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N₂-broadening coefficients of methyl chloride: Measurements at room temperature and calculations at atmospheric temperatures

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ABSTRACT

Infrared spectroscopic study on methyl chloride is the first step for its accurate detection in the atmosphere. In our previous work [Barbouchi Ramchani et al. J Quant Spectrosc Radiat Transfer 2013;120:1–15], line positions, intensities and self-broadening coefficients of both ¹²CH₃³⁵Cl and ¹²CH₃³⁷Cl isotopologues have been studied in the 6.9 μm spectral region. The present work is focused on measurements of N₂-broadening coefficients for transitions of ¹²CH₃³⁵Cl and ¹²CH₃³⁷Cl around 6.9 μm. For that, high-resolution Fourier transform spectra of CH₃Cl–N₂ mixtures have been recorded at room temperature using a rapid scan Bruker IFS 120 HR interferometer at LADIR. The N₂-broadening coefficients have been retrieved using a Voigt profile and a multispectrum fitting procedure. The average accuracy of the N₂-broadening obtained in this work has been estimated to be between 5% and 10% depending on the transitions. The rotational J- and K-dependences of the N₂-broadening coefficients have been clearly observed and modeled using empirical polynomial expansions. The ¹²CH₃³⁵Cl–N₂ line-widths of the ν₅ band have also been computed using a semi-classical approach for the ^pR, ^RR and ^QR sub-branches. A global comparison with the experimental data from this work but also existing in the literature was then performed. Similar J- and K-rotational dependences have been observed while no clear evidence of any vibrational or isotopic dependence has been pointed out. Finally, performing theoretical calculations of the N₂-broadening coefficients at various temperatures of atmospheric interest between 200 and 296 K allowed deducing the temperature exponent of the ¹²CH₃³⁵Cl–N₂ line-widths.

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1. Introduction

The halocarbons, derivatives of methane, are for the greater part natural products found in the atmosphere.

Methyl chloride (CH₃Cl) is the most abundant of them in the Earth's atmosphere. Because this molecule is easily photodissociated, it is an important source of the free chlorine atoms involved in the destruction of the ozone layer [1]. To better analyze the atmospheric spectra collected by satellites and to retrieve accurate concentration of molecules in the atmosphere, accurate laboratory spectroscopic parameters are needed.

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Methyl chloride has been the subject of numerous experimental and theoretical works in various spectral regions [1,2,4–18]. Among this nonexhaustive list of works, the N₂-broadening coefficients of CH₃Cl have been studied (both measurements and calculations) for transitions of the ν_3 band [4–7] around 732 cm⁻¹ at various temperatures, of the ν_1 band [8] around 3000 cm⁻¹ at room temperature and for pure rotational transitions around 12.4 cm⁻¹ at different temperatures [14] and around 45 cm⁻¹ at room temperature [15]. These results will be used in the present paper to be compared with our measurements and calculations.

The previous paper [2] was dedicated to the measurements of positions, intensities and self-broadening coefficients of rovibrational transitions of the ν_5 band around 6.9 μm for both the CH₃³⁵Cl and CH₃³⁷Cl isotopologues. The present work is focused on the measurements of the N₂-broadening coefficients of infrared lines belonging mainly to the strongest ν_5 band but also to weaker bands such as the ν_2 , $2\nu_3$ and $\nu_3 + \nu_5$ bands. The studied spectral range extends from 1286 cm⁻¹ to 1626 cm⁻¹. A multispectrum fitting procedure [3] has been used to fit simultaneously six experimental spectra recorded at various pressures of CH₃Cl and N₂ mixture. In order to study the rotational J - and K -dependences, a large set of measurements has been retrieved at room temperature corresponding to various J and K quantum numbers ($0 \leq J \leq 51$, $0 \leq K \leq 12$). An empirical model and a calculation based on a semi-classical approach have been used to reproduce the observed J - and K -rotational dependences. Comparisons between our measurements of N₂-broadening coefficients and those done for others bands in previous works have been performed. Moreover, to derive the temperature exponents, the ¹²CH₃³⁵Cl–N₂ line-widths of the ν_5 band have also been computed using the semi-classical approach at temperatures of atmospheric interest: 200, 220, 245, 270 and 296 K.

The experimental conditions of the recorded spectra as well as the procedure for the line parameters retrieval are described in Section 2. Section 3 is devoted to the N₂-broadening coefficients measured in this work and to the empirical model used to reproduce the observed J - and K -dependences. Finally, the theoretical approach will be presented in Section 4 together with the temperature exponents deduced from calculations performed at various temperatures.

2. Experiment and preliminary study

2.1. Experimental conditions

Six Fourier transform spectra have been recorded using a rapid scan Bruker IFS 120 HR interferometer. The experimental conditions are summarized in Table 1. The interferometer has been equipped with a Globar source, an MCT photovoltaic detector, and a KBr beamsplitter. No optical filter has been used to cover the whole spectral range between 900 and 5000 cm⁻¹. This allowed us to use transitions of CO₂ near 2300 cm⁻¹ to perform a preliminary study of the apparatus function and the wavenumber calibration (see Section 2.2). The whole optical path has been under vacuum, and a metal multipass White-type cell (1-m base length) has been used to provide absorption path length of (415 ± 1) cm. The cell has been equipped with KCl windows. The sample of the commercial gas, furnished by Alpha Gaz, with a stated of purity of 99.9% in natural abundances (74.894% of ¹²CH₃³⁵Cl and 23.949% of ¹²CH₃³⁷Cl), has been used without any purification. All spectra have been recorded at room temperature (see Table 1). The temperature of the gas inside the cell has been obtained by averaging measurements performed by four platinum probes inside the cell. The accuracy of the average temperature given in Table 1 is estimated to be around the accuracy of the probes (± 0.1 K). The pressure of the gas has been measured using baratron gauges for which the accuracy is better than $\pm 0.15\%$ for the 1 mbar full scale gauge and $\pm 0.25\%$ for the 100 mbar full scale gauge. Around 500 scans have been recorded for each average spectrum, leading to a signal to noise ratio equal to about 180 around 1500 cm⁻¹. The average interferogram has 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. A multiplicative channel spectrum, due to the cell windows, has been observed in all experimental spectra. Its period is around 0.60 cm⁻¹ (corresponding to the thickness of the cell windows) with maximum peak-to-peak amplitude of about 2%. Since the fitted spectral range is smaller than the half-period of the channel, this multiplicative channel has been fitted as part of the background using a second-order polynomial expansion.

Table 1
Experimental conditions.

Spectrum number	CH ₃ Cl pressure (mbar)	N ₂ pressure (mbar)	Resolution ^a (cm ⁻¹)	Temperature (K)
1	0.1241	0	0.005	296.7
2	0.2586	0	0.005	297.1
3	0.5103	0	0.005	297.2
4	0.3059	14.0641	0.006	297.0
5	0.4973	21.0227	0.01	296.8
6	0.5100	54.1700	0.02	296.8

^a Resolution as defined by Bruker = $0.9/\text{Maximum optical path}$.

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