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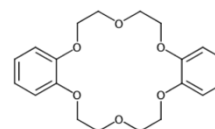
UV and IR spectroscopy of crown ether complexes  
with ammonium ion under cold gas-phase condition

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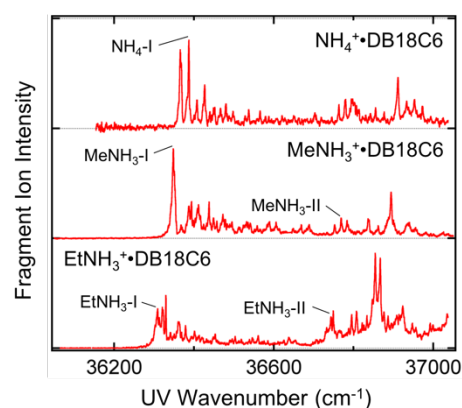
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Crown ethers (CEs) can hold various ions inside the cavity. We have been studying the geometric and electronic structures of CE complexes with alkali metal ions by cold gas-phase spectroscopy [1]. Another type of ions that are effectively encapsulated by CEs is protonated species such as hydronium and ammonium ions. Different from alkali metal ions, which have spherical charge distributions, the protonated systems can have anisotropic interactions with CEs; this will change the encapsulation structure substantially from that of the metal ion complexes. In this study, we investigate dibenzo-18-crown-6 (DB18C6) complexes with ammonium ion, methylammonium ion and ethylammonium ion,  $\text{RNH}_3^+\cdot\text{DB18C6}$  ( $\text{R} = \text{H}, \text{Me}, \text{Et}$ ), under cold gas-phase conditions to elucidate the geometric and electronic structures. We observe UV photodissociation (UVPD) and IR-UV double-resonance (IR-UV) spectra of the complexes with a time-of-flight mass spectrometer equipped with an electrospray ion source and a cold (4 K) ion trap [2].

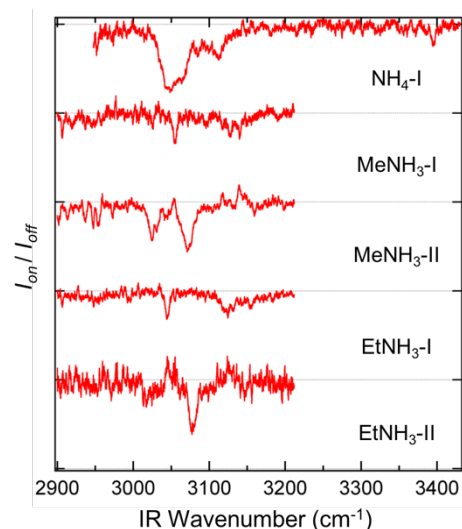
Figure 1 shows the UVPD spectra of the  $\text{RNH}_3^+\cdot\text{DB18C6}$  complexes. All the complexes show many sharp vibronic bands. The position of the origin band is almost the same as that of  $\text{K}^+\cdot\text{DB18C6}$  complex [1], implying a similar encapsulation structure. Figure 2 displays the IR-UV spectra of the  $\text{RNH}_3^+\cdot\text{DB18C6}$  complexes in the NH stretching region. These spectra are measured by tuning the UV probe frequency to the vibronic bands labeled  $\text{NH}_4\text{-I}$ ,  $\text{MeNH}_3\text{-I}$ ,  $\text{MeNH}_3\text{-II}$ ,  $\text{EtNH}_3\text{-I}$  and  $\text{EtNH}_3\text{-II}$  in Figure 1.  $\text{NH}_4\text{-I}$  shows depletions at  $\sim 3050\text{ cm}^{-1}$  and  $\sim 3400\text{ cm}^{-1}$ , which are assigned to the hydrogen-bonded and free NH stretching vibrations, respectively. For the  $\text{MeNH}_3^+\cdot\text{DB18C6}$  and  $\text{EtNH}_3^+\cdot\text{DB18C6}$  complexes, two kinds of IR spectra are obtained. This indicates that there exist at least two isomers for the  $\text{MeNH}_3^+\cdot\text{DB18C6}$  and  $\text{EtNH}_3^+\cdot\text{DB18C6}$  complexes. Quantum chemical calculations suggest that the  $\text{NH}_3^+$  group is effectively encapsulated by the DB18C6 cavity in both isomers, but they have slightly different conformations in the DB18C6 cavity.

[1] Y. Inokuchi *et al.* *J. Am. Chem. Soc.* **133**, 12256 (2011).[2] Y. Inokuchi *et al.* *J. Phys. Chem. A* **119**, 8512 (2015).

DB18C6



**Figure 1** UVPD spectra of the  $\text{RNH}_3^+\cdot\text{DB18C6}$  complexes



**Figure 2** IR-UV spectra of the  $\text{RNH}_3^+\cdot\text{DB18C6}$  complexes