Journal of Quantitative Spectroscopy & Radiative Transfer 129 (2013) 186–192

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

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

Temperature dependence for self- and N_2-broadening coefficients of CH_3Cl

C. Bray [a,b,*], D. Jacquemart [a,b], N. Lacome [a,b]

[a] UPMC Univ Paris 06, Laboratoire de Dynamique, Interactions et Réactivité, UMR 7075, Case Courrier 49, 4 Place Jussieu, 75252 Paris Cedex 05, France
[b] CNRS, UMR 7075, Laboratoire de Dynamique, Interactions et Réactivité, Case Courrier 49, 4 Place Jussieu, 75252 Paris Cedex 05, France

A R T I C L E I N F O

Article history:
Received 22 April 2013
Received in revised form
11 June 2013
Accepted 13 June 2013
Available online 20 June 2013

Keywords:
Methyl chloride
ν_1 band
Temperature dependence
Self- and N_2-broadening coefficients
J dependence

A B S T R A C T

The 3.4 μm-spectral region of methyl chloride was recently studied in terms of line positions, intensities and self- and N_2-broadening coefficients. In this work, the temperature dependence of self- and N_2-broadening coefficients was retrieved from high resolution Fourier transform spectra recorded at temperatures between 200 K and 270 K. 230 self-broadening coefficients and 103 N_2-broadening coefficients were measured using a multispectrum fitting procedure. The accuracy on the widths measurements was estimated to be around 10%. No *K*-rotational was observed on the extracted temperature exponents. The model describing the *J*-rotational dependence of the temperature exponents is available to generate fitted values of both self- and N_2- temperature dependence exponent (from $J=0$ to 40).

1. Introduction

An effort has been devoted by our team to characterize the 3.4 μm-spectral region absorption of methyl chloride. The line positions [1], intensities [1], self- and N_2-broadening coefficients [2,3], and line mixing effects [4] have been measured from room-temperature spectra. A theoretical Hamiltonian model [1] allowed us to generate a complete line list available for atmospheric applications. This list has been transmitted to international databases. The present work is dedicated to the low-temperature measurement of self- and N_2-broadening coefficients in the ν_1 band of both $^{12}CH_3{}^{35}Cl$ and $^{12}CH_3{}^{37}Cl$. Spectra were recorded at temperatures ranging from 200 to 270 K, representative of atmospheric temperatures. The analysis of these low temperature spectra together with those recorded at room temperature [2,3] allow us to derive both self- and N_2-temperature dependence exponents.

Some experimental values of self- and N_2-broadening coefficients at low temperature can be found in the literature [5–7]. Blanquet et al. [5] studied 24 transitions of self-broadened methyl chloride at low temperature in the ν_3 band using a tunable diode-laser spectrometer. All spectra were recorded at 200 K for several pressures allowing retrieval of self-broadening coefficients. Same experimental setup was used to retrieve N_2-brodening coefficients at low temperature in the same spectral region [6]. Colmont et al. [7] obtained N_2-broadening coefficients for a single transition at low temperature using several spectra recorded for N_2 pressures ranging from 0 to 400 mTorr and temperatures from 239 K to 349 K using a millimeter frequency-modulation spectrometer. Recently, semi-classical calculations were performed to calculate temperature-dependence exponents n_{N_2} [8].

In this paper, the broadening coefficients are first retrieved at various temperatures in order to obtain temperature-dependence exponents n_{self} and n_{N_2}. Lines of the ν_1 band of $^{12}CH_3{}^{35}Cl$ and $^{12}CH_3{}^{37}Cl$ around 3.4 μm have been studied

---

* Correspondence to: Interactions et Réactivité, Laboratoire de Dynamique, UPMC Univ Paris 06, Case Courrier 49, 4 Place Jussieu, 75252 Paris Cedex, France. Tel.: +33 1 69 08 36 39.
E-mail address: cedric.bray@cea.fr (C. Bray).

0022-4073/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jqsrt.2013.06.013

from six experimental spectra of CH_3Cl and N_2 mixtures recorded at various temperatures. A fitting procedure [9] was used to adjust the profiles of 333 lines in each spectrum: 230 for self-perturbed transitions and 103 for N_2-perturbed transitions. Rotational dependences upon the quantum number J were observed for both n_{self} and n_{N_2} temperature dependence coefficients.

The experimental conditions and the methodology of the measurements analysis are first presented in Sections 2 and 3, respectively. Section 4 is dedicated to the retrieval of temperature dependence of the measured broadening coefficients. Comparisons with various results from literature are presented in Section 5.

2. Experimental conditions

Six Fourier transform spectra have been recorded at temperatures ranging from 200 to 270 K using the rapid scan Bruker IFS 120 HR interferometer of the LADIR. The experimental conditions are summarized in Table 1. The interferometer was equipped with a CaF_2 beam splitter, an InSb detector, and a Globar source.

For the pure CH_3Cl spectra (#1–3), a single pass cell with an absorption path of (30.00 ± 0.05) cm has been used, whereas for the N_2-broadened spectra (#4–6), a multi-pass White-type cell (1 m base length) with an absorption path of (415 ± 1) cm has been used. Both cells were equipped with KCl windows.

The commercial gas sample of methyl chloride, furnished by Alpha Gaz, with a stated of purity of 99.9% in natural abundance was used without any purification. The pressures of the gases have been measured with 3 baratron gauges with accuracy better than $\pm 0.15\%$ for the 1 mbar full scale thermoregulated gauge and $\pm 0.25\%$ for the 10 and 100 mbar full scales. To record spectra at low temperatures, the cell was first filled with CH_3Cl (and N_2 for spectra #4–6) at room temperature. The gas inside the cells was then cooled using a flow of methylcyclohexane in the second envelop of the cells. To reach the required temperature the methylcyclohexane was cooled by liquid nitrogen. The temperature of the gas has been measured with accuracy equal to 1 K using platinum probes inside the cells. The pressure at low temperature is calculated using the ideal gas equation (the deviation between the ideal gas equation and virial equation of state is 0.02% at 200 K).

No optical filter has been used for recording the whole 1800–5000 cm^{-1} spectral range. This allowed observing CO_2 impurities near 2300 cm^{-1} and H_2O impurities near 1900 and 3700 cm^{-1} present in the cell.

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. The Bruker resolution of 0.01 cm^{-1} corresponds to unapodized full-width at half maximum of the appartus function equal to 0.0056 cm^{-1}.

2.1. *Preliminary treatment of LADIR spectra*

For each spectrum, the apparatus function has been calculated performing numerically the Fourier transform of the interferograms, taking into account the effect of the throughput and of the finite optical path difference [10]. In the definition of the apparatus function, the aperture (nominal value equal to 0.75 mm) and the focal length of the collimator (418 mm) are sensitive parameters. The effective iris radius has been fitted on isolated CH_3Cl and CO_2 transitions. The average effective iris radius has been found equal to (0.80 ± 0.06) mm for the 29 fitted transitions. This average value has been used for the final analysis presented in Section 3.

Concerning the wavenumbers calibration, absolute wavenumbers from HITRAN [11] have been used for 22 isolated transitions of CO_2 near 2300 cm^{-1}. The quantity $\varepsilon = (\nu_{\text{HITRAN2008}} - \nu_{\text{this work}})/\nu_{\text{HITRAN2008}}$ was calculated from measurements in spectrum #1, and an average value was

Table 1
Experimental conditions and characteristics of the recorded spectra.

Unapodized apparatus function:					
Nominal aperture radius	0.75 mm				
Effective aperture radius	0.80 mm				
Collimator focal length	418 mm				
Absorbing sample:					
Natural CH_3Cl	74.89% of $^{12}CH_3{}^{35}Cl$ 23.94% of $^{12}CH_3{}^{37}Cl$				
Stated purity	99.9%				
Experimental conditions:					
S/N ratio	≈100				
#	Pressure CH_3Cl (mbar)	Pressure N_2 (mbar)	Resolution[a] (cm^{-1})	Absorption path (cm)	Temperature (K)
1	4.756	0	0.01	30.00	267 ± 1
2	4.042	0	0.01	30.00	234 ± 1
3	3.455	0	0.01	30.00	200 ± 1
4	0.1976	26.28	0.008	415	271 ± 1
5	0.1709	23.28	0.008	415	240 ± 1
6	0.1546	21.05	0.008	415	217 ± 1

[a] Resolution as defined by Bruker = 0.9/maximum optical path depth.