THE FAR INFRARED SPECTRUM OF THIOPHOSGENE: ANALYSIS OF THE ν_2 FUNDAMENTAL BAND AT 500 cm^{-1}

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Thiophosgene (Cl_2CS) is a model system for studies of vibrational dynamics. Many hundreds of vibrational levels in the ground electronic state have been experimentally observed, allowing a detailed anharmonic force field to be developed including all six vibrational modes.[a] But there have been no previous high resolution studies of this molecule in the infrared, presumably because its mass and multiple isotopic species result in very congested spectra. Here we report a detailed study of the strong ν_2 fundamental band (symmetric $C-Cl$ stretch) based on a spectrum obtained using synchrotron radiation with the Bruker IFS125 FT spectrometer at the Canadian Light Source far infrared beamline. Thiophosgene is an interesting example of an accidentally near-symmetric oblate rotor. Indeed, its inertial axes switch with isotopic substitution: for $^{35}Cl_2CS$, the C_{2v} symmetry axis coincides with the a inertial axis, but for $^{37}Cl_2CS$, this changes to the b axis. Fortunately for us, the ground state microwave spectrum has been well studied.[b] Even so, it has required the full spectral resolution of the present results, with observed line widths of about 0.0008 cm^{-1}, to achieve a true line-by-line analysis.

[a] For example: P.D. Chowdary, B. Strickler, S. Lee, and M. Gruebele, *Chem. Phys. Letters* **434**, 182 (2007).
[b] J.H. Carpenter, D.F. Rimmer, J.G. Smith, and D.H. Whiffen, *J. Chem. Soc. Faraday Trans. 2* **71**, 1752 (1971).