THE MICROWAVE SPECTRA OF SINGLE MOLECULAR EIGENSTATES OF PROPARGYL ALCOHOL

BROOKS H. PATE, DAVID GREEN, REBECCA HOLMBERG, EVAN HUDSPETH and DAVID A. McWHORTER, *Department of Chemistry, University of Virginia, Charlottesville, VA 22901*.

The microwave spectra of single molecular eigenstates of propargyl alcohol ($HCCCH_2OH$) in the region of the acetylenic C-H stretch are presented. Single eigenstates resulting from extensive intramolecular vibrational mixing are accessed through the high resolution (5 MHz) infrared spectrum measured using an electric-resonance optothermal molecular beam spectrometer. Various infrared-microwave double-resonance and infrared-microwave-microwave triple-resonance spectroscopy techniques are used to measure the ”rotational” spectra of the highly mixed molecular eigenstates. These ”rotational” spectra are characterized by a narrow frequency width. The width of the rotational spectrum is much less than the width observed in the single-photon infrared spectrum which results from rapid intramolecular vibrational energy redistribution (IVR). The rotational spectrum of molecular eigenstates in the range of J=0-4 and K_a= 0-2 are investigated. The narrow width of the rotational spectrum of a highly vibrationally excited molecule is explained in terms of the exchange narrowing formalism developed for NMR spectroscopy.