

Line position analysis of the ν_2 band of SO_2F_2 using the C_{2v} Top Data System



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ABSTRACT

A new high-resolution infrared spectrum of the ν_2 band of SO_2F_2 centered at 849.46 cm^{-1} has been recorded with a resolution of 0.00102 cm^{-1} at the AILES beamline of SOLEIL Synchrotron facility. More than 1600 lines up to $J_{\text{max}} = 41$ have been assigned and fitted in line position using a tensorial formalism adapted to the case of XY_2Z_2 asymmetric molecules developed as an extension of the usual one used for spherical tops (Rotger et al., 2002). The analysis has been performed in the $O(3) \supset T_d \supset C_{2v}$ group chain, thanks to the C_{2v} TDS program suite (Wenger et al., 2005). This approach allows a systematic development of rovibrational interaction to study any polyad of SO_2F_2 and makes easier global analysis. Compared to a previous study (Merke et al., 2006), the present fit uses less effective Hamiltonian parameters but we assigned lines up to a lower J value.

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1. Introduction

Sulfuryl fluoride (SO_2F_2) has recently emerged as an important air pollutant [1]. In addition to agriculture and food processing, it is increasingly used as a fumigant of timber, buildings and construction materials. In 2005, chemical industries chose SO_2F_2 as a substitute for methyl bromide, which contributes to the destruction of the ozone layer [2]. The potential atmospheric loss processes of sulfuryl fluoride have been studied and its global warming potential calculated [3]. That is why, modeling the absorption spectrum of this molecule is essential for atmospheric concentration measurements.

SO_2F_2 belongs to the C_{2v} symmetry group and has nine fundamental vibrational bands. Many studies have already been devoted to the analysis of some rovibrational bands using the Watson's Hamiltonian [4,5]. Molecular parameters of the $\nu_8(b_2) = 1$ state have been determined by Bürger et al. [6] with a combined analysis of rotational and rovibrational data. Microwave and high resolution FTIR spectra of the $(\nu_3(a_1)/\nu_7(b_1)/\nu_9(b_2))$ triad at 550 cm^{-1} have also been studied by Bürger et al. [7] with a model that takes into account Coriolis interactions within the triad. Parameters up to the octic centrifugal distortion constants have been determined using Watson's Hamiltonian in S -reduction. A first analysis of the

$\nu_2(a_1)$ band has been performed by Merke et al. [8] combining rotational and rovibrational data, and parameters up to the sextic centrifugal distortion constants have been obtained using a Watson's Hamiltonian in S -reduction.

Yet, the analysis of SO_2F_2 spectra using conventional methods does not seem to provide reliable results as shown by Sarka et al. [9] because sulfuryl fluoride possesses three rotational constants with very close values. The rotational constants of the ground state are as follows: $A = 5134\text{ MHz}$, $B = 5075\text{ MHz}$, $C = 5057\text{ MHz}$. Therefore, this asymmetric top molecule is close to a quasi-spherical species which can be considered as derived from the isoelectronic SO_4^{2-} sulfate ion.

Some years ago, a tensorial formalism adapted to XY_2Z_2 asymmetric top but close to spherical symmetry has been developed by Rotger et al. [10] as a reorientation of the T_d formalism [11] into the C_{2v} subgroup. This approach was extended also for several types of molecules such as XY_5Z and X_2Y_4 . In the meantime, XY_3Z molecules were studied by Nikitin et al. using the MIRS spectroscopic software [12–15] and also by El Hilali et al. [16–19]. More generally, the methods using the tensorial formalism have proved a significant advantage to solve complex molecular spectroscopy problems [20].

The tensorial formalism adapted to XY_2Z_2 asymmetric top was successfully applied to the ground state [21] and to the $(\nu_3/\nu_7/\nu_9)$ bending triad [22] of sulfuryl fluoride.

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We describe here an application of this tensorial formalism to the analysis of the symmetric SF₂ stretching vibration $\nu_2(a_1)$. The results are compared to those obtained with the usual approach [8]. The experimental details are provided in Section 2. The theoretical background is explained in Section 3 and the results are given in Section 4.

2. Experimental details

The spectrum of SO₂F₂ used for this study was recorded at the AILES beam line at the SOLEIL Synchrotron facility, using a high resolution Fourier transform Bruker IFS 125 HR spectrometer. This instrument has all the equipment required to operate from the Mid- to Far Infrared (IR) or Terahertz (THz). In this case, it was equipped with a KBr/Ge beam splitter, a cold optical filter eliminating infrared radiation above 930 cm⁻¹, and an MCT photoconductive detector cooled with liquid Helium down to 4 K [23]. Meanwhile, we have used the SOLEIL synchrotron radiation extracted by the AILES beamline as the continuum source of the interferometer.

A cryogenic multi-pass cell equipped with diamond windows (transparent to IR) was connected to the interferometer [24]. Its base length is 1.41 m but for the current experiment an optical path of 3.14 m was adjusted. The pressure in the cell was maintained at 1.99×10^{-2} mbar at $T = 165$ K. It was measured accurately using a special cryogenic capacitive gauge [25]. The spectrum was recorded with a resolution of 0.00102 cm⁻¹ (according to the Bruker definition, resolution is 0.9/the maximum optical path difference).

The spectrum was obtained by collecting and averaging 120 interferometer scans. Every interferogram was transformed into a spectrum using a Fourier transform procedure included in the Bruker software OPUS package [26] with the Mertz phase error correction method. Calibration was done with CO₂ lines in the same region. An entire spectrum of the ν_2 region is shown at the bottom of Fig. 1. Under the same conditions, alignment but with a reduced resolution (0.05 cm⁻¹), a reference spectrum with an empty cell, was recorded to obtain the absorbance spectrum.

Sulfuryl fluoride in natural abundance was provided by SOLVAY FLUOR GmbH (Hanovre Allemagne) with stated purity of 99%. An overview of the detailed experimental conditions is provided in Table 1.

3. Theoretical model

The theoretical model described below is based on the tensorial formalism and the vibrational extrapolation methods used in Dijon. These methods allow a systematic expansion of the Hamiltonian and dipole moment operator by including all possible interactions for a given rovibrational polyad scheme. They have already been explained for the spherical top [27] and for molecules with

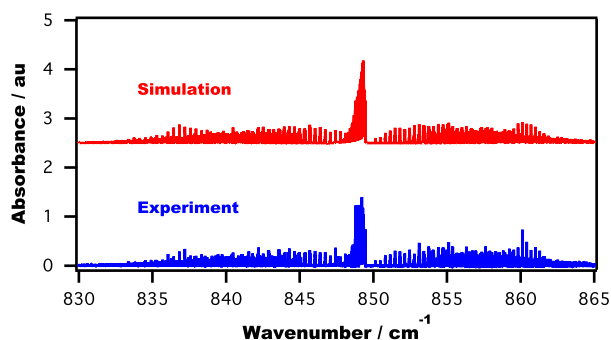


Fig. 1. Infrared spectrum of the ν_2 band of SO₂F₂: experiment and simulation.

Table 1
Experimental details.

Spectral range (cm ⁻¹)	800–950
Resolution (cm ⁻¹)	0.00102
Source	RS
Separator	KBr
Detector	MCT
Cell	Multi-pass
Optical path (m)	3.14
Temperature (K)	165
Pressure (mbar)	1.99×10^{-2}

different symmetries such as C_{4v} [28], D_{2h} [29], C_{3v} [18] and C_{2v} [10]. In this section, we briefly recall the basic principles of these methods and their applications to the analysis of the ν_2 band of SO₂F₂.

3.1. Expression of the Hamiltonian

A tensorial formalism adapted to the case of quasi-spherical XY₂Z₂ asymmetric tops belonging to C_{2v} group has been developed as an extension of the usual one already developed for XY₄ tetrahedral species [10].

The background of this formalism is based on the idea of considering sulfuryl fluoride as deriving from the sulfate ion by substitution of two ligands. It means that the vibrational structure of sulfuryl fluoride can be correlated to that of the sulfate ion. For this reason, we start from the $O(3) \supset T_d$ formalism and we make a symmetry reduction into the C_{2v} subgroup to work in the $O(3) \supset T_d \supset C_{2v}$ chain. After reorientation, the entire C_{2v} tensor operator will be denoted $T^{(K,\Gamma,\tilde{T})}$ with:

$$\begin{aligned} \Gamma &= (A_1, A_2, E, F_1, F_2) \text{ the } T_d \text{ irreducible representations,} \\ \tilde{T} &= (a_1, a_2, b_1, b_2) \text{ the } C_{2v} \text{ irreducible representations.} \end{aligned}$$

Lets consider an XY₂Z₂ molecule for which the vibrational levels are grouped in a series of polyads designed by P_k ($k = 0, 1, 2, 3, \dots, n$), where P_0 is the ground state. After performing some contact transformations (transform completely the Hamiltonian in a diagonal or block diagonal form), the Hamiltonian operators can be written as a sum of contributions of the different polyads:

$$\tilde{\mathcal{H}} = \tilde{\mathcal{H}}_{\{P_0=GS\}} + \tilde{\mathcal{H}}_{\{P_1\}} + \dots + \tilde{\mathcal{H}}_{\{P_n\}}, \quad (1)$$

where the Hamiltonian $\tilde{\mathcal{H}}_{\{P_k\}}$ is formed by a linear combination of rovibrational operators T :

$$\tilde{\mathcal{H}}_{\{P_k\}} = \sum_{\text{all indexes}} \tilde{t}^{\Omega(K,n\Gamma,\tilde{T})} T^{\Omega(K,n\Gamma,\tilde{T})} \Gamma_1 \Gamma_2 \Gamma_v. \quad (2)$$

\tilde{t} are the parameters to be fitted using the experimental data. The T refers to the rovibrational operators obtained through the coupling of a rotational operator (R) of degree Ω (angular momentum components (J_x, J_y, J_z)) and a vibrational operator (V) of degree Ω_v (creation and annihilation operators). The rotational and vibrational operators are symmetrized in the group chain and then coupled in the C_{2v} group. Therefore, T is defined as follows:

$$T = \sum_{\text{all indexes}} \beta \left(R^{\Omega(K,n\Gamma,\tilde{T})} \otimes \varepsilon V^{(\Gamma,\tilde{T})} \right)^{(a_1)}, \quad (3)$$

where $\varepsilon = (-1)^\Omega$ and β the numerical factor defined as $\beta = \sqrt{3}(-\sqrt{3}/4)^{\Omega/2}$ if $(K, n\Gamma) = (0, 0A_1)$.

To obtain the effective Hamiltonian for a given polyad, we should project $\tilde{\mathcal{H}}_{\{P_k\}}$ in the P_n Hilbert subspace:

$$\tilde{H}^{(P_n)} = \tilde{H}_{\{GS\}}^{(P_n)} + \tilde{H}_{\{P_1\}}^{(P_n)} + \dots + \tilde{H}_{\{P_n\}}^{(P_n)}. \quad (4)$$

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