GIANT TORSIONAL SPLITTINGS IN THE PARALLEL FUNDAMENTAL BAND ($v_5=1\leftarrow 0$) OF CH$_3$SiH$_3$

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The lowest frequency parallel fundamental band $\nu_5$ of CH$_3$SiH$_3$ near 700 cm$^{-1}$ has been measured at a resolution of 0.004 cm$^{-1}$ with Fourier transform spectroscopy. The torsional fine structure in the spectrum is increased from $\sim$0.005 to $\sim$1 cm$^{-1}$ by the anharmonic interactions between the torsional stack of levels ($v_5=0,1,2,...$) in the ground vibrational state and the corresponding stack with ($v_5=1$).

For given ($v_5$, $\nu_6$, $J$, $k$), the torsional sub-levels are labelled by the index $\sigma=0,+1,-1$. For several ($k,\sigma$), resonant or near-resonant interactions occur between the vibration-torsion levels ($v_5=0$, $\nu_6=5$) and ($v_5=1$, $\nu_6=0$). For ($k=1$, $\sigma=-1$), the mixing is so severe that perturbation-allowed transitions ($v_5=5\leftarrow 0$) have been observed. In spite of the fact that $\nu_6$ changes by 5 units, the mixing causes the probability density as a function of the torsional angle to have a local maximum for ($v_5=1$, $\nu_6=0$) in the centre of the classically forbidden region inside the torsional barrier. This severe mixing with such large $|\Delta \nu_6|$ has serious implications for vibration-rotation relaxation in molecules with low frequency, highly anharmonic vibrational modes.

A detailed fit to over 3400 transition frequencies has been made to within experimental accuracy using a vibration-torsion-rotation Hamiltonian with 45 parameters. The treatment includes a third stack of torsional levels in the lowest-lying degenerate mode $\nu_{22}$ near 525 cm$^{-1}$. The Hamiltonian is severely constrained by a wide variety of infrared, microwave and molecular beam transitions. The analysis shows that the second term in the Fourier expansion of the hindering potential characterized by the parameter $V_6$ is dominantly due to these Fermi-type interactions. The changes in the effective molecular parameters caused by removing the non-resonant anharmonic interactions by contact transformation will be discussed.

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