Theoretical calculation of CH_3Br/N_2-broadening coefficients at various temperatures

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ABSTRACT

The N_2-broadening coefficients of $CH_3^{79}Br$ and $CH_3^{81}Br$ have been calculated for transitions belonging to the ^PP-, ^PQ-, ^PR-, ^RP-, ^RQ- and ^RR-branches of the ν_6 band near 10 μm, using a semiclassical impact theory. The intermolecular potential used, includes in addition to the overwhelming electrostatic interactions, induction and dispersion energy contributions, which are significant only for low J transitions with K approaching or equal to J. Comparisons have been performed with the extensive set of previous measurements at room temperature [4]. The theoretical results are in satisfactory agreement with the experimental data, and the J and K dependences are reasonably well reproduced. From calculations at 200, 230, 260 and 296 K, the temperature exponent of the collisional broadenings derived from a simple power law has been determined for each transition of each sub-branch and compared with a recent experimental evaluation [5]. Finally the N_2-broadening coefficients calculated at 296 K and their temperature exponents are given as supplementary materials of this paper for atmospheric applications and databases.

1. Introduction

The methyl halides take part in atmospheric chemical reactions and are the subject of very detailed attention in the study of our atmosphere. The methyl bromide, CH_3Br, is a halogen chemical compound that has both industrial and nonindustrial sources to the atmosphere, all of which have highly uncertain magnitudes [1]. This molecule contributes significantly to ozone depletion since CH_3Br is dissociated by UV radiation, producing Br radicals that catalyze the destruction of ozone [2]. These bromide atoms are largely more destructive of ozone than the chlorine atoms coming from chlorofluorocarbon compounds (CFCs) [3]. For this reason, since 2005 the use of CH_3Br has been prevented under the Montreal protocol. Various spectroscopic studies [4–8] on this molecule have led to a complete line list that has recently been added in the atmospheric databases HITRAN [9] and GEISA [10].

In a previous paper [4] absolute line positions and intensities, as well as self- and N_2-broadening coefficients have been measured for about 1200 lines, between 880 and 1050 cm^{-1}, in the ν_6 fundamental band of the isotopic species $CH_3^{79}Br$ and $CH_3^{81}Br$. Theoretical calculations for the self-broadening coefficients of CH_3Br have recently been performed [11], and the present paper is dedicated to the calculation of N_2-broadening coefficients for both isotopic species in the same ν_6 band at 10 μm. These calculations are

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based on the semiclassical Anderson-Tsao-Curnutte (ATC) theory [12] and include some improvements proposed by Robert and Bonamy [13]. They were first applied [14] to the interactions between a symmetric-top molecule (CH_3Cl) and a nonpolar molecule (N_2 or O_2). The intermolecular potential includes, in addition to the strong electrostatic, dipole–quadrupole and quadrupole–quadrupole interactions, the induction and dispersion contributions obtained by Leavitt [15,16]. The calculated N_2-broadening coefficients are compared with a previously measured set of coefficients at room temperature [4]. They have also been calculated at low temperatures (200, 230 and 260 K) in order to deduce the temperature dependence of these broadenings and the resulting temperature exponents are compared with those determined experimentally [5].

The general formulation of the semiclassical formalism and the energy potential considered are similar to those described previously [11] and are briefly presented in Section 2. The theoretical results at 296 K are displayed and compared with measurements [4] in Section 3. Discussions on the different contributions of the potential, the influence of isotopic species, as well as the type of sub-branch are also presented. In Section 4, the temperature exponents of the N_2-broadening coefficients are derived from low temperature results and compared with recent experimental evaluations [5]. Finally, a complete calculation of N_2-broadening coefficients and temperature exponents is proposed as supplementary data for atmospheric applications and databases.

2. General formulation

The N_2-broadening coefficients of CH_3Br are calculated in the framework of the ATC theory [12], which was subsequently developed and applied to the interactions between a symmetric top and a linear molecule [14].

Within this semiclassical model, the collisional half-width γ_{if} of an isolated pressure-broadened $i \rightarrow f$ transition may be expressed as

$$\gamma_{if} = \frac{n_2 \overline{v}}{2\pi c} \sum_{J_2} \rho_{J_2} \int_0^\infty 2\pi b S_{if}(b J_2) \mathrm{db} \qquad (1)$$

where n_2 is the number density of the perturbing molecules, $\overline{v}$ the mean relative speed, ρ_{J_2} the relative population of the $|J_2, v_2 = 0\rangle$ state of the perturber including the nuclear spin factor for N_2, $f(J_2) = [(-1)^{J_2} + 3]/2$, S_{if} the differential cross-section representing the collisional efficiency and b is the impact parameter. The anisotropic potential involves, as in [11], the main electrostatic interactions as well as the main induction and dispersion contributions obtained by Leavitt [15,16] such as

$$V_{aniso} = V_{\mu_1 Q_2} + V_{Q_1 Q_2} + V_{\mu_1^2 \alpha_2} + V_{\alpha_1 \gamma_1 \alpha_2}, \qquad (2)$$

where the index 1 refers to the absorber (CH_3Br) and 2 to the perturber (N_2); α and γ are, respectively, the average polarizability and the dimensionless polarizability anisotropy previously defined [11]. The dispersion interactions are given in terms of $\overline{U} = U_1 U_2 / (U_1 + U_2)$, where U_1 and U_2 are the first ionization energies of molecules 1 and 2, respectively. The strength of the dispersion energy is generally underestimated from the ionization energies and has been re-evaluated, as in [11], by replacing $(3/2)\overline{U}\alpha_1\alpha_2$ by $4\varepsilon\sigma^6$, the long-range part of the Lennard–Jones (LJ) potential. The contribution of this potential to the differential cross-section are derived from the expressions given by Leavitt [16] for interactions of linear molecules by including in the Clebsh–Gordan coefficients the quantum number K_i and K_f with $K_f = K_i \pm 1$ for the perpendicular v_6 band of CH_3Br, together with the appropriate Racah coefficients occurring in the S_2^{middle} term.

In this work, we have only considered the transitions induced by collisions in CH_3Br with $\Delta K = 0$, associated with the usual selection rules $\Delta J = 0, \pm 1$ for a dipolar transition,

Table 1
Spectroscopic constants used (or considered) for the calculations of the N_2-broadening coefficients.

Molecule	State	A (cm^{-1})	B (cm^{-1})	D_J (10^{-7} cm^{-1})	D_{JK} (10^{-6} cm^{-1})	D_K (10^{-5} cm^{-1})
$^{12}CH_3^{79}Br$	Ground	5.180632	0.319160556	3.2932	4.2913	8.47
	v_6	5.2101669	0.31802097	3.3060	4.3243	8.7832
$^{12}CH_3^{81}Br$	Ground	5.180615	0.317947638	3.2694	4.2640	8.48
	v_6	5.2101408	0.3168128	3.2829	4.2961	8.7916
N_2	Ground	—	1.989622[a]	57.63[a]	—	—

Molecule	M (amu)	μ (D)	Q (D.Å)	ε/k_B (K)	σ (Å)	α (Å^3)	γ	U (eV)
$^{12}CH_3^{79}Br$	93.9414	1.82171[b]	3.55[c]	441.9[e]	3.939[e]	5.87[c]	0.115[g]	10.541[c]
$^{12}CH_3^{81}Br$	95.9394	1.82185[b]	3.55[c]	441.9[e]	3.939[e]	5.87[c]	0.115[g]	10.541[c]
N_2	28.0134	0	−1.40[d]	92.91[f]	3.816[f]	1.74[c]	0.137[g]	15.581[c]

Spectroscopic parameters for CH_3Br are taken from [8] for the ground state and from [4] for the v_6 state.
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  [e] [11]
  [f] [14]
  [g] [23].