EIGENSTATE RESOLVED INFRARED SPECTROSCOPY OF PYRROLE IN THE C-H STRETCH OVERTONE REGION

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The infrared spectrum of pyrrole, C_4H_5N, was recorded in the region of the ν_{14} C-H stretch overtone (6150 cm^{-1}), using a resonant cavity enhanced molecular beam laser spectrometer with optothermal detection. The study was carried out to investigate the Intramolecular Vibrational energy Redistribution (IVR) in pyrrole, and compare it with the observed IVR dynamics in benzene, a previously studied aromatic molecule. Of particular interest is the effect of symmetry on the IVR lifetime. Pyrrole and benzene both have a similar density of coupled states, but pyrrole has lower symmetry (C_{2v} versus D_{6h}). Computer simulations and combination differences were used to assign the fairly dense ($\sim$ 1000 lines/cm^{-1}) spectrum of this near oblate asymmetric top. Each rotational line splits into an IVR multiplet of about 10-15 eigenstates spread over an energy range of 0.05-0.1 cm^{-1}. This yields an average density of states of $\sim$100 lines/cm^{-1}, in agreement with the density of vibrational states calculated by a harmonic approximation. The inferred IVR lifetimes for pyrrole range from 100 to 200 ps, about one order of magnitude longer than the IVR lifetime for the comparable excitation in benzene.

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