LINESHAPE ANALYSIS OF DYNAMIC ROTATIONAL SPECTRA IN THE PRESENCE OF INTERNAL ANGULAR MOMENTUM

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In a vibrationally excited molecule there is the possibility for energy flow between the vibrational modes of the molecule (i.e. intramolecular vibrational energy redistribution (IVR)). When a low barrier internal rotor is attached to the frame, the energy in the torsional mode is time dependent. When the energy in this coordinate exceeds the barrier to complete internal rotation, the rotor can generate internal angular momentum. This angular momentum is cancelled by the counter-rotation of the molecular frame about a "gyroscopic" axis. The appearance of the dynamical rotational spectrum depends on the rate of torsional activation-deactivation and the relative orientation of the rotor and the frame. When the internal rotor is asymmetric there is the additional complication that the gyroscopic axis depends on the torsional angle. A description of the overall rotational lineshape for symmetric and asymmetric internal rotors is presented and illustrated by examples of low barrier molecules excited in the region of the C–H stretch fundamentals near 3000 cm^{-1}.