



CH₃Cl self-broadening coefficients and their temperature dependence

A.S. Dudaryonok^a, N.N. Lavrentieva^{a,*}, J.V. Buldyreva^b

^a V.E. Zuev Institute of Atmospheric Optics, Siberian Branch of the Russian Academy of Sciences, 1 Akademichian Zuev square, 634021 Tomsk, Russia

^b Institute UTINAM, UMR CNRS 6213, University of Franche-Comte, 16 Gray road, 25030 Besancon cedex, France

ARTICLE INFO

Article history:

Received 6 March 2013

Received in revised form

1 July 2013

Accepted 12 July 2013

Available online 19 July 2013

Keywords:

Methyl chloride

Self-broadening

Temperature exponent

J- and *K*-dependences

Infrared absorption

Semi-empirical calculations

Semi-classical calculations

ABSTRACT

CH₃³⁵Cl self-broadening coefficients at various temperatures of atmospheric interest are computed by a semi-empirical method particularly suitable for molecular systems with strong dipole–dipole interactions. In order to probe the dependence on the rotational number *K*, the model parameters are adjusted on extensive room-temperature measurements for *K* ≤ 7 and allow reproducing fine features of *J*-dependences observed for *K* ≤ 3; for higher *K* up to 20, the fitting is performed on specially calculated semi-classical values. The temperature exponents for the standard power law are extracted and validated by calculation of low-temperature self-broadening coefficients comparing very favorably with available experimental data. An extensive line-list of self-broadening coefficients at the reference temperature 296 K and associated temperature exponents for 0 ≤ *J* ≤ 70, 0 ≤ *K* ≤ 20 is provided as [Supplementary material](#) for their use in atmospheric applications and spectroscopic databases.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Methyl chloride CH₃Cl is the principle source of chlorine atoms in the terrestrial atmosphere, involved, in particular, in the chemical reactions of ozone layer depletion. Although the main perturbers of this molecule are nitrogen and oxygen, the case of self-perturbation is also of great importance for its line-broadening coefficients because of their high values and their significant contributions to the atmospheric absorption. For radiative transfer calculations, a crucial role is played by the temperature dependence of these coefficients, especially for the range of atmospheric interest (180–300 K).

There are a few experimental studies of methyl chloride self-broadened half-widths. Self-broadening coefficients were initially measured for only one lowest energy

(*J* = 1 ← 0) transition from pure rotational band [1] and for some isolated terahertz lines [2], but the small number of observed lines did not allow any analysis of *J*- or *K*-rotational dependences. Clear *J*-dependences were first observed on the experimental self-broadening coefficients of 29 lines (3 ≤ *J* ≤ 50, 2 ≤ *K* ≤ 9) in the ν_3 band [3,4]. The work [5] reported collisionally broadened CH₃Cl line widths measured at pressures higher than 75 Torr and announced a strong non-linear dependence of line broadening on pressure. Self-broadening coefficients of rovibrational lines (3 ≤ *J* ≤ 27, 3 ≤ *K* ≤ 6) in the ν_5 band were determined [6] for CH₃³⁵Cl and CH₃³⁷Cl at 296 and 200 K, and a *J*-dependent polynomial expression was proposed for their empirical modeling (no specific trends of the broadening coefficients were observed with respect to the rotational quantum number *K*). The same work listed theoretical values of line widths obtained by a semi-classical method, but these values were too high in comparison with the experimental ones. The data obtained by Chackerian et al. [7] for self-perturbed CH₃³⁵Cl and CH₃³⁷Cl line positions, intensities

* Corresponding author.

E-mail address: inn@iao.ru (N.N. Lavrentieva).

and broadening coefficients were included in the HITRAN-2008 database [8]; their values of self-broadening coefficients were also reproduced in the last edition of GEISA [9]. Very recently, CH₃Cl room-temperature self-broadening coefficients in the vibrational ν_1 band as well as in the pure rotational band were studied experimentally ($J \leq 50$, $K \leq 12$) and theoretically ($J \leq 60$, $K \leq 25$) by Bray et al. [10].

From the theoretical point of view, for strongly polar colliders, the standard semi-classical (SC) calculations exhibit an unrealistic overestimation of line widths, as it has been shown for CH₃³⁵Cl [6], CH₃F [11,12], and CH₃Br [13] (treated as linear molecules because of the dominant dipole–dipole interaction). Such semi-classical calculations give a good overall agreement with experimental data only if a cut-off procedure is applied to the maximal value of the intermolecular distance accounted for, as it has been proposed for the CH₃Br case [13] and confirmed by recent calculations for CH₃Cl [10]. The main reason of this line broadening overestimation is the isotropic potential depth much greater than the mean kinetic energy of the relative molecular motion: orbiting collisions occur and the intermolecular interactions cannot be considered as a small perturbation.

The presence of a strong dipole interaction favors however the application of the semi-empirical (SE) method [14] which is also based on the impact theory but enables a realistic prediction of line-broadening and line-shifting parameters via introducing effective correction factors to the interruption functions. For molecular systems with high values of dipole moments (e.g., H₂O–H₂O, H₂O–N₂, H₂O–CO₂) a single (two-parameter) correcting factor for the dipole transitions is sufficient to reproduce the bulk of available experimental data for various vibrational bands and in a wide temperature range. This semi-empirical method has been successfully used for calculations of broadening coefficients, shifting coefficients and their temperature exponents for many collisional partners: H₂O–N₂, O₂, Ar, Xe, H₂, He, H₂O, [15–20]; O₃–N₂, O₂ [21,22]; and CO₂–N₂, O₂, N₂O [23,24]. The results of these calculations were partly included in the freely-available carbon dioxide spectroscopic databank (<ftp://ftp.iao.ru/pub/CSD-1000>), in the “ATMOS” Information System (<http://wadis.saga.iao.ru/>) and in the GEISA database (<http://ara.lmd.polytechnique.fr>). The most extensive calculations concerned the case of water vapor (broadening coefficients, shifting coefficients and their temperature exponents were provided for about two million lines for “ATMOS” and for about forty thousand lines for GEISA).

In the present work, for the first time, we apply the SE method to calculate CH₃³⁵Cl–CH₃³⁵Cl line broadening coefficients for wide ranges of rotational quantum numbers J and K requested for atmospheric applications. We report also the corresponding temperature exponents in the standard form adopted by spectroscopic databases.

The remainder of the paper is organized as follows. In the next section we briefly remind about the main features of the SE method and give the details of its application to the case of CH₃Cl self-broadening. Section 3 provides the results of calculations for room-temperature and their comparison with available experimental data, as well

as determination of the temperature exponents and their testing on the values measured at 200 K. Concluding remarks and perspectives are gathered in the final section.

2. Method and details of calculation

In the framework of the semi-empirical method [14], by analogy with the Anderson theory, the half-width of the spectroscopic line corresponding to the radiative transition $i \rightarrow f$ is expanded into a perturbation series up to the second order:

$$\gamma_{if} = A(i, f) + \sum_l \sum_{i'} D^2(ii'|l) P_l(\omega_{ii'}) + \sum_l \sum_{f'} D^2(ff'|l) P_l(\omega_{ff'}) + \dots \quad (1)$$

Here, $A(i, f) = (n/c) \sum_2 \rho(2) \int_0^\infty v dv b_0^2(v, 2, i, f)$ is the usual term of the Anderson theory due to the cut-off procedure (n is the number density of the perturbing molecules, $\rho(2)$ are their rotational populations, v is the relative velocity and $b_0(v, 2, i, f)$ is the interruption parameter). The summations are performed over transitions of different tensorial ranks l (dipole with $l=1$, quadrupole with $l=2$, etc.). It should be kept in mind that, in general, each transition is due not only to the long-range (electrostatic, induction and dispersion) but also to the short range terms of the same rank in the intermolecular interaction potential. $D^2(ii'|l)$ and $D^2(ff'|l)$ represent the transition strengths corresponding to the scattering channels $i \rightarrow i'$, $f \rightarrow f'$ in the active molecule and are completely determined by the usually well known intramolecular properties (multipole moments, wave functions). The expansion coefficients $P_l(\omega)$ (called also “interruption” or “efficiency” functions) characterize the perturbing molecule (energy levels, wave functions) and the intermolecular interaction (potential, trajectory). These coefficients are known with a much lower precision, so that, using their smooth dependence on frequency, they can be seen as products of the (analytical) interruption functions of the Anderson theory $P_l^A(\omega)$ and a frequency-dependent correction factor $C_l(\omega)$ accounting for the effects of the trajectory curvature, vibrational dependence and deviations of the scattering operator from the perturbative series of Eq. (1):

$$P_l(\omega) = P_l^A(\omega) [1 + a_1 \omega + a_2 \omega^2 + \dots] = P_l^A(\omega) C_l(\omega). \quad (2)$$

For molecular systems with a very strong dipole interaction (such as H₂O active molecule) just one correction factor $C_1(\omega)$ of a simple two-parameter form:

$$C_1 = c_1 / (c_2 \sqrt{J} + 1) \quad (3)$$

is sufficient to reproduce correctly the experimental line-broadening coefficients in various vibrational bands [16–18]. Numerical analyses show that this correction typically changes the broadening value by 1–5% with respect to calculations with $P_l^A(\omega)$.

The CH₃Cl self-broadening is also characterized by the presence of a strong dipole, but has a very specific local minimum in the region of small J values for $K \leq 3$. (This feature has been also observed for CH₃Br [13].) As a result, even if it is always logical to keep just one correction factor with $l=1$, its form should be more complex than

Download English Version:

<https://daneshyari.com/en/article/5428637>

Download Persian Version:

<https://daneshyari.com/article/5428637>

[Daneshyari.com](https://daneshyari.com)