SF_6: THE FORBIDDEN BAND UNVEILED

V. BOUDON, *Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS–Université de Bourgogne, 9 Av. A. Savary, BP 47870, F-21078 Dijon Cedex, France*; L. MANCERON, *Laboratoire de Dynamique, Interactions et Réactivité, CNRS UMR 7075, 4 Place Jussieu, F-75252 Paris Cedex, France*; F. KWABIA-TCHANA, *Laboratoire Interuniversitaire des Systèmes Atmosphériques, UMR CNRS 7583, Université Paris-Est Créteil et Université Paris-Diderot, 61 Avenue du Général de Gaulle, 94010 Créteil Cedex, France*; P. ROY, *Ligne AILES – Synchrotron SOLEIL, L'Orme des Merisiers, F-91192 Gif-sur-Yvette, France*.

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[a] that this band may be slightly activated through 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 multipass 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 $2\nu_6 - \nu_6$ hot band and to reduce the neighboring, stronger $\nu_4 - \nu_2$ 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[b], leading to accurate molecular spectroscopic parameters that should be useful to model the hot bands of SF_6.

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