ROTATIONAL SPECTROSCOPY OF THIOFORMALDEHYDE, H_2CS, IN ITS FOUR LOWEST EXCITED VIBRATIONAL, CORIOLIS-COUPLED STATES

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Rotational spectra of vibrationally excited states of H_2CS below 1500 cm^{-1} have been obtained by long-path absorption spectroscopy between 120 and currently 670 GHz. The highest K_a accessed range from 9 to 12 and correspond to combined rotational and vibrational energies of almost 2400 cm^{-1}. The $v_4 = 1$ (990.185 cm^{-1}) and $v_6 = 1$ (991.019 cm^{-1}) states are almost degenerate and undergo very strong Coriolis interaction ($|\zeta^a_{46}| = 0.5148$) which causes $K_a > 0$ to be mixed completely. The $v_3 = 1$ state is at 1059.204 cm^{-1} and the first order Coriolis terms are smaller ($|\zeta^c_{36}| = 0.2743$ and $|\zeta^b_{34}| = 0.0574$) so that perturbations are more local. Finally, the $v_2 = 1$ state (1455.496 cm^{-1}) is comparatively far away from the three lower states, but there is a large coupling term with $v_4 = 1$: $|\zeta^b_{24}| = 0.8555$. Because of the large energy difference, only higher order effects are pronounced in this case. The initial assignments were greatly facilitated by previous infrared studies on ν_4, ν_6, and ν_3[a] as well as on ν_2.[c] The results from these as well as previous and present pure rotational studies on the ground vibrational state were considered in the global fit. The very satifactory fit required a modest number of vibrational corrections for the four vibrationally excited states and a comparatively large number of Coriolis interaction terms.

[a] D. J. Bedwell and G. Duxbury, *J. Mol. Spectrosc.* **84** (1980) 531−558.
[b] P. H. Turner, L. Halonen, and I. M. Mills, *J. Mol. Spectrosc.* **88** (1981) 402−419.
[c] D. McNaughton and D. N. Bruget, *J. Mol. Spectrosc.* **159** (1993) 340−349.