High-resolution spectroscopy and global analysis of CF4 rovibrational bands to model its atmospheric absorption

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Highlights

- Global analysis of many rovibrational bands of CF4.
- This allows to simulate hot bands in the strongly absorbing 3 region.
- The results allow to model 92 % of the atmospheric absorption of this greenhouse gas.
- They have been used for spectroscopic database updates, including HI-TRAN2016.
High-resolution spectroscopy and global analysis of CF$_4$ rovibrational bands to model its atmospheric absorption

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Abstract

CF$_4$, or tetrafluoromethane, is a chemically inert and strongly absorbing greenhouse gas, mainly of anthropogenic origin. In order to monitor and reduce its atmospheric emissions and concentration, it is thus necessary to obtain an accurate model of its infrared absorption. Such models allow opacity calculations for radiative transfer atmospheric models. In the present work, we perform a
global analysis (divided into two distinct fitting schemes) of 17 rovibrational bands of CF$_4$. This gives a reliable model of many of its lower rovibrational levels and allows the calculation of the infrared absorption in the strongly absorbing $\nu_3$ region (1283 cm$^{-1}$ / 7.8 $\mu$m), including the main hot band, namely $\nu_3 + \nu_2 - \nu_2$ as well as $\nu_3 + \nu_1 - \nu_1$; we could also extrapolate the $\nu_3 + \nu_4 - \nu_4$ absorption. This represents almost 92% of the absorption at room temperature in this spectral region. A new accurate value of the C–F bond length is evaluated to $r_e = 1.314860(21)$ Å. The present results have been used to update the HITRAN, GEISA and TFMeCaSDa (VAMDC) databases.

Keywords: Carbon tetrafluoride, Tensorial Formalism, Spherical Top, Fourier Transform Infrared Spectroscopy, Global fit, Line Positions and Intensities

1. Introduction

Tetrafluoromethane (CF$_4$), also known as Halocarbon 14, PFC-14 or R-14, is a colorless, non-toxic, non-flammable, non-corrosive gas belonging to the group of perfluorocarbons (PFCs). PFCs are extremely powerful greenhouse gases and find themselves among the longest-lived atmospheric trace gases because of their great chemical stability. CF$_4$ is the most abundant PFC in the stratosphere, where it has an estimated lifetime of more than 50,000 years [1, 2]. For these reasons, CF$_4$ is cited in the Kyoto Protocol [3, 4, 5] as a substance whose atmospheric concentration should be monitored and reduced.

Infrared high spectral resolution solar occultation spectrometer measurements (Atmospheric Chemistry Experiment) led to an abundance of 70.45 ± 3.40 pptv (10$^{-12}$ per unit volume) [6]. Part of this is of natural origin [7, 8, 9]. The main source of CF$_4$, however, is anthropogenic and related to aluminum refining and semiconductor manufacturing [10]. Recent studies from the ground and from space [6, 11, 12] detailed the evolution of CF$_4$’s atmospheric concentration.

The in situ detection of atmospheric CF$_4$ is based on infrared solar absorption spectroscopy. The very intense $\nu_3$ vibration-rotation band around 7.8 $\mu$m was used for the first detection of CF$_4$ in the atmosphere from balloon-borne
observations [13]. Volumetric mixing ratio profiles of CF$_4$ were retrieved from satellite-borne [6, 14, 15] and balloon-borne observations [16]. The public spectroscopic databases like HITRAN [17, 18] or GEISA [19, 20], however, are not complete enough for atmospheric applications, since they completely lack hot band lines. This causes huge errors in CF$_4$ concentration retrievals when using these databases, as shows in Ref. [21]. The authors of this paper already pointed out that the lack of hot band lines in the databases is the main problem; thus, they used an empirical list of pseudo lines instead, which is much less flexible for simulations at any temperature.

Table 1 recalls the normal modes of this molecule. Using a simple harmonic approximation, it is easy to evaluate the population $P(v_1, v_2, v_3, v_4)$ of the different vibrational levels, as a function of temperature $T$ [22] as:

$$P(v_1, v_2, v_3, v_4) = \frac{g_v}{Q_v(T)} e^{-\frac{1}{kT}(\tilde{\nu}_1 v_1 + \tilde{\nu}_2 v_2 + \tilde{\nu}_3 v_3 + \tilde{\nu}_4 v_4)},$$

(1)

where $g_v$ is the vibrational level’s degeneracy and $Q_v(T)$ the vibrational partition function. This is plotted for CF$_4$ on Figure 1. We thus see that the sole $\nu_3$ fundamental band, also very strong, represents less than two-thirds of the absorption intensity at 296 K. In order to obtain a correct modelling of the molecule’s opacity, it is thus mandatory to model hot bands, at least the one starting from the first excited vibrational level, $v_2 = 1$ (435.38 cm$^{-1}$), that is the $\nu_3 + \nu_2 - \nu_2$ band.

<table>
<thead>
<tr>
<th>Mode $v$</th>
<th>$v_1$</th>
<th>$v_2$</th>
<th>$v_3$</th>
<th>$v_4$</th>
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<tbody>
<tr>
<td>Symmetry</td>
<td>$A_1$</td>
<td>$E$</td>
<td>$F_2$</td>
<td>$F_2$</td>
</tr>
<tr>
<td>Degeneracy</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Type</td>
<td>Stretching</td>
<td>Bending</td>
<td>Stretching</td>
<td>Bending</td>
</tr>
<tr>
<td>Activity</td>
<td>Raman</td>
<td>Raman</td>
<td>Absorption/Raman</td>
<td>Absorption/Raman</td>
</tr>
<tr>
<td>$\tilde{\nu}_i$ / cm$^{-1}$</td>
<td>909.1</td>
<td>435.4</td>
<td>1283.2</td>
<td>631.1</td>
</tr>
</tbody>
</table>

Table 1: The normal modes of vibration of CF$_4$. Symmetry is the mode’s irreducible representation in the $T_d$ point group. Activity is given for the fundamental band. $\tilde{\nu}_i$ is the approximate wavenumber for $^{12}$CF$_4$ taken from the present study (from Tables A.6 and B.7).

To achieve this goal, it is thus necessary to know at first the lowest vibrational states (like bands with $v_2 = v_3 = 1$ in the above example). The purpose of
the present paper is to perform a global and consistent analysis of as many rovibrational transitions as possible, gathering existing and new experimental data, in order to obtain a reliable modeling of CF$_4$'a absorption spectrum in the $\nu_3$ region, including the most significant hot bands. We complete here our two previous studies [23] and [24] with extensive new experimental data, strongly increasing the number of assigned lines and of studied bands.

Section 2 details the various data used, while Section 3 recalls the spherical-top model used for analysis and modeling. In Section 4, we present line assignments and effective Hamiltonian parameter fits. Line intensities are discussed in Section 5 and, finally, Section 6 presents the recent database updates concerning CF$_4$.

2. Experimental Details

This work gathers different data sources which are summarized in Table 2. We describe here the new spectra that have been recorded recently for this study.

It should be noticed that the uncertainty on line positions associated to high resolution Fourier Transform spectra is typically better than 0.001 cm$^{-1}$, while that of Raman spectra may be somewhat worse. However, knowing that we use here a huge number of lines from various sources, with different pressures, signal-to-noise ratios and apodization functions, we considered in the present study that all the line positions have a similar accuracy.

2.1. Infrared absorption data from Reims

The spectra are recorded with the Fourier Transform Spectrometer (FTS) of the GSMA laboratory already described elsewhere [25, 26]. The different characteristics of the spectra are reported in Table 2 (experimental conditions). The value of the diaphragm is 4 mm. The temperature of the cell was not stabilized, this is a 2 m-long White cell with an equivalent path length of 8.262 m. We
Figure 1: Population of the vibrational levels of CF$_4$, as a function of temperature. Values at 296 K for the four lower levels involved in the hot bands calculated in the present work (see Section 5) are indicated. On the right, vibrational levels are labelled using the vibrational quantum number quadruplet, $(v_1, v_2, v_3, v_4)$, see Table 1 and Section 3.
use two different detectors, a photovoltaic HgCdTe (or MCT) detector cooled at 77 K for the $\nu_2 + (\nu_3/2\nu_4)$ region and an InSb detector cooled at 77 K for the $\nu_1 + (\nu_3/2\nu_4)$ region, a Globar source, and different selected optical filters.

2.2. Infrared absorption data from Braunschweig

Room temperature CF$_4$ spectra were recorded with a high resolution FTS (Bruker IFS120HR) using a White multiple pass absorption cell with a path length of 4 m, equipped with KBr windows. The $\nu_2 + \nu_4$ and $\nu_1 + \nu_4$ bands were recorded using slightly different experimental conditions listed hereafter and grouped in Table 2.

A liquid nitrogen cooled MCT detector and a globar source combination was systematically used for the recording of the two bands. A KBr beam splitter was used for both bands. Gas pressures were monitored with a MKS capacitance gauge. The spectral resolution was 0.003 cm$^{-1}$. The $\nu_1 + \nu_4$ band was monitored at a gas pressure of 15 Torr (20 mbar) by co-adding 70 scans while the $\nu_2 + \nu_4$ band was recorded at a gas pressure of 11.25 Torr (15 mbar) by co-adding 200 scans.

2.3. Far infrared room temperature absorption data from SOLEIL

The far infrared room temperature data were recorded using the synchrotron radiation delivered by the AILES beamline of the synchrotron SOLEIL. The high-resolution FTS (Bruker IFS 125 HR) available on the beamline was connected to a White multiple pass optical cell to achieve an absorption path length of 150 m. The FTS was settled to its maximal resolution (0.00102 cm$^{-1}$) and a 6 $\mu$m thick mylar beam splitter and a bolometer equipped with an internal optical filter were used to record the 40–580 cm$^{-1}$ spectral range. A total of 326 and 274 scans were co-added for a gas pressure of 2.6 and 18 Torr respectively.

2.4. Jet-cooled infrared absorption data from SOLEIL

The jet-cooled absorption spectrum was recorded using the Jet-AILES apparatus implemented on the AILES beamline [27]. The infrared light beam
produced by the internal Globar source of the FTS was focused through a continuous planar supersonic expansion formed by a 30 $\mu$m $\times$ 60 mm slit nozzle. A throughput of about 6 slm (standard liter per minute) of CF$_4$ in 20 slm of argon was regulated by appropriate Bronkhorst mass flow controllers all along the recording. The total stagnation pressure was 1530 Torr and the vacuum chamber pressure was 0.66 Torr. KBr windows were used to isolate the vacuum chamber from the FTS and the detector compartment see Ref. [27]. A combination of a KBr beam splitter, a MCT photovoltaic detector and an adapted optical filter was used to co-add 386 scans in the 900–2700 cm$^{-1}$ spectral range, at a resolution of 0.002 cm$^{-1}$, and a rotational temperature of about 50 K.

2.5. THz rotational absorption data from SOLEIL

We also used newly recorded rotational lines in the $v_3 = 1$ state ($\nu_3 - \nu_3$ hot band) in the THz region (20–36 cm$^{-1}$). This dataset will be described in a forthcoming paper [28].

2.6. Earlier infrared absorption and Raman scattering data

We also use $\nu_3/2\nu_4$ infrared absorption and $\nu_1$, $2\nu_2 - \nu_1$ and $\nu_2$ stimulated Raman data taken from our previous works and described in Refs. [23] and [24], respectively.

3. Theoretical model

CF$_4$, just like CH$_4$ and other tetrahedral spherical top molecules with $T_d$ point group symmetry at equilibrium, possesses four normal modes of vibration: one non-degenerate mode with $A_1$ symmetry ($\nu_1$), one doubly-degenerate mode with $E$ symmetry ($\nu_2$), and two triply-degenerate modes with $F_2$ symmetry ($\nu_3$ and $\nu_4$), see Table 1. Only $F_2$ fundamentals are infrared active, at first approximation, but other vibrational levels can gain some absorption intensity through Coriolis and anharmonic couplings (see for instance [29, 30]).
Table 2: Experimental spectra used for the analyses. They were recorded in different laboratories. $\tilde{\nu}_0$ is the approximate wavenumber, $T$ the temperature, $P$ the pressure, $d$ the optical path and $R$ the spectral resolution.

<table>
<thead>
<tr>
<th>Transitions</th>
<th>Type</th>
<th>$\tilde{\nu}_0$/cm$^{-1}$</th>
<th>Place</th>
<th>$T$/K</th>
<th>$P$/Torr</th>
<th>$d$/m</th>
<th>$R$/cm$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_3 - \nu_3$</td>
<td>THz</td>
<td>35</td>
<td>SOLEIL</td>
<td>296</td>
<td>100</td>
<td>150</td>
<td>0.001</td>
<td>[28]</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>IR</td>
<td>435</td>
<td>SOLEIL</td>
<td>296</td>
<td>18</td>
<td>150</td>
<td>0.001</td>
<td>This work</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>IR</td>
<td>435</td>
<td>IPPR Rennes</td>
<td>296</td>
<td>501</td>
<td>970</td>
<td>0.02</td>
<td>[29]</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>Raman</td>
<td>435</td>
<td>CSIC Madrid</td>
<td>296</td>
<td>1.5</td>
<td>—</td>
<td>0.003</td>
<td>[24]</td>
</tr>
<tr>
<td>$\nu_4$</td>
<td>IR</td>
<td>435</td>
<td>SOLEIL</td>
<td>296</td>
<td>2.6</td>
<td>150</td>
<td>0.001</td>
<td>This work</td>
</tr>
<tr>
<td>$\nu_2 + \nu_4$</td>
<td>IR</td>
<td>1066</td>
<td>Braunschweig</td>
<td>296</td>
<td>11.25</td>
<td>4</td>
<td>0.003</td>
<td>This work</td>
</tr>
<tr>
<td>$2\nu_2$</td>
<td>Raman</td>
<td>870</td>
<td>CSIC Madrid</td>
<td>296</td>
<td>11.3</td>
<td>—</td>
<td>0.003</td>
<td>[24]</td>
</tr>
<tr>
<td>$\nu_3 / 2\nu_4$</td>
<td>IR</td>
<td>1283</td>
<td>Braunschweig</td>
<td>50</td>
<td>—</td>
<td>0.06</td>
<td>0.002</td>
<td>This work</td>
</tr>
<tr>
<td>$\nu_2 + (\nu_3 / 2\nu_4)$</td>
<td>IR jet</td>
<td>1720</td>
<td>SOLEIL</td>
<td>50</td>
<td>—</td>
<td>0.06</td>
<td>0.002</td>
<td>This work</td>
</tr>
<tr>
<td>$\nu_2 + (\nu_3 / 2\nu_4)$</td>
<td>IR</td>
<td>1720</td>
<td>CSMA Reims</td>
<td>295</td>
<td>5</td>
<td>8.262</td>
<td>0.003</td>
<td>This work</td>
</tr>
</tbody>
</table>

Spectra used for the “$\nu_1$” fit

<table>
<thead>
<tr>
<th>Transitions</th>
<th>Type</th>
<th>$\tilde{\nu}_0$/cm$^{-1}$</th>
<th>Place</th>
<th>$T$/K</th>
<th>$P$/Torr</th>
<th>$d$/m</th>
<th>$R$/cm$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1 - \nu_4$</td>
<td>Far-IR</td>
<td>278</td>
<td>SOLEIL</td>
<td>296</td>
<td>18</td>
<td>150</td>
<td>0.001</td>
<td>This work</td>
</tr>
<tr>
<td>$\nu_1$</td>
<td>Raman</td>
<td>969</td>
<td>CSIC Madrid</td>
<td>295</td>
<td>3.75</td>
<td>—</td>
<td>0.003</td>
<td>[24]</td>
</tr>
<tr>
<td>$2\nu_1 - \nu_1$</td>
<td>Raman</td>
<td>966</td>
<td>CSIC Madrid</td>
<td>296</td>
<td>22.5</td>
<td>—</td>
<td>0.003</td>
<td>[24]</td>
</tr>
<tr>
<td>$\nu_1 + \nu_4$</td>
<td>IR</td>
<td>1540</td>
<td>Braunschweig</td>
<td>296</td>
<td>15</td>
<td>4</td>
<td>0.003</td>
<td>This work</td>
</tr>
<tr>
<td>$\nu_1 + (\nu_3 / 2\nu_4)$</td>
<td>IR jet</td>
<td>2180</td>
<td>SOLEIL</td>
<td>50</td>
<td>—</td>
<td>0.06</td>
<td>0.001</td>
<td>This work</td>
</tr>
<tr>
<td>$\nu_1 + (\nu_3 / 2\nu_4)$</td>
<td>IR</td>
<td>2180</td>
<td>CSMA Reims</td>
<td>295</td>
<td>0.5</td>
<td>8.262</td>
<td>0.003</td>
<td>This work</td>
</tr>
</tbody>
</table>

† This spectrum was not used for the present analyses, but it is compared to a high-pressure simulation in Figure 5 below.

3.1. Effective Hamiltonian

In this paper we use the theoretical model based on the tensorial formalism and the vibrational extrapolation concept developed by the Dijon group [31, 32]. It takes full advantage of the molecule’s high symmetry. Let us just recall briefly the principles of this model which have been already detailed in Ref. [32].

Considering an $XY_4$ molecule such as CF$_4$, the vibrational levels are grouped in series of polyads named $P_k$ with $k = 0, \ldots, n$. For $k = 0$, we have $P_0$ which is the ground state (GS). The Hamiltonian operator is written as follows:

$$H = \mathcal{H}_{(P_0=GS)} + \mathcal{H}_{(P_1)} + \ldots + \mathcal{H}_{(P_k)} + \ldots + \mathcal{H}_{(P_{n-1})} + \mathcal{H}_{(P_n)}.$$  \hspace{0.5cm} (2)

where the different $\mathcal{H}_{(P_k)}$ terms are expressed in the following form:

$$\mathcal{H}_{(P_k)} = \sum_{\text{all indexes}} \hat{\Omega}^{(K,n\Gamma)}_{\{s\}\{s'\}} \beta^{(K,n\Gamma)} \left[ \epsilon_{\{s\}\{s'\}} \otimes R^{(K,n\Gamma)} \right] (A_1).$$  \hspace{0.5cm} (3)

In this equation, the $\epsilon_{\{s\}\{s'\}}$ are the parameters to be determined, while $\epsilon_{\{s\}\{s'\}}$ and $R^{(K,n\Gamma)}$ are vibrational and rotational operators, respectively.
For each term, $\Omega_v$ and $\Omega$ represent the degree in elementary vibrational operators (creation $a^+$ and annihilation $a$ operators), and rotational operators (components $J_x$, $J_y$ and $J_z$ of the angular momentum), respectively. $\beta$ is a factor that allows the scalar terms (terms with $\Gamma = A_1$, the totally symmetric irreducible representation of $T_d$) to match the “usual” contributions like $B_0 J^2$, etc. The order of each individual term is defined as $\Omega + \Omega_v - 2$. We deal with the effective Hamiltonians which are obtained, for a given polyad $P_k$, by the projection of $H$ in the $P_n$ Hilbert subspace:

$$H^{<P_n>} = P^{<P_n>} HP^{<P_n>}$$

$$= H^{<P_n>} + H^{<P_{n-1}>} + \ldots + H^{<P_{1}>}_{\{GS\}} + H^{<P_{1}>}_{\{P_1\}} + \ldots + H^{<P_{1}>}_{\{P_{n-1}\}} + H^{<P_{n}>}_{\{P_n\}}.$$  

This effective Hamiltonian contains all the operators, and thus all the parameters, of the lower polyads. Parameters of upper polyads are (presumably) small corrections to those of the lower ones since in our model they are in fact differences between lower and upper state values; this is what we call “vibrational extrapolation”. It enables global fits of data for a series of consecutive polyads, ensures a global consistency and, usually, a better convergence of molecular parameters. Just in order to give a simple illustrative example, if we consider a polyad $P_1$ containing a fundamental band, then the effective Hamiltonian $H^{<P_1>} = H^{<P_{1}>}_{\{GS\}} + H^{<P_{1}>}_{\{P_1\}}$ contains in $H^{<P_{1}>}_{\{GS\}}$ the ground state rotational constant $B_0$ and in $H^{<P_{1}>}_{\{P_1\}}$ the difference $\Delta B = B_1 - B_0$, that is the difference between the upper (say, $B_1$) and lower ($B_0$) state rotational constants, and not $B_1$ itself. We usually have $\Delta B \ll B_0, B_1$.

### 3.2. Polyad scheme definition

Generally speaking, the polyad number $n$ can be defined as

$$n = i_1 v_1 + i_2 v_2 + i_3 v_3 + i_4 v_4,$$  

where $v_1$, $v_2$, $v_3$ and $v_4$ are vibrational quantum numbers for the four normal modes of the molecule, while $i_1$, $i_2$, $i_3$ and $i_4$ are integer numbers chosen to group vibrational levels ($v_1, v_2, v_3, v_4$) into polyads, according to their wavenumbers.
In particular, when some vibrational numbers display simple approximate ratios, a clear polyad structure may appear. For instance, the well-known polyad structure of methane [33] comes from the fact that \( \tilde{\nu}_1 \simeq \tilde{\nu}_3 \simeq 2\tilde{\nu}_2 \simeq 2\tilde{\nu}_4 \), leading to large absorbing bands which are regularly spaced, each 1500 cm\(^{-1}\). In the case of CF\(_4\), however, no such global approximate relation exists. In Ref. [23], it was just noticed that \( \tilde{\nu}_3 \simeq 2\tilde{\nu}_4 \), implying to place the \( v_3 = 1 \) and \( v_4 = 1 \) vibrational levels in the same polyad. Thus, contrary to what is done for CH\(_4\), it appears difficult to include all modes in a single polyad scheme at this stage. We thus decided here to build two separate polyad schemes:

- A “\( \nu_2 \)” polyad scheme implying the \( \nu_2 \) bending mode, its overtones and combinations and related bands linked to it through combinations (in fact, almost “all” the lowest CF\(_4\) bands not linked with the \( \nu_1 \) mode). In this case, we choose:

\[
\begin{align*}
n_{\nu_2} &= 2v_2 + 6v_3 + 3v_4. 
\end{align*}
\]

- A “\( \nu_1 \)” polyad scheme implying the \( \nu_1 \) stretching mode influence into several bands. In this case, we choose:

\[
\begin{align*}
n_{\nu_1} &= 3v_1 + 4v_3 + 2v_4. 
\end{align*}
\]

In both cases, there is no polyad number 1 (this one has no corresponding vibrational level). As we will see later, these two schemes lead to two separate global effective Hamiltonian fits. Tables 3 and 4 list essential details on the polyads including the number of operators for the “\( \nu_2 \)” and “\( \nu_1 \)” schemes, respectively. All vibrational quantum numbers are limited to the values 0, 1 and 2. Except for the (non-existing) polyad number 1, all effective Hamiltonian contributions have been expanded up to the 8th order. In the final analysis, however (see Section 4), only a small subset of all the resulting parameters could be actually determined from the fit, as indicated in the last column of both tables.

Figure 2 shows the transitions included in the two fits, corresponding to the two polyad schemes. These fits are described in Section 4 below.
### Table 3: Effective Hamiltonian for the \( \nu_2 \)” scheme, with the number of parameters in the model. Vibrational levels are denoted using vibrational quantum numbers in the form \((v_1, v_2, v_3, v_3)\). The last column shows the number of parameters that could be fitted (see Section 4.1).

<table>
<thead>
<tr>
<th>Polyad</th>
<th>Vibrational levels</th>
<th>Order</th>
<th>Nb. parameters</th>
<th>Nb. fitted</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(0,0,0,0)</td>
<td>8</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>1</td>
<td>—</td>
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<tr>
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<td>92</td>
</tr>
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<td><strong>Total</strong></td>
<td></td>
<td><strong>887</strong></td>
<td><strong>197</strong></td>
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</table>

3.3. Line intensity calculations

In order to calculate transition intensities, the effective dipole moment transition operator is also determined in a similar way (see Ref. [32] for more detail). This operator is expanded to the lowest possible degree. In the case of the \( \nu_3/2\nu_4 \) dyad, we use the same dipole moment expansion as in our previous paper [23]. Dipole moment derivative values and line intensities in this strongly absorbing \( \nu_4 \) region are discussed in Section 5.

3.4. Basis sets

The calculation of the effective Hamiltonian and effective dipole moment matrix elements are performed in the coupled rovibrational basis

\[
\left[ \Psi_v^{(C_1)} \otimes \Psi_v^{(J,nC_1)} \right]^{(C)} \right],
\]

(8)
Figure 2: Vibrational transitions and levels used in the two fits. Dashed lines correspond to Raman transitions. The $\nu_2$ fundamental band is observed both in infrared absorption and Raman scattering (see text).
<table>
<thead>
<tr>
<th>Polyad</th>
<th>Vibrational levels</th>
<th>Order</th>
<th>Nb. parameters</th>
<th>Nb. fitted</th>
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<td>0</td>
<td>0</td>
</tr>
<tr>
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<td>8</td>
<td>48</td>
<td>0†</td>
</tr>
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<td>(1,0,0,0)</td>
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<td>11</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>(0,0,1,0),(0,0,0,2)</td>
<td>8</td>
<td>224</td>
<td>0†</td>
</tr>
<tr>
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<td>24</td>
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<tr>
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<tr>
<td>Total</td>
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<td></td>
<td>648</td>
<td>107</td>
</tr>
</tbody>
</table>

† Parameters fixed to the values from the “ν2” fit, see Table 3.
‡ Only ν1 = 2 parameters are fitted.

Table 4: Effective Hamiltonian for the “ν1” scheme, with the number of parameters in the model. Vibrational levels are denoted using vibrational quantum numbers in the form (ν1, ν2, ν3, ν4). The last column shows the number of parameters that could be fitted (see Section 4.2).

where Ψ(J,nCr) is a rotational wavefunction with angular momentum J, rotational symmetry species Cr, and multiplicity index n; Ψ(Cv) is a coupled vibrational basis set; C is the overall symmetry species (C = Cv ⊗ Cr). Ψ(Cv) contains the relevant functions for the 4 normal modes of vibration,

$$\left| \Psi(C_v) \right\rangle = \left| \left( \Psi_{v1}^{(A1)} \otimes \Psi_{v2}^{(l_2,C_2)} \otimes \Psi_{v3}^{(l_3,n_3C_3)} \right) \otimes \Psi_{v4}^{(l_4,n_4C_4)} \right\rangle_{C} \right\rangle$$

(9)

For each normal mode number i = 1 to 4, we use a symmetrized harmonic oscillator basis set denoted

$$\left| \psi_{v_i}^{(l_i,n_iC_i)} \right\rangle = \left| v_i, l_i, n_iC_i, \sigma_i \right\rangle,$$

(10)

where

$$l_1 = 0,$$

(11)

$$l_i = v_i, v_i - 2, v_i - 4, \ldots, 0 \text{ or } 1 \ (i = 2, 3 \text{ or } 4),$$

(12)
are the usual vibrational angular momentum quantum numbers for degenerate vibrations. $C_i$ is a $T_d$ irreducible representation (irrep) and $n_i$ a multiplicity index used when $C_i$ appears more than once for a given $(v_i, l_i)$ set. We always have $n_1 = 0$, $n_2 = 0$ and necessarily $C_1 = A_1$. In Equation (9), we have:

$$C_{23} = C_2 \otimes C_3 \quad \text{and} \quad C = C_{23} \otimes C_4,$$

$C_v$ being the overall vibrational symmetry. All $C$ symbols here represent $T_d$ irreps.

4. Global fits of line positions

As already mentioned, the philosophy of this work is to gather many CF$_4$ high-resolution spectroscopic data (see Table 2) to use them in global fits of line positions. Just as explained in Section 3.2, it appears difficult to include all CF$_4$ vibrational levels in a single polyad scheme. As a matter of fact, contrary to methane (CH$_4$) which has a well-defined polyad structure [33, 34, 35], CF$_4$ has fundamental vibrational wavenumber with a more random distribution; we can just notice, as in our previous work [23], that $\tilde{\nu}_3$ is close to $2\tilde{\nu}_4$ leading to a Fermi interaction between the corresponding bands that must be treated as a dyad. This interaction propagates to all combination bands built on $\nu_3/2\nu_4$, for instance when adding $\nu_1$ or $\nu_2$ quanta.

Thus, it appeared wise and more practical to perform assignments and effective Hamiltonian fit following two partial polyad schemes. These two schemes are described in Section 3.2 and the two sections below describe the assignment and fit process in each case.

It should be noticed that during the fits the different sets of data were used with the same weights due to compatible quality of the experimental spectra (see Section 2).

4.1. Global fit based on the $\nu_2$ mode

The fundamental band of the $\nu_2$ mode of tetrahedral XY$_4$ molecules is, at first approximation, only active in Raman scattering. A few years ago, we could
analyze this fundamental band thanks to high-resolution stimulated Raman spectroscopy [24]. This excellent technique can provide essential data for such non-infrared active modes [36, 37, 38, 39, 24] but has also some drawbacks: its spectral resolution (around 0.003 cm$^{-1}$) and sensitivity are significantly lower than what can be achieved using infrared absorption spectroscopy. In some cases, however, $\nu_2$ can gain intensity from rovibrational coupling with another vibrational mode. This is the case for methane, for instance, whose $\nu_2$ and $\nu_4$ wavenumbers are quite close to each other [40], so that the two corresponding fundamentals form a bending dyad. Although these two modes are more separated for CF$_4$, a weak $\nu_2$ fundamental band is observable in the 400–470 cm$^{-1}$ region when a long optical path length is used [29]. In other words, the weakness of this interaction does not necessitate to consider a $v_2 = v_4 = 1$ polyad, but its influence on the $\nu_2$ induced dipole moment is sufficient to let this fundamental band appear in infrared absorption. In the present work, we used such a spectrum (see Section 2 and Table 2), along with the existing Raman data from Ref. [24].

We then included new data concerning the $\nu_2 + \nu_4$ combination band. Analyzing this one implies to know the $v_4 = 1$ level itself, so the previous data on the $\nu_4$ fundamental [23] were necessary. As this one was already a part of a global study including the $\nu_3/2\nu_4$ dyad (see above), we also included data corresponding to this region, coming both from Ref. [23] and from newly recorded spectra (Table 2). Some recently recorded THz lines of the $\nu_3 - \nu_3$ hot band are also used [28]. Finally, a new $\nu_2 + (\nu_4/2\nu_2)$ spectrum was also considered, leading to a global analysis and fit of all rovibrational bands that do not imply the $\nu_1$ mode in the 0 to 1750 cm$^{-1}$ region. We also noticed that the new spectra allowed to assign some hot band lines for $2\nu_2 - \nu_2$ and $\nu_3 - 2\nu_2$ in the $\nu_2$ infrared spectrum, which completed the dataset. As explained in Section 3.2 and Table 3, this is referred as the “$\nu_2$” scheme and fit.

We can notice that this study allowed to refine the GS parameters. It was also necessary to correct some $\nu_3$, $2\nu_2$ and $\nu_3/2\nu_4$ assignments from our previous papers [23, 24]. $\nu_4$ and $\nu_3/2\nu_4$ are now assigned up to slightly higher $J$ values.
The analysis was performed thanks to the STDS [41] package of the XTDS software [42] which allows to calculate and fit XY$_4$ spherical-top spectra. All assignments have been performed with help of the SPVIEW complementary software [42]. A total of 17,626 lines could be assigned (see Table 5) to determine 197 effective Hamiltonian parameters (see Table 3). The overall root mean square deviation is $1.116 \times 10^{-3}$ cm$^{-1}$. For each of the new spectra, initial simulations were performed using the existing effective Hamiltonian parameters from the previous studies which yielded preliminary assignments. Then the new parameters were determined and the assignments refined. Some corrections were also made to the assignments form the previous works. The process was iterated till no more assignment appeared possible.

Table 5 summarizes the fit statistics and Figure 3 displays the fit residuals for line positions. Table A.6 in the Appendix gives the effective Hamiltonian parameter values. Concerning the $\nu_2$ fundamental band itself, it should be noticed that we now have 3.2 times more lines, for $J$ up to 82, instead of 45, compared to Ref. [24].

We give four examples of comparisons between experiment and simulation in spectral regions in infrared absorption, which are analyzed and modeled here for the first time. Figure 4 presents the interaction-induced $\nu_2$ region for which we could analyse and simulate two hot bands, namely $2\nu_2 - \nu_2$ and $\nu_3 - 2\nu_2$. Figure 5 represents the same region at a high pressure, the experimental data being those used for Figure 1 of Ref. [29]. For these first two examples, the vertical scale of the simulations has been adjusted manually to match with the experimental spectra. No attempts to determine absolute intensities has been performed in this case, contrary to what is discussed in Section 5 below for the strongly absorbing $\nu_3$ region. Figure 6 displays the $\nu_2 + \nu_4$ region. Figure 7 shows some details concerning the quite complex $\nu_2 + (\nu_3/2\nu_4)$ region. This one has 8 vibrational sublevels. We illustrate this on Figure 8, which displays the rovibrational sublevels, as a function of the rotational quantum number $J$. 

17
Table 5: Fit statistics for the two polyad schemes. $\sigma$ is the dimensionless standard deviation and $d_{\text{RMS}}$ the root mean square deviation in $10^{-3}$ cm$^{-1}$, except for THz $\nu_3 - \nu_3$ lines for which it is given in MHz.

More precisely, this Figure shows the reduced energy levels, defined by:

$$\tilde{\nu}_{\text{red}} = \tilde{\nu} - \sum_{\Omega} \Omega_{\{\text{GS}\}} \Omega_{\{\text{GS}\}} (J(J+1))^{\Omega/2}$$

$$= \nu - B_0 J(J+1) + D_0 J^2(J+1)^2 - \ldots,$$

i.e. we subtract the dominant scalar polynomial terms in order to enhance levels splittings due to molecular symmetry. We give both the calculated and observed reduced energy levels. Observed levels are simply levels reached by assigned transitions which are included in the fit. This gives a good idea of the sampling of the energy spectrum.
Figure 3: Fit residuals for line positions, in the case of the \( \nu_2 \) fit. In each spectral region, the colors correspond to the different vibrational sublevels.

Figure 4: Measured \( \nu_2 \) spectral region in infrared absorption at 296 K and 18 Torr, compared to the simulation with two hot bands. The insert details a part of the \( P \) branch, around the \( \nu_3 - 2\nu_2 \) region.
Figure 5: Measured $\nu_2$ spectral region at 296 K and high pressure (501 Torr, see Table 2 and Ref. [29]), compared to the simulation with two hot bands.

Figure 6: Measured $\nu_2 + \nu_4$ difference band at 296 K and 11.25 Torr, compared to the simulation. The insert details a part of the $P$ branch.
Figure 7: Measured spectrum in the $\nu_2 + (\nu_3/2\nu_4)$ region (295 K, 5 Torr), compared to the simulation, with detailed view of some parts. Strong lines on the wings are water vapor lines.

4.2. Global fit based on the $\nu_1$ mode

Just as for $\nu_2$, the totally symmetric $\nu_1$ stretching mode is, in first approximation, only Raman-active. Contrary to the CH$_4$ case [43] and to what happens with $\nu_2$ (see previous Section), rovibrational interaction-induced $\nu_1$ lines are too weak to be observed in infrared absorption. Thus, up to now, high-resolution stimulated Raman spectroscopy was the only data source for this mode [24]. The Raman spectrum of $\nu_1$ only displays a narrow Q branch for the $\nu_1$ fundamental band, which strongly limits the number of assignable lines.

Recently, in the case of the SF$_6$ molecule, we have shown another way to access such modes using the difference bands [44]. As a matter of fact, the far infrared region of CF$_4$ near 280 cm$^{-1}$ displays a very nice $\nu_1 - \nu_4$ band with a well-defined $PQR$ branches structure. As described in Section 2, the
Figure 8: Observed and calculated reduced rovibrational energy levels for the $\nu_2 + (\nu_3/2\nu_4)$ region, compared to the simulation. “Observed” levels correspond to those reached by assigned transitions. The colors represent the mixings between the different sublevels.
synchrotron radiation was of great help to obtain spectra with an excellent signal-to-noise ratio in this low wavenumber region.

It made it possible to perform a new global analysis including vibrational levels implying the $\nu_1$ mode. This includes $\nu_1$ and $2\nu_1 - \nu_1$ Raman lines, and new spectra for $\nu_1 - \nu_4$, $\nu_1 + \nu_4$ and $\nu_1 + (\nu_3/2\nu_4)$. As explained in Section 3.2 and Table 4, this is referred as the “$\nu_1$” scheme and fit. Parameters for the ground state, $v_1 = 1$, $v_4 = 2$ and $v_3 = 1$ levels were fixed to the values obtained in the “$\nu_2$” fit. The reason is that, in this second case, we have less data and less parameters to fit. The line assignment and fit and simulation procedures using the XTDS and SPVIEW softwares [42] were totally similar to what we did for the “$\nu_2$” fit (see previous Section).

Table 5 summarizes the fit statistics and Figure 9 displays the fit residuals for line positions. Table B.7 in the Appendix lists the effective Hamiltonian parameter values.
Figure 10: Measured $\nu_1-\nu_4$ difference band at 296 K and 18 Torr, compared to the simulation. Strong lines peaks are water vapor lines. The insert details a part of the $R$ branch.

Figure 10 displays the $\nu_1-\nu_4$ region, compared to the simulation. The insert nicely illustrates the well-defined fine structure in the $P$ branch. Figure 11 shows the $\nu_1+(\nu_3/2\nu_4)$ region. This one has 4 vibrational sublevels. Figure 12 displays the calculated and observed reduced energy levels, as defined by Equation 14.

4.3. Discussion

In Ref. [24], we calculated the equilibrium bond length $r_e$ of CF$_4$. This calculation is possible if one knows the value of the rotational constant $B_0$ in the ground state and rotational constant differences in all the vibrational
Figure 11: Measured spectrum of the $\nu_1 + (\nu_3/2\nu_4)$ region at 295 K and 0.5 Torr, compared to the simulation. The insert details a part of the $R$ branch. The strong $Q$ branch near 2183 cm$^{-1}$ is the $\nu_1 + \nu_3 + \nu_2 - \nu_2$ hot band, which is not simulated here.
Figure 12: Observed and calculated reduced rovibrational energy levels for the $\nu_1 + (\nu_3/2\nu_4)$ region, compared to the simulation. “Observed” levels correspond to those reached by assigned transitions. The colors represent the mixings between the different sublevels.
fundamental levels, say $\Delta B_i = B_i - B_0$ ($i = 1, \ldots, 4$), where $B_i$ is the rotational constant in an excited state with $v_i = 1$. The formula giving $B_e$ is [36]:

$$
B_e = B_0 - \frac{1}{2} \sum_{i=1}^{4} d_i \Delta B_i,
$$

where $d_i$ is the normal mode degeneracy ($d_1 = 1$, $d_2 = 2$, $d_3 = d_4 = 3$). The equilibrium bond length is:

$$
r_e = \sqrt{\frac{3h}{64\pi^2 c m_F B_e}},
$$

$h$ being Planck’s constant and $m_F$ the fluorine atom’s mass. The fitted parameters $\Delta B_i = \Gamma_{\nu_{\nu_{\nu}}}^{[i] [i]}$ result from the two previous global fits. Using their values and standard deviation taken from Tables A.6 and B.7, we get:

$$
B_e = 0.1924649(61) \text{ cm}^{-1},
$$

and thus:

$$
r_e = 1.314860(21) \text{ Å}.
$$

This value is slightly smaller than in Ref. [24], but more precise.

5. Line intensities

Using the present results about the $v_2 = v_3 = 1/v_4 = 2$ level ($v_2 + (v_3/2v_4)$ dyad region) and of $v_1 = v_3 = 1/v_4 = 2$ level ($\nu_1 + (v_3/2v_4)$ dyad region), it becomes possible to calculate the $\nu_3 + \nu_2 - \nu_2$, $2\nu_4 + \nu_2 - \nu_2$, $\nu_3 + \nu_1 - \nu_1$ and $2\nu_3 + \nu_1 - \nu_1$ hot bands, in the $\nu_3/2\nu_4$ region. In order to calculate absolute line intensities, we can use the $\nu_3$ and $2\nu_4$ dipole moment derivative parameters from Ref. [45] (see also Section 5 of Ref. [23] for more explanations). These two values are sufficient and common to both cold and hot bands, when limiting the dipole moment operator expansion to degree 1. No further dipole moment refinement is possible, since no individual line intensity measurement is available, due to the spectroscopic congestion for this molecules, for which almost all observed lines result from the overlap of several transitions.
Figure 13: Experimental spectrum in the $\nu_3$ region (296 K, 17 Torr), including hot bands, compared to the simulation. The insert details a part of the $R$ branch. Most of the absorption intensity is well reproduced by the model.

It is even possible to extrapolate the $\nu_3 + \nu_4 - \nu_4$ and $3\nu_4 - \nu_4$ hot bands, although the corresponding vibrational levels could not be assigned in the current work. These would be a part of the polyad number 9 in the “$\nu_2$” polyad scheme, whose effective Hamiltonian can expanded up to order two only, leading to purely vibrational parameters only. We just set up the four parameters of the $v_3 = v_4 = 1$ vibrational level (corresponding to the anharmonicity coefficient of its four sublevels) to a constant value of $-4.7 \text{ cm}^{-1}$, corresponding to a correct positioning of the $\nu_3 + \nu_4 - \nu_4$ $Q$ branch (see Figures 13 and 14 below).

The resulting simulation at high resolution is shown on Figure 13, compared to the corresponding spectrum recorded in the present work. Figure 14 shows a low-resolution simulation, compared to a band profile from the PNNL database [46].
It appears clearly that we can now simulate a significant part (almost 92 %, see Figure 1) of the $\nu_3$ region absorption intensity at room temperature, compared to the sole $\nu_3$ fundamental simulation (which represents only 65.8 % of the intensity).

6. HITRAN and TFMeCaSDa updates

Although the present work was not fully ready on time for the recent HITRAN 2016 \cite{18} and GEISA 2015 \cite{20} updates, a new partial calculated line list including $\nu_3$ and $\nu_3 + \nu_2 - \nu_2$ only could be used for the HITRAN 2016 update itself. Then, the complete CF$_4$ line list in the $\nu_3$ region, including hot bands based on $\nu_1$, $\nu_2$ and $\nu_4$ (see previous Section) has now been accepted by these databases for an intermediate online update.

Moreover, we have previously setup a database named TFMeCaSDa (Tetra-Fluoro-Methane Calculated Spectroscopic Database) of the calculated CF$_4$ spectroscopic lines in the framework of the Virtual Atomic and Molecular Data Cen-

Figure 14: PNNL (see text and Ref. \cite{46}) spectrum of the $\nu_3$ region, including hot bands, at low resolution, compared to the simulation.
7. Conclusion

The two global fits presented in this study constitute the most extensive study of CF\textsubscript{4} rovibrational levels to date. This enables a significant update of the public spectroscopic databases concerning this molecule. Our results should allow a much better modeling of the atmospheric absorption and improved concentration retrievals from satellite, balloon-borne and ground-based data.

The next step will be to include even more bands in the analysis, possibly in a unique global polyad scheme, if possible. In particular, the \( \nu_3 + \nu_4 \) band should be assigned and analyzed in detail. The knowledge of this one would lead to the calculation of the \( \nu_3 + \nu_4 - \nu_4 \) hot band, which is the second one in terms of absorption intensity, representing 9.2\% of it in the \( \nu_3 \) region at room temperature (here, we could just extrapolate this band). This kind of rovibrational system is quite challenging to analyze, since the \( \nu_3 = \nu_4 = 1 \) vibrational level has four sublevels whose exact position is still unknown. Presumably, \textit{ab initio} calculations would be of help to get initial values for these anharmonicity coefficients. Moreover, this band should interact with \( 3\nu_4 \).

Another important challenge would be to accurately measure the line intensities and to determine the experimental dipole moment parameters, instead of using previously calculated values. This is not an easy task, for such a heavy molecule with a very congested spectrum consisting mostly of many overlapping lines.

8. Acknowledgements

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Appendix A. Effective Hamiltonian parameters from the “$\nu_2$” fit.

Table A.6 below gives the fitted values of the effective Hamiltonian parameters of CF$_4$ for the “$\nu_2$” fit (see Section 4.1). Notations correspond to Equation (3). Standard deviation is given in parentheses in the unit of the last two digits.

| Parameter | Polyad | Order | $\Omega(K,nC)$ | $|s\rangle$ | $C_v$ | $|s'\rangle$ | $C_v'$ | Value $\pm$ Value |
|-----------|--------|-------|----------------|-----------|-------|-----------|-------|------------------|
| 1         | GS     | 0     | 2(0.0A$_1$)    | 0000.A$_1$| 0000.A$_1$| 1.911952(35) | 3.00$^{-1}$ |
| 2         | GS     | 2     | 4(0.0A$_1$)    | 0000.A$_1$| 0000.A$_1$| -6.360(33)    | 3.00$^{-8}$ |
| 3         | GS     | 2     | 4(4.0A$_1$)    | 0000.A$_1$| 0000.A$_1$| 7.433(37)     | 3.00$^{-9}$ |
| 4         | GS     | 4     | 6(0.0A$_1$)    | 0000.A$_1$| 0000.A$_1$| -2.390(10)    | 3.00$^{-12}$|
| 5         | GS     | 4     | 6(4.0A$_1$)    | 0000.A$_1$| 0000.A$_1$| -1.982(14)    | 3.00$^{-13}$|
| 6         | GS     | 4     | 6(6.0A$_1$)    | 0000.A$_1$| 0000.A$_1$| -1.010(12)    | 3.00$^{-13}$|
| 7         | GS     | 6     | 8(0.0A$_1$)    | 0000.A$_1$| 0000.A$_1$| 5.544(92)     | 3.00$^{-10}$|
| 8         | GS     | 6     | 8(4.0A$_1$)    | 0000.A$_1$| 0000.A$_1$| 4.654(30)     | 3.00$^{-17}$|
| 9         | GS     | 6     | 8(6.0A$_1$)    | 0000.A$_1$| 0000.A$_1$| -1.054(11)    | 3.00$^{-17}$|
| 10        | GS     | 6     | 8(8.0A$_1$)    | 0000.A$_1$| 0000.A$_1$| 4.73(45)      | 3.00$^{-19}$|
| 16        | $\nu_2$| 0     | 0(0.0A$_1$)    | 0100.E    | 0100.E | 435.380220(40) | 3.00$^{-4}$ |
| 17        | $\nu_2$| 2     | 2(0.0A$_1$)    | 0100.E    | 0100.E | -3.37820(67)  | 3.00$^{-4}$ |
| 18        | $\nu_2$| 2     | 2(2.0E)        | 0100.E    | 0100.E | -1.04544(70)  | 3.00$^{-4}$ |
| 19        | $\nu_2$| 3     | 3(3.0A$_1$)    | 0100.E    | 0100.E | 2.9171(54)    | 3.00$^{-7}$ |
| 20        | $\nu_2$| 4     | 4(0.0A$_1$)    | 0100.E    | 0100.E | 7.96(32)      | 3.00$^{-10}$|
| 21        | $\nu_2$| 4     | 4(2.0E)        | 0100.E    | 0100.E | 1.440(26)     | 3.00$^{-9}$ |
| 22        | $\nu_2$| 4     | 4(4.0A$_1$)    | 0100.E    | 0100.E | 2.681(45)     | 3.00$^{-10}$|
| 23        | $\nu_2$| 4     | 4(6.0E)        | 0100.E    | 0100.E | -1.95(14)     | 3.00$^{-10}$|
| 24        | $\nu_2$| 5     | 5(3.0A$_1$)    | 0100.E    | 0100.E | -2.270(77)    | 3.00$^{-12}$|
| 25        | $\nu_2$| 6     | 6(0.0A$_1$)    | 0100.E    | 0100.E | -7.66(36)     | 3.00$^{-14}$|
| 26        | $\nu_2$| 6     | 6(2.0E)        | 0100.E    | 0100.E | 1.243(19)     | 3.00$^{-13}$|
| 28        | $\nu_2$| 6     | 6(4.0E)        | 0100.E    | 0100.E | -3.50(14)     | 3.00$^{-14}$|
| 32        | $\nu_4$| 0     | 0(0.0A$_1$)    | 001F$_2$  | 001F$_2$ | 631.059781(74)| 3.00$^{-4}$ |
| 33        | $\nu_4$| 1     | 1(1.0F$_1$)    | 001F$_2$  | 001F$_2$ | -2.947805(68)| 3.00$^{-1}$ |
| 34        | $\nu_4$| 2     | 2(0.0A$_1$)    | 001F$_2$  | 001F$_2$ | 1.0277(17)    | 3.00$^{-4}$ |
| 35        | $\nu_4$| 2     | 2(2.0E)        | 001F$_2$  | 001F$_2$ | -8.569(17)    | 3.00$^{-5}$ |
| 36        | $\nu_4$| 2     | 2(2.0F$_2$)    | 001F$_2$  | 001F$_2$ | 1.7218(35)    | 3.00$^{-4}$ |
| 47        | $\nu_4$| 3     | 3(1.0F$_1$)    | 001F$_2$  | 001F$_2$ | -3.327(35)    | 3.00$^{-7}$ |
| 48        | $\nu_4$| 3     | 3(3.0F$_1$)    | 001F$_2$  | 001F$_2$ | -5.081(15)    | 3.00$^{-7}$ |
| 49        | $\nu_4$| 4     | 4(0.0A$_1$)    | 001F$_2$  | 001F$_2$ | -2.01(20)     | 3.00$^{-9}$ |

Table A.6: Effective Hamiltonian parameters.
Table A.6 (continued).

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Table A.6 (continued).

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<th>( {C_v} )</th>
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<th>( {C_v'} )</th>
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Table A.6 (continued).

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<th>{s′} C'_v</th>
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<td>${s'}$</td>
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Appendix B. Effective Hamiltonian parameters from the “ν₁” fit.

Table B.7 below gives the fitted values of the effective Hamiltonian parameters of CF₄ for the “ν₁” fit (see Section 4.2). Notations correspond to Equation (3). Standard deviation is given in parentheses in the unit of the last two digits.

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<th>Parameter</th>
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<th>Order</th>
<th>(\Omega(K,nC))</th>
<th>({s})</th>
<th>(C_{\nu})</th>
<th>({s'})</th>
<th>(C_{\nu}')</th>
<th>Value</th>
<th>(\text{cm}^{-1})</th>
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<td>1001 F₂</td>
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Table B.7: Effective Hamiltonian parameters.
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Table B.7 (continued).

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<th>$C_v$</th>
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<td>$\times 10^{-7}$</td>
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<tr>
<td>$\nu_2 + \nu_3/\nu_2 + 2\nu_4$</td>
<td>7</td>
<td>3(1, 0, $F_{1}$)</td>
<td>1002E</td>
<td>1002F$_2$</td>
<td>$-1.741(26)$</td>
<td>$\times 10^{-7}$</td>
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<tr>
<td>$\nu_2 + \nu_3/\nu_2 + 2\nu_4$</td>
<td>7</td>
<td>3(3, 0, $F_{1}$)</td>
<td>1002E</td>
<td>1002F$_2$</td>
<td>2.512(22)</td>
<td>$\times 10^{-7}$</td>
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<tr>
<td>$\nu_2 + \nu_3/\nu_2 + 2\nu_4$</td>
<td>7</td>
<td>3(3, 0, $E_{2}$)</td>
<td>1002E</td>
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<tr>
<td>$\nu_2 + \nu_3/\nu_2 + 2\nu_4$</td>
<td>8</td>
<td>4(2, 0, $F_{2}$)</td>
<td>1002E</td>
<td>1002F$_2$</td>
<td>1.136(33)</td>
<td>$\times 10^{-7}$</td>
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<tr>
<td>$\nu_2 + \nu_3/\nu_2 + 2\nu_4$</td>
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<td>4(4, 0, $F_{1}$)</td>
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<td>4(4, 0, $F_{2}$)</td>
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<td>$\nu_2 + \nu_3/\nu_2 + 2\nu_4$</td>
<td>5</td>
<td>1(1, 0, $F_{1}$)</td>
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<td>$\nu_2 + \nu_3/\nu_2 + 2\nu_4$</td>
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<td>2(0, 0, $A_{1}$)</td>
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<td>1002F$_2$</td>
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<td>2(2, 0, $E$)</td>
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