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+, Cs+) with a cold (~4 K) 22-pole ion trap

Crown Ether Complexes with Metal Ions

Wide use for applications
- Phase transfer catalysis
- Ionophores
- Symmetric “sandwich”
- Asymmetric “sandwich”

Selective encapsulation

UV and IR spectroscopy

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+)

Experimental

Analysis with quantum chemical calculations

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

Zwier and coworkers,

Ebata and coworkers,

Hiroshima University and École Polytechnique Fédérale de Lausanne

Crown Ether Complexes

Selective encapsulation

Previous studies in the gas phase
- Mass spectrometric studies
- IR spectroscopy
  - Lisy (2009), Martinez-Haya (2009)
- UV and IR spectroscopy of jet-cooled complexes

• UV spectroscopy
  - Kim (2009)

Show broad features at 150 K due to thermal congestion.

Widely used for applications
- Phase transfer catalysis
- Ionophores
- etc...

M+ + 18C6

M+ •18C6

K

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

M+ + B15C5

M+ •B15C5

M+ •B18C6

M+ •(CE)2 Complexes

Analysis with quantum chemical calculations in progress

Na+ •B15C5 IR-UV

Only one isomer for Na+ •B15C5

Rb+ •B15C5 IR-UV

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

Structure of M+ •B15C5

Structure of K+ •B15C5

Three 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.)

These calculation results well explain the UVPD results.

Symmetric “sandwich”

Asymmetric “sandwich”

M+ •(CE)2 Complexes

Analysis with quantum chemical calculations in progress

UVA spectrum of neutral B15C5