THE MICROWAVE SPECTRUM OF A MOLECULAR EIGENSTATE I

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When a molecule is excited to a region of high state density, the rovibrational spectrum becomes much more complicated due to the intramolecular vibrational energy redistribution process (IVR). The single rovibrational transition expected in the harmonic normal mode approximation appears as a set of transitions forming the IVR multiplet. Each transition corresponds to a different eigenstate of the full molecular Hamiltonian. The molecular eigenstates are superpositions of the coupled normal mode vibrational basis states. The rotational spectrum of a single eigenstate is discussed. Even when only anharmonic coupling is present, the microwave spectrum of the eigenstate contains a series of transitions. This result reflects the fact that a molecular eigenstate at one value of J is not an eigenstate at a different value, such as J+1, because of the vibration-rotation terms usually incorporated in the vibrational dependence of the rotational constant. The dynamics following coherent excitation from a single eigenstate are further complicated by the vibrational dependence of the molecular dipole moment. The effects of these terms, and also the effects of the anharmonic coupling strength, are investigated to determine the appearance of the high resolution spectrum and the nature of the coherent state produced by broad band excitation.