MEASURING THE RATE OF ENERGY FLOW ACROSS THE SEPARATRIX USING A MOLECULAR GYROSCOPE

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The dynamics of methyl group rotation qualitatively change when the energy in the torsional coordinate exceeds the barrier to internal rotation. This problem is similar to the simple pendulum. Below the barrier, the motion of the methyl top is torsional oscillation while above the barrier the top undergoes full rotation about its symmetry axis. In a phase space description, a separatrix divides the phase space between these two characteristic types of motion. Recent nonlinear dynamics studies of isomerization reactions indicate that there is a barrier to energy flow across the separatrix that leads to violations of transition state theory rate predictions. We apply our technique of dynamical rotational spectroscopy to measure the energy flow rate across the separatrix for Z-pentenyne at a total energy of 3330 cm^{-1}. This energy greatly exceeds the barrier to internal rotation (V3 = 390 cm^{-1}). Through the process of intramolecular vibrational energy redistribution (IVR), the energy localized in the torsional coordinate is time-dependent. Unlike conformational isomerization reactions, there is no geometry change associated with going over the barrier for the threefold-symmetric rotor. However, there is a change in the characteristic rotational frequencies when the energy in the torsional coordinate exceeds the barrier. This change is caused by molecular gyroscope effects. As a result, the kinetics of energy flow across the separatrix lead to a modulation of the rotational frequency. This frequency modulation modifies the frequency-domain rotational spectrum of the molecule through coalescence of the overall line shape. From a line shape analysis we determine the time scale for energy flow across the separatrix to be 39 ps for Z-pentenyne. This time scale is significantly longer than predicted by quantum transition state theory (0.35 ps).