SYSTEMATIC DEGENERACIES AS A GUIDE TO THE VIBRATIONAL DYNAMICS OF METHANOL

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The vibrational dynamics of highly excited CH stretch and torsional vibrations of methanol are explored using a 4-dimensional effective Hamiltonian. The model parameters are constrained by a combination of low-resolution CH overtone spectra and high-resolution spectra of the three CH fundamentals and of the torsional levels of the vibrational ground state. Systematic patterns of degeneracies are found in four regions of quantum number space: (i) At low excitation energies, the torsion-vibration states are at most 2-fold degenerate as expected for the combination of the E-type torsional tunneling species with the $A'$ and $A''$ (in $C_s$) CH stretch vibrations. (ii) At high torsional energies, we find a series of approximate 4-fold degeneracies characteristic of a degenerate E-type asymmetric CH stretch in combination with a decoupled free internal rotation. (iii) When a single CH bond is excited to a high level, torsional tunneling is quenched causing all such levels to be 3-fold degenerate. (iv) When both a local CH stretch and internal rotation are highly excited, we find systematic 6-fold degeneracies characterized by free internal rotation decoupled from three equivalent local CH stretches.