UV Spectroscopic Studies of Cold Alkali Metal Ion–Crown Ether Complexes in the Gas Phase

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Summary

UV photodissociation spectroscopy of benzo-crown ether complexes with alkali metal ions (M^+ = Li^+, Na^+, K^+, Rb^+, and Cs^+) with a cold (~4 K) 22-pole ion trap

Conformation of benzo-crown ether components (folded or open)
Location of M^+ in 1:1 complexes (inside or outside)

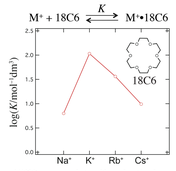
	Dibenzo-18-crown-6	Benzo-15-crown-5	Benzo-18-crown-6
Li^+	folded, inside	folded, inside	folded
Na^+		open, inside	folded open open
K^+	open, inside	open, outside	open open
Rb^+	open, outside	folded, outside	open
Cs^+		folded, outside	

UV spectra of 1:2 complexes under analysis with quantum chemical calculations

Crown Ether Complexes with Metal Ions

■ **Widely used for applications**
Phase transfer catalysis
Ionophores
etc...

■ **Selective encapsulation**



18C6 encapsulates K^+ selectively because of the optimim size matching.

■ **Previous studies in the gas phase**

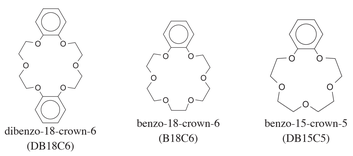
- Mass spectrometric studies
  Dearden (1991), Brodbelt (1992), Armentrout (1996), Brutschy (1997), Bowers (1995)
- IR spectroscopy
  Lisy (2009), Martinez-Haya (2009)
- UV and IR spectroscopy of jet-cooled complexes
  Zwier (2007), Ebata (2007)
- UV spectroscopy
  Kim (2009)
  shows broad features at 150 K due to thermal congestion.

In This Study

UV photodissociation (UVPD) spectroscopy with electrospray and cooled (~4 K) 22-pole ion trap

IR-UV double resonance spectroscopy

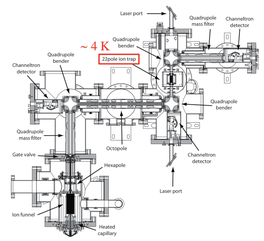
Benzo-crown ether complexes with alkali metal ions (Li^+, Na^+, K^+, Rb^+, Cs^+)



dibenzo-18-crown-6 (DB18C6) | benzo-18-crown-6 (B18C6) | benzo-15-crown-5 (DB15C5)

Examination of relation between selective encapsulation and complex structure

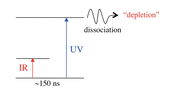
Experimental



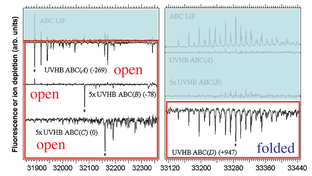
Svendsen, Lorenz, Boyarkin, and Rizzo, *Rev. Sci. Instrum.*, **2010**, *81*, 073107.

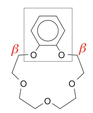
■ nanoelectrospray
B15C5, B18C6, DB18C6
LiCl, NaCl, KCl, RbCl, CsCl
in Methanol
20–200 μM

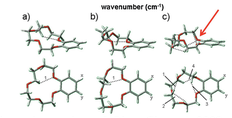
■ UV spectroscopy
■ IR-UV spectroscopy
UV power 1–1.5 mJ/pulse
IR power 4–5 mJ/pulse



UV Spectra of Neutral B15C5



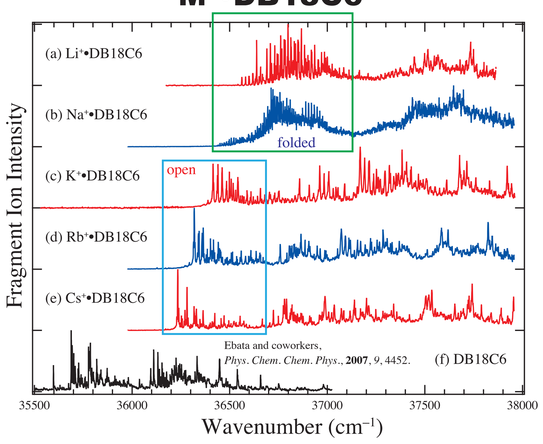




Folded conformations with β carbon atoms out-of-plane of the phenyl ring show congested UV spectra with extensive low-frequency progressions.

Zwier and coworkers, *J. Phys. Chem. A*, **2009**, *113*, 8055.

M^+•DB18C6

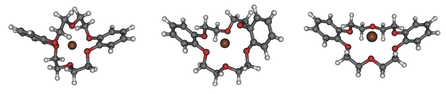


Ebata and coworkers, *Phys. Chem. Chem. Phys.*, **2007**, *9*, 4452.

Calculations of M^+•DB18C6

Number of stable structures

	Li^+•DB18C6	Na^+•DB18C6	K^+•DB18C6	
Molecular Mechanics (< 10 kcal/mol)	219	201	123	MacroModel ver 9.1 MMFF94s
Quantum Mechanics (< 3 kcal/mol)	6	7	2	GAUSSIAN09 M05-2X/6-31+G(d)

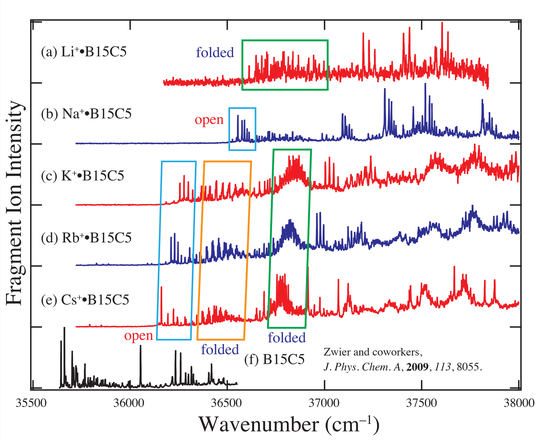


(a) Li^+•DB18C6 folded | (b) Na^+•DB18C6 folded | (c) K^+•DB18C6 open

These structures are consistent with those predicted on the basis of the UVPD spectra.

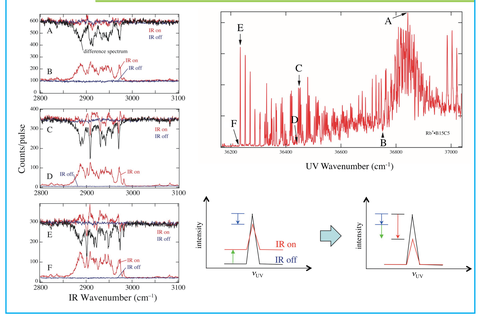
Bowers and coworkers suggested the existence of similar structures for 18C6. (*J. Am. Chem. Soc.*, **1995**, *117*, 10159.)

M^+•B15C5

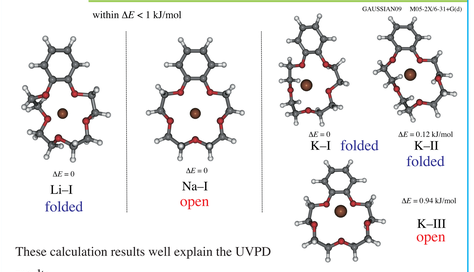


Zwier and coworkers, *J. Phys. Chem. A*, **2009**, *113*, 8055.

Rb^+•B15C5 IR-UV



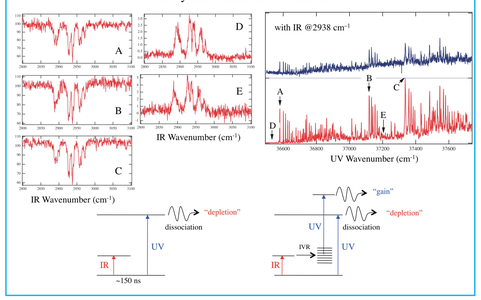
Structure of M^+•B15C5



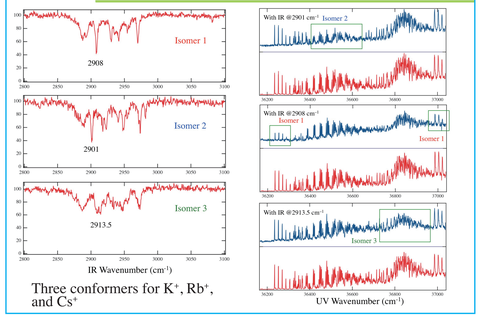
These calculation results well explain the UVPD results.

Na^+•B15C5 IR-UV

Only one isomer for Na^+•B15C5

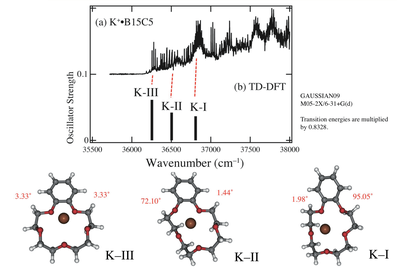


Rb^+•B15C5 IR-UV



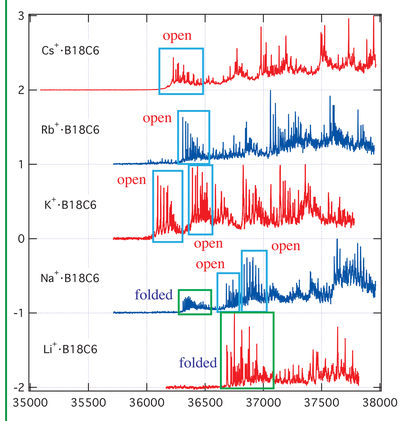
Three conformers for K^+, Rb^+, and Cs^+

Structure of K^+•B15C5



The more tightly the ether ring is folded, the higher the transition energy is and the more congested the vibronic structure is.

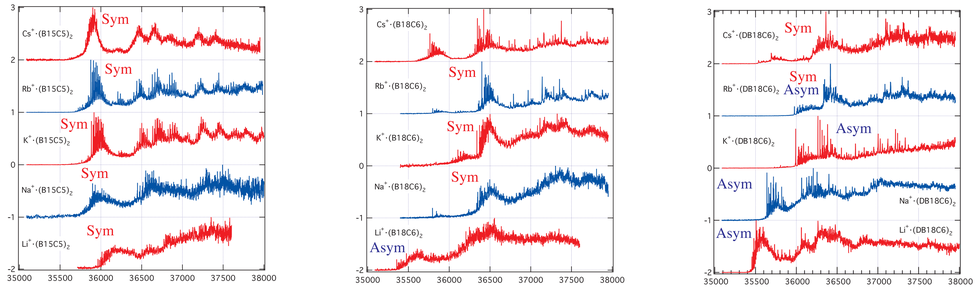
M^+•B18C6

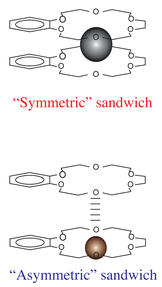


Analysis with quantum chemical calculations in progress

M^+•$(CE)_2$ Complexes

Analysis with quantum chemical calculations in progress





"Symmetric" sandwich

"Asymmetric" sandwich