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FTIR Synchrotron Spectroscopy of the Lower Modes of Methyl-D3 Mercaptan (CD₃SH) –Where is the C-S Stretch?

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The infrared Fourier transform spectrum of the lower vibrational modes of CD₃SH has been recorded in the 400-1200 cm⁻¹ region using synchrotron radiation at the FIR beamline of the Canadian Light Source in Saskatoon. Torsion-rotation assignments have been made for a relatively strong parallel band centred at 644 cm⁻¹ and a weaker perpendicular band centred at 727 cm⁻¹. Comparison with the spectra for the normal CH₃SH species as well as the analogous CD₃OH and CH₃OH methanol molecules would suggest an obvious association of the 644 cm⁻¹ band with the C-S stretching mode, with the 727 cm⁻¹ mode likely to be the out-of-plane methyl rock. However, a previous vibrational normal mode analysis [Byler & Gerasimowicz, J. Mol. Struct. 112 (1984) 207-219] showed strong coupling between the C-S stretch and CSH bending modes. They assign the 644 cm⁻¹ band to the latter, and attribute the C-S stretch instead to a supposed feature at 688 cm⁻¹ that we find no clear evidence for in our spectrum. For normal CH₃SH, the CSH bend is very weak and lies between the strong C-S stretch and CH₃-rocking bands. A Gaussian quantum chemistry calculation was carried out to explore this mystery, and indeed there is a mode predicted to lie in between our two observed bands with almost vanishing intensity and a reduced mass and effective force constant corresponding closely to those calculated for the C-S stretch for normal CH₃SH. This apparent dramatic extinction of the normally very strong C-S stretching band is quite remarkable!

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