STRUCTURALLY MIXED MOLECULAR EIGENSTATES OF 2-FLUOROETHANOL RESULTING FROM CONFORMATIONAL ISOMERIZATION

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Using a newly developed method of molecular-beam, infrared-microwave double-resonance spectroscopy, we are able to measure the rotational spectra of single molecular eigenstates of the molecular Hamiltonian near 3000 cm^{-1} of energy above the ground rovibrational state. For the asymmetric -CH_2(F) stretch of Gg' 2-fluoroethanol, near 2983 cm^{-1}, the molecular eigenstates lie about 2000 cm^{-1} above the $Gg' \rightarrow$ Tt conformational isomerization barrier. The rotational spectra of these eigenstates reflect the contribution of vibrational states localized around the Tt conformer structural minimum to the individual molecular eigenstates. This result demonstrates the ability of isolated molecules to use vibrational excitation to achieve geometrical rearrangement when the bright state normal mode lies above the barrier to conformational isomerism. The microwave spectra are characterized by two sets of transitions. One set lies near the transition frequencies of the pure rotational spectrum of the less stable Tt conformer. A second set lies approximately 1 GHz higher and is intermediate between the expected Tt and Gg' rotational frequencies. This second set of transitions may originate from vibrationally excited states whose torsional energy is above the barrier to conformational isomerism.