INTERACTION OF THE TORSION AND C-H STRETCH VIBRATIONS IN METHANOL: A LOCAL MODE TREATMENT

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Torsional tunnelling about the C-O bond splits the vibrational ground state of methanol into A and E states. For K=0, the A state is 9.11 cm^{-1}below the E state; for K >0, the torsional energies follow the expected cosine pattern. For the ν_2 asymmetric C-H stretch, the splitting is inverted, i.e., E below A at K=0, and smaller in magnitude (-3.26 cm^{-1}), but the torsional energies still follow an approximately regular cosine pattern. The limited information available on the ν_9 asymmetric C-H stretch indicates that it is also inverted (about -5 cm^{-1}). However, the ν_3 symmetric C-H stretch is normal with A below E (+9.07 cm^{-1}).

In order to treat the inverted torsional tunnelling behavior, a local mode Hamiltonian with G_6 symmetry has been developed. Three parameters are sufficient to fit the frequencies of the three C-H stretch band origins. These are the harmonic local C-H stretch frequency ω=2935.8 cm^{-1}, the local-local coupling λ=-43.9 cm^{-1}, and the lowest order torsion-vibration interaction constant μ=10.5 cm^{-1}. Qualitatively, the torsion-vibration interaction μ results from the fact that the force constant for the C-H bond $trans$ to the O-H is higher than for the $gauche$ C-H bonds. When combined with the known ground state torsional potential, the same three parameters are sufficient to account for the sign and magnitude of the torsional tunnelling splitting of all three C-H stretch fundamentals. The inversion of the torsional tunnelling for the ν_2 and ν_9 vibrations is a systematic property of the Hamiltonian and not the result of an accidental stretch-torsion resonance. Therefore, the inverted torsional tunnelling is a general result attributable to the molecular symmetry.