SYNCHROTRON SPECTROSCOPY AND TORSIONAL STRUCTURE OF THE CSH-BENDING AND CH_3-ROCKING BANDS OF METHYL MERCAPTAN

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The Fourier transform spectra of the CSH-bending and CH_3-rocking infrared bands of CH_3SH have been investigated at 0.001 cm^{-1} resolution employing synchrotron radiation at the Canadian Light Source in Saskatoon. The relative band strengths and structures are remarkably different from those for the analogous CH_3OH relative, with the CSH bend being very weak and both the in-plane and out-of-plane CH_3 rocks being strong with comparable intensities. The CSH bend, centered at 801.5 cm^{-1}, has parallel a-type character with no detectable b-type component. The out-of-plane CH_3 rock at 957.0 cm^{-1} is a purely c-type perpendicular band, whereas the in-plane rock around 1074 cm^{-1} is of mixed a/b character. The K-reduced v_t = 0 sub-state origins for the CSH bend follow the normal oscillatory torsional pattern as a function of K with an amplitude of 0.362 cm^{-1}, as compared to 0.653 cm^{-1} for the ground state and 0.801 cm^{-1} for the C-S stretching mode. The torsional energy curves for the out-of-plane rock are also well-behaved but are inverted, with an amplitude of 1.33 cm^{-1}. In contrast, the sub-state origins for the in-plane rock do not display a clear oscillatory structure but are scattered over a range of about 2 cm^{-1}, with indications of some significant perturbations. The assignments for the three bands all extend up to about K = 10 and are well-determined from GSCD relations, particularly for the a/b in-plane rock for which ΔK = 0, +1 and -1 transitions are all observed.