Evolutionary Algorithm-Based Analysis Of The Rovibrational SCl_2 Stretching Bands Of Thionyl Chloride

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Thionyl chloride ($SOCl_2$) is a volatile inorganic compound extensively used in the industry and whose monitoring in the gas phase is critical both from environmental and military concerns. Pure rotational and rovibrational spectra of $SOCl_2$ and several of its isotopologues, were characterized recently in the microwave, submillimeter, and far-infrared spectral regions [1] [2]. The rotationally resolved vibrational spectra of the $SOCl_2$ asymmetric υ_5 (459 cm^{-1}) and symmetric υ_2 (500 cm^{-1}) SCl_2 stretching fundamental bands have been measured by means of high resolution (R = 0.001 cm^{-1}) FT-FIR spectroscopy on the AILES beamline of the SOLEIL synchrotron facility. These two bands overlap with a strong SO_2 band (520 cm^{-1}) arising from the very efficient hydrolysis of $SOCl_2$ with residual traces of water [3].

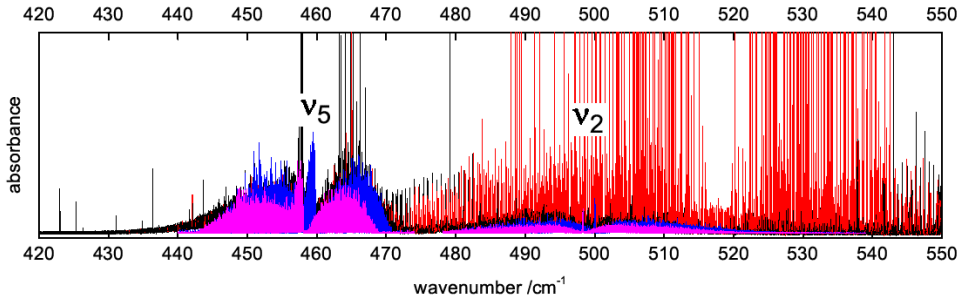

Fig. 1. Synchrotron-Based FT-FIR spectrum of υ_5 and υ_2 bands of $SOCl_2$ mixed with a strong SO_2 band (in red)

Evolutionary algorithms implemented in the automated fit programs developed by the Nijmegen and Düsseldorf groups [4] have enabled the analysis of the υ_5 and υ_2 bands of two isotopologues ($^{32}S^{16}O^{35}Cl_2$ and $^{32}S^{16}O^{35}Cl^{37}Cl$), despite the presence of the SO_2 band and thus demonstrating the power of evolutionary algorithms applied to the spectroscopic analysis of congested spectra. This work helped to identify the pure rotational structure of the v_2=1 and v_5=1 vibrational states of $^{32}S^{16}O^{35}Cl_2$ in the submillimeter spectrum of Ref.[2], as well as the v_4=1 state (not-active in the FIR region). A global fit gathering all the microwave, submillimeter and Far-IR data of thionyl chloride has been performed. Almost all reachable excited rovibrational energy levels have been included in assigned transitions suggesting that no effective interaction was observed.

References

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