クラウンエーテルの金属イオン包接に対する溶媒効果の研究

（広大院理，EPFL）

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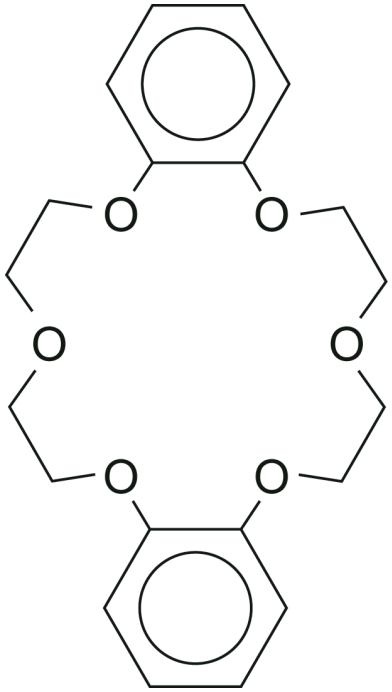
Ion Selectivity of Crown Ethers



Dibenzo-18-crown-6
(DB18C6)

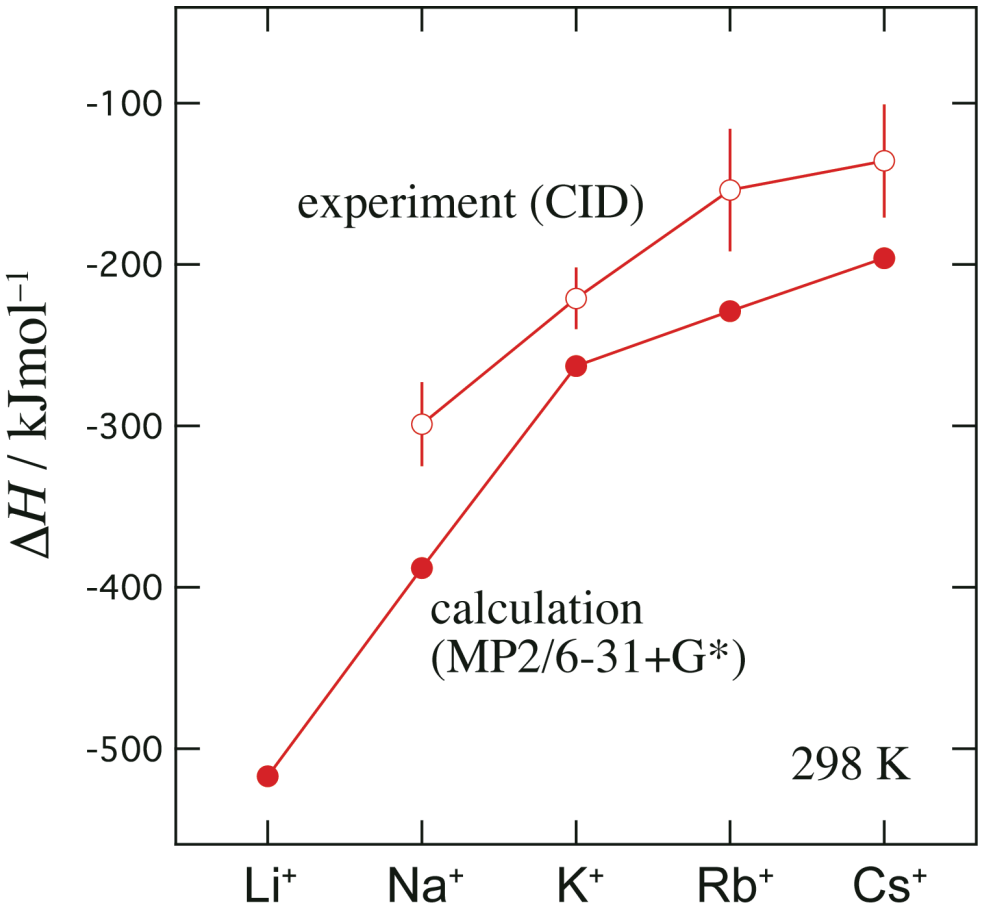
(fits K^+ among alkali metal ions)

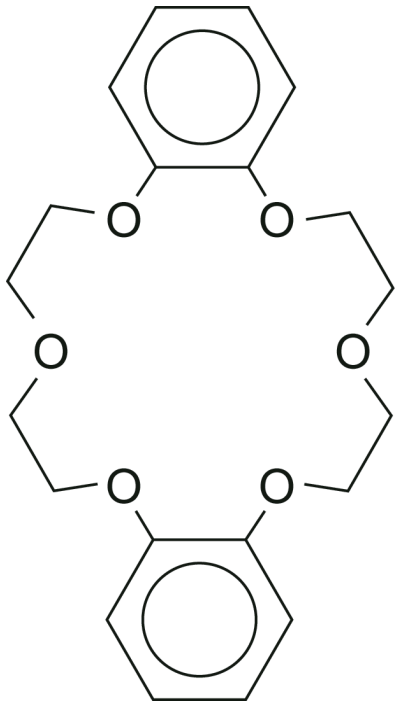
Our final goal is
to reveal the origin of ion selectivity
in terms of quantum chemistry.

ΔH for Complex Formation

Bare complexes cannot explain the ion selectivity in solution.

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





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.

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

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

$$\boxed{(M^+ \bullet CE) \bullet (H_2O)_k}$$

Relation between *K*, ΔG, ΔH, and ΔS

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

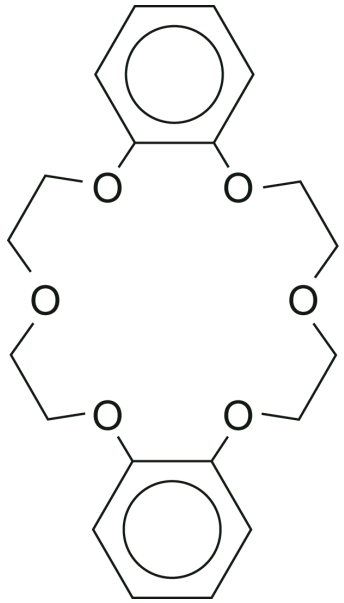
$$K = \exp\left(-\frac{\Delta G}{RT}\right)$$

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

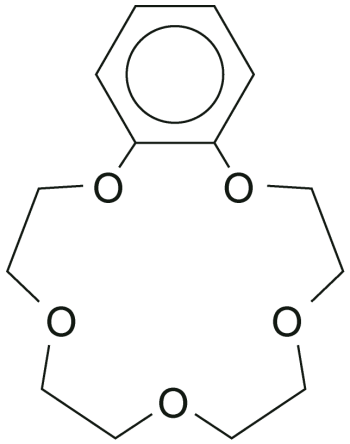
- *H* and *S* depend on the structure.
- The more conformations a complex takes, the more stable it is.

This Study

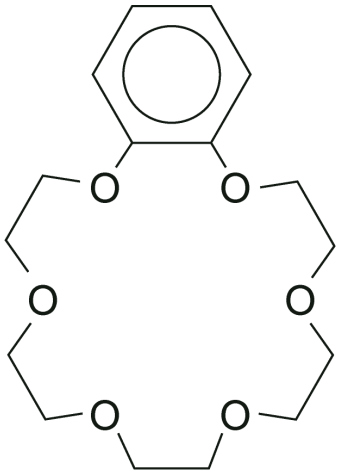
- M^+•DB18C6•$(H_2O)_n$ (M = alkali metal)
- M^{2+}•B15C5•L and M^{2+}•B18C6•L



DB18C6



B15C5

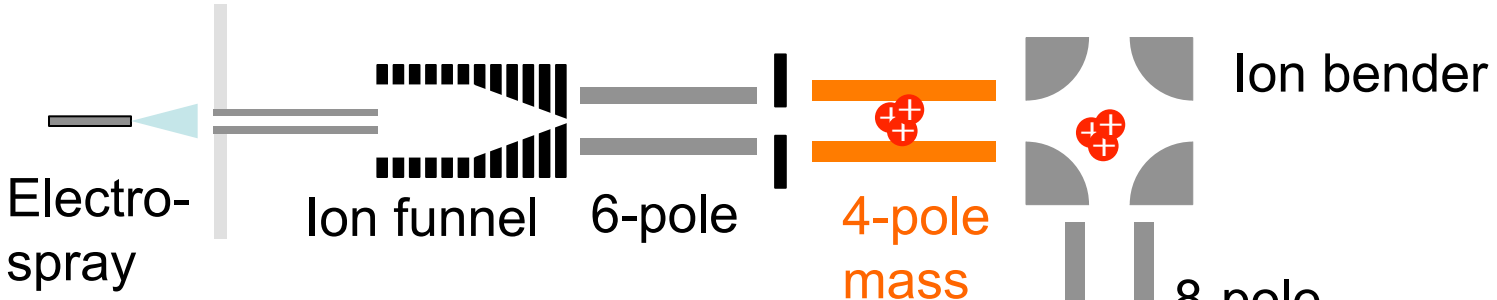


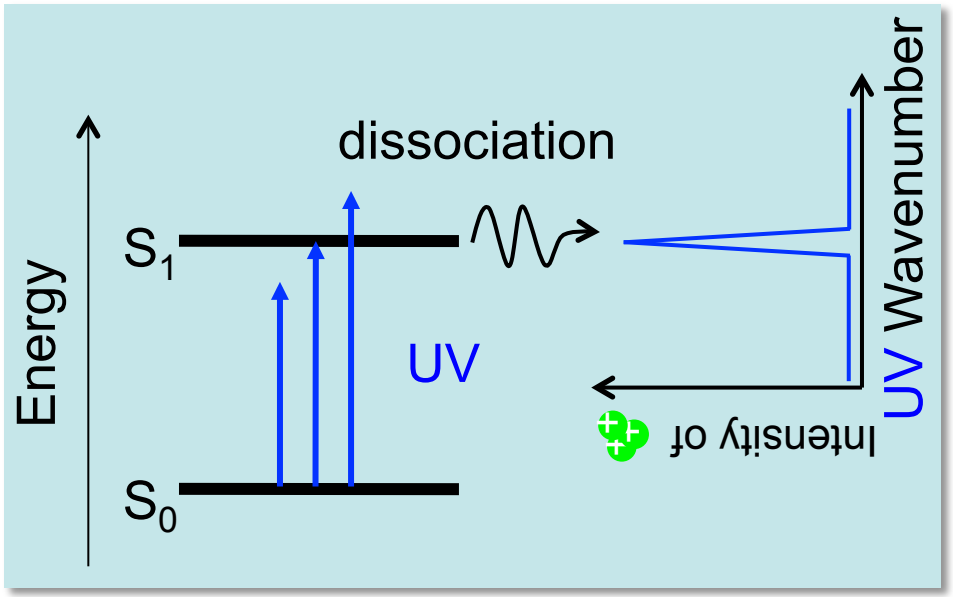
B18C6

- UV and IR spectroscopy in a cold, 22-pole ion trap
- Relation between ion selectivity and the number of conformers.

Experimental

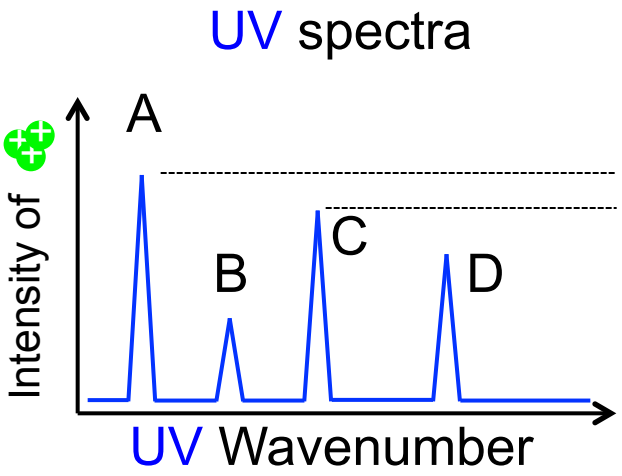
UV and IR spectra of ions are measured under cold (~10 K) conditions in the gas phase.

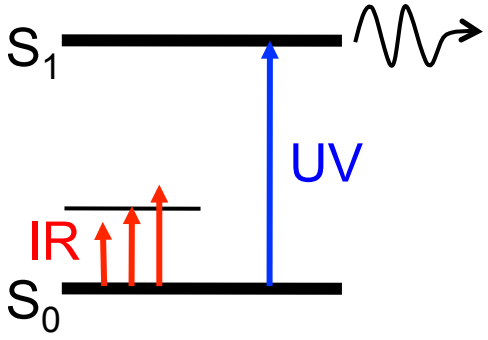




IR-UV Double-Resonance

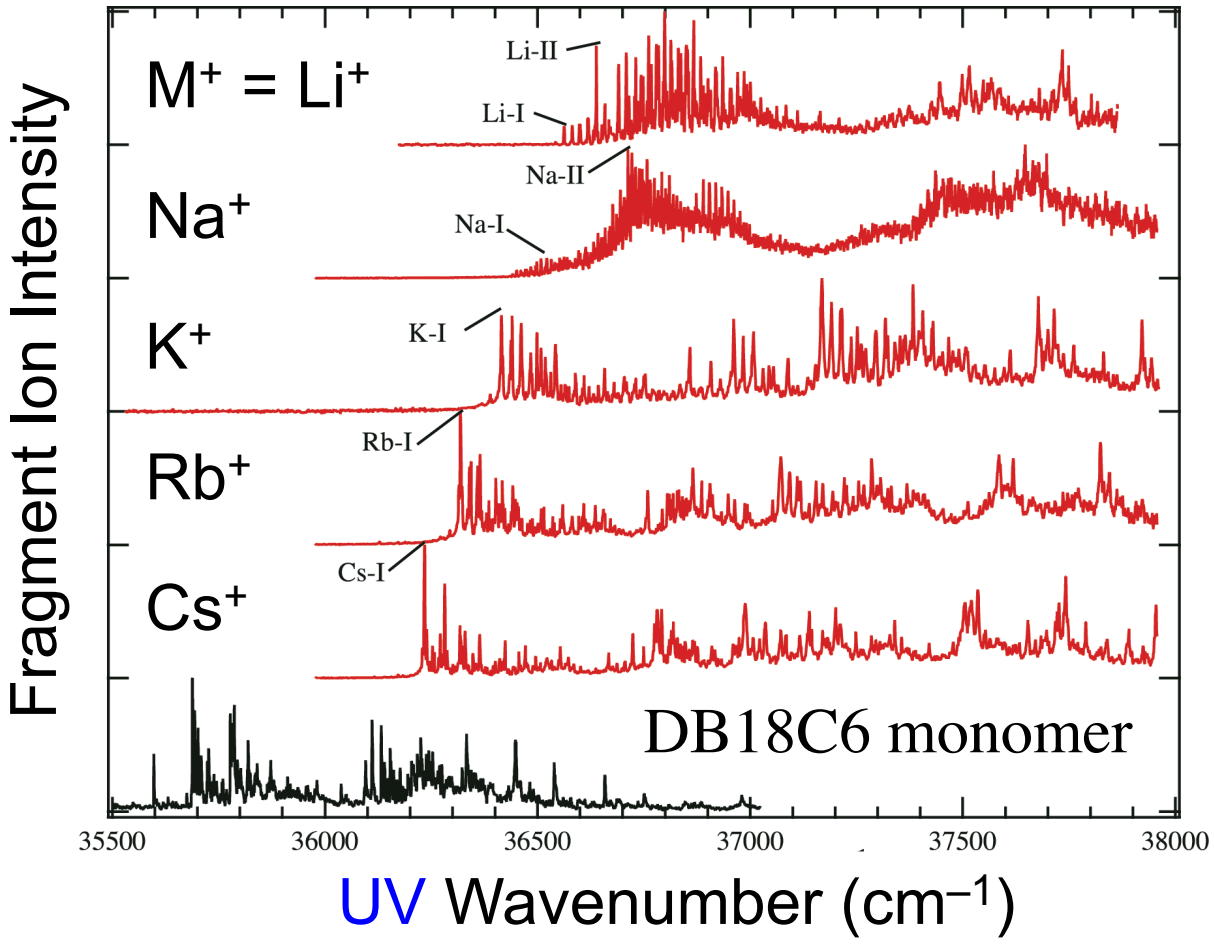
Conformer-specific IR spectra can be measured by IR-UV double-resonance.

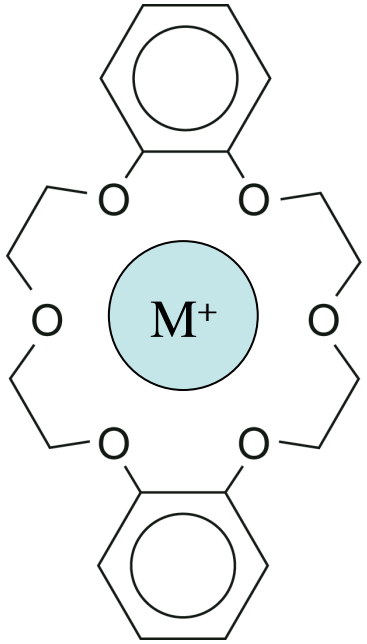




UV Spectra of M^+•DB18C6

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



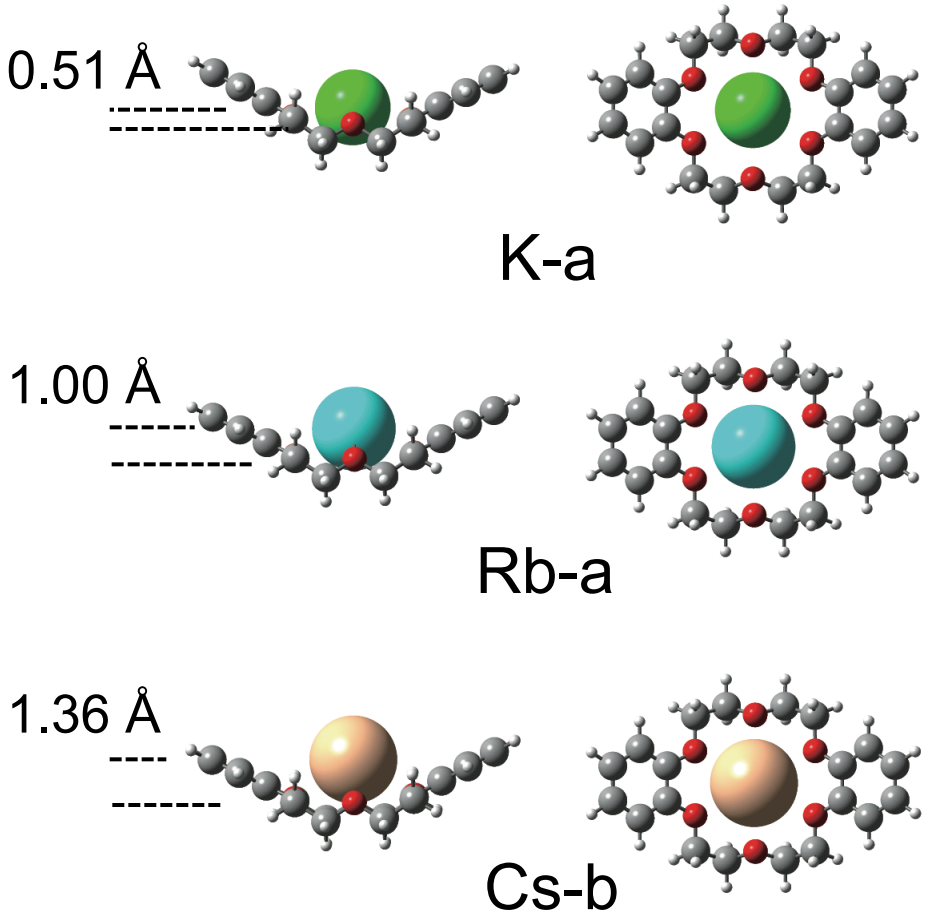


M^+•DB18C6

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

Structure of M^+•DB18C6

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

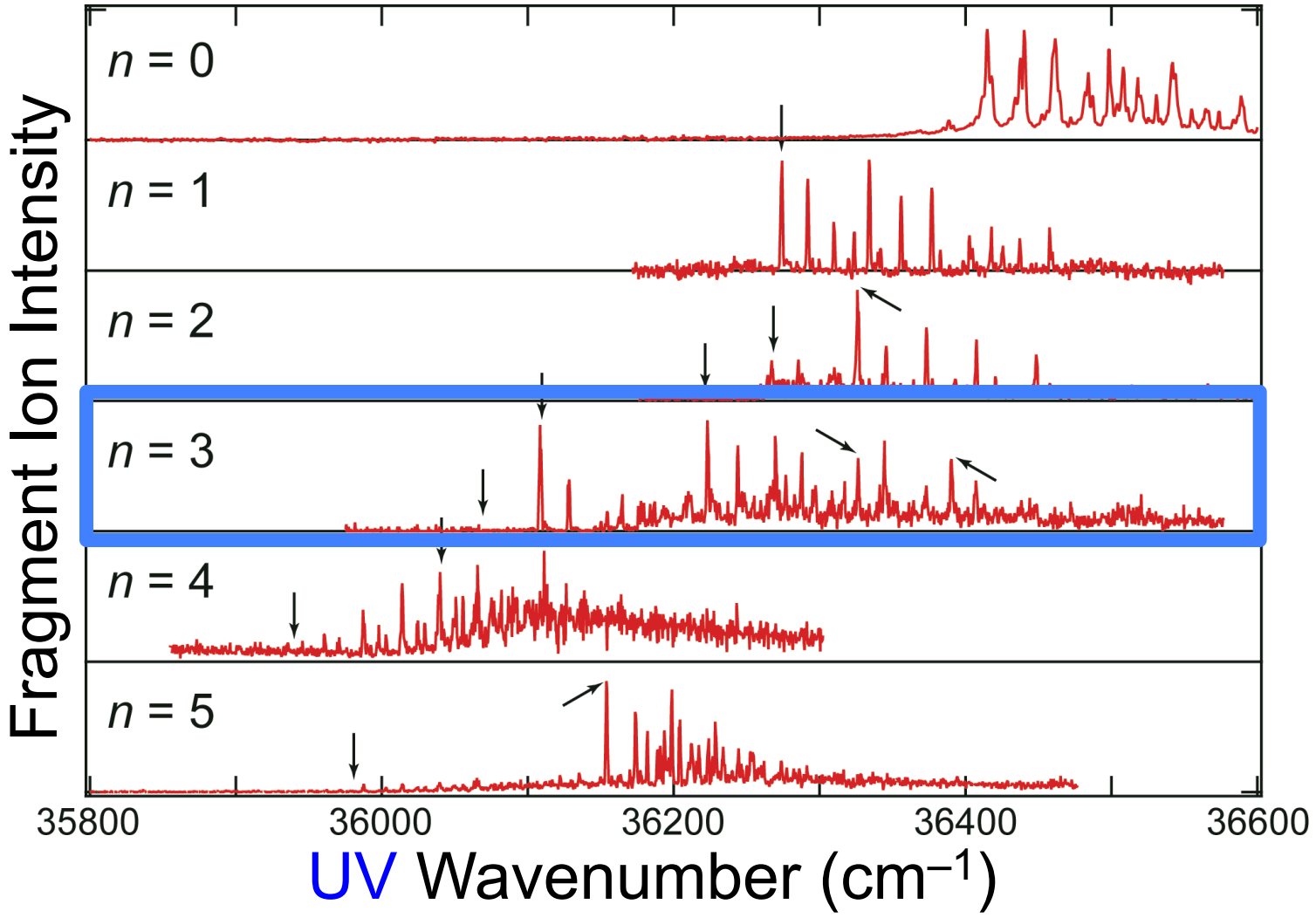


Inokuchi et al., *JACS*, **2011**, *133*, 12256.

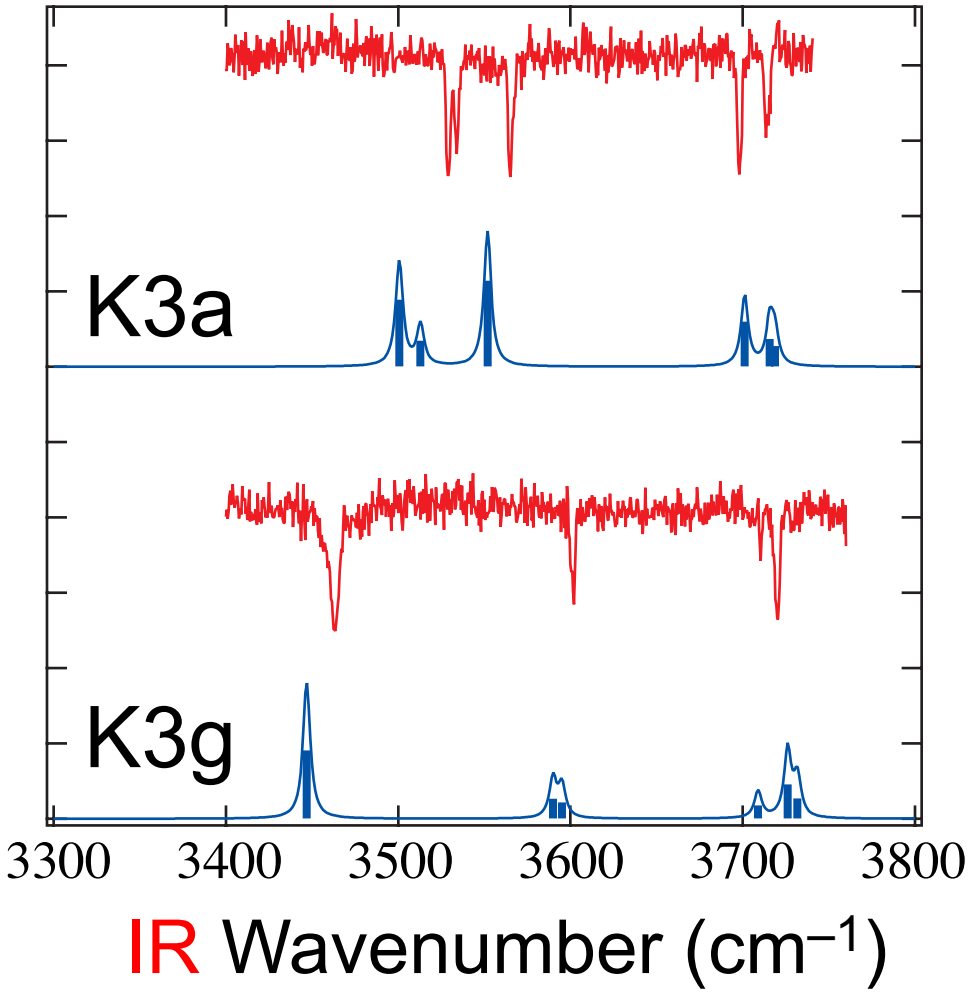
UV Spectra of $K^+ \cdot DB18C6 \cdot (H_2O)_n$

UV spectra also show sharp bands.

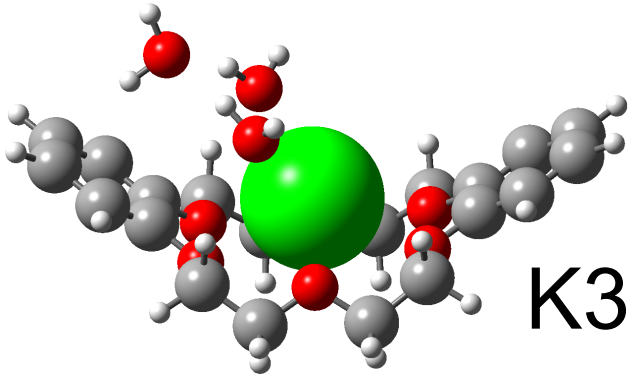
Conformer-specific IR spectra can be measured.

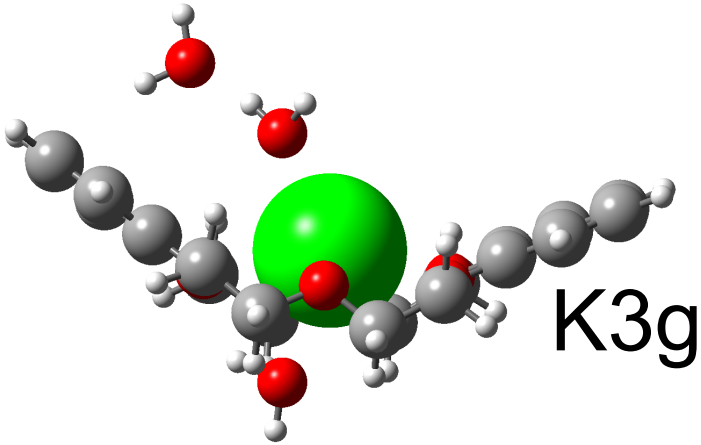


Conformers of $K^+ \cdot DB18C6 \cdot (H_2O)_3$



Two conformers for K^+.



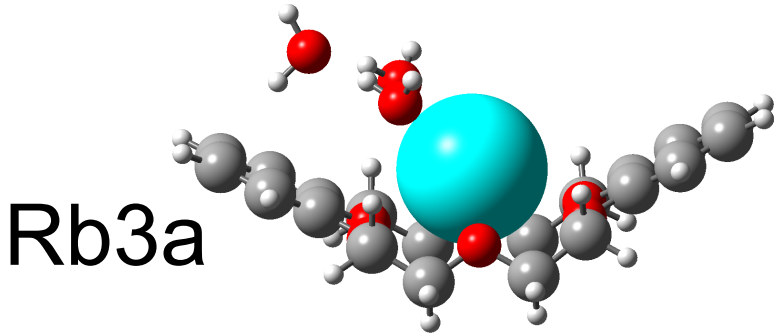


Inokuchi et al., *JACS*, **2014**, *136*, 1815.

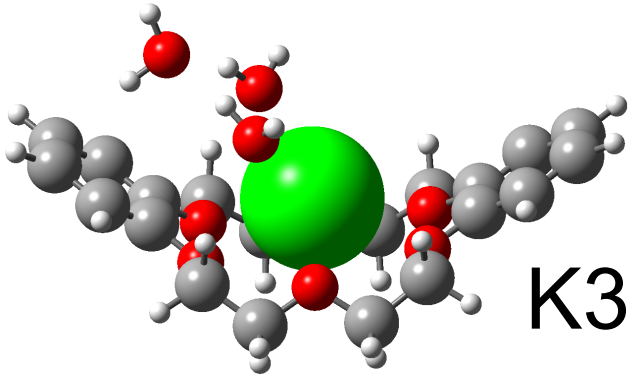
Conformers of $M^+ \cdot DB18C6 \cdot (H_2O)_3$

One conformer for Rb^+ and Cs^+.

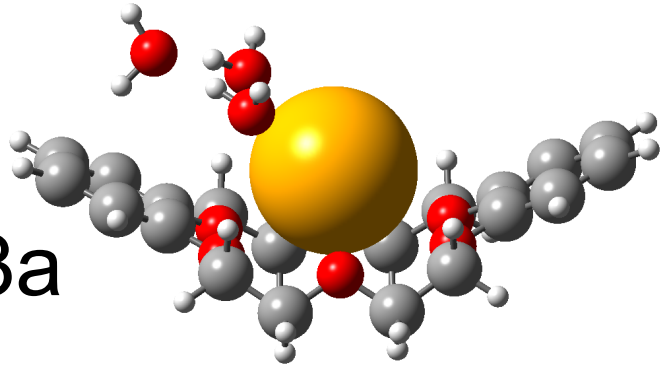
Two conformers for K^+.



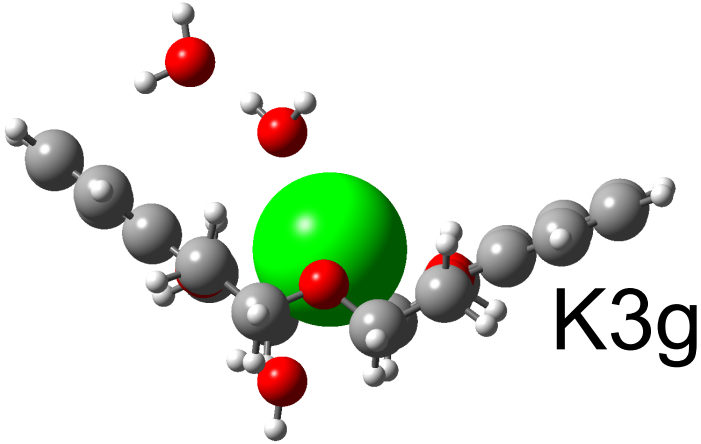
Rb3a



K3a



Cs3a

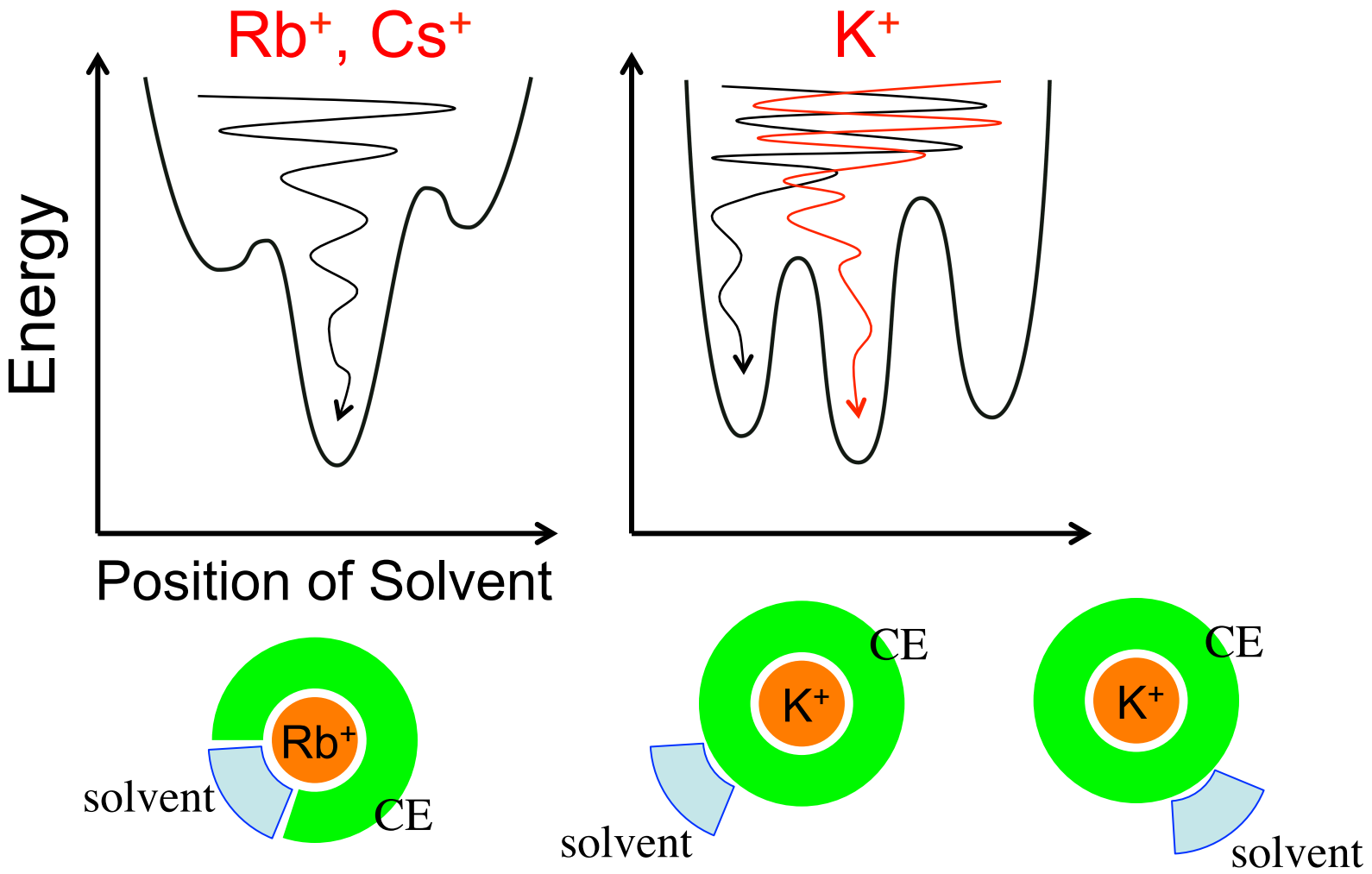


K3g

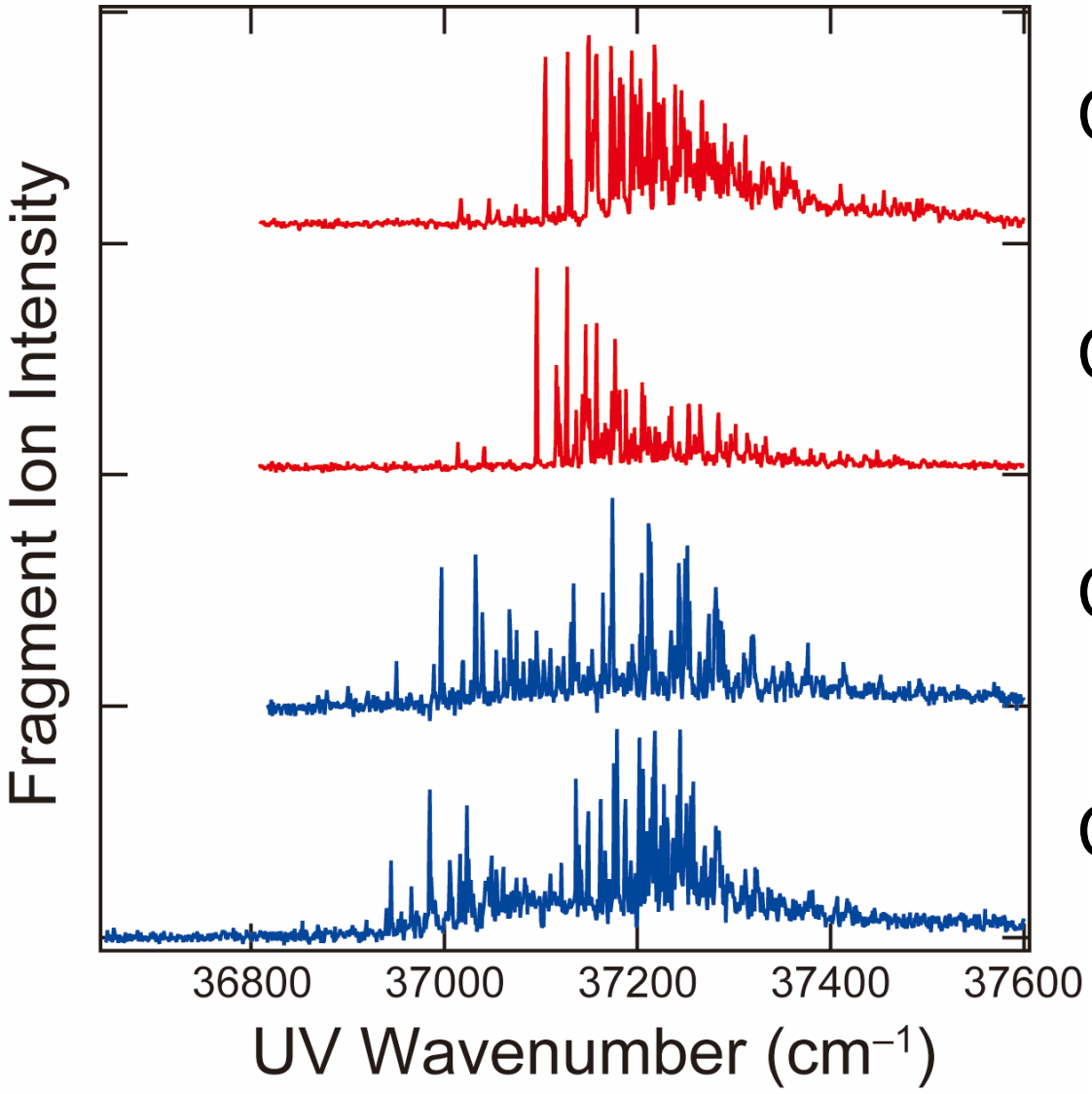
Inokuchi et al., *JACS*, **2014**, *136*, 1815.

The Number of Conformers

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



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



Ca^{2+}•B15C5•H_2O

Ca^{2+}•B15C5•CH_3OH

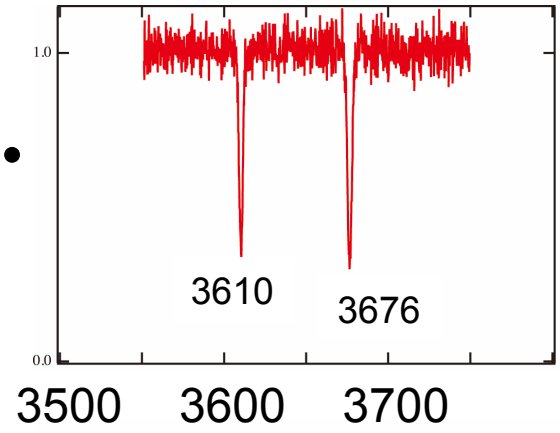
Ca^{2+}•B18C6•H_2O

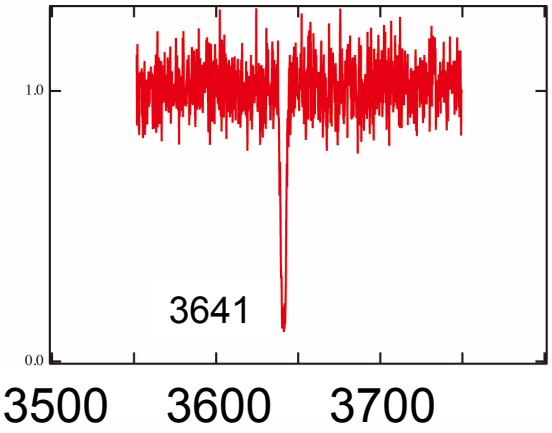
Ca^{2+}•B18C6•CH_3OH

Inokuchi et al., in preparation.

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

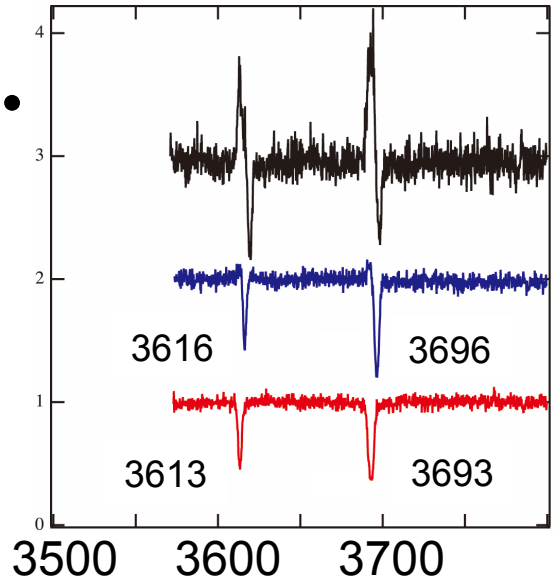
Ca^{2+}•B15C5•H_2O

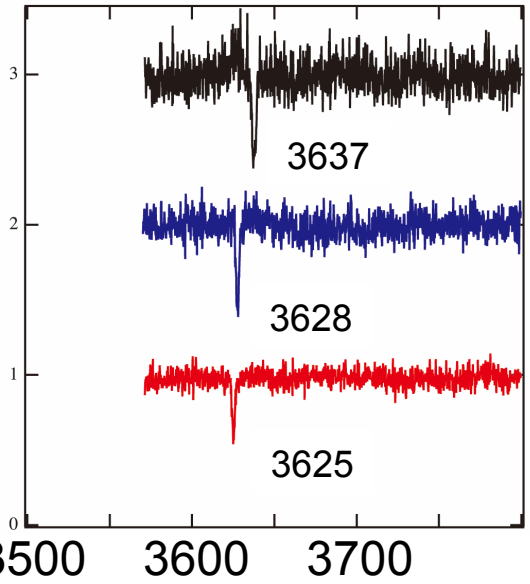




Ca^{2+}•B15C5•CH_3OH

Ca^{2+}•B18C6•H_2O





Ca^{2+}•B18C6•CH_3OH

IR wavenumber (cm^{-1})

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

M^{2+}•CE•H_2O

	B15C5	B18C6
Ca^{2+}	1	3
Sr^{2+}	2	3
Ba^{2+}	2	1
Mn^{2+}	1	2

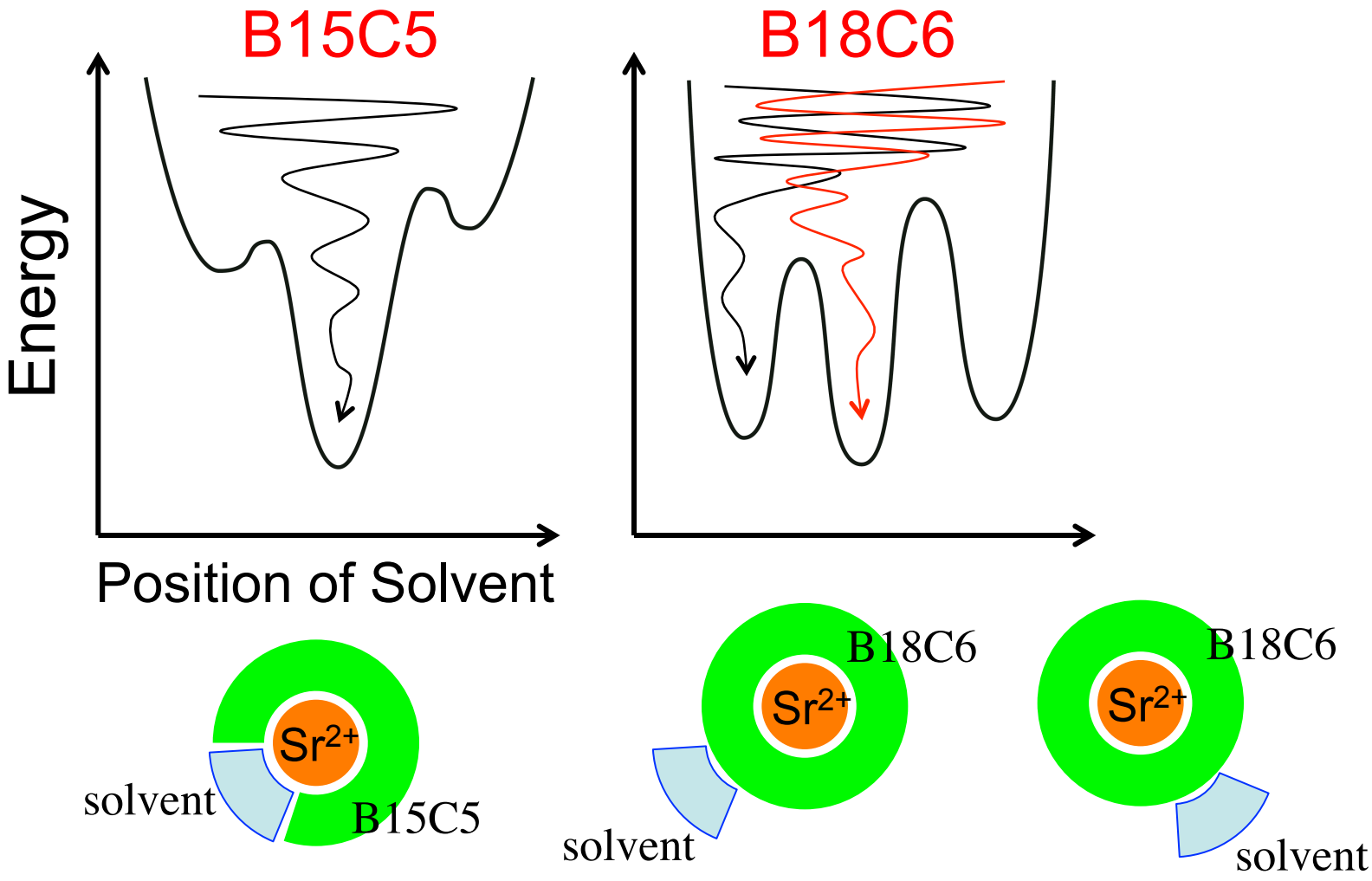
M^{2+}•CE•CH_3OH

	B15C5	B18C6
Ca^{2+}	1	3
Sr^{2+}	2	5
Ba^{2+}	1	2
Mn^{2+}	1	3

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

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

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



Summary

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

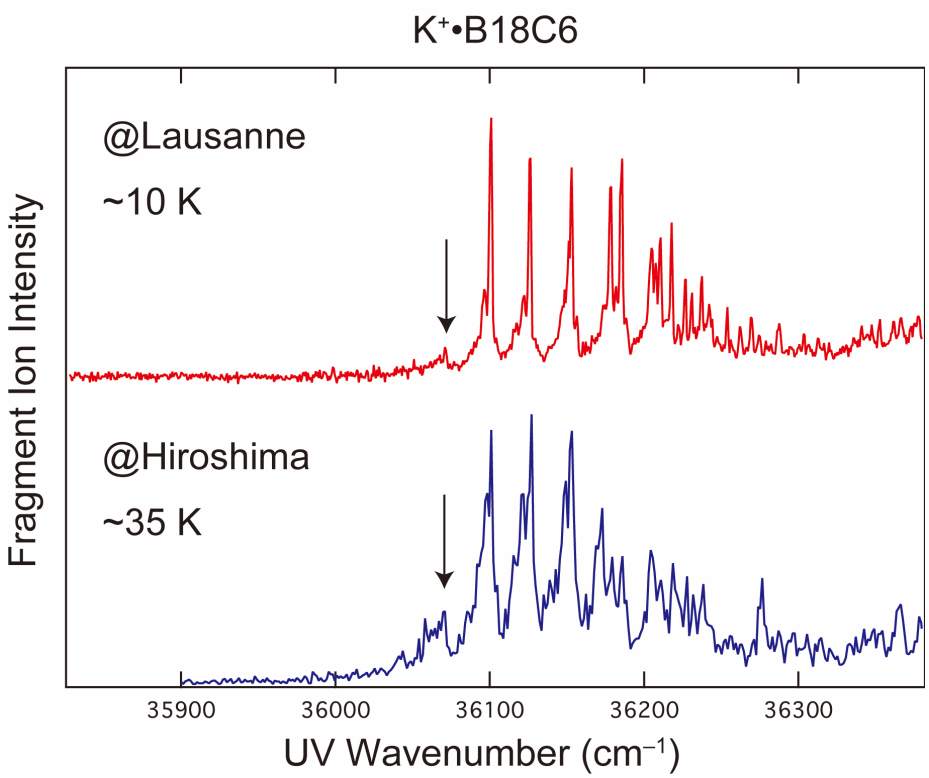
- M^+•DB18C6•$(H_2O)_n$
- M^{2+}•B15C5•L and M^{2+}•B18C6•L (L = H_2O, CH_3OH)
- UV and IR spectroscopy in a cold, 22-pole ion trap

- 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.

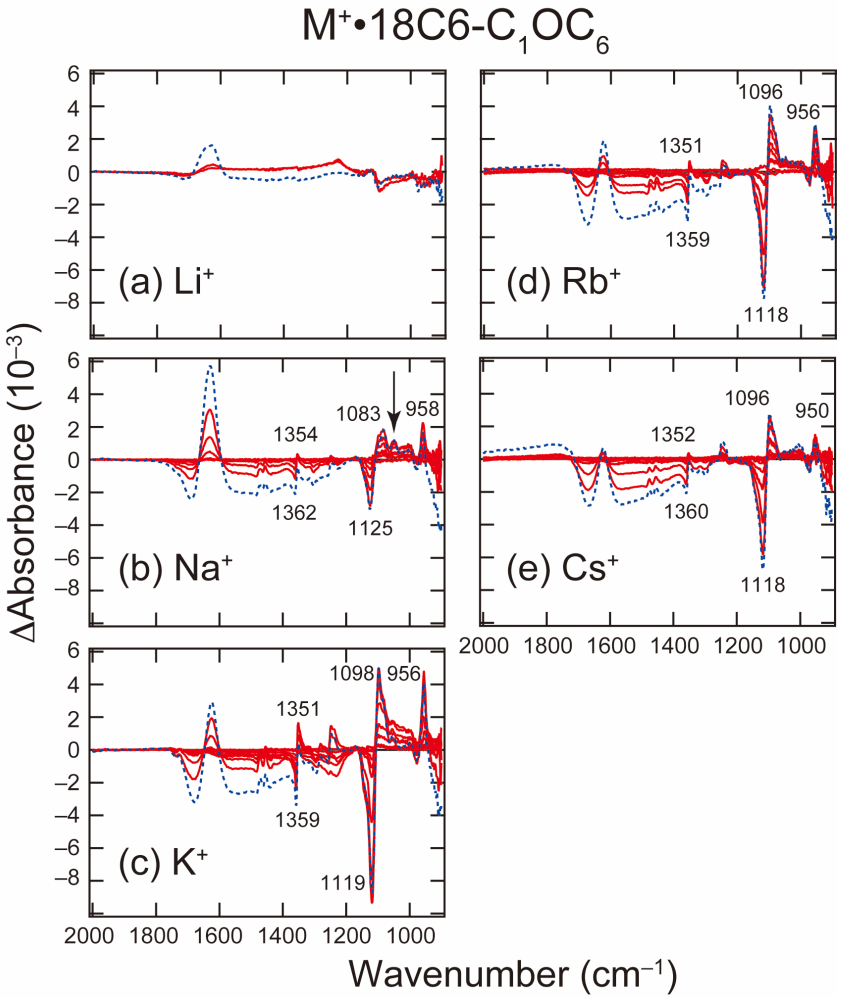
Future Prospects

Quantum chemical approaches in host-guest chemistry

Gas phase



On gold surface



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