



# Analysis of self-broadened pure rotational and rovibrational lines of methyl chloride at room temperature



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## ABSTRACT

Rovibrational absorption spectra of methyl chloride in the spectral region between 2800 and 3200  $\text{cm}^{-1}$  were recorded with a high-resolution Fourier transform spectrometer. A multi-spectrum fitting procedure was used to analyze 527 transitions of the  $\nu_1$  band and to retrieve the self-broadening coefficients for various  $J$ - and  $K$ -values with an estimated accuracy around 8%. Pure rotational transitions of  $\text{CH}_3\text{Cl}$  in the submillimeter/terahertz region (0.2–1.4 THz) were also investigated using two complementary techniques of frequency-multiplication and continuous-wave photomixing. Forty-three pure rotational self-broadening coefficients were extracted with the accuracy between 3 and 5%. The whole set of measured values was used to model the  $J$ - and  $K$ -rotational dependences of the self-broadening coefficients by second-order polynomials. In addition, semi-classical calculations were performed, based on the real symmetric-top geometry of the active molecule, an intermolecular potential model including not only the dominant electrostatic but also the short-range forces, as well as on an exact classical treatment of the relative translational motion of the colliding partners. Comparison of all experimental and theoretical results shows similar rotational dependences and no significant vibrational dependence, so that extrapolations to other spectral regions should be straightforward.

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## 1. Introduction

Methyl chloride is one of the most abundant organohalogen, anthropogenic or natural in the Earth's atmosphere, so that its quantification and monitoring are of great

importance for atmospheric studies [1–4]. It has a rather strong signature around 3000  $\text{cm}^{-1}$  ( $\nu_1$  band region) which was recently used by the atmospheric chemistry experiment (ACE) satellite mission to produce the first global distribution of methyl chloride in the upper troposphere and stratosphere [5]. Prior to a precise quantification of  $\text{CH}_3\text{Cl}$  in the atmosphere, the accurate determination of line profile parameters of  $\text{CH}_3\text{Cl}$  is required. These parameters have to be determined from laboratory experiments. For the symmetric top  $\text{CH}_3\text{Cl}$ , numerous measurements have to be performed in order to reach transitions with various  $J$  and  $K$  values and obtain the rotational  $J$ - and  $K$ -dependences of line broadening coefficients.

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Self-broadening coefficients of methyl chloride infrared transitions have been previously studied experimentally for the  $\nu_2$ ,  $2\nu_3$  and  $\nu_5$  bands [6] as well as for the  $\nu_3$  band [7–9]. In Ref. [6], Chackerian et al. recorded high-resolution Fourier transform spectra and retrieved 423 self-broadening coefficients exhibiting well-pronounced dependences on the quantum number  $J$ , but no dependence on the quantum number  $K$ . In Refs. [7–9] a diode laser spectrometer characterized by a high signal-to-noise ratio but limited to a narrow spectral range was used to obtain 29 self-broadening coefficients. In Ref. [9] semi-classical calculations were also performed to evaluate the  $J$ - and  $K$ -dependences of self-broadening  $\text{CH}_3\text{Cl}$  coefficients at 200 and 296 K but a strong over-estimation of calculated line widths was stated. The determination of self-broadening coefficients of  $\text{CH}_3\text{Cl}$  lines from pure rotational transitions using electronic sources was limited to old studies focused on the lowest energy ( $J=0\rightarrow 1$ ) transition [10]. Using far infrared lasers, some measurements [11] were performed on isolated terahertz (THz) lines but without any possibility to study the  $J$ - and  $K$ -rotational dependences. More recently, Harde et al. [12] via THz coherent transients and THz time-domain spectroscopy were able to study the  $J$  dependence of collisional-broadened  $\text{CH}_3\text{Cl}$  line-widths. Limited by the resolution of the spectrometer, the  $J$  dependence was retrieved with measurements at pressures higher than 75 Torr where strong nonlinear broadenings pressure dependences are observed.

This work is dedicated to the study of room-temperature  $\text{CH}_3\text{Cl}$  self-broadening coefficients in different spectral regions and by various experimental techniques. Self-broadening coefficients have been measured in the “Laboratoire de Dynamique, Interactions et Réactivité” (LADIR) for transitions of  $\nu_1$  band around  $3000\text{ cm}^{-1}$  from the analysis of infrared Fourier-transform (FT) spectra. Self-broadening coefficients of pure rotational transitions have also been measured in the “Laboratoire de Physico-Chimie de l’Atmosphère” (LPCA) in terahertz region using a continuous-wave photomixing spectrometer and in the “Laboratoire de Physique des Lasers, Atomes et Molécules” (PhLAM) using a frequency-modulation spectrometer. The observed  $J$ - and  $K$ -rotational dependences are also modeled by a second-order polynomial with empirical coefficients deduced from fitting to the bulk of obtained experimental data. In addition, semi-classical calculations of self-broadening coefficients are performed in order to compare with the empirical model but mainly to be able to calculate self-broadening coefficients for transitions with high  $K$ - and  $J$ -values that have not been observed.

In the next section the experimental conditions and brief descriptions of the instrumental setups used in the present work are presented. The retrieval of self-broadening coefficients is described in Section 3. The modeling of the measurements by an empirical polynomial function and the details of the semi-classical calculations are presented in Sections 4 and 5, respectively. Section 6 is dedicated to comparisons of our results with those available in the literature. The final section outlines

the general conclusions and some perspectives of the present study.

## 2. Experimental conditions

### 2.1. Infrared Fourier transform spectrometer

Fourier transform spectra have been recorded between  $2800$  and  $3200\text{ cm}^{-1}$  using the rapid scan Bruker IFS 120 h interferometer of the LADIR. The experimental conditions are summarized in Table 1. This set of spectra have been already analyzed [13] with a multispectrum fitting procedure to measure line positions and intensities of around 500 transitions in the  $3.4\text{ }\mu\text{m}$  spectral region. More details concerning the experimental setup and conditions can be found in Ref. [13].

### 2.2. THz photo-mixing spectrometer

A photomixing CW-THz spectrometer was also used at LPCA to record  $\text{CH}_3\text{Cl}$  spectra between  $0.8$  and  $1.4\text{ THz}$  corresponding to  $31 \leq J \leq 50$ . This spectrometer is based on an ultra fast photomixer converting a beating between two near infrared laser diodes into the THz domain. This opto-electronic frequency-conversion provides a THz radiation at the frequency difference between the two infrared sources keeping their spectral purities. The diodes were locked onto a frequency comb generated from a femtosecond laser itself locked onto a frequency standard (provided by a GPS). The synthesized THz source exhibits metrological characteristics (a relative frequency accuracy of  $10^{-8}$  and an apparatus function in the order of  $30\text{ kHz FWHM}$ ). More details can be found in [14,15]. Different stainless steel absorption cells, with various lengths ( $25, 65, 85, 120\text{ cm}$ ), equipped with PTFE windows were used depending on the line intensity (see Table 1). For  $J=31$ , a room temperature Schottky diode detector (VDI) has been used. For the other values of  $J$ , the detection has been performed with a liquid He-cooled bolometer (QMC Instruments). The spectra were recorded at room temperature ( $293 \pm 1\text{ K}$ ). The pressure was measured with a  $1\text{ mbar}$  full scale pressure gauge (Alcatel ADS-1004) with a stated accuracy of  $0.25\%$ . A total of  $130\text{ CW-THz}$  spectra in a  $75\text{--}1000\text{ mTorr}$  pressure range were recorded. More details on the experiments are available in Refs. [16,17] dealing with the  $\text{O}_2$  and  $\text{N}_2$  broadening coefficient measurements of  $\text{CH}_3\text{Cl}$ .

### 2.3. Millimeter frequency-modulation spectrometer

The measurements on the  $J=6\rightarrow 7$  rotational line of  $^{12}\text{CH}_3\text{ }^{35}\text{Cl}$  at  $186\text{ GHz}$  were performed with the PhLAM frequency-modulation spectrometer that has been described in details in previous papers [17,18], so we only recall its principal features. The electromagnetic (e.m.) source consisted of a synthesizer (Agilent E8257D) locked onto a GPS receiver and followed by an active sextupler (Spacek Inc.). The e.m. power was detected by an InSb liquid He-cooled bolometer (QMC Instruments) and the corresponding signal, demodulated by a lock-in amplifier (Ametek 7270DSP) operating at

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