HYDROGEN BONDED OH–C_2H_2 REACTANT COMPLEX CHARACTERIZED BY INFARED ACTION SPECTROSCOPY

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The entrance channel to the OH + $C_2H_2 \rightarrow$ 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–C_2H_2 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 ($v = 1$ or 0) fragments from vibrational predissociation are detected by laser-induced fluorescence. The pure OH overtone band of OH–C_2H_2 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 $\frac{1}{2}(B + C)$ for the upper and lower vibrational states, and yield a center of mass separation between the two subunits of $3.34(3)$ Åin 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.