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Theoretical calculations of self-broadening coefficients in the ν_6 band of CH_3Br

L. Gomez [a,b], D. Jacquemart [a,b,*], J.-P. Bouanich [c], Z. Boussetta [d], H. Aroui [d]

[a] UPMC Univ Paris 06, UMR 7075, Laboratoire de Dynamique Interactions et Réactivité, Case courrier 49, Bât. F 74, 4, place Jussieu, 75252 Paris Cedex 05, France
[b] CNRS, UMR 7075, Laboratoire de Dynamique Interactions et Réactivité, Case courrier 49, Bât. F 74, 4, place Jussieu, 75252 Paris Cedex 05, France
[c] Institut des Sciences Moléculaires d'Orsay, CNRS Université Paris Sud 1191405 Orsay Cedex, France
[d] Laboratoire de Physique Moléculaire, Ecole Supérieure des Sciences et Techniques de Tunis, 5 Av Taha Hussein 1008 Tunis, Tunisia

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ABSTRACT

A semiclassical impact theory based upon the Anderson–Tsao–Curnutte formalism has been used to calculate the self-broadening coefficients in the ^PP-, ^PQ-, ^PR-, ^RP-, ^RQ- and ^RR-branches of the ν_6 band of $^{12}CH_3{}^{79}Br$ and $^{12}CH_3{}^{81}Br$ near 10 μm. Comparisons have then been performed with the extensive set of previous measurements [3] (Jacquemart et al., 2007). The intermolecular potential used, involving the overwhelming electrostatic contributions, leads to larger results than the experimental data for middle J values. By arbitrarily limiting the integration of the differential cross-section to an impact parameter equal to 29 Å, quite satisfactory results have been obtained, and the J and K dependences are in reasonable agreement with those observed experimentally. The theoretical results are, on the whole, slightly larger for $CH_3{}^{79}Br$ than for $CH_3{}^{81}Br$ and for same J and K initial states of the transitions they depend on the sub-branch considered. These differences and dependencies were not observed in the previous measurements due to scatter in the experimental data. Finally, the theoretical results obtained for all sub-branches of $^{12}CH_3{}^{79}Br$ and $^{12}CH_3{}^{81}Br$ are given as supplementary materials of this paper.

1. Introduction

Methyl bromine is of interest for atmospheric applications, since this molecule is directly involved in the catalytic destruction of ozone in the lower stratosphere. Methyl bromide (CH_3Br) has been identified as the major contributor to stratospheric bromine and the primary organobromine species in the lower atmosphere. Many works have been devoted to CH_3Br, concerning mainly the line positions. An extensive review of this molecule is given by Graner [1] for works prior to 1981. More recent references may be found in [2]. In a previous paper [3] 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 $CH_3{}^{81}Br$. The present paper is dedicated to the theoretical calculation of self-broadening coefficients for both isotopic species in the same ν_6 band at 10 μm. Such a calculation for interactions of symmetric-top molecules was first applied to the ν_3 band of CH_3Cl [4] and is based on the semiclassical Anderson–Tsao–Curnutte (ATC) theory [5] and include some improvements proposed by Robert and Bonamy [6]. For methyl bromide, which has a strong dipole moment, the potential used for the calculation of self-broadening coefficients is essentially limited to the main electrostatic interactions dipole–dipole, dipole–quadrupole and quadrupole–quadrupole. The

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[*] Corresponding author at: UPMC Univ Paris 06, UMR 7075, Laboratoire de Dynamique Interactions et Réactivité, Case courrier 49, Bât. F 74, 4, place Jussieu, 75252 Paris Cedex 05, France. Tel.: +33 1 44 27 36 82; fax: +33 1 44 27 30 21.
E-mail address: david.jacquemart@upmc.fr (D. Jacquemart).

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calculated self-broadening coefficients are compared to the previously set of measured coefficients [3] as a means for testing the theoretical model as well as the intermolecular potential used.

The general formulation of the semiclassical formalism and the energy potential considered are presented in Section 2. The theoretical results are displayed and compared to the experimental measurements [3] in Section 3. Discussions on the isotopic species, the type of sub-branch and the electrostatic interactions considered, are also presented there. Finally, a complete calculation of the self-broadening coefficients is proposed as supplementary data for databases.

2. General formulation for the calculation of the self-broadening coefficients

The broadening coefficients of CH_3Br are calculated in the frame of the semiclassical Anderson–Tsao–Curnutte theory [5], which was subsequently developed and applied to the interactions between a symmetric top and a linear molecule [7], and between two symmetric top molecules [4]. This theory is based on binary collisions, the impact approximation and assumes that the interacting molecules follow classical trajectories while their internal degrees of freedom are treated with quantum mechanics. Within this model, the collisional half-width γ_{if} of an isolated self- (pressure) broadened $i \rightarrow f$ line $(v_iJiK_i \rightarrow v_fJ_fK_f)$ may be expressed as

$$\gamma_{if} = \frac{n_2\overline{v}}{2\pi c}\sum_{J_2}\sum_{K_2=0}^{J_2}\rho_{J_2K_2}\int_0^{\infty}2\pi b S_{if}(b,J_2,K_2)\,db, \tag{1}$$

where n_2 is the number density of the perturbing molecules, $\overline{v}$ is the mean relative speed, $\rho_{J_2K_2}$ is the relative population of the perturber in the $|J_2,K_2,v_2=0\rangle$ state, S_{if} is the differential cross-section representing the collisional efficiency, and b is the impact parameter. For a rigid symmetric-top molecule, $\rho_{J_2K_2}$ is given by

$$\rho_{J_2K_2} = \frac{2J_2+1}{Q_r}f(K_2)\exp\left\{-\frac{hc}{k_BT}[B_0J_2(J_2+1)+(A_0-B_0)K_2^2]\right\}, \tag{2}$$

where k_B is the Boltzmann constant, A_0 and B_0 are the rotational constants for the fundamental vibrational state, $f(K_2)$ is a nuclear spin factor (1 for K_2=0,1,2,4,… and 2 for K_2=3,6,…) and Q_r the rotational partition function is evaluated from

$$\sum_{J_2=0}^{J_{2\max}}\sum_{K_2=0}^{K_{2\max}}\rho_{J_2K_2} = 1. \tag{3}$$

In our calculations, we have considered $J_{2\max}=70$, $K_{2\max}=J_2$ if $J_2 \leq 15$ and $K_{2\max}=15$ if $J_2 > 15$. By neglecting any imaginary parts in S_{if} and any contribution arising from the isotropic part of the potential, the differential cross-section is given by Leavitt and Korff [8]

$$S_{if}(b,J_2,K_2) = 1-\exp[-(S_{2,i}^{outer}+S_{2,f}^{outer}+S_2^{middle})], \tag{4}$$

where $S_{2,i}^{outer}$, $S_{2,f}^{outer}$ and S_2^{middle} are the second-order terms of the perturbation development of S_{if} derived from the anisotropic part V_{aniso} of the intermolecular potential [5]. Note that this exponential form is very close to that proposed by Robert and Bonamy [6]. For V_{aniso} we have considered in addition to the electrostatic dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interactions [5], the main induction and dispersion contributions obtained by Leavitt [9,10] such as

$$V_{aniso} = V_{\mu_1\mu_2}+V_{\mu_1Q_2}+V_{Q_1\mu_2}+V_{Q_1Q_2}+V_{\mu_1^2\alpha_2}+V_{\mu_2^2\alpha_1\gamma_1}+V_{\alpha_1\gamma_1\alpha_2}, \tag{5}$$

where the index 1 refers to the absorber and 2 to the perturber, μ and Q are the dipole and quadrupole moments of the molecules, α is the average polarizability $[\alpha=(\alpha_{||}+2\alpha_{\perp})/3]$ of CH_3Br and γ here represents its dimensionless polarizability anisotropy $[\gamma=(\alpha_{||}-\alpha_{\perp})/3\alpha]$. The dispersion potential $V_{\alpha_1\gamma_1\alpha_2}$ is given in terms of $\overline{U}=U_1U_2/(U_1+U_2)$, where U_1 and U_2 are the first ionization energies of molecules 1 and 2 [9]. The strength of the dispersion energy is generally underestimated from the ionization energies and has been revaluated, as proposed by Giraud et al. [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; such a procedure leads to a dispersion energy about twice greater.

The trajectory model [12] includes the influence of the isotropic potential taken as the LJ (6–12) potential, in energy conservation and in the equation of motion around the distance of closest approaches r_c. The actual trajectory is replaced by an equivalent straight-line trajectory described at the velocity v_c'. Since the dipole–dipole long range interaction is predominant in this case, this model is close to the straight-path trajectory with constant relative velocity $\overline{v}$, as used in the ATC theory. The equivalent impact parameter b_0 for which $S_2(b_0)=1$ (Anderson cut-off) increases here from ≈ 8.5 Å for J=5 to ≈ 14.8 Å for J=20 and then decreases up to ≈ 6.8 Å for J=60. The LJ parameters ε and σ of CH_3Br have been calculated, as in [13], by fitting five values of the second virial coefficients $B(T)$ in the temperature range 287.8–321.1 K [14]. The resulting parameters are ε/k_B=441.9 K and σ=3.939 Å.

The values used for the rotational constants of the absorber ($CH_3{}^{79}Br$ or $CH_3{}^{81}Br$) in the ν_6 and fundamental bands, the dipole and quadrupole moments of the molecules, the LJ parameters, the average polarizability and the dimensionless polarizability anisotropy of CH_3Br are given in the Table 1.

The contributions to S_2 include, through the Clebsch–Gordan coefficients, the quantum number K_i and K_f with $K_f=K_i \pm 1$ for the perpendicular ν_6 bands of CH_3Br. For the transitions induced by collisions in the initial and final states, we have only considered $\Delta K=0$ for the absorber, associated with the usual selection rules $\Delta J=0$, ± 1 for a dipolar transition and $\Delta J=0$, ± 1, ± 2 for a quadrupolar transition. It should be noted that the broadening coefficients for A-type transitions are calculated the same way as for E-type transitions, i.e., we ignore the A_1-A_2 doublet splitting in transitions with K=3, 6, 9.