A preliminary study of the frequencies infrared spectrum of the ϑ_4 band of monoisotopic $^{34}\mathbf{SF}_6$

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Abstract

Octahedral formalism based on the notions of molecular symmetry is used in the calculation of the position lines of the ϑ_4 band of $^{34}SF_6$; we used an experimental spectrum near 650 cm^{-1}. This spectrum was analysed using XTDS and SPVIEW software's, developed in Dijon, France. We have 37 parameters to determined at the six order and for $J_{max} = 95$, using 1497 data. We have obtained an $RMS = 0.598 \times 10^{-3}$ cm^{-1}.

Key Words: Octahedral molecule, tensorial formalism, Hamiltonian, XTDS, SPVIEW

1. Introduction

Sulphur hexafluoride is one of heaviest gases known, its density being 139 kg/m^3 at 20 °C and 0.1 Mpa (approximately one atmosphere) pressure, five times heavier than air. Its molecular mass is 146.06 g, it is colourless, odourless non-toxic and inflammable. The SF$_6$ is octahedral with Sulphur at the molecule's centre and the six fluorine atoms at each vertex. S-F and F-F bond lengths are 1.5 Å and 2.21 Å. Sulphur hexafluoride having a long lifetime and being a strong absorber of infrared in the atmosphere makes it an atmospheric and thermal antagonist. In fact, this molecule is classified among gases contributing to greenhouse warming at the 1997 conference on the climatic change in Kyoto, Japan. With this in mind, we have undertook a systematic study of the υ_4 absorption band of monoisotopic $^{34}SF_6$ (4.21% in the atmosphere).

The υ_4 absorption band comprises the six vibration modes ϑ_1, ϑ_2 , ϑ_3 , ϑ_4 , ϑ_5 and ϑ_6 of symmetry A$_{1g}$, E$_g$, F$_{1u}$, F$_{1u}$, F$_{2g}$, F$_{2u}$, respectively (given in Table 1) [1]. We used the tensorial form of the Hamiltonian to calculate all possible frequencies of the rovibrational spectrum of this molecule. This form make it is possible to developed the Hamiltonian as a linear combination of the rovibrational operators, obtained by coupling in O$_h$ group. On the basis of experimental spectrum (the experimental conditions are given in Table 2) [2], we determined the parameters of the Hamiltonian to sixth order and $J_{max} = 95$. XTDS and SPVIEW developed

in Dijon, French and freely downloadable via the Internet* make it possible to carry out most of studies of octahedral molecules [3].

Table 1. The vibration normal modes of SF_6.

Normal mode	ϑ_1	ϑ_2	ϑ_3	ϑ_4	ϑ_5	ϑ_6
Symmetry in O_h	A_{1g}	E_g	F_{1u}	F_{1u}	F_{2g}	F_{2u}
Degeneracy	1	2	3	3	3	3
Activity	Raman	Raman	Infrared	Infrared	Raman	Inactive
Type		Stretching			Bending	

Table 2. Experiment conditions.

Experiment		
Temperature	Pressure	Resolution
213 °K	2.8 mbar	0.0028 cm^{-1}

2.   Theoretical model

The theoretical model used in this work is based on the tensorial form of the Hamiltonian and vibrational extrapolation methods developed in Dijon. The effective Hamiltonian for polyad P_n is obtained by projection in the corresponding subspace [4]:

$$H^{\langle P_n \rangle} = P^{\langle P_n \rangle} H P^{\langle P_n \rangle} \tag{1}$$

$$H^{\langle P_n \rangle} = H_{\{GS\}}^{\langle P_n \rangle} + H_{\{P_1\}}^{\langle P_n \rangle} + \cdots + H_{\{P_k\}}^{\langle P_n \rangle} + \cdots + H_{\{P_n\}}^{\langle P_n \rangle} \tag{2}$$

The various terms are written like [5]:

$$H_{\{P_k\}} = \sum_{\text{over all indices}} t_{\{n_s\}\{m_s\}}^{\Omega(k,n\Gamma)\Gamma_1\Gamma_2} \otimes T_{\{n_s\}\{m_s\}}^{\Omega(k,n\Gamma)\Gamma_1\Gamma_2}, \tag{3}$$

where $t_{\{n_s\}\{m_s\}}^{\Omega(k,n\Gamma)\Gamma_1\Gamma_2}$ are the model parameters; and $T_{\{n_s\}\{m_s\}}^{\Omega(k,n\Gamma)\Gamma_1\Gamma_2}$ are the model rovibrational operators, obtained by coupling in the molecule's group rotational operators $R^{\Omega(k,n\Gamma)}$ and the vibrational operators $V_{\{n_s\}\{m_s\}}^{\Omega(k,n\Gamma)\Gamma_1\Gamma_2}$ [6]:

$$T_{\{n_s\}\{m_s\}}^{\Omega(k,n\Gamma)\Gamma_1\Gamma_2} = \beta(R^{\Omega(k,n\Gamma)} \otimes V_{\{n_s\}\{m_s\}}^{\Omega(k,n\Gamma)\Gamma_1\Gamma_2}), \tag{4}$$

where

$$\beta = \begin{cases} \sqrt{\Gamma_1}\left(\frac{-\sqrt{3}}{4}\right)^{\frac{\Omega}{2}} & \text{for } (k,n\Gamma) = (0, nA_1), \\ 1 & \text{for } (k,n\Gamma) \neq (0, nA_1). \end{cases} \tag{5}$$

The vibrational operator is also obtained by coupling in the group of covering of the molecule:

$$V_{\{n_s\}\{m_s\}}^{\alpha_1\Gamma_1\alpha_2\Gamma_2(\Gamma)} = \frac{1}{N}e^{i\varphi} \times \left(A_{\{n_s\}\{m_s\}}^{\alpha_1\Gamma_1\alpha_2\Gamma_2(\Gamma)} + \varepsilon(-1)^{\Gamma_1+\Gamma_2+\Gamma} \times B_{\{n_s\}\{m_s\}}^{\alpha_2\Gamma_2\alpha_1\Gamma_1(\Gamma)} \right) \tag{6}$$

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*XTDS and SPVIEW can be freely downloaded from http://www.u-bourgogne.fr/LPUB/shTDS.html.

In this formula,

$$\varepsilon = \begin{cases} -1 \text{ if this operator is an odd polynomial} \\ +1 \text{ if this operator is an even polynomial,} \end{cases} \tag{7}$$

N is the factor of standardization, and

$$e^{i\varphi} = \begin{cases} +i \text{ for } \varepsilon = 1 \\ -i \text{ for } \varepsilon = -1. \end{cases} \tag{8}$$

The stages followed in construction of the vibrational operators are as a follows [7]. By coupling operators n_s to creations operators $a_s^{+(C)}$, one gets

$$a_s^{+(C)} = \frac{1}{2} \left(q_{s\sigma} - ip_{s\sigma} \right)^{(C)}, \tag{9}$$

$$\left(a_s^{+(C)} \times a_s^{+(C)} \times \ldots \times a_s^{+(C)} \right)^{\alpha_1 \Gamma_1} = a_{\{n_s\}}^{+(\alpha_1 \Gamma_1)}. \tag{10}$$

By coupling operators m_s to annihilation operators $a_s^{(C)}$, one gets

$$a_s^{(C)} = \frac{\sqrt{2}}{2} \left(q_{s\sigma} + ip_{s\sigma} \right)^{(C)}, \tag{11}$$

$$\left(a_s^{(C)} \times a_s^{(C)} \times \ldots \times a_s^{(C)} \right)^{\alpha_2 \Gamma_2} = a_{\{m_s\}}^{(\alpha_2 \Gamma_2)}. \tag{12}$$

By coupling the two tensors obtained to build two vibrational operators, we get

$$A_{\{n_s\}\{m_s\}}^{\alpha_1 \Gamma_1 \alpha_2 \Gamma_2 (\Gamma)} = \left(a_{\{n_s\}}^{+(\alpha_1 \Gamma_1)} \times a_{\{m_s\}}^{(\alpha_2 \Gamma_2)} \right)^{(\Gamma)}, \tag{13}$$

$$B_{\{n_s\}\{m_s\}}^{\alpha_2 \Gamma_2 \alpha_1 \Gamma_1 (\Gamma)} = \left(a_{\{m_s\}}^{(\alpha_2 \Gamma_2)} \times a_{\{n_s\}}^{+(\alpha_1 \Gamma_1)} \right)^{(\Gamma)}. \tag{14}$$

V is a non-homogeneous polynomial of degree

$$d_v = \sum_s \left(n_s + m_s \right) \tag{15}$$

The rotational operator is obtained by the coupling of the elementary rotational operators [7]:

$$R^{\Omega(k,n\Gamma)} = \left[A^{(l_g)} \times A^{(l_g)} \times \ldots \times A^{(l_g)} \right]^{(k,n\Gamma)} \tag{16}$$

Where the row K takes the values:

$$k = \Omega, \Omega 2, \ldots, 1 and 0. \tag{17}$$

The degree of $R^{\Omega(k,n\Gamma)}$ is Ω.

3.   Analysis and discussion

The XTDS package provides the facility to fit Hamiltonian parameters using experimental data; this necessitates an assignment file (obtained via the SPVIEW software) bearing lines of the form given in Table 3. In practicality, we performed two tasks: First task is to calculate the Hamiltonian operator's matrix elements to six orders, for both ground state and the ϑ_4 band of monoisotopic $^{34}SF_6$. The second task performs an iteration to determine a new parameter set.

Table 3. The assignments file form.

N°	Exp. freq	Intensity	RMS	.... Assignment..........
8764	631.907032	− 0.6708E+00	0.001004	91 A2g 5 92 A2u 20 SPVIEW_EXASG
8765	631.912319	+ 0.7093E+00	0.000793	91 E g 10 92 E u 41 SPVIEW_EXASG
8766	631.926309	+ 0.6775E+00	0.000958	91 E g 12 92 E u 43 SPVIEW_EXASG
8767	631.931345	+ 0.6872E+00	0.000953	91 F2g 18 92 F2u 64 SPVIEW_EXASG
8768	631.935326	+ 0.5724E+00	0.000891	91 A2g 7 92 A2u 22 SPVIEW_EXASG
8769	631.940063	+ 0.6761E+00	0.000668	91 F2g 20 92 F2u 66 SPVIEW_EXASG
8770	631.945002	+ 0.6833E+00	0.000968	91 E g 14 92 E u 45 SPVIEW_EXASG

Fitting of the frequencies of spectral lines was conducted using the least squares iterative method, where the calculated frequencies are functions of the set of parameters $\{P\}$ of Hamiltonian tensorial form [8]:

$$S = S_0 + \frac{\partial S}{\partial P_i} + \frac{1}{2}\frac{\partial S}{\partial P_i \partial P_j} \cdot \delta P_i \delta P_j + \cdots, \tag{18}$$

where S is the mean square deviation [9]

$$S = \sum (\sigma_{obs} - \sigma_{cal})^2 / \sigma^2. \tag{19}$$

Here, σ is the experimental accuracy. S was taken as the sum of square deviations of the observed frequencies from the calculated ones over all measured lines.

The parameters are correlated if we can express their variations via the variation along a direction x as

$$\delta P_i = a_i \cdot \delta_x, \tag{20}$$

where a_i is the direction cosines.

In this analysis, we have 10 parameters for the ground states (Table 4) [2] and we have determined 22 other parameters for the ϑ_4 band; these values are given in Table 5. We adjusted parameter $t^{2(2,0E_g)F_{1u}F_{1u}}_{\{n_s\}\{m_s\}}$ manually and fixed it to the value 0.752654×10^{-04} cm^{-1}, to get a correct profile for the Q branch.

Figure 1 shows the root mean square deviation of the frequencies lines; the statistics of fit are given in Table 6.

These computed parameters of fit makes it possible to calculate simulated spectra, and subsequently compare with experimental spectrum, as shown in Figure 2. Figures 3–5 illustrate various areas of Figure 2 in the three regions of spectrum $P(\Delta J = -1)$, Q ($\Delta J = -0$) and R ($\Delta J = +1$) branches. We give some details in Table 7.
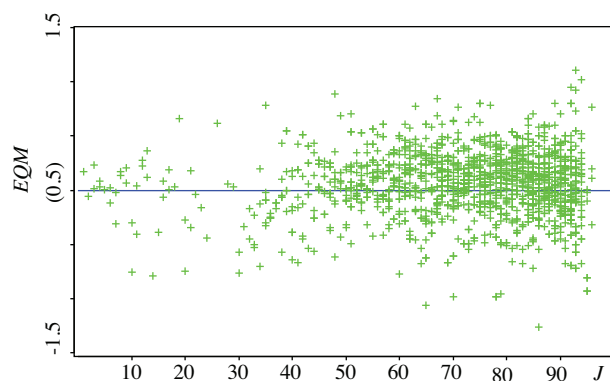
Figure 1. The root mean square deviation of the frequencies lines.

Table 4. Effective Hamiltonian parameters of the Ground State of monoisotopic $^{34}SF_6$.

| $\Omega(k, n\,\Gamma)$	n_s Γ_1	n_s Γ_2	Γ Hmn	value / cm^{-1}	St.Dev. / cm^{-1}
2(0,0A1g)	000000A1g	000000A1g	A1g 02	0 0.91078389192E-01	0.0000000E+00
4(0,0A1g)	000000A1g	000000A1g	A1g 04	0 -0.63369998149E-08	0.0000000E+00
4(4,0A1g)	000000A1g	000000A1g	A1g 04	0 0.18196943510E-09	0.0000000E+00
6(0,0A1g)	000000A1g	000000A1g	A1g 06	0 -0.15890094350E-12	0.0000000E+00
6(4,0A1g)	000000A1g	000000A1g	A1g 06	0 0.10083389785E-13	0.0000000E+00
6(6,0A1g)	000000A1g	000000A1g	A1g 06	0 -0.10615255469E-15	0.0000000E+00
8(0,0A1g)	000000A1g	000000A1g	A1g 08	0 0.59060087823E-18	0.0000000E+00
8(4,0A1g)	000000A1g	000000A1g	A1g 08	0 0.65795734511E-19	0.0000000E+00
8(6,0A1g)	000000A1g	000000A1g	A1g 08	0 -0.89391941374E-20	0.0000000E+00
8(8,0A1g)	000000A1g	000000A1g	A1g 08	0 -0.96703402824E-21	0.0000000E+00
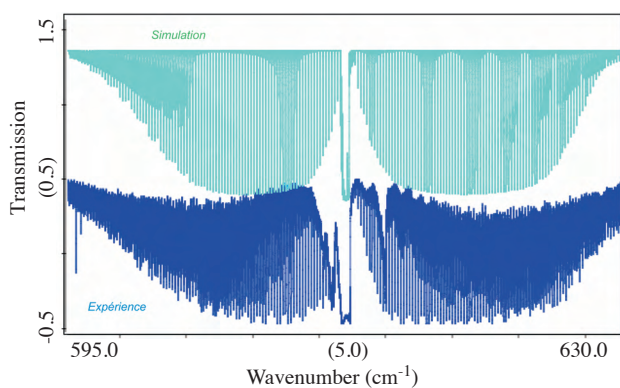
Figure 2. Experimental and simulated spectra of the ϑ_4 band of monoisotopic $^{34}SF_6$.
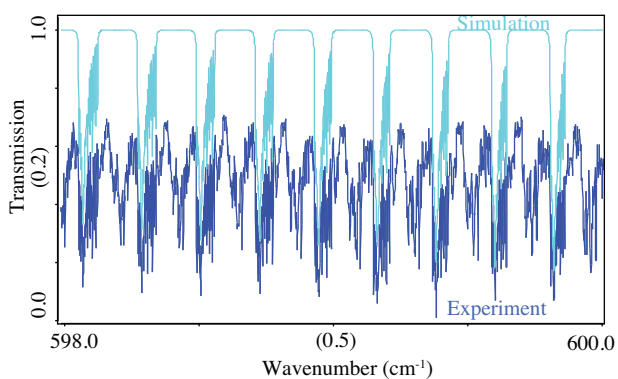

Figure 3. Part of experimental and simulated spectra in the P branch.

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Table 5. Effective Hamiltonian parameters of the ϑ_4 band of monoisotopic $^{34}SF_6$.

$\Omega(k, n\, \Gamma)$	$n_s\ \Gamma_1$	$n_s\ \Gamma_2$	Γ Hmn		value / cm^{-1}	St.Dev. / cm^{-1}
0(0,0A1g)	000100F1u	000100F1u	A1g 20	190	0.61221079379E+03	0.1666360E−04
1(1,0F1g)	000100F1u	000100F1u	F1g 21	37	−0.73013123539E−01	0.2381399E−05
2(0,0A1g)	000100F1u	000100F1u	A1g 22	18	−0.66476812969E−04	0.2851683E−07
2(2,0E g)	000100F1u	000100F1u	E g 22	0	0.75265400000E−04	0.0000000E+00
2(2,0F2g)	000100F1u	000100F1u	F2g 22	18	0.82794503615E−04	0.1224230E−06
3(1,0F1g)	000100F1u	000100F1u	F1g 23	12	−0.16115633194E−07	0.4684374E−09
3(3,0F1g)	000100F1u	000100F1u	F1g 23	25	0.53485801653E−07	0.2981333E−09
4(0,0A1g)	000100F1u	000100F1u	A1g 24	1	0.34330541579E−08	0.5441896E−10
4(2,0E g)	000100F1u	000100F1u	E g 24	1	0.56743622674E−08	0.8056314E−10
4(4,0A1g)	000100F1u	000100F1u	A1g 24	1	0.18397850831E−08	0.2888642E−10
4(4,0E g)	000100F1u	000100F1u	E g 24	1	0.72566848215E−09	0.1064078E−09
4(4,0F2g)	000100F1u	000100F1u	F2g 24	2	0.99165757983E−09	0.8109295E−10
5(1,0F1g)	000100F1u	000100F1u	F1g 25	9	0.12089800863E−11	0.3400066E−13
5(3,0F1g)	000100F1u	000100F1u	F1g 25	1	0.47165060223E−11	0.4285519E−12
5(5,0F1g)	000100F1u	000100F1u	F1g 25	1	0.38452415508E−11	0.4774977E−12
5(5,1F1g)	000100F1u	000100F1u	F1g 25	10	0.19626782148E−11	0.6613854E−13
6(0,0A1g)	000100F1u	000100F1u	A1g 26	1	0.18562222357E−12	0.6348078E−14
6(2,0F2g)	000100F1u	000100F1u	F2g 26	2	−0.12560950916E−12	0.4052106E−14
6(4,0A1g)	000100F1u	000100F1u	A1g 26	1	0.45838094452E−13	0.1886891E−14
6(4,0E g)	000100F1u	000100F1u	E g 26	1	0.77176985730E−13	0.5596607E−14
6(4,0F2g)	000100F1u	000100F1u	F2g 26	2	0.69343761394E−13	0.4287391E−14
6(6,0E g)	000100F1u	000100F1u	E g 26	13	−0.64226981343E−14	0.5223495E−15

One use of spectrum calculation is to calculate the energy values of both upper and lower levels; we calculate the transition moment between these two levels and, finally, the spectrum line frequencies and intensities are calculated from specific conditions (frequency range, temperature, pressure, etc.) [3].

Figure 6 show the calculated spectrum used by the Hamiltonian parameters determined in this work. This spectrum extends from 591.219543 cm^{-1} to 632.593073 cm^{-1}. It contains 12933 lines.

The reduced energies levels (Figure 7) are calculated via the relation

$$E_{red} = E - B_0 J(j+1) + \cdots, \tag{21}$$

where $B_0 = 9.1073389192 \times 10^{-2}$ cm^{-1} (the rotational constant) [8].

Table 6. The statistics of fit.

| J	NUMBER OF DATA	THEORETICAL PRECISION	CUMULATIVE NB OF DATA	PARTIAL STD. DEV.	MEAN DEV.	CUMULATIVE STD. DEV.
10	2	0.000000	17	0.000292	−0.000172	0.000034
20	1	0.000000	33	0.000349	−0.000349	0.000072
40	5	0.000000	88	0.000328	0.000172	0.000123
60	22	0.000000	343	0.000150	0.000104	0.000167
80	42	0.000002	920	0.000284	0.000181	0.000128
90	45	0.000004	1343	0.000180	0.000113	0.000121
95	11	0.000006	1496	0.000412	0.000289	0.000122
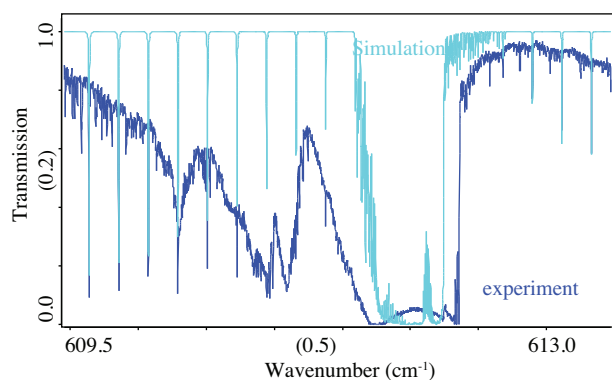
Figure 4. Part of experimental and simulated spectra in the Q branch.
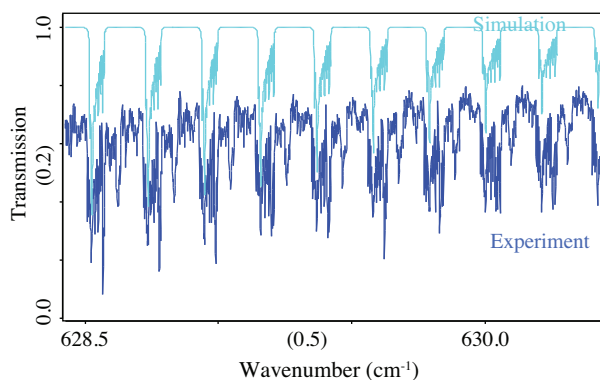
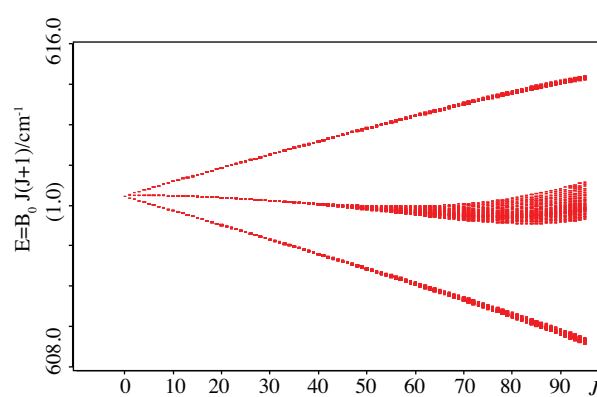
Figure 5. Part of experimental and simulated spectra in the R branch.

Table 7. Details on the simulated spectrum.

Simulation			
Development order	J_{max}	number of Data	RMS
06	95	1497	0.598×10^{-3} cm^{-1}
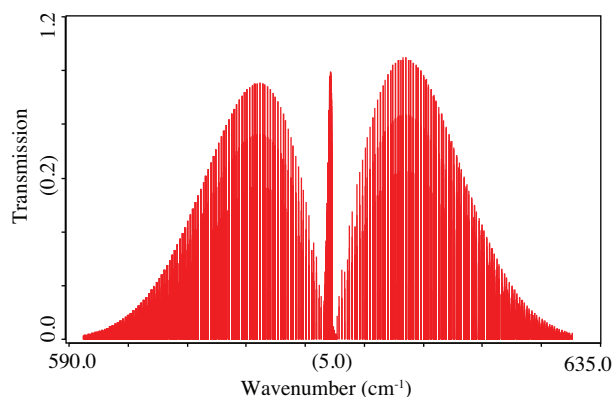
Figure 6. Calculated spectra of the ϑ_4 band of monoisotopic ^{34}SF$_6$.

Figure 7. Reduced energies for calculated levels of the ϑ_4 band of monoisotopic ^{34}SF$_6$.

4. Conclusion and perspectives

In the present work, we have analyzed the ϑ_4 band frequencies of monoisotopic $^{34}\mathrm{SF}_6$. The fitting of parameters and calculation of infrared spectrum are made using software programs XTDS and SPVIEW developed in Dijon.

We used 10 parameters of the ground state given in reference [2]. These parameters were fixed during analysis; 22 others parameters were also determined for the υ_4 band associated with the six orders of the rovibrational Hamiltonian, and for $J_{max} = 95$, using 1497 observed data with an root mean square equal to 0.598×10^{-3} cm^{-1}.

These parameters make it possible to calculate rovibrational spectrum used the tensorial form of the Hamiltonian adapted to the octahedral molecules. The study of the infrared spectrum is very important for the modelling of the atmospheric absorption of this species, since SF_6 is now recognized as a pollutant that can contribute to the greenhouse effect [9]. Its concentration in earth's atmosphere is presently small, but increases at a rate of around 7% per year due to industrial emissions [10].

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