High-resolution spectroscopy of difference and combination bands of SF_6 to elucidate hot band structures in the ν_3 region

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The strong infrared absorption in the ν_3 S–F stretching region of sulfur hexafluoride (SF_6) near 948 cm^{-1} makes it a powerful greenhouse gas. Although its present concentration in the atmosphere is very low, it is increasing rapidly, due to industrial pollution. The ground state population of this heavy species is only 30 % at room temperature and thus many hot bands are present. Consequently, a reliable remote-sensing spectroscopic detection and monitoring of this species requires an accurate modeling of these hot bands.

We used two experimental setups at the SOLEIL French synchrotron facility to record some difference and combination bands of SF_6: (i) a new cryogenic multiple pass cell with 93 m optical path length and regulated at 165±2 K temperature and (ii) the Jet-AILES supersonic expansion jet setup. With this, we could obtain high-resolution absorption spectra of the ν_3–ν_2, ν_3–ν_1, ν_3+ν_2 and ν_3+ν_1 bands at low temperature. These spectra could be assigned and analyzed thanks to the SPVIEW and XTDS software [1]. We performed two global fits of effective Hamiltonian parameters:

- A global fit of the present ν_3–ν_1 and ν_3+ν_1 lines, together with previous ν_1 Raman data [2], in order to obtain refined ν_1 parameters and also ν_3+ν_1 parameters in a consistent way. This allows to simulate the ν_3+ν_1–ν_1 hot band.

- A global fit of the ground state, ν_2, ν_3, ν_3–ν_2, ν_3+ν_2, 2ν_3 and 2ν_3–ν_3 lines, using the present spectra and previous infrared, Raman and two-photon absorption data [3–5]. This allows a consistent refinement of the effective Hamiltonian parameters for all the implied vibrational levels and a new simulation of the ν_3+ν_2–ν_2 hot band.

Thanks to these results and to the recent investigation of the ν_6 "forbidden" band, we can present a new global simulation of SF_6 hot bands in the ν_3 region.

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