# COMPETITION BETWEEN INTRAMOLECULAR VIBRATIONAL ENERGY REDISTRIBUTION AND METHYL GROUP INTERNAL ROTATION OBSERVED THROUGH DYNAMIC ROTATIONAL SPECTROSCOPY

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Model Hamiltonian calculations of the overall rotational spectrum of a highly vibrationally excited molecule with a symmetric threefold rotor are presented. For the highly excited molecule, the total vibrational energy exceeds the barrier to internal rotation. The amount of energy localized in the torsional coordinate is time-dependent because of the intramolecular vibrational energy redistribution (IVR) process. As the torsional energy fluctuates, the rotor makes transitions from librational to full internal rotational motion. When the rotor can execute complete internal rotation, the overall rotational frequencies change from the asymmetric top to the gyroscope rotational limit. The modulation of the rotational frequencies between these two limits by the IVR process causes coalescence in the overall rotational spectrum. However, as the IVR rate becomes very rapid, such that the rotor no longer has time to execute a complete internal rotation cycle before the energy leaves the torsional coordinate, the overall rotational spectrum reverts to the standard asymmetric top rotational frequencies. An analytical lineshape that includes coalescence and motional narrowing effects is presented that accurately describes the overall rotational spectrum through the full range of IVR rates. Experimental spectra of molecules in various limits of the dynamics are presented to illustrate the basic effects.