

Air-broadening coefficients of $\text{CH}_3^{35}\text{Cl}$ and $\text{CH}_3^{37}\text{Cl}$ rovibrational lines and their temperature dependence by a semi-classical approach

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ABSTRACT

Air-broadening coefficients and associated temperature exponents for $\text{CH}_3^{35}\text{Cl}$ and $\text{CH}_3^{37}\text{Cl}$ (vib)rotational transitions of $^{\circ}R$ -type branches are calculated by a semi-classical approach previously validated on extensive room-temperature measurements. Contrary to the theoretical methods used in the literature for the CH_3X -type absorbers, the active molecule is rigorously treated as a symmetric top with long- as well as short-range interactions and the exact classical trajectories are employed for the relative molecular motion. Analogous parameters additionally computed for N_2 - and O_2 -broadening provide a very favorable comparison with available low-temperature experimental results and ensure the reliability of the reported values in the interval of atmospheric interest 200–300 K. Numerical data for $0 \leq J \leq 70$ and $K \leq 20$ are given as supplementary materials for use in atmospheric applications and spectroscopic databases.

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1. Introduction

Methyl chloride CH_3Cl is known as the main source of extremely reactive atomic chlorine ions in the terrestrial atmosphere [1,2]. Together with bromine ions and hydroxyl and nitric oxide radicals, these ions are the most important catalysts of chemical reactions leading to the depletion of the stratospheric ozone layer [3]. Retrieval of accurate atmospheric concentrations by remote sensing requires therefore a precise knowledge of CH_3Cl line broadening and shifting induced by the main atmospheric gases N_2 and O_2 , i.e. by air. The line broadening and line shifting coefficients should be known for various spectral regions (various vibrational bands) and for wide temperature ranges of atmospheric interest (at least between 200 and 300 K).

Whereas the information available in spectroscopic databases [4,5] on CH_3Cl line positions and intensities is

quite extensive [6] and continues to be completed [7], the data on its air-broadening are limited to $J \leq 50$, $K \leq 15$ ¹ and the temperature exponents are taken as constant for all the lines. Such lack of spectroscopic parameters is due to the absence of exhaustive direct measurements and calculations at temperatures other than the reference temperature 296 K. Even for the room temperature the air-broadening coefficients are deduced from their N_2 - and O_2 -broadening values.

The case of perturbation by nitrogen is the most investigated in the literature from both experimental and theoretical points of view. Besides the early ν_3 -band measurements [8,9] ($3 \leq J \leq 46$, $3 \leq K \leq 9$ and $J=3$, $0 \leq K \leq 3$) and corresponding semi-classical calculations with a long-range interaction potential [10] for 296 K, analogous studies [11] ($2 \leq J \leq 22$, $0 \leq K \leq 6$) have been also realized for the low temperature of 203 K. Ref. [12] and also Refs. [9,10] considered the oxygen-broadening. The

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¹ In the standard notations for the rotational quantum numbers of a symmetric top, J is associated with the total angular momentum whereas K represents the projection of the latter on the molecular axis.

$K=5$ component of the purely rotational transition $J=14-13$ in $\text{CH}_3^{35}\text{Cl}$ colliding with both N_2 and O_2 has been extensively examined by Colmont et al. [13] in the temperature range 240–350 K and the associated, experimental as well as theoretical, temperature exponents have been deduced. In the same work, almost complete K -dependence ($0 \leq K \leq 11$) has been obtained for the N_2 -broadening at 301 K. Owing to increased performances of terahertz-spectroscopy techniques, the cases of room-temperature $\text{CH}_3^{35}\text{Cl}$ rotational lines broadened by nitrogen and oxygen have been recently revisited [14,15] in an extended range of quantum numbers: $6 \leq J \leq 50$, $0 \leq K \leq 18$. Similar studies of the ν_1 -band region ($0 \leq J \leq 50$, $0 \leq K \leq 9$) and far-infrared transitions of the pure rotational band ($55 \leq J \leq 67$, $0 \leq K \leq 12$) have been reported by Bray et al. [16]. These extensive experimental data obtained for the room temperature enabled rigorous tests of the improved semi-classical approach detailed for the molecular systems of $\text{CH}_3\text{X}-\text{Y}_2$ type in Ref. [15] and employed also in Refs [14,16] (in addition to the previous symmetric-top studies on NO [17–19] and OH [20]). With respect to the previous semi-classical calculations of Bouanich et al. [10,11] and Colmont et al. [13], this approach takes into account the real symmetric-top geometry of methyl chloride molecule and includes the (non-negligible) contributions from the short-range forces; the usual parabolic trajectories for the relative molecular motion are moreover replaced by the exact ones [21]. The very good agreement stated between these new semi-classical results and experimental data for both N_2 and O_2 perturbers makes extremely worthy extensive systematic calculations of such kind for other temperatures in order to provide the missing data on air-broadening.

The present work is focused on theoretical estimation, with the formalism of Ref. [15], of air-broadening coefficients and temperature exponents for both $\text{CH}_3^{35}\text{Cl}$ and $\text{CH}_3^{37}\text{Cl}$ isotopologues in wide ranges of quantum numbers and temperatures requested by atmospheric applications. The studied J - and K -values ($0 \leq J \leq 70$, $0 \leq K \leq 20$) match the transitions considered for a line strengths and positions update [22]. Since no evident vibrational dependence has been observed so far for the CH_3Cl lines [16], these calculations are expected to be valid for rotational as well as vibrotational transitions. Moreover, N_2 - and O_2 -broadening temperature exponents – computed for performing tests with available experimental data [11,13] – are reported too.

2. Semi-classical calculations

The theoretical expressions and molecular parameters required for semi-classical calculations of methyl chloride line widths broadened by N_2 and O_2 can be found in Refs. [14,15]. In addition to the data already obtained at room temperature, new calculations have been performed for K values up to 20 at 296 K as well as for all J and K of the considered intervals at three lower temperatures (260, 240 and 220 K) representative of the terrestrial stratosphere. For the $\text{CH}_3^{37}\text{Cl}$ isotopologue it was supposed that the intermolecular potential parameters remain the same as those for $\text{CH}_3^{35}\text{Cl}$ (a similar assumption has been also made for a theoretical analysis of N_2 -broadening of CH_3Br isotopologues [23]), and the rotational constants have been taken from Ref. [7].

As the case of temperature-dependent nitrogen-broadening has already been addressed in the literature [11,13], it is worthy to extract first the $\text{CH}_3^{35}\text{Cl}-\text{N}_2$ temperature exponents N determined by the standard relation between the line-broadening coefficients:

$$\gamma(T) = \gamma(T_{\text{ref}}) \left(\frac{T}{T_{\text{ref}}} \right)^{-N} \quad (1)$$

(with $T_{\text{ref}}=296$ K) and to use them for evaluating line widths at lower and higher temperatures. Since the classical path approximation loses gradually its validity with decreasing temperature (the isotropic potential depths are 185 K and 208 K for $\text{CH}_3\text{Cl}-\text{N}_2$ and $\text{CH}_3\text{Cl}-\text{O}_2$, respectively), two series of fits have been realized: the first one excluding the lowest temperature 220 K (which approaches the isotropic potential depth) and the second one accounting for all four temperatures. These two sets of N values (noted as N_{3T} and N_{4T}) extracted by the standard least-squares procedure for $0 \leq J \leq 70$, $0 \leq K \leq 20$ as well as the broadening coefficients $\gamma(296)$ for $\text{CH}_3^{35}\text{Cl}-\text{N}_2$ lines are given as [Supplementary material](#) (the quoted uncertainties correspond to one standard deviation issued from fitting). N_{3T} and N_{4T} have very close values (maximal relative difference about 3% for 107 lines among 1281 studied), which confirms the validity of our calculations and of Eq. (1) in the considered temperature interval. The root-mean-square deviations are however slightly smaller for N_{3T} which favors the use of this set. Fig. 1 shows examples of N_{3T} values plotted as functions of J for $K=0-6$; the data for $J=13$, $K=5$ [13] are also added, but only a visual comparison can be made with Fig. 7 of Ref. [11] since the authors did not provide the numerical values. It can be seen from Fig. 1 that our value calculated for $J=13$, $K=5$ (0.650) is very close to the theoretical datum of Ref. [13] (0.659) but is quite far from their experimental results. This discrepancy can be explained by the following reasons: first, by a larger temperature interval studied in [13] and the well known fact that Eq. (1) holds only in limited temperature ranges; second, by a probable underestimation of experimental broadening coefficients [13] in comparison with recent measurements (clearly seen in Fig. 11 of Ref. [14]), and, finally, by experimental error bars greater than one

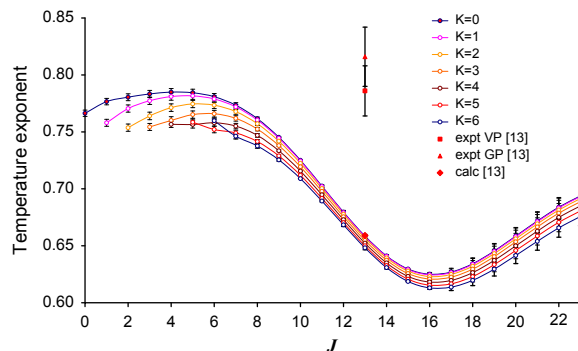


Fig. 1. Temperature exponents N_{3T} for the N_2 -broadening coefficients of $\text{CH}_3^{35}\text{Cl}$ calculated in the present work (the error bars correspond to one standard deviation determined from the fitting procedure). The experimental values obtained with Voigt profile (VP) and Galatry profile (GP) as well as the theoretical value of Ref. [13] for $J=13$, $K=5$ are also shown.

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