CONFORMATION-SPECIFIC ELECTRONIC AND VIBRATIONAL SPECTROSCOPY OF JET COOLED 4'-AMINOBENZO-15-CROWN-5 ETHER

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Crown ethers are ubiquitous throughout chemistry and are especially notable in their abilities to selectively bind guest substrates. The cyclic structure, symmetry, and multiple oxygen sites form a well-defined 'pocket' that make it ideal for studies of substrate binding. Although the chemical structure of crown ethers might suggest they are rigid, in the absence of a tight-binding ion or substrate they can exist in multiple conformations. Little is known about the inherent conformational preferences, relative populations, interconversion barriers, or spectroscopic signatures of the individual crown ether conformations. In order to gain insight into these conformational preferences, we have carried out a first spectroscopic characterization of a model crown ether, 4'-aminobenzo-15-crown-5 ether (ABC), under jet-cooled conditions. One color resonant two photon ionization (R2PI), laser induced fluorescence (LIF), UV-UV holeburning, resonant ion dip infrared spectroscopy (RIDIRS), and single vibronic level fluorescence (SVLF) have been employed, taking advantage of the aromatic tag built into ABC's structure. We report the conformation-specific electronic and infrared spectra of four resolved conformations. The origins of these four conformations are spread over 1250 cm^{-1}, with three of the origins within 300 cm^{-1} of each other and the fourth 1250 cm^{-1} blue of the red-most origin. As an aid toward conformational assignment, B3LYP geometry optimization and harmonic vibrational frequency calculations have been carried out, followed by single-point MP2 calculations on the DFT optimized structures. Single point TDDFT calculations were also performed in order to understand the basis for the large electronic frequency shifts of the conformers. Tentative conformational assignments of the four conformations of ABC will be discussed.