

クラウンエーテルの金属イオン包接錯体の 極低温気相分光

—イオン選択性の分子論的理解をめざして—

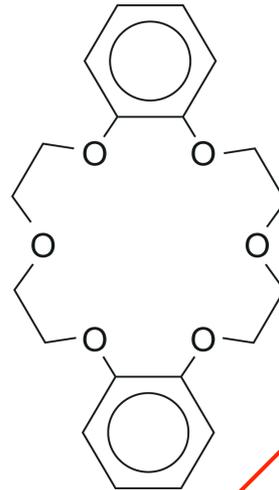
(広大院理, ローザンヌ連邦工科大)

○井口佳哉, 江幡孝之, T. R. Rizzo

Outline

- Introduction
 - What are **crown ethers**? Why in the gas phase?
- Experimental and computational
 - Tandem mass spectrometer with **a cold 22-pole ion trap**
 - UV and IR spectroscopy
 - Quantum chemical calculations
- Complex structure and its relation with **ion selectivity**
 - $M^+ \cdot (\text{Crown Ether})_1$ (M = Li, Na, K, Rb, and Cs)

What Are Crown Ethers?



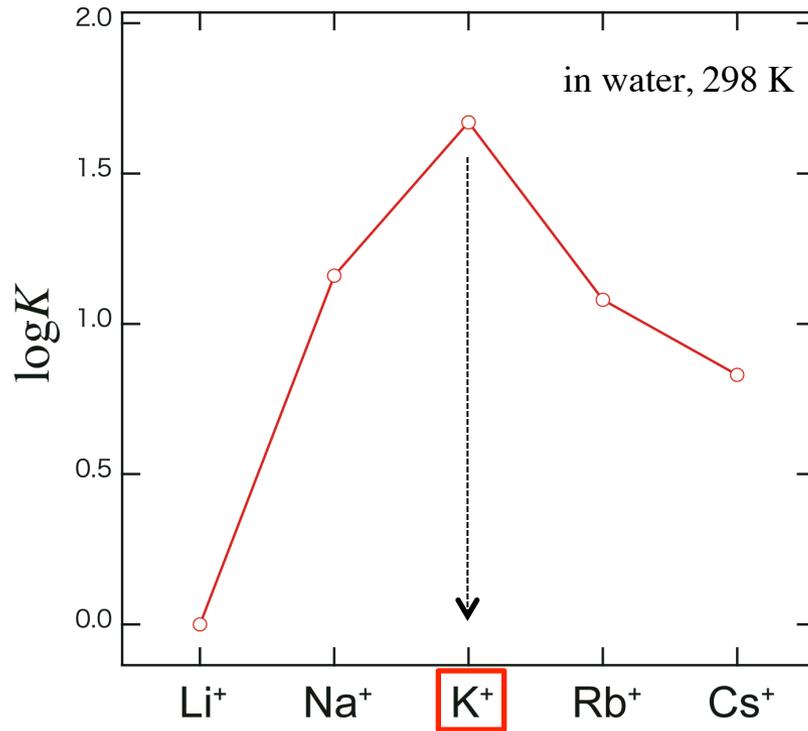
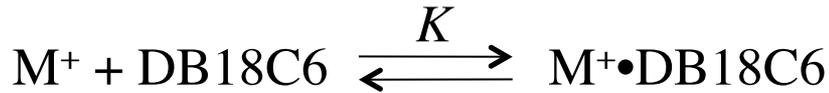
Dibenzo-18-crown-6
(DB18C6)

リングを形成している全原子数

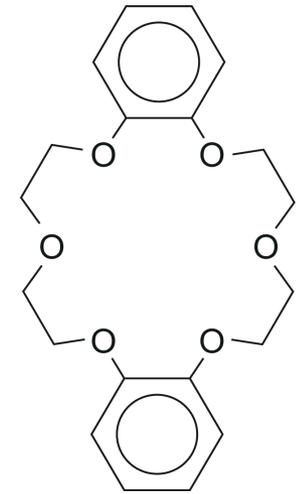
リング中のO原子数

イオンを**選択的に**トラップする

Ion Selectivity

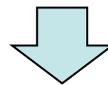


Izatt et al., *Chem. Rev.*,
1985, 85, 271.



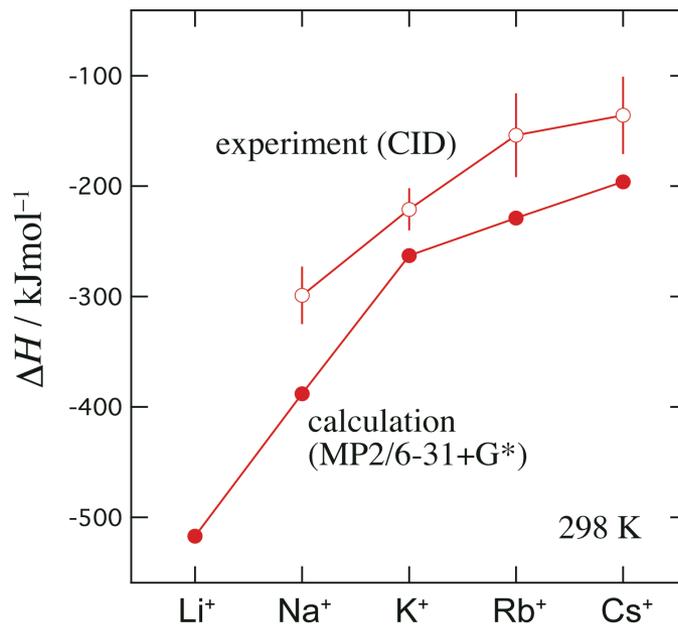
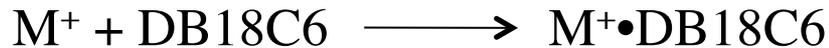
DB18C6

K⁺に高い選択性をしめす



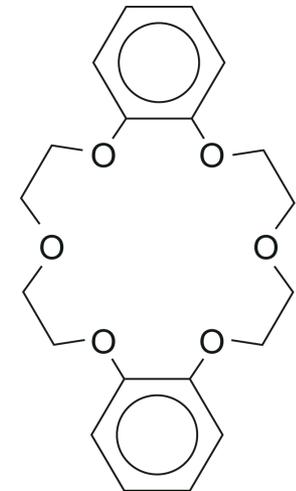
K⁺とDB18C6の**大きさの一致**に由来する
なぜ大きさが一致すると良いのか？

ΔH for Complex Formation



in the gas phase

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



DB18C6

K⁺に特異性は見られない

選択性の起源は？構造にあるのか？
包接錯体の構造を決める必要がある

Pedersen's Study -UV spectra-

DB18C6
with alkali metal ions

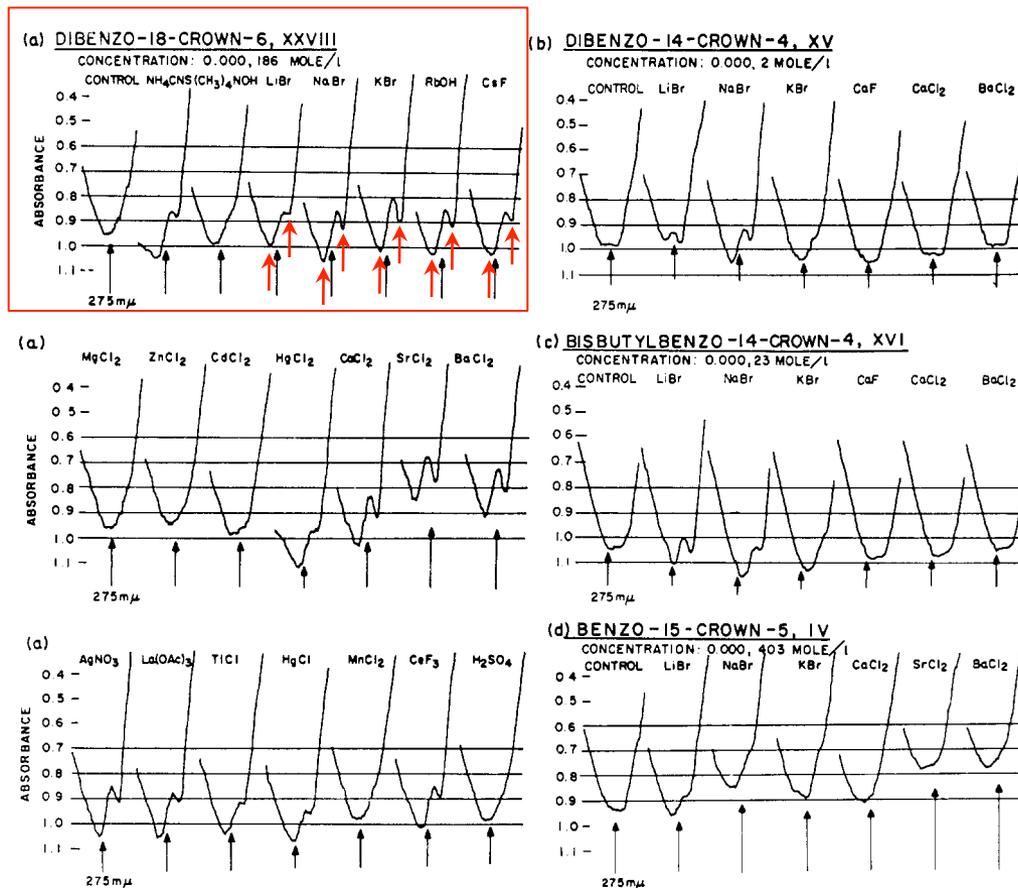
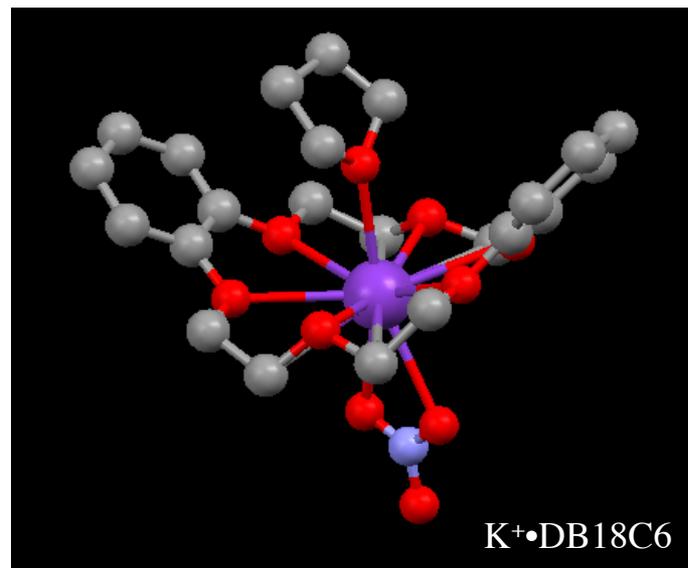
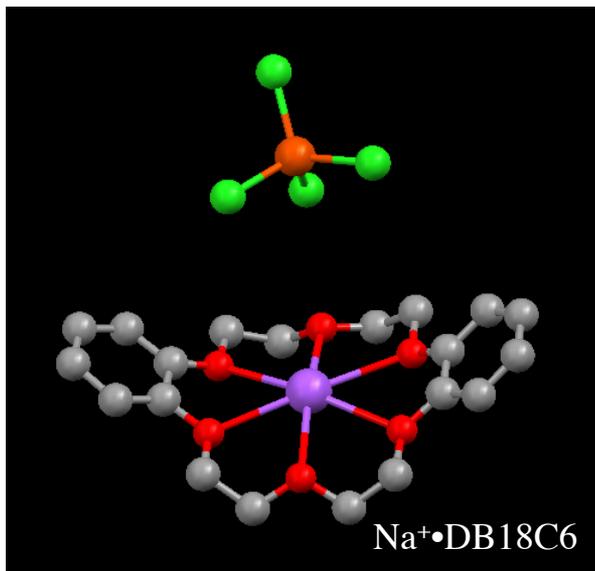


Figure 13. Effects of salts on ultraviolet spectrum.

C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, 89, 7017.

溶液の吸収スペクトルから構造の情報を引き出すのは難しい

Crystal Structure



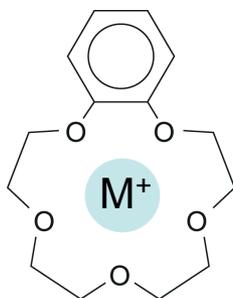
結晶中では、カウンターアニオンも金属カチオンに配位している

気相で構造を決定する必要がある

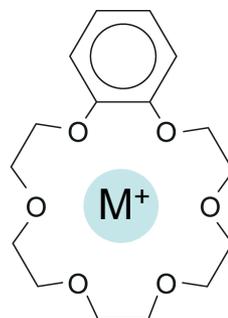
This Study

- DB18C6, B18C6, B15C5
 $M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+$

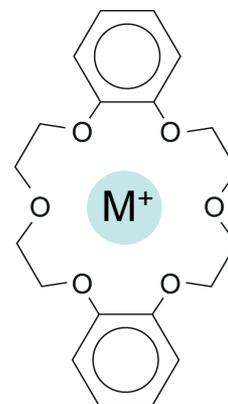
1:1 complexes



B15C5



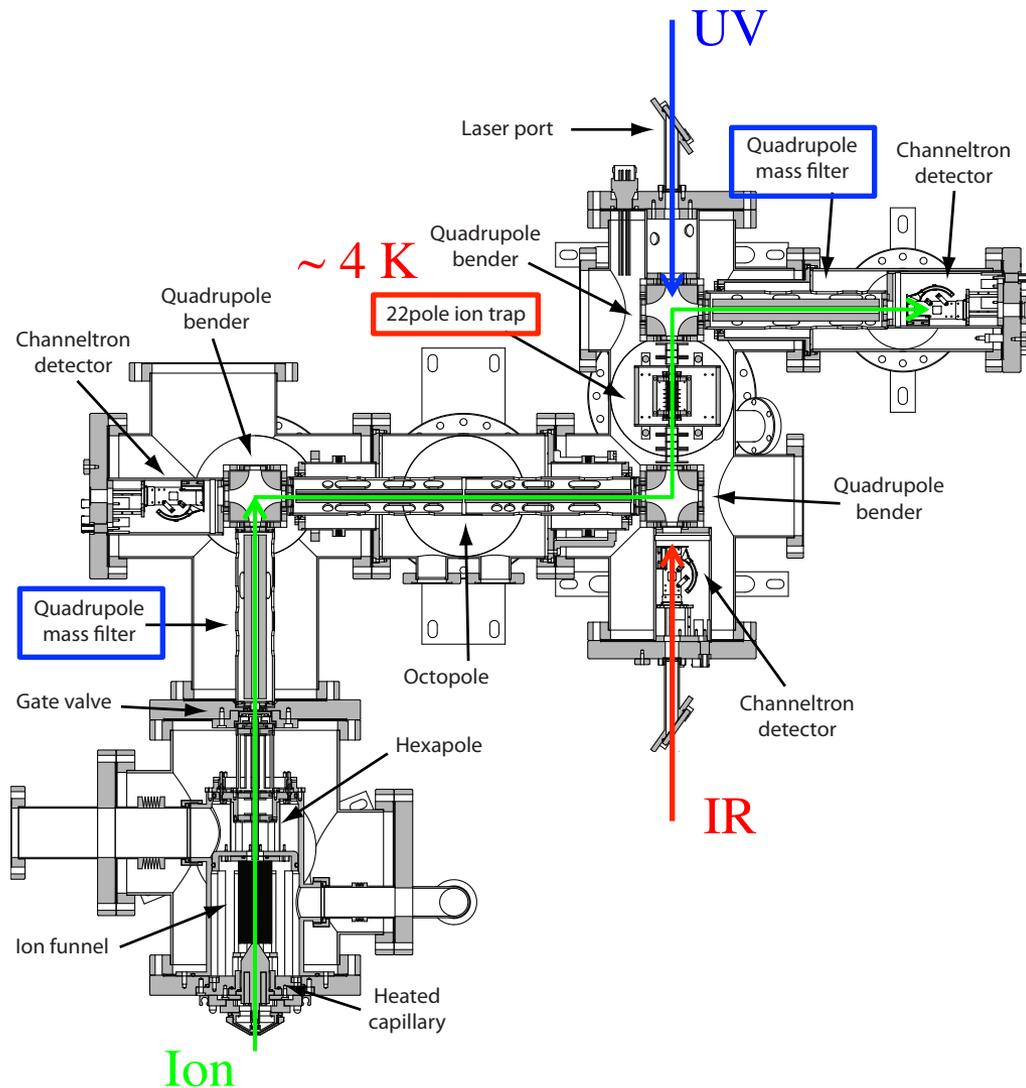
B18C6



DB18C6

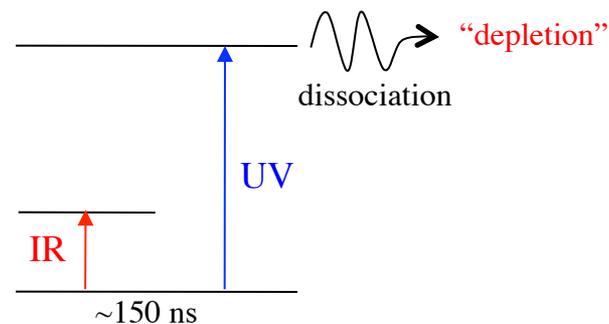
- **UV** and **IR** spectroscopy in a cold, 22-pole ion trap
DFT, TD-DFT
- コンフォマーの数, 構造の決定
金属イオン選択性との関係

Experimental

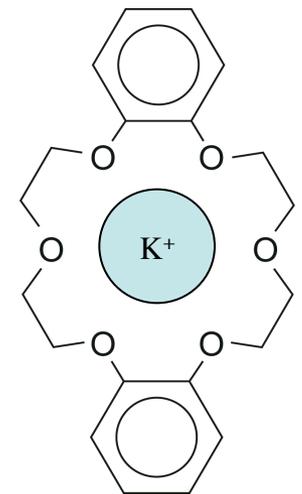
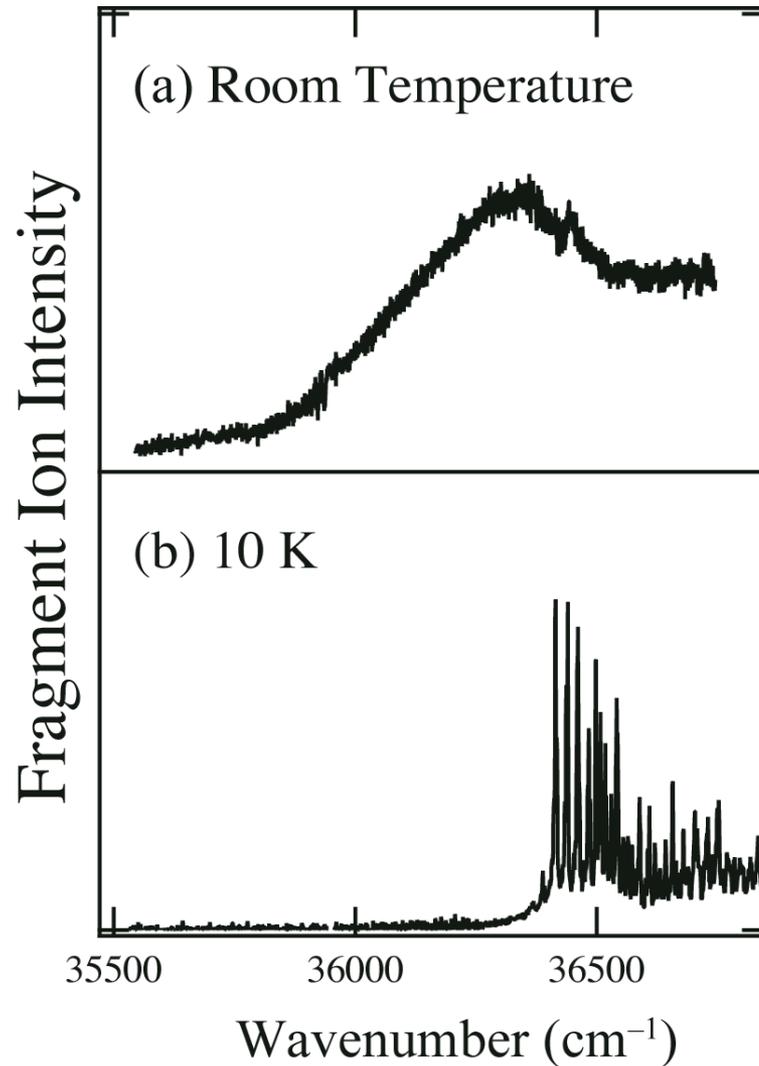


- nanoelectrospray
DB18C6, B18C6, B15C5
LiCl, NaCl, KCl, RbCl, CsCl
in Methanol
20–200 μM

- UV spectroscopy
- IR-UV spectroscopy
UV power 1–1.5 mJ/pulse
IR power 4–5 mJ/pulse



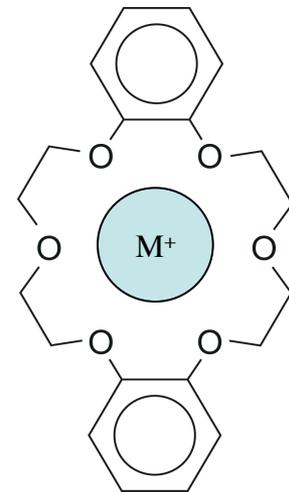
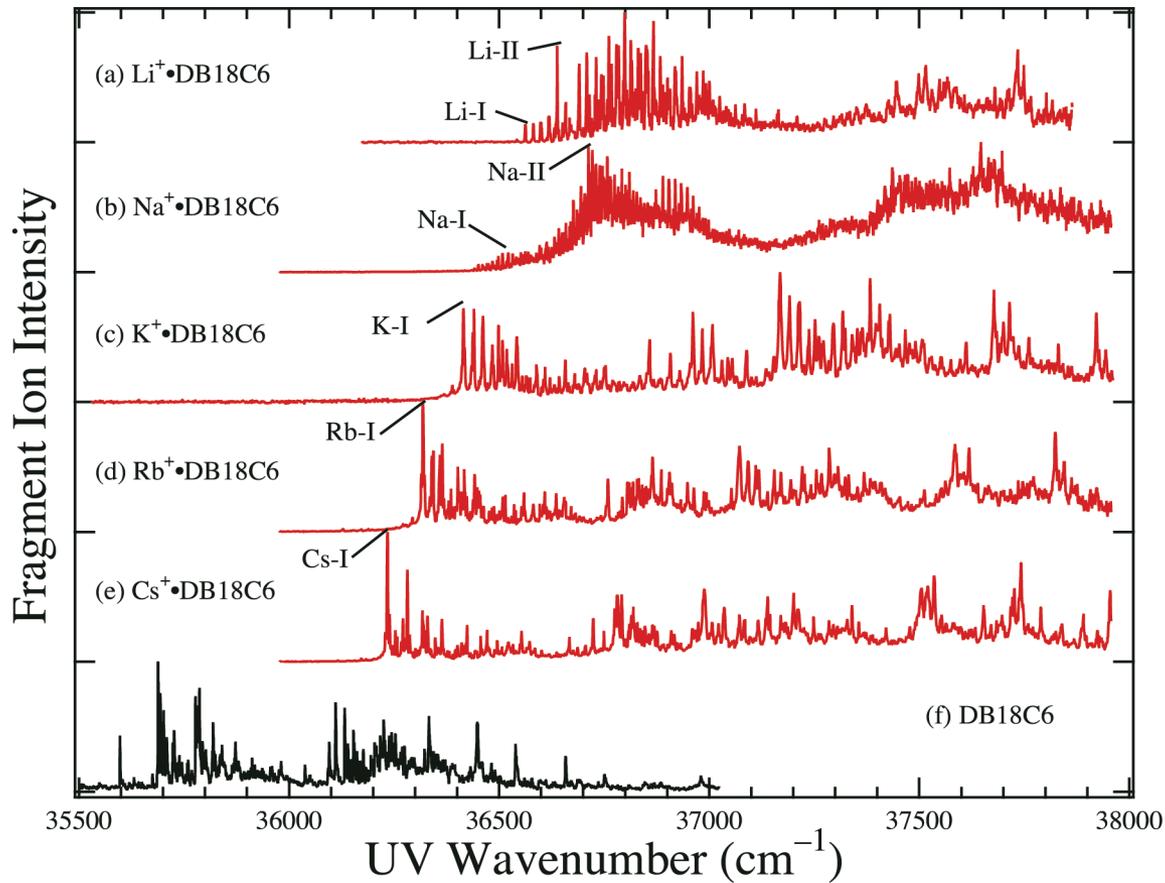
UV Spectra of $K^+ \cdot DB18C6$



$K^+ \cdot DB18C6$

冷却することによりシャープな振電構造が出現している

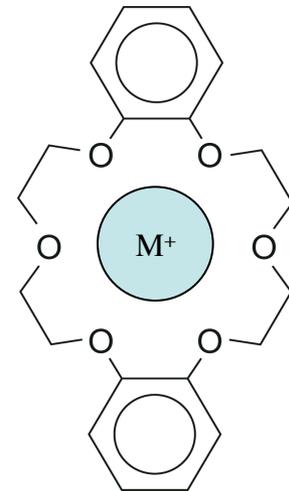
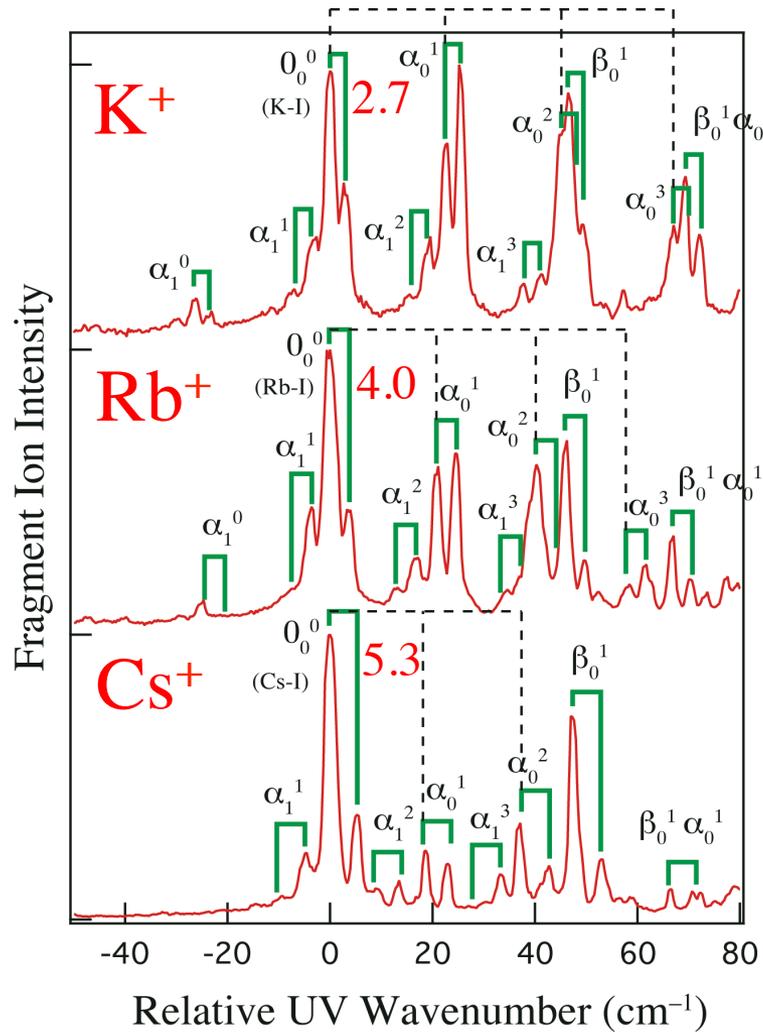
UV Spectra of $M^+ \cdot DB18C6$



$M^+ \cdot \text{DB18C6}$

シャープな振電バンドが多数観測されている

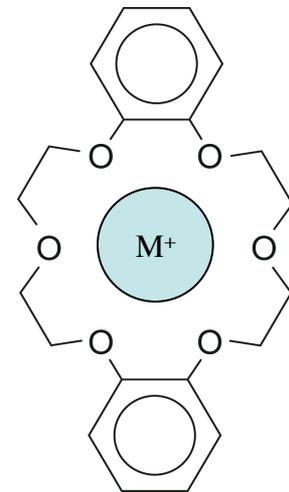
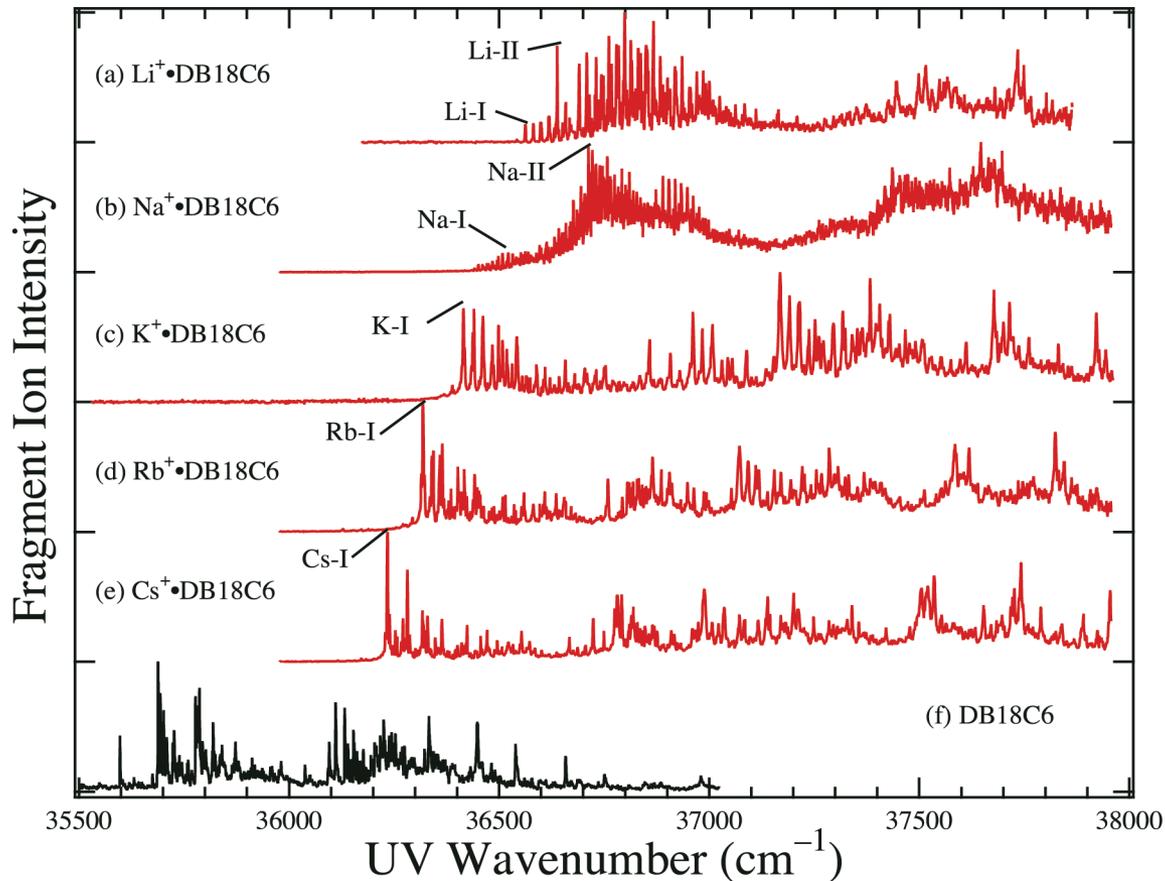
Exciton Splitting



$M^+\cdot DB18C6$

$K^+ \sim Cs^+$ で Exciton Splitting が明瞭に観測された

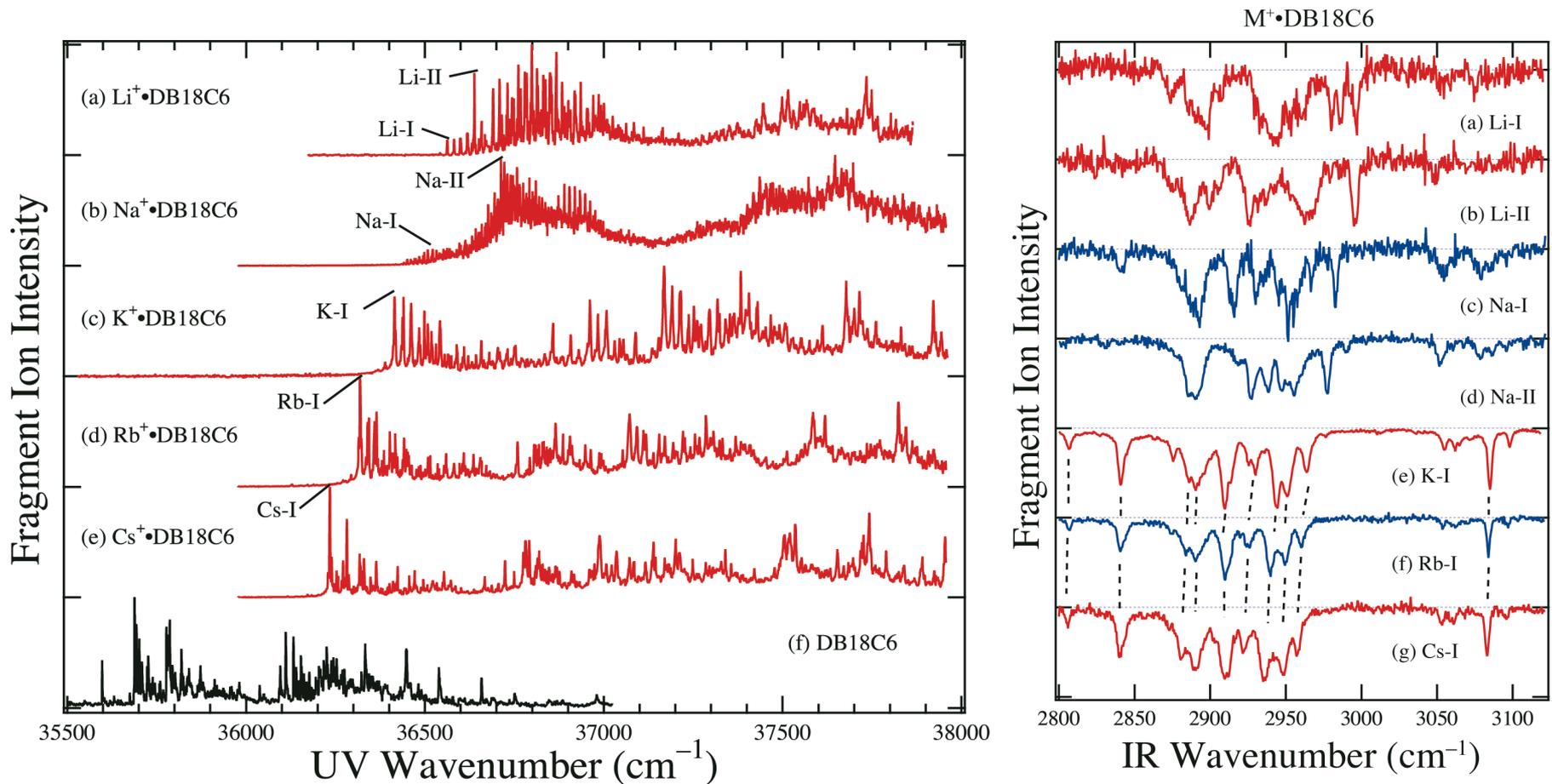
UV Spectra of $M^+ \cdot DB18C6$



$M^+ \cdot \text{DB18C6}$

$\text{Li}^+ \sim \text{K}^+$ でUVスペクトルが大きく変化する → 構造が大きく異なる
 $\text{K}^+ \sim \text{Cs}^+$ はUVスペクトルが似ている → 類似の構造をもつ

IR Spectra of $M^+ \cdot DB18C6$

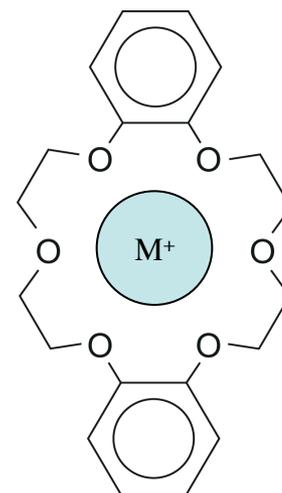


IRスペクトルにより異性体の数を決定できる

$K^+ \sim Cs^+$ はIRスペクトルが似ている → 類似の構造をもつ

The Number of Conformers

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

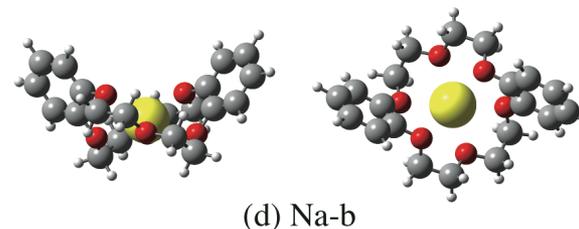
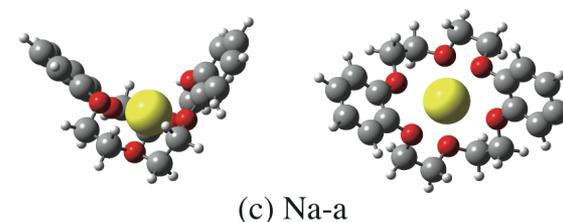
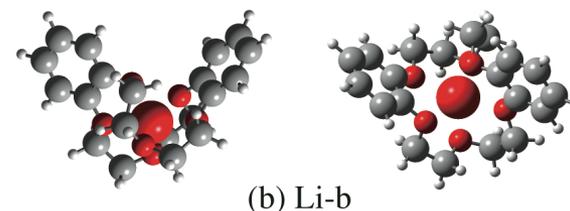
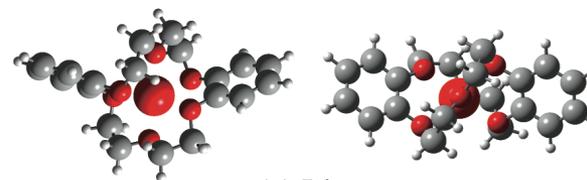
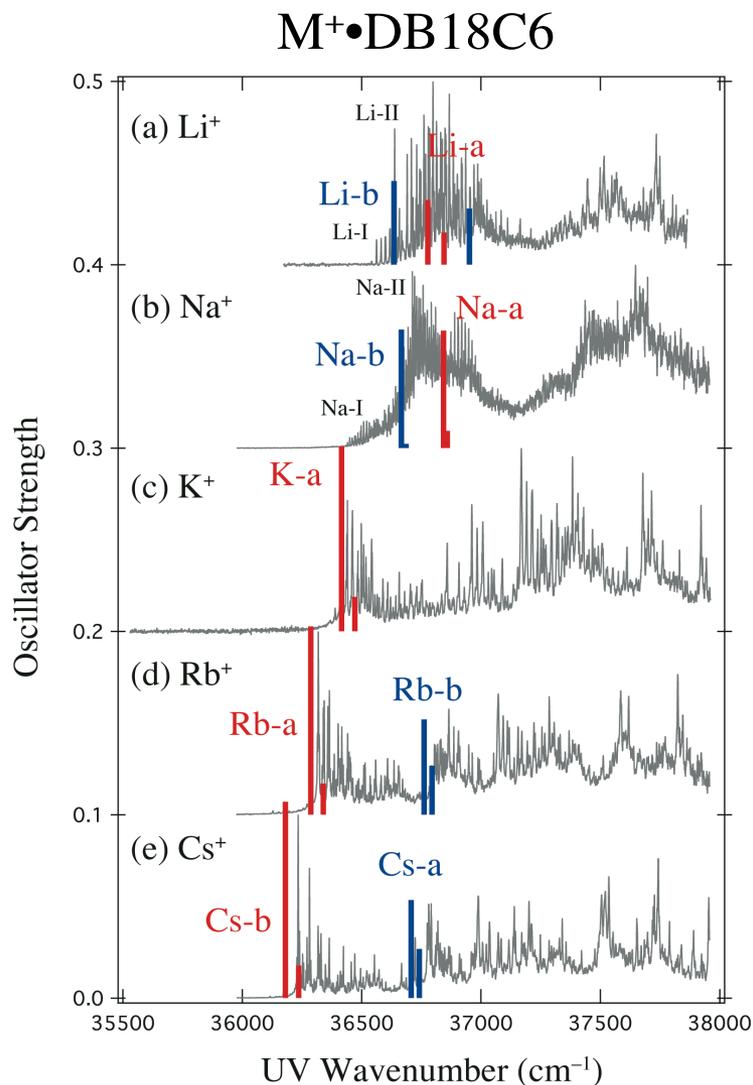


M⁺•DB18C6

IR-UVスペクトル
エネルギー
電子スペクトル計算

に基づいて構造を同定

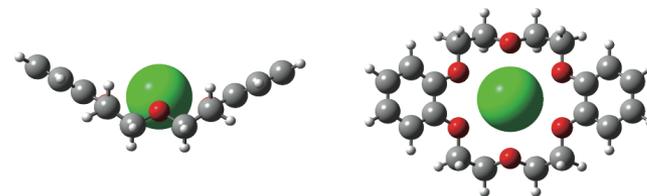
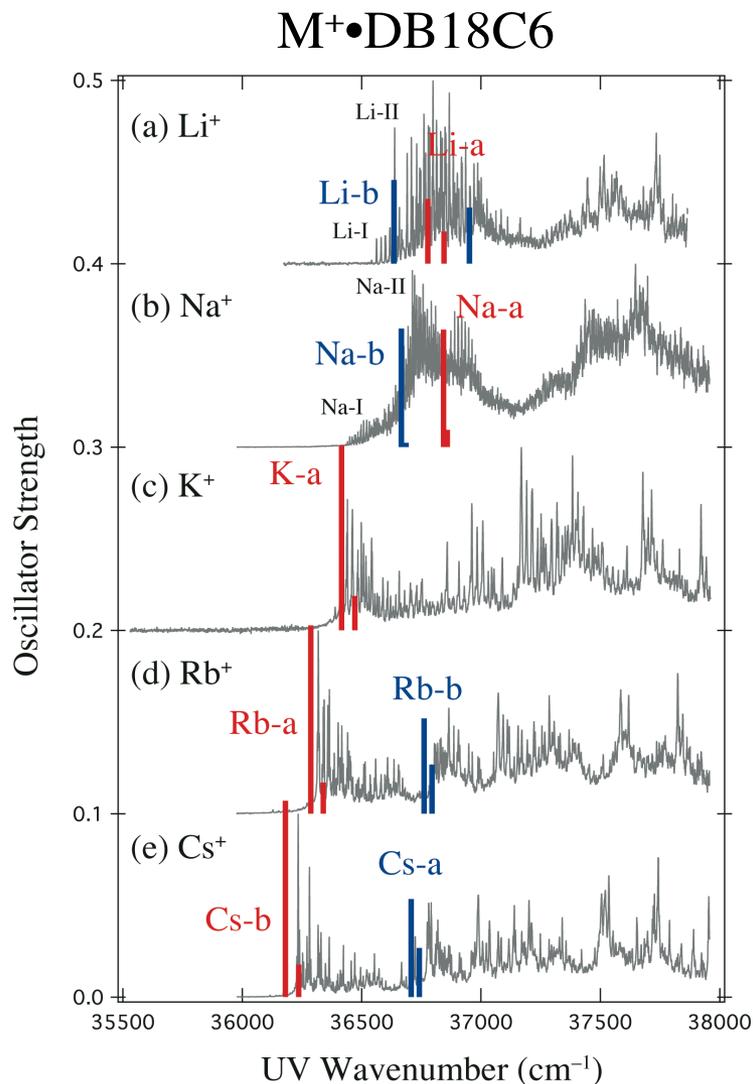
Structure of $M^+ \cdot DB18C6$ ($M = Li, Na$)



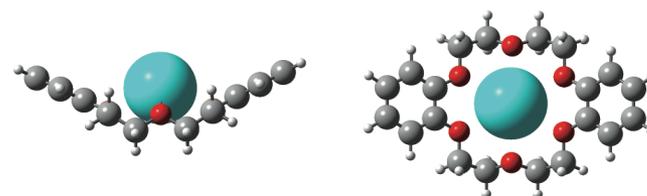
M05-2X/6-31+G(d) with Stuttgart RLC ECP
A scaling factor of 0.8340 is used.

エーテル環を歪めて捕捉

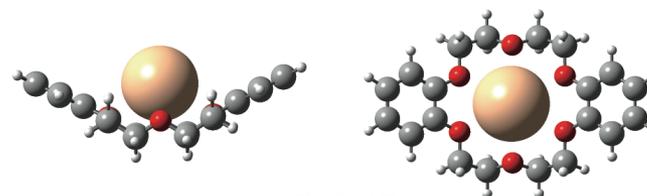
Structure of $M^+ \cdot \text{DB18C6}$ (M = K, Rb, Cs)



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



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



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

エーテル環を最大限開いている

K^+ エーテル環に入っている

Rb^+ , Cs^+ エーテル環から大きくはみ出ている

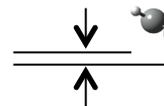
Structure of $M^+ \cdot \text{DB18C6}$ ($M = \text{K}, \text{Rb}, \text{Cs}$)

イオン半径/ \AA

K^+

1.52

0.51

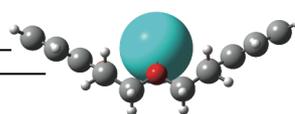
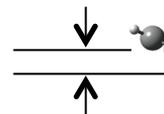


(a) K-a (C_{2v})

Rb^+

1.66

1.00

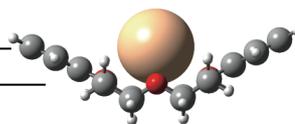
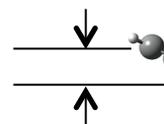


(b) Rb-a (C_{2v})

Cs^+

1.81

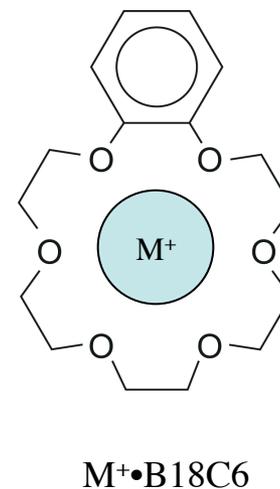
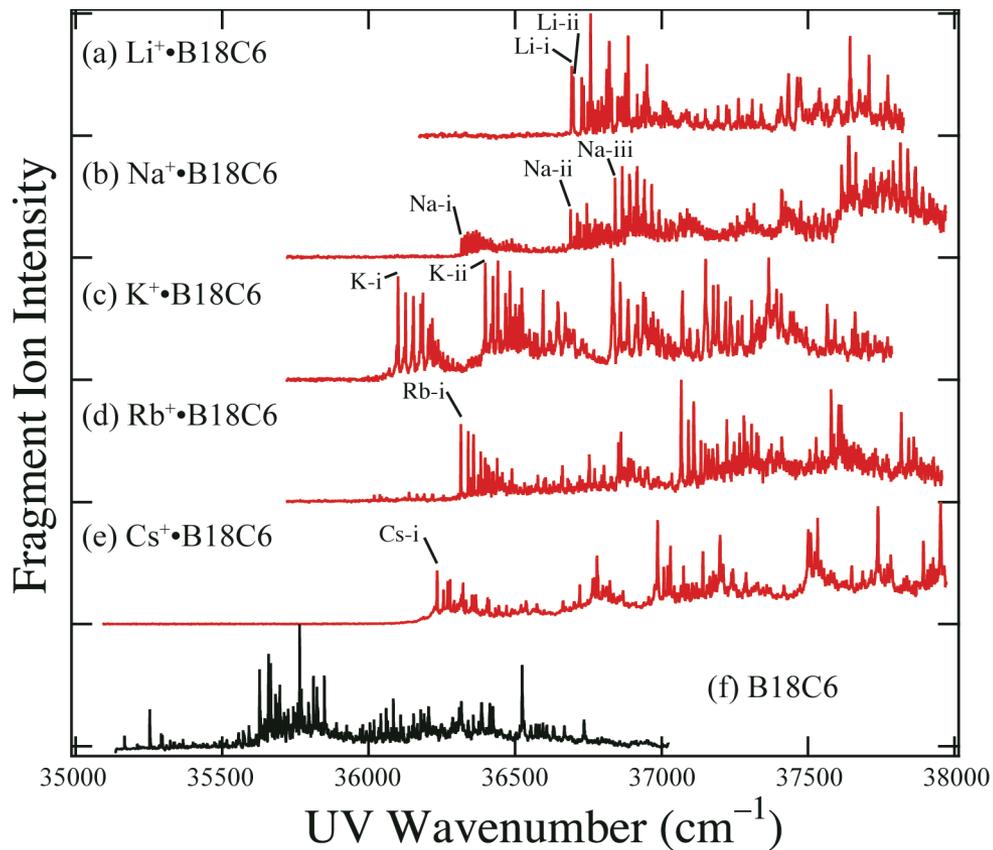
1.36



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

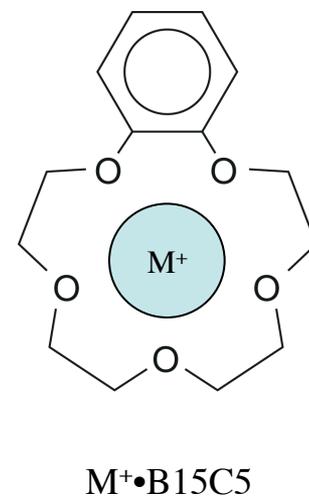
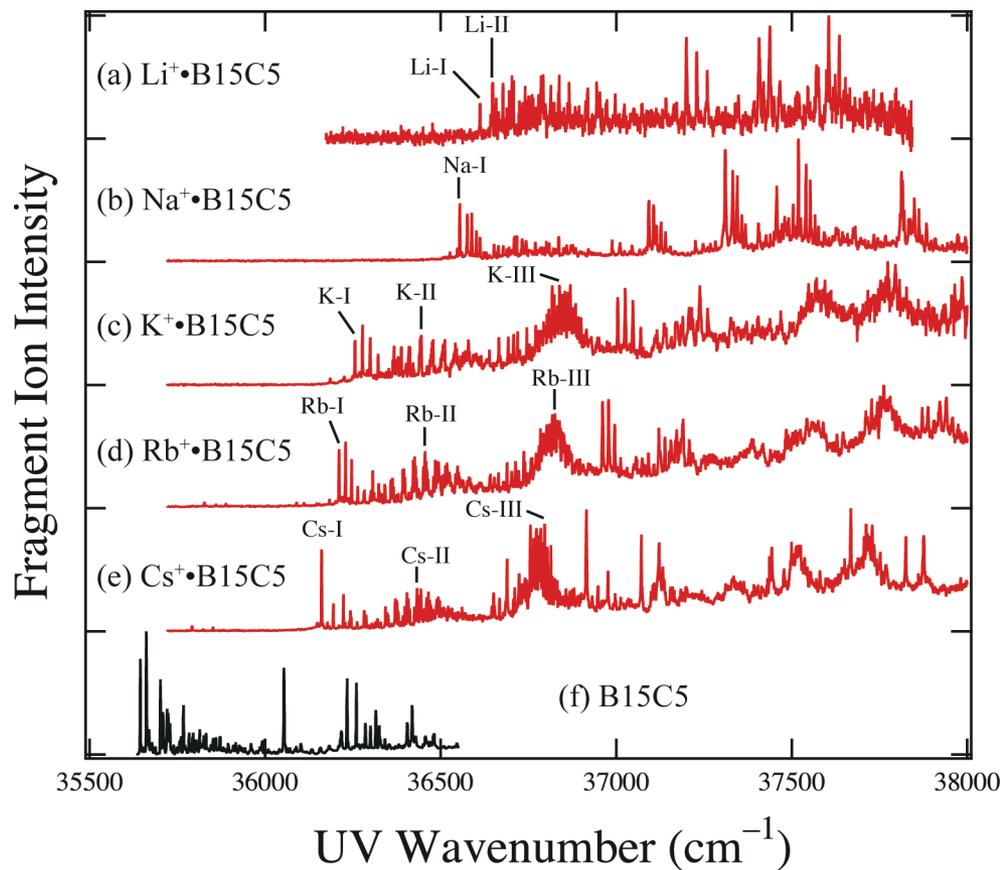
cf. Li^+ (0.90 \AA), Na^+ (1.16 \AA)

UV Spectra of $M^+ \cdot B18C6$



DB18C6と同様に
コンフォーマー数とその構造
を決定

UV Spectra of $M^+ \cdot B15C5$

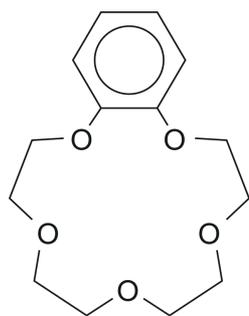


The Number of Conformers

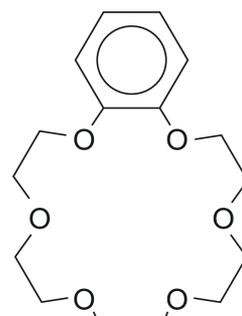
M ⁺	M ⁺ •B15C5	M ⁺ •B18C6	M ⁺ •DB18C6
Li ⁺	2	2	2
Na ⁺	1	3	2
K ⁺	3	2	1
Rb ⁺	3	1	1
Cs ⁺	3	1	1
(monomer)	3 ^a	4 ^b	2 ^b

^aZwier and co-workers, *J. Phys. Chem. A*, **2009**, *113*, 8055.

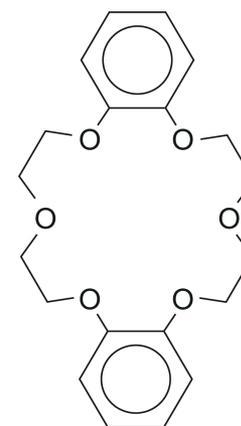
^bEbata and co-workers, *Sensors*, **2010**, *10*, 3519.



B15C5



B18C6

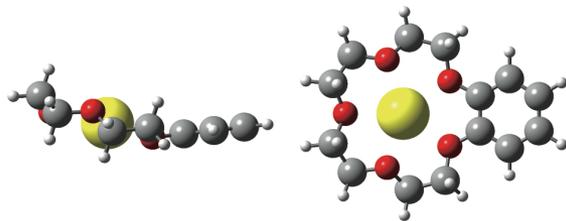


DB18C6

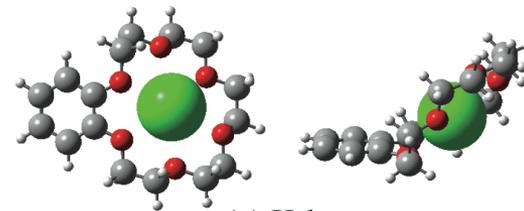
エーテル環が小さくても
必ずしもコンフォーマー数は減少しない

ベンゼンがエーテル環の自由度を下げ
コンフォーマー数を減少させる

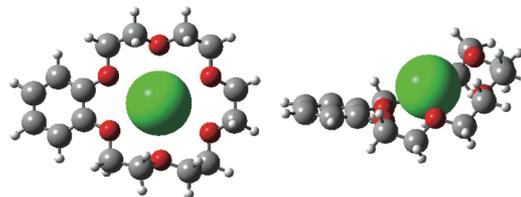
Structure of 1:1 Complexes



Na⁺•B15C5

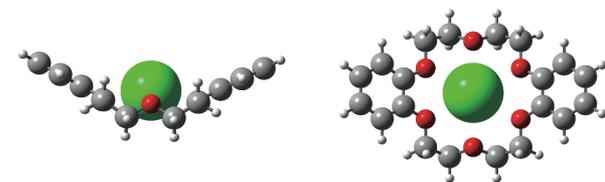


(a) K-b



(b) K-a

K⁺•B18C6



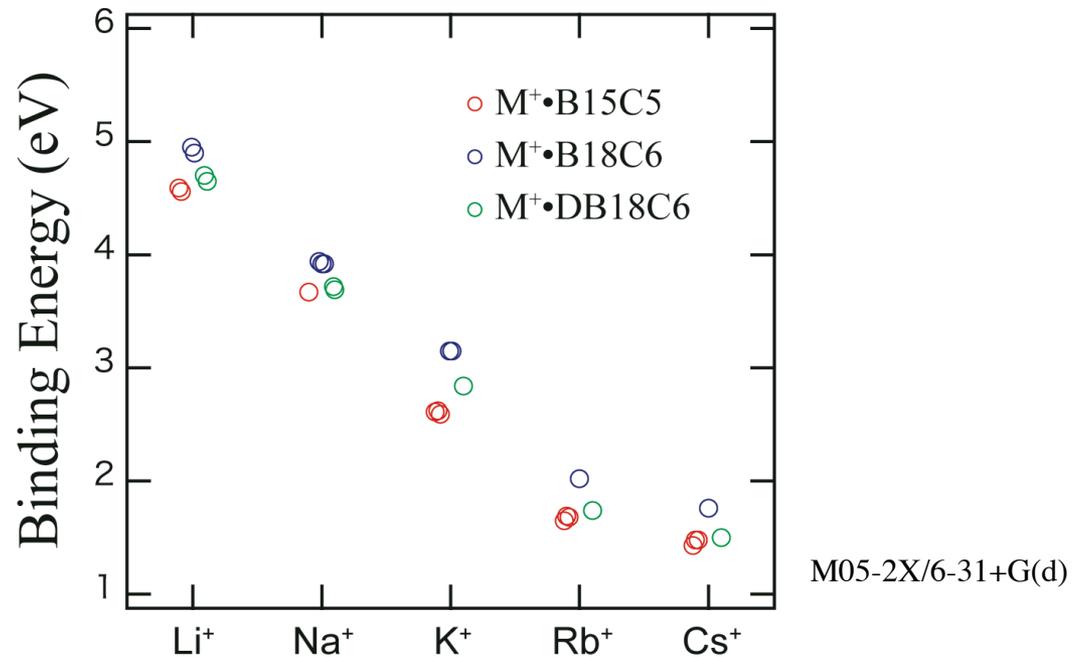
(a) K-a (C_{2v})

K⁺•DB18C6

エーテル環とイオンのサイズが適合
開いたエーテル環にきれいに収まっている

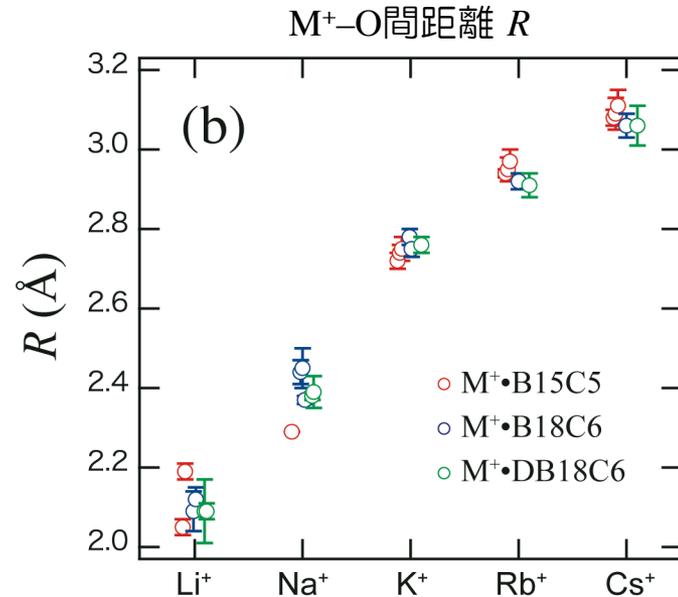
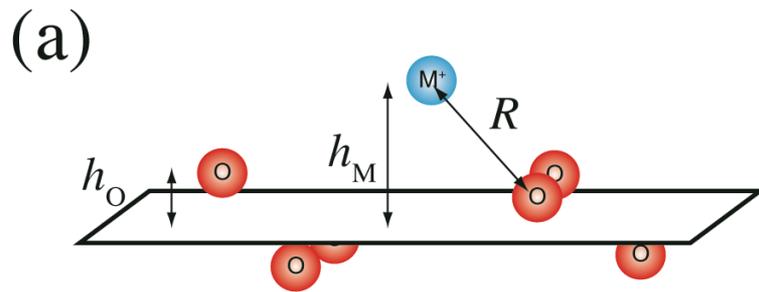
これらの組み合わせに特異性があるか？

Calculated Binding Energy



いずれも単調に減少
特異性はみられない

Structural Parameters



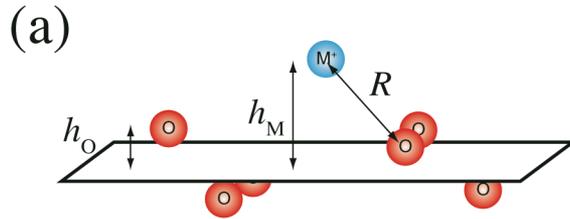
Rは単調に増加

エーテル環のサイズ，ベンゼン環の数に依存しない

Rのばらつきが小さい

M⁺はすべてのO原子に均等に結合している

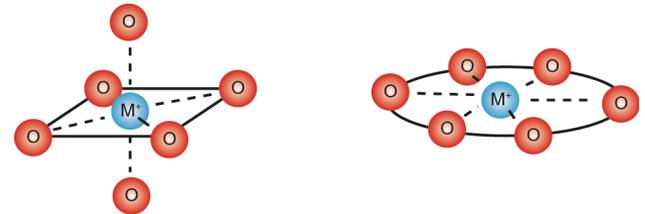
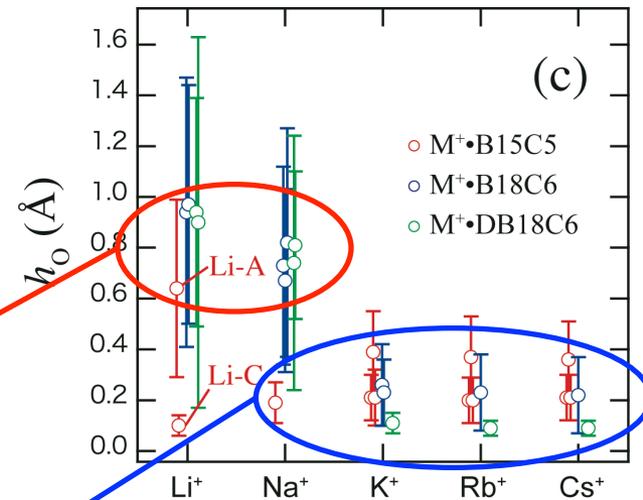
Structural Parameters



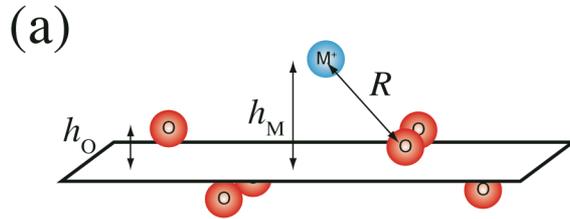
小さいイオンの錯体
O原子が3次的に配列

大きいイオンの錯体
O原子が平面にならび

O原子の平均面とO原子間距離



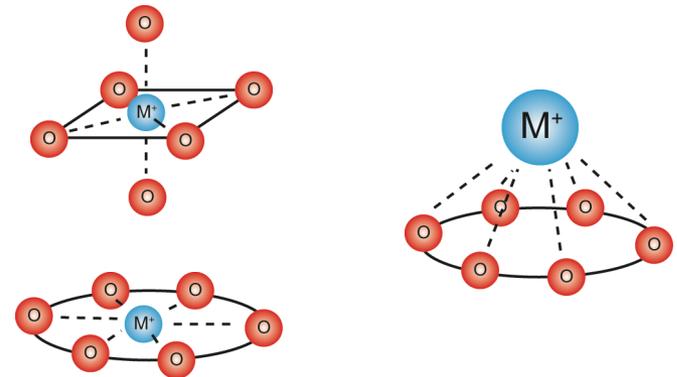
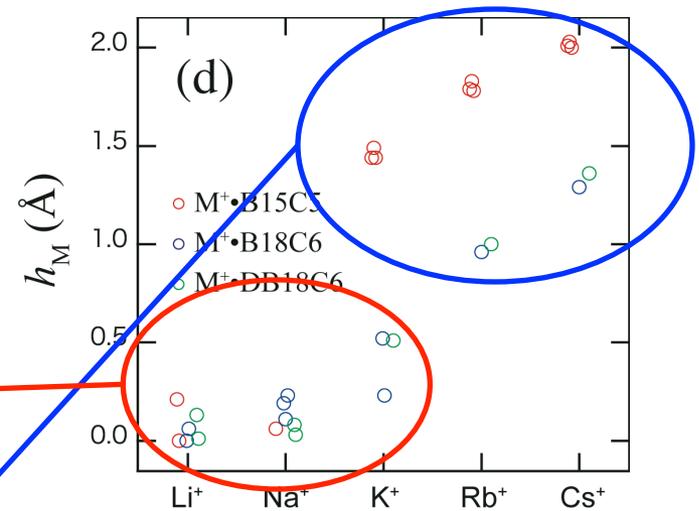
Structural Parameters



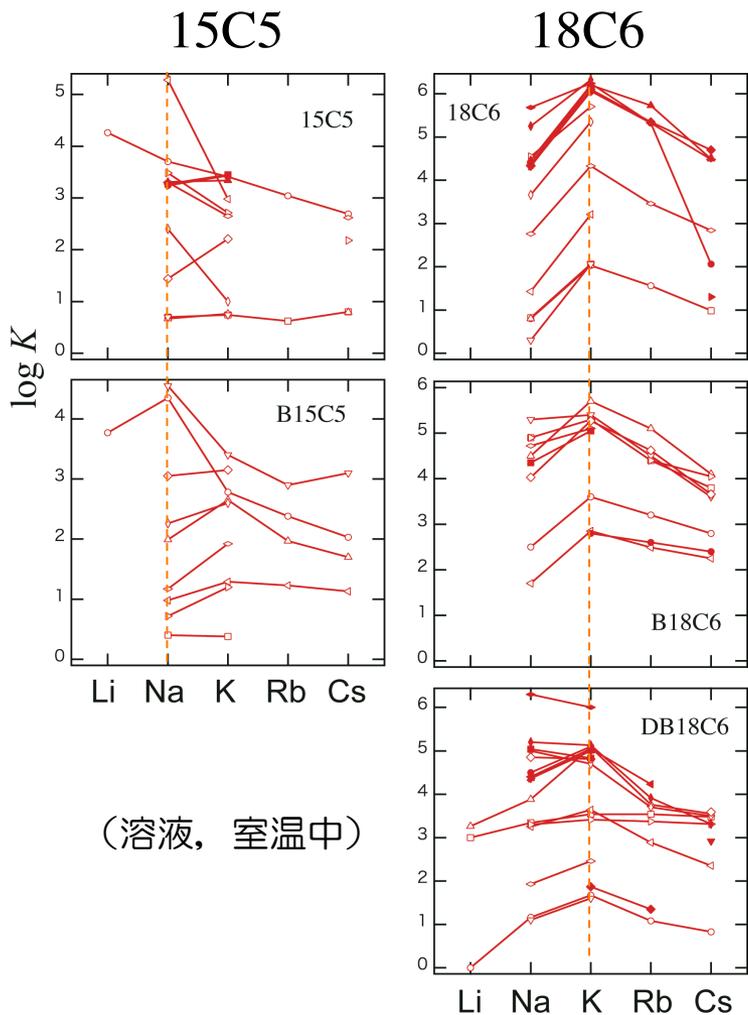
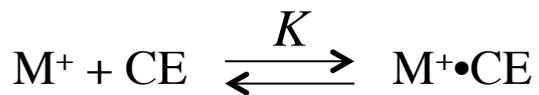
小さいイオン
O原子の集団の中心に捕捉

大きいイオン
O原子の平面から外れている

O原子の平均面とM⁺原子間距離



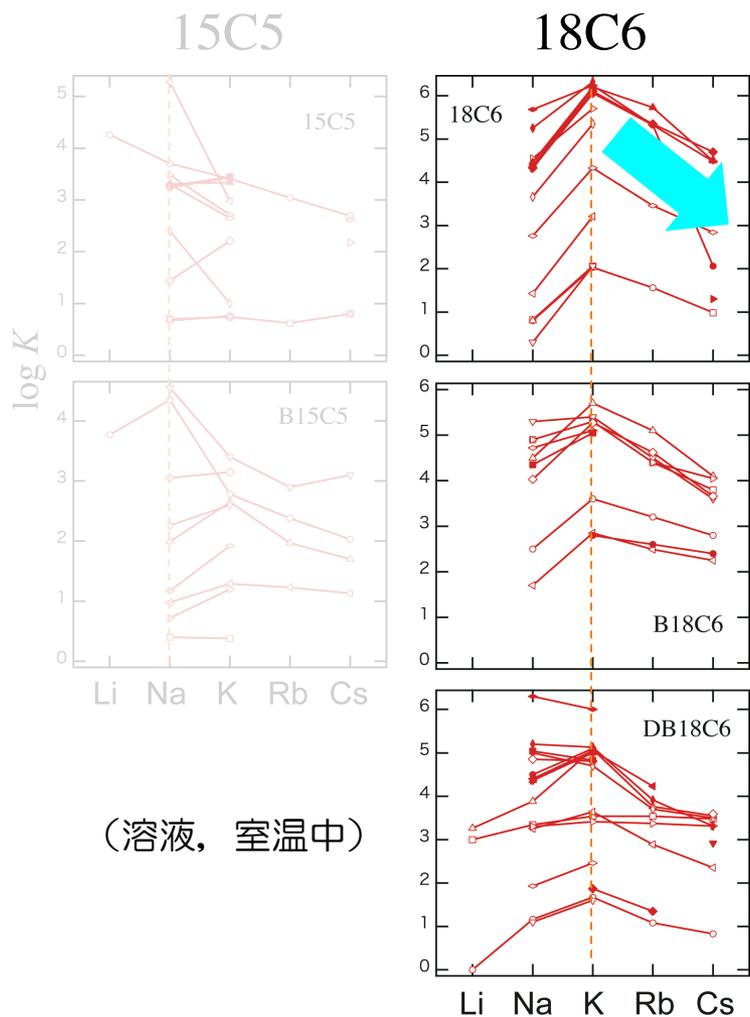
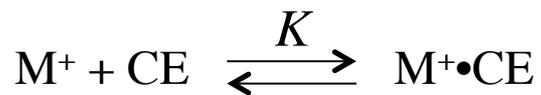
Relation between Complex Structure and Selectivity



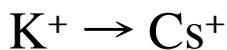
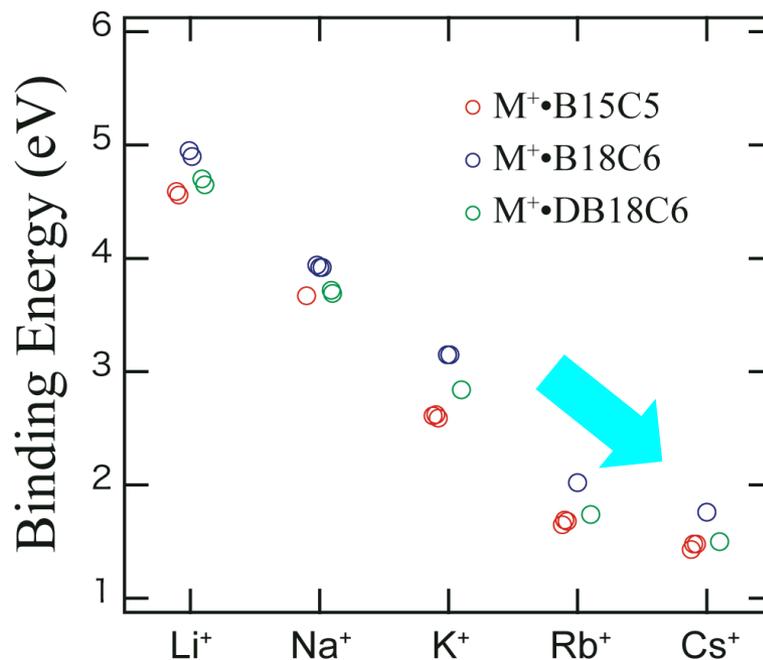
包接錯体の構造から
溶液中の選択性について
何か言えるか？

- 18C6, B18C6, DB18C6
K⁺に対して明確な特異性
- 15C5, B15C5
特異性あまり明瞭ではない

Relation between Complex Structure and Selectivity

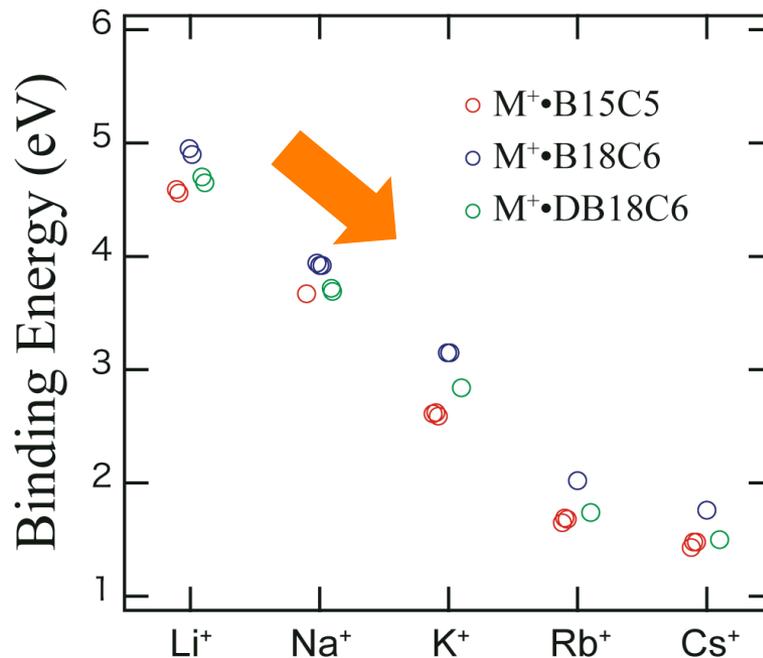
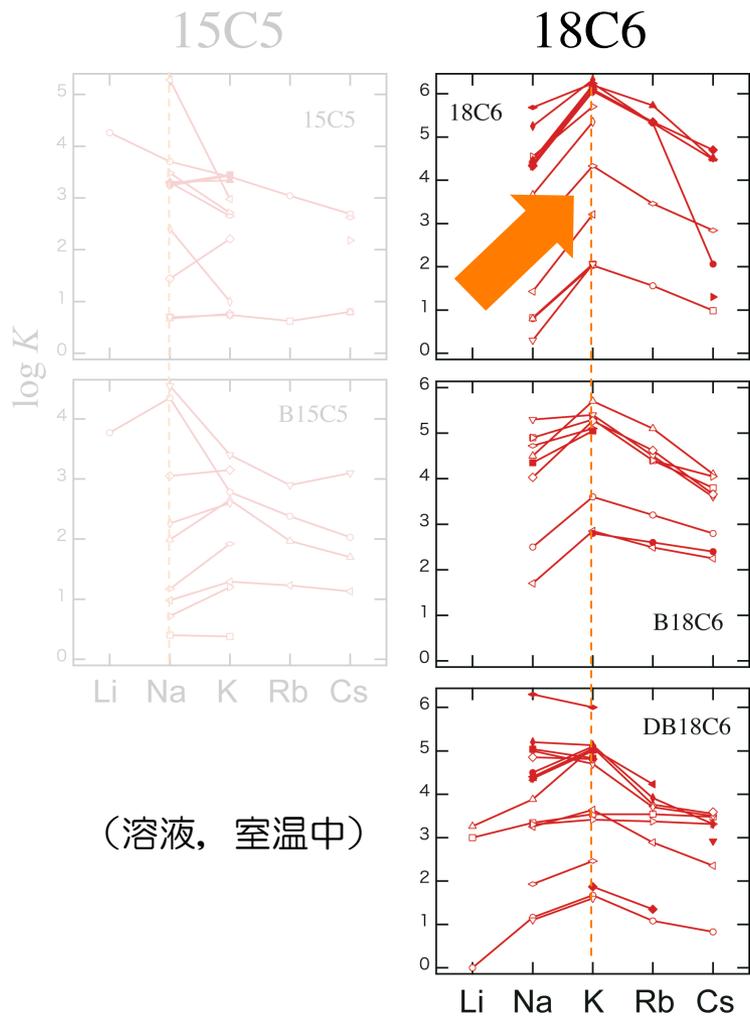
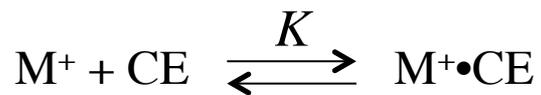


(溶液, 室温中)



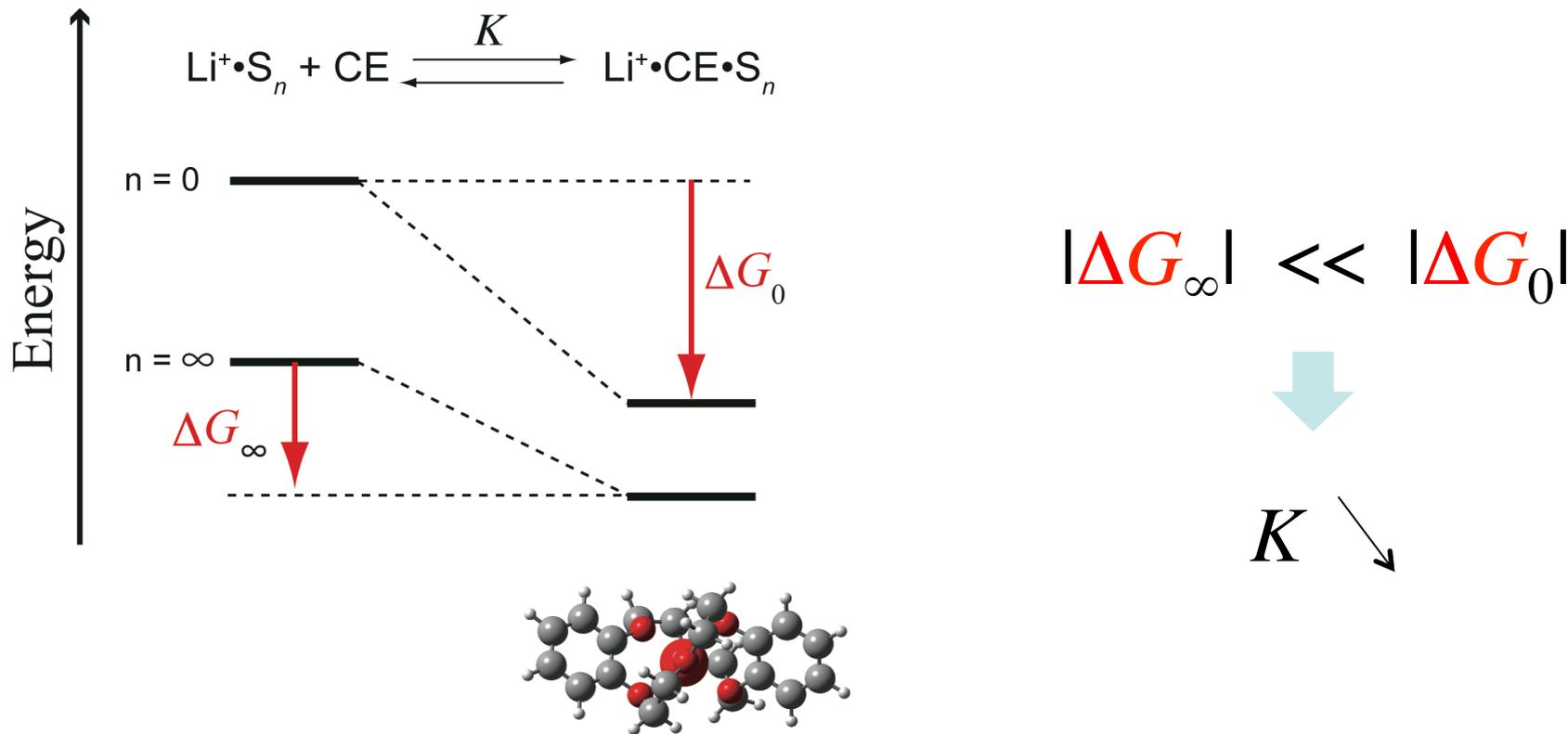
結合エネルギーは減少
平衡定数も減少

Relation between Complex Structure and Selectivity



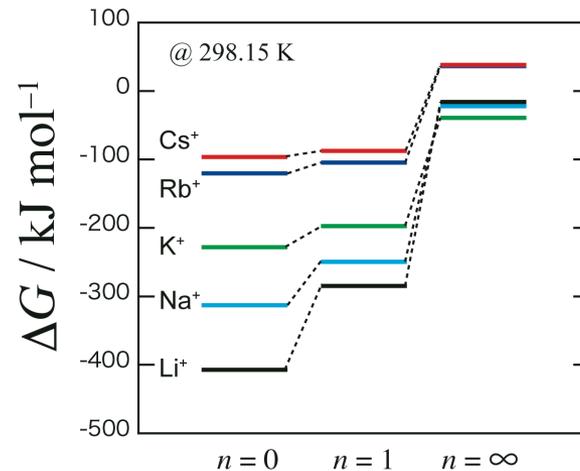
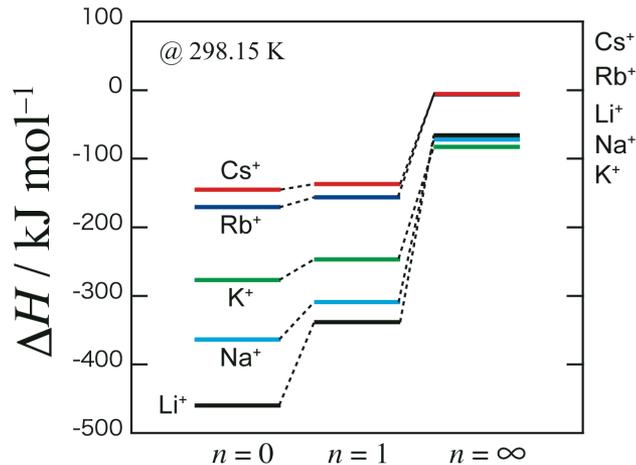
Li⁺ → K⁺
 結合エネルギーは減少
 平衡定数は増加

Relation between Complex Structure and Selectivity



小さいイオンは
エーテル環に3次的に取り囲まれ
溶媒との相互作用が小さくなる

ΔH , ΔS , and ΔG for DB18C6



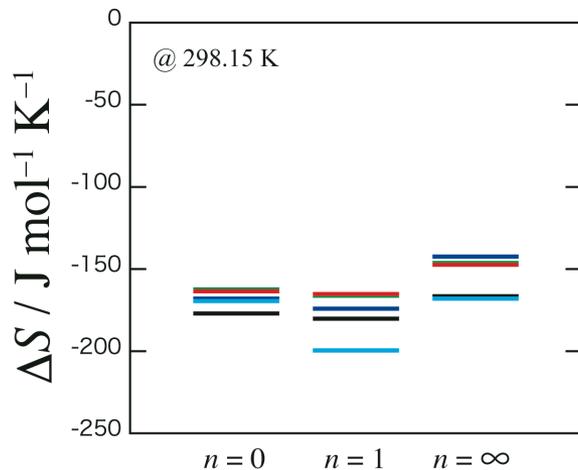
Cs⁺

Rb⁺

Li⁺

Na⁺

K⁺



■ 溶媒和により ΔH は大きく変化

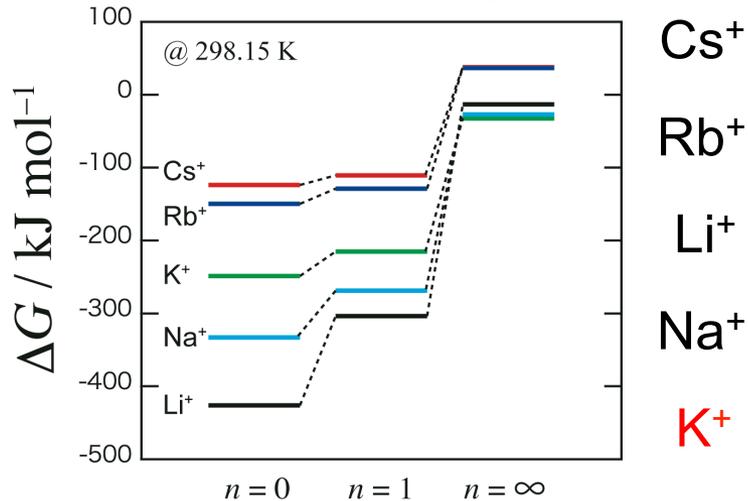
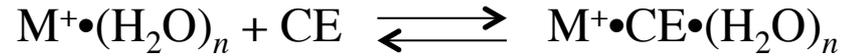


溶液中の ΔG はK⁺に対して最も有利
選択性を再現

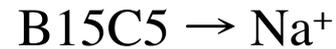
■ ΔS はほぼ一定

M05-2X/6-31+G*. $n = \infty$ の計算は分極連続体モデル (PCM) による。

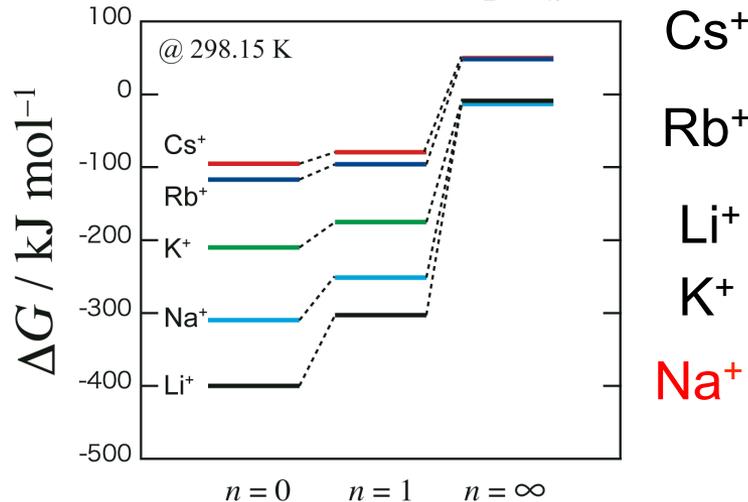
ΔG for B18C6 and B15C5



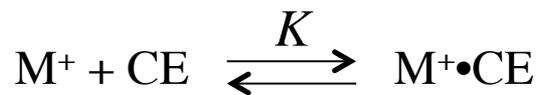
溶液中で



の選択性が再現されている

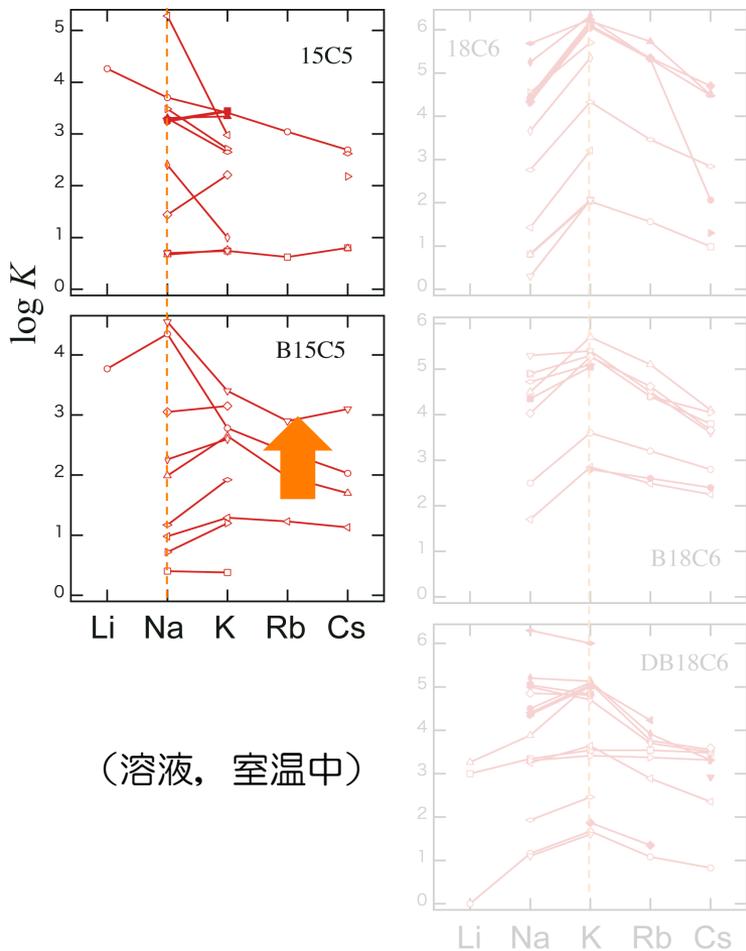


Relation between Complex Structure and Selectivity



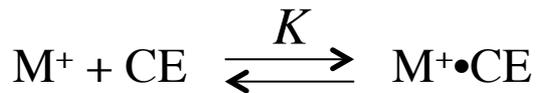
15C5

18C6



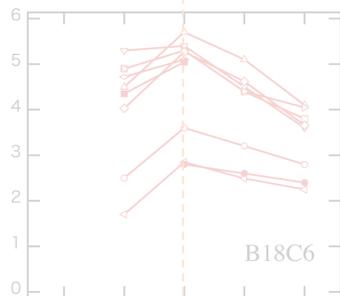
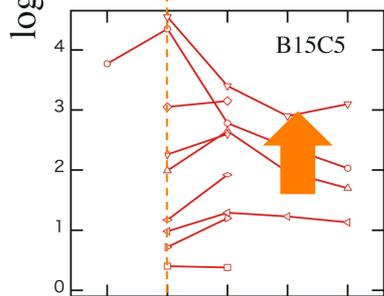
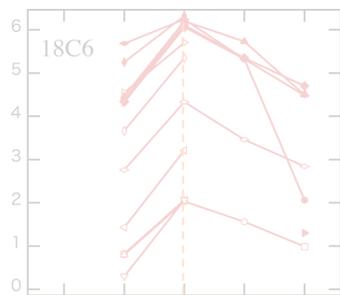
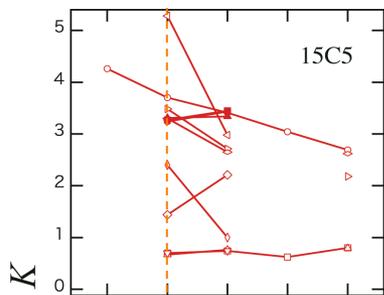
■ 15C5, B15C5
 特異性あまり明瞭ではない
 K⁺~Cs⁺のKが比較的大きい

Relation between Complex Structure and Selectivity



15C5

18C6



Li Na K Rb Cs

Li Na K Rb Cs

(溶液, 室温中)

Li Na K Rb Cs

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

大きいイオン

B15C5のコンフォメーション数が多い
エントロピー的に有利



$K \nearrow$

Summary

■ イオン選択性は包接錯体の溶媒和の大きさによりコントロール
エーテル環とイオンのサイズ適合にのみ由来するのではない

■ 小さいイオン

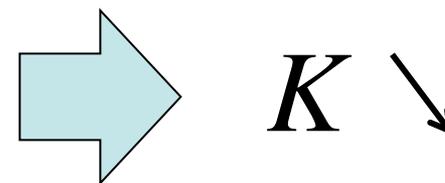
クラウンエーテルに3次的に取り囲まれる

イオンと溶媒との相互作用が小さい

→ 溶液中での ΔG が小さくなる

■ 大きいイオン

包接錯体の ΔG がもともと小さい



■ 今後の展開

温度可変の実験

溶媒和した包接錯体

溶液中での構造決定