SF_6: The forbidden band unveiled

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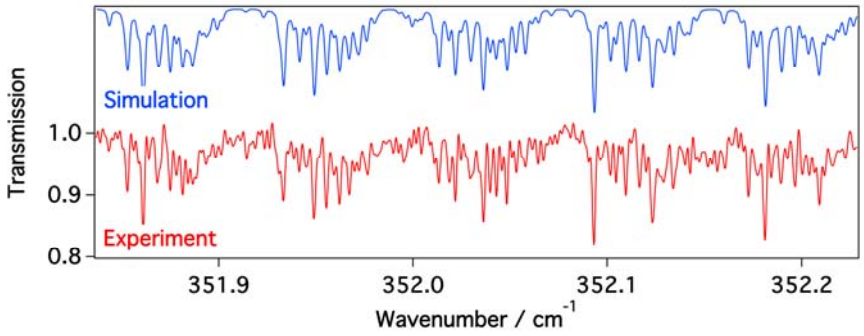
Sulfur hexafluoride (SF_6) is a greenhouse gas of anthropogenic origin, whose strong infrared absorption in the ν_3 S–F stretching region near 948 cm^{-1} induces a global warming potential 23900 times bigger than CO_2. This heavy species features many hot bands at room temperature (at which the ground state population is only 30 %), especially those originating from the v_6=1 state. Unfortunately, the ν_6 band itself (near 347 cm^{-1}) being, in first approximation, both infrared and Raman inactive, no reliable information could be obtained about it up to now. A long time ago, some authors suggested [1,2] that this band may be slightly activated through a Coriolis interaction and may appear as a very faint band, with an integrated intensity about 2 millionths of that of ν_3. Using a new cryogenic multiple pass cell with 93 m optical path length and regulated at 165±2 K temperature, we recorded a spectrum of the ν_6 far-infrared region thanks to the performances of the AILES Beamline at the SOLEIL French synchrotron facility. Low temperature was used to avoid the presence of the $2\nu_6$–ν_6 hot band and to reduce the neighboring, stronger ν_3-ν_2 difference band. We are thus able to confirm that the small feature in this region, previously viewed at low-resolution is indeed ν_6. We present its fully resolved spectrum. It appears to be activated thanks to unidentified faint interactions resulting in the presence of a first-order dipole moment term that induces unusual selection rules. This spectrum was analyzed thanks to the XTDS software package [3], leading to accurate molecular spectroscopic parameters that should be useful to model the hot bands of SF_6.



Detail in the R branch of the ν_6 band.

[1] W. B. Person, B. J. Krohn, J. *Mol. Spectrosc*. **1983**, 98, 229–257.
[2] C. Chappados, G. Birnbaum, *J. Mol. Spectrosc.* **1984**, 105, 206–214.
[3] Ch. Wenger, V. Boudon, M. Rotger, M. Sanzharov, J.-P. Champion, *J. Mol. Spectrosc.* **2008**, 251, 102–113.