# 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 $\mathrm{cm}^{-1}$below the $E$ state; for $K$ >0, the torsional energies follow the expected cosine pattern. For the $\nu_2$ asymmetric C-H stretch, the splitting is inverted, i.e., $E$ below $A$ at $K$=0, and smaller in magnitude (-3.26 $\mathrm{cm}^{-1}$), but the torsional energies still follow an approximately regular cosine pattern. The limited information available on the $\nu_9$ asymmetric C-H stretch indicates that it is also inverted (about -5 $\mathrm{cm}^{-1}$). However, the $\nu_3$ symmetric C-H stretch is normal with $A$ below $E$ (+9.07 $\mathrm{cm}^{-1}$).

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 $\omega$=2935.8 $\mathrm{cm}^{-1}$, the local-local coupling $\lambda$=-43.9 $\mathrm{cm}^{-1}$, and the lowest order torsion-vibration interaction constant $\mu$=10.5 $\mathrm{cm}^{-1}$. Qualitatively, the torsion-vibration interaction $\mu$ 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 $\nu_2$ and $\nu_9$ 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.