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# Analysis and modeling of combination bands of sulfur hexafluoride $^{32}\text{SF}_6$ based on global fits. Update of the SHeCaSDa database.

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## Abstract

Sulfur hexafluoride is a powerful greenhouse gas of industrial origin. Remote-sensing detection of this heavy species requires a detailed knowledge of its infrared absorption spectra that features many hot bands at room temperature. It is thus necessary to study many of its rovibrational levels which are implied in such hot band transitions. Based on our previous results reporting global fits of many rovibrational bands [M. Faye *et al.*, *J. Quant. Spectrosc. Radiat. Transfer* **190**, 38–47 (2017)], we present here detailed analyses of three combination bands, namely  $\nu_1 + \nu_4$ ,  $\nu_2 + \nu_6$  and  $\nu_5 + \nu_6$ . The  $\nu_2 + \nu_6$  combination band has been already investigated some years ago, but the present analysis represents a strong improvement; the two other bands are analyzed in detail for the first time. The results contribute to improve the simulation of hot bands in the strongly absorbing  $\nu_3$  and  $\nu_4$  regions and they have been used to update the SHeCaSDa database (<http://vamdc.icb.cnrs.fr/PHP/shecasda.php>).

*Keywords:* Sulfur hexafluoride, Greenhouse gases, Combination bands, Tensorial formalism, Spectroscopic database update

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## 1. Introduction

Sulfur hexafluoride ( $\text{SF}_6$ ) is a very strong greenhouse gas of industrial origin and whose concentration should be monitored and reduced, according to the Kyoto Protocol [1, 2, 3, 4, 5, 6, 7, 8]. It has a very long lifetime in the atmosphere of around 3200 years [9], since it is chemically inert. It is also used as an atmospheric tracer [10, 11, 12, 13, 14]. In order to perform remote-sensing detection of this molecule, one needs a very good modeling and/or a complete rovibrational line database for its infrared absorption spectrum. This is, however, quite difficult for  $\text{SF}_6$ . This heavy species possesses a dense and complex spectrum. Due to the presence of low-lying vibrational states, the ground state population is only 32 % at room temperature [15] and, as a consequence, a large number of hot band transitions constitutes the major part of the absorption spectrum of  $\text{SF}_6$ . At present, public databases HITRAN [16] and GEISA [17] are largely incomplete for this molecule: they only contain  $\nu_4$  and  $\nu_3$  cold band lines and  $\nu_4 + \nu_6 - \nu_6$  hot band lines for the main isotopologue,  $^{32}\text{SF}_6$ , as calculated from our previous works and given as supplementary files.

In order to compute hot band spectra, one needs to get a detailed knowledge of the different rovibrational levels implied in these transitions. For this, for many years, we have undertaken a systematic study of as many as possible vibrational bands [15]. As a matter of fact, despite some early pioneering works using simplified models [18, 19, 20], no detailed systematic and quantitative study existed before the very end of the 1990's. Our first work was dedicated to the first analysis of a combination band of  $\text{SF}_6$ , namely  $\nu_2 + \nu_6$ , using supersonic jet-cooled infrared absorption spectroscopy [21]. Then, high-resolution stimulated Raman spectroscopy from the CSIC group in Madrid was of great importance to access vibrational levels with  $g$  parity of this centrosymmetric species [22, 23, 24, 25]. The  $\nu_4$  bending region in the infrared could be studied, along with the first hot band to be analyzed for this species, namely  $\nu_4 + \nu_6 - \nu_6$  [26]. Different combination and difference bands could also be analyzed [27, 28, 29, 30]. The low-lying “forbidden” mode  $\nu_6$ , which is the origin

of many hot bands, could be studied in detail for the first time, since it gains a very weak intensity through Coriolis couplings with other vibrational modes [31]. Finally, we recently published a detailed study of many stretching bands using global fits [32].

35 Some works were also dedicated to SF<sub>6</sub>'s minor isotopologues <sup>33</sup>SF<sub>6</sub> [21], <sup>34</sup>SF<sub>6</sub> [21, 24, 25] and even <sup>36</sup>SF<sub>6</sub> [33].

All these studies were carried out thanks to the tensorial formalism tools developed in the Dijon group [34, 35, 36, 37, 38] and to the XTDS and SPVIEW dedicated softwares [39].

40 Relying on the results of our recent global fits [32], we present in this paper new analyses of three combination bands of <sup>32</sup>SF<sub>6</sub>, namely  $\nu_1 + \nu_4$ ,  $\nu_2 + \nu_6$  (as a strong improvement compared to Refs. [21, 22]) and  $\nu_3 + \nu_5$ . This continues the “SF<sub>6</sub> combination level quest”.

Section 2 presents some general considerations about the theoretical model  
45 and tools used. We present the experimental details in Section 3, while Section 4 gives the analysis, assignment and simulation results. Section 5 explains the recent update of the SheCaSDa (**S**ulfur **H**exafluoride **C**alculated **S**pectroscopic **D**atabase) database of SF<sub>6</sub> calculated line lists that is built in the framework of the VAMDC international portal [40, 41, 42, 43]. Finally, Section 6 concludes  
50 and gives some perspectives to this work.

## 2. Theoretical elements

### 2.1. Generalities about SF<sub>6</sub> vibrations

In its equilibrium configuration, SF<sub>6</sub> is a centrosymmetric regular octahedron, belonging to the  $O_h$  point group. The SF<sub>6</sub> molecule has six normal vibra-  
55 tional modes [15]:

- $\nu_1$  is a non-degenerate stretching mode with  $A_{1g}$  symmetry (band center: 774.5 cm<sup>-1</sup>);
- $\nu_2$  is a doubly degenerate stretching mode with  $E_g$  symmetry (band center: 643.4 cm<sup>-1</sup>);

- 60 •  $\nu_3$  is a triply degenerate stretching mode with  $F_{1u}$  symmetry (band center: 948.1  $\text{cm}^{-1}$ );
- $\nu_4$  is a triply degenerate bending mode with  $F_{1u}$  symmetry (band center: 615.0  $\text{cm}^{-1}$ );
- $\nu_5$  is a triply degenerate bending mode with  $F_{2g}$  symmetry (band center: 523.5  $\text{cm}^{-1}$ );
- 65 •  $\nu_6$  is a triply degenerate bending mode with  $F_{2u}$  symmetry (band center: 346.9  $\text{cm}^{-1}$ ).

Among those vibrations, only the  $F_{1u}$  fundamental vibrational modes ( $\nu_3$  and  $\nu_4$ ) are IR active, while  $A_{1g}$ ,  $E_g$  and  $F_{2g}$  vibrational modes ( $\nu_1$ ,  $\nu_2$  and  $\nu_5$ ) are Raman scattering active only, in first approximation. The  $F_{2u}$  fundamental ( $\nu_6$ ) is inactive in both IR absorption and Raman scattering, again in first approximation, although it can get a faint intensity through Coriolis couplings with the other modes [31].

Following group theoretical symmetry rules, harmonic and combination bands 75 of the above-described normal modes usually possess several vibrational sublevels, which are separated through anharmonic interactions. For instance, the three combination bands studied in this article have the following sublevels:

- Combination band  $\nu_1 + \nu_4$  contains only one sublevel, since

$$A_{1g} \otimes F_{1u} = F_{1u}. \quad (1)$$

- Combination band  $\nu_2 + \nu_6$  contains two sublevels, since

$$E_g \otimes F_{2u} = F_{1u} \oplus F_{2u}. \quad (2)$$

- 80 • Combination band  $\nu_5 + \nu_6$  contains four sublevels, since

$$F_{2g} \otimes F_{2u} = A_{1u} \oplus E_u \oplus F_{1u} \oplus F_{2u}. \quad (3)$$

(in the above expressions,  $\otimes$  represents the direct product and  $\oplus$  the direct sum of  $O_h$  group irreducible representations).

Vibrational transitions follow the parity selection rule: since the dipole moment operator has  $u$  parity, dipolar absorption or emission imply a parity change ( $u \rightarrow g$  or  $g \rightarrow u$ ) between the initial and final vibrational state, while a Raman scattering transition implying the polarizability operator with  $g$  parity implies parity conservation ( $g \rightarrow g$  or  $u \rightarrow u$ ). The IR absorption active vibrational bands have thus  $u$  parity and the Raman scattering active vibrational bands have  $g$  parity. In other words, when starting from the ground state ( $g$  parity), one can only reach  $u$  parity vibrational levels through IR absorption, or  $g$  parity vibrational levels by using Raman spectroscopy. The sublevels of  $\nu_1 + \nu_4$ ,  $\nu_2 + \nu_6$  and  $\nu_5 + \nu_6$  have  $u$  parity, and are thus observable through IR absorption. Since SF<sub>6</sub> is a heavy molecule with low-lying vibrational levels that are heavily populated at room temperature, however, it is necessary to cool down the molecules in order to simplify the spectrum by removing as many as possible of these hot band transitions.

## 2.2. Effective Hamiltonian

We use here the tensorial formalism and vibrational extrapolation methods developed in the Dijon group [34, 35, 36] and that were specially adapted to octahedral molecules in Ref. [37]. This formalism is implemented in the XDTS software [39]. We summarize here the essential points which are important for the present study.

We can construct the rovibrational Hamiltonian for the SF<sub>6</sub> molecule in the following manner. The rovibrational Hamiltonian operator for a given group of vibrational levels, of polyad, say  $P_k$  (see below), is expanded in the form:

$$H_{\{P_k\}} = \sum_{\text{all indices}} t_{\{s\}\{s'\}}^{\Omega(K,n\Gamma)\Gamma_v\Gamma'_v} T_{\{s\}\{s'\}}^{\Omega(K,n\Gamma)\Gamma_v\Gamma'_v}. \quad (4)$$

In this equation, all indices stand for intermediate quantum numbers and symmetries. Briefly,  $\Gamma$ ,  $\Gamma_v$  and  $\Gamma'_v$  are a rotational and two vibrational irreducible representations, respectively, while  $K$  is an integer (rotational degree),  $n$  is a multiplicity index (counting identical irreducible representations  $\Gamma$  for a given

110  $K$  value), while  $\{s\}$  and  $\{s'\}$  represent intermediate symmetry labels in the construction of vibrational operators [34];  $\Omega$  is defined below. The term  $t_{\{s\}\{s'\}}^{\Omega(K,n\Gamma)\Gamma_v\Gamma'_v}$  represents numerical parameters of the model to be fitted using experimental line assignments. The term  $T_{\{s\}\{s'\}}^{\Omega(K,n\Gamma)\Gamma_v\Gamma'_v}$  refers to totally symmetric rovibrational operators:

$$T_{\{s\}\{s'\}}^{\Omega(K,n\Gamma)\Gamma_v\Gamma'_v} = \beta(R^{\Omega(K,n\Gamma)} \otimes \varepsilon V_{\{s\}\{s'\}}^{\Gamma_v\Gamma'_v(\Gamma)})^{(A_{1g})}, \quad (5)$$

115 where  $\beta$  is a numerical factor used to modify the scalar terms so that they get a standard form:

$$\beta = \begin{cases} \sqrt{[\Gamma]}(-\sqrt{3}/4)^{\Omega/2} & , \text{ if } (K, n\Gamma) = (0, 0A_{1g}), \\ 1 & , \text{ otherwise,} \end{cases} \quad (6)$$

where  $[\Gamma]$  is the dimension of irreducible representation  $\Gamma$ .  $R^{\Omega(K,n\Gamma)}$  is a rotational operator of degree  $\Omega$  in the angular momentum components  $(J_x, J_y, J_z)$ , while  $\varepsilon V_{\{s\}\{s'\}}^{\Gamma_v\Gamma'_v(\Gamma)}$  is a vibrational operator of degree  $\Omega_v$  in vibration creation and annihilation operators. The order of each individual term is defined as 120  $\Omega + \Omega_v - 2$ . The recursive construction of these operators has been described elsewhere [44, 34, 36].

Consider a species whose molecular vibrational levels are grouped into a series of polyads named  $P_k$  ( $k = 0, \dots, n$ ),  $P_0$  being the ground state. We can 125 expand the rovibrational effective Hamiltonian operator as follows, after performing some Van Vleck [45] contact transformations to isolate polyads [34]:

$$\tilde{H} = H_{\{P_0\}} + H_{\{P_1\}} + \dots + H_{\{P_n\}}, \quad (7)$$

where  $H_{\{P_k\}}$  contains rovibrational operators with no matrix element within the  $P_{k' < k}$  basis sets. The effective Hamiltonian for polyad  $P_n$  is obtained by 130 projecting  $H$  in the  $P_n$  Hilbert subspace:

$$\tilde{H}^{\langle P_n \rangle} = P^{\langle P_n \rangle} H P^{\langle P_n \rangle} = H_{\{GS\}}^{\langle P_n \rangle} + \dots + H_{\{P_k\}}^{\langle P_n \rangle} + \dots + H_{\{P_n\}}^{\langle P_n \rangle}. \quad (8)$$

### 2.3. SF<sub>6</sub> polyad schemes

The SF<sub>6</sub> molecule has a quite complex vibrational level distribution, with no clear polyad structure, the six fundamental vibrational wavenumbers being ran-

domly distributed without simple ratios between them. It is possible, however,  
 135 to define some partial polyad schemes in order to treat together several levels  
 showing specific interactions. This was done in our previous work about excited  
 states of this molecule [32]. In particular, we used in this paper a scheme allow-  
 ing a global fit of lines from 12 rovibrational bands, giving fitted parameters for  
 10 different stretching vibrational levels. Figure 10 in the Appendix illustrates  
 140 this polyad scheme. It was then possible to reconsider the  $\nu_6$  “forbidden band”  
 [31] together with the  $\nu_4$  and  $\nu_4 + \nu_6 - \nu_6$  bands [26] altogether using a second  
 polyad scheme, as described in Figure 11 in the Appendix. Schemes number 3  
 and 4 are also used for levels implying bending modes, as in Ref. [46] and [30],  
 see Figure 12 in the Appendix.

145 At each step, the parameters determined in previous fits are fixed, as indi-  
 cated in Figures 10 to 13 in the Appendix. Results of these global fits can be  
 found in Table 5 of Ref. [32] and Table 2 of Ref. [46]. Using all these results  
 to get reliable effective Hamiltonian parameters for the Ground State,  $\nu_1$ ,  $\nu_4$ ,  
 $\nu_5$  and  $\nu_6$ , levels it was then possible to define new simple polyad schemes (see  
 150 Figure 13 in the Appendix) in order to assign and fit three additional combina-  
 tion bands, namely  $\nu_1 + \nu_4$ ,  $\nu_2 + \nu_6$  and  $\nu_5 + \nu_6$ . It should be again noticed that  
 $\nu_2 + \nu_6$  has been studied previously [21, 22], but that the new spectra used in  
 the present work allowed a very strong improvement, as we detail it below. We  
 thus only detailed here the effective Hamiltonians used for the study of these  
 155 three bands, that are:

- The ground state effective Hamiltonian,

$$H^{<GS>} = H_{\{GS\}}^{<GS>}. \quad (9)$$

- The  $\nu_i$  ( $i = 1, 2, 4, 5, 6$ ) fundamental band effective Hamiltonians,

$$H^{<\nu_i>} = H_{\{GS\}}^{<\nu_i>} + H_{\{\nu_i\}}^{<\nu_i>}. \quad (10)$$

- The  $\nu_1 + \nu_4$  combination level effective Hamiltonian,

$$H^{<\nu_1+\nu_4>} = H_{\{GS\}}^{<\nu_1+\nu_4>} + H_{\{\nu_4\}}^{<\nu_1+\nu_4>} + H_{\{\nu_1\}}^{<\nu_1+\nu_4>} + H_{\{\nu_1+\nu_4\}}^{<\nu_1+\nu_4>}. \quad (11)$$



- The  $\nu_2 + \nu_6$  combination level effective Hamiltonian,

$$H^{<\nu_2+\nu_6>} = H_{\{GS\}}^{<\nu_2+\nu_6>} + H_{\{\nu_6\}}^{<\nu_2+\nu_6>} + H_{\{\nu_2\}}^{<\nu_2+\nu_6>} + H_{\{\nu_2+\nu_6\}}^{<\nu_2+\nu_6>}. \quad (12)$$

- The  $\nu_5 + \nu_6$  combination level effective Hamiltonian,

$$H^{<\nu_5+\nu_6>} = H_{\{GS\}}^{<\nu_5+\nu_6>} + H_{\{\nu_6\}}^{<\nu_5+\nu_6>} + H_{\{\nu_5\}}^{<\nu_5+\nu_6>} + H_{\{\nu_5+\nu_6\}}^{<\nu_5+\nu_6>}. \quad (13)$$

#### 2.4. Basis sets

To calculate line positions and strengths, we use a coupled vibrational basis set taking into account the different vibrational modes of  $XY_6$  molecules. The Hamiltonian and dipole moment matrix elements are then calculated in the coupled rovibrational basis set with symmetry  $C$  ( $O_h$  group irreducible representation):

$$\left| (\Psi_r^{(J,nC_r)} \otimes \Psi_v^{C_v})^{(C)} \right\rangle, \quad (14)$$

where  $\Psi_r^{(J,nC_r)}$  is a rotational wavefunction with symmetry  $C_r$  ( $n$  being a multiplicity index to distinguish identical representations  $C$  for a given rotational quantum number value  $J$ ) and  $\Psi_v^{(C_v)}$  is a vibrational wavefunction with symmetry  $C_v$ . The latter ones are constructed [37, 36] by coupling harmonic oscillator basis sets:

- The  $\nu_1$  vibrational functions are all totally symmetric,

$$\left| \Psi_{\nu_1}^{(A_{1g})} \right\rangle. \quad (15)$$

- The doubly degenerate mode basis set is

$$\left| \Psi_{\nu_2}^{(l_2, C_2)} \right\rangle, \quad (16)$$

where  $l_2 = \nu_2, \nu_2 - 2, \dots, -\nu_2$ .

- The vibrational basis set for the triply degenerate modes is written as

$$\left| \Psi_v^{(l, n_v C_n)} \right\rangle, \quad (17)$$

where  $n_v$  is a multiplicity index (counting identical representations  $C_n$  for a given  $l$  value) and the quantum number is  $l = \nu, \nu - 2, \dots, 0$  or 1.

### 2.5. Line intensities

In order to calculate line intensities for dipolar absorption transitions, the  
180 dipole moment operator is expanded using the same tensorial formalism. Its  
construction has been described previously for octahedral  $XY_6$  molecules [37,  
47, 36]. Since in the present study we only consider relative intensities for  
the rovibrational lines of the three combination bands under investigation, the  
dipole moment was only expanded to a low order. It includes a first-order term  
185 (main dipole moment derivative) and a second order term (Herman-Wallis term)  
used to “equilibrate” the  $P$  and  $R$  branch intensities when performing synthetic  
spectrum simulations. Thus, we do not detail more the dipole moment formalism  
here.

### 3. Experimental setup

190 The experimental high resolution spectra were recorded at the AILES Beam-  
line at Synchrotron SOLEIL on the Synchrotron light source[48, 49] by Mbaye  
Faye during his PhD thesis [50]. The line is coupled to the Bruker 125HR inter-  
ferometer and uses a cryogenic multipass cell set on a 15 m optical path length  
and regulated at  $153 \pm 2$  K temperature along the entire optical path. This  
195 setup is fully described in Ref. [51]. The cell optical set-up is based on a 1.5 m  
base length Barskaya-Chernin five-mirrors arrangement[52].

The cell is mounted inside a triple jacket-liquid nitrogen cryostat. The cool-  
ing power from a liquid nitrogen-filled surrounding envelope is transmitted by  
an annular space filled by helium as convection gas, whose pressure can be var-  
200 ied to adjust the cooling power. Additional heaters are distributed along the  
gas cell body for temperature homogenization. The cell and the outside Dewar  
jacket are fitted with diamond windows brazed on stainless steel flanges to en-  
able operation of the cell between 80 K and 400 K from the near IR to the THz  
range. A spectrum with a gas pressure of 0.09 mbar of  $SF_6$  (Air Liquide, France,  
205 99.9% purity) was recorded at  $0.0025 \text{ cm}^{-1}$  resolution in the  $700 - 2000 \text{ cm}^{-1}$   
region with no apodization, 5.06 cm/s mirror velocity, a Ge/KBr beamsplitter

and a HgCdTe detector. 1426 interferograms were averaged in a total recording time of about 38 hours and processed against a background of the empty cell taken at the same 153 K temperature at  $0.01 \text{ cm}^{-1}$  resolution. Spectra were zero-filled, corrected for channelling effects and calibrated using well-known water rotational lines [53, 54]. The frequency accuracy is here  $3 \times 10^{-4} \text{ cm}^{-1}$  (one sigma).

#### 4. Analysis of simulation results

Thanks to the XTDS and SPVIEW softwares [39] developed in the Dijon group that implement the above-described formalism (XTDS) and that allow on-screen line assignments (SPVIEW), the simulation and analysis of combination bands  $\nu_1 + \nu_4$ ,  $\nu_2 + \nu_6$  and  $\nu_5 + \nu_6$  is a relatively easy.

First of all, we calculate in each case an approximate spectrum with pre-existing parameters taken from previous works for the lower levels (GS,  $\nu_1$ ,  $\nu_2$ ,  $\nu_5$  and  $\nu_6$ ). In this first step, anharmonicity parameters for the combination bands are fixed by hand in order to match the correct band center, as detailed for instance in Section 4.1. Next, we assign the simulated absorption peaks to the experimental spectrum by using the SPVIEW software (this one allows to assign experimental lines to calculated transitions by comparing the two spectra and by clicking on the lines). After that, the effective Hamiltonian parameters are fitted thanks to a non-linear least-squares fit method (Levenberg-Marquardt algorithm). To correct the simulated spectrum, and assign more lines, these steps were repeated several times until a good simulation spectrum is obtained and considered as perfectly similar to the experimental spectrum (with no further assignment being possible and a root-mean-square deviation of a few  $10^{-4} \text{ cm}^{-1}$  for the fit of the effective Hamiltonian parameters). Table 1 gives the effective Hamiltonian parameters we obtain. Please refer to Table 5 of Ref. [32] and Table 2 of Ref. [46] for lower state parameters. The following paragraphs give more detailed explanations for the three different combination bands under study.

Table 1: Fitted effective Hamiltonian parameters for the  $\nu_1 + \nu_4$ ,  $\nu_2 + \nu_6$  and  $\nu_5 + \nu_6$  combination bands. Lower-state parameters are fixed from previous global fits (see text).

Band	Parameter (notations of Section 2.2)			Value / $\text{cm}^{-1}$	Comments
	$\Omega(K, n\Gamma)$	$(s)\Gamma_v$	$(s')\Gamma'_v$		
$\nu_1 + \nu_4$	0(0,0 $A_{1g}$ )	100100 $F_{1u}$	100100 $F_{1u}$	-1.145635(56)	Anhrmonicicity $X_{14}$
	1(1,0 $F_{1g}$ )	100100 $F_{1u}$	100100 $F_{1u}$	$-5.358(39) \times 10^{-4}$	Coriolis interaction
	2(0,0 $A_{1g}$ )	100100 $F_{1u}$	100100 $F_{1u}$	$-9.2(2.1) \times 10^{-8}$	$\Delta B_{14}$
	2(2,0 $E_g$ )	100100 $F_{1u}$	100100 $F_{1u}$	0.0 <sup>†</sup>	
	2(2,0 $F_{2g}$ )	100100 $F_{1u}$	100100 $F_{1u}$	0.0 <sup>†</sup>	
	3(1,0 $F_{1g}$ )	100100 $F_{1u}$	100100 $F_{1u}$	$-5.14(48) \times 10^{-9}$	
	3(3,0 $F_{1g}$ )	100100 $F_{1u}$	100100 $F_{1u}$	$-3.22(25) \times 10^{-9}$	
$\nu_2 + \nu_6$	0(0,0 $A_{1g}$ )	010001 $F_{1u}$	010001 $F_{1u}$	$1.64179(77) \times 10^{-1}$	$F_{1u}$ sublevel
	1(1,0 $F_{1g}$ )	010001 $F_{1u}$	010001 $F_{1u}$	$-1.3065(63) \times 10^{-3}$	Coriolis interaction
	2(0,0 $A_{1g}$ )	010001 $F_{1u}$	010001 $F_{1u}$	$-5.269(56) \times 10^{-5}$	
	2(2,0 $E_g$ )	010001 $F_{1u}$	010001 $F_{1u}$	$-3.779(41) \times 10^{-5}$	
	2(2,0 $F_{2g}$ )	010001 $F_{1u}$	010001 $F_{1u}$	$8.169(65) \times 10^{-5}$	
	3(1,0 $F_{1g}$ )	010001 $F_{1u}$	010001 $F_{1u}$	$1.052(18) \times 10^{-7}$	
	3(3,0 $F_{1g}$ )	010001 $F_{1u}$	010001 $F_{1u}$	$5.28(18) \times 10^{-8}$	
	4(0,0 $A_{1g}$ )	010001 $F_{1u}$	010001 $F_{1u}$	$-1.44(28) \times 10^{-10}$	
	4(2,0 $E_g$ )	010001 $F_{1u}$	010001 $F_{1u}$	$-2.6(1.4) \times 10^{-11}$	
	4(2,0 $F_{2g}$ )	010001 $F_{1u}$	010001 $F_{1u}$	$-3.10(26) \times 10^{-10}$	
	4(4,0 $A_{1g}$ )	010001 $F_{1u}$	010001 $F_{1u}$	$2.37(63) \times 10^{-11}$	
	4(4,0 $E_g$ )	010001 $F_{1u}$	010001 $F_{1u}$	$9.9(1.1) \times 10^{-11}$	
	4(4,0 $F_{2g}$ )	010001 $F_{1u}$	010001 $F_{1u}$	0.0 <sup>†</sup>	
	1(1,0 $F_{1g}$ )	010001 $F_{1u}$	010001 $F_{2u}$	$7.261(19) \times 10^{-3}$	$F_{1u} - F_{2u}$ interaction
	2(2,0 $E_g$ )	010001 $F_{1u}$	010001 $F_{2u}$	$4.196(40) \times 10^{-5}$	
	2(2,0 $F_{2g}$ )	010001 $F_{1u}$	010001 $F_{2u}$	$2.725(77) \times 10^{-6}$	
	3(1,0 $F_{1g}$ )	010001 $F_{1u}$	010001 $F_{2u}$	0.0 <sup>†</sup>	
	3(3,0 $A_{2g}$ )	010001 $F_{1u}$	010001 $F_{2u}$	0.0 <sup>†</sup>	
	3(3,0 $F_{1g}$ )	010001 $F_{1u}$	010001 $F_{2u}$	0.0 <sup>†</sup>	
	3(3,0 $F_{2g}$ )	010001 $F_{1u}$	010001 $F_{2u}$	0.0 <sup>†</sup>	
	0(0,0 $A_{1g}$ )	010001 $F_{2u}$	010001 $F_{2u}$	-1.92162(13)	$F_{2u}$ sublevel
	1(1,0 $F_{1g}$ )	010001 $F_{2u}$	010001 $F_{2u}$	$3.8380(76) \times 10^{-3}$	Coriolis interaction
	2(0,0 $A_{1g}$ )	010001 $F_{2u}$	010001 $F_{2u}$	$4.243(57) \times 10^{-5}$	
	2(2,0 $E_g$ )	010001 $F_{2u}$	010001 $F_{2u}$	$2.960(43) \times 10^{-5}$	
	2(2,0 $F_{2g}$ )	010001 $F_{2u}$	010001 $F_{2u}$	$-5.932(63) \times 10^{-5}$	
	3(1,0 $F_{1g}$ )	010001 $F_{2u}$	010001 $F_{2u}$	$-9.26(16) \times 10^{-8}$	
3(3,0 $F_{1g}$ )	010001 $F_{2u}$	010001 $F_{2u}$	$-7.08(14) \times 10^{-8}$		
4(0,0 $A_{1g}$ )	010001 $F_{2u}$	010001 $F_{2u}$	0.0 <sup>†</sup>		
4(2,0 $E_g$ )	010001 $F_{2u}$	010001 $F_{2u}$	0.0 <sup>†</sup>		
4(2,0 $F_{2g}$ )	010001 $F_{2u}$	010001 $F_{2u}$	0.0 <sup>†</sup>		
$\nu_5 + \nu_6$	0(0,0 $A_{1g}$ )	000011 $A_{1u}$	000011 $A_{1u}$	$-1.389(79) \times 10^{-1}$	$A_{1u}$ sublevel

<sup>†</sup> Fixed value.

Continued from Table 1.

Band	Parameter (notations of Section 2.2)			Value / $\text{cm}^{-1}$	Comments
	$\Omega(K, n\Gamma)$	$(s)\Gamma_v$	$(s')\Gamma'_v$		
	2(0,0A <sub>1g</sub> )	000011A <sub>1u</sub>	000011A <sub>1u</sub>	0.0 <sup>†</sup>	
	4(0,0A <sub>1g</sub> )	000011A <sub>1u</sub>	000011A <sub>1u</sub>	0.0 <sup>†</sup>	
	4(4,0A <sub>1g</sub> )	000011A <sub>1u</sub>	000011A <sub>1u</sub>	0.0 <sup>†</sup>	
	2(2,0E <sub>g</sub> )	000011A <sub>1u</sub>	000011E <sub>u</sub>	$-1.10(21) \times 10^{-4}$	A <sub>1u</sub> - E <sub>u</sub> interaction
	4(2,0E <sub>g</sub> )	000011A <sub>1u</sub>	000011E <sub>u</sub>	$-3.36(33) \times 10^{-8}$	
	4(4,0E <sub>g</sub> )	000011A <sub>1u</sub>	000011E <sub>u</sub>	0.0 <sup>†</sup>	
	1(1,0F <sub>1g</sub> )	000011A <sub>1u</sub>	000011F <sub>1u</sub>	0.0 <sup>†</sup>	
	3(1,0F <sub>1g</sub> )	000011A <sub>1u</sub>	000011F <sub>1u</sub>	0.0 <sup>†</sup>	
	3(3,0F <sub>1g</sub> )	000011A <sub>1u</sub>	000011F <sub>1u</sub>	0.0 <sup>†</sup>	
	4(4,0F <sub>1g</sub> )	000011A <sub>1u</sub>	000011F <sub>1u</sub>	0.0 <sup>†</sup>	
	2(2,0F <sub>2g</sub> )	000011A <sub>1u</sub>	000011F <sub>2u</sub>	$3.58(35) \times 10^{-4}$	A <sub>1u</sub> - F <sub>2u</sub> interaction
	3(3,0F <sub>2g</sub> )	000011A <sub>1u</sub>	000011F <sub>2u</sub>	$2.52(21) \times 10^{-6}$	
	4(2,0F <sub>2g</sub> )	000011A <sub>1u</sub>	000011F <sub>2u</sub>	$-2.88(37) \times 10^{-8}$	
	4(4,0F <sub>2g</sub> )	000011A <sub>1u</sub>	000011F <sub>2u</sub>	$1.71(25) \times 10^{-8}$	
	0(0,0A <sub>1g</sub> )	000011E <sub>u</sub>	000011E <sub>u</sub>	$-3.901(53) \times 10^{-1}$	E <sub>u</sub> sublevel
	2(0,0A <sub>1g</sub> )	000011E <sub>u</sub>	000011E <sub>u</sub>	0.0 <sup>†</sup>	
	2(2,0E <sub>g</sub> )	000011E <sub>u</sub>	000011E <sub>u</sub>	0.0 <sup>†</sup>	
	3(3,0A <sub>2g</sub> )	000011E <sub>u</sub>	000011E <sub>u</sub>	0.0 <sup>†</sup>	
	4(0,0A <sub>1g</sub> )	000011E <sub>u</sub>	000011E <sub>u</sub>	0.0 <sup>†</sup>	
	4(2,0E <sub>g</sub> )	000011E <sub>u</sub>	000011E <sub>u</sub>	0.0 <sup>†</sup>	
	4(4,4A <sub>1g</sub> )	000011E <sub>u</sub>	000011E <sub>u</sub>	0.0 <sup>†</sup>	
	4(4,0E <sub>g</sub> )	000011E <sub>u</sub>	000011E <sub>u</sub>	0.0 <sup>†</sup>	
	1(1,0F <sub>1g</sub> )	000011E <sub>u</sub>	000011F <sub>1u</sub>	$-9.25(46) \times 10^{-3}$	E <sub>u</sub> - F <sub>1u</sub> interaction
	2(2,0F <sub>2g</sub> )	000011E <sub>u</sub>	000011F <sub>1u</sub>	$-1.27(11) \times 10^{-4}$	
	3(1,0F <sub>1g</sub> )	000011E <sub>u</sub>	000011F <sub>1u</sub>	$-4.03(42) \times 10^{-7}$	
	3(3,0F <sub>1g</sub> )	000011E <sub>u</sub>	000011F <sub>1u</sub>	$-2.45(42) \times 10^{-7}$	
	3(3,0F <sub>2g</sub> )	000011E <sub>u</sub>	000011F <sub>1u</sub>	0.0 <sup>†</sup>	
	4(2,0F <sub>2g</sub> )	000011E <sub>u</sub>	000011F <sub>1u</sub>	0.0 <sup>†</sup>	
	4(4,0F <sub>1g</sub> )	000011E <sub>u</sub>	000011F <sub>1u</sub>	0.0 <sup>†</sup>	
	4(4,0F <sub>2g</sub> )	000011E <sub>u</sub>	000011F <sub>1u</sub>	0.0 <sup>†</sup>	
	1(1,0F <sub>1g</sub> )	000011E <sub>u</sub>	000011F <sub>2u</sub>	0.0 <sup>†</sup>	
	2(2,0F <sub>2g</sub> )	000011E <sub>u</sub>	000011F <sub>2u</sub>	0.0 <sup>†</sup>	
	3(1,0F <sub>1g</sub> )	000011E <sub>u</sub>	000011F <sub>2u</sub>	0.0 <sup>†</sup>	
	3(3,0F <sub>1g</sub> )	000011E <sub>u</sub>	000011F <sub>2u</sub>	0.0 <sup>†</sup>	
	3(3,0F <sub>2g</sub> )	000011E <sub>u</sub>	000011F <sub>2u</sub>	0.0 <sup>†</sup>	
	4(2,0F <sub>2g</sub> )	000011E <sub>u</sub>	000011F <sub>2u</sub>	0.0 <sup>†</sup>	
	4(4,0F <sub>1g</sub> )	000011E <sub>u</sub>	000011F <sub>2u</sub>	0.0 <sup>†</sup>	
	4(4,0F <sub>2g</sub> )	000011E <sub>u</sub>	000011F <sub>2u</sub>	0.0 <sup>†</sup>	
	0(0,0A <sub>1g</sub> )	000011F <sub>1u</sub>	000011F <sub>1u</sub>	-1.365364(67)	F <sub>1u</sub> sublevel
	1(1,0F <sub>1g</sub> )	000011F <sub>1u</sub>	000011F <sub>1u</sub>	$4.3826(74) \times 10^{-3}$	Coriolis interaction
	2(0,0A <sub>1g</sub> )	000011F <sub>1u</sub>	000011F <sub>1u</sub>	$4.88(20) \times 10^{-5}$	
	2(2,0E <sub>g</sub> )	000011F <sub>1u</sub>	000011F <sub>1u</sub>	$3.3(1.5) \times 10^{-6}$	

<sup>†</sup> Fixed value.

Continued from Table 1.

Band	Parameter (notations of Section 2.2)			Value / $\text{cm}^{-1}$	Comments
	$\Omega(K, n\Gamma)$	$(s)\Gamma_v$	$(s')\Gamma'_v$		
	2(2,0 $F_{2g}$ )	000011 $F_{1u}$	000011 $F_{1u}$	$3.968(99) \times 10^{-5}$	
	3(1,0 $F_{1g}$ )	000011 $F_{1u}$	000011 $F_{1u}$	$-2.73(29) \times 10^{-7}$	
	3(3,0 $F_{1g}$ )	000011 $F_{1u}$	000011 $F_{1u}$	$4.73(44) \times 10^{-7}$	
	4(0,0 $A_{1g}$ )	000011 $F_{1u}$	000011 $F_{1u}$	0.0 <sup>†</sup>	
	4(2,0 $E_g$ )	000011 $F_{1u}$	000011 $F_{1u}$	0.0 <sup>†</sup>	
	4(2,0 $F_{2g}$ )	000011 $F_{1u}$	000011 $F_{1u}$	0.0 <sup>†</sup>	
	4(4,0 $A_{1g}$ )	000011 $F_{1u}$	000011 $F_{1u}$	0.0 <sup>†</sup>	
	4(4,0 $E_g$ )	000011 $F_{1u}$	000011 $F_{1u}$	0.0 <sup>†</sup>	
	4(4,0 $F_{2g}$ )	000011 $F_{1u}$	000011 $F_{1u}$	0.0 <sup>†</sup>	
	1(1,0 $F_{1g}$ )	000011 $F_{1u}$	000011 $F_{2u}$	$6.03(55) \times 10^{-3}$	$F_{1u} - F_{2u}$ interaction
	2(2,0 $E_g$ )	000011 $F_{1u}$	000011 $F_{2u}$	$-4.38(10) \times 10^{-5}$	
	2(2,0 $F_{2g}$ )	000011 $F_{1u}$	000011 $F_{2u}$	$2.75(15) \times 10^{-4}$	
	3(1,0 $F_{1g}$ )	000011 $F_{1u}$	000011 $F_{2u}$	$-2.07(78) \times 10^{-7}$	
	3(3,0 $A_{2g}$ )	000011 $F_{1u}$	000011 $F_{2u}$	$4.12(31) \times 10^{-7}$	
	3(3,0 $F_{1g}$ )	000011 $F_{1u}$	000011 $F_{2u}$	$2.38(91) \times 10^{-7}$	
	3(3,0 $F_{2g}$ )	000011 $F_{1u}$	000011 $F_{2u}$	0.0 <sup>†</sup>	
	4(2,0 $E_g$ )	000011 $F_{1u}$	000011 $F_{2u}$	0.0 <sup>†</sup>	
	4(2,0 $F_{2g}$ )	000011 $F_{1u}$	000011 $F_{2u}$	$-6.12(26) \times 10^{-9}$	
	4(4,0 $E_g$ )	000011 $F_{1u}$	000011 $F_{2u}$	0.0 <sup>†</sup>	
	4(4,0 $F_{1g}$ )	000011 $F_{1u}$	000011 $F_{2u}$	$1.012(65) \times 10^{-8}$	
	4(4,0 $F_{2g}$ )	000011 $F_{1u}$	000011 $F_{2u}$	0.0 <sup>†</sup>	
	0(0,0 $A_{1g}$ )	000011 $F_{2u}$	000011 $F_{2u}$	$-9.75(48) \times 10^{-2}$	$F_{2u}$ sublevel
	1(1,0 $F_{1g}$ )	000011 $F_{2u}$	000011 $F_{2u}$	$-9.52(51) \times 10^{-3}$	Coriolis interaction
	2(0,0 $A_{1g}$ )	000011 $F_{2u}$	000011 $F_{2u}$	$5.36(73) \times 10^{-5}$	
	2(2,0 $E_g$ )	000011 $F_{2u}$	000011 $F_{2u}$	0.0 <sup>†</sup>	
	2(2,0 $F_{2g}$ )	000011 $F_{2u}$	000011 $F_{2u}$	$-4.5(1.6) \times 10^{-5}$	
	3(1,0 $F_{1g}$ )	000011 $F_{2u}$	000011 $F_{2u}$	$5.2(2.0) \times 10^{-7}$	
	3(3,0 $F_{1g}$ )	000011 $F_{2u}$	000011 $F_{2u}$	$7.9(1.2) \times 10^{-7}$	
	4(0,0 $A_{1g}$ )	000011 $F_{2u}$	000011 $F_{2u}$	$8.2(1.2) \times 10^{-9}$	
	4(2,0 $E_g$ )	000011 $F_{2u}$	000011 $F_{2u}$	0.0 <sup>†</sup>	
	4(2,0 $F_{2g}$ )	000011 $F_{2u}$	000011 $F_{2u}$	$-2.00(16) \times 10^{-8}$	
	4(4,0 $A_{1g}$ )	000011 $F_{2u}$	000011 $F_{2u}$	0.0 <sup>†</sup>	
	4(4,0 $E_g$ )	000011 $F_{2u}$	000011 $F_{2u}$	0.0 <sup>†</sup>	
	4(4,0 $F_{2g}$ )	000011 $F_{2u}$	000011 $F_{2u}$	0.0 <sup>†</sup>	

<sup>†</sup> Fixed value.

#### 4.1. The $\nu_1 + \nu_4$ combination band (band center: $1388.382 \text{ cm}^{-1}$ )

As shown in Figure 1,  $\text{H}_2\text{O}$  molecules were present in the  $\text{SF}_6$  sample, resulting in a  $\text{H}_2\text{O}$  line in the  $P$  branch of  $\nu_1 + \nu_4$  band spectrum. We can see that the  $P$  and  $R$  branches are well resolved with a quite clear structure. This band being, in first approximation, a simple shift of the well-known  $\nu_4$  one [26] (the  $\nu_1$  mode being totally symmetric), its assignment starting from  $\nu_4$  parameters is quite straightforward. The  $Q$  branch is very dense and less resolved but it was possible to assign some lines and reproduce its structure correctly. The simulated spectrum agrees well and ensures the accuracy of the effective Hamiltonian that has been determined. 1322 line positions up to  $J = 76$  were assigned and effective Hamiltonian was developed up to order 6 for the ground state,  $\nu_1$  and  $\nu_4$  vibrational levels and up to order 5 for the  $\nu_1 + \nu_4$  level itself. The band center is located at  $1388.382 \text{ cm}^{-1}$ . Only 5 Hamiltonian parameters were fitted as shown in Table 1. The root-mean-square deviation is  $0.456 \times 10^{-3} \text{ cm}^{-1}$ . This is the first detailed study and modeling of this band. The parameters obtained here, allow the calculation of the  $\nu_4 + \nu_1 - \nu_1$  hot band in the  $\nu_4$  region for the SHeCaSDa database (see Section 5).

Figure 2 displays the fit residuals for line positions. Figure 3 displays reduced calculated and observed rovibrational energy levels for this band, after subtraction of scalar terms in the effective Hamiltonian. Observed levels are those reached by assigned transitions. They show the sampling of the energy level spectrum for this level used in the fit.

#### 4.2. The $\nu_2 + \nu_6$ combination band (band center: $991.274 \text{ cm}^{-1}$ )

As mentioned above, this band has already been studied a long time ago thanks to a cold supersonic molecular jet spectrum [21, 22]. This previous study was a good starting point for the present work. It was then possible to assign here many more lines: 4194 lines up to  $J = 78$ , instead of 521 lines up to  $J = 37$  only.

For this  $\nu_2 + \nu_6$  combination band, the spectrum structure is quite complicated and dense as shown in the Figure 4. We should firstly assign several

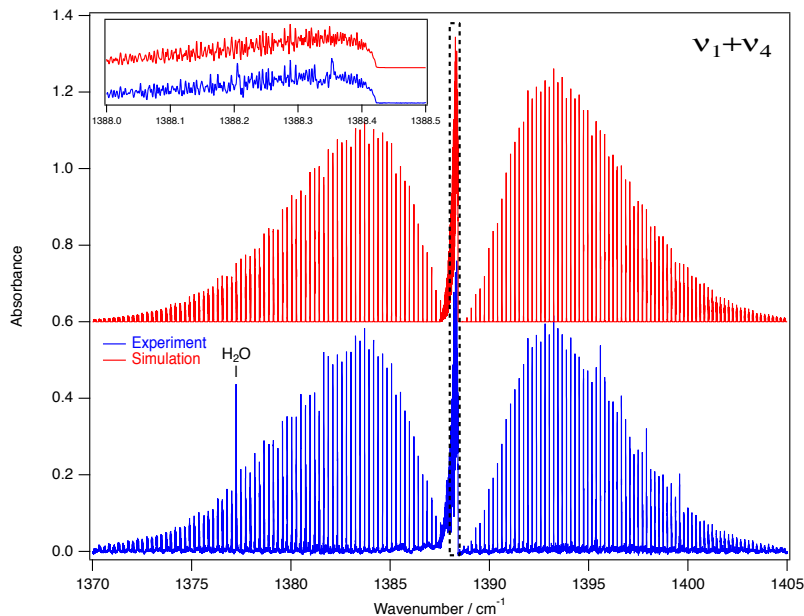


Figure 1: Experimental and simulated spectra for the  $\nu_1 + \nu_4$  combination band of  $\text{SF}_6$  at 153 K. The insert shows the  $Q$  branch. The presence of a  $\text{H}_2\text{O}$  line in the experimental spectrum is indicated.

obvious absorption peaks in both the  $P$  and  $R$  branch, and then add more absorption peaks, step by step. After repeating the procedure many times, the dense parts were also well simulated. The effective Hamiltonian was developed up to order 6 for the ground state,  $\nu_2$ ,  $\nu_6$  and  $\nu_2 + \nu_6$  vibrational levels. The  $F_{1u}$  and  $F_{2u}$  vibrational sublevels are located at  $991.274$  and  $989.119$   $\text{cm}^{-1}$ , respectively. The  $F_{1u}$  sublevel corresponds to the “active” or “allowed” band center (same symmetry as the dipole moment operator) and the strong visible  $Q$  branch is centered on it. A total of 22 Hamiltonian parameters were fitted at the same time as shown in Table 1. The root-mean-square deviation is very small:  $0.259 \times 10^{-3}$   $\text{cm}^{-1}$  only.

Figure 5 displays the fit residuals for line positions. Figure 6 displays reduced calculated and observed rovibrational energy levels for this band, as in the previous case.



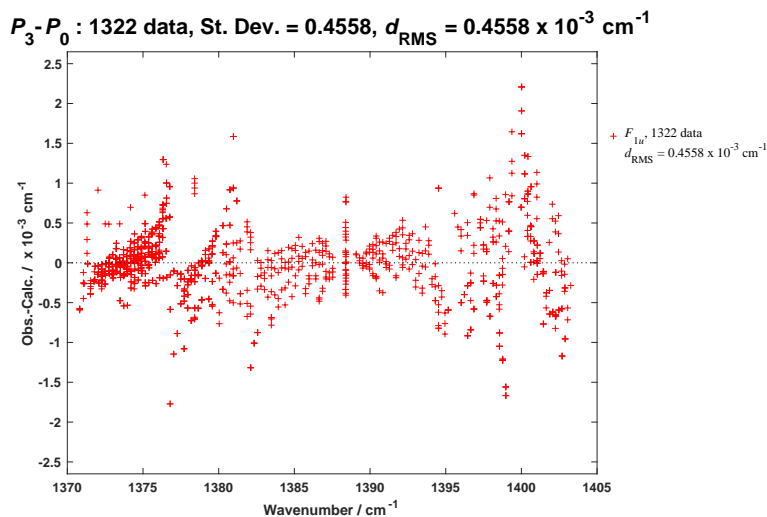


Figure 2: Fit residuals for line positions in the  $\nu_1 + \nu_4$  combination band of  $\text{SF}_6$ .

280 4.3. The  $\nu_5 + \nu_6$  combination band (band center:  $870.399 \text{ cm}^{-1}$ )

As for the  $\nu_5 + \nu_6$  combination band, the spectrum structure looks quite simple, although we have here a problem with four sublevels. This indicates that the anharmonic interactions should not split them very much. After assignment and fit, all the peaks were well matched (see Figure 7), even for some peaks with an anomalous intensity in the  $R$  branch. We could assign 2992 line positions up to  $J = 71$ . The effective Hamiltonian was developed up to order 6 for the ground state,  $\nu_5$ ,  $\nu_6$  and  $\nu_5 + \nu_6$  vibrational levels. The “active”  $F_{1u}$  band center is located at  $870.399 \text{ cm}^{-1}$ , while the three others are located around  $871.5 \text{ cm}^{-1}$ . The positions of these  $A_{1u}$ ,  $E_u$  and  $F_{2u}$  should, however, be considered with care. They were obtained through couplings fitted with essentially  $F_{1u}$  sublevel assigned peaks. The final result matches remarkably well for the whole band, but the data about these “inactive” levels (or “dark states”) may not be very accurate. A total of 35 Hamiltonian parameters were fitted as shown in

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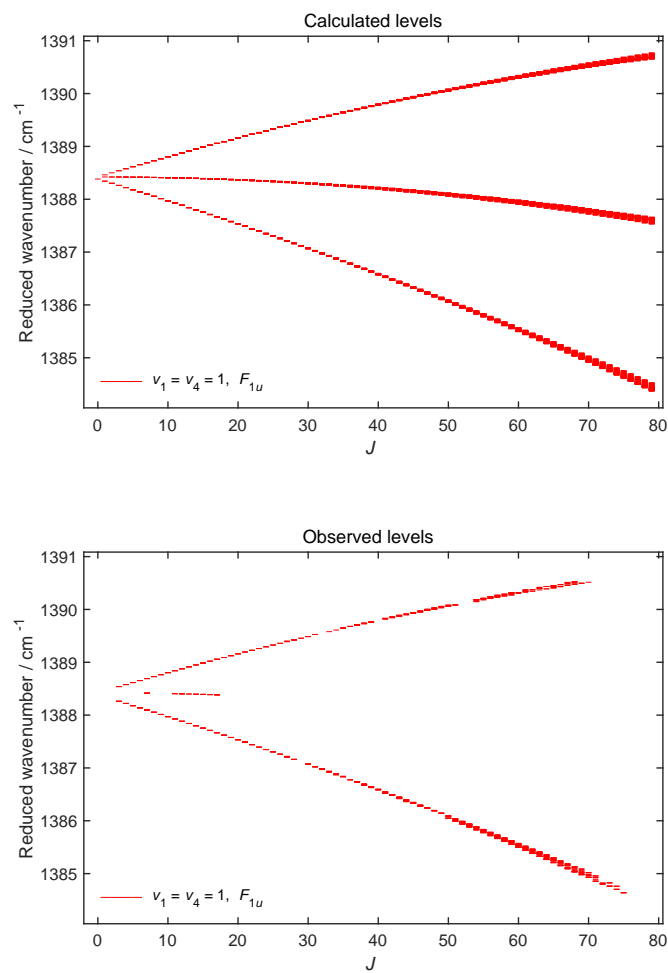


Figure 3: Calculated and observed (*i.e.* reached by assigned transitions) rovibrational energy levels for the  $\nu_1 + \nu_4$  combination band of  $\text{SF}_6$ .

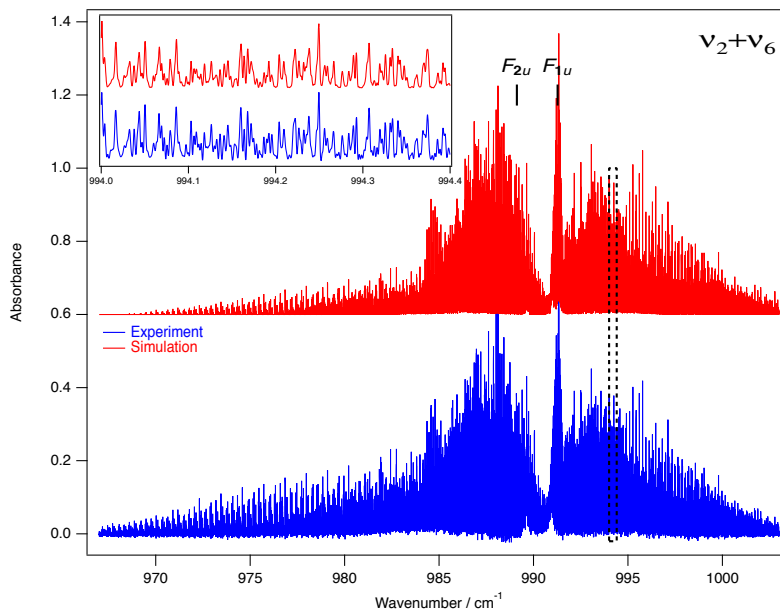


Figure 4: Experimental and simulated spectra for the  $\nu_2 + \nu_6$  combination band of  $\text{SF}_6$  at 153 K. The insert shows a detail in the  $R$  branch. The positions of the two sublevels are also marked.

Table 1, with a root-mean-square deviation of  $0.451 \times 10^{-3} \text{ cm}^{-1}$ . This is the  
 295 first detailed study and modeling of this band.

Figure 8 displays the fit residuals for line positions. Figure 9 displays reduced  
 calculated and observed rovibrational energy levels for this band, as in the  
 previous cases. We can see, as mentioned above, that the observed levels only  
 sample the  $F_{1u}$  sublevels, but that some faint mixings appear. These are due to  
 300 couplings with the other sublevels that allowed to fit some of their parameters.

## 5. SHeCaSDa database update

As explained in section 2.3, because of  $\text{SF}_6$ 's complex vibrational level dis-  
 tribution, we have updated the SHeCaSDa database by using 6 different polyad  
 305 schemes (see Table 2). Four schemes are dedicated to the  $^{32}\text{SF}_6$  main isotopo-

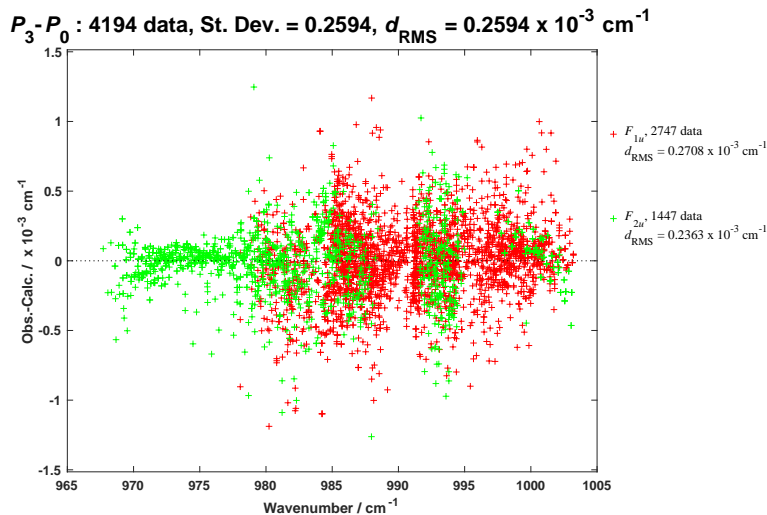


Figure 5: Fit residuals for line positions in the  $\nu_2 + \nu_6$  combination band of  $\text{SF}_6$ .

logue. They correspond to previously defined schemes 1, 2, 4 and 5 (see Section 2.3; scheme 3 is not calculated in the database; see Figures 10 to 12 in the Appendix). The two other simple schemes contain data about the  $\nu_3$  fundamental bands of the  $^{33}\text{SF}_6$ ,  $^{34}\text{SF}_6$  and  $^{36}\text{SF}_6$  isotopologues and about the  $\nu_4$  band of the  $^{34}\text{SF}_6$  isotopologue, respectively (in these schemes, the ground state is  $P_0$  and the fundamental band is  $P_1$ ). This is a complete refactoring of the previous revision of the base and the old data should be considered as obsolete. It should be noticed that the database only contains lines for which absolute line intensities can be calculated, that are the  $\nu_6$ ,  $\nu_4$  and  $\nu_3$  cold fundamental bands and some of the associated hot bands; but these calculations result from the energy levels obtained thanks to all the above-described fits.

A total of 491 500 calculated lines have been included in a new version of the database (see Table 3). The calculated data are accessible either through our website at <http://vamdc.icb.cnrs.fr/PHP/shecasda.php> or on the VAMDC

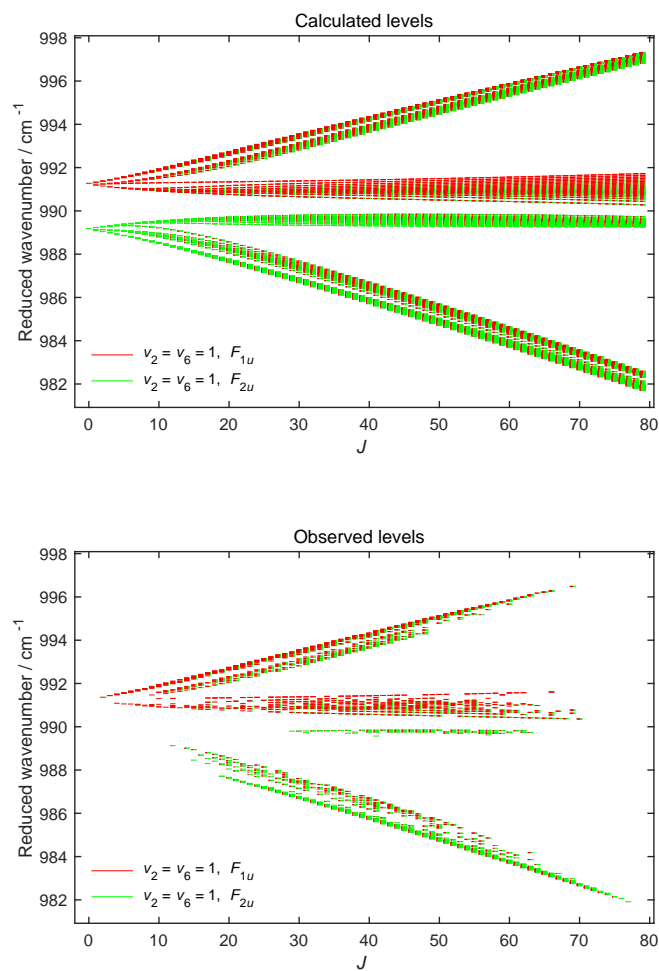


Figure 6: Calculated and observed (*i.e.* reached by assigned transitions) rovibrational energy levels for the  $\nu_2 + \nu_6$  combination band of SF<sub>6</sub>. Colors show the mixings between the two vibrational sublevels.

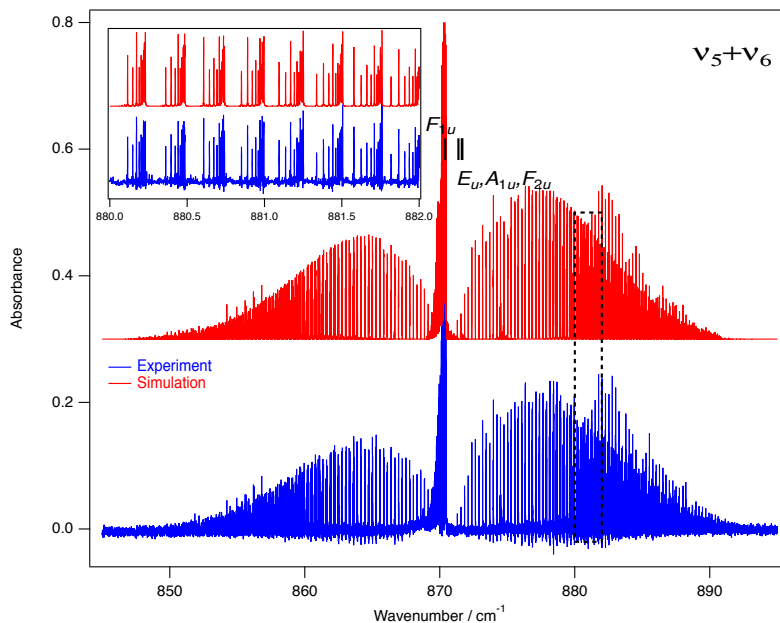


Figure 7: Experimental and simulated spectra for the  $\nu_5 + \nu_6$  combination band of  $\text{SF}_6$  at 153 K. The insert shows a detail in the  $R$  branch. The positions of the four sublevels are also marked.

portal at [https://portal.vamdc.eu/vamdc\\_portal](https://portal.vamdc.eu/vamdc_portal). On the first one, it is possible to plot the data and download two sorts of file formats. The line by line list is given following the HITRAN 2004 format[54], while cross section is a simple 2-column flat file.

## 6. Conclusion and perspectives

This work is a continuation of our previous studies of the rovibrational levels of  $^{32}\text{SF}_6$  in order to gather information allowing a correct simulation of hot bands in the  $\nu_3$  strongly absorbing region. Based on previous global fits, we could model three combination bands:  $\nu_2 + \nu_6$ , which has been strongly improved from the previous studies, while  $\nu_1 + \nu_4$  and  $\nu_5 + \nu_6$  were analyzed in detail for the first time. These results and those from other recent papers from our group allowed to update the SHeCaSDa database of calculated  $\text{SF}_6$  lines. For this

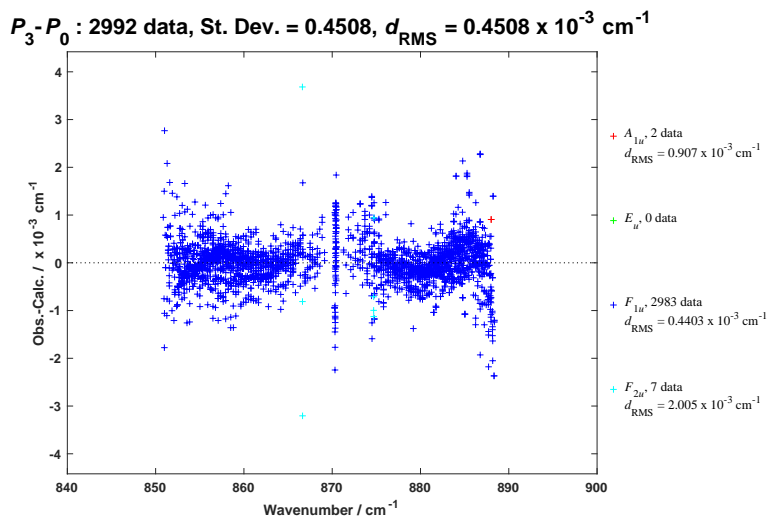


Figure 8: Fit residuals for line positions in the  $\nu_5 + \nu_6$  combination band of  $\text{SF}_6$ .

molecule, some work is still needed, as mentioned in Ref. [46], in order to analyze the  $\nu_3 + \nu_6 - \nu_4$  difference band. This one is quite weak and complex, but will lead to the knowledge of the  $\nu_3 + \nu_6$  combination level and thus to the calculation of the main hot band in the  $\nu_3$  region, namely  $\nu_3 + \nu_6 - \nu_6$ . Only after that, updates of the HITRAN and GEISA databases for  $\text{SF}_6$  would be valuable (knowing also that line-broadening studies would be needed).

### Acknowledgements

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### Appendix: Polyad schemes

Figures 10 to 13 illustrate the vibrational structure of  $\text{SF}_6$  and display the different transitions already analyzed or calculated for this molecule, along with

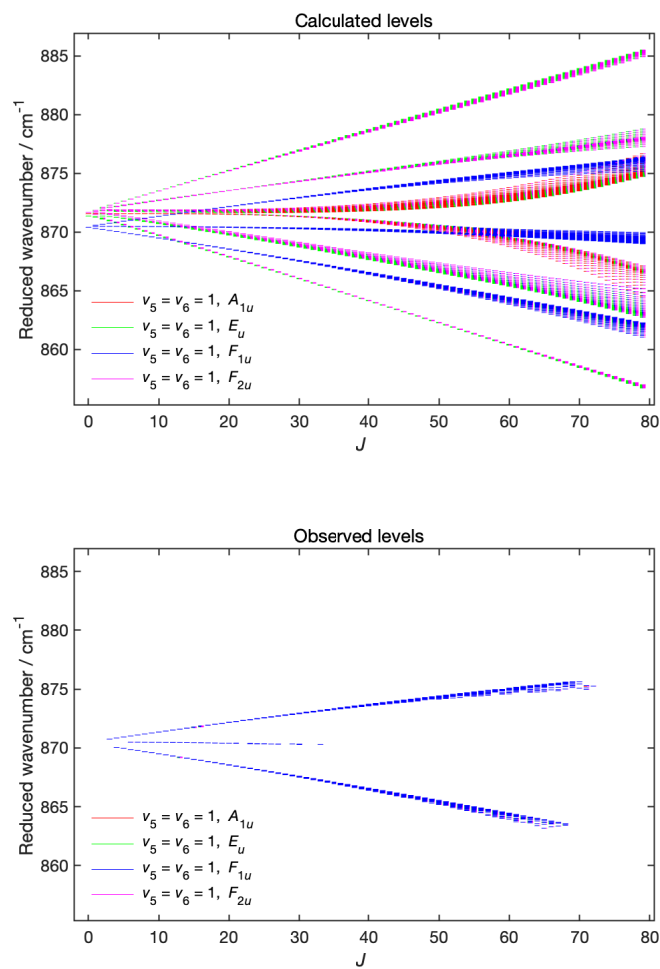


Figure 9: Calculated and observed (*i.e.* reached by assigned transitions) rovibrational energy levels for the  $\nu_5 + \nu_6$  combination band of  $\text{SF}_6$ . Colors show the mixings between the four vibrational sublevels.



Table 2: Number of calculated molecular states in the SHeCaSDa database for the different polyad schemes defined in Section 2.3 and in the Appendix, plus two other simple schemes for the minor isotopologues ( $P_0 = \text{GS}$  and  $P_1 = \nu_3$  or  $\nu_4$  in this case). In “Scheme 5”, we consider here the  $\nu_1 + \nu_4$  band from Figure 13.

Scheme	Levels	Molecular States	Scheme	Levels	Molecular States
Scheme 1 (Figure 10)			Scheme 5 ( $\nu_1 + \nu_4$ , Figure 13)		
$^{32}\text{SF}_6$	$P_0$	9 501	$^{32}\text{SF}_6$	$P_1$	18 301
	$P_1$	19 001		$P_2$	5 901
	$P_2$	9 501		$P_3$	17 701
	$P_3$	28 501	$\nu_3$ of minor isotopologues		
	$P_4$	66 503	$^{34}\text{SF}_6$	$P_0$	571
	$P_5$	28 501		$P_1$	1 620
Scheme 2 (Figure 11)			$^{33}\text{SF}_6$	$P_0$	571
$^{32}\text{SF}_6$	$P_0$	4 251	$P_1$	1 620	
	$P_1$	12 751	$^{36}\text{SF}_6$	$P_0$	2 734
	$P_2$	12 751		$P_1$	82 01
	$P_3$	38 254	$\nu_4$ of minor isotopologues		
Scheme 4 (Figure 12)			$^{34}\text{SF}_6$	$P_0$	1 354
$^{32}\text{SF}_6$	$P_0$	6 101	$P_1$	3 920	
	$P_1$	17 701			
	$P_3$	51 334			

the different polyad schemes that were used. In each case, arrows representing  
345 transitions follow the following plot code:

- Continuous lines represent assigned and fitted bands.
- Dashed lines represent calculated bands (typically: a hot band calculated from the difference between two levels that were analyzed on their own).
- Red lines correspond to dipolar absorption.
- 350 • Green lines correspond to stimulated Raman transitions.
- Blue lines correspond to two-photo absorption [55].

Table 3: Rovibrational transitions included in the SHeCaSDa database (see Table 2 and Appendix for polyad definitions).

Transitions	Nb. dipolar	Dipolar wavenumber range / $\text{cm}^{-1}$	Dipolar intensity range / $\text{cm}^{-1}/(\text{molecule cm}^{-2})$	Polarisability intensity range / arbitrary unit
Scheme 1 (Figure10)				
$^{32}\text{SF}_6$				
$P_1 - P_0$	42 983	600–687		$2.0 \times 10^{18} - 6.0 \times 10^{20}$
$P_2 - P_0$	7 861	773–775		$2.0 \times 10^{17} - 3.0 \times 10^{21}$
$P_4 - P_0$	11 797	770–773		$2.0 \times 10^{17} - 2.0 \times 10^{20}$
$P_3 - P_0$	53 996	935–957	$8.0 \times 10^{-24} - 1.6 \times 10^{-20}$	
$P_4 - P_1$	32 371	932–959	$8.0 \times 10^{-24} - 8.0 \times 10^{-22}$	
$P_5 - P_2$	11 473	937–949	$8.0 \times 10^{-24} - 3.6 \times 10^{-22}$	
Scheme 2 (Figure11)				
$^{32}\text{SF}_6$				
$P_2 - P_0$	14 941	593–637	$8.0 \times 10^{-24} - 1.2 \times 10^{-21}$	
$P_3 - P_1$	34 575	593–637	$8.0 \times 10^{-24} - 2.0 \times 10^{-22}$	
$P_1 - P_0$	62 895	320–374	$8.0 \times 10^{-29} - 4.0 \times 10^{-26}$	
Scheme 4 (Figure12)				
$^{32}\text{SF}_6$				
$P_1 - P_0$	59 842	475–562		$2.0 \times 10^{18} - 4.0 \times 10^{20}$
$P_3 - P_0$	12 1841	932–964		
Scheme 5 ( $\nu_1 + \nu_4$ , Figure13)				
$^{32}\text{SF}_6$				
$P_3 - P_1$	17 987	772–773		$3.0 \times 10^{17} - 2.0 \times 10^{20}$
$P_3 - P_1$	3 935	599–630	$8.0 \times 10^{-24} - 2.8 \times 10^{-23}$	
$\nu_3$ of minor isotopologues				
$^{34}\text{SF}_6$				
$P_1 - P_0$	1 620	928–933	$2.0 \times 10^{-22} - 1.6 \times 10^{-20}$	
$^{33}\text{SF}_6$				
$P_1 - P_0$	1 620	937–941	$2.0 \times 10^{-22} - 1.6 \times 10^{-20}$	
$^{36}\text{SF}_6$				
$P_1 - P_0$	7 843	908–920	$1.2 \times 10^{-21} - 1.6 \times 10^{-20}$	
$\nu_4$ of minor isotopologues				
$^{34}\text{SF}_6$				
$P_1 - P_0$	3 920	600–624	$1.6 \times 10^{-23} - 1.2 \times 10^{-21}$	

- Orange lines on Figure 12 also represent dipolar absorption transitions from Ref. [30]; this color is used to distinguish polyad schemes 3 and 4.

It should be noticed that, in scheme 1 (Figure 10),  $2\nu_1$  and  $\nu_2 + \nu_3$  are  
355 grouped into polyad  $P_4$ , while  $2\nu_3$  and  $\nu_1 + \nu_2 + \nu_3$  are grouped into polyad  $P_6$ .  
This is for convenience and consistency with lower polyads, but, in each case,  
both bands having opposite parity, there is no interaction between them (no  
intra-polyad interaction). There is no polyad  $P_7$  nor  $P_8$  in this scheme.

Concerning polyad schemes 5 (Figure 13), used for the study of each com-  
360 bination band of the present work, the polyad definition is given in Section  
2.3.

### Step 1 – Scheme 1

Simultaneous fit of 12 transitions:

- $P_1 - P_0$      $P_3 - P_1$
  - $P_2 - P_0$      $P_3 - P_2$
  - $P_3 - P_0$      $P_4 - P_2$
  - $P_5 - P_0$      $P_6 - P_3$
  - $P_6 - P_0$
  - $P_9 - P_0$      $P_4 - P_1$  and  $P_5 - P_2$
- are also calculated

to get parameters for:

- GS,  $\nu_2$ ,  $\nu_1$ ,  $\nu_3$ ,  $2\nu_1$ ,  $\nu_2 + \nu_3$ ,  $\nu_1 + \nu_3$ ,  $2\nu_3$ ,  $\nu_1 + \nu_2 + \nu_3$ ,  $3\nu_3$

GS is fixed in steps 3 to 5 to the values obtained here.

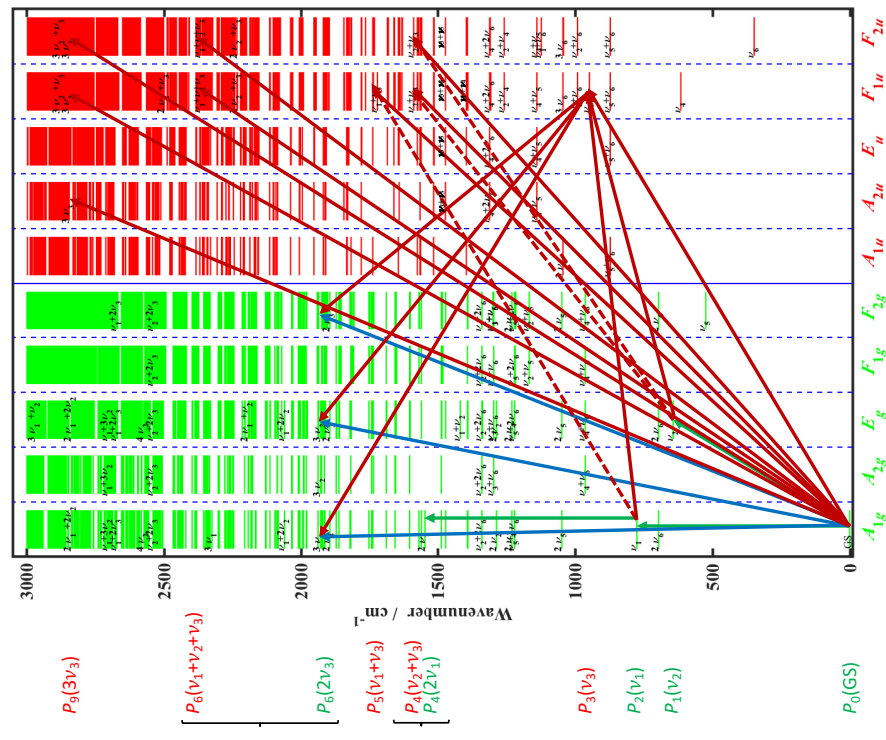


Figure 10: First polyad scheme implying stretching modes  $\nu_1$ ,  $\nu_2$  and  $\nu_3$ . For instance, the  $\nu_3$  cold fundamental band constitutes  $P_3 - P_0$  transitions in this scheme;  $P_5 - P_2$  transitions are  $\nu_3 + \nu_1 - \nu_1 - \nu_1$  hot band lines.

## Step 2 – Scheme 2

Simultaneous fit of 3 transitions:

$$\begin{aligned} P_1 - P_0 \\ P_2 - P_0 \\ P_3 - P_1 \end{aligned}$$

to get parameters for:

$$\begin{aligned} \nu_6 \\ \nu_4 \\ \nu_4 + \nu_6 \end{aligned}$$

which are fixed in steps 3 and 5 to the values obtained here.

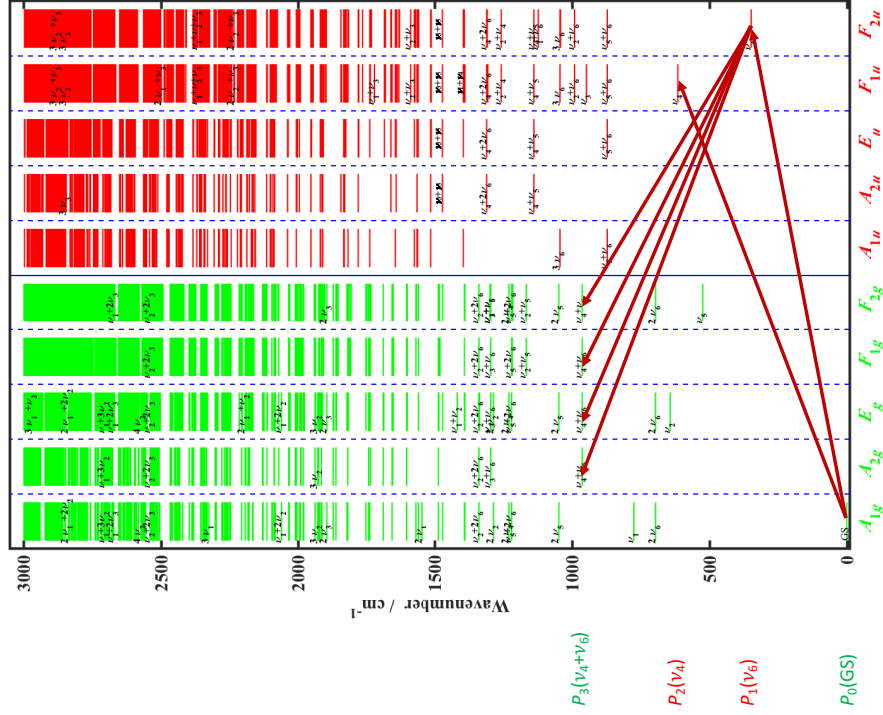


Figure 11: Second polyad scheme implying bending modes  $\nu_4$  and  $\nu_5$ . For instance, the  $\nu_6$  and  $\nu_4$  cold fundamental bands constitute  $P_1 - P_0$  and  $P_2 - P_0$  transitions in this scheme, respectively;  $P_3 - P_1$  transitions are  $\nu_4 + \nu_6 - \nu_6$  hot band lines.

### Step 3 – Scheme 3

Fit of 1 transition:

$$P_6 - P_1$$

to get parameters for:

$$\nu_5, \nu_2 + \nu_4$$

$\nu_5$  are fixed in steps 4 and 5 to the values obtained here.

Scheme 3  
 $P_6(\nu_2 + \nu_4)$   
 $P_5(\nu_2 + \nu_5)$   
 $P_3(\nu_4 + \nu_5)$

### Step 4 – Scheme 4

Fit of 1 transition:

$$\nu_3 + \nu_5 - \text{GS}$$

$\nu_3 + \nu_5 - \nu_5$  is then calculated.

$P_4(\nu_2)$   
 $P_2(\nu_4)$   
 $P_1(\nu_5)$

$P_0(\text{GS})$   $P_0(\text{GS})$

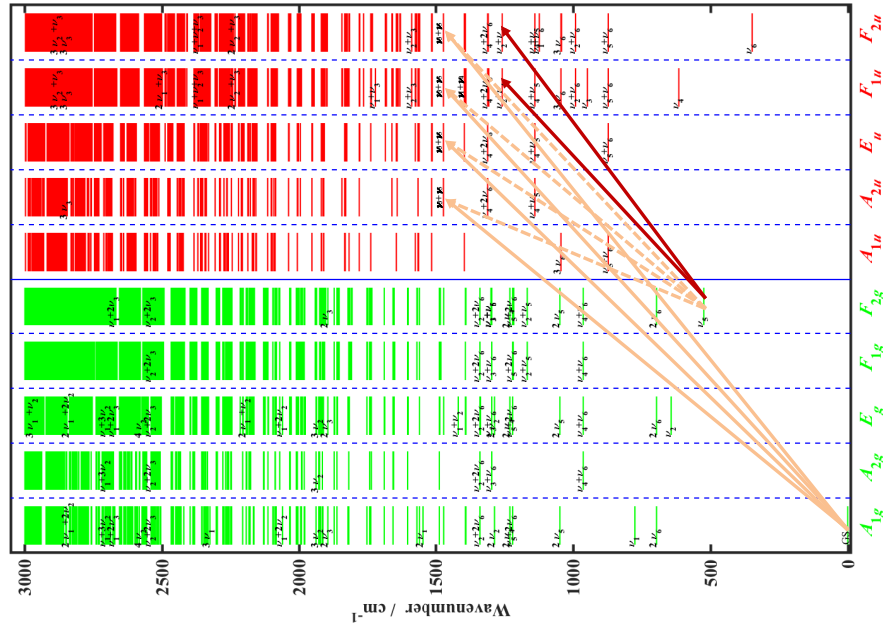


Figure 12: Third and fourth polyad schemes implying bending mode  $\nu_5$ .

### Step 5 – Other schemes

Fit of 3 transitions :

- $\nu_1+\nu_4$ -GS
- $\nu_2+\nu_6$ -GS
- $\nu_5+\nu_6$ -GS

Using previous parameters for  $\nu_1$ ,  $\nu_2$ ,  $\nu_5$  and  $\nu_6$ .

At this stage, they are considered as isolated, with a simple polyad scheme in each case.

The  $\nu_4+\nu_1-\nu_1$  hot band can be calculated.

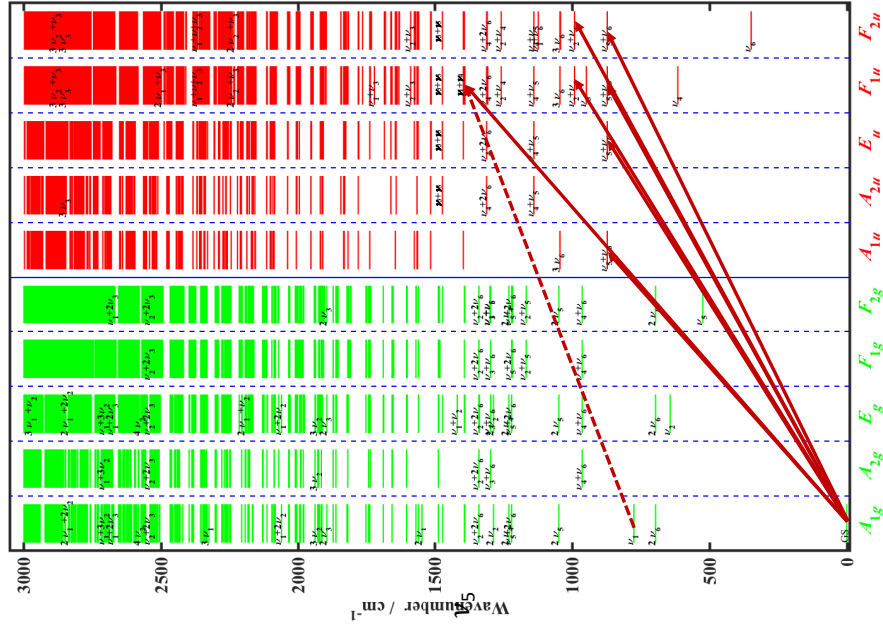


Figure 13: Fifth polyad schemes used for the combination bands fitted in the present work.

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