High resolution terahertz and far-infrared spectroscopy of $SOCl_2$

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Thionyl chloride ($SOCl_2$) is an extremely powerful oxidant widely used in industrial processes and playing a role in the chemistry of the atmosphere [1]. In addition, it is of particular interest for security and defense applications. Low resolution vibrational spectra of gas phase $SOCl_2$ [2] as well as high resolution pure rotational transitions up to 25 GHz [3] have previously been investigated. To date no high resolution data are reported at frequencies higher than 25 GHz.

We have investigated the THz absorption spectrum of $SOCl_2$ in the spectral region 70-650 GHz using a frequency multiplier chain coupled to a 1 m long single path cell containing a pressure of about 15 μbar of the molecule. On this spectrum transitions of both $SO^{35}Cl^{35}Cl$ and $SO^{35}Cl^{37}Cl$ isotologues have been observed. 15993 pure rotational transitions of the main isotopologue $SO^{35}Cl^{35}Cl$ have been assigned up to $J_{max}=127$ and $Ka_{max}=64$. 13708 pure rotational transitions of $SO^{35}Cl^{37}Cl$ have also been observed with $J_{max}=117$ and $Ka_{max}=65$. Effective molecular parameters have been obtained for these two isotopologues using the SPFIT/SPCAT suite [4].

We also have recorded the high resolution FIR spectra of $SOCl_2$ in the spectral range 50-700 cm^{-1} using synchrotron radiation at the AILES beamline of SOLEIL facility. A White-type cell aligned with an absorption path length of 150 m has been used to record, at a resolution of 0.001 cm^{-1}, two spectra at pressures of 5 and 56 μbar of $SOCl_2$. On these spectra four FIR modes of $SO^{35}Cl_2$ are observed (ν_2, ν_3, ν_5 and ν_6) and present a resolved rotational structure. Their analysis has been realized using accurate ground state molecular parameters derived from our new pure rotational measurements and MP2/6-311^{++}G(3df,3pd) anharmonic calculations.

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