

## FTIR SYNCHROTRON SPECTROSCOPY OF THE LOWER MODES OF METHYL-D<sub>3</sub> MERCAPTAN (CD<sub>3</sub>SH) – WHERE IS THE C-S STRETCH?

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The infrared Fourier transform spectrum of the lower vibrational modes of CD<sub>3</sub>SH has been recorded in the 400-1200 cm<sup>-1</sup> 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 centered at 644 cm<sup>-1</sup> and a weaker perpendicular band centered at 727 cm<sup>-1</sup>. Comparison with the spectra for the normal CH<sub>3</sub>SH species as well as the analogous CD<sub>3</sub>OH and CH<sub>3</sub>OH methanol molecules would suggest an obvious association of the 644 cm<sup>-1</sup> band with the C-S stretching mode, with the 727 cm<sup>-1</sup> mode likely to be the out-of-plane methyl rock. However, a previous vibrational normal mode analysis [Byler and 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<sup>-1</sup> band to the latter, and attribute the C-S stretch instead to a feature at 688 cm<sup>-1</sup> that we find no clear evidence for in our spectrum. For normal CH<sub>3</sub>SH, the CSH bend is very weak and lies between the strong C-S stretch and CH<sub>3</sub>-rocking bands. A Gaussian quantum chemistry calculation of the vibrational frequencies and transition moments was carried out, 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 of normal CH<sub>3</sub>SH. This apparent dramatic extinction of the normally very strong C-S stretching band is quite remarkable!