GIANT TORSIONAL SPLITTINGS IN THE PARALLEL FUNDAMENTAL BAND (ν_5=1←0) OF CH_3SiH_3

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The lowest frequency parallel fundamental band ν_5 of CH_3SiH_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 ∼0.005 to ∼1 cm^{-1} by the anharmonic interactions between the torsional stack of levels (v_6=0,1,2..) in the ground vibrational state and the corresponding stack with (v_5=1). For given (v_5, v_6, J, k), the torsional sub-levels are labelled by the index σ=0,+1,–1. For several (k,σ), resonant or near-resonant interactions occur between the vibration-torsion levels (v_5=0, v_6=5) and (v_5=1, v_6=0). For (k=1, σ=–1), the mixing is so severe that perturbation-allowed transitions (v_6=5←0) have been observed. In spite of the fact that v_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, v_6=0) in the centre of the classically forbidden region inside the torsional barrier. This severe mixing with such large $|\Delta v_6|$ 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 ν_{12} 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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