

HYDROGEN BONDED OH-C₂H₂ REACTANT COMPLEX CHARACTERIZED BY INFARED ACTION SPECTROSCOPY

JAMES B. DAVEY, MARGARET E. GREENSLADE, MARSHA I. LESTER, *Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323.*

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 (*v* = 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 $\frac{1}{2}(B + C)$ for the upper and lower vibrational states, and yield a center of mass separation between the two subunits of 3.34(3) 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.