DIABATIC, ADIABATIC, AND NONADIABATIC BEHAVIORS IN THE TORSION-VIBRATION SPECTRUM OF METHANOL

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The Born-Oppenheimer approximation, which is an adiabatic separation of the electronic (fast) and nuclear (slow) degrees of freedom, is the foundation on which the language of molecular spectroscopy rests and the starting point for the treatment of nonadiabatic effects. Similarly within the domain of nuclear motion, the separation of fast and slow nuclear degrees of freedom may be a useful, even essential, approximation for the treatment of high dimensional problems. This presentation is an exploration of the adiabatic concept in the context of a low-dimensional model system for which the fully coupled solutions are known. The model system is a 4-dimensional torsion-vibration Hamiltonian for methanol fit to the fundamentals and high overtones of the CH stretches as well as the torsionally excited levels of the CH ground state. We find that the adiabatic approximation is satisfactory for the lowest torsional levels of the CH fundamentals; however, the high-overtone CH local mode region exhibits diabatic behavior. Intramolecular vibrational redistribution (IVR) is recognized as a nonadiabatic effect and the source of the scaling behavior of the IVR coupling matrix elements in this torsional molecule is identified.