ELECTRONIC AND VIBRATIONAL SPECTROSCOPY OF CROWN ETHER WATER COMPLEXES: 4'-AMINOBENZO-15-CROWN-5-ETHER$(H_2O)_n$, n=1,2

V. ALVIN SHUBERT and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907*.

Crown ethers have long been noted for their ability to selectively bind substrates, especially cations. Much of this work has been performed in aqueous solution with a focus on the structure and binding energy of the crown-cation complex. While it is understandable that the majority of these studies have focused on ion binding, the oxygen-rich pocket is also ideally suited to binding other types of substrates, including water. From a fundamental viewpoint, it is worthwhile to study the binding of water to crown ethers in the absence of ions, a task that can be profitably pursued using gas-phase spectroscopy of crown ether-$(H_2O)_n$ clusters. As a first step in this direction, we present the infrared and ultraviolet spectra of water clusters of 4'-aminobenzo-15-crown-5 ether (ABC) containing 1 and 2 waters. One-color resonant two-photon ionization (R2PI) spectroscopy and UV-UV holeburning spectroscopy have been used to record the ultraviolet spectra of these complexes. Despite the fact that there are four conformations of the ABC monomer, only one conformation was observed in each of the n=1 and n=2 complexes. This result demonstrates that binding even a single water molecule can strongly influence the conformational preferences of the crown ether. Resonant ion-dip infrared spectroscopy (RIDIRS) is used to characterize the n=1 and n=2 clusters in the OH and alkyl CH stretch regions of the infrared. In ABC-H_2O, the two OH stretch fundamentals are shifted down to 3569 and 3637 cm^{-1}, indicating that both OH groups are involved in H-bonds with crown ether oxygens. The splitting between the two fundamentals is only 68 cm^{-1}, one-third less than the splitting in the H_2O monomer. Detailed studies of the ABC-HDO complex prove unequivocally that there are two conformations of this complex, one in which the OH group is in a more strongly bound environment (and OD weaker), while the other has the reverse. Finally, ABC-$(H_2O)_2$ has resolved OH stretch transitions shifted down to 3566, 3578, and 3637 cm^{-1} with a shoulder at 3639 cm^{-1}, indicating that all OH groups are involved H-bonds. As an aid toward understanding the observed spectra, B3LYP geometry optimizations and frequency calculations followed by higher level computations were performed. Tentative assignments are made and interesting features of the infrared specta will be discussed.