HIGH RESOLUTION INFRARED SPECTRUM AND GLOBAL ANALYSIS OF ν_{12}, ν_5, AND $\nu_{12}+\nu_6-\nu_6$ IN CH_3SiH_3

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The rotation-torsion-vibration spectrum of CH_3SiH_3 has been investigated at the Canadian Light Source from 400 to 750 cm^{-1} with a resolution of 0.0009 cm^{-1}. The spectra were obtained with a Bruker IFS 125HR Fourier transform spectrometer using the synchrotron radiation as the continuum source. Three bands were investigated: the silyl rock ν_{12} centred near 525 cm^{-1} with $\Delta K = \pm 1$, its first torsional hot band $\nu_{12} + \nu_6 - \nu_6$ near 534 cm^{-1} again with $\Delta K = \pm 1$, and the C−Si stretch ν_5 near 703 cm^{-1} with $\Delta K = 0$. For the two fundamentals, the spectra are much improved over those in the earlier studies,[1] with many of the torsional triplets now being clearly resolved even for the unperturbed cases. The main interest is in the hot band, here reported for the first time, where the torsional effects are much larger. Using a Fourier transform waveguide spectrometer at E.T.H., the three σ-components of the $(J = 1 \leftarrow 0)$ transition in $\nu_{12} + \nu_6$ have been resolved, where $\sigma = 0, +1, -1$ labels the torsional sub-levels. In addition, direct l-doubling transitions in $\nu_{12} + \nu_6$ have been measured for $\sigma = 0$ and $19 \leq J \leq 27$. In a global fit, all the new data have been analysed along with the frequencies obtained in earlier investigations.[1] The analysis includes all the important interactions among the torsional stacks of levels for the ground state (gs), for ν_{12}, and for ν_5. These include the previously known (gs, ν_5) Fermi and (gs, ν_{12}) Coriolis interactions[1], along with a higher order (ν_{12}, ν_5) Coriolis coupling introduced here. This last is responsible for the strong perturbation of the hot band series with $\Delta K = -1$ for $9 \leq K \leq 12$. A good fit was obtained. The Hamiltonian will be discussed with emphasis on the terms required for treating the hot band.

[1] I. Ozier and N. Moazzen-Ahmadi, Internal rotation in symmetric tops, in: E. Arimondo, P. R. Berman, C. C. Lin (Eds.), Advances in Atomic, Molecular and Optical Physics, vol. 54, Elsevier, Amsterdam, 2007.