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Conformation of alkali metal ion-B12C4 complexes studied by UV spectroscopy under cold gas-phase conditions

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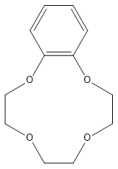
[Introduction] Crown ethers (CEs) are known as host molecules which can hold various guests inside the cavity. In the present work, we investigate the number and the structure of conformers of benzo-12-crown-4 (B12C4) complexes with alkali metal ions, $M^+ \cdot$B12C4 (M = Li, Na, K, Rb, Cs) by UV spectroscopy under cold gas-phase conditions.



B12C4

[Experimental] We measure UV photodissociation (UVPD) spectra of $M^+ \cdot$B12C4 complexes under cold (~10 K) conditions in the gas phase. Then we apply UV-UV hole-burning (HB) spectroscopy to the $M^+ \cdot$B12C4 complexes to discriminate vibronic bands of a single conformer. We also perform quantum chemical calculations.

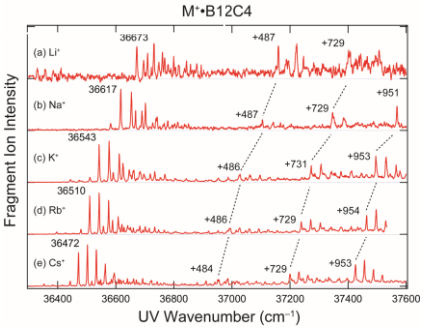


Figure 1. UVPD spectra of the $M^+ \cdot$B12C4

[Results and Discussion] Figure 1 shows the UVPD spectra of the $M^+ \cdot$B12C4 complexes in the 36300-37600 cm^{-1} region. Thanks to the cooling of ions to ~10K, all the $M^+ \cdot$B12C4 complexes show sharp vibronic bands. The UV spectra of $M^+ \cdot$B12C4 show a strong origin band at 36673, 36617, 36543, 36510, and 36472 cm^{-1} for M = Li, Na, K, Rb, Cs, respectively. The vibronic bands at ~487, ~729, and ~953 cm^{-1} can be assigned to the vibrations of the benzene ring.

Figure 2 shows the UV-UV HB spectra of the $M^+ \cdot$B12C4 (M = Na, K, Rb, Cs) complexes. Only one conformer is found for each complex. The vibronic structure around the origin band of the UVPD spectra is quite similar for all the complexes, indicating close resemblance of the complex structure. The most stable structures calculated for the $M^+ \cdot$B12C4 complexes also have a similar conformation among them, which coincides with the UVPD results. In these conformers the metal ions are too big to enter the cavity of B12C4, even for the Li^+ ion.

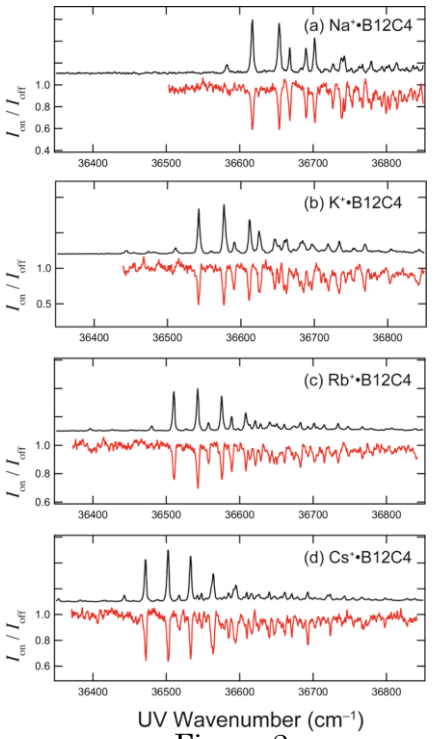


Figure 2. UV-UV HB spectrum (red) and the UVPD spectrum (black)