A BLOCH MODEL DESCRIPTION OF THE OVERALL ROTATIONAL LINESHAPE OF A HIGHLY VIBRATIONALLY EXCITED MOLECULE WITH A METHYL GROUP INTERNAL ROTOR

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A general theory for the rotational lineshape of a highly vibrationally excited molecule containing a rigid, threefold rotor is described. The model that is investigated is a molecule with total vibrational energy that exceeds the barrier to internal rotation. Intramolecular vibrational energy redistribution (IVR) is assumed to occur between the internal rotation coordinate and the other 3N-7 vibrational modes of the molecule. This process is modeled using random matrix techniques. The rotational spectrum of a single quantum state of the molecule is examined as the energy exchange rate between the internal rotation coordinate and other vibrational modes is varied. A somewhat unusual Bloch model formulation is presented that quantitatively describes the lineshape evolution of the rotational spectrum. The peculiar feature of the Bloch model is that signed rate constants are required to reproduce the evolution of the molecular rotational frequency and spectral intensity as the energy in the internal coordinate is increased from below-to-above the internal rotation barrier. The analytic lineshape model is compared to simulations to examine its limitations. The analytic lineshape theory correctly recovers the quenching of internal rotation by intramolecular friction in the reaction coordinate. However, it cannot recover features associated with coherent rotational sidebands that accompany complete internal rotation of the top. These effects are only important in the intermediate range of the dynamics where the IVR damping rate is on the order of the frame rotational frequency.