THE INFLUENCE OF METHYL GROUP INTERNAL ROTATION ON THE INTRAMOLECULAR VIBRATIONAL ENERGY REDISTRIBUTION DYNAMICS OF E-PENTENYNE

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The intramolecular vibrational energy redistribution (IVR) dynamics of E-pentenyne are studied using high-resolution, molecular-beam infrared spectroscopy and dynamical rotational spectroscopy at a total energy of 3330 cm^{-1}. The combination of large molecular size (27 vibrational modes) and a low barrier to internal rotation (V_3 = 670 cm^{-1}) leads to a situation where there is a high density of torsional states with energy exceeding the barrier to internal rotation (>10 states/cm^{-1}) at the energy investigated. Spectral evidence for the participation of these highly excited torsional states is found in both the infrared and single-eigenstate rotational spectra. These features can be attributed to the strong a-type Coriolis interactions caused by the nearly free internal rotation. Because the methyl group is directly predominantly along the a-principal axis, these interactions between internal rotation and overall rotation dominate. One result of the participation of the above barrier states is the collapse of the molecular asymmetry. Through analysis of the correlation of infrared spectra originating from different Ka=1 asymmetry levels in the ground vibrational state we estimate the time scale of energy flow between below- and above-barrier torsional states to be 6 ps. This time scale for IVR is much faster than the IVR rate of the acetylenic C-H stretch (lifetime of 70 ps) indicating mode-specific energy flow. From the analysis we conclude that the interaction between internal rotation and overall molecular rotation does not enhance the IVR rate, but does redirect anharmonic interactions into apparent Coriolis interactions. These effects are illustrated through statistical modeling of the spectrum that includes the torsion-rotation interaction.