Journal of Quantitative Spectroscopy & Radiative Transfer 177 (2016) 49–58

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Improved spectroscopic line list of methyl chloride in the 1900–2600 cm^{-1} spectral region

A.V. Nikitin [a,*], T.A. Dmitrieva [b], I.E. Gordon [c]

[a] Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, SB RAS, 1, Academician Zuev square, 634021 Tomsk, Russia
[b] National Research Tomsk Polytechnic University, 30 Lenin Avenue, 634050 Tomsk, Russia
[c] Harvard – Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge, MA 02138, USA

ARTICLE INFO

Article history:
Received 30 October 2015
Received in revised form
3 March 2016
Accepted 3 March 2016
Available online 10 March 2016

Keywords:
Methyl chloride
High resolution molecular spectroscopy
Infrared
Global analysis
Vibrational polyad
Line positions
Line intensities

ABSTRACT

Parameters of line positions and line intensities up to 2×10^{-25} $cm^{-1}/(molecule\ cm^{-2})$ for $^{12}CH_3{}^{35}Cl$ and $^{12}CH_3{}^{37}Cl$ were retrieved from the Fourier transform spectra in the range of 1900–2600 cm^{-1}. Line intensities were scaled with measurements from literature. Measured line positions and intensities were treated using global effective Hamiltonian and dipole moment model. The RMS of intensity fitting was 7.4% for $^{12}CH_3{}^{35}Cl$ and 6.6% for $^{12}CH_3{}^{37}Cl$. List of positions and intensities were calculated for 22,098 and 21,014 lines between 1900 and 2600 cm^{-1} for $^{12}CH_3{}^{35}Cl$ and $^{12}CH_{33}{}^{7}Cl$, respectively. Updated intensities allow extending assignments. The new line list of positions and intensities for both isotopologues in this spectral region was calculated. The calculations from the line list of this work have been compared with values from the HITRAN2012 database and PNNL spectra.

1. Introduction

The methyl chloride (CH_3Cl) is a subject of much interest for experimental and theoretical spectroscopic researches [1–7] and atmospheric applications [8]. It is also considered as a potential biosignature on the exoplanets [9].

First of all, it should be mentioned that chlorine-containing molecules are of huge interest for the purposes of monitoring the Earth's atmosphere. Because of its atmospheric abundance methyl chloride is the prevalent important source of free chlorine atoms in the stratosphere and consequently this molecule is involved in the catalytic destruction of the ozone layer [10]. In addition biomass burning, oceanic emissions, wood-rotting fungi, and higher plants have been identified as an important natural sources of CH_3Cl [11]. However, the global chloromethane budget is uncertain, and that is the problem of great importance in modeling studies for atmospheric applications [12]. Therefore, accurate and high-precision parameters of the spectral lines are necessary for the remote detection of CH_3Cl and to correctly determine its concentration in the Earth's atmosphere.

Moreover, in order to study the rotational *J*-and *K*-dependences of chloromethane line broadening coefficients, a large set of measured line positions with assignments are required. Therefore high accuracy CH_3Cl spectral lines parameters in large spectral regions are required for the cases of theoretical calculation self- and air/N_2-broadening coefficients of methyl chloride at various temperatures [13–20].

The present study addresses the problem of previous global effort to improve and update the spectroscopic line positions and intensities of methyl chloride in the infrared spectral region. For that, high resolution FTIR spectra recorded with enriched samples of $^{12}CH_3{}^{35}Cl$ and

* Corresponding author. Tel.: +3822 491111 1208.
E-mail address: avn@lts.iao.ru (A.V. Nikitin).

http://dx.doi.org/10.1016/j.jqsrt.2016.03.007
0022-4073/

$^{12}CH_3{}^{37}Cl$ were used. Significant progress in line position analysis and assignment of methyl chloride has been achieved in works [21–23]. Over 20,000 transitions of each isotopologue $^{12}CH_3{}^{35}Cl$ and $^{12}CH_3{}^{37}Cl$ in 1900–2600 cm^{-1} spectral range were assigned and fitted with a standard deviation of about 3×10^{-4} cm^{-1} in previous work [22]. It should be noted that in our study the theoretical basis described in previous work was also used.

Intensities of lines in the HITRAN2008 spectroscopic database [24] were based on values from Ref. [22]. However, it was recognized that these intensities had to be scaled to reproduce observations. Therefore, in the HITRAN2012 [25] database these intensities were scaled to roughly reproduce the N_2-broadened spectra (under normal atmospheric conditions) from the PNNL database [26]. The present study focuses on the 1900–2600 cm^{-1} spectral region where the relative intensities for both species were found from the fitting of the line parameters in this spectral range. The intensity analysis significantly improved the prediction accuracy. New assignments have been performed for both isotopic species.

New analysis of the investigated spectral region in this work includes measured positions and intensities of lines. A precise analysis of the relative intensities reported here can be used to update the atmospheric databases [25,27].

2. Experimental details and intensity retrieval

Spectra were recorded in Wuppertal using a Bruker 120HR interferometer equipped with a Globar source and an InSb detector. Enriched samples, 99.32% ^{35}Cl (98.21% ^{37}Cl, values for this species henceforth in parentheses) were used. Two spectra denoted here as F35 (F37) and I35 (I37) were recorded in the 1770–2420 cm^{-1} and 2250–3800 cm^{-1} spectral regions, respectively, covering the 1900–2600 cm^{-1} interval investigated here. White-type multipass cell with a basis length of 80 cm and adjusted to an effective path length of 19.2 m was used. Pressures were 1.4 (1.2) mbar in spectra F and 1.7 (1.2) mbar in spectra I. Low pass and high pass filters and KBr and CaF_2 beam splitters were mounted for experiments corresponding to spectra F and I, respectively. The number of scans was 130 (170) and 350 (750) for spectra F and I, respectively. The resolution (0.9/maximum optical path difference) was set to 3.0×10^{-3} and 4.1×10^{-3} cm^{-1} in spectra F and I, respectively, and trapezoidal apodization chosen. Spectra G and H were recorded with the same filter as I but with shorter optical paths. Spectra G were used only for intensity calibration here.

Details of spectra used in this work are summarized in Table 1. These spectra have been recorded mainly for assignments purpose [21–23] and are not specifically adapted for intensity study. The pressure was not measured with high precision especially for spectra H35 and H37 whose pressure is given only with one significant digit.

In the region of 1900–2260 cm^{-1}spectra F35 and F37 are most informative. However comparing spectra F35 and F37 with I35 and I37 shown that there was a small admixture of $^{12}CH_3{}^{35}Cl$ at F37 spectrum. Also a foreign gas that was not either $^{12}CH_3{}^{35}Cl$/$^{12}CH_3{}^{37}Cl$, nor calibration gases (CO_2 and H_2O) was present in all the spectra in small amounts. In F35 spectra $^{12}CH_3{}^{37}Cl$ lines were almost completely absent, but same foreign gas as in the F37 spectra, was present, although in much smaller amounts. This gas was clearly noticeable only in the 1900–2260 cm^{-1} spectral region, where the lines of two principal isotopologue CH_3Cl are very weak and less noticeable under the strong bands. It could be rare isotopologue of CH_3Cl.

The SpectraPlot program [28] was used for visualization and assignment correction (see Fig. 1). The spectra F and I were virtually superposed in the 2250–2300 cm^{-1}spectral range.

For the intensity comparison a set of selected isolated lines was found for each isotopologue. The intensities of these isolated lines measured from spectra H and I in the 2260–2600 cm^{-1} spectral region for $^{12}CH_3{}^{35}Cl$ and for $^{12}CH_3{}^{37}Cl$ were compared and the results are shown in Tables 2 and 3.

The Table 2 confirmed pressure values defined in Table 1 for $^{12}CH_3{}^{35}Cl$. For $^{12}CH_3{}^{37}Cl$ intensities from

Table 1
Experimental details of the FTR spectra.

File	TSM2081	TSM2966	TSM2879	TSM2879B
No. of spectrum	F35	G35	H35	I35
Spectral range	1770–2420	2250–3800	2250–3800	2250–3800
Resolution (10^{-3} cm^{-1})	3.0	4.1	4.1	4.1
Path length (m)	19.2	0.28	9.6	19.2
Pressure (mbar)	1.4	1.0	0.40 [a](0.4)	1.7
File	TSM2080	TSM2967	TSM2878	TSM2878B
No. of spectrum	F37	G37	H37	I37
Spectral range	1770–2420	2250–3800	2250–3800	2250–3800
Resolution (10^{-3} cm^{-1})	3.0	4.1	4.1	4.1
Path length (m)	19.2	0.28	9.6	19.2
Pressure (mbar)	1.2	1.2	0.42[a] (0.5)	1.2

[a] These values were obtained from intensity comparison, old values [21–23] are in parenthesis.

Table 2
Comparison of the line intensities of $^{12}CH_3{}^{35}Cl$ for H35 and I35 spectra.

WvNm (cm^{-1})	Intensity I35 (cm^{-1}/(molecule cm^{-2}))	Intensity H35 (cm^{-1}/(molecule cm^{-2}))	Intensity ratio I35/H35
2368.36336	1.02E-22	1,.03E-22	0.991237
2368.54229	1.01E-22	1.04E-22	0.972089
2369.50432	8.88E-23	9.55E-23	0.929731
2369.75916	6.74E-23	6.44E-23	1.047064
2375.37585	4.89E-23	4.85E-23	1.008254
2375.56761	5.13E-23	5.04E-23	1.017053
2400.63596	5.59E-23	5.62E-23	0.994664
2401.37441	5.53E-23	5.41E-23	1.021619
2402.81485	5.17E-23	5.22E-23	0.990998
2404.88527	4.52E-23	4.43E-23	1.021459
Average			**0.9994**