RO-VIBRATIONAL ANALYSIS OF THE \( \nu_4, \nu_0 \) and \( \nu_3 \) BANDS OF THIOFORMALDEHYDE: EXAMPLE OF A MASSIVE Z-TYPE CORIOLIS RESONANCE

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The infrared spectrum of thioformaldehyde (CH\(_2\)S) 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, \( \nu_0 \) (B\(_2\)), and the out-of-plane wagging mode, \( \nu_4 \) (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, \( \nu_2 \), with A\(_1\) 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\(_2\)S was produced by low pressure thermolysis of a gas flow of C\(_3\)H\(_2\)SCH\(_3\)/Ar (560° C) and CH\(_3\)SCl/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.

\(^b\)D.J. Bedwell and G. Duxbury, J. Mol. Spectrosc. 64, 531 (1980)