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Line positions and intensities in the ν_2 fundamental band of Sulfuryl Fluoride using the C_{2v} Top Data System

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Abstract

New experimental high-resolution Fourier-Transform infrared spectra of the infrared active fundamental ν_2 band of sulfur dioxide SO_2 , have been recorded at a temperature of 193 K and at resolution of 0.00102 cm^{-1} at the AILES (Advanced Infrared Line Exploited for Spectroscopy) beamline of the SOLEIL ((Source Optimisée de Lumière d'Énergie intermédiaire du LURE) Synchrotron facility. A detailed analysis has been performed both in line positions and intensities with the C_{2v} TDS (Top Data System) program suite, based on the tensorial formalism developed in Dijon for quasi-spherical top molecules. The effective Hamiltonian was developed up to fourth order. The parameter of the effective dipole moment operator has been determined using the wavefunctions of the effective Hamiltonian operator. 2407 line positions have been measured with global root mean square deviation of about $0.19 \times 10^{-3} \text{ cm}^{-1}$. Using 71 lines intensities, we estimate the uncertainty on calculated line intensities to 10 %. To the extent of our knowledge, this is the first time that an absolute intensity analysis has been carried out for sulfur dioxide.

Key words:

Quasi-spherical top molecules, tensorial formalism, molecular spectroscopy, line intensities, sulfuryl fluoride

1 Introduction

Sulfuryl fluoride (SO_2F_2) is an industrial chemical released into the atmosphere in significant quantities [1]. It is used increasingly as a fumigant of timber, buildings and construction materials. SO_2F_2 is also used in agriculture and food processing as a replacement for CH_3Br [2]. Modeling its absorption spectrum is thus essential both for atmospheric concentration measurements and for theoretical aspects of spectroscopy, since SO_2F_2 is close to a spherical rotor and can be considered as derived from tetrahedral SO_4^{2-} 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.

The spectroscopy of sulfuryl fluoride is still quite unexplored. Only quite a limited number of spectroscopic works exist for this rather heavy molecule which is one of the few quasi-spherical species [3–11]. Existing studies have been devoted to investigate line positions in the pure rotation and fundamental band spectra of SO_2F_2 . No absolute intensity experimental study existed up to now. Only two room temperature IR cross section studies exist [12,13] and a computational quantum chemical study reported prediction of band intensities [14].

The band of interest in the present work, namely the ν_2 fundamental band, has been the subject of two previous studies. The first one has been performed by Merke *et al.* [8] who analysed this band at room temperature. Using rotational and rovibrational data, parameters up to the sextic centrifugal distortion constants have been determined with Watson's Hamiltonian in S -reduction. For IR-transitions, the standard deviation was about $0.40 \times 10^{-3} \text{ cm}^{-1}$. This result was obtained by using about 1900 lines with rotational quantum number up to $J = 68$. This study showed that the ν_2 band can be treated as isolated.

The second one has been performed by Hmida *et al.* [10] using an oriented tensorial formalism in the $O(3) \supset T_d \supset C_{2v}$ group chain adapted to XY_2Z_2 asymmetric tops close to spherical symmetry. This formalism has been developed by Rotger *et al.* [15] and has been derived from the formalism developed for tetrahedral (T_d) XY_4 molecules [16,17]. This tensorial model uses the so-called vibrational extrapolation, which makes global analyses much easier

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and enables studying any rovibrational band or polyad with a systematic development of all rovibrational interactions. Using a high-resolution spectrum recorded at the SOLEIL synchrotron facility at $T = 165$ K, the root-mean-square deviation (RMS) for IR-transitions was about $0.20 \times 10^{-3} \text{ cm}^{-1}$. This result was obtained by using about 1668 lines up to $J_{max} = 41$.

In the course of this intensity study, new data were acquired which permitted a reexamination of the line position model developed previously [10]. More lines could be assigned and an improved set of parameters could be obtained. In this paper, we report on the line position analysis and on the first line intensity analysis of the symmetric SF₂ stretching vibration ν_2 which belongs to the symmetry species A_1 of the C_{2v} point group. This band centered at 849.46 cm^{-1} is located at the limit of the 10 microns atmospheric windows. The analysis was performed using the C_{2v} TDS software developed in Dijon [18]. The experimental details are described in Section 2 and the basic elements of the theoretical model are briefly recalled in Section 3. The details of the analysis are presented in section 4 in which we compare results with previous contributions. We will show in this paper that the tensorial approach is again more appropriate for the analysis of quasi-spherical molecules.

2 Experimental details

The Fourier Transform Infrared (FTIR) spectra of the ν_2 band of a commercial sample of sulfuryl fluoride (SOLVAY FLUOR GmbH, 99 % purity) were recorded in the $830 - 930 \text{ cm}^{-1}$ spectral range at different pressures using the Bruker IFS125HR spectrometer on the far-infrared AILES beamline, located at the SOLEIL Synchrotron facility [19].

The instrument was installed with a KBr/Ge beam splitter and a HgCdTe 4K-cooled detector, achieving an eightfold increase in signal-to-noise ratio versus commercially available detectors in this region [20]. The detector was equipped with a low pass optical filter with a 930 cm^{-1} cutoff. The interferometer was coupled to a simple-pass gas cell with base length of about $51 \pm 1 \text{ mm}$. The SOLEIL synchrotron light source extracted by the AILES beamline has been used as the continuum source of the interferometer.

A total of three spectra were recorded at the temperature $T = 193 \pm 2 \text{ K}$ and at pressures of 0.52, 1 and 2.89 mbar. Low temperature was used to limit the presence of hot bands. An overview of the ν_2 region recorded at the different pressures is shown in Fig. 1. The resolution was set to 0.00102 cm^{-1} (according to the Bruker definition, resolution is $0.9/882 \text{ cm}$, 882 cm being the maximum optical path difference).

An empty cell spectrum recorded under the same conditions and alignment was used as reference in order to limit the baseline variations which may cause errors on the measured absolute intensities. More than 80 interferome-

ter scans were collected for each pressure. No apodization was applied (boxcar option in the Bruker software). The aperture used was 1.15 mm. The interferogram was transformed into a spectrum using a Fourier transform procedure included in the Bruker software Opus package [21]. Spectra were calibrated using 40 known (with sub-MHz accuracy) carbon dioxide lines and with the HITRAN2016 [22] values used as reference. The average RMS deviation after calibration was $1.04 \times 10^{-4} \text{ cm}^{-1}$ (1σ). We thus retained three times the standard deviation (about $3.1 \times 10^{-4} \text{ cm}^{-1}$) as a conservative estimate of our frequency accuracy. Taking into account the precision of measurements, the wavenumber accuracy (3σ) and the line intensities accuracy are estimated to be about 0.00031 cm^{-1} and 5%, respectively.

Peak positions and lines intensities in the ν_2 band of SO_2F_2 were determined for each pressure by non-linear least-squares curve fitting of the spectra using the program “WSpectra” [23]. For the spectra recorded at 0.52 and 1 mbar, each line was given a Gaussian profile and we take into account the instrumental line shape of the Fourier Transform Spectrometer in the modeling of the spectra by including the input diaphragm diameter as a fixed parameter. For the spectrum recorded at 2.89 mbar, each line was given a Voigt profile. The Doppler width of about $0.84 \times 10^{-3} \text{ cm}^{-1}$ is slightly larger than the width of the instrumental lineshape (about $0.68 \times 10^{-3} \text{ cm}^{-1}$), giving a Gaussian profile for the low pressure spectra. For the higher pressure, a small collisional contribution of about $0.57 \times 10^{-3} \text{ cm}^{-1}$ has been taken into account, so that, the line profile can be approximated by a Voigt profile.

3 Theoretical model

The theoretical model used in this paper is based on the tensorial formalism specific to an XY_2Z_2 asymmetric top close to spherical symmetry and the vibrational extrapolation method developed in Dijon [17,24]. The tensorial formalism adapted to XY_2Z_2 asymmetric molecules has been developed by Rotger *et al.* [15] as a reorientation of the T_d formalism [25] into the C_{2v} subgroup. It means that the vibrational structure of sulfuryl fluoride can be correlated to that of the tetrahedral sulfate ion. The basic idea is the use of the $O(3) \supset T_d \supset C_{2v}$ group chain in order to unambiguously label molecular states. This approach follows closely the same steps as those used for C_{4v} and C_{3v} molecules [26–29].

This model, which allows a systematic expansion of the Hamiltonian and dipole moment operator by including all possible interactions for a given rovibrational polyad scheme, has been described in Refs. [6,7,15,17,30]. We just briefly recall here the basic principles of this formalism.

3.1 Tensorial model for the Hamiltonian

Let's consider an XY_2Z_2 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. Consequently, we assume that intra-polyad interactions are strong and should be treated exactly, while inter-polyad interactions can be considered as small perturbations. After performing contact transformations in order to eliminate inter-polyad interactions, the resulting hamiltonian operators can be written as a sum of contributions of the different polyads:

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

The effective Hamiltonian for polyad P_n is obtained by projection in the corresponding subspace,

$$\tilde{H}^{(P_n)} = P^{(P_n)} \tilde{\mathcal{H}} P^{(P_n)} \quad (2)$$

$$\tilde{H}^{(P_n)} = \tilde{H}_{\{\text{GS}\}}^{(P_n)} + \tilde{H}_{\{P_1\}}^{(P_n)} + \dots + \tilde{H}_{\{P_n\}}^{(P_n)} \quad (3)$$

This corresponds to the so-called vibrational extrapolation method. This one allows analysing molecular spectra by climbing up the polyad ladder, one polyad after the other: the effective hamiltonian for a given polyad contains all the parameters for the lower polyads (the terms that are added to the effective hamiltonian are a smaller contributions accounting for vibrational corrections to the lower polyad terms).

The different terms being written as:

$$\tilde{\mathcal{H}}_{\{P_k\}} = \sum_{\text{all indexes}} \tilde{t}_{\{n_s\}\{m_s\}}^{\Omega(K,n\Gamma,\tilde{\Gamma})\Gamma_1\Gamma_2\Gamma_\nu} T_{\{n_s\}\{m_s\}}^{\Omega(K,n\Gamma,\tilde{\Gamma})\Gamma_1\Gamma_2\Gamma_\nu} \quad (4)$$

$\tilde{\mathcal{H}}_{\{P_k\}}$ is expressed as a linear combination of rovibrational operators T and it must be symmetric, Hermitian and time reversal invariant in the C_{2v} molecular point group.

The \tilde{t} are the effective hamiltonian parameters to be determined by fitting experimental line positions. T refers to the rovibrational operators obtained by coupling of a rotational operator (R) of degree Ω (in angular momentum components (J_x, J_y, J_z)) [31–33] and a vibrational operator (V) of degree Ω_v (in creation and annihilation operators) constructed through recursive coupling of elementary creation and annihilation operators of the corresponding modes of the tetrahedral molecule. The order of each operator $T^{\Omega(K,n\Gamma,\tilde{\Gamma})\Gamma_1\Gamma_2\Gamma_\nu}$ is $\Omega + \Omega_v - 2$. The rotational and vibrational operators are symmetrized in the

group chain and then coupled in the C_{2v} group.

$$T_{\{n_s\}\{m_s\}}^{\Omega(K,n\Gamma,\tilde{\Gamma})\Gamma_1\Gamma_2\Gamma_\nu} = \sum_{\text{all indexes}} \beta \left(R^{\Omega(K,n\Gamma_r,\tilde{\Gamma})} \otimes \varepsilon V_{\{n_s\}\{m_s\}}^{\Gamma_1\Gamma_2(\Gamma_\nu,\tilde{\Gamma})} \right)^{(a_1)}. \quad (5)$$

where $\varepsilon = (-1)^\Omega$. β is the numerical factor that allows a straightforward comparison between the conventional and the tensorial notations and is defined as $\beta = \sqrt{3}(-\sqrt{3}/4)^{\Omega/2}$ if $(K, n\Gamma) = (0, 0A_1)$ and 1 otherwise. $\Gamma = (A_1, A_2, E, F_1, F_2)$ and $\tilde{\Gamma} = (a_1, a_2, b_1, b_2)$ denoting T_d and C_{2v} irreducible representations, respectively, Γ_1 and Γ_2 are the symmetries of vibrational operators formed by coupling creation and annihilation operators.

Matrix elements of the effective hamiltonian are calculated in a coupled rovibrational basis using the Wigner-Eckart theorem and uncoupling tensorial relations [17].

In order to analyze the ν_2 (a_1) band of sulfuryl fluoride, considered as isolated and derived from the ν_1 (A_1) fundamental of SO_4^{2-} , we use the following effective Hamiltonians:

- The ground state effective Hamiltonian

$$\tilde{H}^{\langle \text{GS} \rangle} = \tilde{H}_{\{\text{GS}\}}^{\langle \text{GS} \rangle} \quad (6)$$

- The ν_2 band effective Hamiltonian

$$\begin{aligned} \tilde{H}^{\langle \nu_2 \rangle} &= \tilde{H}_{\{\text{GS}\}}^{\langle \nu_2 \rangle} + \tilde{H}_{\{\nu_2\}}^{\langle \nu_2 \rangle} \\ &= \tilde{H}_{\text{Moret-Bailly}} \\ &\quad + \sum_{\text{all indexes}} \beta \tilde{t}^{\Omega(K,n\Gamma_r)\Gamma'} \left(R^{\Omega(K,n\Gamma_r,a_1)} \otimes \varepsilon V_{\{1\}\{1\}}^{A_1A_1(A_1,a_1)} \right)^{(a_1)}, \end{aligned} \quad (7)$$

where $\tilde{H}_{\text{Moret-Bailly}}$ is the effective ground state purely rotational contribution of degree Ω [6,34,35].

After diagonalization, the Hamiltonian eigenfunctions obtained are denoted:

$$|J, \tilde{C}, \alpha\rangle, \quad (8)$$

α has no particular physical meaning. It's a running index that numbers eigenstates with the same C_{2v} symmetry \tilde{C} within a given J block, in increasing energy order. J is the quantum number associated to the total angular momentum of the molecule. This labelling is related to the group chain choice, which is an orientation from $O(3) \supset T_d$ into the symmetry subgroup C_{2v} of the XY_2Z_2 asymmetric molecule.

3.2 Tensorial model for the dipole moment

To calculate line intensities, the dipole moment operator (in the case of infrared absorption spectroscopy) is expanded using the same methods as discussed above [15].

The components μ_{Θ} ($\Theta = X, Y, Z$) in the laboratory fixed frame (LFF) can be related to the components μ_{θ} ($\theta = x, y, \text{ or } z$) in the molecule-fixed frame (MFF) as follows:

$$\mu_{\Theta} = \sum_{\theta} \lambda_{\Theta\theta} \mu_{\theta}, \quad (9)$$

where $\lambda_{\Theta\theta}$ are the direction cosines.

The transformed LFF components can be expressed in terms of the MFF transformed components as follows:

$$\tilde{\mu}_{\Theta} = \sum_{\theta} (\lambda_{\Theta\theta} \tilde{\mu}_{\theta} + \tilde{\mu}_{\theta} \lambda_{\Theta\theta}). \quad (10)$$

The effective dipole moment operator $\tilde{\mu}_{\theta}^{(\tilde{\Gamma})}$ is expanded in a tensorial form similar to that of the effective Hamiltonian. Thus $\tilde{\mu}_{\theta}^{(\tilde{\Gamma})}$ is expressed in terms of rovibrational operators [16], as:

$$\tilde{\mu}_{\theta}^{(\tilde{\Gamma})} = \sum_{\{i\}} \tilde{\mu}^{\{i\}} (R^{\Omega(K, n\Gamma_r, \tilde{\Gamma}_r)} \otimes \varepsilon V_{\{n_s\}\{m_s\}}^{\Gamma_1\Gamma_2(\Gamma_v, \tilde{\Gamma}_v)})_{\theta}^{(\tilde{\Gamma})} \quad (11)$$

$\tilde{\mu}^{\{i\}}$ are the effective dipole moment parameters to be determined using experimental intensities. The index i collects all the parameters of the operators R and V , i.e. $i = \Omega, K, n\Gamma_r, \tilde{\Gamma}_r, \Gamma_1, \Gamma_2, \Gamma_v, \tilde{\Gamma}_v$. The order of the individual terms is $\Omega + \Omega_v - 1$.

In the present study of the isolated ν_2 fundamental band of SO_2F_2 , the effective dipole moment is expanded up to order one, leading to a set of three parameters: $\tilde{\mu}^{0(0, A_1, a_1)}$, $\tilde{\mu}^{1(1, F_1, b_1)}$ and $\tilde{\mu}^{1(1, F_1, b_2)}$. However, the last two turned out to be non-determinable using the present data and were fixed to zero; as we show below, only the order zero parameter can be fitted.

4 Analysis and results

The analysis of line positions and intensities in the ν_2 band of SO_2F_2 involved a two-step process. We first assigned the line positions to determine parameters

involved in the Hamiltonian. Then, parameters involved in the dipole moment operator are obtained using the experimental line intensities and the corresponding wavefunctions of the effective Hamiltonian. Analysis were performed using the SPVIEW (Spectrum View) and C_{2v} TDS packages [18] dedicated to the simulation and to the fit of high-resolution molecular spectra.

4.1 *Line positions analysis*

4.1.1 *Line assignments*

As already mentioned, we performed a simultaneous analysis of the ground state and of the ν_2 fundamental band of sulfuranyl fluoride. For the ground state, we have used the microwave assignments of Ref. [6]. The infrared transitions of the ν_2 band, reported in the present work, were recorded at the SOLEIL Synchrotron at $T = 193$ K and at the pressure of 1 mbar where the lines are intense and unsaturated in the P and R branches (Fig. 1). The contributions of the ground state (GS) and of the ν_2 band to the effective Hamiltonians have been expanded up to order 4. The dipole moment has been expanded up to order one, leading to a set of 3 parameters.

To analyze the ν_2 fundamental band of SO_2F_2 , we needed as an initial step a first guess of the tensorial parameters. Initial assignments were based on parameters available in the literature. The results of the tensorial analysis performed by Hmida *et al.* [10] have been the starting point for the work explained here. The parameters of the GS have been fixed to the values of Table 1 of Ref. [11] whereas those of the ν_2 have been fixed to the values of Table 2 of Ref. [10]. These preliminary values allow a correct reproduction of the experimental spectrum when taking into account the experimental details such as temperature, resolution, pressure and path length. The initial set of tensorial parameters allowed us to start the analysis procedure which was rather straightforward. We made a preliminary simulation and assigned a few lines with the SPVIEW software by comparing the positions of experimental and calculated spectrum [36]. Following this step, a new set of parameters was determined. This set of parameters provided us a more accurate simulation of the spectrum and allowed us to continue the analysis by assigning transitions with higher J quantum numbers. This process was repeated until no more experimental lines could be assigned.

4.1.2 *Effective Hamiltonian fit and discussion*

This analysis is based on the use of the MW data of the ground state [6] and the IR data of the ν_2 band recorded at the SOLEIL Synchrotron. Among 29 parameters involved in the effective Hamiltonians of Eqs. (6) and (7), only 26

parameters are fitted. In this analysis, the ground state parameters are fitted except $\tilde{t}^{6(2,0F_2,a_1)}$ and $\tilde{t}^{6(4,0E,a_1)}$ are fixed to the value obtained in Ref. [11]. All possible parameters of the ν_2 band are fitted except $\tilde{t}^{4(4,0F_2,a_1)}$, which is kept to zero because its standard deviation being too high compared to its value. We notice that the $\tilde{t}^{4(0,0A_1,a_1)}$ and $\tilde{t}^{4(4,0A_1,a_1)}$ have now been fitted, knowing that in our previous work [10], they have been fixed to zero.

It should be noticed that keeping some parameters fixed is not equivalent to fixing the parameters in the two well-known A and S reductions defined by Watson [37,38]. As a matter of fact, fixing one parameter of the ν_2 band to zero in the present model does not mean to fix the corresponding parameter to zero in the Watson Hamiltonian.

Table 1 lists the tensorial rovibrational parameters obtained in this global fit. As it can be seen all parameters are well determined. In this analysis, the fit leads to more precise parameter values because we were able to assign significantly more lines (739 new weak lines were added and the value of J_{max} becomes 45 instead of 41) than in our previous study [10]. The ground state and the ν_2 parameters are very similar to previous works [10,11].

The corresponding values in the Watsonian model are given in Table 2. In this Table, we also compare the values of the ν_2 parameters up to the quadratic order in the Watsonian model as recalculated from our results with those of Refs. [8,10]. The tensorial parameters are converted to the Watson's ones thanks to formulas given in Ref. [30]. In this Reference, a detailed correspondence between the tensorial formalism and the usual approach of Watson is presented for asymmetric tops.

We can note from this Table that the Watson's rovibrational constants derived from this fit are in reasonably good agreement with previous works [8,10]. The current analysis gives very similar results with no significant differences for A , B and C constants and the quadratic centrifugal distortion constants are close to those obtained with the usual approach but no sextic parameters are used in our fit. The variation of the value of d_1 is due to the fact that the fixed parameters in both fits are not equivalent.

Using about 1070 MW data of the ground state up to $J = 98$ of Ref. [6] combined with our 2407 IR data of the ν_2 band up to $J = 45$, we obtained a RMS deviation of about $0.002 \times 10^{-3} \text{ cm}^{-1}$ and $0.19 \times 10^{-3} \text{ cm}^{-1}$, respectively. The results obtained are satisfactory. The RMS values of IR data is within the spectral resolution and frequency accuracy margins. The statistics for line positions analysis (number of lines included in the fit, maximum value of the quantum number J and standard deviations achieved for the ν_2 band) are reported in Table 3. In the same Table, we compare different analyses of the ν_2 band of SO_2F_2 . As it can be seen, more rovibrational transitions have been assigned, more parameters have been fitted and we have obtained better root mean square deviation (RMS) with less free adjustable parameters than in Ref. [8]. The present analysis also confirms that there is no need to develop the Hamiltonian to order 6 because the fit converges with lower order parameters.

Fig. 2 shows the experimental spectrum in comparison to the simulated one under the same experimental conditions ($T = 193$ K and $P = 1$ mbar) using the line list built in this work. As it can be seen, the calculation of intensities with the terms of zero order of the dipole moment was enough to get a rough profile and identify each line, as well. The detailed views in Figs. 3, 4 and 5 reveal the achieved accuracy of the calculated positions in the spectrum.

The infrared spectrum of the ν_2 band of sulfuryl fluoride has a PQR structure with well-separated J clusters which makes it relatively straightforward to analyze. These clusters are extremely dense for the higher values of the J quantum number. Compared to the P and R branches, only a few assignments have been performed in the very crowded Q branch. As it can be seen in Figs. 2 and 3 a hot band is visible, especially in the Q -branch region. Having no information about this hot band, it has neither been analysed, nor simulated. It should be noticed that the strong Q branch is saturated in the experimental spectrum.

The fit residuals of IR data for line positions in the ν_2 band are shown by black markers at the bottom of the Fig. 2. These observed minus calculated wavenumber errors appear to be homogeneous over the whole ν_2 band. The transitions are regularly distributed in the wavenumber range which implies a correct sampling of the whole band. The ($\nu_{obs} - \nu_{cal}$) differences do not exceed 0.001 cm^{-1} . No systematic deviation is observed and the results of the fit are reliable.

Fig. 6 displays the dependence of the fit residuals for line positions in the ground state rotational spectrum [6] as a function of the wavenumber which allows to give a global idea about the quality of the fit in this region.

Fig. 7 displays the calculated and observed reduced energy levels for the ν_2 fundamental band of sulfuryl fluoride. Observed reduced energy levels for ν_2 band, reached by assigned transitions, are obtained by subtracting the scalar terms, i.e.

$$E_{\text{red}} = E(J, n, \tilde{C}) - t^{2(0,0A_1,a_1)} J(J+1) - t^{4(0,0A_1,a_1)} J^2(J+1)^2 \quad (12)$$

This figure gives an idea of the ν_2 band energy spectrum used in the present fit.

4.2 Intensity analysis

The above-described line position analysis was a mandatory first step for the analysis of line intensities: the measured line intensities have been fitted using the wavefunctions of the effective Hamiltonian obtained from the line positions analysis. In this step, the hamiltonian parameters obtained from the fit position are fixed.

In this analysis, it was difficult to fit intensity parameters for such a heavy

molecule with a very congested spectrum consisting mostly of many overlapping lines. The IR spectra of the ν_2 band recorded at different pressures were very congested with no isolated lines. In addition, we have no information in the literature on the ν_2 dipole moment parameters. As an initial step, the dipole moment was roughly estimated by searching for the value reproducing the experimental spectra. Using the three spectra recorded at different pressure, we have built our experimental assignment file in averaging intensities and line positions over the three experimental spectra for a same theoretical label. This file has been used for our intensity analysis.

The effective dipole moment operator has been developed up to order one, leading to a set of three parameters. Using 71 experimental line intensities, only one parameter is determined. It is the parameter of order zero, the purely vibrational parameter, which corresponds to the traditional dipole moment derivative. The two parameters of order one are kept to zero because their standard deviation being too high compared to their value. The value of the fitted parameter $\tilde{\mu}^{(0,A_1,a_1)}$ is equal to 0.10257(30) Debye.

Fig. 8 presents the resulting residuals for the 71 line intensities fitted with a global root mean square deviation of 4.55 %. This RMS deviation is consistent with the uncertainty of the measurement which is around 5 %. Fig. 8 also shows that the residuals are smaller than 10 % on the calculated line intensities and that they do not exhibit systematic trends. Most of the absorption intensities for the very dense ν_2 band is well reproduced by the model. However, some problems remain, especially in the P branch. This is mainly due to the hot band lines not included in this analysis. In order to improve the results obtained, it will be interesting to model these hot bands or to improve the experimental conditions by recording spectra at a temperature below 193 K.

The parameter of the dipole moment, obtained in the present work, allows us to estimate the value of the integrated band intensity. As specified by previous work, the integrated band intensity has been determined for the bands observed in the 800 - 930 cm^{-1} spectral range of the sulfuryl fluoride spectrum [12,13] (Table 4) which corresponds mostly to the symmetric SF_2 stretching vibration ν_2 and the asymmetric SF_2 stretching vibration ν_8 . According to values computed at the MP2 level with the 6-31G(df) basis, these two bands, which fall within the atmospheric window and make the sulfuryl fluoride an efficient atmospheric greenhouse, possess infrared intensities of about 118.6 km/mol and 231.5 km/mol , respectively [14]. In our team, all electrons *ab initio* intensities calculations were carried out at the level MP2/cc-pV(T+d)Z. We obtained for ν_2 and ν_8 , 126.9 km/mol ($2.10 \times 10^{-17} \text{ cm}^{-1}/(\text{molecule cm}^{-2})$) and 246.0 km/mol ($4.08 \times 10^{-17} \text{ cm}^{-1}/(\text{molecule cm}^{-2})$), respectively. These results are in agreement with those of the reference [14].

In the present work, we calculated the integrated band intensity S_{band} for the ν_2 band using the line list generated as described in Section 4.1 and the following approximate relation:

$$S_{band} = \frac{Q_{vib}}{I_a} \sum_k S_k \quad (13)$$

Q_{vib} is the vibrational partition function computed within the harmonic approximation. For SO_2F_2 , Q_{vib} is estimated to 1.5157 at 296 K. $I_a = 0.99$ is the isotopic abundance of $^{32}\text{S}^{16}\text{O}_2\text{F}_2$. S_k is the intensity of line k .

The integrated band intensity calculated at 296 K for the ν_2 band of SO_2F_2 is about 85 km/mol or $1.41 \times 10^{-17} \text{ cm}^{-1}/(\text{molecule cm}^{-2})$ which is less than the value predicted by the *ab initio* calculation.

In Table 4 are compared the intensities for the ν_2/ν_8 region from cross section studies of references [12] and [13] with the integrated band intensity derived from the present study. Note that the total intensity estimated from the cross sections corresponds to the sum of the ν_2 and ν_8 contributions. Compared to the cross sections reported in the literature [12,13] merging the intensities of both ν_2 and ν_8 , of quite unequal relative intensities, it seems reasonable to estimate that the integrated intensity for ν_2 is of the order of $2 \times 10^{-17} \text{ cm}^{-1}/(\text{molecule cm}^{-2})$ or less. This value is to be compared to our more reliable estimate of $1.41 \times 10^{-17} \text{ cm}^{-1}/(\text{molecule cm}^{-2})$.

5 Conclusion

A complete line position and intensity analysis of the ν_2 band of SO_2F_2 was performed using the $C_{2v}\text{TDS}$ software. This is the first time that an intensity analysis has been carried out for this molecule. 2407 line positions and 71 intensities were fitted.

The IR spectrum of the ν_2 band was analyzed up to $J = 45$ and provided a set of 26 tensorial parameters without the need to include any sextic parameters. These parameters allow us to calculate the line positions with a precision of about $0.19 \times 10^{-3} \text{ cm}^{-1}$. The parameter for the expansion of the transition dipole moment yields to intensities correct to within 4.55 %. We can thus estimate to 10 % the accuracy of calculated line intensities using the present tensorial model.

6 Acknowledgments

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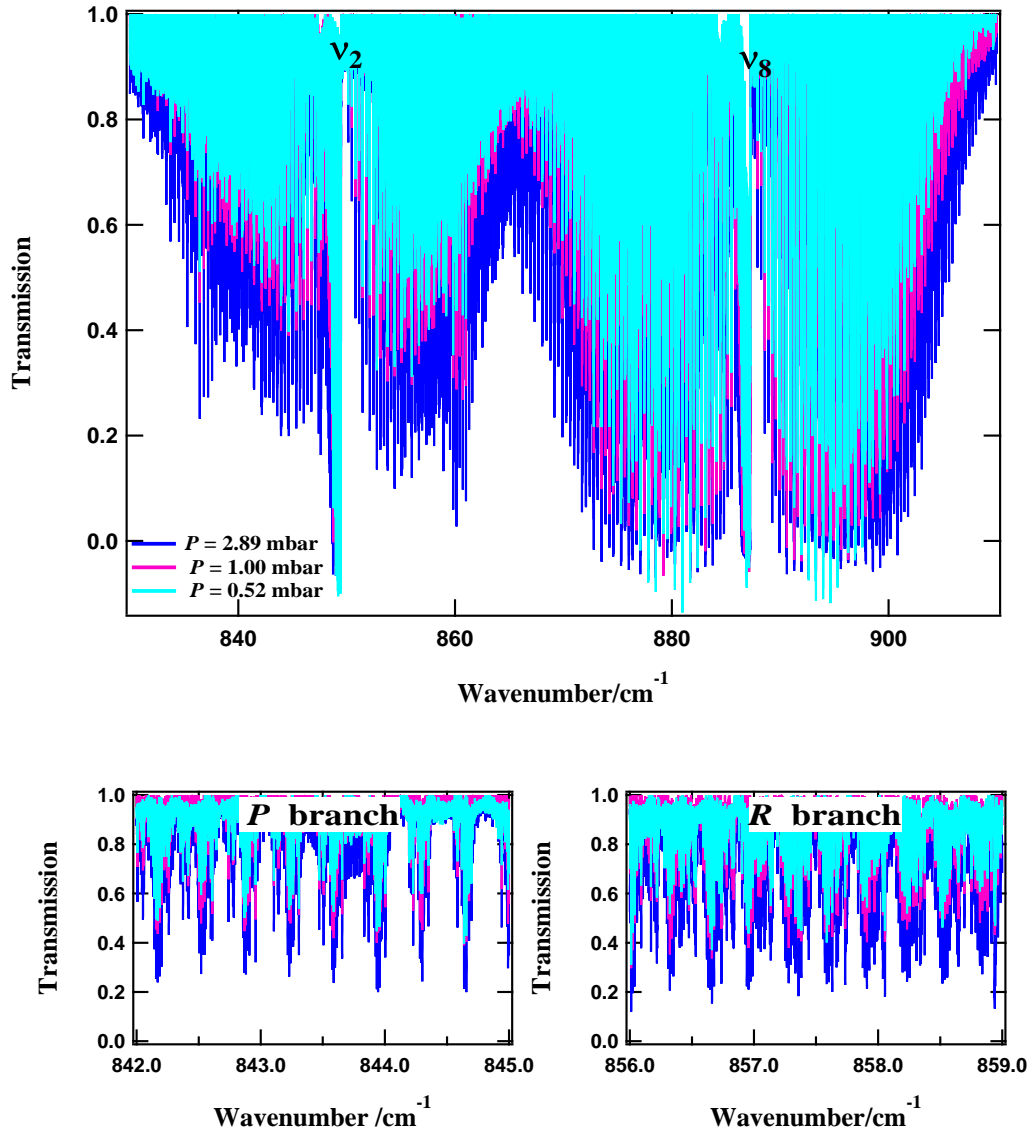


Fig. 1. Survey spectra of the ν_2 and ν_8 bands of SO_2F_2 recorded at $T = 193$ K at the AILES beamline of SOLEIL Synchrotron. These two bands overlap in the $860\text{-}870\text{ cm}^{-1}$ region.

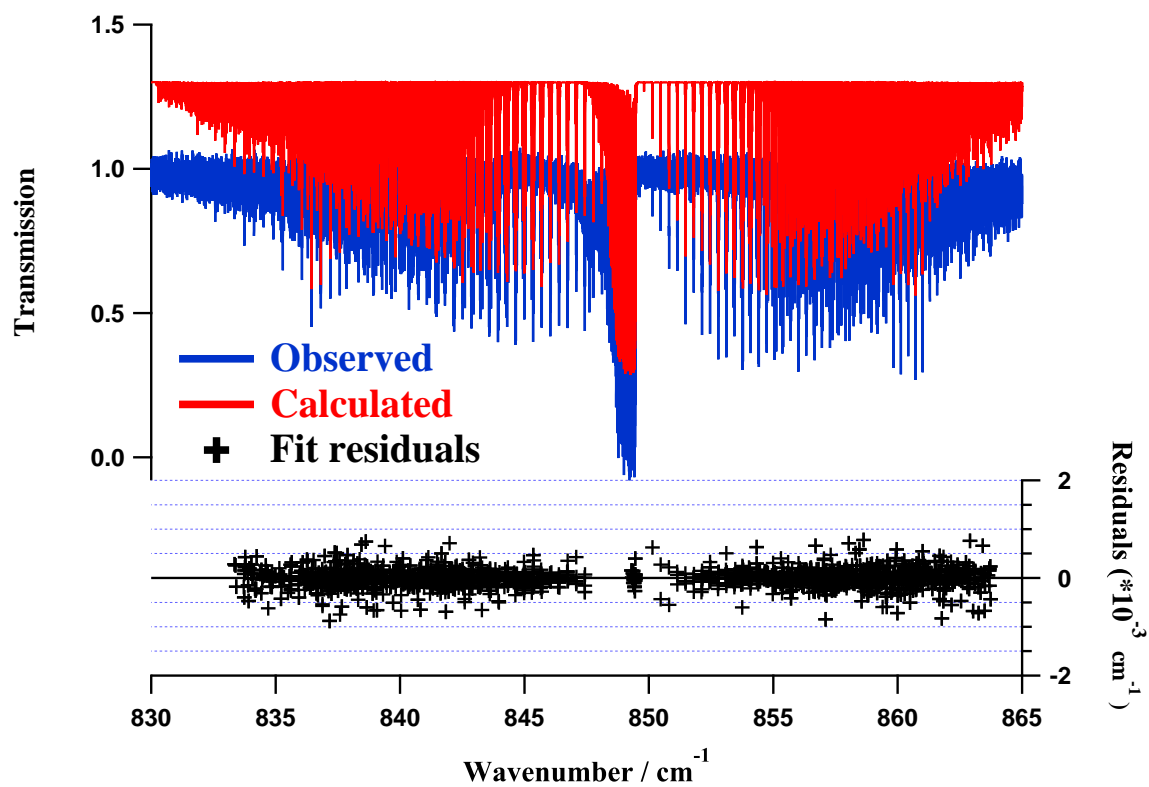


Fig. 2. Comparison of the observed spectrum of the ν_2 band of SO_2F_2 recorded at $T = 193$ K and $P = 1$ mbar (blue) with simulation using results of the present work (red). The corresponding difference between the observed and calculated line positions is presented in the lower panel. The simulated spectra is offset by 0.25 for clarity.

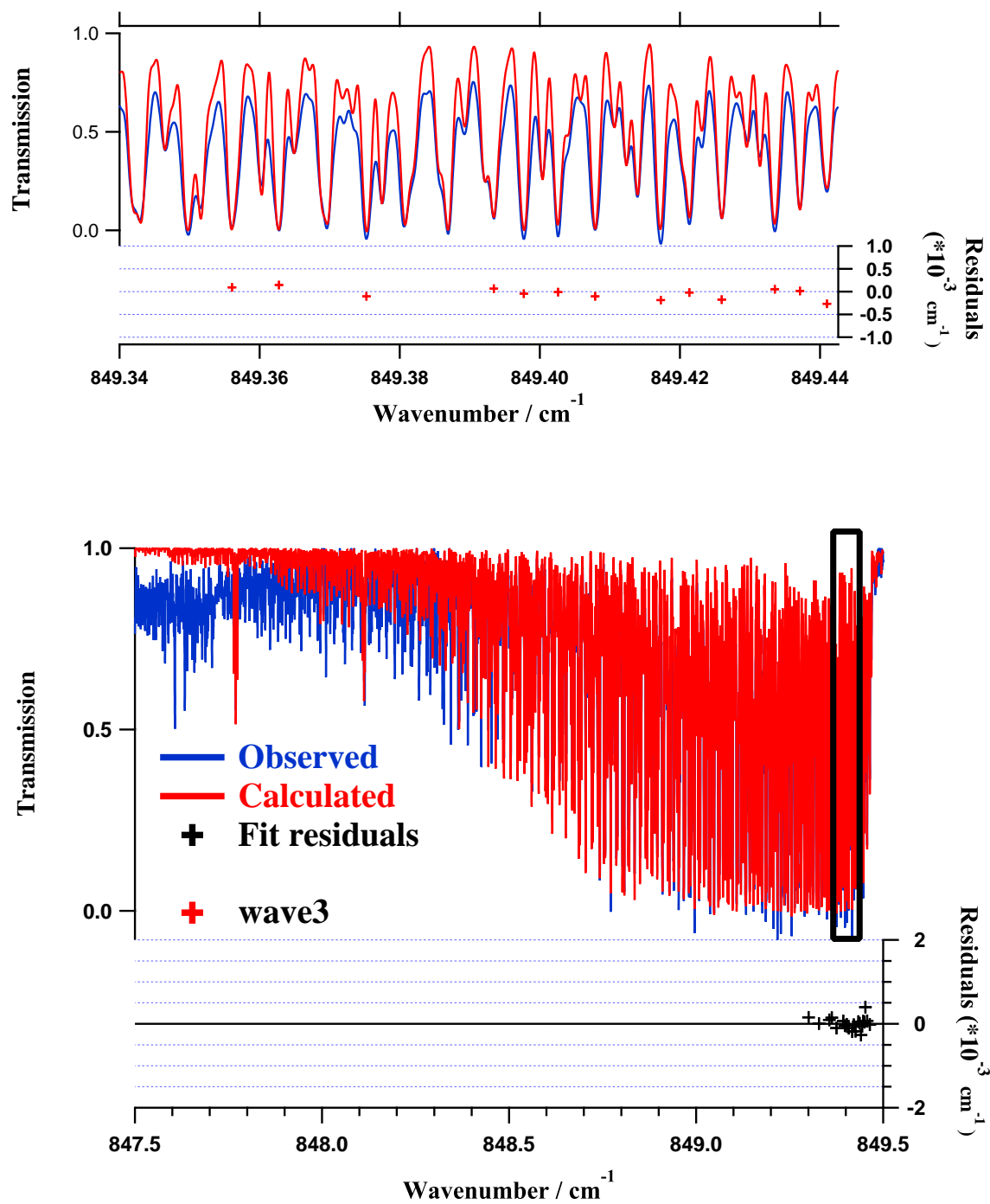


Fig. 3. Overview of the Q branch of the ν_2 band of SO_2F_2 , compared to the simulation at $T = 193 \text{ K}$ and $P = 1 \text{ mbar}$.

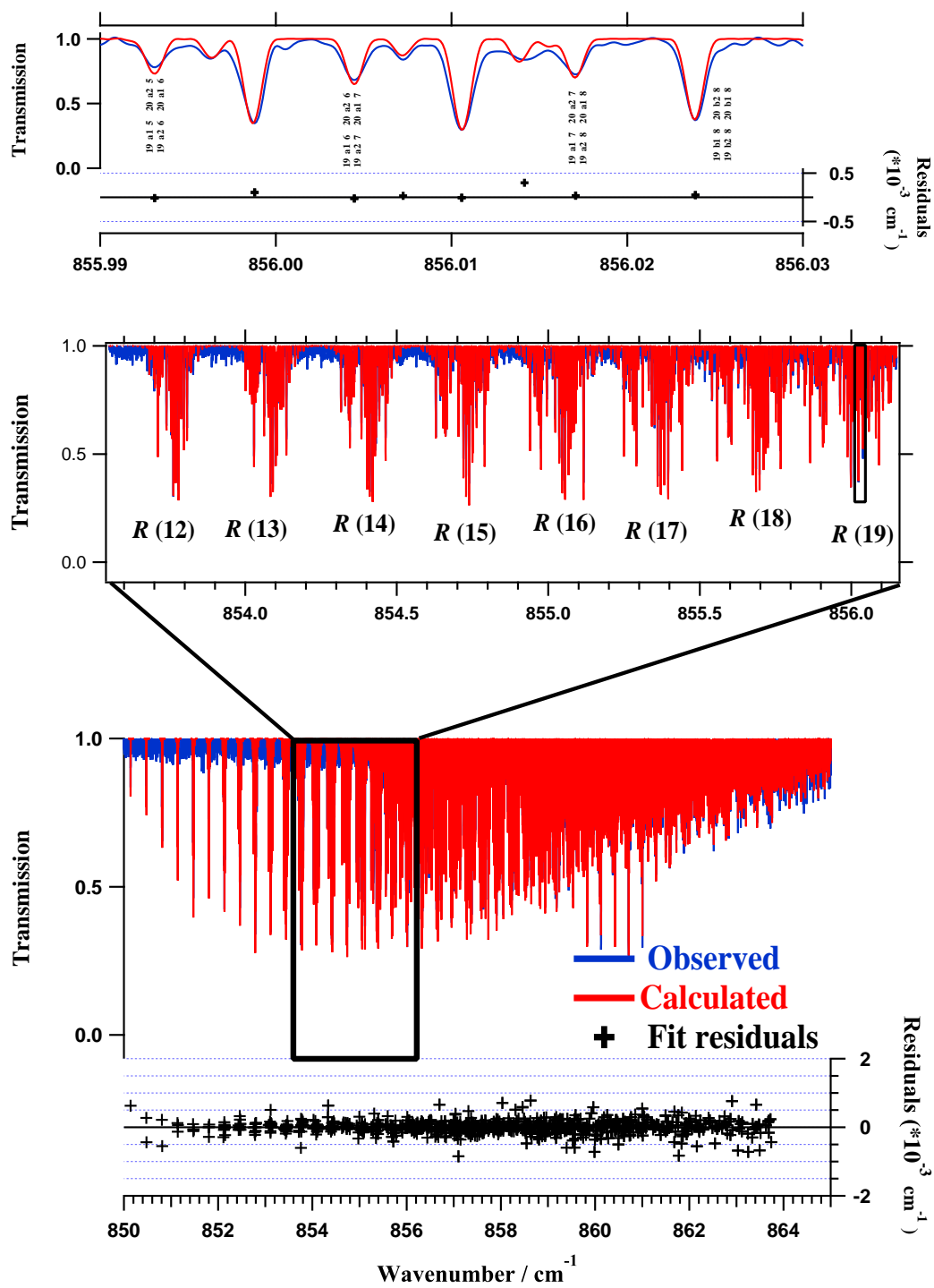


Fig. 4. Comparison between the experiment spectrum and the simulation in the R branch of the ν_2 band, showing the good agreement of the fit.

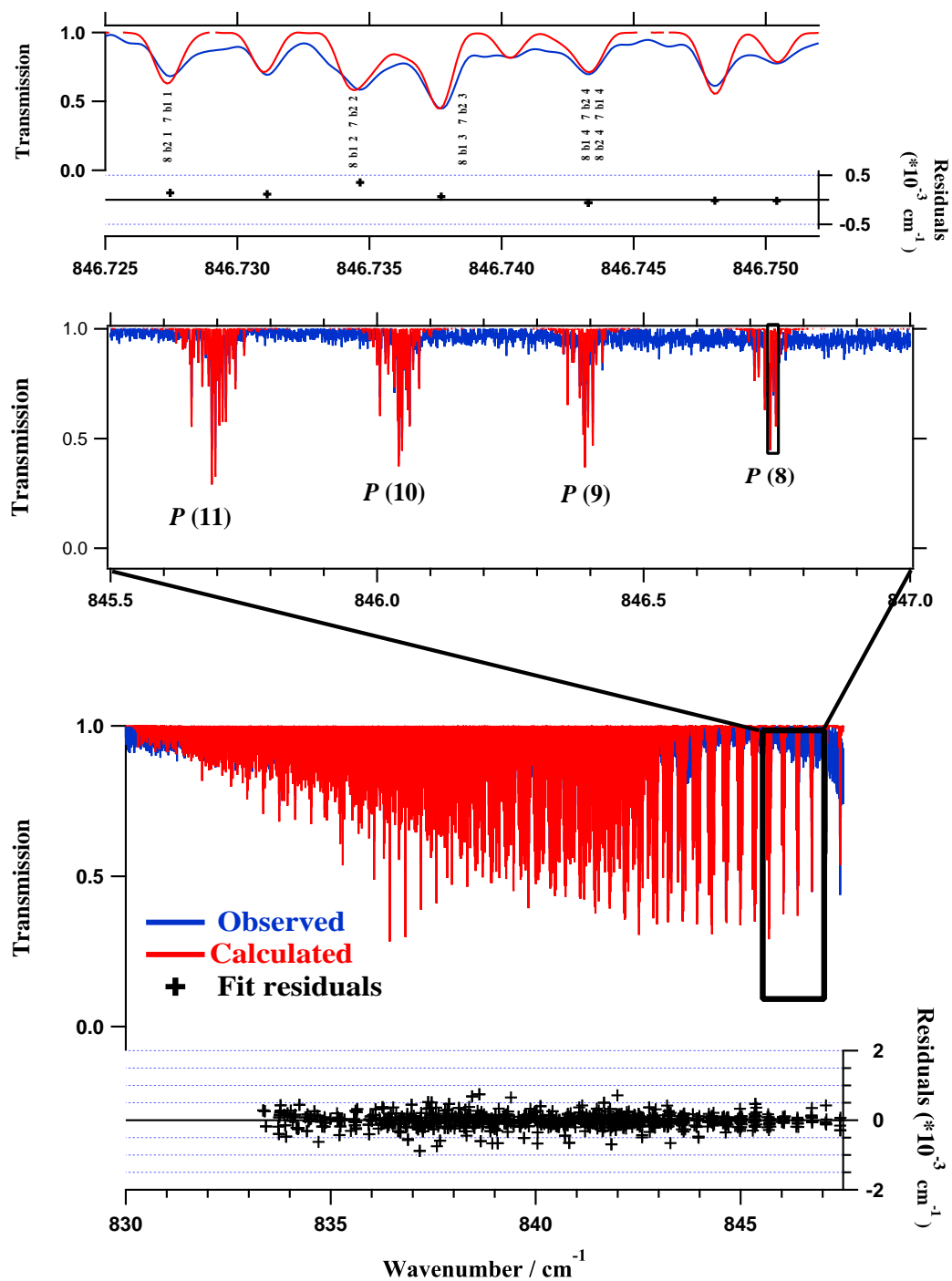


Fig. 5. Comparison between the experiment spectrum and the simulation in the P branch of the ν_2 band, showing the good agreement of the fit

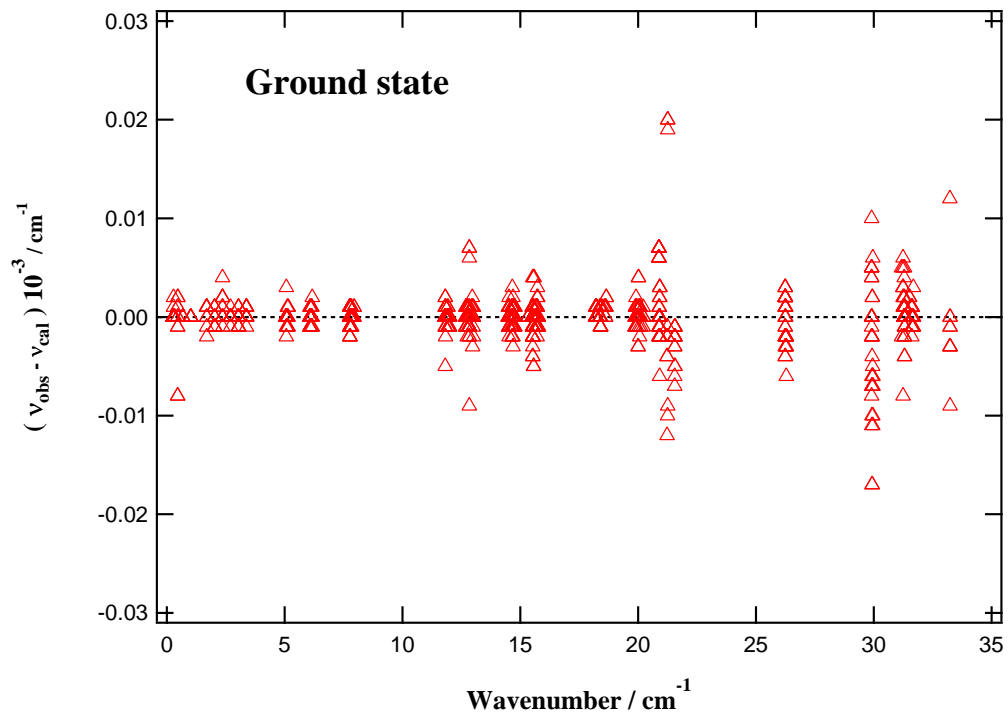


Fig. 6. Fit residuals for line positions in the case of the ground state of SO_2F_2 with the tensorial model.

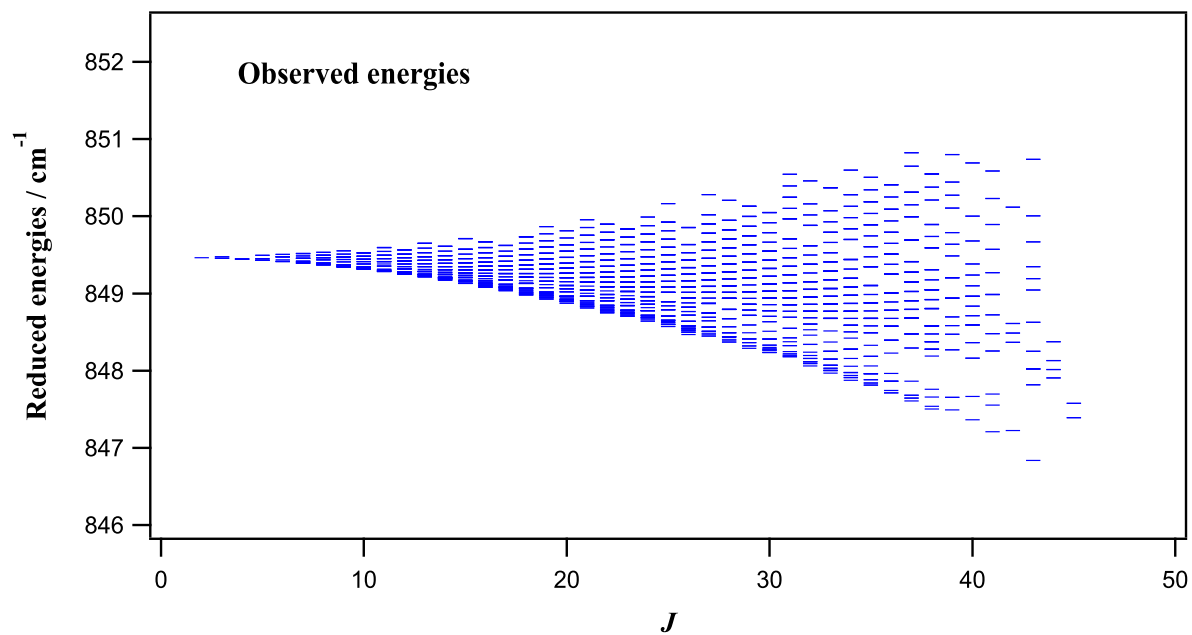
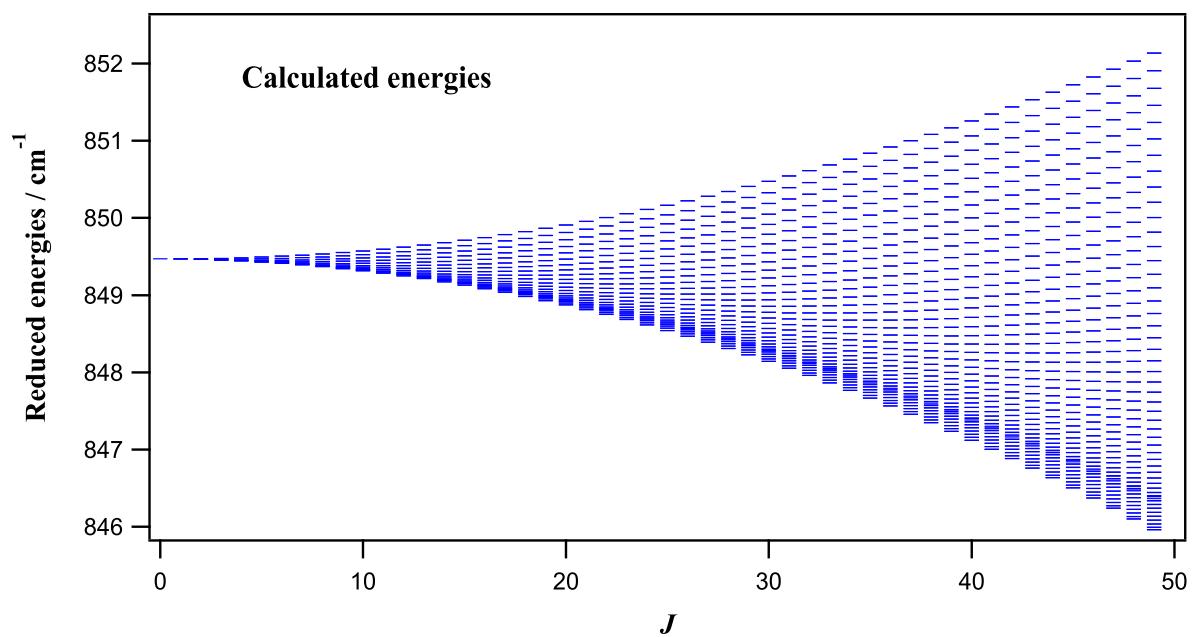


Fig. 7. Observed and calculated reduced energies for the ν_2 band of SO_2F_2 using the tensorial model. "Observed" levels correspond to those reached by assigned transitions.

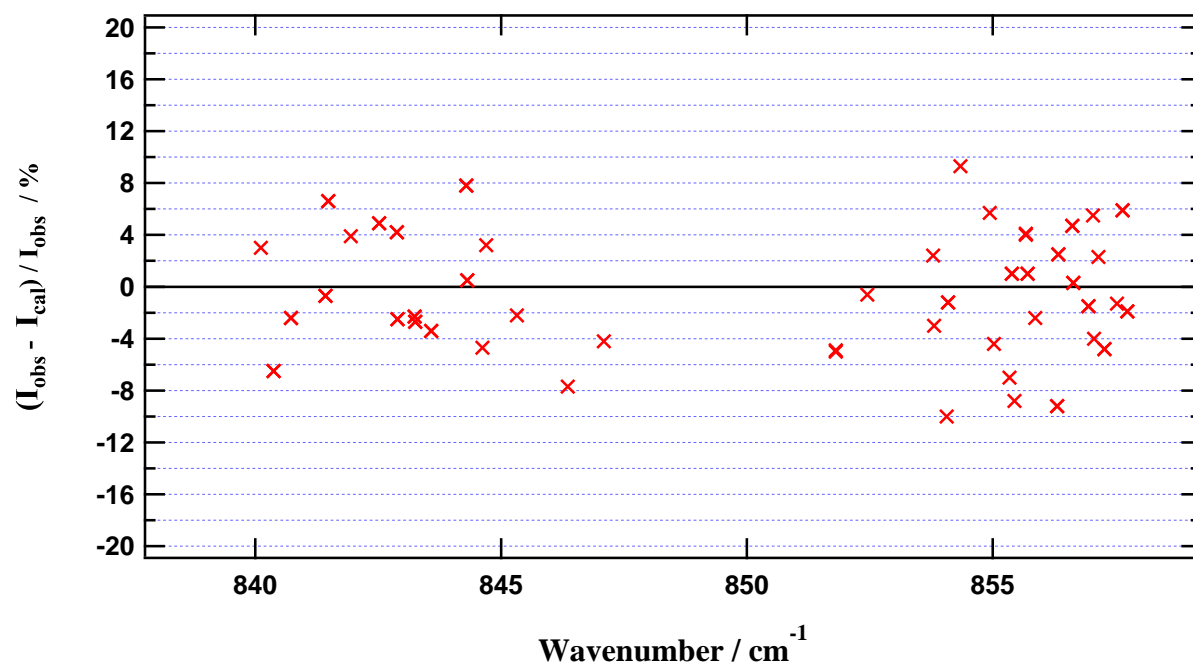


Fig. 8. Residuals on the line intensities versus the wavenumber for the ν_2 band of SO_2F_2 .

Table 1
Values of the effective Hamiltonian parameters of the ground state and the ν_2 band with the tensorial formalism.

Polyad	Order	$\Omega(K, m\Gamma, \tilde{\Gamma})$	Parameter $t_{\{ns\}\{ms'\}}^{\Omega(K, m\Gamma, \tilde{\Gamma})\Gamma_v \Gamma'_v}$	$\{s\}\Gamma_v$	$\{s'\}\Gamma'_v$	This work	Value (cm^{-1})	Ref. [10]
GS	0	$2(0, 0A_1, a_1)$	0000A ₁	0000A ₁	0000A ₁	0.1697286568(28)	0.1697286576(24)	
	0	$2(2, 0E, a_1)$	0000A ₁	0000A ₁	0000A ₁	$4.7533510(86) \times 10^{-4}$	$4.7533462(71) \times 10^{-4}$	
	0	$2(2, 0F_2, a_1)$	0000A ₁	0000A ₁	0000A ₁	$9.447574(55) \times 10^{-5}$	$9.447533(49) \times 10^{-5}$	
	2	$4(0, 0A_1, a_1)$	0000A ₁	0000A ₁	0000A ₁	$-4.465470(88) \times 10^{-8}$	$-4.465489(76) \times 10^{-8}$	
	2	$4(2, 0E, a_1)$	0000A ₁	0000A ₁	0000A ₁	$9.45(17) \times 10^{-11}$	$9.443(21) \times 10^{-11}$	
	2	$4(2, 0F_2, a_1)$	0000A ₁	0000A ₁	0000A ₁	$6.781(91) \times 10^{-10}$	$6.7748(16) \times 10^{-10}$	
	2	$4(4, 0A_1, a_1)$	0000A ₁	0000A ₁	0000A ₁	$-2.5638(27) \times 10^{-9}$	$-2.563650(74) \times 10^{-9}$	
	2	$4(4, 0E, a_1)$	0000A ₁	0000A ₁	0000A ₁	$-6.368(45) \times 10^{-11}$	$-6.3672(70) \times 10^{-11}$	
	2	$4(4, 0F_2, a_1)$	0000A ₁	0000A ₁	0000A ₁	$-5.64(14) \times 10^{-10}$	-5.635×10^{-10} (Fixed)	
	4	$6(0, 0A_1, a_1)$	0000A ₁	0000A ₁	0000A ₁	$1.742(11) \times 10^{-14}$	$1.7420(91) \times 10^{-14}$	
	4	$6(2, 0E, a_1)$	0000A ₁	0000A ₁	0000A ₁	$-5.8(2.9) \times 10^{-17}$	$-6.4(17) \times 10^{-17}$	
	4	$6(2, 0F_2, a_1)$	0000A ₁	0000A ₁	0000A ₁	1.93×10^{-16}	$1.93(66) \times 10^{-16}$	
	4	$6(4, 0A_1, a_1)$	0000A ₁	0000A ₁	0000A ₁	$-6.16(18) \times 10^{-16}$	$-6.14(34) \times 10^{-16}$	
	4	$6(4, 0E, a_1)$	0000A ₁	0000A ₁	0000A ₁	-2.50×10^{-17}	$-2.5(28) \times 10^{-17}$	
	4	$6(4, 0F_2, a_1)$	0000A ₁	0000A ₁	0000A ₁	$8.8(1.6) \times 10^{-16}$	$8.85(76) \times 10^{-16}$	
	4	$6(6, 0A_1, a_1)$	0000A ₁	0000A ₁	0000A ₁	$3.38(16) \times 10^{-16}$	$3.33(37) \times 10^{-16}$	
	4	$6(6, 0E, a_1)$	0000A ₁	0000A ₁	0000A ₁	$-3.59(26) \times 10^{-16}$	$-3.64(13) \times 10^{-16}$	
	4	$6(6, 0F_2, a_1)$	0000A ₁	0000A ₁	0000A ₁	$1.09(11) \times 10^{-15}$	$1.11(21) \times 10^{-15}$	
	4	$6(6, 1F_2, a_1)$	0000A ₁	0000A ₁	0000A ₁	$6.63(56) \times 10^{-16}$	$6.660(80) \times 10^{-16}$	
	$\nu_2 = 1$	0	$0(0, 0A_1, a_1)$	1000A ₁	1000A ₁	1000A ₁	849.469601(18)	849.469409(78)
2		$2(0, 0A_1, a_1)$	1000A ₁	1000A ₁	1000A ₁	$-5.19716(48) \times 10^{-4}$	$-5.1945(13) \times 10^{-4}$	
2		$2(2, 0E, a_1)$	1000A ₁	1000A ₁	1000A ₁	$4.3216(19) \times 10^{-5}$	$4.322(16) \times 10^{-5}$	
2		$2(2, 0F_2, a_1)$	1000A ₁	1000A ₁	1000A ₁	$-1.25014(67) \times 10^{-4}$	$-1.2503(28) \times 10^{-4}$	
4		$4(0, 0A_1, a_1)$	1000A ₁	1000A ₁	1000A ₁	$2.28(31) \times 10^{-10}$	0.0	
4		$4(2, 0E, a_1)$	1000A ₁	1000A ₁	1000A ₁	$1.851(71) \times 10^{-10}$	$1.87(67) \times 10^{-10}$	
4		$4(2, 0F_2, a_1)$	1000A ₁	1000A ₁	1000A ₁	$-3.11(40) \times 10^{-10}$	$-3.2(13) \times 10^{-10}$	
4		$4(4, 0A_1, a_1)$	1000A ₁	1000A ₁	1000A ₁	$3.6(1.5) \times 10^{-10}$	0.0	
4		$4(4, 0E, a_1)$	1000A ₁	1000A ₁	1000A ₁	$-1.53(20) \times 10^{-10}$	$-1.83(49) \times 10^{-10}$	
4		$4(4, 0F_2, a_1)$	1000A ₁	1000A ₁	1000A ₁	0.0	0.0	

Table 2

The ν_2 Watson parameters up to the quadratic order calculated from the fitted values of the tensorial parameters in table 2.

Parameters	Calculated values / cm^{-1}	Ref. [10] / cm^{-1}	Ref. [8] / cm^{-1}
E_0	849.469601(18)	849.469409(78)	849.4696554(58)
A	0.17090248(18)	0.1709028(12)	0.170902455(24)
B	0.16844854(27)	0.1684488(12)	0.168448698(12)
C	0.16827577(11)	0.16827598(40)	0.168275651(12)
$D_J \times 10^8$	4.851(14)	4.875(35)	4.86287(25)
$D_{JK} \times 10^8$	-4.822(87)	-4.84(17)	-4.8971(15)
$D_K \times 10^8$	5.994(90)	6.02(11)	6.0517(22)
$d_1 \times 10^8$	-0.001(19)	-0.003(42)	-0.01334(29)
$d_2 \times 10^8$	0.5082(77)	0.521(11)	0.51554(29)

Table 3

Statistical details on the comparison of the analysis of the ν_2 band with Refs. [8,10].

	Ref. [8]	Ref. [10]	This work
Experimental details			
Temperature (K)	296	165	193
Pressure (mbar)	10 SO ₂ F ₂ - 1000 He	1.99×10^{-2}	1
Resolution cm^{-1}	0.0024	0.00102	0.00102
Fit analysis			
Degree of development	6	4	4
Number of IR assignments	1873	1668	2407
Fitted parameters	13/16	7/10	9/10
Fixed parameters	3	3	1
J_{max}	68	41	45
RMS (cm^{-1})	0.40×10^{-3}	0.20×10^{-3}	0.19×10^{-3}

Table 4

The integrated band intensity at 296 K determined for the ν_2 band of SO_2F_2 within the ν_2/ν_8 region.

Integration range (cm^{-1})	Band strength ($10^{-17} \text{ cm}^2 \text{ molecule}^{-1} \text{ cm}^{-1}$)		
	Dillon <i>et al.</i> : [13] (2008)	Papadimitriou <i>et al.</i> : [12] (2008)	This work
820 - 865	-	-	1.41
800.8 - 927.6	5.7	5.84	-

The 820 - 865 cm^{-1} spectral range corresponds to the ν_2 band which represents about 1/3 of the total intensity.

The 800.8 - 927.6 cm^{-1} spectral range corresponds to the ν_2 and ν_8 bands. The ν_8 represents about 2/3 of the total intensity.

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