

MICROWAVE AND MMWAVE STUDY OF CH_3SiH_3 INCLUDING THE PERTURBATION-ALLOWED TORSION-VIBRATION DIFFERENCE BAND ($v_{12} = 0, v_6 = 3$) \leftrightarrow ($v_{12} = 1, v_6 = 0$)

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The vibration-torsion-rotation Hamiltonian in CH_3SiH_3 has been investigated using Fourier transform microwave methods and tunable sideband far-infrared spectroscopy. Four different studies have been carried out. First, the Q -branch of the torsion-vibration difference band ($v_{12} = 0, v_6 = 3$) \leftrightarrow ($v_{12} = 1, v_6 = 0$) has been measured between 17.8 and 26.6 GHz. When three quanta of the torsional mode ν_6 are excited in the ground vibrational state (gs) for ($\sigma = -1$) torsional sublevels with $K = 6$, these transitions become allowed through resonant Coriolis-like coupling to the lowest lying degenerate mode ν_{12} with no quanta of ν_6 excited. Second, direct l -doubling transitions in the state ($v_{12} = 1, v_6 = 0$) have been observed between 8.3 and 17.5 GHz for both $\sigma = 0$ and $\sigma = \pm 1$. In the limit that the intervibrational interactions vanish, the σ -splitting between lines of the same J would be difficult to resolve, but frequency differences of more than 1 GHz due to these interactions have been determined. Third, the ($J = 1 \leftarrow 0$) spectrum just below 22 GHz has been re-measured with higher resolution for $0 \leq v_6 \leq 4$ in the gs and for ($v_6 = 0$) in ν_{12} . Finally, the ($J = 45 \leftarrow 44$) spectrum near 1 THz has been obtained for $0 \leq v_6 \leq 2$ in the gs. A global data set of 3423 frequencies has been formed by merging the present 123 measurements with the data set used recently in the simultaneous analysis of the ν_{12} and ν_5 bands. By refining the (gs/ ν_{12} / ν_5) Hamiltonian developed in this earlier work, a good fit to within experimental error has been obtained by varying 45 parameters. The grouping of the torsional motion with rotational rather than vibrational degrees of freedom will be discussed.