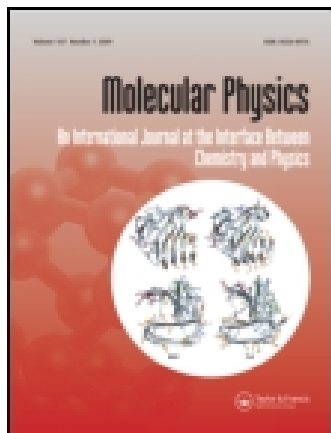


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## INVITED ARTICLE

### The high resolution infrared spectrum of the $\nu_4$ band of 1,1,1-trifluoroethane

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The  $\nu_4$  band of 1,1,1-trifluoroethane ( $\text{CH}_3\text{CF}_3$ ) has been studied using synchrotron radiation at the far-infrared beamline, Canadian Light Source. The spectra were recorded at a resolution of  $0.00096\text{ cm}^{-1}$  in the spectral range 800 to  $860\text{ cm}^{-1}$  using a Bruker IFS125 FT spectrometer. Altogether 2785 lines were assigned to  ${}^qP_K(J)$  and  ${}^qR_K(J)$  transitions with  $J''$  up to 71 and  $K$  up to 45. The  ${}^qQ_K(J)$  sub-branches are too congested and overlapped to other hot-band  $Q$  branches to be analysed. A Watson-type Hamiltonian containing the usual terms up to the 6th power in the angular momentum operators was used in the analysis. The spectroscopic parameters obtained from the fit reproduce 2636 transitions with a standard deviation of about  $0.00016\text{ cm}^{-1}$ .

**Keywords:**  $\text{CH}_3\text{CF}_3$ ; 1,1,1-trifluoroethane; high resolution; infrared spectrum;  $\nu_4$  fundamental

#### 1. Introduction

The 1,1,1-trifluoroethane,  $\text{CH}_3\text{CF}_3$ , has been the subject of several spectroscopic investigations [1–7]. It attracted the interest of spectroscopists because of the presence of torsional splitting in the ground and excited vibrational states. Besides, the low energy torsional motion affects the whole infrared spectrum allowing the observation of many hot bands involving vibrationally excited torsional states. This molecule (HFC-143a) is also interesting from the environmental point of view since it could replace HCFC-22 ( $\text{CHClF}_2$ ), eventually in mixture with other less flammable HFC [1]. The microwave and millimetre-wave rotational spectra in the ground and excited torsional states up to  $\nu_6 = 3$  have been reported in the literature [2–4]. The high resolution infrared spectra of several fundamental and combination bands have been recorded and analyzed. In 1993 Fraser *et al.* [5] studied the molecular-beam spectrum of the Fermi triad  $2\nu_6 + \nu_{11}$ ,  $\nu_5 + \nu_{12}$  and  $\nu_{10}$  located near  $970\text{ cm}^{-1}$ . The  $\nu_2$  and  $\nu_8$  fundamentals and the combination bands  $\nu_4 + \nu_5$  and  $\nu_6 + \nu_9$  were analysed by Duxbury *et al.* [6]. Later, Wang *et al.* [4] studied the high resolution infrared spectrum of the first overtone of the  $\nu_6$  at  $423\text{ cm}^{-1}$  together with the millimetre-wave rotational spectra in the four lowest torsional states. Wang *et al.* [7] also recorded and analysed the  $\nu_5$  band together with the  $(\nu_5 + \nu_6) - \nu_6$  hot band. In this paper we report

the analysis of the high resolution infrared spectrum of the  $\nu_4$  fundamental band, namely the C–C stretching, centred at  $831\text{ cm}^{-1}$ , recorded using synchrotron radiation. This band was already reported by Nivellini *et al.* [8] at a resolution of  $0.004\text{ cm}^{-1}$ , but no  $K$  structure was observed (see Figure 7 in [8]). It was obvious that detailed information could have been obtained only using a high resolution spectrometer equipped with a very brilliant source. These experimental conditions can only be fulfilled by a synchrotron radiation facility equipped with a very high resolution infrared spectrometer.

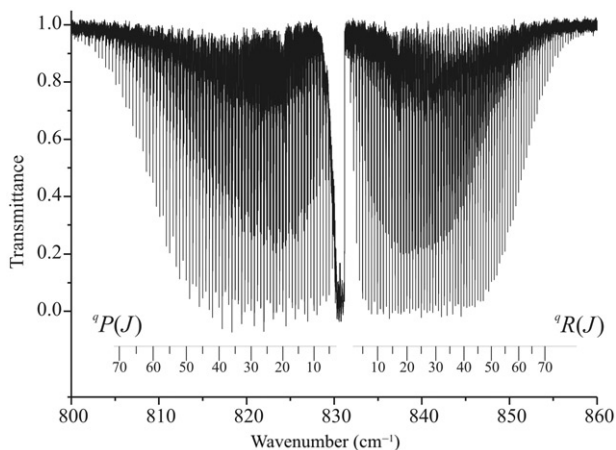
#### 2. Experimental

For this study we recorded four absorption spectra at an unapodized resolution of  $0.00096\text{ cm}^{-1}$  in the  $510\text{--}1000\text{ cm}^{-1}$  spectral range using the Bruker IFS 125 Fourier transform spectrometer located at the far-infrared beamline, Canadian Lightsource. A summary of the experimental conditions for each spectrum is given in Table 1. All the 1,1,1-trifluoroethane,  $\text{CH}_3\text{CF}_3$ , spectra were recorded using a multipass coolable absorption cell with a 2 m base length. Figure 1 shows an overview of the vibrational band of interest. The cell was equipped with wedged KBr windows. The radiation generated by either the synchrotron source (SR) or an infrared globar (GB)

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Table 1. Summary of experimental conditions of CH<sub>3</sub>CF<sub>3</sub> spectra.

	Source	Pressure (mTorr)	Temperature (K)	Pathlength (m)	Scanning speed (KHz)	Resolution (cm <sup>-1</sup> )	Optical filter (cm <sup>-1</sup> )	Detector filter (cm <sup>-1</sup> )	Detector gain	No. scans
1	SR <sup>a</sup>	85	298.25	24.15	40	0.00096	510–1000	490–1190	64	104
2	SR <sup>a</sup>	200	298.25	72.15	60	0.00096	510–1000	490–1190	64	142
3	GB <sup>b</sup>	200	298.45	24.15	40	0.00096	None	490–1190	64	350
4	SR <sup>a</sup>	301	216.75	24.15	40	0.00096	300–1250	300–1200	16	374

Notes: <sup>a</sup>Synchrotron source.<sup>b</sup>Global source.Figure 1. Infrared spectrum of CH<sub>3</sub>CF<sub>3</sub> in the region between 800 and 860 cm<sup>-1</sup> showing the  $\nu_4$  fundamental band centred at 831 cm<sup>-1</sup>. The  $J$  numbering of the  ${}^Q P_K(J)$  and  ${}^Q R_K(J)$  branches is indicated. Experimental conditions, see Table 1, spectrum 4.

was detected using a Ge : Cu detector fitted with a cold filter. The diameter of the iris was 1.15 mm. A 5 kHz electronic filter was used in the experiments. The CH<sub>3</sub>CF<sub>3</sub> sample of 98% purity was supplied by the Cambridge Isotope Laboratories and was used without further purification. Besides the CH<sub>3</sub>CF<sub>3</sub> lines, a few lines belonging to residual water vapour present in the evacuated spectrometer were identified in the spectra. The gas sample temperature and pressure were monitored continuously during the data recording. A T-type thermocouple mounted inside the cell was used to monitor the gas sample temperatures. The gas pressures ranged between 85 to 301 mTorr and were measured using a 0–1 Torr capacitance gauge (Baratron). The calibration of the wavenumber scale of each spectrum was performed relative to well determined positions of the  $\nu_2$  band carbon dioxide lines [9]. These lines appeared in the spectra due to residual amounts of carbon dioxide in the evacuated spectrometer tank. The gain in S/N by adopting a SR instead of a GB source can be demonstrated by

comparing spectra 3 and 4 (see Table 1). In fact, an increase of at least a factor of 4 in the S/N can be observed in the spectrum recorded with the SR source as shown in Figure 2.

### 3. Description of the spectrum and analysis

The CH<sub>3</sub>CF<sub>3</sub> molecule is a prolate symmetric top close to the spherical limit,  $\gamma = (A-B)/\frac{1}{2}(A+B) = 0.06$ . The  $\nu_4 = 1$  state (C–C stretching) is of A<sub>1</sub> symmetry. As a consequence, the  $\nu_4$  band appears as a well behaved parallel band of medium-weak intensity, with a strong Q branch centred at about 830 cm<sup>-1</sup> and a series of  ${}^Q P_K(J)$  ( $J$ ) branches in the lower wavenumber side, and the corresponding  ${}^Q R_K(J)$  branches in the higher wavenumber side, as can be seen in Figure 1. The  $P$  and  $R$  branches appear as a comb structure with a separation between successive  $J$  of about 0.345 cm<sup>-1</sup> ( $2B$ ) and could be analysed up to  $J'' = 69$  in the  $R$  side and up to  $J'' = 71$  in the  $P$  side. Because of the small size (0.0005726 cm<sup>-1</sup>) and of the positive sign of the difference  $[(A' - A'') - (B' - B'')]$  the  $K$  structure of all the  $R$  and  $P$  branches appears very congested and blue degraded. In fact, up to  ${}^Q P_K(12)$  on the low energy side, and up to  ${}^Q R_K(13)$  on the high energy one, the  $K$  structure cannot be resolved at all. Even at high  $J$  values,  $K = 12$  is usually the lowest  $K$  resolved transition, and below  $K = 9$  the branch generally appears as a strong unresolved band feature. For the same reason the central Q branch appears completely unresolved and overlapped with other Q branches belonging to many hot bands appearing in the spectrum. The only characteristic feature in this branch is the very sharp edge on the high wavenumber side at 831.177 cm<sup>-1</sup> which denotes the band origin. Starting from this point, by measuring the average spacing between the  ${}^Q R$  branches, a tentative assignment of the  $J$  numbering of the  ${}^Q R_K(J)$  branches was attempted. Because of the presence of two groups of three identical fermions in the molecule an intensity alternation can be seen in the  $K$  structure of branches. The transitions with  $K = 3n$

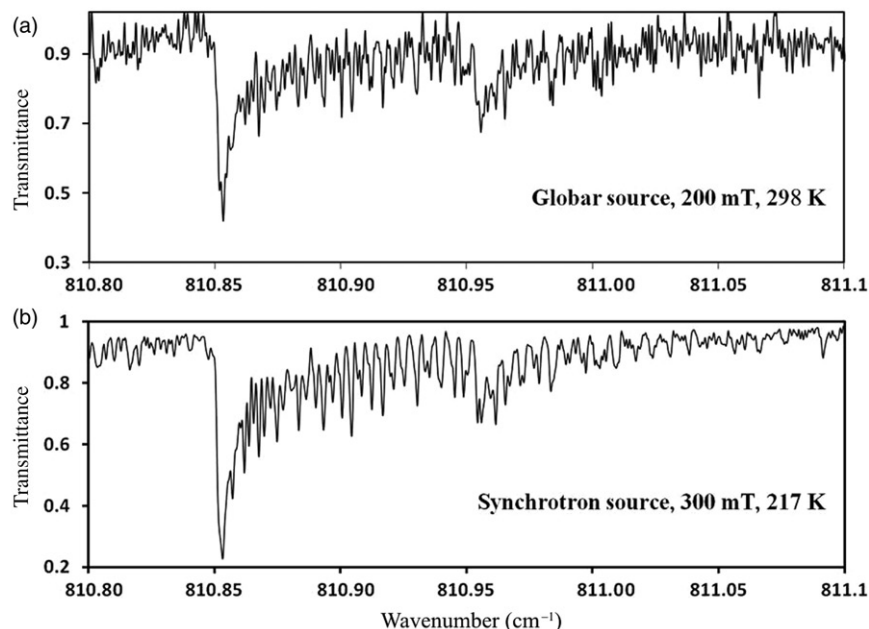


Figure 2. Portion of the  $\text{CH}_3\text{CF}_3$   $\nu_4$  band recorded at the far-infrared beamline using the (a) global source and (b) the synchrotron. See Table 1, spectra 3 and 4, for more detailed experimental conditions.

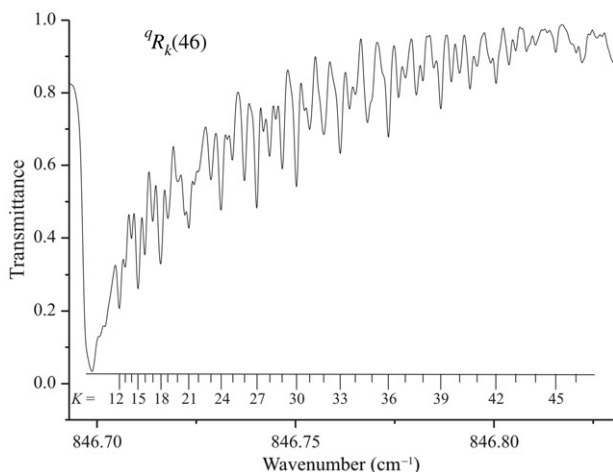


Figure 3. Section of the infrared spectrum of  $\text{CH}_3\text{CF}_3$  in the region between  $846.70$  and  $846.83\text{ cm}^{-1}$  showing the  $K$  structure of the  ${}^qR_K(46)$  branch. Experimental conditions, see Table 1, spectrum 4.

with  $n=0, 1, 2, \dots$  have twice the intensity of those with  $K \neq 3n$  owing to the statistical weight of the corresponding  $K$  levels. Figure 3 illustrates the  ${}^qR_K(46)$  in the region  $846.70$ – $846.83\text{ cm}^{-1}$  where the intensity alternation is evident. Since  $K$  cannot be larger than  $J$  and because of the blue degradation of the branches, the line at higher wavenumber in a  ${}^qR$  branch is the one with  $J'' = K''$ , which is a strong line when  $J'' = 3n$ .

In this way we were able to confirm the  $J$  numbering of the  ${}^qR$  branch and assign the  $K$  structure. The  $J$  numbering was performed analogously in the  ${}^qP_K(J)$  region, but with less confidence for the first few  $J$  values because of the strong overlap with the  ${}^qQ$  branches. In order to assist the assignments, the method of the ground state combination differences (GSCD) was adopted. Satellites branches accompany each  $P$ ,  $Q$  and  $R$  branch of the  $\nu_4$  fundamental band. They arise from hot bands involving the first few vibrational states  $\nu_6$ ,  $\nu_{12}$  and  $2\nu_6$  with origin at  $223$ ,  $366$  and  $423.15\text{ cm}^{-1}$ , respectively [4,8]. The large majority of the assignments were made in spectrum 4 (see Table 1), with a few exceptions for high  $J$  high  $K$  values where the spectrum 2 was used.

Spectroscopic parameters for the ground state were already reported by Wang *et al.* [4,7] in studies of the microwave and millimetre-wave rotational spectrum in the ground and in excited torsional states up to  $\nu_6=4$  adopting an effective torsional-rotational Hamiltonian.

No torsional splitting was ever observed in the  $\nu_4$  band and a torsional splitting of the order of  $0.01\text{ MHz}$  was reported in the distortion moment-allowed  $Q$  branch transitions in the pure rotational spectrum [3]. The spectroscopic parameters for the ground state could thus be determined, by neglecting the splitting, from the fit of all the data available in the literature. The usual Hamiltonian for a prolate symmetric top

with terms up to the sixth power in  $J$ ,  $K$  was adopted. In addition, the  $\Delta k = \pm 3$  interaction terms leading to the  $K=3$  split transitions observed in the forbidden rotational  $Q$  branches [3] and, in a few cases, in the millimetre-wave spectrum at very high values of  $J$  [2] was taken into account.

The diagonal matrix elements for a prolate rotor, including terms up to the sixth power in the angular momentum, are given by

$$E(J, k)/hc = B[J(J+1) - k^2] + Ak^2 - D_J[J(J+1)]^2 - D_{JK}[J(J+1)]k^2 - D_K k^4 + H_J[J(J+1)]^3 + H_{JK}[J(J+1)]^2 k^2 + H_{KJ}[J(J+1)]k^4 + H_{KK}k^6, \quad (1)$$

and off-diagonal elements by

$$\langle J, k | H/hc | J, k \pm 3 \rangle = \{[\varepsilon + \varepsilon_J J(J+1)](2k \pm 3) + \varepsilon_K [k^3 + (k \pm 3)^3]\} F_{\pm 3}(J, k), \quad (2)$$

where

$$F_{\pm 3}(J, k) = \{[J(J+1)] - (k(k \pm 1))[J(J+1)] - (k \pm 1)(k \pm 2)[J(J+1) - (k \pm 2)(k \pm 3)]\}^{1/2}$$

and the signed quantum number  $k = \pm K$ .

The data in Table 2 of [2] were treated according to the suggestions of Ozier [3]. It was also decided not to consider the GSCD obtained from the data for the  $\nu_4$  band presently analysed, since their accuracy is of the order of 5 MHz while that of microwave and

millimetre-wave measurements is 0.2 MHz, in the worst case. The spectroscopic parameters for the vibrational ground state obtained from the fit are reported in column 2 of Table 2. They are in good agreement with those obtained taking into account the torsional splitting [7].

After completing the analysis of the  ${}^qP_K(J)$  branches, all the  $\nu_4$  transitions were fitted using for the  $\nu_4=1$  state the same Hamiltonian adopted for the ground state. Columns 3 and 4 in Table 2 list the spectroscopic parameters obtained from transition wavenumbers whose corresponding observed – calculated values do not exceed a chosen limit set to 0.0002 (fit I) and 0.0004  $\text{cm}^{-1}$  (fit II), respectively. In the former case 694 out of 2785 fitted transitions (about 25%) exceeded the rejection limit and the obtained standard deviation of the fit was 0.00010  $\text{cm}^{-1}$ . When a tolerance of 0.0004  $\text{cm}^{-1}$  was adopted only 150 data (about 5%) were discarded but the standard deviation raised to 0.00016  $\text{cm}^{-1}$ . It should be pointed out that the discarded transitions do not follow any specific trend but are scattered over all the assigned  $J$  and  $K$  values. Generally, in a spectrum taken at a resolution of 0.001  $\text{cm}^{-1}$  with a  $S/N \geq 50$  one would expect, with a well-behaved Hamiltonian, to fit the large majority of the transitions ( $\geq 90\%$ ) with a limit for rejection of 0.0001  $\text{cm}^{-1}$ , obtaining a standard deviation of the fit of the order of 0.00006–0.00009  $\text{cm}^{-1}$  (i.e. 2–3 MHz). If this is not the case, as in the present analysis, it means that either in the Hamiltonian some important interaction terms are not considered or in the spectrum most of the transitions are overlapped, or both. The

Table 2. Spectroscopic parameters (in  $\text{cm}^{-1}$ ) for the ground state and the  $\nu_4=1$  state of  $\text{CH}_3\text{CF}_3$ .

	Ground state	$\nu_4=1$ fit I <sup>a</sup>	$\nu_4=1$ fit II <sup>b</sup>
$\nu_0$	–	831.1769618 (191)	831.1769049 (147)
$A$	0.18342224765 (679)	0.1831688643 (668)	0.1831692008 (482)
$B$	0.172957554120 (378)	0.1726383363 (289)	0.1726383572 (217)
$D_J \times 10^9$	42.184614 (487)	42.2685 (130)	42.27015 (962)
$D_{JK} \times 10^9$	66.78631 (169)	66.8795 (194)	66.9199 (138)
$D_K \times 10^9$	–65.783 (114)	–65.6094 (688)	–65.3255 (485)
$H_J \times 10^{15}$	18.336 (682)	17.38 (162)	17.32 (119)
$H_{JK} \times 10^{15}$	–0.866 (282)	–0.866 <sup>c</sup>	–0.866 <sup>c</sup>
$H_{KJ} \times 10^{12}$	0.148304 (820)	0.1350 (115)	0.15254 (810)
$H_K \times 10^{12}$	2.480 (615)	2.3751 (234)	2.4458 (165)
$\varepsilon \times 10^9$	8.32004 (442)	8.32004 <sup>c</sup>	8.32004 <sup>c</sup>
$\varepsilon_J \times 10^{15}$	–14.782 (868)	–14.782 <sup>c</sup>	–14.782 <sup>c</sup>
Total number of data	478	2785	2785
Number of data retained in the fit	447	2635	2091
Weighted standard deviation	$1.42 \times 10^{-7} \text{ cm}^{-1}$	$1.56 \times 10^{-4} \text{ cm}^{-1}$	$1.00 \times 10^{-4} \text{ cm}^{-1}$

Notes: <sup>a</sup>Tolerance for rejection = 0.0004  $\text{cm}^{-1}$ .

<sup>b</sup>Tolerance for rejection = 0.0002  $\text{cm}^{-1}$ .

<sup>c</sup>Fixed to the ground state value.

refinement of higher order coefficients ( $L_K$  and  $P_K$ ) which could effectively account for the effect of perturbations, due to anharmonic or Coriolis interactions, did not improve significantly the quality of the fit. In fact, by adopting a rejection limit of  $0.0002\text{ cm}^{-1}$ , the number of fitted transitions increased from 2091 to 2256 and the standard deviation of the fit remained almost unchanged. Moreover, the additional 165 transitions which were retained in the fit are randomly distributed over all  $J$  and  $K$  quantum numbers. This observation suggests that the high density of the lines, which leads to a large number of overlapping features in the spectra, is responsible for the quality of the fit. Although perturbations cannot be excluded *a priori*, they should be extremely small. All the diagonal parameters for the  $\nu_4=1$  state have been determined, with the exception of  $H_{JK}$  which has been set equal to the corresponding value of the ground state. Also the  $\Delta k = \pm 3$  interaction constants,  $\varepsilon$  and  $\varepsilon_J$ , have been fixed to the corresponding ground state values, since no  $K=3$  transition has been identified in the spectrum due to the congestion of the low  $K$  lines.

The spectroscopic parameters in columns 3 and 4 of Table 2 are very similar, most of their values being within  $3\sigma$  or less. Moreover, their values are close to the corresponding ones in the ground state, further supporting the hypothesis that the  $\nu_4=1$  state is practically unperturbed. All line wavenumbers from the ro-vibrational analyses can be made available from the Bologna author.

#### 4. Conclusions

The  $\nu_4=1$  vibrational state (C–C stretching) of  $\text{CH}_3\text{CF}_3$  has been spectroscopically characterized through the observation and the analysis of the  $\nu_4$  – GS band at  $831\text{ cm}^{-1}$ . An improved set of ground state spectroscopic parameters, however neglecting torsional splitting, was obtained from the analysis of all the data available in the literature. Two sets of spectroscopic

parameters for the excited state have been evaluated. They differ for the chosen rejection limit ( $0.0002$  or  $0.0004\text{ cm}^{-1}$ ), for the number of data excluded in the final fit (694 or 150), leading to a standard deviation of the fit of  $0.00010$  and  $0.00016\text{ cm}^{-1}$ , respectively.

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