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# Spectroscopy of a Low Global Warming Power Refrigerant. Infrared and Millimeter-wave Spectra of Trifluoroethene (HFO-1123) in the Ground and some Vibrational Excited States

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## Abstract

In the present work we carried out a combined rotational and ro-vibrational investigation on 1,1,2-trifluoroethene, a relevant unsaturated hydrofluoroolefin recently proposed as refrigerant in mixture with other halogenated compounds (like difluoromethane). By employing a frequency-modulation millimeter-wave spectrometer, the rotational spectra were recorded in the frequency ranges 80–96 GHz and 245–260 GHz for the ground and also the vibrationally excited states  $\nu_8 = 1$ ,  $\nu_9 = 1$ ,  $\nu_{12} = 1$ ,  $\nu_9 = 2$ ,  $\nu_{12} = 2$ , and  $\nu_9 = \nu_{12} = 1$ . In addition, the infrared spectra in the region of the  $\nu_6$  band (centered at  $929.8\text{ cm}^{-1}$ ) were measured with a high-resolution Fourier transform spectrometer. The data coming from the detailed rotational and ro-vibrational assignments were combined in a global fit, taking into account also the ground state transitions available in the literature. From this analysis, a very accurate set of rotational and centrifugal distortion constants was determined for the ground state and for all the vibrationally excited states here investigated.

*Keywords:* Rotational Spectroscopy, Ro-vibrational spectra, Hydrofluoroolefins, Trifluoroethene, HFO-1123

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## 1. Introduction

In the last decades, great attention has been devoted to the search for suitable replacements of the gases used for domestic and industrial purposes which strongly contribute to the atmospheric pollution, the ozone hole and the greenhouse effect. Unsaturated hydrofluoroolefins (HFO’s) are an interesting alternative to chlorofluorocarbons (CFC’s). Indeed, such molecules have a very short atmospheric lifetime, an almost zero Ozone Depletion Potential (ODP) and a low Global Warming Potential (GWP) [1]. The search of an ideal candidate for refrigerants is nowadays a crucial issue, considering that recent studies showed that a very limited number of fluids exhibit the required environmental properties [2]. 1,1,2-trifluoroethene ( $\text{CF}_2=\text{CHF}$ , HFO-1123, hereafter referred as TFE) is used nowadays in heat pumps and conditioning systems, often in mixtures with difluoromethane ( $\text{CH}_2\text{F}_2$ , HFC-32). In these mixtures self-decomposition does not occur [1]; also, they have low toxicity and are only mildly flammable [1, 3], proving therefore to be a valuable alternative to R-410A, a common refrigerant with high GWP. The atmospheric importance of  $\text{CF}_2=\text{CHF}$  has stimulated a number of spectroscopic studies in the past. Low resolution infrared (IR) spectra were first recorded by Mann *et al.* [4] and later by McKean [5]. In 2002

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15 Jiang *et al.* [6] calculated the vibrational fundamental wavenumbers and the relative intensities using the  
16 Scaled Quantum Mechanical (SQM) force field procedure in combination with the hybrid three-parameter  
17 B3-PW91 density functional. Microwave transitions of the ground and some vibrationally excited states  
18 were reported a long time ago by Bhaumik *et al.* [7] and Wellington Davis & Gerry [8].

19 More recently, Leung & Marshall recorded rotational transitions of TFE between 6 and 22 GHz by Fourier  
20 transform (FT) spectroscopy for the most abundant isotopologue and the two singly  $^{13}\text{C}$ -substituted species.  
21 From the determined spectroscopic constants they also derived the structural parameters of the molecule  
22 [9]. High-resolution infrared studies are however limited to the very strong fundamentals  $\nu_3$ ,  $\nu_4$ , and  $\nu_5$  in  
23 the atmospheric window, centered at 1360, 1265, and 1173  $\text{cm}^{-1}$ , respectively. These high-resolution spectra  
24 were recorded with a tunable diode laser and analysed by Visinoni *et al.* [10, 11, 12]. The authors pointed  
25 out the presence of several resonances and determined some parameters for the interacting states.

26 The infrared atmospheric window has been only partially analysed and this work aims to a more complete  
27 spectroscopic characterization of this region and of the low-lying vibrational states. The goal is to provide  
28 the necessary laboratory data useful for the atmospheric detection of this molecule. The infrared spectrum  
29 was recorded at high resolution ( $0.004\text{ cm}^{-1}$ ) by FT-IR spectroscopy between 500 and 1500  $\text{cm}^{-1}$ , where  
30 the  $\nu_3$ ,  $\nu_4$ ,  $\nu_5$ ,  $\nu_6$  ( $929\text{ cm}^{-1}$ ),  $\nu_7$  ( $623\text{ cm}^{-1}$ ) and  $\nu_{10}$  ( $750\text{ cm}^{-1}$ ) fundamental bands are located with the  
31 objective to assign and analyse for the first time  $\nu_6$ ,  $\nu_7$ , and  $\nu_{10}$  and to re-investigate  $\nu_3$ ,  $\nu_4$ , and  $\nu_5$ . Given the  
32 complexity of the ro-vibrational structure, in this paper we focused only on the  $\nu_6$  fundamental vibrational  
33 band and on the detection of pure rotational transitions in the ground state and in the low energy  $\nu_8 = 1$ ,  
34  $\nu_9 = 1$ ,  $\nu_{12} = 1$ ,  $\nu_9 = 2$ ,  $\nu_{12} = 2$ , and  $\nu_9 = \nu_{12} = 1$  excited vibrational states. The rotational spectra were  
35 recorded in the frequency ranges 80-96 GHz and 245-260 GHz using a frequency-modulation millimeter-wave  
36 spectrometer.

37 In this work we present therefore a combined rotational and ro-vibrational investigation from which very  
38 accurate spectroscopic parameters were determined for the ground state and the investigated excited vibra-  
39 tional states.

## 40 2. Experimental details

### 41 2.1. Millimeter spectrometer

42 Rotational spectra were recorded in the frequency ranges 80-96 GHz and 245-260 GHz using a frequency-  
43 modulation millimeter-wave spectrometer [13, 14]. The radiation source is a Gunn diode (J.E. Carlstrom  
44 Co.) emitting in the spectral range 80-115 GHz with an output power up to 50 mW. A passive multiplier  
45 (WR3.4X2, Virginia Diodes) is used to reach the higher frequencies. The diode's radiation is phase-locked to  
46 a harmonic of a digital frequency synthesizer (HP8672A, 2-18 GHz) and its frequency is sine-wave modulated  
47 by a 75 MHz reference signal. Each synthesizer is referenced to a rubidium atomic-clock which guarantees the  
48 frequency stability of the radiation. A 3.25 m-long free-space glass absorption cell, filled with trifluoroethene  
49 vapor at a static pressure between 1 and 2.5 Pa, was employed for the measurements. The output signal was  
50 sensed by two different zero-biased Schottky diode detectors (Millitech, Inc. below 100 GHz and Virginia  
51 Diodes above 240 GHz) and demodulated at twice the modulation frequency by an analog lock-in amplifier.  
52 The signal is then filtered into an ohmic RC circuit, analog-to-digital converted and sent to a computer.  
53 Typically, the spectra were recorded using a frequency modulation  $f = 48\text{ kHz}$ , a modulation depth (FM)  
54 between 90 and 300 kHz, a RC constant of 3 ms, and a frequency step sufficiently small to provide at least  
55 twenty points across the expected linewidths.

### 56 2.2. Infrared spectra

57 The vibrational spectra were recorded with a FT-IR Bomem spectrometer [15], equipped with an MCT  
58 detector and a Globar source. The resolution of the spectra was  $0.004\text{ cm}^{-1}$  and the optical pathlength,  
59 obtained with a multipass absorption cell, was 3 meters. Sample pressures ranged between 0.06 and 1 hPa.  
60 Several hundreds scans were co-added in order to improve the signal-to-noise ratio of the spectra. The  
61 absolute calibration of the wavenumber axis was attained by referencing ro-vibrational transitions of  $\text{H}_2\text{O}$   
62 and  $\text{CO}_2$  from the HITRAN database [16]. An overview of the high-resolution infrared spectrum between  
63 500 and 1500  $\text{cm}^{-1}$  is shown in Figure 1.

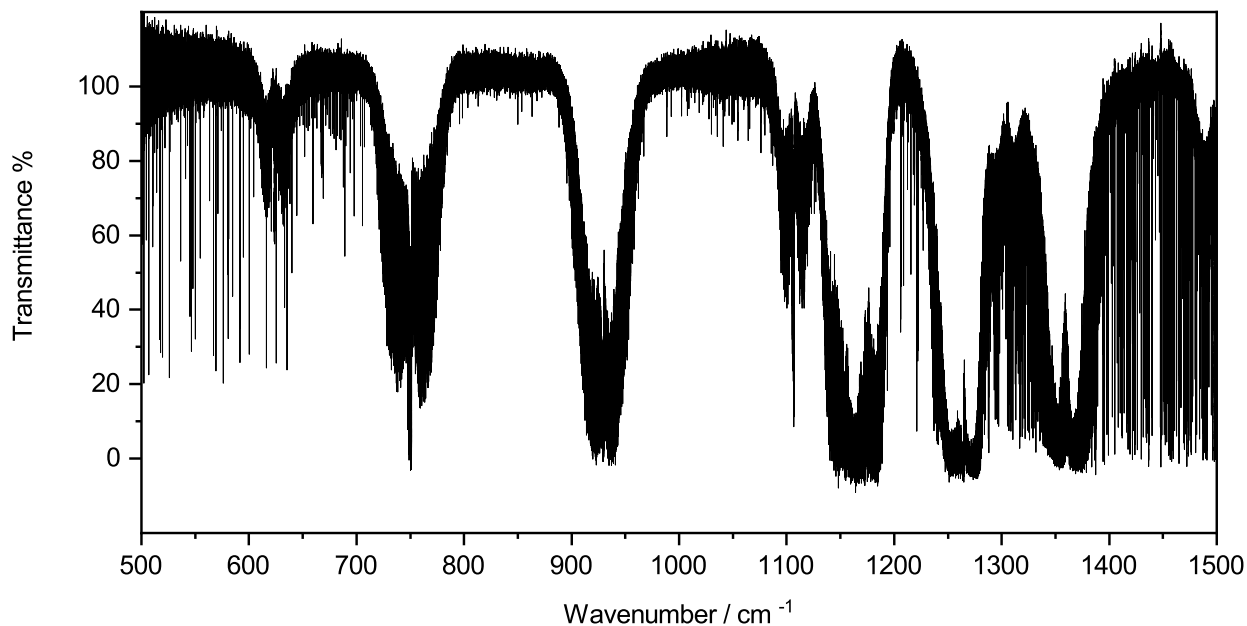


Figure 1: Portion of the infrared spectrum (P=1 hPa, L=3 m, 800 scans, room temperature). The assignment of all fundamental bands is given in Table 1.

### 64 3. Analysis and results

#### 65 3.1. General features

66 From a spectroscopic point of view, trifluoroethene is a planar near-prolate asymmetric-top molecule belong-  
 67 ing to the  $C_s$  symmetry point group, having an asymmetry parameter  $\kappa=-0.74$ . The molecular geometry of  
 68 TFE with respect to its principal axes is shown in Figure 2.

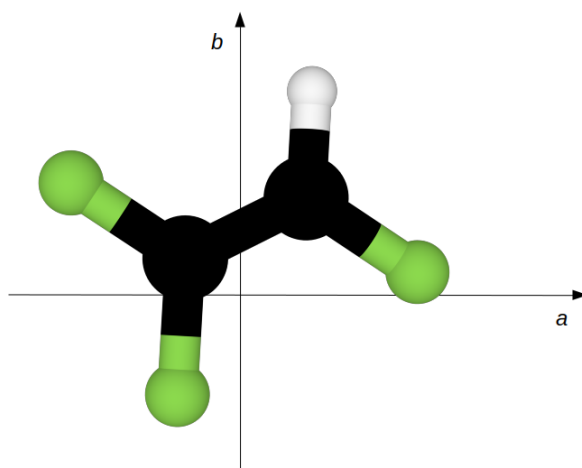


Figure 2: Trifluoroethene in its principal axis system.

69 Its permanent electric dipole moment ( $\mu=1.30(6)$  D) lies in the  $ab$  plane, with the  $b$  component ( $\mu_b=1.30(6)$  D)  
 70 much greater than that of the  $a$  component ( $\mu_a=0.075(15)$  D) [7]. Of the 12 fundamentals, all infrared active,  
 71 9 are classified as  $A'$  modes ( $\nu_1 - \nu_9$ ), whereas the other 3 are  $A''$  ( $\nu_{10} - \nu_{12}$ ). The former give rise to  $a/b$

72 hybrid bands, while the latter produce *c*-type band contours. The vibrational modes and their description  
73 are summarized in Table 1.

Table 1: Vibrational modes.

Symmetry	Mode	Envelope	Rel. intensity <sup>a</sup>	Description	Wavenumber <sup>b</sup>	Reference
<i>A'</i>	$\nu_1$	a/b	m	C–H stretch.	3150	[4]
	$\nu_2$		s	C=C stretch.	1788	[4]
	$\nu_3$		vs	CF <sub>2</sub> antisym. stretch.	1361.3684(1)	[10]
	$\nu_4$		vs	C–F stretch.	1264.86188(4)	[11]
	$\nu_5$		vs	CHF bend.	1172.6730(1)	[12]
	$\nu_6$		s	CF <sub>2</sub> sym. stretch.	928.80082(6)	This work
	$\nu_7$		m	C–F bend.	623	[4]
	$\nu_8$		w	CF <sub>2</sub> bend.	485	[4]
	$\nu_9$		w	CF <sub>2</sub> rock.	232	[4]
<i>A''</i>	$\nu_{10}$	c	s	CHF oop bend.	750	[4]
	$\nu_{11}$		vw	CF <sub>2</sub> wag.	555	[4]
	$\nu_{12}$		w	Torsion	305	[4]

<sup>a</sup> Abbreviations are used as follows: vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

<sup>b</sup> Units are cm<sup>-1</sup>. Numbers in parenthesis represent quoted uncertainties.

74 The ro-vibrational energies have been modeled by the standard semi-rigid Watson’s *A*-reduced Hamiltonian  
75 [17] in the *I'* representation:

$$\mathcal{H} = \mathcal{H}_{\text{vr}} + \mathcal{H}_{\text{cd}}^{(4)} + \mathcal{H}_{\text{cd}}^{(6)} + \dots, \quad (1)$$

76 where  $\mathcal{H}_{\text{vr}}$  contains the vibrational energy  $E_v$  and the rotational constants  $A$ ,  $B$ , and  $C$ :

$$\mathcal{H}_{\text{vr}} = E_v + \frac{1}{2} (B + C) \mathbf{P}^2 + \left[ A - \frac{1}{2} (B + C) \right] \mathbf{P}_a^2 + \frac{1}{2} (B - C) (\mathbf{P}_b^2 - \mathbf{P}_c^2). \quad (2)$$

77  $\mathbf{P}$  is the operator of the total angular momentum and  $\mathbf{P}_a$ ,  $\mathbf{P}_b$ , and  $\mathbf{P}_c$  its components along the principal  
78 inertial axes in the molecule-fixed coordinate system. The  $\mathcal{H}_{\text{cd}}^{(4)}$  part accounts for the centrifugal distortion  
79 terms up to 4<sup>th</sup> power of the angular momentum

$$\mathcal{H}_{\text{cd}}^{(4)} = -\Delta_J \mathbf{P}^4 - \Delta_{JK} \mathbf{P}^2 \mathbf{P}_a^2 - \Delta_K \mathbf{P}_a^4 - \delta_J \mathbf{P}^2 (\mathbf{P}_b^2 - \mathbf{P}_c^2) - \delta_K [\mathbf{P}^2 (\mathbf{P}_b^2 - \mathbf{P}_c^2) + (\mathbf{P}_b^2 - \mathbf{P}_c^2) \mathbf{P}^2], \quad (3)$$

80 while  $\mathcal{H}_{\text{cd}}^{(6)}$  contains operator with 6<sup>th</sup> power of  $\mathbf{P}$  [see Ref. 18, Eq. (8.100)], and so on. For the ground  
81 state only the analysis has also been performed in the Watson’s *S*-reduced Hamiltonian [17]. Its form is not  
82 reported here and can be found in Ref. [18], Eqs. (8.110)–(8.113).

83 Since hydrogen and fluorine possess a non-vanishing nuclear spin ( $I = 1/2$ ), rotational energy levels can  
84 exhibit a hyperfine-structure due to nuclear spin-spin interactions. These effects were observed for few  
85 transitions recorded with a pulsed Fourier-transform microwave spectrometer [9], but they are too small to  
86 be detected at high frequencies or in infrared spectra.

### 87 3.2. Rotational spectra

88 Initially, the rotational spectrum of TFE in its ground vibrational state has been predicted using the spec-  
89 troscopic constants reported in Ref. [8]. Literature data were limited to rotational transitions recorded at

90 frequencies below 66 GHz, corresponding to energy levels with  $J$  up to 75. Therefore, the available set of  
 91 spectroscopic parameters (rotational constants and centrifugal distortion terms) provided reliable predictions  
 92 in our spectral coverage.  
 93 In the 80–96 GHz window, rotational transitions have been recorded mostly line-by-line, scanning few MHz  
 94 around the predicted transition frequencies. On the other hand, in the 245–260 GHz range, where the lines  
 95 are more spread out, scanning broader portions was more convenient (see Figure 3).

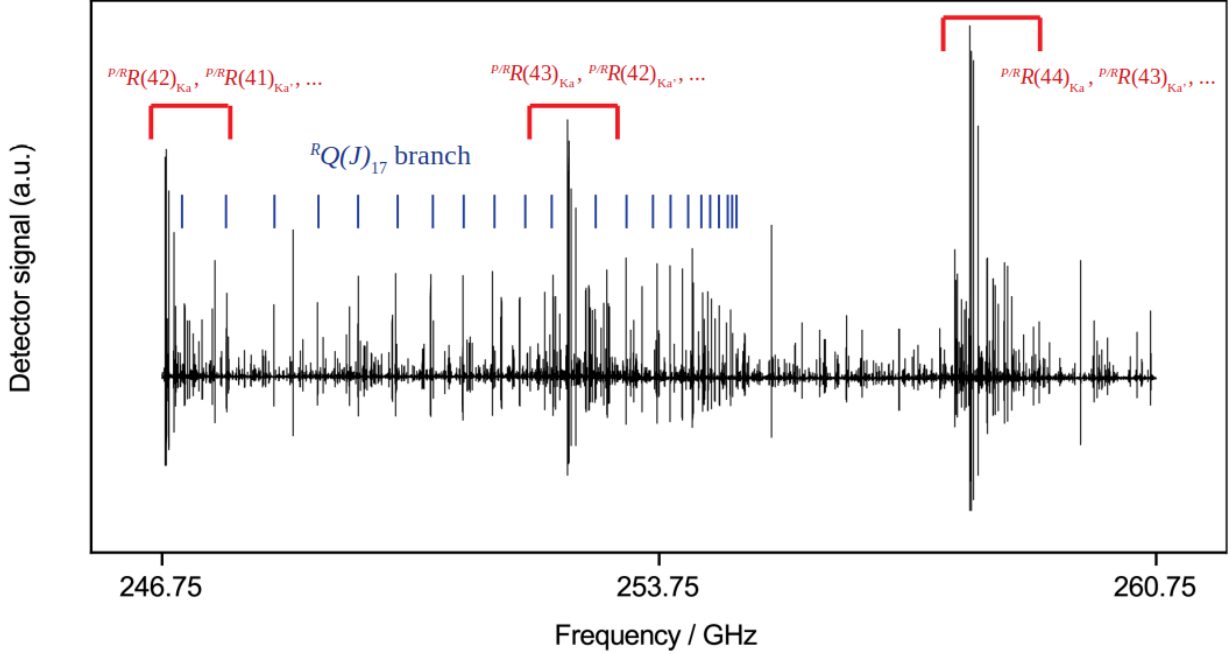


Figure 3: Portion of the millimeter spectrum of trifluoroethene. The spectrum has been obtained by adding consecutive 250 MHz-long scans, all of which were recorded sweeping the frequency upward and downward for an integration time of *ca.* 200 s. The figure shows the complexity of the rotational spectrum, where some  $P/R R(J)_{K_a}$  transitions are grouped at certain frequencies. Also, the  $RQ(J)_{17}$  branch is reported.

96 A number of 260  $b$ -type transition frequencies have been recorded and added to the previous data set [7, 8, 9],  
 97 expanding the data up to  $J = 106$  and requiring the inclusion of higher order centrifugal distortion terms.  
 98 Singly excited states ( $\nu_8 = 1$ ,  $\nu_9 = 1$ , and  $\nu_{12} = 1$ ) transitions up to 96 GHz were predicted by using  
 99 the spectroscopic constants of Refs. [7, 8]. More precise spectral predictions were later produced in order  
 100 to assign the broad spectrum between 245 and 260 GHz. The transitions relative to the doubly excited  
 101 vibrational states ( $\nu_9 = 2$ ,  $\nu_{12} = 2$ , and  $\nu_9 = \nu_{12} = 1$ ) were initially calculated with rotational parameters  
 102 derived from the rotational constants of the corresponding singly excited vibrational states and the derived  
 103 ro-vibrational coupling constants  $\alpha$ . Although the  $\nu_{11} = 1$  state is lower in energy than the  $\nu_{12} = 2$  and  
 104 its rotational lines should be detected more easily because of the higher Boltzmann population, it was not  
 105 possible to confidently assign any transitions of the  $\nu_{11} = 1$  state. Indeed, the density of lines in the spectrum  
 106 and the lack of reliable predictions for the  $\nu_{11} = 1$  state made the assignment of transitions belonging to this  
 107 excited vibrational state very difficult. On the other hand, it was easier to recognize transitions of  $\nu_{12} = 2$ ,  
 108 despite its higher vibrational energy, because the knowledge of the  $\alpha$  constants derived from the singly  
 109 excited  $\nu_{12} = 1$  state allowed rather precise predictions.

### 110 3.3. The $\nu_6$ fundamental band

111 The structure of the  $Q$  branch of the  $\nu_6$  fundamental, degrading to lower wavenumbers, appears very dense  
 112 and the even ( $K_a'' + K_c'' = J''$ ) and odd ( $K_a'' + K_c'' = J'' + 1$ ) transitions are mostly overlapped. Anyway, the

113 high-wavenumber edge of the  $Q$  branch allowed us to estimate the band origin; this datum, combined with  
 114 the ground state constants, led to the identification near the band center of several  ${}^Q P_K(J)$  and  ${}^Q R_K(J)$   
 115 groups, which are approximately separated by  $(B + C) \simeq 0.22 \text{ cm}^{-1}$ . As the  $J$  values increase, the lines  
 116 belonging to a given cluster start to overlap to a great extent with those of the neighboring manifolds, thus  
 117 leading to a very packed structure where the resolved details are very difficult to identify. The most relevant  
 118 information for the analysis of the band was yielded by the assignment of groups of lines having high  $J$   
 119 and low  $K_a$  values. In both the  $P$  and  $R$  branches, the spectrum is dominated by distinct bandheads; they  
 120 are separated by about  $2C \simeq 0.18 \text{ cm}^{-1}$  and consist of a series of transitions having the  $J$  values differing  
 121 by one unit between successive lines, each one involving the levels with  $K_a^+$  and  $(K_a + 1)^-$ , which are  
 122 almost degenerate (the superscripts + and - refer to even and odd transitions, respectively). These spectral  
 123 features are characteristic of planar molecules; Borchert[19] and Kisiel[20] are the first who investigated  
 124 these patterns highlighting that they are due to the near-coincidence of transitions between energy levels  
 125 which become degenerate in the oblate symmetric top limit. Figure 4 reproduces a section of the  $R$  branch  
 126 near  $940.3 \text{ cm}^{-1}$  with the resolved  $J$  lines in the  ${}^Q R_K(J = 50 - 59)$  bandheads. The series starts with the  
 127 transition having  $J'' = K_c''$ , and then proceeds toward the higher frequency side with the line sequences of  
 128 the two degenerate even and odd components given, in the  $R$  branch, by

$$(J - k + 1)_{k, J-2k+1} \leftarrow (J - k)_{k, J-2k} \quad (4)$$

$$(J - k + 1)_{k+1, J-2k+1} \leftarrow (J - k)_{k+1, J-2k} \quad (5)$$

129 where  $k = 0, 1, 2, 3, \dots$

130 By using the constants derived from the analysis of the  $a$ -type component we tried to identify also the  
 131  $b$ -type transitions, but they could not be reliably assigned given their lower intensities and the very packed  
 132 structure of the spectrum.

#### 133 4. Discussion

134 The fitting procedure, the spectral simulation and the calculation of the ro-vibrational term values were  
 135 carried out by employing the ATIRS software [21] and the SPFIT/SPCAT program suite [22]. The rotational  
 136 and ro-vibrational data were analysed in a global fit together with the literature data for the ground state  
 137 only [7, 8, 9]. The transition frequencies of Ref. [7] relative to vibrationally excited states were not used in  
 138 our global fit, not only because they are less precise than our measurements, but also because they show  
 139 residuals much greater than the stated uncertainties.

140 In Tables 2– 4 the spectroscopic parameters determined for the ground and vibrationally excited states are  
 141 reported. Although the global fit was performed using the Watson  $A$ -reduced Hamiltonian, in the case of  
 142 the ground state (Table 2), the fits have been performed in both the  $A$  and  $S$  reductions and are compared  
 143 with the literature results of Ref. [8]. The quality of the two procedures is equivalent, in terms of root-mean-  
 144 square (RMS) error and standard deviation  $\sigma$ , but the precision of the individual parameters is greatly  
 145 improved in both cases, with respect to previous determination [8, 9]. This is consistent with the much  
 146 wider range of  $J$  and  $K_a$  values observed in this work, which allowed precise derivations even for high-order  
 147 centrifugal distortion terms. As can be seen from inspection of Table 2, our rotational constants ( $A$ ,  $B$ ,  
 148  $C$ ) as well as our set of quartic centrifugal distortion terms agree well with those reported in the literature  
 149 [8, 9]. On the other hand, the values of all the sextic centrifugal constants are totally different from those  
 150 of Ref. [8] because (i) our analysis includes a more various sample of transitions and (ii) most of the sextic  
 151 constants were completely undetermined in Ref. [8] (i.e., the uncertainty on the constants were greater than  
 152 the constants themselves).

153 In Table 3 the results for the singly excited vibrational states  $\nu_9 = 1$ ,  $\nu_{12} = 1$ ,  $\nu_8 = 1$  and  $\nu_6 = 1$  are  
 154 presented. As discussed previously, only the  $\nu_6$  fundamental ro-vibrational band has been analysed, while  
 155 pure rotational transitions were observed for the other vibrational states.

156 For the fundamental  $\nu_6$ , the analysis carried out in the  $P$  and  $R$  branches led to the assignment of many  
 157 transitions (belonging to the  $a$ -type component) having  $J \leq 85$  and  $K_a \leq 11$ . Only well resolved features



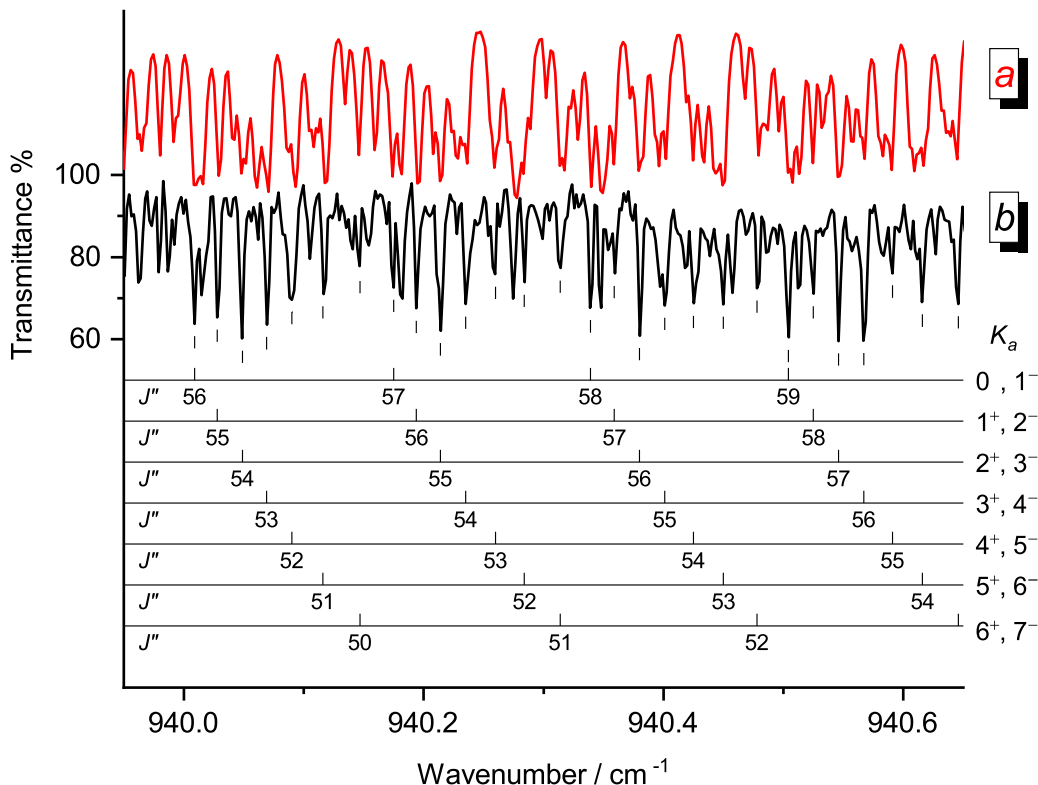


Figure 4: Details of the FT-IR spectrum of the  $\nu_6$  band around  $940.3\text{ cm}^{-1}$ . Lower (black) trace *b* refers to the experimental spectrum, upper (red) trace *a* refers to the computed one using our best parameters. The line sequences in the  $Q_{R_K}(J'' = 50 - 59)$  band heads are reported.

158 were included in the analysis, while badly overlapped features were not considered. It is worthwhile to  
 159 point out that the ro-vibrational assignments in the *P* and *R* branches were checked out by ground state  
 160 combination differences (GSCDs) as implemented in the Visual Loomis Wood program (a part of the ATIRS  
 161 package [21]). The RMS error shown from the final fit of 1622 ro-vibrational transitions is  $7.5 \times 10^{-4}\text{ cm}^{-1}$ .  
 162 In addition to accurate values for band origin and rotational constants, all the quartic centrifugal distortion  
 163 constants were refined in the fit, with the exception of  $\Delta_K$ , due to the fact that  $K_a$  does not change in  
 164 the observed transitions. The value of  $\Delta_K$  was fixed to the ground state value. In addition, the sextic  
 165 terms could not be reliably determined. It is useful to point out that the excited rotational and centrifugal  
 166 distortion terms agree reasonably well with those of the ground state, thus confirming that the set of assigned  
 167 transitions for the  $\nu_6 = 1$  state is essentially free of perturbations. As a further check of the reliability of  
 168 the results, spectral simulations were performed in different portions of the spectrum, as it can be seen by  
 169 looking at Figure 4. The computed spectrum compares reasonably well with the experimental one (residual  
 170 discrepancies are mainly due to signals coming from hot-bands and the weaker *b*-type component), thus  
 171 pointing out the accuracy of the spectroscopic parameters here presented.  
 172 Finally, Tables 4 reports the parameters obtained from the analysis of the rotational transitions observed  
 173 for the doubly excited vibrational states  $\nu_9 = 2$ ,  $\nu_{12} = 2$ , and  $\nu_9 = \nu_{12} = 1$ . For these states, only a  
 174 limited number of lines have been detected. Nevertheless, also in these cases precise sets of rotational and

Table 2: Spectroscopic parameters determined for trifluoroethene in the ground vibrational state.

Parameter <sup>[a]</sup>	Unit	Previous <sup>[b]</sup>		Present work	
		<i>A</i> -reduction		<i>S</i> -reduction	
<i>A</i>	MHz	10665.481287(51)	10665.47731(63)	10665.482129(54)	10665.47809(60)
<i>B</i>	MHz	3872.406579(24)	3872.40538(23)	3872.396511(26)	3872.39542(23)
<i>C</i>	MHz	2837.960953(29)	2837.95990(18)	2837.970162(31)	2837.96926(17)
$\Delta_J(D_J)$	kHz	0.731145(12)	0.73066(24)	0.560036(10)	0.56001(23)
$\Delta_{JK}(D_{JK})$	kHz	7.671250(62)	7.6757(29)	8.698079(51)	8.6985(23)
$\Delta_K(D_K)$	kHz	4.92912(16)	4.9248(15)	4.07290(17)	4.07168(66)
$\delta_J(d_1)$	kHz	0.1831457(50)	0.18353(16)	0.1831675(55)	-0.18346(18)
$\delta_K(d_2)$	kHz	4.83607(14)	4.8228(41)	0.0855201(26)	-0.085327(79)
$\Phi_J(H_J)$	mHz	0.2010(29)	0.038(20)	-0.0951(14)	0.056(89)
$\Phi_{JK}(H_{JK})$	Hz	0.019977(56)	0.0027(105)	0.005288(14)	0.0026(22)
$\Phi_{KJ}(H_{KJ})$	Hz	-0.05529(18)	0.0025(288)	-0.864(88)	0.0007(16)
$\Phi_K(H_K)$	Hz	0.07534(20)	0.033(21)	0.03395(17)	0.0306(27)
$\phi_J(h_1)$	mHz	0.0765(15)	-0.02(18)	0.0125(14)	-0.46(29)
$\phi_{JK}(h_2)$	mHz	9.352(55)	14.4(63)	0.1387(10)	0.59(25)
$\phi_K(h_3)$	Hz	0.11635(37)	-0.041(78)	0.07287(19)	0.00014(10)
$\Lambda_{JK}(L_{JK})$	nHz	-3.61(68)		23.05(71)	
Lines		484	182	484	182
$J_{\max}, K_{a\max}$		106, 38	75, 38	106, 38	75, 38
RMS error	kHz	21.6	16.0	21.6	15.8
$\sigma$		0.99	0.80	0.99	0.79

**Notes:** Numbers in parentheses are one standard deviation and apply to the last significant digits. **[a]** *S*-reduction parameters are reported in parentheses. **[b]** Ref. [8].

175 centrifugal distortion constants could be derived. The analysis of the rotational data in excited vibrational  
176 states highlighted the presence of accidental perturbations in all the states except  $\nu_9 = 1$  and  $\nu_{12} = 1$ . A  
177 correct interpretation of perturbed transitions and their inclusion in the global analysis would require a  
178 detailed ro-vibrational analysis of the lowest excited states [23], not available at the moment. Therefore,  
179 only unperturbed transitions were included in the final analysis.

## 180 5. Conclusions

181 In this paper we report the detection of the rotational spectrum of TFE in the ground and in the vibrationally  
182 excited states  $\nu_9 = 1$ ,  $\nu_{12} = 1$ ,  $\nu_8 = 1$ ,  $\nu_9 = 2$ ,  $\nu_{12} = 2$ , and  $\nu_9 = \nu_{12} = 1$ . Moreover, the fundamental  $\nu_6$   
183 ro-vibrational band has been observed. All the data were analysed in a global fit and sets of spectroscopic  
184 parameters for each state were determined in the *A*-reduction scheme. The quality of the fit is very good, as  
185 shown by the values of the statistical errors, the precision of the parameters and the overall good agreement  
186 between calculated and observed spectra. As far as the infrared bands are concerned, only a small portion  
187 of the recorded high-resolution spectrum has been analysed. In this light, this should be considered as an  
188 ongoing work.

189 We are already planning to study in the near future all the fundamentals not yet investigated, especially  
190 the ones falling below  $500\text{ cm}^{-1}$ , for which a synchrotron-based experiment would be most appropriate.

Table 3: Spectroscopic parameters determined for trifluoroethene in the singly-excited vibrational states.

Parameter	Unit	$\nu_9 = 1$	$\nu_{12} = 1$	$\nu_8 = 1$	$\nu_6 = 1$
$E$	$\text{cm}^{-1}$	232 <sup>[a]</sup>	305 <sup>[a]</sup>	485 <sup>[a]</sup>	929.800817(68)
$A$	MHz	10624.33115(21)	10698.10053(46)	10673.4129(13)	10641.54(43)
$B$	MHz	3870.682459(76)	3879.11980(11)	3874.51307(24)	3867.839(43)
$C$	MHz	2835.673154(87)	2841.51433(10)	2835.73608(17)	2831.9027(19)
$\Delta_J$	kHz	0.717141(44)	0.740172(89)	0.73194(26)	0.6934(89)
$\Delta_{JK}$	kHz	6.72388(32)	8.33244(86)	7.6312(25)	8.66(23)
$\Delta_K$	kHz	4.8686(22)	5.1612(33)	5.1076(32)	4.92907 <sup>[b]</sup>
$\delta_J$	kHz	0.179378(16)	0.186624(31)	0.184212(84)	0.1656(44)
$\delta_K$	kHz	4.38568(48)	5.22666(72)	4.8513(33)	5.049(44)
$\Phi_J$	mHz	0.178(11)	0.223(26)	0.742(87)	
$\Phi_{JK}$	mHz	4.18(24)	34.27(51)	26.16(59)	
$\Phi_{KJ}$	Hz	-0.08034(91)	-0.0313(14)	-0.0220(47)	
$\Phi_K$	Hz	0.0488(45)	0.0698(61)	0.07529 <sup>[b]</sup>	
$\phi_J$	mHz	0.0308(56)	0.1015(99)	0.0768 <sup>[b]</sup>	
$\phi_{JK}$	mHz	1.11(21)	17.02(34)	12.7(16)	
$\phi_K$	Hz	0.0439(15)	0.1812(22)	0.11635 <sup>[b]</sup>	
$\Lambda_{JKK}$	$\mu\text{Hz}$		0.336(52)	-0.00332 <sup>[b]</sup>	
$\Lambda_{JK}$	$\mu\text{Hz}$	-2.75(31)	-2.48(60)		
$\Lambda_{KKJ}$	mHz	0.0278(25)			
Lines		266	194	67	1622
RMS error	kHz	13.3	19.8	13.5	$7.5 \times 10^{-4} \text{ cm}^{-1}$
$\sigma$		0.97	0.98	1.01	1.00

**Notes:** Numbers in parenthesis are one standard deviation and apply to the last significant digits. **[a]** From Ref. [4]. **[b]** Fixed to ground state value.

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206

Table 4: Spectroscopic parameters determined for trifluoroethene in the overtone and combination states.

Parameter	Unit	$\nu_9 = 2$	$\nu_{12} = 2$	$\nu_9 = \nu_{12} = 1$
$E$	$\text{cm}^{-1}$	464	610	537
$A$	MHz	10582.13248(78)	10730.4962(22)	10656.5591(41)
$B$	MHz	3868.72306(23)	3885.44476(24)	3877.20485(78)
$C$	MHz	2833.35089(10)	2844.51620(12)	2839.28342(14)
$\Delta_J$	kHz	0.70320(11)	0.76091(17)	0.72476(77)
$\Delta_{JK}$	kHz	5.8417(18)	9.2032(25)	7.4041(52)
$\Delta_K$	kHz	4.7432(44)	5.794(39)	4.844(57)
$\delta_J$	kHz	0.175477(52)	0.192589(97)	0.18200(36)
$\delta_K$	kHz	3.9355(15)	5.7471(21)	4.7743(26)
$\Phi_J$	mHz	0.2014 <sup>[a]</sup>		0.2014 <sup>[a]</sup>
$\Phi_{JK}$	Hz	0.019974 <sup>[a]</sup>		0.027(11)
$\Phi_{KJ}$	Hz	-0.163(14)		-0.05527 <sup>[a]</sup>
$\Phi_K$	Hz	0.07529 <sup>[a]</sup>		0.07529 <sup>[a]</sup>
$\phi_J$	mHz	0.0768 <sup>[a]</sup>		0.0768 <sup>[a]</sup>
$\phi_{JK}$	mHz	9.348 <sup>[a]</sup>		9.348 <sup>[a]</sup>
$\phi_K$	Hz	0.11635 <sup>[a]</sup>		0.322(201)
Lines		67	25	25
RMS error	kHz	11.5	11.9	11.8
$\sigma$		0.96	1.17	0.95

**Notes:** Numbers in parenthesis are one standard deviation and apply to the last significant digits. The values for the vibrational energy levels ( $E$ ) were estimated by using the data listed in Table 1 and without considering the anharmonicity constants. [a] Fixed to ground state value.

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