THE SPECTROSCOPIC CONSEQUENCES OF C-H$\cdots\pi$ HYDROGEN BONDING: THE C_6H_6-C_4H_2 COMPLEX

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Resonant two-photon ionization spectroscopy and resonant ion-dip infrared spectroscopy are used to structurally characterize the C_6H_6-C_4H_2 complex. The complex takes on a T-shaped geometry in which the diacetylene molecule sits on the six-fold axis of benzene, with one of its C-H groups hydrogen bonded to the π cloud of benzene. The direction and magnitude of the electronic frequency shift of the complex's transitions relative to benzene monomer, the forbidden S_0-S_1 origin transition, and the acetylenic C-H stretch vibrational fundamentals are all consistent with this structure. The complexation with benzene localizes the C-H stretch vibrations of the two acetylenic C-H groups. Both C-H stretch fundamentals are clearly observed, one unshifted and one shifted from its frequency in C_4H_2 monomer. The C-H stretch fundamental of the hydrogen bonded C-H group is shifted down in frequency by about 45 cm^{-1} and gains significant intensity, as one would expect from a hydrogen bonded XH group. This complex is a good candidate for half-collision reaction dynamics following excitation of the C_4H_2 molecule in the complex.