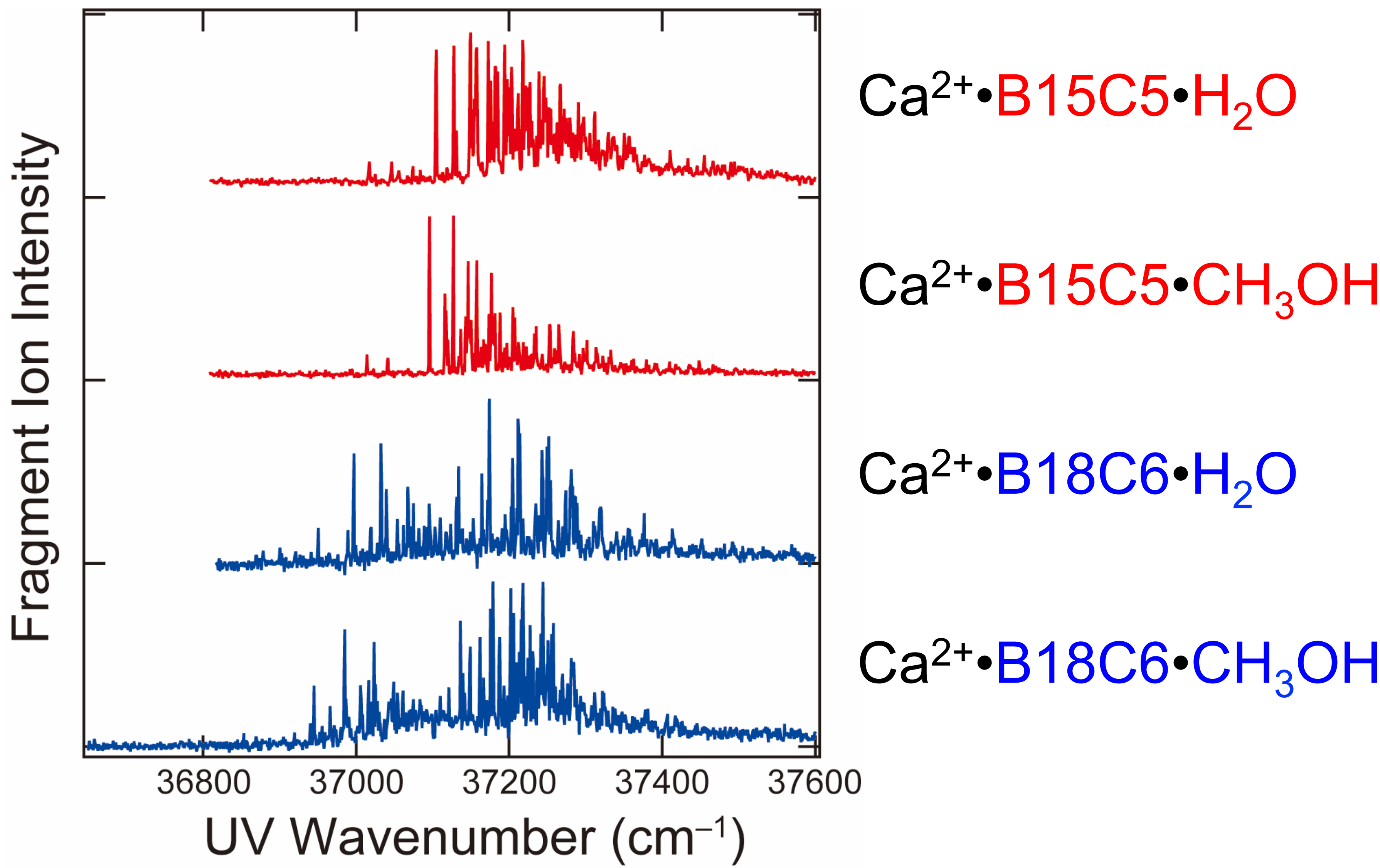
Inokuchi et al., *JACS*, **2014**, *136*, 1815.

The Number of Conformers

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



UV Spectra of Ca^{2+}•CE•L



Inokuchi et al., J. Phys. Chem. A, **2015**, *119*, 8097.

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

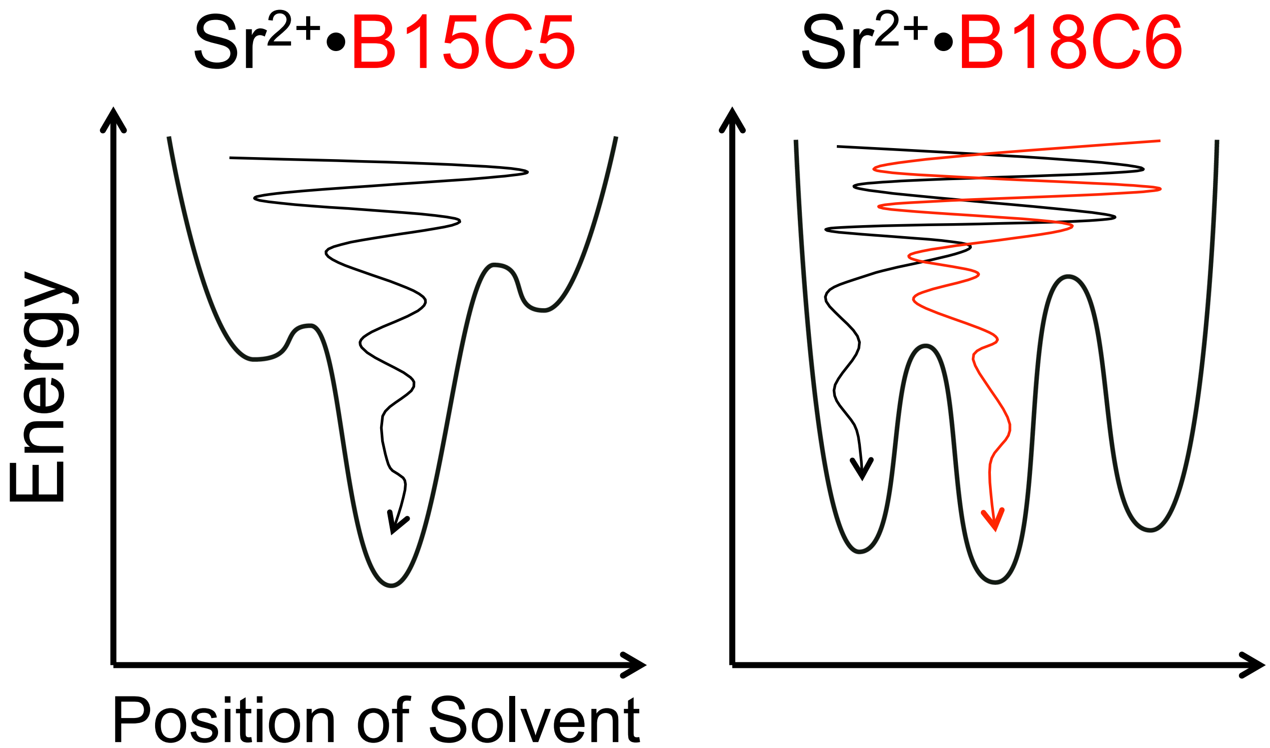
L	H_2O		CH_3OH		Ion radii (Å)
CE	B15C5	B18C6	B15C5	B18C6	
Ca^{2+}	1	3	1	3	1.14
Sr^{2+}	2	3	2	5	1.32
Ba^{2+}	2	1	1	2	1.49
Mn^{2+}	1	2	1	3	0.97

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

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

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

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



Summary

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.

Acknowledgment

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Prof. Takayuki Ebata　　Dr. Ryoji Kusaka

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