

UV Spectroscopic Studies on Cold Host-Guest Complexes in 22-Pole Ion Trap

極低温イオントラップを用いた、ホスト-ゲスト錯体の気相分光

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【Introduction】 After the discovery of crown ethers (CEs) by Pedersen in 1967 (Pedersen, *J. Am. Chem. Soc.*, **1967**), these have been used in host-guest chemistry for the selective capture of metal cations. In his study, UV spectroscopy was used as one of three criteria to verify the complex formation. However, since UV spectra of complexes were measured in methanol at room temperature, the absorption showed only broad features due to solvent effect and thermal congestion, and it was not possible to determine the structure of the complexes from the UV spectra. More recently, Kim and coworkers reported UV spectra of alkali metal ion-CE complexes produced by electrospray (Kim et al., *J. Phys. Chem. A*, **2009**). In their experiments, the complexes were cooled down to 150 K in the gas phase, but they still showed broad features in the UV spectra. In this study, we report UV photodissociation (UVPD) spectra of CE complexes with metal ions. The complexes are cooled down to ~10 K in a 22-pole ion trap. We use dibenzo-18-crown-6 (DB18C6), benzo-18-crown-6 (B18C6), and benzo-15-crown-5 (B15C5) as host CE molecules.

【Experiment】 UVPD spectra of $M\cdot(CE)_n$ complexes ($M = Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ni^{2+}, Mn^{2+}, Cu^+$; $CE = DB18C6, B18C6, B15C5$; $n = 1, 2$) are measured with a tandem mass spectrometer equipped with a cold, 22-pole ion trap (Svendsen et al., *Rev. Sci. Instrum.*, **2010**). The $M\cdot(CE)_n$ complexes are produced *via* nanoelectrospray, isolated by a quadrupole mass filter, and cooled down to ~10 K in the 22-pole ion trap. The cooled complexes are irradiated with a UV laser, and resulting fragment ions are detected with a second quadrupole mass spectrometer. UVPD spectra are obtained by plotting yields of fragment ions as a function of UV wavelength.

【Results and discussion】 FIG. 1 shows the UVPD spectra measured with the 22-pole ion trap at room temperature and 10 K. The uncooled complex has a broad absorption around 36300 cm^{-1} , whereas the UVPD spectrum of the cooled $K^+\cdot DB18C6$ complex consists of many sharp bands, with the band origin clearly observed at 36415 cm^{-1} . This result indicates that isolating the complexes and cooling them in the gas phase greatly simplify the UV spectra and hence facilitate structure determination. FIG. 2 displays the structure of the Li^+ and K^+ complexes expected on the basis of the UVPD spectra. In the $Li^+\cdot DB18C6$ complex, the DB18C6 component shrinks the ether ring and holds the Li^+ ion, because the hole size of DB18C6 is too large to catch Li^+ . For the K^+ complex, the DB18C6 component takes a boat-like open conformation because of the optimum size matching between the cavity of the open conformer and K^+ ion.

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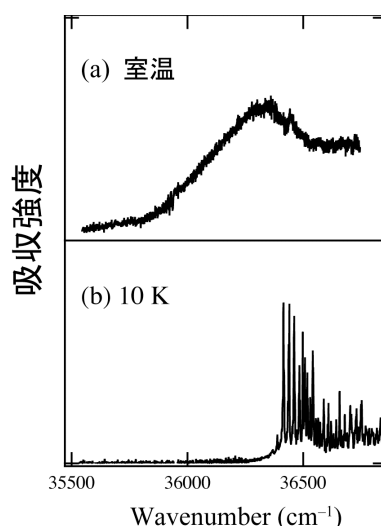


FIG. 1. UV spectra of $K^+\cdot DB18C6$

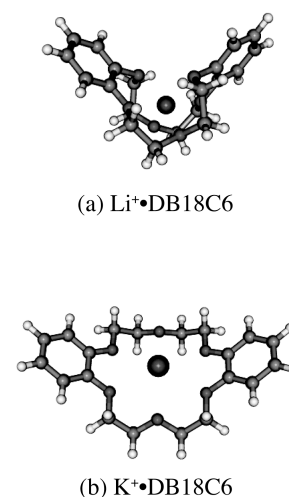


FIG. 2 Structure of (a) $Li^+\cdot DB18C6$ and (b) $K^+\cdot DB18C6$