HYDROGEN BONDED OH–C₂H₂ REACTANT COMPLEX CHARACTERIZED BY INFRARED ACTION SPECTROSCOPY

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The entrance channel to the OH + C₂H₂ → HOCHCH reaction has been characterized by infrared spectroscopy of a binary hydrogen-bonded complex between the chemically reactive partners. Infrared action spectra of the OH–C₂H₂ reactant complex have been recorded using an optical parametric oscillator operating in the OH overtone region near 1.4 μm and the asymmetric acetylenic fundamental region near 3.0 μm. The OH (υ = 1 or 0) fragments from vibrational predissociation are detected by laser-induced fluorescence. The pure OH overtone band of OH–C₂H₂ is observed at 6885.6 cm⁻¹ (band origin), shifted 85.7 cm⁻¹ to lower energy of the OH monomer transition. The pure OH overtone band exhibits rotationally resolved structure that is characteristic of an A-type transition of a near-prolate asymmetric top. The spectrum also shows interesting gaps between the P, Q and R branches, indicating that the orbital and spin angular momentum of the unpaired electron of OH is unquenched. The P and R line positions have been used to determine values of ½(B + C) for the upper and lower vibrational states, and yield a center of mass separation between the two subunits of 3.34(3) Å in both vibrational states. The spectroscopic data, taken together with the results of ab initio calculations and previous work on the HF–acetylene and HCl–acetylene complexes, show that the OH–acetylene complex is T-shaped, with a hydrogen bond formed between the H atom of OH and the π system of the C–C bond. The infrared spectrum in the asymmetric stretch region of acetylene is centered at 3281 cm⁻¹, with a much smaller spectral red shift of 14 cm⁻¹, but exhibits more complicated band structure with multiple Q-branches arising from a B-type transition.