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FTIR Synchrotron Spectroscopy of the Asymmetric C-H Stretching Bands of Methyl Mercaptan (CH₃SH) –A Perplexity of Perturbations

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The infrared Fourier transform spectrum of the asymmetric C-H stretching bands of CH₃SH has been recorded in the 2950-3100 cm⁻¹ region using synchrotron radiation at the FIR beamline of the Canadian Light Source in Saskatoon. Assignment of numerous torsion-rotation sub-bands for the asymmetric stretches has revealed a surprising pseudo-symmetric behavior, in which each band is seen in only one of the two possible ΔK selection rules. The upper states of the two asymmetric stretching vibrational bands thus appear to behave more like $l = \pm 1$ components of a degenerate E state of a symmetric top rather than distinct vibrational states. The two components are separated by about 1.5 cm⁻¹ at $K = 0$, and then diverge linearly at higher K with torsional oscillation amplitude similar to that of the ground state of about 1.3 cm⁻¹. The divergence is consistent with an a -type Coriolis splitting picture with an effective Coriolis constant $\zeta \approx 0.075$.

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