

UV spectroscopy of cryogenically cooled Ag⁺-benzo-crown ether complexes in the gas phase

Yuma Kitamura,¹ Motoki Kida,¹ Satoru Muramatsu,¹

Takayuki Ebata,^{1,2} Yoshiya Inokuchi¹

¹ Department of Chemistry, Graduate School of Science, Hiroshima University

² National Chiao Tung University

In host-guest chemistry, crown ethers play important roles for the selective capture of guest species such as metal ions. We have reported UV spectra of benzo-18-crown-6 (B18C6), dibenzo-18-crown-6 (DB18C6), and dibenzo-15-crown-5 (DB15C5) (Figure 1) complexes with alkali metal ions in the gas phase.^{1,2} In the present work, we study UV photodissociation (UVPD) spectroscopy of Ag⁺ ion complexes, (Ag-B18C6)⁺, (Ag-DB18C6)⁺, and (Ag-DB15C5)⁺.³ Ag⁺ ion is classified into soft acid; some macrocycles having aromatic rings can encapsulate Ag⁺ ion efficiently because of strong Ag⁺- π interactions. In addition, Ag atom has substantially higher ionization energy than alkali metals; this can also strongly affect the electronic structure/charge distribution in the complexes.

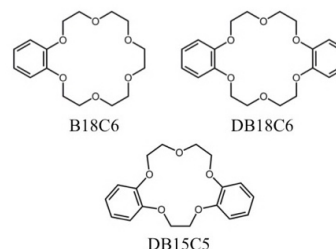


Figure 1. Benzo-crown ether

UVPD spectroscopy of the Ag⁺ complexes is performed using a time-of-flight mass spectrometer equipped with an electrospray ion source and a cold (4 K) quadrupole ion trap.³ The geometric and electronic structures of the Ag⁺ complexes are also analyzed by density functional theory (DFT) calculations. The electronic transitions of the complexes are predicted by time-dependent DFT (DFT) calculations.

Figure 2 displays the UVPD spectra of the complexes. The (Ag-B18C6)⁺ and (Ag-DB18C6)⁺ complexes show sharp vibronic bands, while the UVPD spectrum of the (Ag-DB15C5)⁺ complex is very broad. These UV bands are assigned to the π - π^* transition. Quantum chemical calculations suggest that the broad feature of the (Ag-DB15C5)⁺ complex can be attributed to short lifetimes of optically excited $\pi\pi^*$ states due to internal conversion to low-lying excited states present only for (Ag-DB15C5)⁺. The appearance of the π - π^* transition indicates that the positive charge in the complexes is localized on Ag. However, the main fragment ions subsequent to the UV excitation of these complexes are B18C6⁺, DB18C6⁺, and DB15C5⁺ radical ions; the charge transfer (CT) occurs from Ag⁺ to the benzo-crown ethers after the UV excitation. The CT during the fragmentation is attributed to higher ionization energy of Ag atom than that of the benzo-crown ethers. We will talk about the structure of (Ag-B18C6)⁺, (Ag-DB18C6)⁺, and (Ag-DB15C5)⁺ complexes in the gas phase and the mechanism of charge transfer from Ag⁺ ions to the crown ethers after the UV excitation.

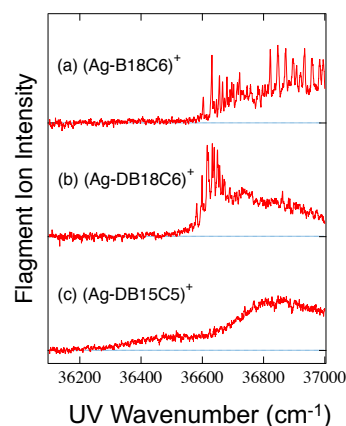


Figure 2. UVPD spectra

(1) Inokuchi et al., *J. Am. Chem. Soc.*, 133, 12256 (2011). (2) Inokuchi et al., *J. Phys. Chem. A.*, 116, 4057 (2012). (3) Kitamura et al., *J. Phys. Chem. A.*, 123, 9185 (2019).