RO-VIBRATIONAL ANALYSIS OF THE ν_4, ν_6 and ν_3 BANDS OF THIOFORMALDEHYDE: EXAMPLE OF A MASSIVE Z-TYPE CORIOLIS RESONANCE

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The infrared spectrum of thioformaldehyde (CH_2S) is of interest since this species is one of the myriad of molecules found in the interstellar space. From a spectroscopic point of view, it is of even more interest since the two lowest vibrational modes, the in-plane rocking mode, ν_6 (B_2), and the out-of-plane wagging mode, ν_4 (B_1), fall at 990.18 and 991.02 cm^{-1} respectively. This separation of only 0.84 cm^{-1} leads to a massive z-type Coriolis resonance where many of the rotational levels of each of the two vibrational states are mixed nearly 50% with each other. To make the situation even more interesting the C=S stretching vibration, ν_3, with A1 symmetry occurs nearby at 1059 cm^{-1}. This vibrational level also interacts with the two low frequency modes which complicates the assignment and analysis. CH_2S was produced by low pressure thermolysis of a gas flow of $C_3H_5SCH_3$/Ar (560° C) and CH_3SCl/Ar (1150° C) in the entrance of the multipath white cell (optical path length 32 m). At a total pressure of 0.15 mbar, 40 scans were recorded for the range 750 to 1400 cm^{-1} on a Bruker HR120 TFIR spectrometer at a resolution of 0.005 cm^{-1} (maximum optical path difference). The initial line assignment was not straightforward. There are strong series apparent in the spectrum, but the features expected for a b-type and c-type bands were not obvious near the band center. The centers of these three vibrations have been determined from medium resolution FT spectra[a] as well as laser Stark measurements[b]. An initial calculation was made using this information as well as guessed values for the band intensities. This permitted the identification of several low K_a series. Finally after numerous iterations, the transitions in the spectrum were identified leading to an excellent set of ro-vibrational constants.

[a] C. Clouthier, D.C. Moule, D.A. Ramsay and F.W. Birss, Can. J. Phys 60, 1212 (1982)
[b] D.J. Bedwell and G. Duxbury, J. Mol. Spectrosc. 64, 531 (1980)