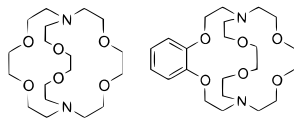


EXPLORING THE CH STRETCH SPECTRAL REGION OF CRYPTAND/ION COMPLEXES WITH IR-UV DOUBLE RESONANCE SPECTROSCOPY AND LOCAL MODE HAMILTONIANS

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The infrared spectroscopy of cryptands containing Na^+ , K^+ , Rb^+ , Sr^{+2} , and Ba^{+2} ions are studied both theoretically and experimentally. Specifically, [2, 2, 2] cryptand complexes are modified to contain a phenyl group as shown below.



The complexes are formed in solution and brought into the gas phase by electrospray methods. After mass selection, the complexes are introduced into a cryo-cooled octupole ion trap and cooled to 5 K. The aromatic chromophore in the cryptand provides a UV absorption that is used to record a UV photofragment spectrum that shifts to unique wavelengths depending on size and charge of the embedded ion. Infrared spectra in the alkyl CH stretch region are recorded using IR-UV double resonance. The UV wavelength is fixed on the S_0 - S_1 origin of the complex, while a tunable IR laser records the IR spectrum in the ground electronic state by depleting the photofragment ion signal. The resulting spectra are investigated theoretically by first searching for low-lying conformers and subsequently modeling the CH stretch fundamentals of these conformers with local mode Hamiltonians which include anharmonic coupling between CH stretches and nearby background states. In contrast to our previous work on alkanes, the ethoxy bridges enhance both CH_2 scissor and wag vibrational frequencies, with the result that scissor overtones and combination bands are detuned from the CH stretch vibrations. The increase in the wag frequencies leads to these modes playing a significant role in the spectral patterns of the CH stretch spectral region. These spectra are used to identify those conformers that are observed experimentally and to explore the role of the central ion's size in altering the structure of the cryptand, consequently, the peak patterns in the CH stretch spectral region.