Observation and analysis of $\nu 1 + \nu 3$ and $\nu 1 + 2\nu 4$ bands of CF4 molecule

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Abstract

Infrared spectra of CF_4 molecule were measured for three different temperatures in the range 2160–2210 cm^{-1} using Fourier transform spectrometer. Non-empirical effective Hamiltonian obtained from the potential energy surface using the contact transformation method was used for the modeling of line positions. The origins of two bands $\nu_1 + \nu_3$ (F_2) and $\nu_1 + 2\nu_4$ (F_2) at 2186.97 and 2168.21 cm^{-1} were experimentally determined for the first time. The experimental origin of the weak $\nu_1 + 2\nu_4$ (E) sub-band was tentatively evaluated near 2169.84 cm^{-1}. Ab initio line intensities were calculated from high order dipole moment surface by variational method using the TENSOR computational code in the normal mode representation. The analyses of experimental spectra were carried out using the MIRS program suite accounting for the full tetrahedral symmetry of the molecule.

Key words: Carbon tetrafluoride, CF_4, ab initio, analysis spectra, intensities, position

Introduction

Tetrafluoromethane (CF_4), also known as Halocarbon 14, PFC-14 or R-14 etc., is a colorless, non-toxic, non-flammable, non-corrosive gas belonging to the family of perfluorocarbons (PFCs). The concentration of the carbon tetrafluoride in the troposphere is low [1] [2] [3], however its growth in recent decades has been associated with industrial blowouts, the most significant of which is the production of aluminum [4].

Recently, the amount of CF_4 in the Earth's atmosphere has increased, and its lifetime in the atmosphere could reach 50 thousand years according to evaluations of Ref. [5]. This is because CF_4 molecules, compared to other freons, are not chemically active that leads to their accumulation in the atmosphere. CF_4 is a highly absorbing molecule in the infrared ~~range~~ and has one of the largest known global warming potentials (GWP) [6]. Consequently, tetrafluoromethane can play an active role in global climate change and falls under the directives of Kyoto Protocol of the United Nations Framework Convention on Climate Change (UNFCCC) for species recommended for environmental monitoring [2] [3] [7].

To determine the concentration of CF_4 in the atmosphere related to above mentioned climatic issues, it is necessary to compare remote measurements of the absorption function with the spectra obtained by the modeling of laboratory experiments at various temperature conditions. To this end, it is necessary to make an accurate calculation of frequencies and intensities, accounting for the selection rules for absorption lines, which strongly depend on the symmetry of the molecule.

CF_4 molecule belongs to the tetrahedral Td point group, like methane, but ~~it~~ is heavier than CH_4. It has thus lower vibrational modes and rotational levels populated at higher J quantum numbers, even at room temperature. The spectra of this molecule are characterized by the presence of complex Fermi resonance interactions, which significantly complicates the description of their vibrational-rotational patterns. The spectra of the CF_4 molecule have been studied over the past decades both theoretically and experimentally [8] [9] [10] [11]. However, currently available versions of databases such as HITRAN [12] [13] and GIESA [14] [15], include information for strong bands only.

The purpose of this work is to analyze the strong band $\nu_1 + \nu_3$ as well as the nearby band $\nu_1 + 2\nu_4$, which are couples by strong interactions. These bands are part of the 9-th polyad (heptad) of CF_4, containing seven bands in the spectral range 2120–2260 cm^{-1}. These seven bands correspond to unevenly localized upper state vibrational levels, as shown in figure 1. The weak band $2\nu_2 + 2\nu_4$ having ten upper state vibrational sublevels

($A_1, A_2, 2F_1, 3F_2, 3E$) is localized near 2130 cm^{-1}. The band $2\nu_2 + \nu_3$ has three upper state vibrational sublevels ($F_1, 2F_2,$). The corresponding transitions to one of two F_2 sublevels are well identified in experimental spectra. The resonance interaction of $2\nu_2 + \nu_3$ with $\nu_1 + \nu_3$ is less pronounced compared to the coupling $\nu_1 + 2\nu_4$ / $\nu_1 + \nu_3$. The strong $\nu_1 + \nu_3$ band has only one upper state vibrational levels (F_2), whereas the $\nu_1 + 2\nu_4$ has three vibrational sub-levels (A_1, F_2, E). Both bands investigated in this work lie near the $5\nu_2$ (A_1, A_2, E) sub-bands, but the corresponding perturbations were not found. Another two bands $\nu_1 + 3\nu_2$ with (A_1, A_2, E) upper sate sublevels and $2\nu_1 + \nu_2$(E) are located at the upper edge of the polyad.

The analyses of experimental spectra were carried out using the MIRS program suite [16] [17] accounting for the full symmetry of the molecule using tetrahedral tensorial formalism [18] [19].

Similarly to our previous work [20], we applied a mixed approach involving an Effective Hamiltonian (EH) model obtained from the ab initio potential energy surface (PES) using high-order contact transformations (CT) [21], [22], [23]. An alternative version of numerical transformations from PES to EH is presented in the work [24].

To construct an ab initio line list of CF_4 we used the potential energy surfaces and the dipole moment surfaces (DMS), which were described in detail in [11]. This work is part of the TheoReTS project [25], devoted to the development of complete theoretical line lists for polyatomic molecules based on ab initio PESs and DMSs.

For experimental study of the spectra of greenhouse gases at low temperatures, single- and multi-pass low-temperature cells have been created in the Institute of Atmospheric Optics in Tomsk. The theoretical line lists obtained in this work were validated with success by a direct comparison with the infrared Fourier spectra recorded at T = 113 K and T = 296 K in the region of 2160–2210 cm^{-1}.

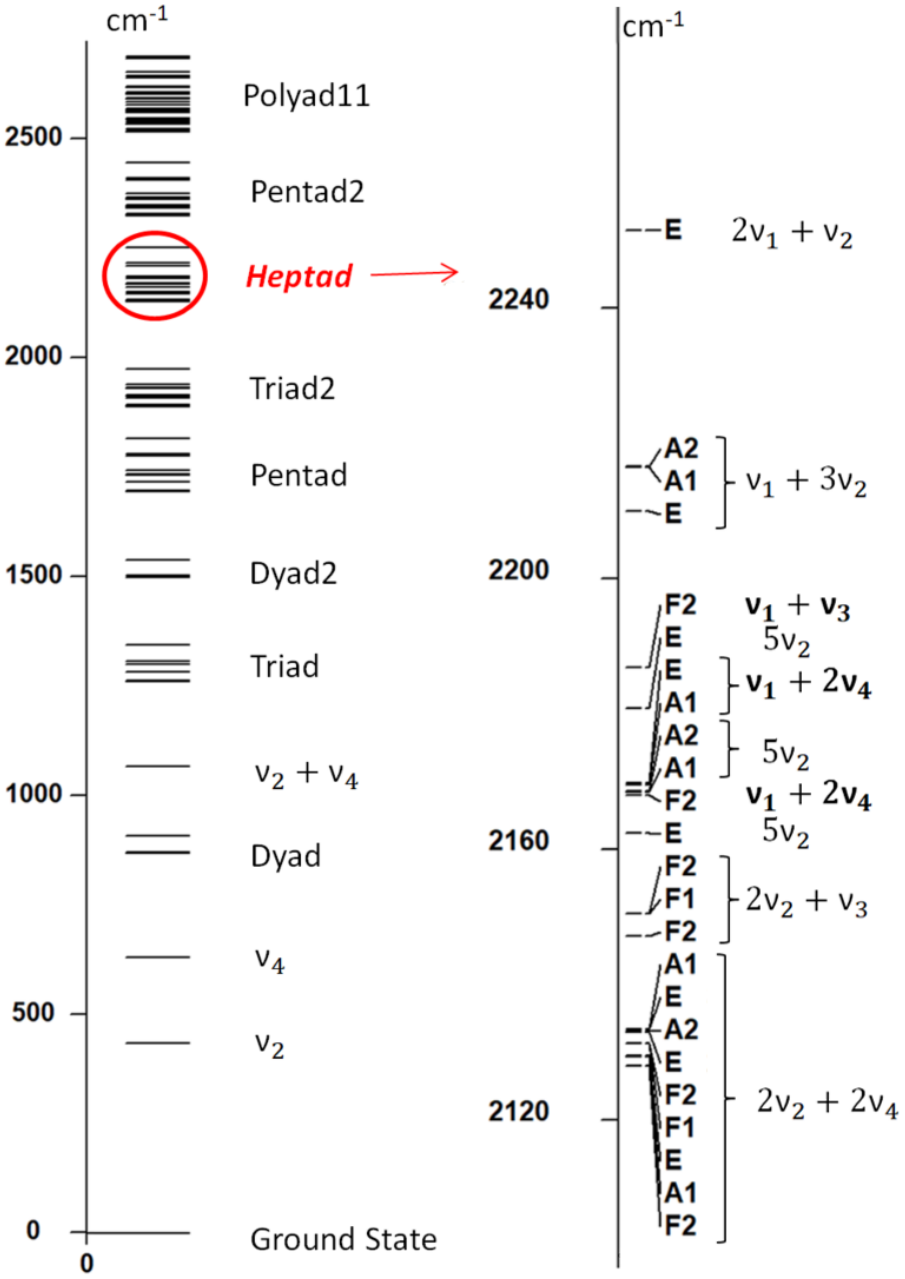

Figure1. Scheme of vibrational polyads of the CF_4 molecule (left) and vibrational sublevels of the hexad (right). The states investigated in this work are distinguished by boldface script.

Experimental spectra recorded in this work are described in Section 2. Section 3 gives an overview of the theoretical model for tetrahedral molecules used for our analysis. The last Section 4 contains the conclusions and discussions of the results.

2 Experiment

The absorption spectra of carbon tetrafluoride were recorded using a Bruker IFS 125-M Fourier spectrometer with two single-pass cells. The first cell, 220 cm long, with windows made of ZnSe and KBr and the possibility of cooling by liquid alcohol, was used to record spectra at room temperature and the temperature of 196 K. The second cell, 20 cm long, cooled with liquid nitrogen was used to record spectra at the temperature of 113 K. In total, the spectra were recorded for three temperatures 296, 196 and 113 K. In the range 2160–2210 cm^{-1} CF_4 has strong absorption bands with line intensities up to 10^{-21} cm^{-1}/molecule $\times$ cm^{-2}. The MIR globe was used as the radiation source, the beam splitter was made of CaF_2, and an MST cooled with liquid nitrogen was used as a photodetector. Pressure measurements were made by an AIR-20 M pressure sensor with a pressure measurement range of 0–100 kPa and an accuracy of about 0,1%. The temperature stabilization in the measurement room with a volume of 75 m^3 was carried out using a Midea MSE-24HR air conditioner with an error of less than 1 K that allowed for long time measurements. The radiation after the cell was introduced into the Fourier spectrometer through the radiation channel. The spectrometer was not evacuated, so the recorded spectra show strong water vapor lines broadened by air pressure at one atmosphere. The 113 K spectrum was calibrated using four lines 2114.4255, 2115.0160, 2136.1433, 2161.7255 cm^{-1}. Calibration of the spectra for temperatures of 296 K and 196 K was made according to the positions of several CF_4 transitions obtained from the 113 K spectrum. All spectra were recorded with a spectral resolution of 0,005 cm^{-1} (Table 1) using the diaphragm with the diameter of 1.1 mm. 350 scans were recorded with a scanner position measurement frequency of 20 kHz. The pressure was measured at room temperature to give 1.6775 and 6.7 mbar for the spectra with an optical path length of 220 and 20 cm, respectively. The signal-to-noise ratio in the recorded spectra was about 1000 in the measurement region. The uncertainty of the pressure measurements at low temperatures inside the cell significantly contributed to the errors of line intensity determination. The total error of the line intensities measurements did not exceed 10%. The experimental spectra recorded in the specified range are shown in Figure 2. Note that only the bands $\nu_1 + \nu_3$, $\nu_1 + 2\nu_4$, $2\nu_2 + \nu_3$ and $5\nu_2$ fall within the range of our experiment. The spectra at a temperature of 113 K contain several water absorption features.

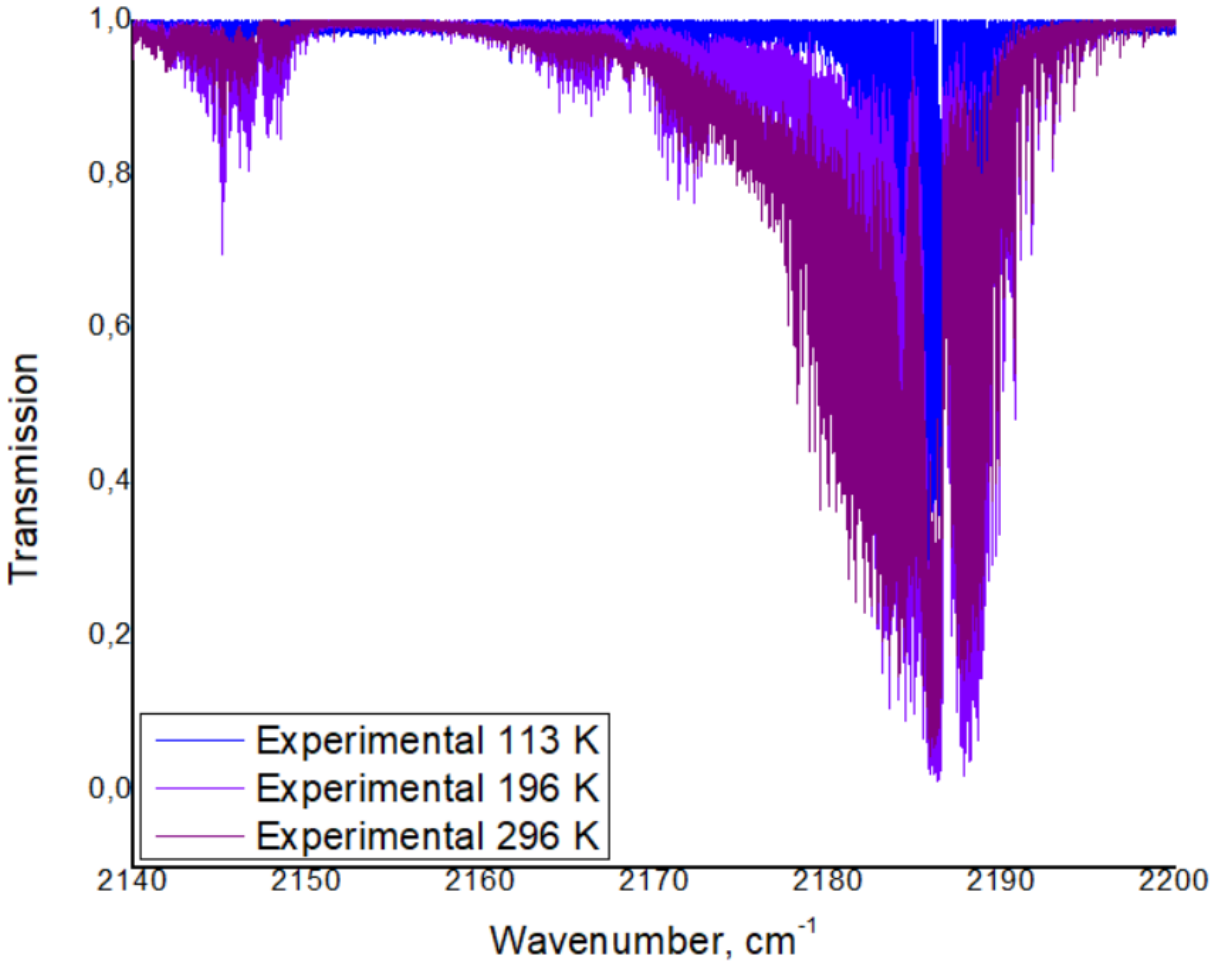

Figure 2. Transmittance spectrum of CF_4, recorded at temperatures 296 K (black), 196 K (magenta) and 113 (blue) K in the spectral range between 2130 and 2200 cm^{-1}.

Table 1. Experimental details

Spectra Range (cm^{-1})	2137-2205	2112-2205
Resolution (cm^{-1})	0.005	0.005
Source	Globar	Globar
Separator	CaF2	CaF2
Detector	MCT	MCT
Cell	220cm low temperature vacuum cell	20cm low temperature vacuum cell
Optical Path (cm)	220	20
Temperatures K	296±2, 196±2	113±4
Initial Pressure (mbar) at 296K	1.775±0.0025	6.7±0.002
Aperture Diameter (mm)	1.1	1.1

3. Theoretical modeling of the observed spectrum in the range 2160 – 2210 cm^{-1}

Despite a significant progress in the construction of accurate ab initio PESs and DMSs and and in variational calculations for band origins and line intensities, the bands under study have not been identified in experimental spectra so far. Due to its high tetrahedral symmetry, CF4 exhibits degenerate normal modes of vibration while the closely lying rovibrational levels are grouped into so-called polyads, leading to strong and complex resonance interactions. A well-known difficulty in purely empirical effective models is that the parameters of the resonance interactions may be ambiguously determined from the least-square fits [23] [26]. In this work, a non-empirical effective Hamiltonian - initially derived in [20] - was constructed from the optimized ab initio PES [11] by applying high-order contact transformations (CT) [21], [22] [23] [24] and was used in the analyses. This approach allowed us to calculate resonance parameters fairly accurately, which significantly simplifies the process of fitting parameters compared to purely empirical models [23]. A detailed description of ab initio calculations of potential energy and dipole moment surfaces, as well as global variational calculations is given in [11].

The MIRS computational code [16] was used to obtain the parameters of the effective Hamiltonian in the same way as it was described in previous papers to fully account for the properties of the tetrahedral symmetry of the molecule. Then these parameters were refined by a fine tuning using the fit to experimental line positions and CF_4 energy levels.

In this paper, transitions from the ground state (GS) to the states $\nu_1 + \nu_3$, $\nu_1 + 2\nu_4$ and $2\nu_2 + \nu_3$ of the Heptad (9th polyad) are investigated. The effective vibration-rotation Hamiltonian adapted to the polyad structure of CF_4 is expressed as follows:

$$H = \sum H_k = \widetilde{H}_{P_0} + \widetilde{H}_{v_2} + \widetilde{H}_{v_4} + \widetilde{H}_{Dyad} + \widetilde{H}_{v_2+v_4} + \widetilde{H}_{Tetrad} + \widetilde{H}_{Dyad2} + \widetilde{H}_{Pentad} + \widetilde{H}_{Heptad} + \widetilde{H}_{Pentad2} + \widetilde{H}_{Polyad11}$$

A comparison of the band origins obtained using the high-order CT method with previously determined experimental values of CF_4 was given in Table 11 and Figure 9 of ref [11] The RMS deviation between variational [11] and CT calculations [20] using the same PES was very small, about 0.003 cm^{-1} in the range 0–2700 cm^{-1}. This allowed us to safely use the corresponding mixed ab initio / effective approach to analyses the observed spectra.

A schematic representation of the polyad structure as well as the scheme of vibrational levels for tetrafluoromethane is shown in Figure 1. The enlarged scale on the right-hand side represents the vibrational sublevels and their symmetry types in the range under consideration. At the first stage, the centers of the two strongest bands were adjusted using several observed transitions. This made it possible to significantly improve the calculated positions of most transitions in the spectral range 2160–2205 cm^{-1}.

At the second stage, we determined the line intensities. The infrared spectra of CF_4 are very dense due to the large number of transitions belonging to both cold and hot bands that significantly complicates the analysis of experimental spectra. The variational method using the ab initio DMS [11] made it possible to accurately determine line intensities from first principles calculations. Consequently, we adjusted the parameters of the effective dipole moment (EDM) directly to the variational intensities calculated in [11]. This approach has already been successfully applied in our previous work [20]. The obtained EDM parameters are shown in Table 2. As a result, a good agreement between the variational and experimental intensity of the lines, was achied (achieved) as shown in Figure 5.

Table 2. Effective dipole transition moment parameters for the $\nu_1 + \nu_3$, $\nu_1 + 2\nu_4$ and $2\nu_2 + \nu_3$ bands

Tonsorial nomenclature			Parameter value
	Rotational	Vibrational	
1	9 R 0(0, 0A1)	0000 0210	3.0677673220E-04
2	9 R 0(0, 0A1)	0000 0210	-7.0097729574E-05
3	9 R 0(0, 0A1)	0000 1002	-0.5582053784E-04
4	9 R 0(0, 0A1)	0000 1010	7.4121145986E-03
5	9 R 1(1, 0F1)	0000 1002	-8.0011070683E-06
6	9 R 1(1, 0F1)	0000 1010	1.3437943401E-07
7	9 R 2(0, 0A1)	0000 1010	9.8005076990E-09
8	9 R 2(2, 0E)	0000 1010	1.8003881577E-08
9	9 R 2(2, 0F2)	0000 1010	-3.0670244770E-08

At the third stage, a more detailed optimization of the effective Hamiltonian using the observed transitions was made.

Table 3. Bands origins and integrated band intensities

Sub-bands	band origins computed [11], [24] from the PES, cm^{-1}	Vibrational band centers, cm^{-1}, TW	Integrated band intensity, cm / molecule
$2\nu_2 + 2\nu_4$ F_2	2128.14	2128.129140	2.967E-21
$2\nu_2 + 2\nu_4$ A_1	2129.41	2129.406546	
$2\nu_2 + 2\nu_4$ E	2129.67	2129.673834	
$2\nu_2 + 2\nu_4$ F_1	2131.42	2131.412124	
$2\nu_2 + 2\nu_4$ F_2	2131.46	2131.457598	
$2\nu_2 + 2\nu_4$ E	2133.07	2133.066099	
$2\nu_2 + 2\nu_4$ A_2	2133.29	2133.291210	
$2\nu_2 + 2\nu_4$ E	2133.54	2133.538461	
$2\nu_2 + 2\nu_4$ A_1	2133.59	2133.592973	
$2\nu_2 + \nu_3$ F_2	2147.34	2147.263493	4.892E-22
$2\nu_2 + \nu_3$ F_2	2150.65	2150.571641	-
$2\nu_2 + \nu_3$ F_1	2150.60	2150.528037	1.620E-20
$5\nu_2$ E	2162.46	2162.464206	7.416E-22
$5\nu_2$ A_1	2168.54	2168.546631	
$5\nu_2$ A_2	2168.65	2168.653221	
$5\nu_2$ E	2180.86	2180.861649	
$\nu_1 + 2\nu_4$ F_2	2168.21	2168.013546	5.620E-20
$\nu_1 + 2\nu_4$ A_1	2169.55	2169.551443	4.243E-21
$\nu_1 + 2\nu_4$E	2169.84	2169.836080	4.972E-20
$\nu_1 + \nu_3$ F_2	2186.97	2186.871327	5.228E-19
$\nu_1 + 3\nu_2$ F_2	2209.97	2209.974243	1.767E-21
$\nu_1 + 3\nu_2$ A_2	2216.56	2216.559310	

The complexity of the CF_4 spectra in the range 2137–2205 cm^{-1} is due to overlapping cold and hot bands, including the transitions with three-, four-, and five vibrational quanta. Theoretical and experimentally determined band origin belonging to heptad band system are summarized in Table 3. The integrated intensities of cold bands given in the last columns of Table 3 correspond to ab initio calculations of ref [11]. The centers of the hot bands could not be accurately determined without a detailed analysis of the upper polyads. In addition, due to the high density of transitions, it was not possible to find the positions of individual lines. Instead, the spectra show peaks corresponding, at best, to a combination of strong transitions with certain values of the upper and lower J of one vibrational band. Similar sets of transitions were observed in the multiplets of the band $2\nu_3$ (F_2) of methane [27] [28]. In the case of methane many individual transitions in the multiplets could still be identified. However, in the case of the heavier CF_4 molecule, the spectra are much more crowded, and it was not possible to resolve individual transitions in this range. Most likely, it would be possible to identify individual transitions with $J< 5$ at lower temperatures with longer optical paths, but at the

temperature of 113 K, the transitions with J< 5 were noticeably weaker than the transitions with J= 10–20 and, as a rule, were not visible. Either some multiplets of a band were blended by transitions of another bands, or the multiplets of one band with different J values overlapped each other. Such multiplets could not be used for assignments of individual lines. However, in many cases, the multiplets consisted of closely spaced transitions with the same values of J, and the center of the multiplet was determined quite accurately from the experiment. Several of these multiplets are shown in Figure 3.

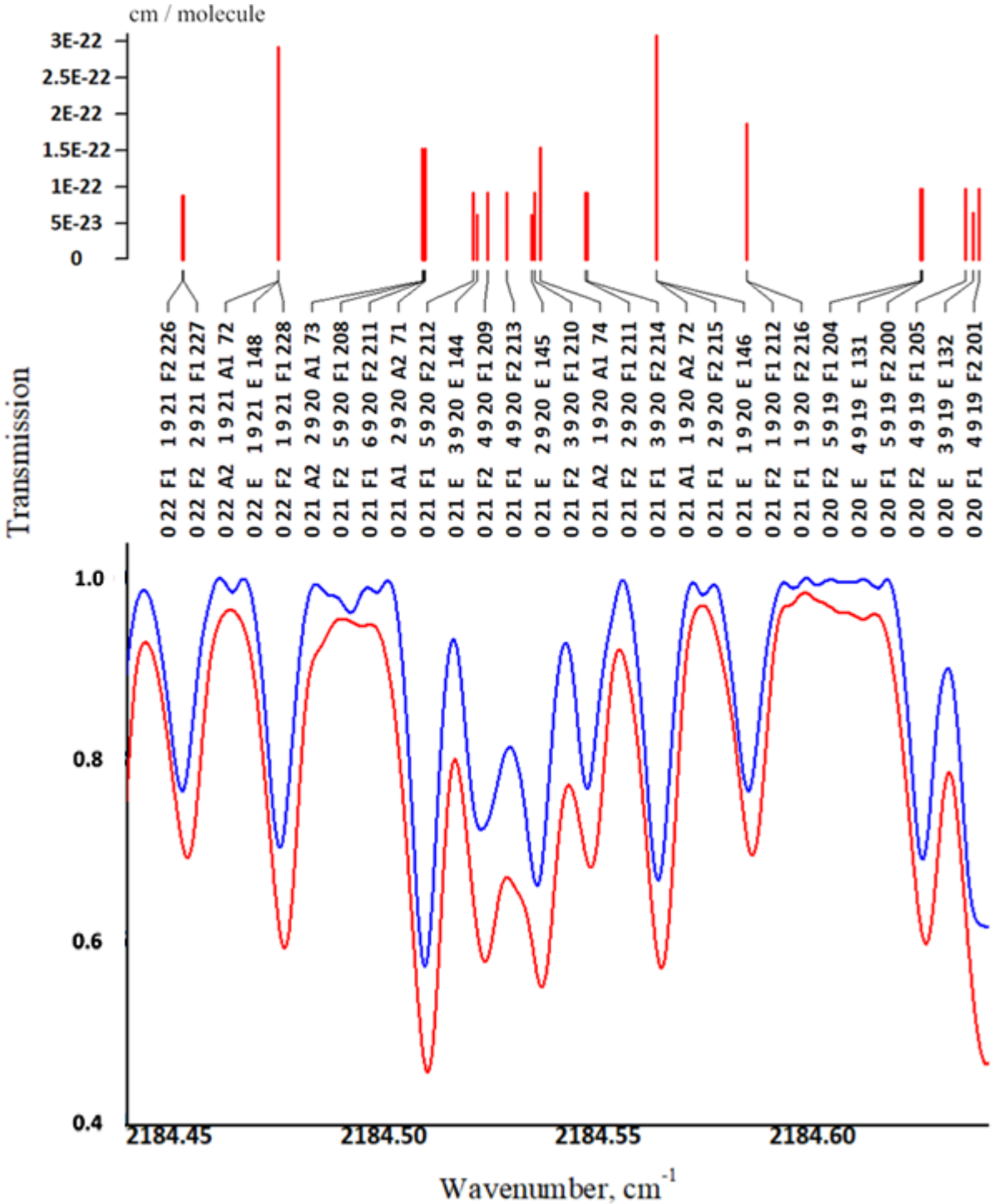

Figure 3. Comparison of the simulated spectra with the measurements at T = 113 K in the 2184.4–2184.7 cm^{-1} region: upper panel –spectral lines from our line list at T = 113 K (red); lower panel – observed spectra (blue) and simulations using our line list (red).

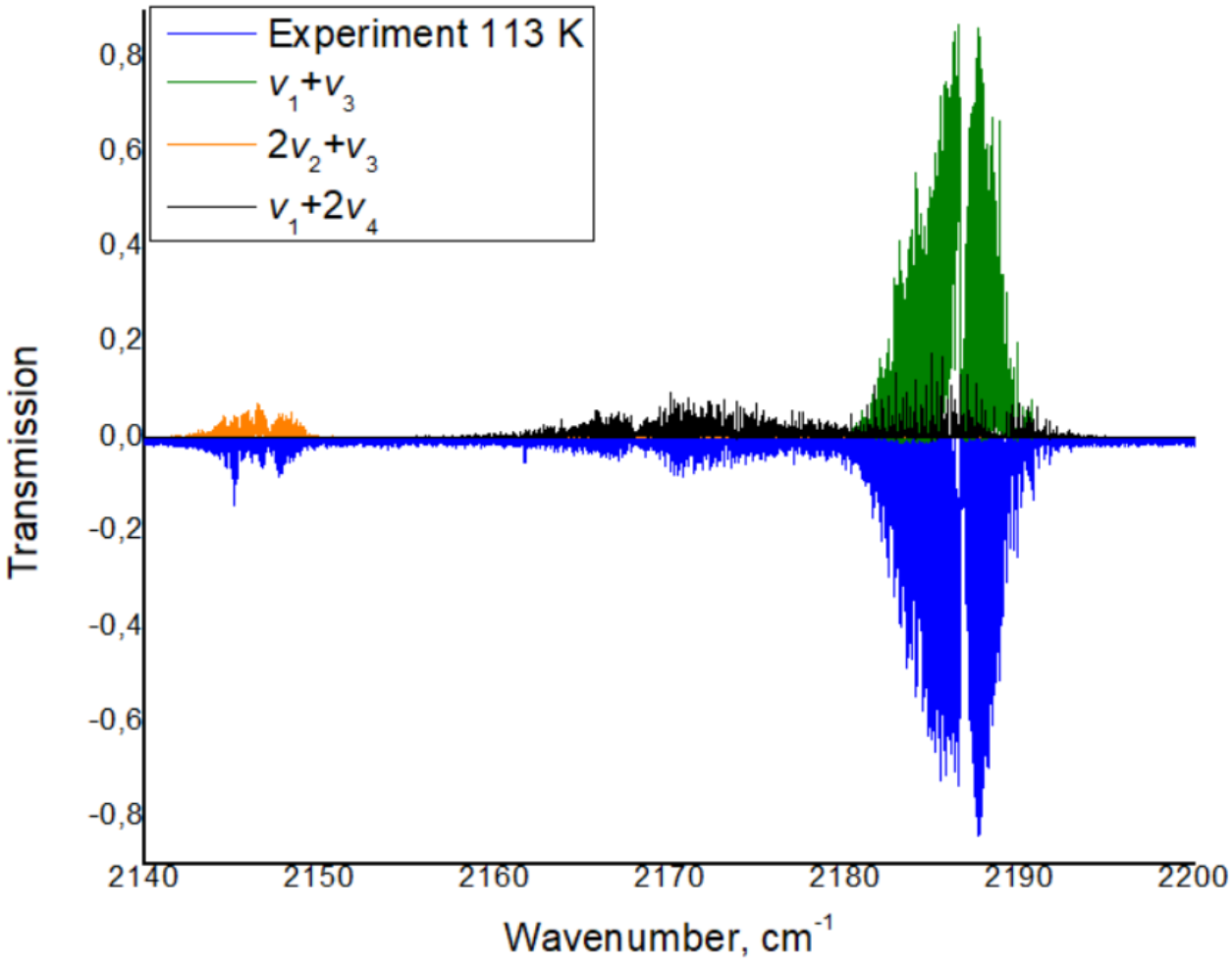

Figure 4. Comparison of the spectra simulations of CF_4 using our calculated line list with measurements at T= 113 K in the 2140.0 –2200.0 cm^{-1} region: upper panel $\nu_1+\nu_3$ (green), $2\nu_2+\nu_3$ (black) and $\nu_1+2\nu_4$ (orange); lower panel –experimental (blue) spectra T = 113 K.

The strongest absorption in this range is due to the $\nu_1 + \nu_3$ band with the integrated intensity of more than $5.2^{x}10^{-19}$ cm/molecule. The origin of this band predicted from the PES [11] was 2186.97 cm^{-1}. To fit the effective Hamiltonian, 284 multiplets were identified for the R and P branches in the range 2184.737–2188.023 cm^{-1} with J_{max}= 20 and J_{min}= 4. Most of the multiplets at the R and P branches were well separated from each other and their assignment using ab initio predictions was often streightforvard. A slight adjustment of the interaction parameter between the upper states of $\nu_1 + \nu_3$ and $\nu_1 + 2\nu_4$ (F_2) noticeably improved the quality of fit for the positions of the strong $\nu_1 + \nu_3$ band. Then, we tried to find some assignements of weak band $\nu_1 + 2\nu_4$ (F_2) transitions.

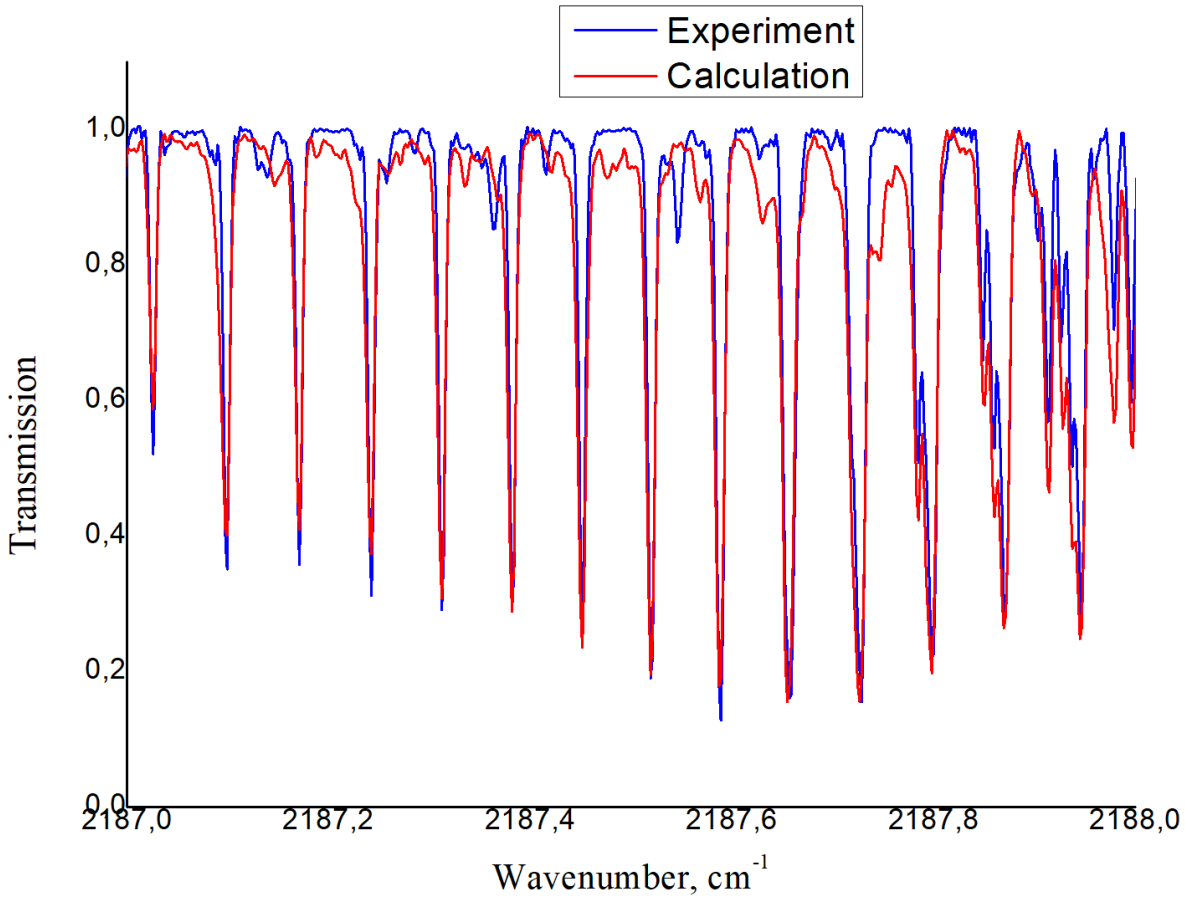

Figure 5. Detailed comparisons of the transmission in experimental and simulated spectra of CF_4 at 113 K in the R branch of $\nu_1 + \nu_3$.

The absorption of the $\nu_1 + 2\nu_4$ band is five times weaker, with the ab initio estimation of the integrated intensity of 1.027×10^{-19} cm/molecule. The transitions to the sublevel $\nu_1 + 2\nu_4$ (F_2) provide the largest contribution to the absorption for this band. However, an assignment of transitions corresponding to this sublevel turned out to be much more difficult than for $\nu_1 + \nu_3$. It was possible to find a good match only in the spectral range 2169.5–2170.5 cm^{-1} (see Figure 6). In this range, the multiplets of the R branch are well visible in the observed spectra for the upper state rotational quantum numbers J=7–19.

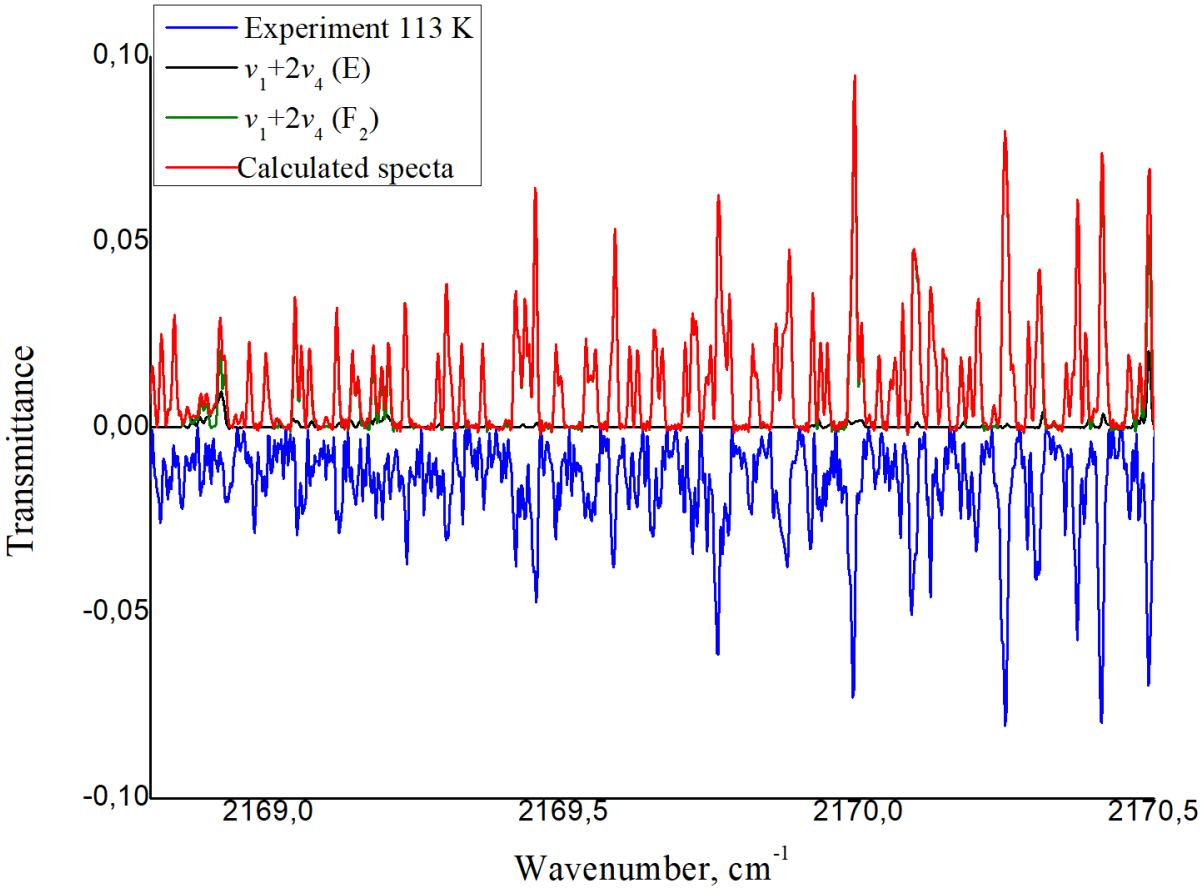

Figure 6. The comparison of simulated and observed spectra of CF_4 for *T*= 113 K in the 2169.8 –2170.5 cm^{-1} region: calculated (red) spectra and $\nu_1 + 2\nu_4$ (E) (black); lower panel – experimental (blue) spectra *T* = 113 K.

The center origin of $\nu_1 + 2\nu_4$ (F_2) was predicted from the PES at 2168.21 cm^{-1} [11]. A total of 117 multiplets for the R and P branches were identified to fit the effective Hamiltonian in the range 2169.0481 - 2170.4171 cm^{-1} with J_{max}= 19 and J_{min}=7. Considering that the levels with J<7 were not identified, the uncertainty of empirically determined band origin was estimated as 0,01 cm^{-1}. The identification of $J \leq 7$ is a rather difficult task due to the high density of lines in this range. After fitting the parameters of the effective Hamiltonian to assigned transitions, the origins of the bands $\nu_1 + \nu_3$ and $\nu_1 + 2\nu_4$ (F_2) were deremined at 2186.87 cm^{-1} and 2168.007 cm^{-1} correspondingly. Note that the empirical values of some sublevels of the F_2 symmetry of the heptad were slightly changed with respect to the previous works, see Table 3.

Multiplets for the $\nu_1 + 2\nu_4$ (E) sub-band could not be identified, because of the weakness of the corresponding transitions compared to $\nu_1 + 2\nu_4$ (F_2), see Figure 7. The value of the vibrational $\nu_1 + 2\nu_4$ (E) sublevel did not change (2169.836 cm^{-1}), but the positions of

the transitions with large J slightly changed compared to the initial non-empirical CT Hamiltonian due to the interactions with other sublevels.

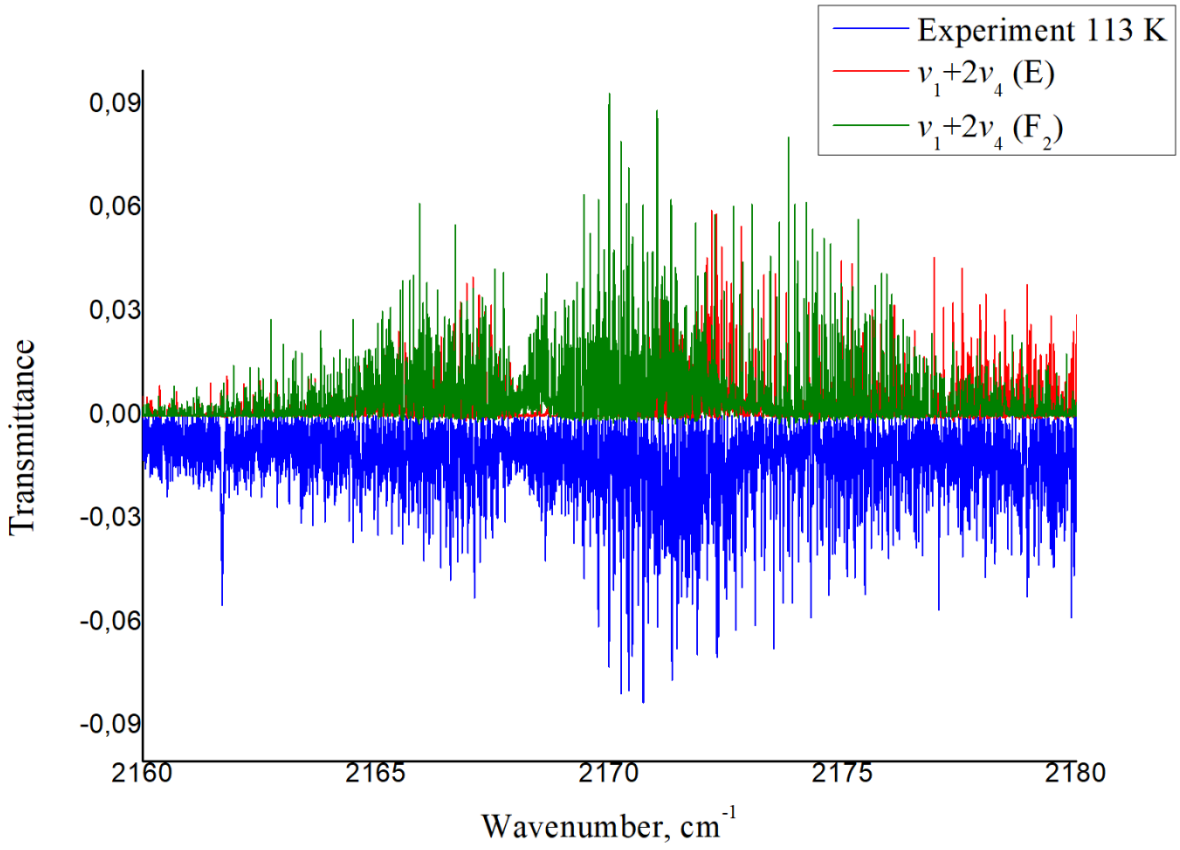

Figure 7. The comparison of simulated and observed spectra of CF_4 for T= 113 K in the 2169.8 –2170.5 cm^{-1} region: calculated (red) spectra and v1-2v4 (E) (black); lower panel – experimental (blue) spectra T = 113 K.

Transitions of $\nu_1 + 2\nu_4$ (E) provide a noticeable absorption in the ranges 2172-2173 cm^{-1} and 2177-2180 cm-1, but the transitions $\nu_1 + 2\nu_4$ (F_2) are also quite strong in both ranges. The statistics of fitting the effective Hamiltonian are given in Table 4, and the modified parameters of the effective Hamiltonian (compared to those initially computed from the PES by contact transformations) are given in Table 5.

Table 4. Information on the fit of EH to the experimental transitions

Band	RMS deviation * 10^{-3}	Number of data	J_{max}/J_{min}
$\nu_1 + \nu_3$	1.195	284	20/4
$\nu_1 + 2\nu_4$ (F2)	1.921	117	19/7

Table 5. Effective Hamiltonian parameters for the $\nu_1 + \nu_3$ and $\nu_1 + 2\nu_4$ bands.

Tensorial nomenclature			Parameter value
	Rotational	Vibrational	
1	R 0(0, 0A1)	1010 1010	-1.0571136851E+01
2	R 1(1, 0F1)	1010 1010	-7.3098294025E-03

3	R 2(0, 0A1)	1010 1010	7.3935706176E-06
4	R 0(0, 0A1)	1010 1002	4.8915047905E-01
5	R 0(0, 0A1)	1002 1002	-2.7618876735E-01
6	R 1(1, 0F1)	1002 1002	-4.6380494756E-03
7	R 2(0, 0A1)	1002 1002	-3.9785009339E-04
8	R 2(2, 0F2)	1002 1002	1.1713093142E-04

Another $2\nu_2 + \nu_3$ band corresponding to three vibrational upper-state sublevels is visible in the 2146 cm^{-1} region, see Figure 8. It is quite weak with more than 95% of absorption at 113 K due to transitions to the lower F_2 vibrational sublevel at 2147.34 cm^{-1}. This band was not analyzed. Variational calculations qualitatively well reproduce the spectrum, but slight distortions of the intensities were observed. No combinational differences for this band were found.

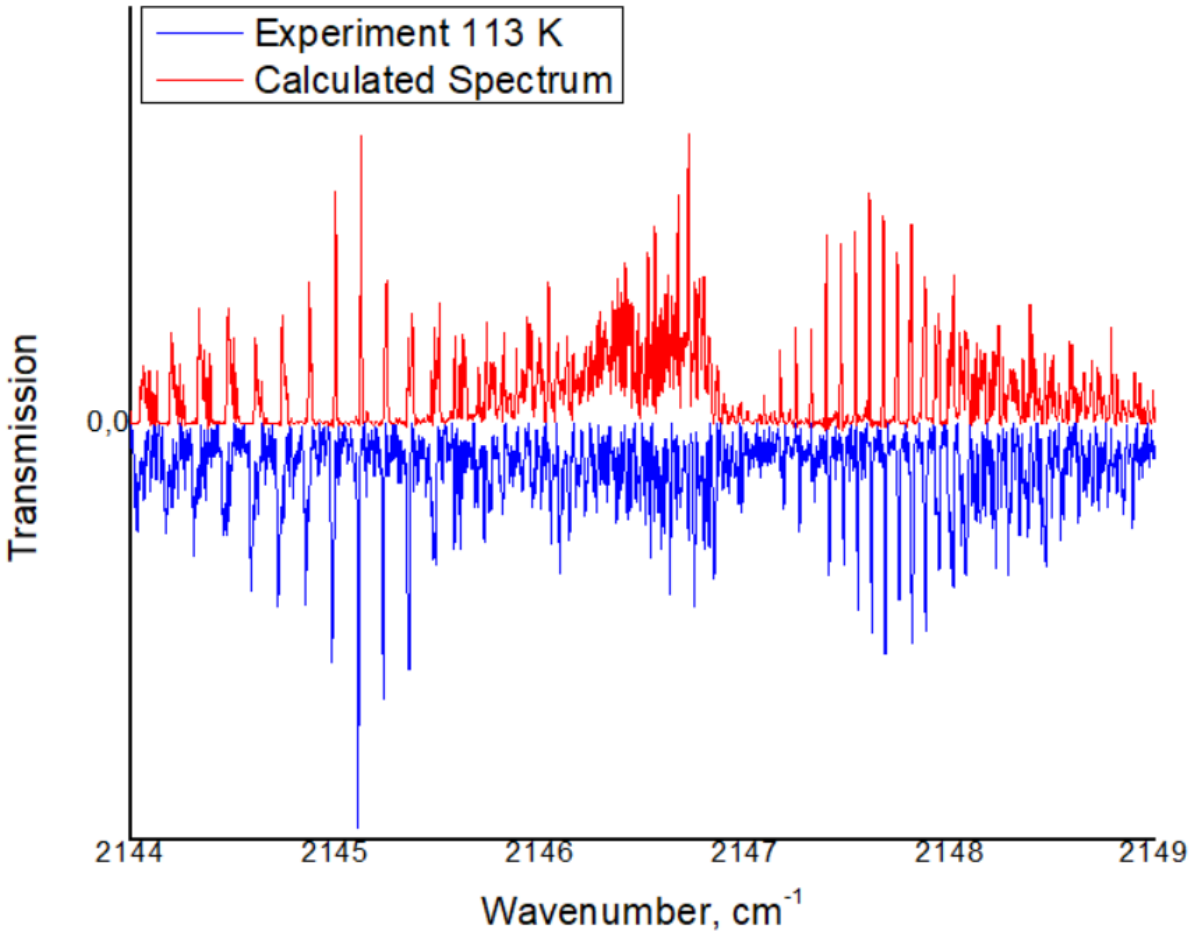

Figure 8. The comparison of simulated and observed spectra of CF_4 for T= 113 K in the 2144. –2149. cm^{-1} region: calculated (red) spectra of 2v+v3 shifted by -0.13 cm-1; lower panel –experimental (blue) spectra T = 113 K.

Conclusion

The main result of this work is the first high-resolution observation and analyses of the infrared spectrum of CF_4 in the region of 2160–2210 cm^{-1}. The strong $\nu_1 + \nu_3$ band of this range practically does not overlap with strong water lines and can be used for a remote sensing of CF_4 in the atmosphere. For these purposes, a list of transitions was calculated with noticeably more accurate line positions compared to initial ab initio based variational calculations of [11]. An example of a computed list is shown in Table 6.

Table 6. An example of electronic supplementary data.

Key[a]	Position, cm^{-1} [b]	Intensity, cm/molecul[c]	Rotational assignment[d]		K[i]	Vibrational assigment[j]	E_{lower}, cm/molecule[k]
			Lower state	Upper state			
+	2169.300541	4.545e-24	0 7 F1 1	9 8 F2 64	K 0 1	1002F2	10.706588
+	2169.300601	5.347e-24	0 8 F2 2	9 9 F1 71	K 0 1	1002 F2	13.765624
+	2169.307311	3.545e-24	0 8 E 2	9 9 E 46	K 0 1	1002 F2	13.765619
+	2169.326621	5.174e-24	0 8 F1 2	9 9 F2 70	K 0 2	1002 F2	13.765603
+	2169.335560	2.258e-25	0 14 F2 3	9 14 F1 122	K 1 2	1002 E	40.148104
-	2171.228600	3.383e-24	0 11 F2 1	9 12 F1 93	K 0 2	1002 F2	25.236247

[a]"+" assigned line, "-" unassigned line.

[b] calculated line position.

[c] calculated line intensities at T = 296 K.

[d]rotational identification for bottom and top states.

[i] lower and upper rotational quantum number K .

[j] vibrational identification.

[k] calculated energy of the lower state.

The calculated list of lines was verified by comparison with high resolution measurements at T = 113 K and T = 196 K. All results will be included in the TheoReTS information system.

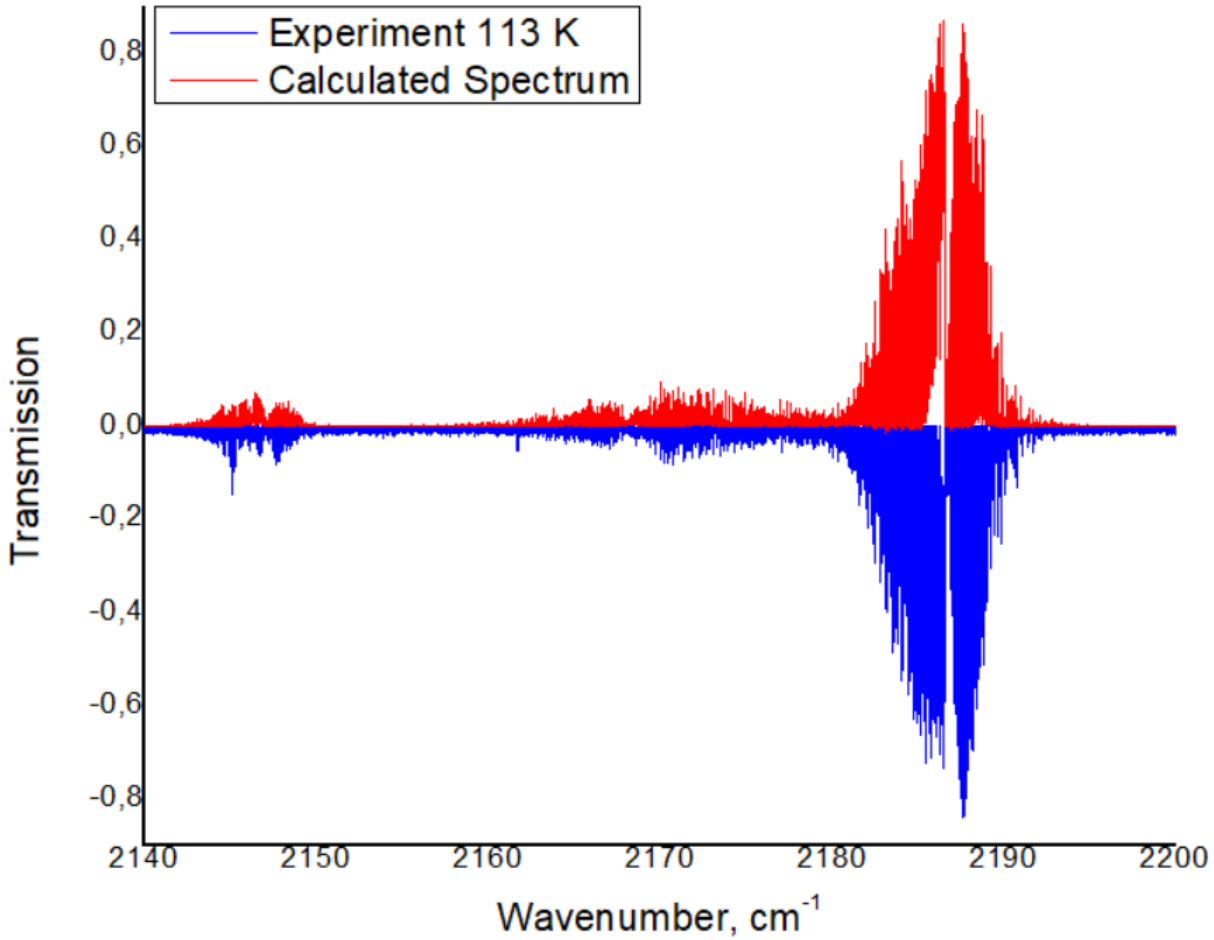

Figure 8. The comparison the simulations using our line list (red) with the experimental spectrum of CF4 (blue) at 113 K.

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