

## Cold Spectroscopy of Metal Ion-Crown Ether Complexes in the Gas Phase

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Crown ethers play important roles in host-guest chemistry for the selective capture of guest species, especially metal cations.<sup>1</sup> For instance, dibenzo-18-crown-6 (DB18C6) captures K<sup>+</sup> ion preferentially among alkali metal ions in solution. The goal of this study is to elucidate the mechanism of the ion selectivity of crown ethers with gas-phase spectroscopy under very cold conditions.<sup>2-4</sup>

In the experiment, metal ion-crown ether complexes are produced by electrospray, and a specific complex is mass-selected by a quadrupole mass filter. The parent ions are introduced into a cold 22-pole ion trap, where the parent ions are cooled down to ~10 K. The cold ions are irradiated by a UV laser in the trap, and resultant fragment ions are mass analyzed by the second quadrupole mass filter. UV photodissociation (UVPD) spectra of the parent species are obtained by plotting yields of fragment ions as a function of the UV laser. IR spectra of conformer-specific ions are measured by IR-UV double resonance.

Firstly we measure UVPD and IR-UV double-resonance spectra of DB18C6 complexes with alkali metal ions, M<sup>+</sup>•DB18C6 (M = Li, Na, K, Rb, and Cs). All the complexes show a number of vibronically resolved UV bands in the 36000–38000 cm<sup>-1</sup> region. The Li<sup>+</sup> and Na<sup>+</sup> complexes each exhibit two stable conformations in the cold ion trap (as verified by IR-UV double-resonance), whereas the K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> complexes exist in a single conformation. We analyze the structure of the conformers with the aid of DFT calculations. In the Li<sup>+</sup> and Na<sup>+</sup> complexes, DB18C6 distorts the ether ring to fit the cavity size to the small diameter of Li<sup>+</sup> and Na<sup>+</sup>. In the complexes with K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>, DB18C6 adopts a boat-type (C<sub>2v</sub>) open conformation. The K<sup>+</sup> ion is captured in the cavity of the open conformer thanks to the optimum matching between the cavity and the ion. The Rb<sup>+</sup> and Cs<sup>+</sup> ions sit on top of the ether ring, because they are too large to enter the open conformer.

Furthermore, we extend our measurement to hydrated complexes, M<sup>+</sup>•DB18C6•(H<sub>2</sub>O)<sub>n</sub>, in order to examine the solvent effect to the encapsulation. The K<sup>+</sup>•DB18C6•(H<sub>2</sub>O)<sub>n</sub> complexes have a few conformers even under the cold condition, whereas the Rb<sup>+</sup> and Cs<sup>+</sup> complexes show only one conformation for each size. These results imply that the K<sup>+</sup>•DB18C6 complex in solution will take many kinds of conformations with solvent molecules involved, which can lead to entropic preference for the K<sup>+</sup> encapsulation.

<sup>1</sup>C. Pedersen, *J. Am. Chem. Soc.* **1967**, *89*, 7017. <sup>2</sup>Y. Inokuchi et al., *J. Am. Chem. Soc.* **2011**, *133*, 12256. <sup>3</sup>Y. Inokuchi et al., *J. Phys. Chem. A* **2012**, *116*, 4057. <sup>4</sup>Y. Inokuchi et al., *ChemPhysChem* **2013**, *14*, 649.