"Cold" Ion Spectroscopy of Host-Guest Complexes in the Gas Phase

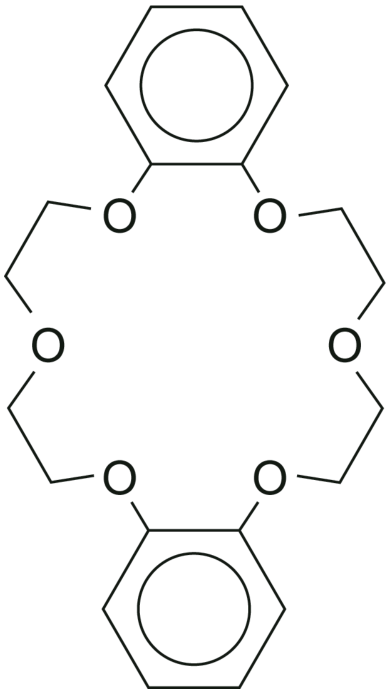
Yoshiya INOKUCHI

Hiroshima University

in collaboration with Prof. Tom Rizzo

Crown Ethers (CEs)

Crown ethers (CEs) show ion selectivity.

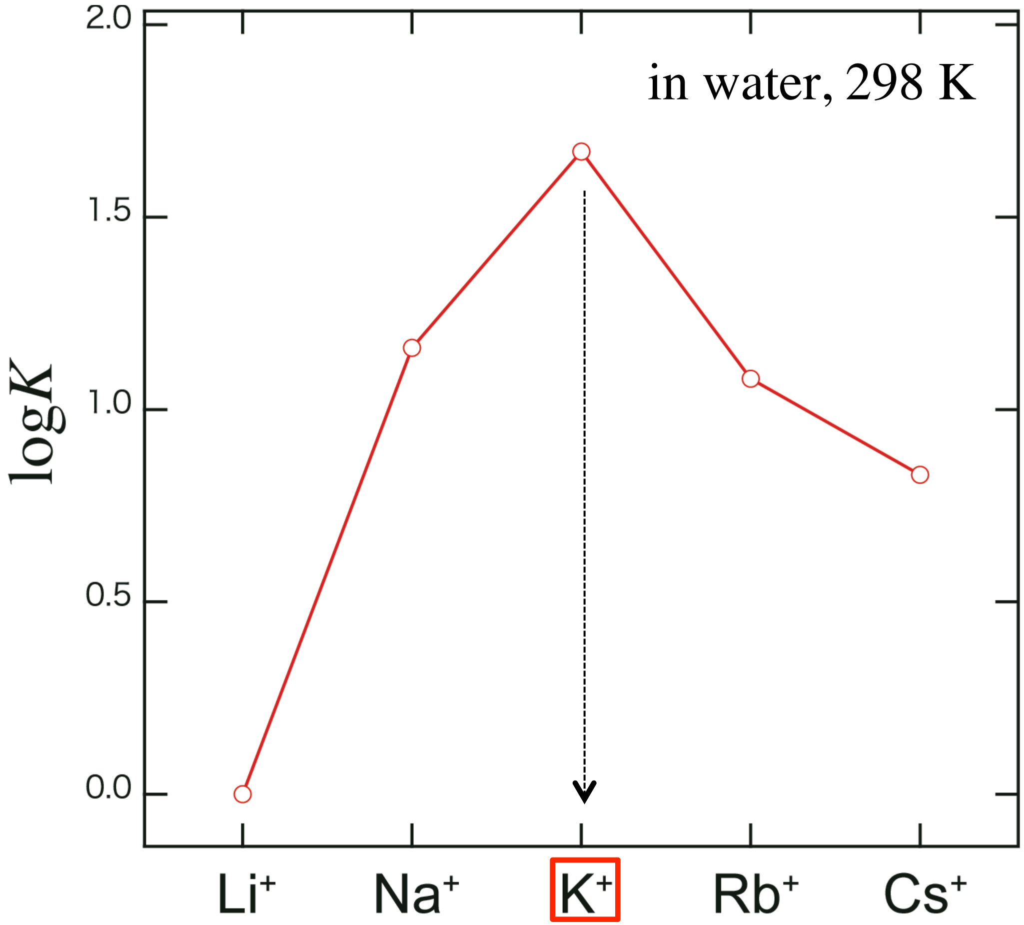


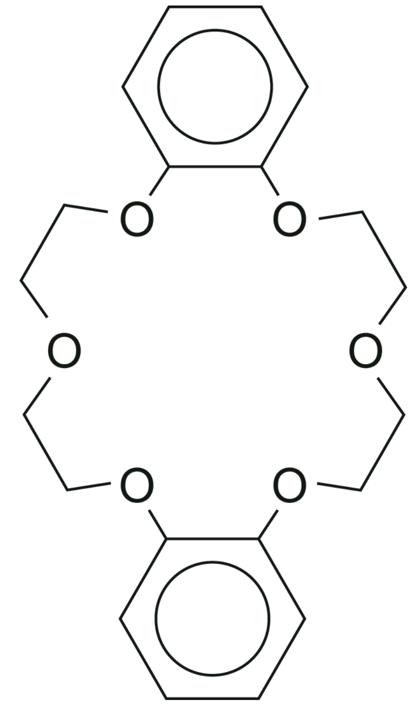
Dibenzo-18-crown-6
(DB18C6)

Ion Selectivity of CE

DB18C6 captures K^+ selectively in water.

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



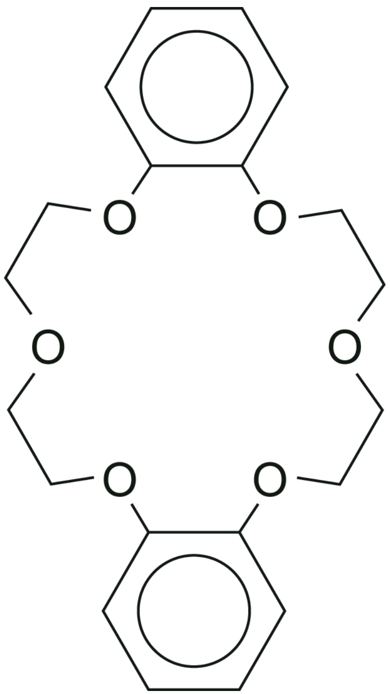


DB18C6

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

Our Final Goal

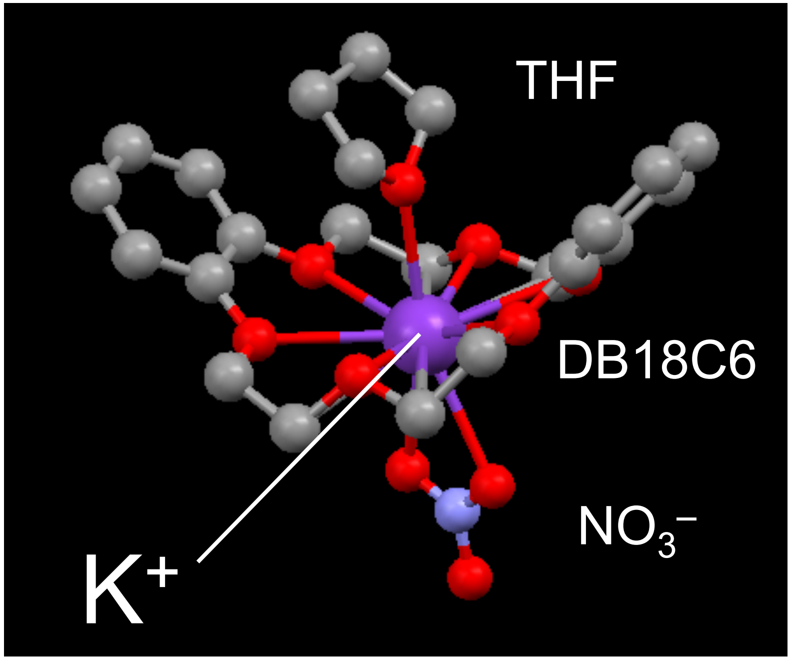
Our final goal is
to reveal the origin of ion selectivity
in terms of quantum chemistry.



Dibenzo-18-crown-6
(DB18C6)

Crystal Structure of M^+•DB18C6

X-ray analysis of crystal tells us the relation in size, but…
no information on the origin of ion selectivity in solution.

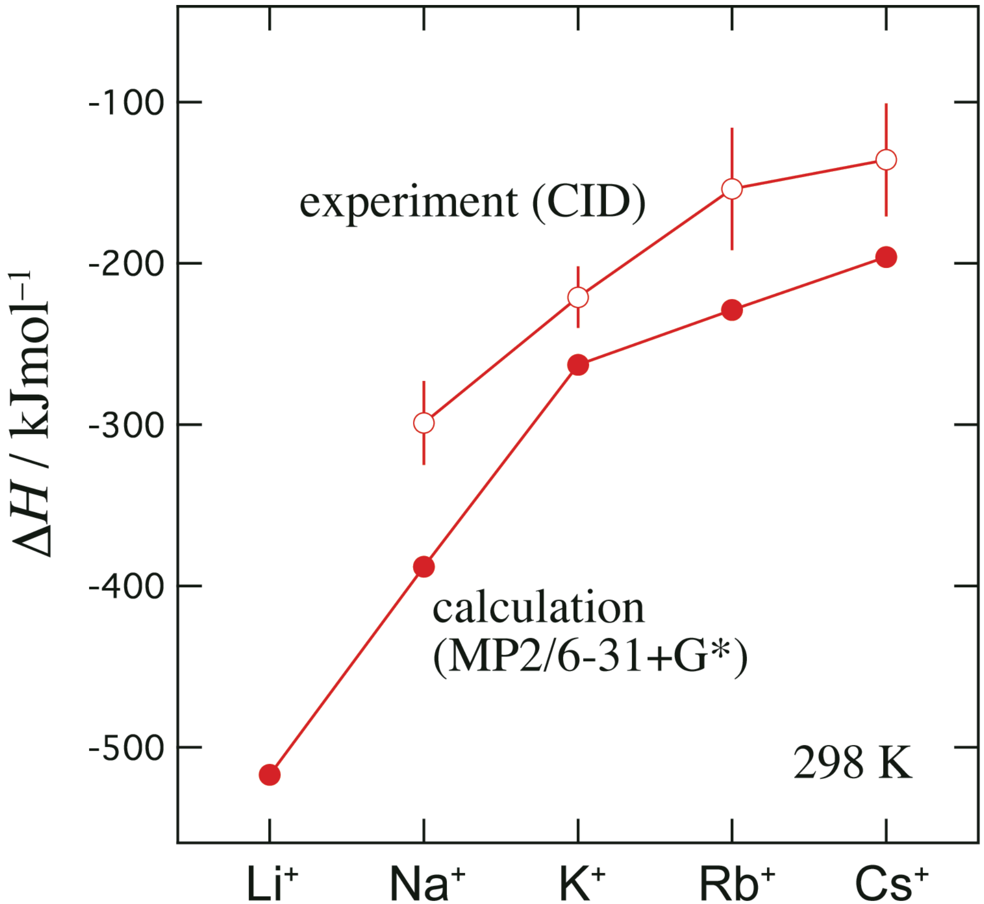


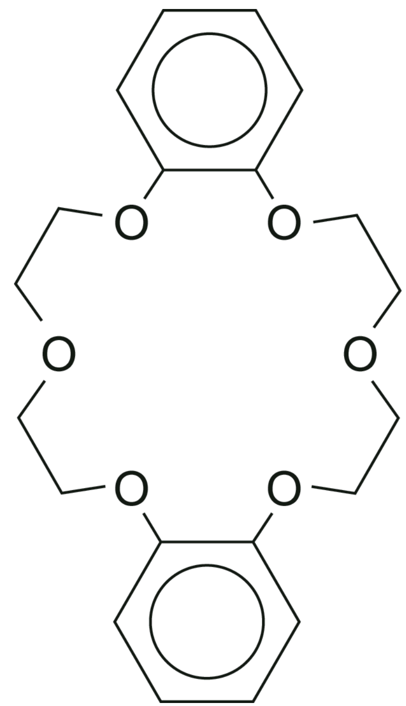
(Cambridge Structural Database)

ΔH for Complex Formation

Bare complexes cannot explain the ion selectivity in solution.

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





DB18C6

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

Solvated Complexes

Solvated complexes are used to examine the solvent effect at a molecular level.

$$M^+_{aq} + CE_{aq} \underset{}{\overset{K}{\rightleftharpoons}} (M^+\bullet CE)_{aq}$$

$$M^+\bullet(H_2O)_m + CE\bullet(H_2O)_n \overset{K}{\rightleftharpoons} (M^+\bullet CE)\bullet(H_2O)_k$$

Relation between K, ΔG, ΔH, and ΔS

We have to determine the structure and the number of conformers to evaluate the ion selectivity.

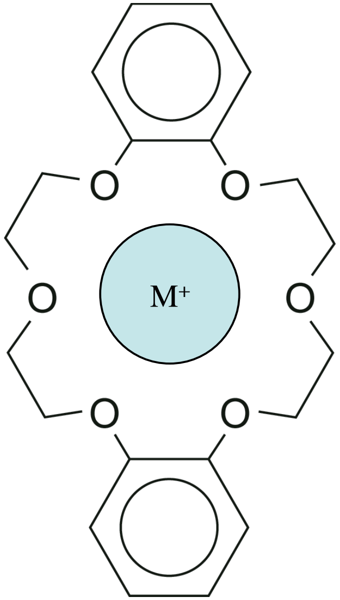
$$K = \exp\left(-\frac{\Delta G}{RT}\right)$$

$$\Delta G = \Delta H - T\Delta S$$

- *H* and *S* depend on the structure.
- The more conformations a complex takes, the more stable it is.

This Study

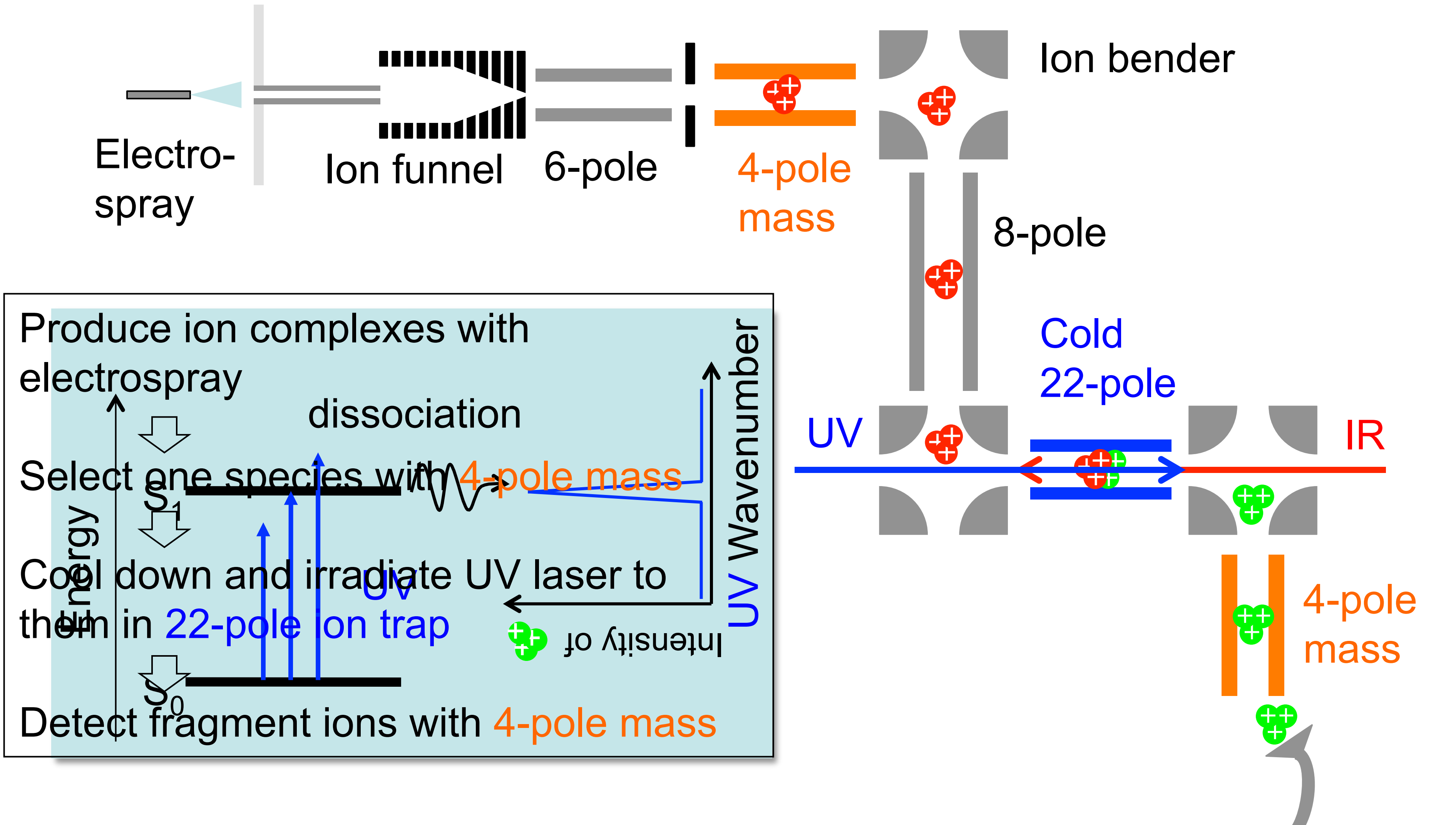
- M^+•DB18C6 (M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+)
- M^+•DB18C6•$(H_2O)_n$ (n = 1–5)



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

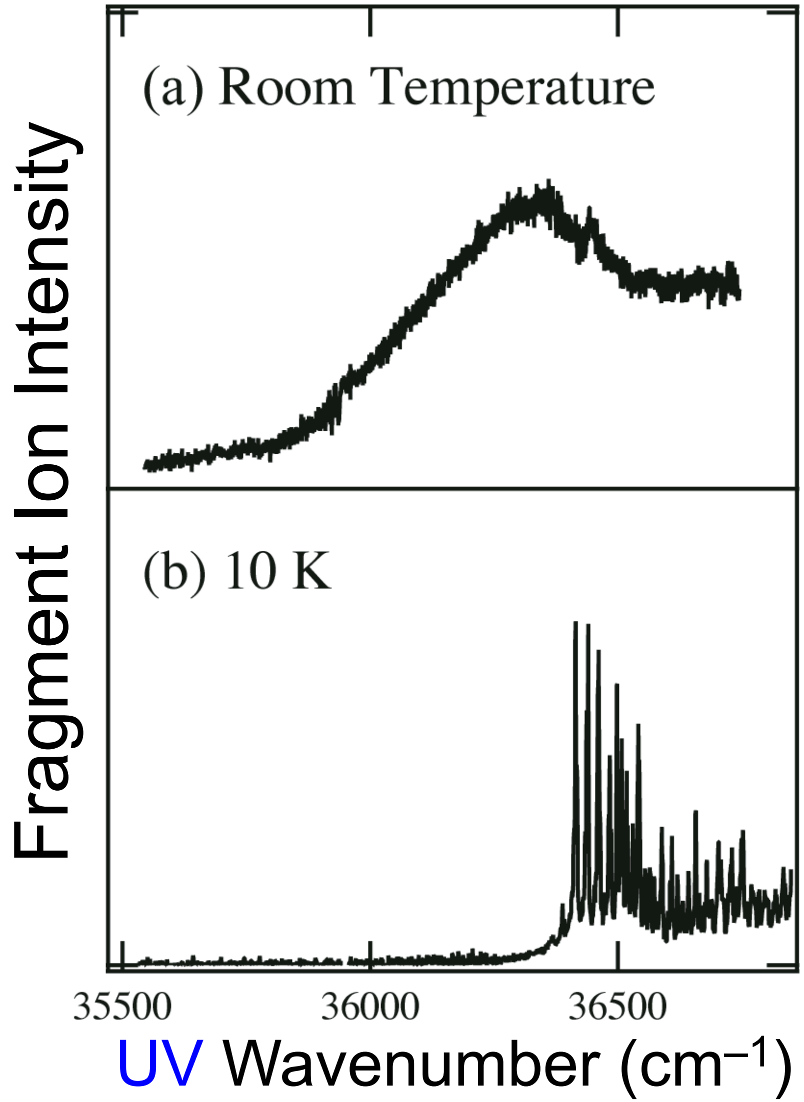
Experimental (simple ver.)

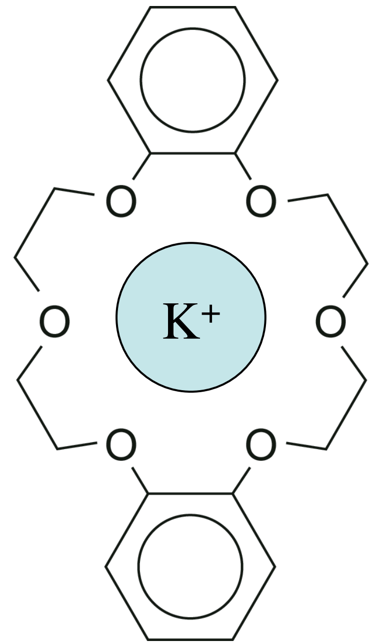
UV and IR spectra of ions are measured under cold (~10 K) conditions in the gas phase.



Effect of the Cooling on UV Spectra

Sharp UV bands are observed thanks to the cooling.



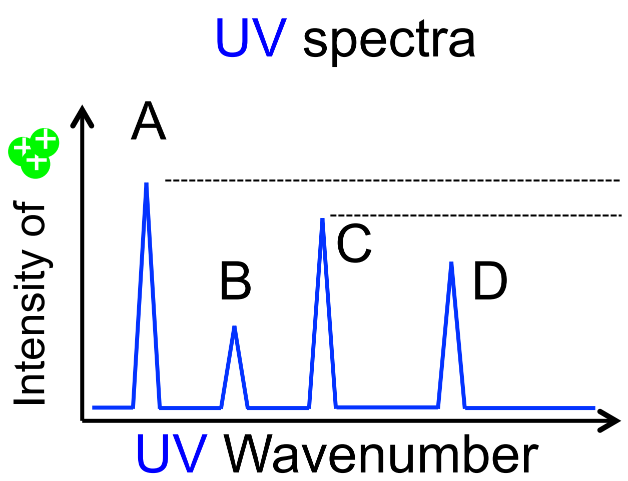


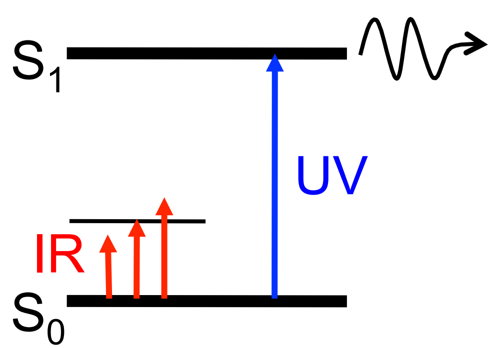
K$^+$•DB18C6

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

IR-UV Double-Resonance

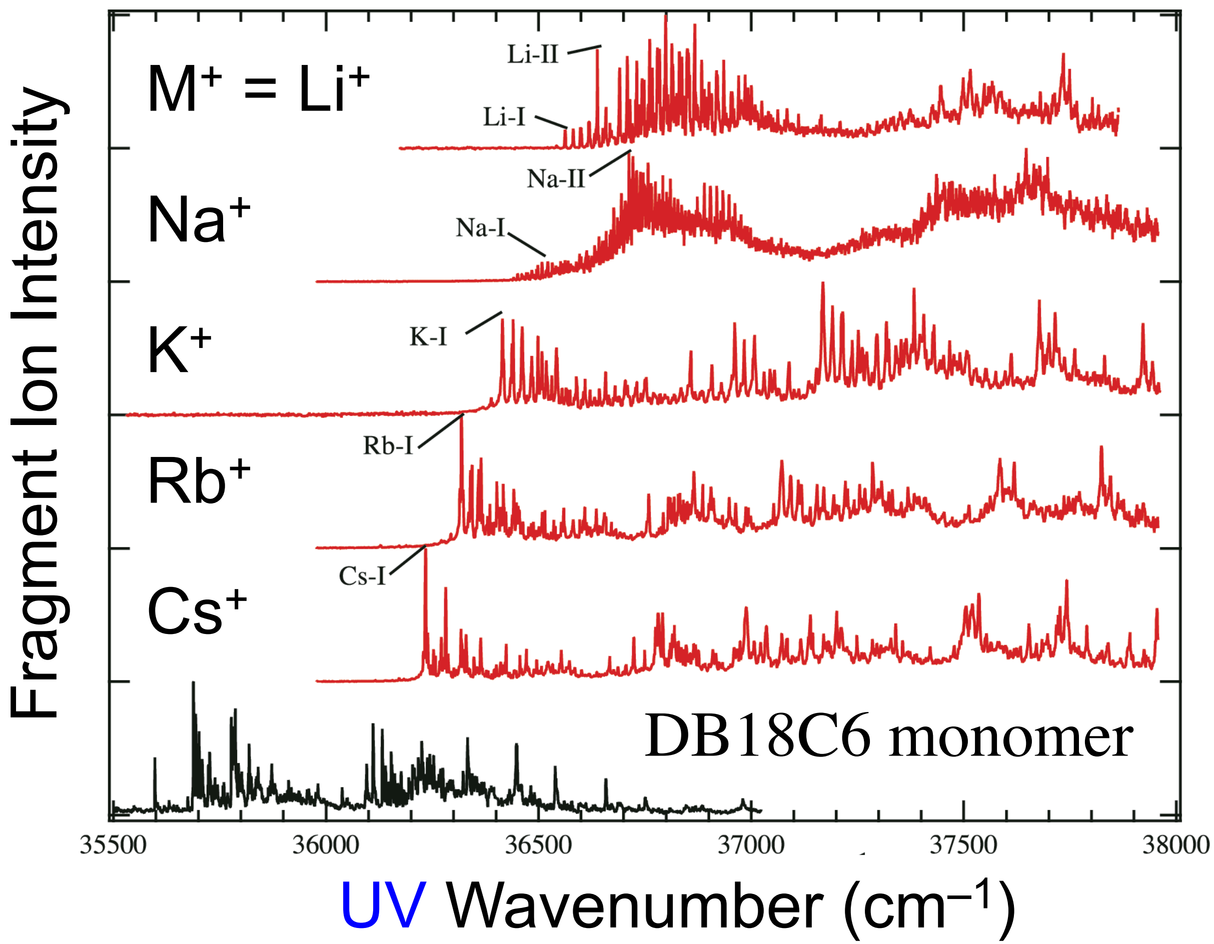
Conformer-specific IR spectra can be measured by IR-UV double-resonance.

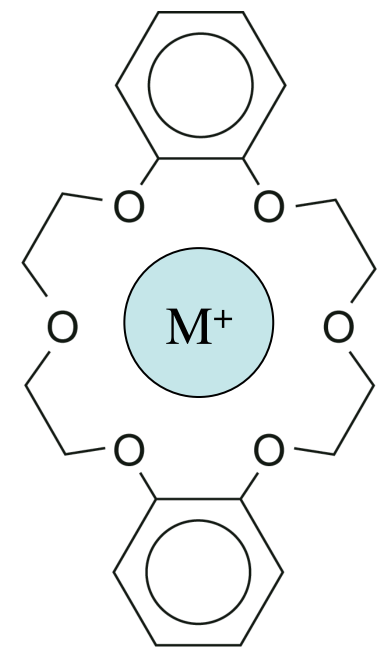




UV Spectra of M^+•DB18C6

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



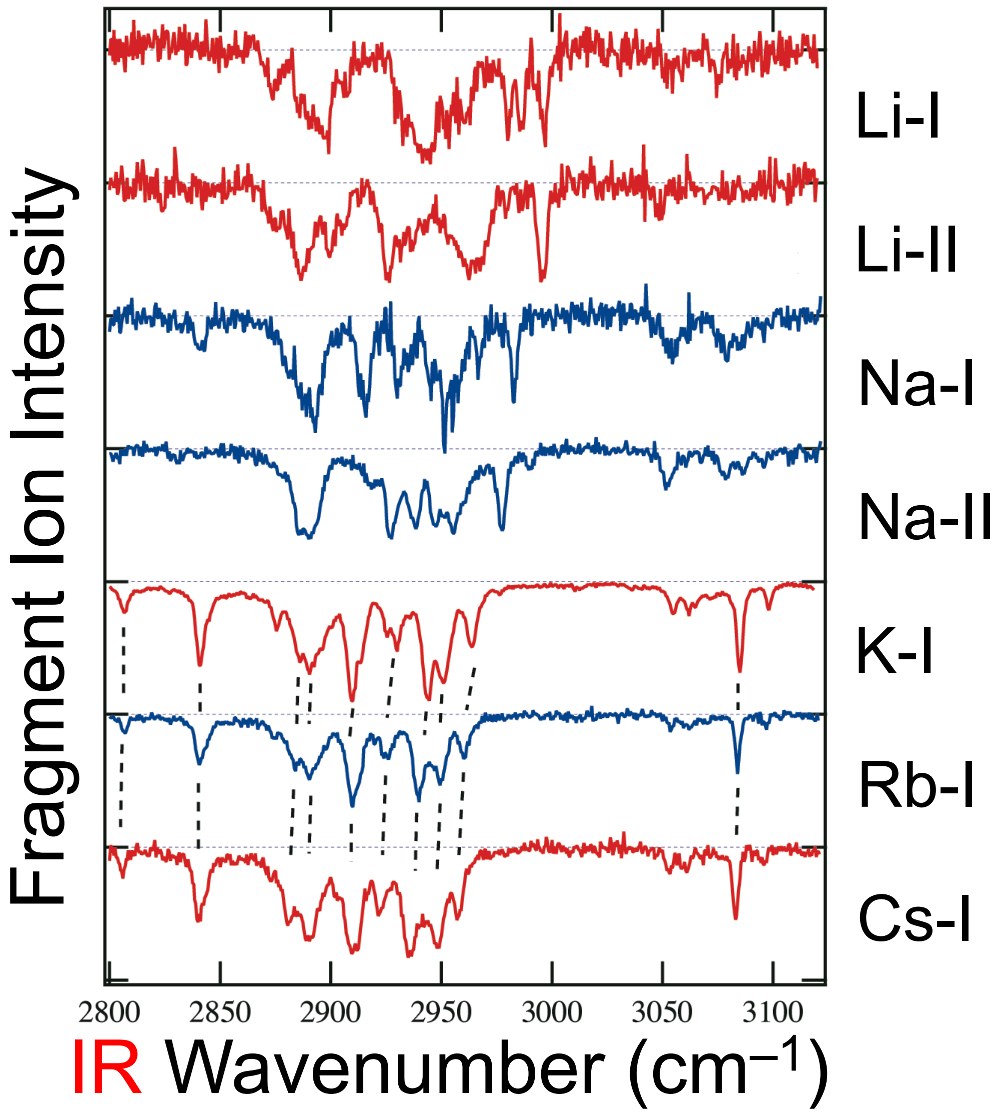


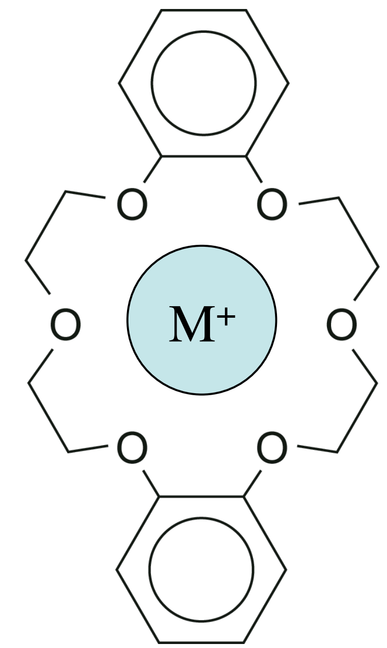
M^+•DB18C6

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

IR Spectra of M^+•DB18C6

Different IR features originate from different conformers.



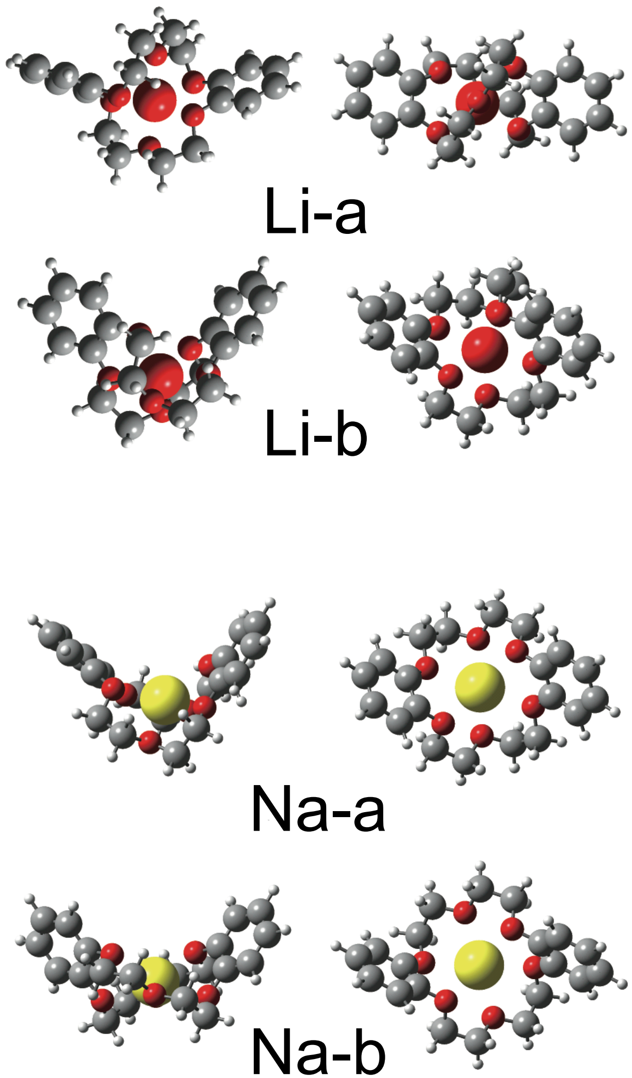


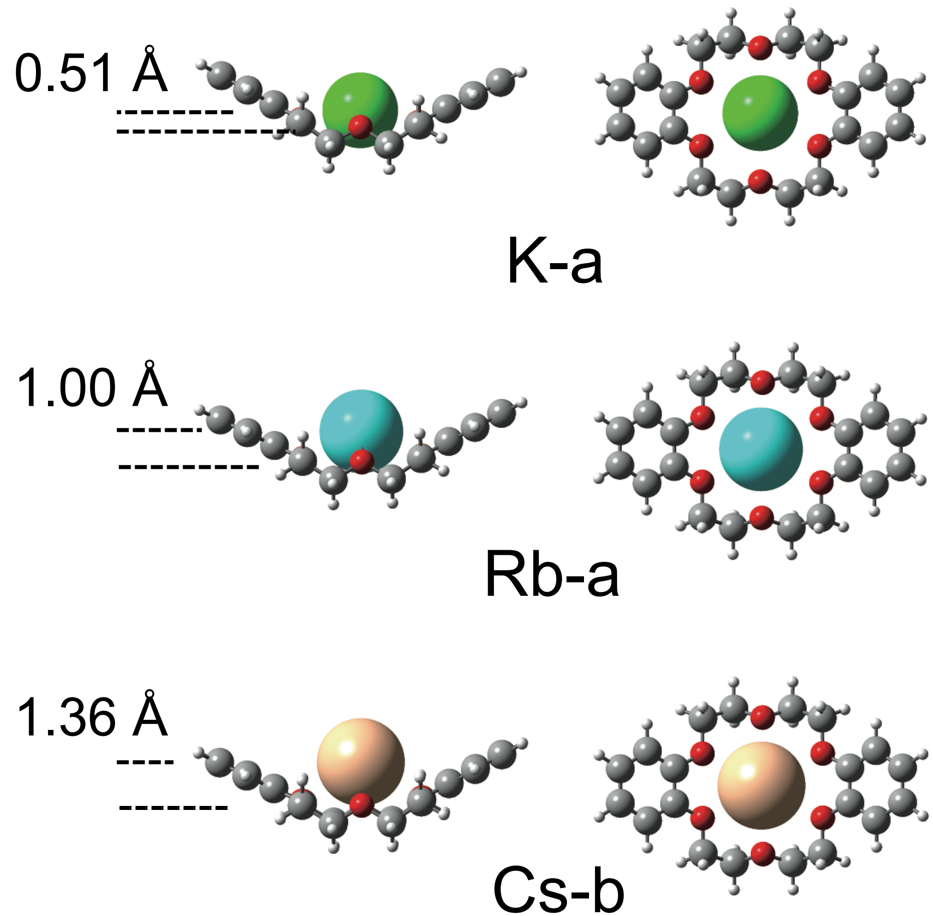
M^+•DB18C6

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

Structure of M^+•DB18C6

The conformer structure is determined with the aid of quantum chemical calculations.



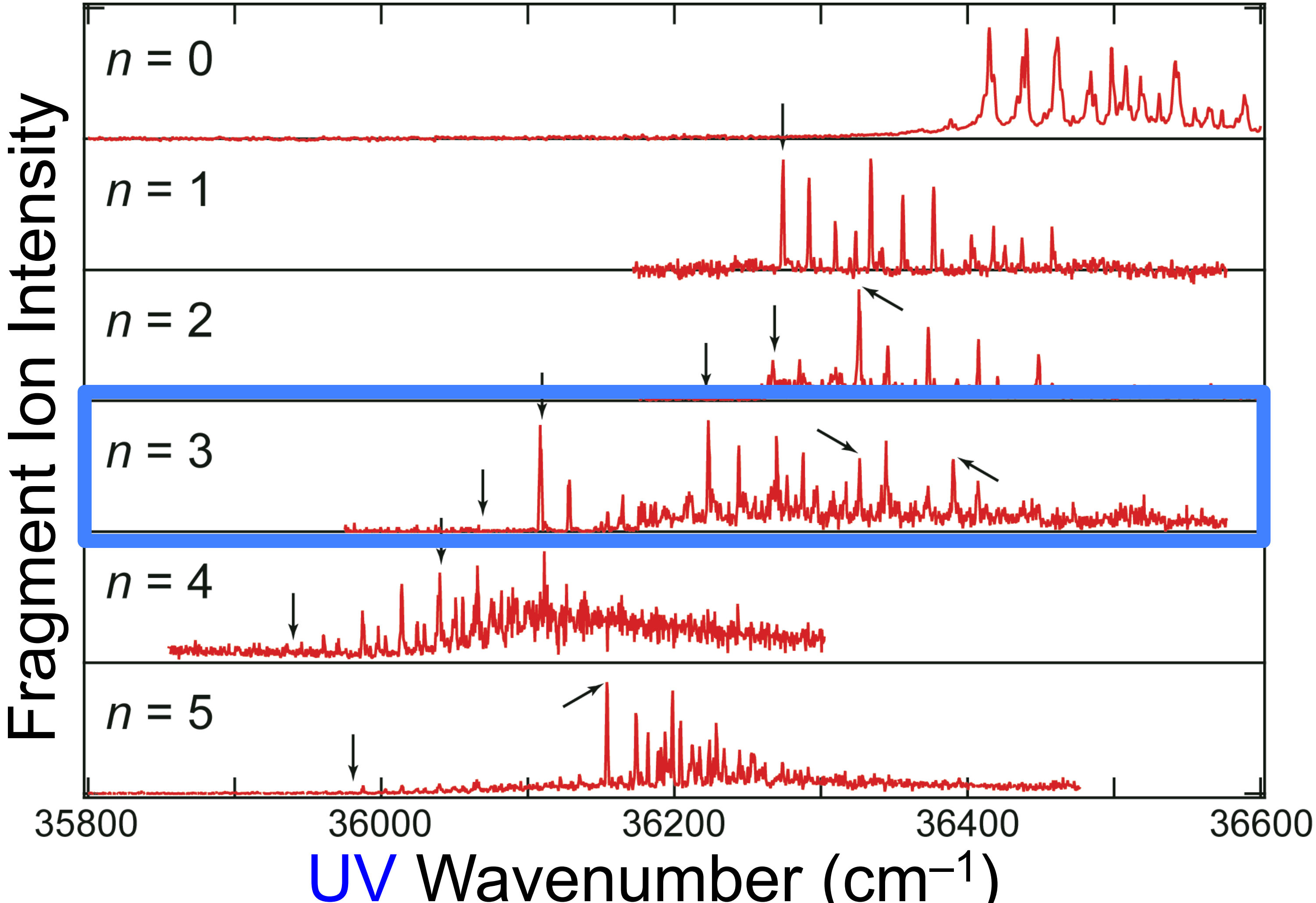


Inokuchi et al., *JACS*, **2011**, *133*, 12256.

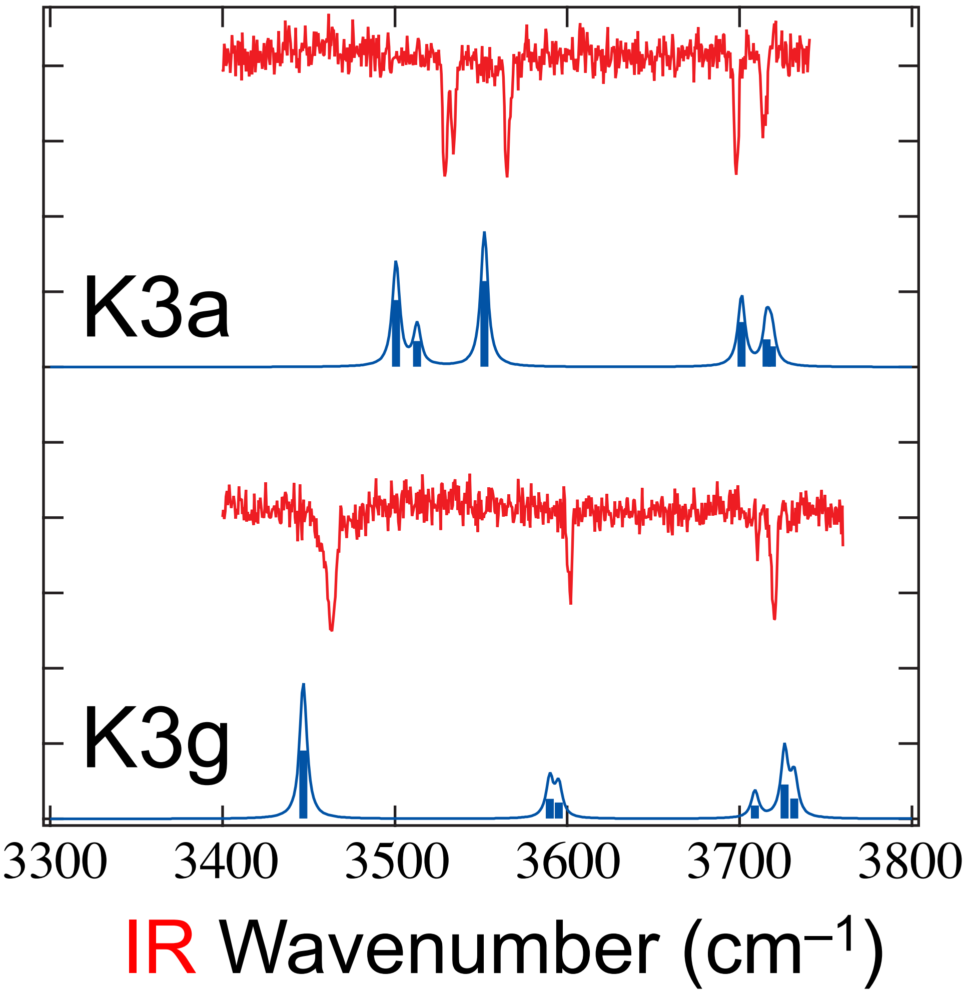
UV Spectra of $K^+ \cdot DB18C6 \cdot (H_2O)_n$

UV spectra also show sharp bands.

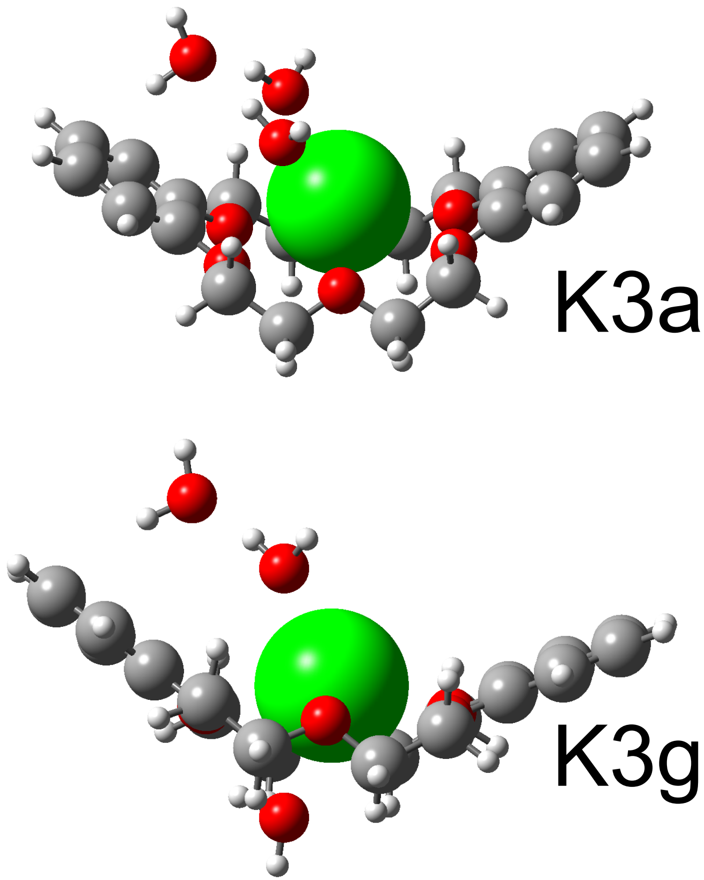
Conformer-specific IR spectra can be measured.



Conformers of K^+•DB18C6•$(H_2O)_3$

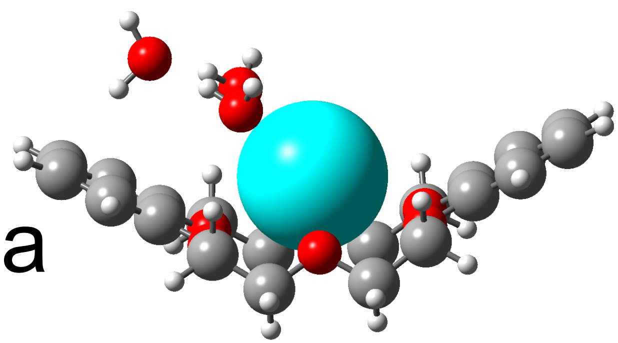


Two conformers for K^+.

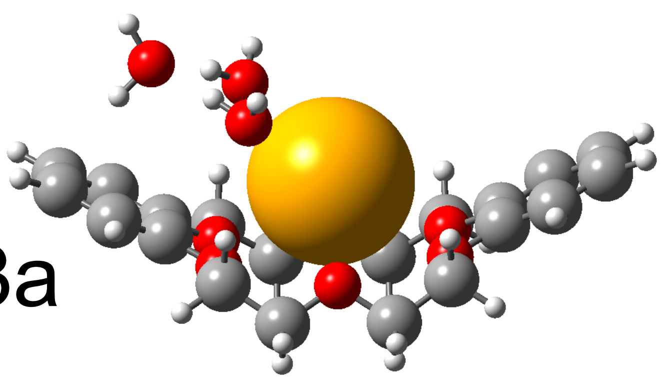


Conformers of M^+•DB18C6•$(H_2O)_3$

One conformer for Rb^+ and Cs^+.

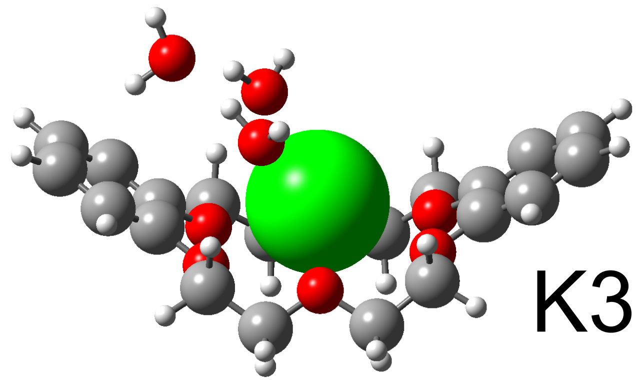


Rb3a

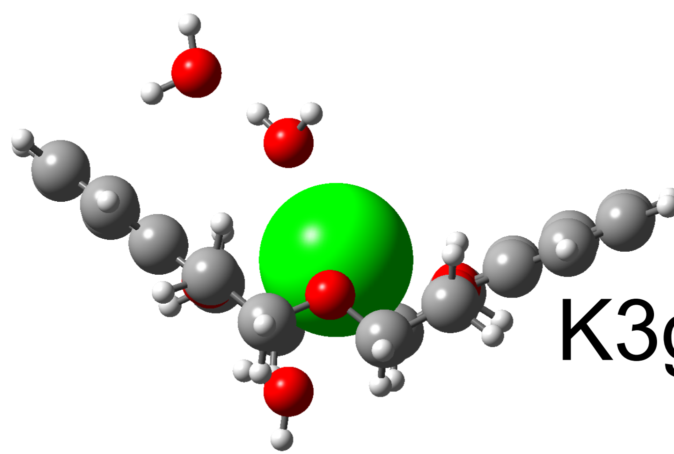


Cs3a

Two conformers for K^+.



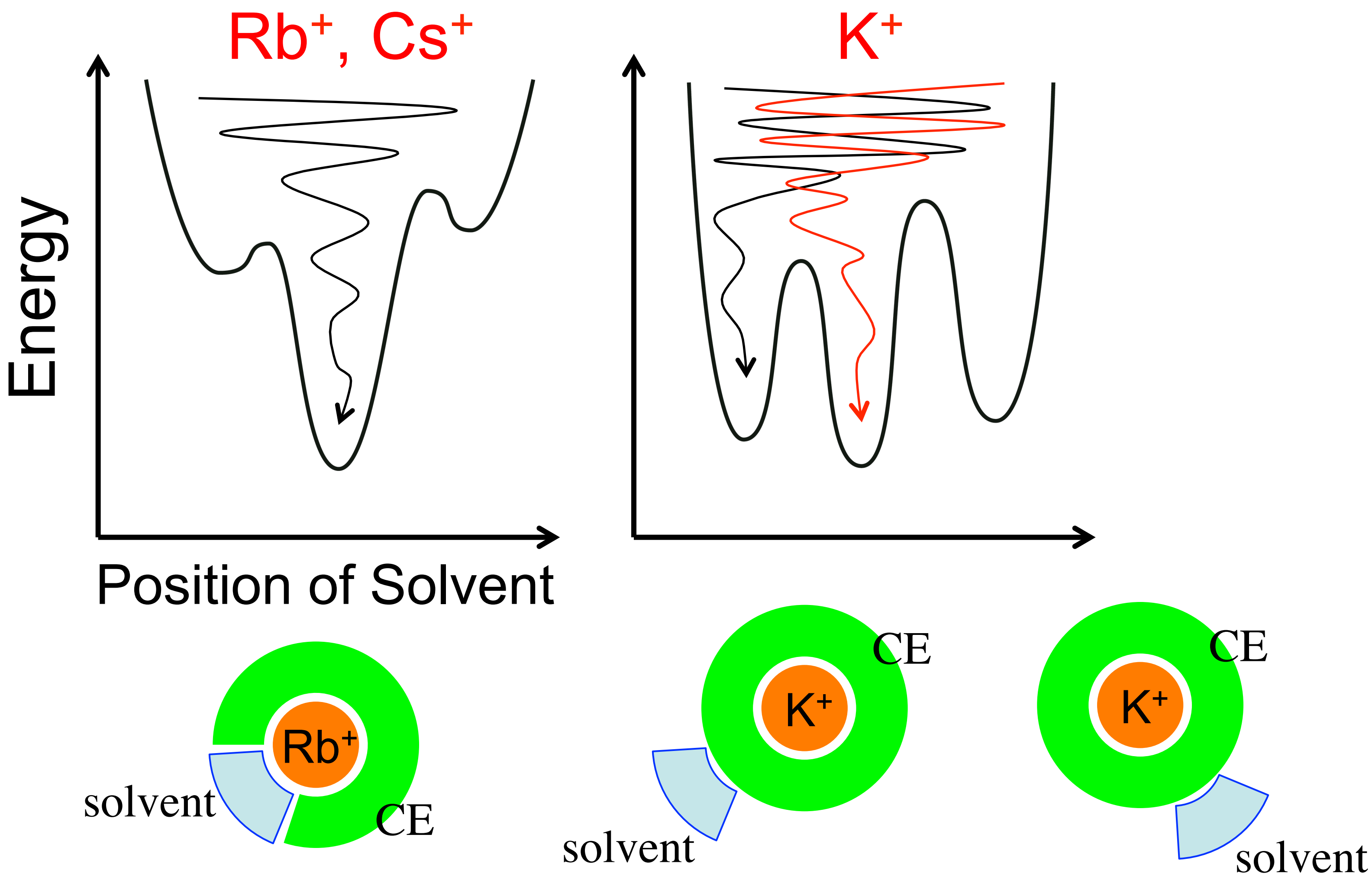
K3a



K3g

The Number of Conformers

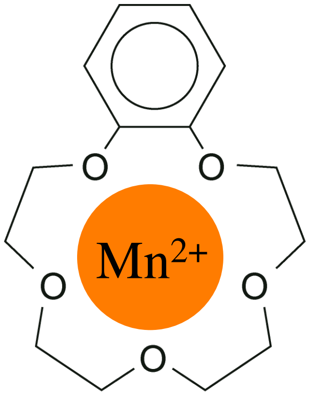
If the metal ion is completely surrounded by CE, multiple conformers can exist for solvated complexes.



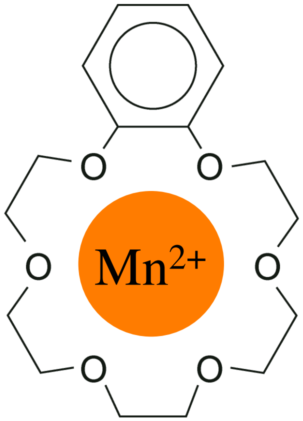
The Number of Conformers of Mn^{2+}•CE

B18C6 occupies all the coordination sites, resulting in multiple conformers with CH_3OH.

CE	Mn^{2+}•CE•CH_3OH
B15C5	1
B18C6	3



B15C5



B18C6

What's happening in encapsulation?

We have just started understanding the relation between encapsulation and solvation.

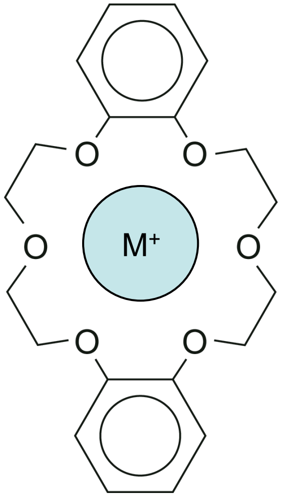
$$M^+ \bullet (H_2O)_m + CE \bullet (H_2O)_n \underset{}{\overset{K}{\rightleftarrows}} (M^+ \bullet CE) \bullet (H_2O)_k$$

We can determine the structure and the number of conformers at the same time.

Summary

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

- M^+•DB18C6 (M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+)
- M^+•DB18C6•$(H_2O)_n$
- 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

■École Polytechnique Fédérale de Lausanne (EPFL)

Prof. Thomas R. Rizzo

Dr. Oleg V. Boyarkin

LCPM members

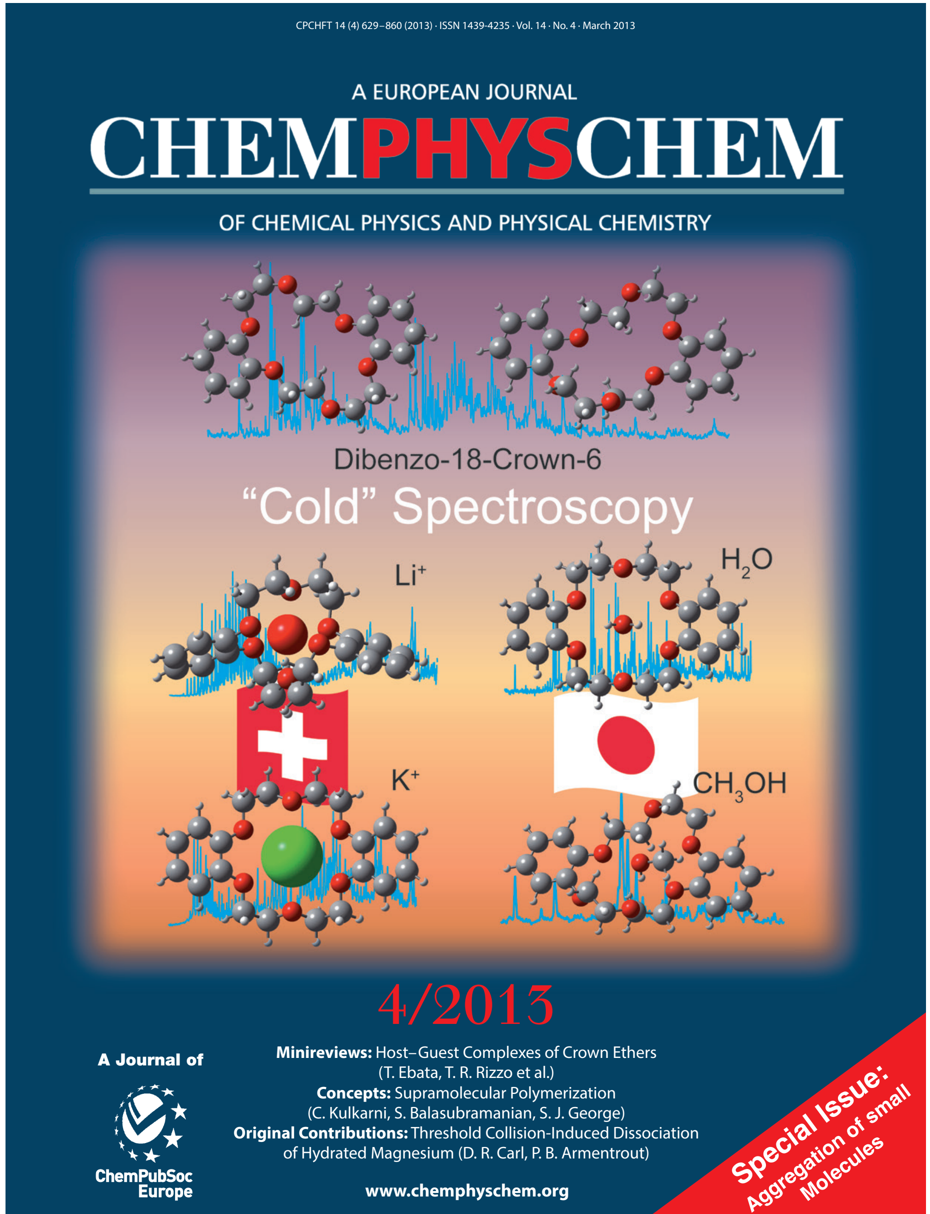
■Hiroshima University

Prof. Takayuki Ebata

Prof. Takeharu Haino

Dr. Ryoji Kusaka

Suisse-Japon Coopération



http://doi.org/10.1002/cphc.201390015

Thank You

Thank you
for your attention!