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# Line parameters measurements and modeling for the $\nu_6$ band of $CH_3F$: Generation of a complete line list for atmospheric databases

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ABSTRACT

The 8.5 μm-spectral region of methyl fluoride was studied in terms of line positions, intensities and self-broadening coefficients at room temperature. A multispectrum fitting was used to retrieve from 7 high-resolution Fourier transform spectra line parameters for 787 transitions belonging to the $\nu_6$ band between 1078 and 1240 $cm^{-1}$. The accuracy of line intensities and widths measurements were estimated to be around 5% and 5–10% respectively. *J*- and *K*-rotational dependences of the transition dipole moment squared and the self-broadening coefficients were observed and modeled from the measurements. A complete line list of almost 1500 transitions was generated for atmospheric or industrial detection of $CH_3F$. Comparisons with previous studies from the literature were also performed.



## 1. Introduction

A recent effort has been made by our group to characterize spectral-absorption regions of $CH_3X$ gases: $CH_3Br$ around 7 μm [1] and 10 μm [2–7],$CH_3Cl$ around 3 μm [8–11] and 6.9 μm [12,13]. The line positions [1,2,8,12], intensities [1,2,8,12], room-temperature self- and $N_2$-broadening coefficients [2,7,9,10,13], temperature exponent [4,7,13], and line mixing effects [3,5,11] have been studied for these two molecules in order to generate complete line list for atmospheric applications. Most of these spectroscopic data have been included in the recent HITRAN [14] and GEISA [15] databases.

The present work concerns methyl fluoride spectrum around 8.5 μm where the $\nu_6$ band absorbs closely to the strong $\nu_3$ band at 9.5 μm. Concerning the weaker $\nu_6$ band, previous spectroscopic studies have already been performed: one can cite the works of Papoušek et al. [16,17] for line positions and interactions between states, and the work of Lepère et al. [18] for the measurements of line intensities using tunable diode laser spectrometer. Concerning self-broadening coefficients, measurements have been performed in Ref. [18] for 13 transitions of the $\nu_6$ band. One can also notice the works of Lerot et al. [19,20], Lepère et al. [21], Lance et al. [22] and Guerin et al. [23] for the self-, $N_2$-, $O_2$-, and air-widths and their temperature dependences [19,20] for transitions of the $\nu_2$ and $\nu_5$ bands.

In this work, a line list has first been generated using from the literature positions and assignments [24], intensities [18], and energy of the lower state of the transition [25]. Then, a global analysis using multispectrum fitting procedure has been performed on seven experimental spectra recorded with various pressures and previously calibrated in wavenumbers. The results have been analyzed and compared to the literature for finally generating for the $\nu_6$ band of $^{12}CH_3F$ a complete line list of positions, intensities and self-broadening coefficients. Most of the

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spectroscopic data published in the literature for the $\nu_6$ band of $CH_3F$ have been confirmed and improved especially for line intensities and self-broadening coefficients.

This study has been performed as a continuation of our previous works on $CH_3X$ molecules [1–13]. Note that semi-empirical models have been used both in the previous works as in the present one to analyze the rotational dependence of transition dipole moments squared (Herman-Wallis factors depending on $J$ and $K$) and the broadening coefficients ($K$-rotational modeling $\gamma_J(K)=a_J^0+a_J^2K^2$ for each set of measurements with same $J$ value).

The experimental conditions are first presented in Section 2. Section 3 is dedicated to the measurements, their analysis and comparisons to literature for line positions, intensities, and self broadening coefficients respectively. Finally, the generation of various line lists will be described in Section 4.

## 2. Experimental spectra

Eight Fourier transform spectra have been recorded at room temperature using the Bruker IFS 120 HR interferometer of the MONARIS. The experimental conditions are summarized in Table 1.

The interferometer was equipped with a KBr beam splitter, a MCT photovoltaic detector, and a Globar source. A $(68.8\pm0.1)$ cm path length cell has been used to record all spectra. For all of them (except spectrum 8, see Table 1) an optical filter covering the 860–1320 $cm^{-1}$ spectral region has been used. The cell was equipped with KBr windows. The overview of the $CH_3F$ absorption region in spectrum 5 is presented in Fig. 1 between 950 and 1250 $cm^{-1}$. The $\nu_3$ band is saturated under experimental conditions of this work but the focus of the present study is the weaker $\nu_6$ band. Fig. 2 illustrates the structure of the $R^Q$ sub-branches between 1180 and 1240 $cm^{-1}$. Note that the first letter refers to the $K$ variation ($R$ for $\Delta K=1$), the second one in upper case corresponds to the $J$ variation ($Q$ for $\Delta J=0$). The sub-branch noted $R_0^Q$ refers to various $R_0^Q(J)$ transitions with $K=0$ ($J$ and $K$ being the rotational quantum numbers of the lower state of the transition).

The commercial gas sample of methyl fluoride, furnished by Alpha Gaz, with a stated of purity of 99.0% in natural abundance was used without any purification. The pressures of $CH_3F$ (ranging from 0.1 to 10 mbar) inside the cell have been measured with 2 baratron gauges with accuracy better than $\pm0.15\%$ for the 1 mbar full scale thermoregulated gauge and $\pm0.25\%$ for the 10 mbar full scale. Note that due to the low pressures used in this work, no attempt has been done to measure self-shifting parameters. The temperature of the gas sample has been measured with accuracy equal to $\pm0.1$ K using platinum probes inside the cell.

The first seven spectra of Table 1 have been recorded with optical filter covering the 800–1300 $cm^{-1}$ spectral region. For spectrum 8, recorded with no optical filter from 800 to 4000 $cm^{-1}$, the observed $CO_2$ transitions near 2300 $cm^{-1}$ and $H_2O$ transitions near 1900 and 3700 $cm^{-1}$ (present as impurities in the tank of the interferometer) allowed to perform an accurate wavenumber calibration (see Section 3.1).

The average interferograms have been Fourier transformed using the procedure included in the Bruker software OPUS package, selecting a Mertz phase error correction. The spectra have not been numerically apodized. An average signal-to-noise ratio (peak to peak) between 150 and 200 has been obtained for the various experimental spectra of Table 1. Note that a weak multiplicative channel, due to the cell windows, was observed in all recorded spectra with maximum peak-to-peak amplitude about 2% (see Fig. 2). The period of the channel (about 2.2 $cm^{-1}$) being larger than the adjusted spectral domains (from 0.1 to 0.2 $cm^{-1}$), the multiplicative channel can be taken into account with a linear background.

## 3. Measurements, analysis and comparisons with literature

A multispectrum fitting procedure [26] has been applied to adjust simultaneously 7 experimental (spectra 1–7, see Table 1 for experimental conditions) of $CH_3F$, constraining the adjustment of a transition by using the same set of line parameters for the calculation of this transition in every spectra. As a final result the line position, the line intensity and the self broadening coefficient have been retrieved for 787 transitions of the $\nu_6$ band of $^{12}CH_3F$. The broadening coefficients of $^{12}CH_3F$ transitions by $^{13}CH_3F$ have been considered equal to the self-broadening coefficients of $^{12}CH_3F$. An example of the multispectrum fitting procedure for a spectral range containing 3 transitions is presented in Fig. 3. A Voigt profile has been used without observing any significant signatures in the residuals of the fit. One can observe the well reproduced wings of the sinus cardinal apparatus function. For each spectrum, the apparatus function $f(\sigma)$ has been calculated performing numerically the Fourier transform of the optical weighting of the interferograms, taking into account the finite optical path difference $\Delta_{max}$ and the optical weighting due do the size of the beam inside the interferometer (finite entrance beam with a beam radius $R$ and a focal distance $f$).

$$f(\sigma)=TF\left[\prod_{\Delta_{\max}}(\Delta).P_{opt}(\Delta)\right],$$

where

$$\prod_{\Delta_{max}}(\Delta)=1 \text{ for } 0\le\Delta\le\Delta_{max},$$

$$\prod_{\Delta_{max}}(\Delta)=0 \text{ for } \Delta>\Delta_{max},$$

and

$$P_{opt}(\Delta)=\left|\mathrm{sinc}\left(\frac{\sigma_0\Omega\Delta}{2}\right)\right|, \text{with } \Omega=\pi\frac{R^2}{f^2}.$$

Measurements, analysis and comparisons with literature performed in this work for line positions, intensities and self-broadening coefficients will be presented in the next sub-sections.