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Measurements and modeling of N_2-broadening coefficients for the ν_6 band of CH_3F, comparison with CH_3Cl and CH_3Br molecules

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ABSTRACT

The 8.5-µm spectral region of methyl fluoride was recently studied in terms of line positions, intensities and self-broadening coefficients at room temperature [JQSRT 2016;185:58–69]. The present work is dedicated to measurements of N_2-broadening coefficients for transitions of the ν_6 band. Based on new set of Fourier transform spectra using various mixtures of CH_3F and N_2, a multispectrum fitting procedure was used to retrieve N_2-broadening for 1189 transitions between 1105 and 1291 cm^{-1}. 899 transitions have been studied to model the *J*- and *K*-rotational quantum number dependences of the N_2-broadening coefficients in order to generate any transitions of CH_3F assuming no vibrational dependence. The accuracy of the retained N_2-broadening coefficients was estimated to be between 2–5%. These measurements have been compared with previous studies from the literature obtained for other bands of CH_3F. Comparison with the results obtained for similar empirical *J*- and *K*-rotational model applied to CH_3Cl, CH_3Br and CH_3F (this work) molecules is also presented.

1. Introduction

A recent effort has been made by our group to characterize spectral absorption of CH_3Br and CH_3Cl gases: CH_3Br around 7 µm [1] and 10 µm [2–7] and CH_3Cl around 3 µm [8–11] and 6.9 µm [12–15]. The line positions [1,2,8,12], intensities [1,2,8,12,15], self-and N_2-broadening coefficients [2,7,9,10,12,13,14,15], temperature dependence exponents [4,7,13,14], and line mixing effects [3,5,11] have been studied for CH_3Br and CH_3Cl in order to generate complete line list for atmospheric applications. Some of these spectroscopic data [1,2,4,8,12] have been included in the recent HITRAN [16,17] and GEISA [18,19] databases. Recently, a line list of positions, intensities and self-broadening coefficients has been published for the ν_6 band of CH_3F [20].

The present work is the continuation of our recent effort on the ν_6 band of CH_3F [20]. New spectra were recorded with various mixtures of CH_3F and N_2 in order to retrieve N_2-broadening parameters and to study their rotational dependences. Such measurements have been performed for the first time for the ν_6 band of CH_3F. In order to detect a possible vibrational dependence of CH_3F broadening coefficients by N_2, our measurements will be compared with those obtained by Lepère et al. [21,22] and Lerot et al. [23] at room temperature for transitions of the ν_2 and ν_5 bands using tunable diode laser spectrometer setup. As performed previously for CH_3Br and CH_3Cl broadening coefficients [2,9,10,12,14], a semi-empirical model has been used to analyze the *J*- and *K*-rotational dependence of the measured self- and N_2-broadening coefficients of CH_3F: $\gamma_J(K) = a_J^0 + a_J^2 K^2$ for each set of measurements with same *J* value. The *K*-rotational dependence of the N_2-broadening parameters obtained for $^RR_K(3)$, $^RR_K(8)$ and $^RQ_K(17)$ transitions in Ref. [21] will be especially useful to be compared with the rotational dependences modeled in the present work.

The experimental conditions of the recorded spectra are presented in Section 2. Section 3 is dedicated to the measurements of N_2-broadening coefficients of CH_3F and their analysis. Comparisons between the present measurements and the measured and calculated line widths reported in literature and obtained for other bands of CH_3F are discussed in Section 4 together with comparisons between results from our model for CH_3F with those published in literature for other bands of CH_3Cl and CH_3Br.

2. Experimental spectra

Five Fourier transform spectra have been newly recorded at room temperature using the Bruker IFS 120 HR interferometer of MONARIS. The experimental conditions are summarized in Table 1. For the multispectrum analysis performed in this study, a pure CH_3F spectrum from Ref. [20] has been added in order to be fitted together with the five spectra recorded with var-

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Table 1
Experimental conditions of the FT spectra used in this work.

#	Pressure of CH_3F (in mbar)	Pressure of N_2 (in mbar)	Absorption path (in cm)	Bruker resolution (in cm^{-1})
0[a]	2.236	0	68.8	0.004
1	6.147	50.3	59.8	0.01
2	8.214	105.0	59.8	0.01
3	4.533	128.5	59.8	0.01
4	8.631	149.3	59.8	0.01
5	12.278	304.5	59.8	0.01

Notes: The purity of the CH_3F sample is 99%. Bruker resolution corresponds to $0.9/\Delta$ max, where Δ max is the maximum optical path difference.

[a] This spectrum has been recorded previously in Ref. [20].

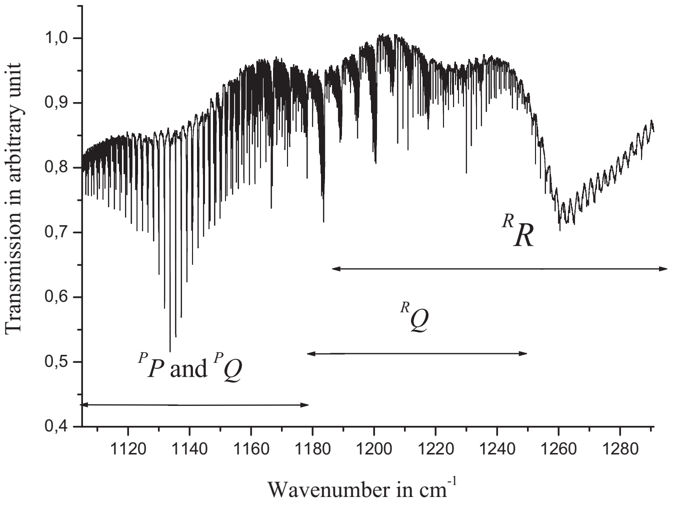

Fig. 1. Overview of the ν_6 band in spectrum #3 (see Table 1). The spectral ranges of the strongest sub-branches have been indicated.

ious mixtures of CH_3F and N_2. This pure CH_3F spectrum, for which line widths are much smaller than those of spectra 1–5, is useful through multispectrum fitting procedure to accurately fit transitions that may be blended in spectra 1–5 broadened by N_2. The collisional broadening in spectrum 0 is around 0.002 cm^{-1}/atm (FWHM: full width at half maximum), and is a little bit smaller than the Doppler width equal to 0.0025 cm^{-1} (FWHM) at 1200 cm^{-1} and room temperature. Note that for spectrum 5, the collisional width due to CH_3F/CH_3F collisions is around 0.01 cm^{-1} (FWHM) whereas the collisional width due to CH_3F/N_2 collisions is around 0.06 cm^{-1} (FWHM). The resolution of the interferometer has been chosen according to the widths of the transitions depending on the experimental conditions.

The interferometer was equipped with a KBr beam splitter, a MCT photovoltaic detector, and a Globar source. A (59.8 ± 0.1) cm path length cell has been used to record all CH_3F-N_2 mixture spectra. For all of them an optical filter covering the 860–1320 cm^{-1} spectral region has been used. The cell was equipped with KBr windows. The aperture radius from the iris in front of the source is equal to 0.75 mm for spectra 1–5 and to 0.65 mm for spectrum 0 from Ref. [20], whereas the focal length is equal to 418 mm for all spectra.

The "weak" ν_6 band under study in the present work is located around 8 µm. Under the experimental conditions of this work the "strong" ν_3 band located around 9.6 µm is saturated. The overview of the CH_3F studied absorption region between 1105 and 1291 cm^{-1} is presented in Fig. 1 for spectrum #3. This figure illustrates the global structure of the different sub-branches ^PP, ^RP, ^PQ, ^RQ, ^PR and ^RR with strong ^PQ and ^RQ sub-branches between 1160 and 1240 cm^{-1}. Note that the ^RP *and* ^PR sub-branches are weak compared to other sub-branches. The transitions are noted $\Delta^K\Delta J_K(J)$ where J and K the rotational quantum numbers of the lower state of the transition, and ΔK and ΔJ represent the variation of these quantum numbers between the upper and lower levels. The sub-branch noted $^RQ_0$ refers to various $^RQ_0(J)$ transitions with $K = 0$.

The commercial gas sample of methyl fluoride was furnished by Alphagaz with a stated of purity of 99.0% in natural abundance. It was used without any purification. The pressures of CH_3F (ranging from 2 to 300 mbar) inside the cell have been measured with 2 Baratron gauges with accuracy better than ±0.25% for the 10 and 1000 mbar full scale pressure readings. The temperature of the gas sample has been measured with accuracy equal to ±0.1 K using platinum probes inside the cell.

The average interferograms (co-addition of 1500 scans for each spectrum 1–5, and 800 scans for spectrum 0) have been Fourier transformed using the procedure included in the Bruker software OPUS package, selecting a Mertz phase error correction. The spec-

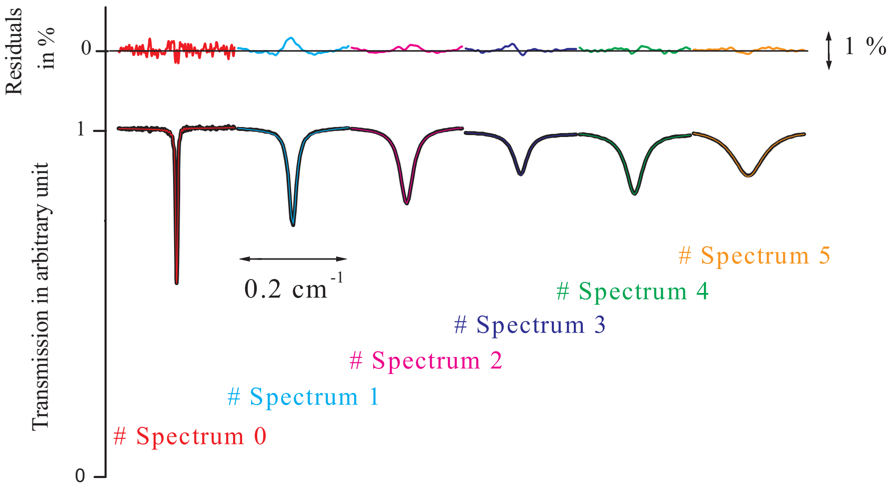

Fig. 2. Multispectrum fitting of the isolated $^PP(21,6)$ transition centered at 1113.6578 cm^{-1} using 6 spectra: 1 of pure CH_3F (# 0) and 5 with various mixtures of CH_3F and N_2 (# 1–5), see experimental conditions listed in Table 1. The residuals are (calc – obs)/calc in %. Note that the same spectral range (0.2 cm^{-1}) has been used for fitting the various spectra. Spectrum # 0 has more experimental points since its resolution is higher than the other 5 spectra broadened by N_2.

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