Jet-cooled diode laser spectrum and FTIR integrated band intensities of CF₃Br: rovibrational analysis of $2\nu_5$ and $\nu_2 + \nu_3$ bands near 9 μm and cross section measurements in the 450 - 2500 cm⁻¹ region

Andrea Pietropolli Charmet, Nicola Tasinato, Paolo Stoppa, Agostino Baldacci, Santi Giorgianni

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Jet-cooled diode laser spectrum and FTIR integrated band intensities of CF₃Br: rovibrational analysis of 2v₅ and v₂ + v₃ bands near 9 μm and cross section measurements in the 450 - 2500 cm⁻¹ region

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Complete List of Authors:	PIETROPOLLI CHARMET, Andrea; Universita' Ca' Foscari di Venezia, Dipartimento di Chimica Fisica TASINATO, Nicola; Universita' Ca' Foscari di Venezia, Dipartimento di Chimica Fisica STOPPA, Paolo; Universita' Ca' Foscari di Venezia, Dipartimento di Chimica Fisica BALDACCI, Agostino; Universita' Ca' Foscari di Venezia, Dipartimento di Chimica Fisica GIORGIANI, Santi; Universita' Ca' Foscari di Venezia, Dipartimento di Chimica Fisica
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**Jet-cooled diode laser spectrum and FTIR integrated band intensities of CF₃Br:
rovibrational analysis of 2ν₅ and ν₂ + ν₃ bands near 9 μm and cross section
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A. PIETROPOLLI CHARMET, N. TASINATO, P. STOPPA, A. BALDACCI
and S. GIORGIANNI

Dipartimento di Chimica Fisica, Università Ca' Foscari di Venezia
D.D. 2137, I-30123 Venezia, Italy

Proposed running head: rovibrational analysis of CF₃Br and integrated cross sections

Corresponding author: Andrea PIETROPOLLI CHARMET
Università Ca' Foscari di Venezia
Dipartimento di Chimica Fisica
Dorsoduro 2137
I-30123 VENEZIA (Italy)
Tel: +39 041 2348541
Fax: +39 041 2348594
E-mail: jacpnike@unive.it

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Abstract

The high resolution (up to 0.0007 cm^{-1}) infrared diode laser spectrum of CF_3Br (Halon 1301) with natural isotopic abundance has been investigated in the region $1090 - 1130\text{ cm}^{-1}$, characterized by the presence of the $2\nu_5$ and $\nu_2 + \nu_3$ absorptions and several weaker hot bands. The rovibrational analysis of the data, obtained employing a slit-jet system (rotational temperature of about 50 K) together with those recorded at 200 K, led to a complete and accurate set of spectroscopic constants for the bands of both the bromine isotopologues. Integrated band intensities have been obtained for all the absorptions in the spectral range $450 - 2500\text{ cm}^{-1}$. The high resolution data and the information about the cross sections of this molecule can be useful for its remote sensing and for better modelling its contribution to the global warming.

Keywords: Bromotrifluoromethane; slit-jet diode laser spectroscopy; rovibrational analysis; integrated cross sections; FTIR spectroscopy.

1. Introduction

Once they have reached the stratosphere, brominated organic compounds undergo photochemical oxidation thus releasing bromine atoms that critically affect the Earth's protective ozone layer. Known bromine sources include the long-lived anthropogenic halons and methyl bromide: between 1980 and the late 1990s emissions of these compounds have resulted in more than a doubling of the atmospheric bromine loading [1]. Bromotrifluoromethane (CF_3Br , Halon 1301, Freon 13B1), characterized by a long stratospheric lifetime (about 65 years), has the highest Ozone Depletion Potential among the sources of bromine (12 referred to CFC 11, as reported in Ref. [2]), and therefore it has been banned by the Montreal Protocol since 2003. Its averaged global tropospheric mixing ratio has been estimated equal to 2.6 ppt [3]: this value may seem rather low but it must be underlined that bromine is considered up to 45 – 70 times more efficient than chlorine as a catalyst of stratospheric ozone depletion [4].

The mid infrared spectrum of bromotrifluoromethane shows two strong absorption bands (ν_1 and ν_4 located at 1085 and 1210 cm^{-1} , respectively) and a number of weaker fundamental, overtone and combination features, so this compound can heavily contribute to the greenhouse effect. In addition to its importance in the atmospheric chemistry, CF_3Br has been proposed as prototype molecule for infrared laser chemistry and isotopically selective multiphoton induced dissociation (see Refs. [5 – 9] and references therein).

Owing to the severe environmental effects and the suggested variety of applications, CF_3Br has been the subject of many spectroscopic studies in the last decades. Concerning the microwave and the millimetre regions, the ^{12}C species has been

extensively analyzed in the past [10 – 15] thus leading to the determination of the dipole moment and to an accurate set of ground state constants for both the $^{79/81}\text{Br}$ isotopologues; the bromine nuclear quadrupole constants have been theoretically investigated employing several DFT and hybrid HF/DFT methods [16]. Recently also the ^{13}C species have been studied [17] employing both radiofrequency-microwave double resonance (RFMWDR) and conventional microwave spectroscopic techniques.

The infrared spectrum of CF_3Br has been originally assigned by Plyler and Acquista [18] and subsequently by Polo and Kent Wilson [19]; the structure of many fundamental, overtone and combination bands has been analysed at medium resolution employing grating [20 – 23] and Fourier transform spectrometers [24]. The advent of tunable diode laser and FTIR spectrometers with a greater resolving power has allowed a more accurate rovibrational analysis of the fine structure of the infrared spectrum (see for example Refs. [25 – 27]).

The last years have seen a renewed interest in the spectroscopic studies of similar halogenated pollutants (see for example Ref. [28] and references therein) since an accurate rovibrational analysis of the bands falling in the mid infrared region could support the quantitative detection and the temperature profiles modelling of these compounds. Furthermore, since a better understanding of their radiative forcing needs accurate information about absorption strengths, integrated cross section measurements in a wavenumber range as wide as possible could be useful. Recently [29] we have employed a slit-jet supersonic expansion to simplify the spectrum of the ν_1 band around 1085 cm^{-1} recorded with a tunable diode laser spectrometer, resolving almost completely the K -structure of many $P(J)$ and $R(J)$ multiplets and so improving our earlier results [30]. Here we complete the jet-cooled high-resolution study of the region

around this fundamental reporting the rovibrational analysis of the weaker absorptions coming from $2\nu_5$ and $\nu_2 + \nu_3$ for both the bromine isotopologues.

The previous rovibrational investigations of these bands carried out several years ago [31, 32] with a diode laser spectrometer were lacking of some important spectral regions: for example, the P branch of $2\nu_5$ at 200 K was completely overlapped by the stronger R branch of the ν_1 fundamental, so the analysis was restricted to the R branch transitions. In addition, the K -structure of both these bands appeared not completely resolved even at a resolution of about 0.002 cm^{-1} and the accuracy of the measurements, limited by the secondary standards employed, was estimated around 0.003 cm^{-1} . In the present work the use of a slit-jet expansion has allowed us to access for the first time to the resolved P branch transitions recording the high-resolution spectrum (up to 0.0007 cm^{-1}) of $2\nu_5$ in the region $1090 - 1102\text{ cm}^{-1}$. In the region of $\nu_2 + \nu_3$ a new and more complete data set has been obtained from the analysis of the cold (about 50 K) free-jet spectrum and that recorded at stratospheric temperature (200 K). The measurements cover about 85% of the range $1110 - 1130\text{ cm}^{-1}$, thus furnishing P and R transitions at higher J values than our previous data. As a consequence, a more reliable and accurate set of spectroscopic parameters has been obtained for $2\nu_5$ and $\nu_2 + \nu_3$ of both the bromine isotopologues. Furthermore, many features belonging to various hot bands have been identified, and the corresponding sets of molecular constants have been determined. We have also measured the integrated cross sections for all the absorptions of CF_3Br falling in the spectral range $450 - 2500\text{ cm}^{-1}$ and we have obtained accurate values for many fundamental and combination bands thus extending the analysis to spectral regions not previously investigated [33 – 36].

2. Experimental aspects

Details of our home built slit-jet system have been given previously [29], so only a brief description will be reported here. The main part of the radiation emitted by a lead salt diode laser (Laser Components), after being collimated and mode filtered, entered a large (1.5 m^3) vacuum chamber evacuated by a set of large Roots blower. The pulsed supersonic planar expansion of the gas sample (15% of CF_3Br in Helium) has been regulated by a modified solenoid valve (General Valves, Series 9) driven by a controller (Iota One, General Valve Corporation). Laser scans (about 0.3 cm^{-1} wide, duration of about 1 ms) and gas pulses (about 2 ms) have been properly synchronized by using an electronic delay generator: a fast four channel digital oscilloscope (Tektronix TDS 3014) has been used to acquire simultaneously the jet spectrum and the signals employed for reference purpose. Up to 128 scans have been averaged together without appreciably increasing the observed linewidths. The stagnation pressure has been varied between 150 and 180 kPa, while the pump system kept the background pressure below 0.3 Pa, thus minimizing absorptions coming from the rotationally warm background gas. Linewidths up to 0.0007 cm^{-1} (FWHM) have been measured in the free-jet spectrum, mainly limited by residual Doppler broadening and laser jitter noise. From spectral simulations we have estimated a rotational temperature of about 50 K. For the spectrum at reduced temperature (200 K) we used a homemade 92 cm path cell. Observed linewidths were generally better than 0.0012 cm^{-1} . The wavenumber calibration has been based on SO_2 line positions measured in a room temperature reference cell. Since the frequencies reported by the HITRAN 2004 [37] database are calculated without taking into account all the rovibrational resonances, to obtain a reliable wavenumber

accuracy (estimated better than 0.0007 cm^{-1} for resolved single lines) of the diode laser data, we have used the frequencies of the SO_2 lines obtained by high resolution FTIR spectrum calibrated versus H_2O [38].

The infrared absorption cross sections have been obtained from experiments carried out in a $134.0 (\pm 0.5)$ mm path-length stainless steel cell, equipped with KBr windows; the temperature in the cell, continuously monitored, has been kept constant at $298.0\text{ K} (\pm 0.5\text{ K})$. The infrared spectrum has been recorded on a Bruker Vertex 70 FTIR instrument, equipped with DLaTGS detector covering the $250 - 12000\text{ cm}^{-1}$ region. A total of 128 interferograms for both the sample and the background spectra have been co-added and transformed into the corresponding absorbance spectrum using boxcar apodization and Mertz phase correction. The wavenumber accuracy in the range investigated has been estimated to be better than 0.05 cm^{-1} . The spectra have been recorded at resolution of 0.2 and 0.5 cm^{-1} : different pressures of CF_3Br (Matheson, purity $> 99\%$) have been used, both pure and mixed with N_2 (SIAD, purity $> 99\%$) to a total pressure of 101 kPa . The pressures have been measured employing different capacitance vacuum gauges (Alcatel model ARD 1001, 1002 and 1003 with a full scale range of 1000 , 100 and 10 mbar , respectively), each with a quoted manufacturer's full scale accuracy of 0.15% . A 15 minute delay between the filling of the cell and the recording of the spectrum has been adopted. A diffusion pump backed by a double stage rotary pump evacuated the cell down to about 10^{-4} Pa before and after each sample measurement, and the corresponding background scans have been acquired. Adsorption of the sample gas on the cell walls has been checked both by direct measurement of the pressure, and by monitoring of the absorption spectrum: it has been found negligible

over a period of 2 hours, which is far longer than the typical time required to obtain a spectrum.

3. High-resolution spectra

The CF_3Br molecule is a prolate symmetric rotor belonging to the C_{3v} point group. Due to the presence of two bromine isotopologues in almost equal proportion, the diode laser spectrum of natural CF_3Br appears rather crowded, being also present features coming from several hot bands.

3.1. Description of the $2\nu_5$ band region

The region between 1090 and 1102 cm^{-1} is characterized by the ν_1 band R branch and the parallel component of the $2\nu_5$ overtone, centred at about 1095 cm^{-1} . The proximity of the bromine isotopologue band origins (about 0.12 cm^{-1}) causes a considerable overlapping of the K -structure. Furthermore, even at 200 K , the P branch transitions appear completely buried under the stronger absorption features of the near ν_1 fundamental (band origin at 1084.76902 and $1084.52168\text{ cm}^{-1}$ for $\text{CF}_3^{79}\text{Br}$ and $\text{CF}_3^{81}\text{Br}$, respectively [29]). Only the spectrum recorded in a free-jet expansion has allowed us to access this spectral region, leading to the assignment of some $P(J)$ multiplets which were completely masked by the $R(J)$ features of ν_1 . Figure 1 reproduces the spectrum around 1093.6 cm^{-1} where are located the multiplets $P(14 - 15)$ and $P(13 - 14)$ of $\text{CF}_3^{79}\text{Br}$ and $\text{CF}_3^{81}\text{Br}$, respectively. The upper trace, referring to the 200 K spectrum, clearly shows how the absorptions of the ν_1 fundamental completely

cover the weaker $2\nu_5$ transitions which, conversely, are evident in the colder (50 K) slit-jet spectrum. A similar spectral simplification is achieved in the Q branch region, where transitions with high and low (J, K) values occur together. This effect can be observed in figure 2: at 200 K (upper trace) the structure appears congested and partially masked by the R branch transitions belonging to the ν_1 fundamental, while in the supersonic expansion (lower trace) the two bandheads of $\text{CF}_3^{79/81}\text{Br } 2\nu_5$ overtone are well separated.

Figure 3 reports a wide portion of the free-jet spectrum: owing to the noticeable cooling, it closely resembles that of a parallel band, with a rather dense Q branch extending to lower wavenumbers and well-defined clusters separated by about $2B$ that constitute the P and R branches. In the same figure it is shown the computed spectrum calculated employing the spectroscopic parameters obtained in the present investigation: as it can be seen, there is a good agreement between the computed and experimental spectra. No transitions belonging to the perpendicular component of this overtone (i.e. $2\nu_5^{\pm 2}$) have been observed in the range $1090 - 1102 \text{ cm}^{-1}$.

3.2. Description of the $\nu_2 + \nu_3$ band region

The $\nu_2 + \nu_3$ combination band shows the typical structure of a parallel-type absorption: compared to the $2\nu_5$ overtone the density of lines is greater, because the term $\Delta(A - B)$ mainly ruling the K -component positions within a given multiplet is much smaller. Another difference is the presence of many hot bands, whose intensities are still considerable even at low temperature: the strongest identified features belong to the $\nu_2 + 2\nu_3 - \nu_3$ and $\nu_2 + \nu_3 + \nu_6 - \nu_6$ hot bands of both the isotopologues whose lower

vibrational states have at 200 K a relative Boltzmann population to the ground state of about 16% and 22%, respectively. The rotational cooling can be highlighted by comparing the width of the Q branch of the $\nu_2 + \nu_3$ of $\text{CF}_3^{79}\text{Br}$ at 200 K and in the supersonic jet (figure 4).

3.3. *Rovibrational analysis of the $2\nu_5$ and $\nu_2 + \nu_3$ bands*

For the $2\nu_5$ and the $\nu_2 + \nu_3$ parallel bands, the rovibrational analysis has been carried out employing the following equation, which computes the energy of the rovibrational levels up to the quartic centrifugal distortion terms:

$$\frac{E(\nu, J, K)}{hc} = \tilde{\nu}_0 + (A_\nu - B_\nu)K^2 + B_\nu J(J+1) - D_J^\nu J^2(J+1)^2 - D_{JK}^\nu J(J+1)K^2 - D_K^\nu K^4 \quad (1)$$

where $\tilde{\nu}_0$ is the band origin and ν represents the vibrational state. As fitting program, we have used the SPFIT software [39]: an uncertainty of 0.0007 cm^{-1} has been attributed to well resolved single lines, whereas for blended or scarcely resolved features, an uncertainty of 0.0020 cm^{-1} has been assumed.

Table 1 gives the spectroscopic parameters of the $2\nu_5^0$ band for the $^{79/81}\text{Br}$ isotopologues obtained from the free-jet spectrum together with the molecular constants obtained by the whole set of data (slit jet and 200 K spectra). The complete analysis has led to the identification of 375 and 353 lines for $\text{CF}_3^{79}\text{Br}$ and $\text{CF}_3^{81}\text{Br}$, respectively. Although the overall agreement between the experimental and the computed spectra is

good, concerning the $K \leq 3$ transitions small discrepancies from the computed line positions have been observed in some of the multiplets analyzed of both the isotopologues. Because no irregularities have been found in the near ν_1 and $\nu_2 + \nu_3$ bands, as possible perturber we have considered the $2\nu_5^{\pm 2}$ vibration with different rotational interactions; the inclusion of the corresponding terms in the Hamiltonian did not improve the overall results. The lack of directly observed transitions of the $2\nu_5^{\pm 2}$ as well as of other bands in the region investigated has made a better characterization impossible: furthermore this interacting scheme may be complicated by the interaction of $2\nu_5^{\pm 2}$ with other dark states (i.e. $\nu_5 + 2\nu_6$).

Regarding the $\nu_2 + \nu_3$ band, different spectral sections in the P, Q and R branches have been investigated and the K -structure in the $P(J)$ and $R(J)$ multiplets has been resolved and unambiguously assigned. Table 2 reports the spectroscopic parameters for the $^{79/81}\text{Br}$ isotopologues obtained from the free-jet spectrum and that obtained by the whole set of data (slit jet together with 200 K spectra). The complete analysis has led to the identification of 347 and 635 lines for $\text{CF}_3^{79}\text{Br}$ and $\text{CF}_3^{81}\text{Br}$, respectively.

In addition, in the region $1100 - 1130 \text{ cm}^{-1}$ the spectrum recorded at 200 K reveals several absorptions coming from different hot bands. The strongest identified absorptions belong to $\nu_2 + 2\nu_3 - \nu_3$ and $\nu_2 + \nu_3 + \nu_6 - \nu_6$: for the hot band of ν_6 the perpendicular component is too weak to be observed and therefore the analysis has dealt only with the A_1 type component. Since the observed features are very weak and generally the K -structure is unresolved, the rotational

analysis has been limited to the J peaks. The analysis has been carried out using the polynomial method, and the J peaks have been fitted to the following equation:

$$\tilde{\nu}(m) = A + Bm + Cm^2 + Dm^3 \quad (2)$$

with

$$A = \tilde{\nu}_0$$

$$B = B' + B''$$

$$C = B' - B''$$

$$D = -2(D_J' + D_J'')$$

and $m = -J$ for the P branch and $J + 1$ for the R branch. The set of spectroscopic parameters obtained for $\text{CF}_3^{79}\text{Br}$ and $\text{CF}_3^{81}\text{Br}$ is reported in table 3.

A complete list of the assigned transitions is available upon request from the authors.

4. Cross section measurements by medium resolution FTIR spectra

The absorbance cross-section per molecule ($\text{cm}^2 \text{ molecule}^{-1}$) of the sample, $\sigma(\tilde{\nu})$, has been calculated from the measured infrared absorbance using the following relationship:

$$\sigma(\tilde{\nu}) = \frac{\ln 10 A(\tilde{\nu})}{N_A c l} \quad (3)$$

where $A(\tilde{\nu})$ is the absorbance (at wavenumber $\tilde{\nu}$) of an optical path length l (cm), c is the gas concentration (mol cm^{-3}) and N_A is the Avogadro's constant. Assuming the validity of the ideal gas law, in the range of pressures used in the present work, the concentration is related to the pressure and the temperature by:

$$c = \frac{10^{-6} P}{RT} \quad (4)$$

where R is the molar gas constant ($\text{J K}^{-1} \text{mol}^{-1}$), P is the pressure (Pa) and T is the temperature (K). The integrated cross section G_{int} ($\text{cm}^2 \text{molecule}^{-1} \text{cm}^{-1}$) is then derived from the absorbance cross section by the following equation:

$$G_{int} = \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} \sigma(\tilde{\nu}) d\tilde{\nu} = \frac{10^6 RT \ln 10}{N_A l P} \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} A(\tilde{\nu}) d\tilde{\nu} \quad (5)$$

where $\tilde{\nu}_1$ and $\tilde{\nu}_2$ are the integration limits corresponding to the wavenumbers where the absorption is negligible. If two or more strongly overlapped bands without a clear separation are present in the spectral interval, a single integration has been performed. Following a procedure similar to that reported by Nemtchinov and Varanasi [40], the experimental uncertainty in the cross sections has been estimated by taking into account the uncertainties of the pressure and temperature of the sample, of the optical path length, of the photometric accuracy of the FTIR spectrometer and of the evaluation of absorbance.

At the beginning of the experiments some spectra have been recorded at two different resolutions (0.2 and 0.5 cm^{-1}) for different pressures of both the pure CF_3Br and its mixture with N_2 . A linear dependence of the absorbance with the pressure of the sample has been observed over all the concentration range used in the present investigation. The calculated band intensities corresponding to the same concentration of the sample and different spectral resolution have been found to be equal within the error of the measurements; therefore we have chosen to determine the integrated cross sections from the spectra of the pure gas measured at the resolution of 0.5 cm^{-1} because they generally have a better signal-to-noise ratio, especially for the weaker absorption features.

The survey spectrum of bromotrifluoromethane in the range $450 - 2500\text{ cm}^{-1}$ reveals several absorption bands: by taking into account their different intensities, we have divided the infrared spectrum into three main regions. The first is located between 450 and 715 cm^{-1} and it is characterized by the weak absorptions originating from the ν_5 (at 548 cm^{-1}) fundamental and the $2\nu_3$ overtone (at 700 cm^{-1}): here the pressure of the sample has been kept in the range $10 - 80\text{ hPa}$. The second range, located between 720 and 1250 , shows two strong fundamentals (ν_1 and ν_4), a medium one (ν_2) and some weak combination ($\nu_1 + \nu_3$, $\nu_5 + \nu_6$, $\nu_2 + \nu_3$) and overtone bands ($2\nu_5$): here the intensities have been measured with the pressure in the range $10 - 300\text{ Pa}$. Finally, between 1250 and 2500 cm^{-1} the spectrum contains many very weak features, corresponding to various combination and overtone bands: here the pressure has been varied in the range $10 - 80\text{ hPa}$.

By using the equations reported earlier, the integrated absorption cross sections have been determined and the resulting averaged values, together with their statistical

errors are reported in table 4; our estimated experimental uncertainty in the integrated cross section is 5.5%. For comparison, the most recent available data [35, 36] are listed in the same table. In the range $720 - 1250 \text{ cm}^{-1}$ the integration limits have been chosen to facilitate the comparison. In the other regions many bands appear not completely resolved and so the data refer to several bands grouped together: in the range $1360 - 1800 \text{ cm}^{-1}$ the absorptions appear so strongly overlapped that the integration limit has been extended to measure their overall intensities. Figure 5 shows the resulting averaged spectrum for some regions investigated in the present analysis. A mean value of $0.300 \text{ W m}^{-2} \text{ ppbv}^{-1}$ (with an estimated accuracy of 5.5% and a standard deviation of 2%) for the radiative forcing has been obtained by employing a narrowband model [41] and considering all the data in the range $450 - 2500 \text{ cm}^{-1}$. **This result is in very good agreement with the most recent value of $0.31 \text{ W m}^{-2} \text{ ppbv}^{-1}$ determined by Drage et al. [36] who took into account only the absorptions falling into the range $720 - 1250 \text{ cm}^{-1}$. This occurs since this region is characterised by the strongest bands of CF_3Br and by the maximum radiative forcing for average Earth sky [41], as it can be seen in figure 6.**

5. Conclusion

The high resolution diode laser spectrum of CF_3Br in the region $1090 - 1130 \text{ cm}^{-1}$ has been recorded in a supersonic planar expansion (rotational temperature of about 50 K) and at 200 K. The combination of supersonic slit-jet expansion data with those recorded at 200 K has been successfully employed to obtain a reliable set of

parameters for the $2\nu_5^0$ and $\nu_2 + \nu_3$ bands of both bromine isotopologues. The improved accuracy of the present analysis compared to those previously published [31, 32] is based on many factors: a better wavenumber calibration (0.0007 cm^{-1} instead of 0.003 cm^{-1}), a more extended spectral range investigated, especially for the $2\nu_5$ band where the new P-branch data led to more reliable results, and a greater resolution. All the fits have a standard deviation that compares well with our estimated wavenumber accuracy and the statistical errors of the parameters are significantly lower than those previously obtained. In addition, being the assignments more complete, some constants have been determined for the first time. Together with the data of the near ν_1 fundamental previously reported [29], these molecular constants should provide a complete understanding of the spectral fine structure of CF_3Br in the region around $9\text{ }\mu\text{m}$ and the ability to simulate and predict the detailed temperature dependence of these absorptions at a variety of atmospheric temperatures. The determined absorption band intensities could be used by the radiative transfer models of the atmosphere employed for global climate calculations.

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Figure captions

Fig. 1 CF_3Br spectrum around 1093.6 cm^{-1} . Upper trace: spectrum recorded at 200 K showing the $R_K(J)$ multiplets of the ν_1 fundamental. Lower trace: slit-jet spectrum illustrating the $P_K(J)$ lines of $2\nu_5^0$ overtone. i refers to $\text{CF}_3^{79}\text{Br}$, ii refers to $\text{CF}_3^{81}\text{Br}$.

Fig. 2 Portion of the $2\nu_5^0$ Q branch around 1095.6 cm^{-1} . Upper trace: spectrum recorded at 200 K. Lower trace: slit-jet spectrum; $Q_K(J)$ bandheads labelled by i and ii refer to $\text{CF}_3^{79}\text{Br}$ and $\text{CF}_3^{81}\text{Br}$, respectively.

Fig. 3 Portion of the survey free-jet spectrum of the $2\nu_5^0$ overtone. Upper trace: experimental spectrum. Lower trace: simulated spectrum ($T = 50 \text{ K}$, $\text{FWHM} = 0.0007 \text{ cm}^{-1}$).

Fig. 4 Portion of the $\nu_2 + \nu_3$ band of CF_3Br around 1120.0 cm^{-1} . Upper trace: spectrum recorded at 200 K, $Q_K(J)$ branch of $\text{CF}_3^{79}\text{Br}$ is indicated. Lower trace: slit-jet spectrum, $R_K(J)$ multiplets of $\text{CF}_3^{81}\text{Br}$ $\nu_2 + \nu_3$ are labelled.

Fig. 5 Averaged absorption cross sections (0.5 cm^{-1} resolution, $T = 298 \text{ K}$) of CF_3Br in the region $700 - 1250 \text{ cm}^{-1}$ and $1800 - 2500 \text{ cm}^{-1}$.

Fig. 6 Narrow band radiative forcing F (dashed line) for average Earth sky and averaged absorption cross section G (full line) of CF_3Br (0.5 cm^{-1} resolution, $T = 298 \text{ K}$).

Table 1. Spectroscopic constants (cm^{-1}) for the $2\nu_5^0$ band of CF_3Br ^a.

	$\text{CF}_3^{79}\text{Br}$		$\text{CF}_3^{81}\text{Br}$	
	Slit jet	Slit jet and 200 K	Slit Jet	Slit Jet and 200 K
$\tilde{\nu}_0$	1095.6276(2)	1095.62746(11)	1095.4955(2)	1095.49544(11)
B'	0.0700141(9)	0.0700150(2)	0.0693629(8)	0.0693639(2)
B''	0.069985970 ^b	0.069985970 ^b	0.069333439 ^b	0.069333439 ^b
$\Delta(A - B) \times 10^3$	-0.532(2)	-0.5314(12)	-0.530(3)	-0.5341(13)
$D_J' \times 10^8$	0.75(8)	0.794(9)	0.69(7)	0.788(9)
$D_J'' \times 10^8$	0.8989 ^b	0.8989 ^b	0.8868 ^b	0.8868 ^b
$D_{JK}' \times 10^7$	0.41(3)	0.440(5)	0.42(3)	0.375(6)
$D_{JK}'' \times 10^7$	0.43393 ^b	0.43393 ^b	0.42720 ^b	0.42720 ^b
$\Delta D_K \times 10^8$	-	-	-	0.22(7)
N. of data	188	375	179	353
$\sigma \times 10^3$	0.35	0.46	0.59	0.55
J_{max}	32	53	33	53
K_{max}	15	33	15	36

^a Quoted errors are one standard deviation.^b From Ref. [15].

Table 2. Spectroscopic constants (cm^{-1}) for the $\nu_2 + \nu_3$ band of CF_3Br ^a.

	$\text{CF}_3^{79}\text{Br}$		$\text{CF}_3^{81}\text{Br}$	
	Slit jet	Slit jet and 200 K	Slit Jet	Slit Jet and 200 K
$\tilde{\nu}_0$	1120.0511(2)	1120.05110(10)	1118.0000(2)	1117.99994(10)
B'	0.0698300(7)	0.06983037(10)	0.0691789(5)	0.06917932(8)
B''	0.069985970 ^b	0.069985970 ^b	0.069333439 ^b	0.069333439 ^b
$\Delta(A - B) \times 10^4$	-0.35(3)	-0.383(4)	-0.42(2)	-0.444(2)
$D_J' \times 10^8$	0.87(5)	0.900(2)	0.87(3)	0.8890(12)
$D_J'' \times 10^8$	0.8989 ^b	0.8989 ^b	0.8868 ^b	0.8868 ^b
$D_{JK}' \times 10^7$	0.44(4)	0.4070(9)	0.41(2)	0.3989(6)
$D_{JK}'' \times 10^7$	0.43393 ^b	0.43393 ^b	0.42720 ^b	0.42720 ^b
$\Delta D_K \times 10^8$	0.24 ^c	0.25(3)	0.24 ^c	0.257(12)
N. of data	86	347	99	635
$\sigma \times 10^3$	0.49	0.49	0.39	0.49
J_{max}	37	85	43	88
K_{max}	21	42	24	48

^a Quoted errors are one standard deviation.

^b From Ref. [15].

^c From Ref. [32].

Table 3. Spectroscopic constants (cm^{-1}) for the $\nu_2 + 2\nu_3 - \nu_3$ and $\nu_2 + \nu_3 + \nu_6 - \nu_6$ hot bands of CF_3Br ^a.

	$\text{CF}_3^{79}\text{Br}$		$\text{CF}_3^{81}\text{Br}$	
	$\nu_2 + 2\nu_3 - \nu_3$	$\nu_2 + \nu_3 + \nu_6 - \nu_6$	$\nu_2 + 2\nu_3 - \nu_3$	$\nu_2 + \nu_3 + \nu_6 - \nu_6$
$\tilde{\nu}_0$	1120.9422(5)	1118.5611(4)	1119.1300(4)	1116.5180(4)
B'	0.069767(6)	0.069703(6)	0.069131(6)	0.069047(7)
B''	0.069934(6)	0.069861(6)	0.069298(6)	0.069204(7)
$(D_J' + D_J'') \times 10^8$	1.84(14)	2.4(2)	2.44(15)	1.9(2)
N. of data	63	50	52	48
$\sigma \times 10^3$	0.51	0.27	0.39	0.33
J_{max}	64	85	52	71

^a Quoted errors are three standard deviations.

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Table 4. Integrated absorption cross sections ($\times 10^{18} \text{ cm}^2 \text{ molecule}^{-1} \text{ cm}^{-1}$) of CF_3Br in the range 450 – 2500 cm^{-1}

INTEGRATION LIMITS		INTEGRATED ABSORPTION CROSS SECTION		
[cm^{-1}]		This work ^a	Drage et al. ^b	Orkin et al. ^c
720 – 790		5.6(2)	5.5 (8%)	5.45 (4%)
1040 – 1150		77.8(1.4)	74 (7%)	79.7 (2%)
1150 – 1250		78.7(9)	74 (7%)	78.3 (2%)
500 – 600		0.380(4)	^a In parentheses standard deviations in units of the last significant digits are given. The estimated experimental uncertainties are 5.5% the reported value.	
670 – 715		0.379(2)		
810 – 880		0.150(2)		
1250 – 1360		1.249(5)	^b From Ref. [36]. The estimated uncertainty includes the statistical as well as the systematic uncertainty.	
1360 – 1800		0.624(17)		
1800 – 1910		0.177(8)	^c From Ref. [35]. Uncertainties are the 95% confidence intervals and do not include the systematic uncertainty.	
1940 – 2000		0.131(3)		
2120 – 2240		0.125(7)		
2240 – 2340		0.717(10)		
2340 – 2480		0.65(2)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6