# Theoretical calculations of self-broadening coefficients in the nu6 band of CH3Br

Laura Gomez, David Jacquemart, Jean-Pierre Bouanich, Zouhaier Boussetta, Hassen Aroui

# Theoretical calculations of self-broadening coefficients in the $\nu_6$ 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] *Laboratoire de Photophysique Moléculaire, UPR3361 du CNRS, Université de Paris-Sud, Bâtiment 350, 91405 Orsay cedex, France*

[d] *Laboratoire de Physique Moléculaire, Ecole Supérieure des Sciences et Techniques de Tunis, 5 Av Taha Hussein 1008 Tunis, Tunisia.*

Received 2009

Manuscript pages: 22

Figures: 5

Tables: 3

[*] Corresponding author. Tel.: + 33-1-44-27-36-82; fax: + 33-1-44-27-30-21.

*E-mail address*: david.jacquemart@upmc.fr (D. Jacquemart).

**Abstract**

A semiclassical impact theory based upon the Anderson-Tsao-Curnutte formalism has been used to calculate the self-broadening coefficients in the ${}^{P}P$-, ${}^{P}Q$-, ${}^{P}R$-, ${}^{R}P$-, ${}^{R}Q$- and ${}^{R}R$-branches of the $\nu_6$ 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 [*J. Quant. Spectrosc. Radiat. Transfer* **105** (2007) 264]. 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.

*Keywords:* Methyl bromide; Self-broadening coefficients; Semiclassical formalism; Databases

## 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 $\nu_6$ 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 $\nu_6$ band at 10 μm. Such a calculation for interactions of symmetric-top molecules was first applied to the $\nu_3$ 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 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 $\gamma_{if}$ of an isolated self- (pressure) broadened $i \rightarrow f$ line ($v_i J_i K_i \rightarrow v_f J_f K_f$) may be expressed as

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

where $n_2$ is the number density of the perturbing molecules, $\bar{v}$ is the mean relative speed, $\rho_{J_2 K_2}$ 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, $\rho_{J_2 K_2}$ is given by

$$\rho_{J_2 K_2} = \frac{2J_2 + 1}{Q_r} f(K_2) \exp\left\{ -\frac{hc}{k_\mathrm{B} T} \left[ B_0 J_2 (J_2 + 1) + (A_0 - B_0) K_2{}^2 \right] \right\}, \qquad (2)$$

where $k_\mathrm{B}$ 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

$$\sum_{J_2=0}^{J_{2\max}} \sum_{K_2=0}^{K_{2\max}} \rho_{J_2 K_2} = 1 \, . \qquad (3)$$

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]

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

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 $V_\mathrm{aniso}$ of the intermolecular potential [5]. Note that this exponential form is very close to that proposed by Robert and Bonamy [6]. For $V_\mathrm{aniso}$ 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

$$V_{aniso} = V_{\mu_1 \mu_2} + V_{\mu_1 Q_2} + V_{Q_1 \mu_2} + V_{Q_1 Q_2} + V_{\mu_1^2 \alpha_2} + V_{\mu_2^2 \alpha_1 \gamma_1} + V_{\alpha_1 \gamma_1 \alpha_2} \, , \qquad (5)$$

where the index 1 refers to the absorber and 2 to the perturber, $\mu$ and $Q$ are the dipole and quadrupole moments of the molecules, $\alpha$ is the average polarizability [$\alpha = (\alpha_{//} + 2\alpha_\perp)/3$] of $CH_3Br$ and $\gamma$ here represents its dimensionless polarizability anisotropy [$\gamma = (\alpha_{//} - \alpha_\perp)/3\alpha$].

The dis persion potential $V_{\alpha_1\gamma_1\alpha_2}$ is 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 [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 $\varepsilon/k_B$ = 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 $\nu_6$ 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 $\nu_6$ 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 $\Delta J = 0, \pm 1$ for a dipolar transition and $\Delta J = 0, \pm 1, \pm 2$ 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.

## 3. Results and comparison with experimental data

The self-broadening coefficients $\gamma_0$ (in $cm^{-1}$ $atm^{-1}$) have been calculated at 296 K for transitions in the ${}^PP$-, ${}^PQ$-, ${}^PR$-, ${}^RP$-, ${}^RQ$-, and ${}^RR$-branches of the $\nu_6$ bands of $CH_3{}^{79}Br$ and

$CH_3{}^{81}Br$. The notation $^{P}Q$ corresponds to a $P$ branch for $K$ ($\Delta K=K'-K''=-1$) and to a $Q$ branch for $J$ ($\Delta J = J'-J''= 0$). In the following text, the notations $J$ and $K$ have been used for the quantum numbers $J''$ and $K''$ of the lower state of the transitions. We have considered separately the perturbers $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$ and the broadening coefficients for each isotopic species have been derived from

$$\begin{aligned}\gamma_0(\mathrm{CH_3}{}^{79}\mathrm{Br}) &= 0.5054\,\gamma_0(\mathrm{CH_3}{}^{79}\mathrm{Br\text{-}CH_3}{}^{79}\mathrm{Br}) + 0.4946\,\gamma_0(\mathrm{CH_3}{}^{79}\mathrm{Br\text{-}CH_3}{}^{81}\mathrm{Br}) \\ \gamma_0(\mathrm{CH_3}{}^{81}\mathrm{Br}) &= 0.5054\,\gamma_0(\mathrm{CH_3}{}^{81}\mathrm{Br\text{-}CH_3}{}^{79}\mathrm{Br}) + 0.4946\,\gamma_0(\mathrm{CH_3}{}^{81}\mathrm{Br\text{-}CH_3}{}^{81}\mathrm{Br})\end{aligned}, \qquad (6)$$

where 0.5054 and 0.4946 are the natural abundances of $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$, respectively. As is generally the case for interactions between molecules like OCS [19], $CH_3Cl$ [4], ClCN [20] and $CH_3F$ [21] with strong dipole and/or quadrupole moments, the theoretical results for $\gamma_0(\mathrm{CH_3}{}^{79}\mathrm{Br})$ as well as for $\gamma_0(\mathrm{CH_3}{}^{81}\mathrm{Br})$ are larger than the measurements though their $J$-dependences are similar (see Fig. 1 for the case of the $^{R}R(K=6)$ transitions). 'The results presented here are overestimated, especially for middle $J$ values where the broadening coefficient is largest. The induction and dispersion potential considered in Eq. (5) provides a negligible contribution to $\gamma_0$, except for a slight increase for small $J$ values with $K$ close or equal to $J$ (about 0.05% for $\gamma_0(J=2,K=0)$ and 0.25% for $\gamma_0(J=2,K=2)$ in $^{R}R$ sub-branch). Note that the dispersion energy is not well known and could be several times larger than that considered [22]. As shown in Fig. 1 the main contribution arises from the dipole-dipole interaction, but the quadrupole moment provides a significant contribution, especially for high $J$ transitions.

### 3.1. Effect of the impact parameter limit on the broadening coefficients

The disagreement between calculations and measurements probably arises from the great interaction distances ($b$ > 50 Å) in the integral of Eq. (1) because of the strong dipole-dipole contribution to $S_2(b)$. For such large impact parameters, the impact approximation in binary collisions may not be valid. To obtain a good agreement between the theoretical results and the experimental values given in [3], we have, as in Refs. [20, 21], calculated the integral over $r_c$ from $r_c(b = 0)$ to an arbitrary limit of $r_{c(lim)}$ instead of the infinite. The effects of the choice of different $r_{c(lim)}$ or $b_{lim}$ values (for large $r_c$ values, $b \approx r_c$) are displayed in Fig. 2 for transitions with $K$=1 and 9. The convergence of the calculation is obtained from $r_{c(lim)}$ □ 100 Å for the most pressure-broadened lines ($J \approx 20$). The $r_{c(lim)}$ value equal to 29 Å is quite empirical and has been chosen in order to better match the experimental measurements obtained in [3]. The differences between the results derived from $r_{c(lim)}$ = 29 Å and the results obtained from the convergence (around 100 Å) can reach 15% for $J$ values around 20. As it can be seen in Fig. 2 these differences are greater for middle $J$ values, for which the broadenings are the largest. The agreement between theoretical results with $r_{c(\lim)}$ = 29 Å with experimental data is then satisfactory (Fig. 3), in view of the estimated accuracy on the experimental data. As presented in Fig. 10 of [3], the scattering of the experimental measurements is quite important (around 5% in average, but can achieve 10%). We have done several tests to check that this experimental dispersion is not due to the isotopic dependence, to the various sub-branches or to the $K$-dependence of the broadenings.

3.2. Isotopic dependence of the broadenings

The calculation performed for both isotopic species shows that the self-broadening coefficients are practically the same for high $J$ transitions and slightly larger for $CH_3{}^{79}Br$ and $J$ < 35 (average difference = 0.3%). This result is in agreement with the experimental data [3], where the differences between the broadenings of each isotopic species are quite insignificant. A sample of the theoretical results for $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$ is given in Table 2 for the $^{R}R$ sub-branch.

3.3. Sub-branch- and $K$-dependencies of the broadenings

For transitions with same $J$, samples of theoretical results of $\gamma_0$ for different sub-branches are presented in Fig. 4 as decreasing curves with increasing $K$ values. This decrease of $\gamma_0$ is much more significant at low and middle $J$ values than at high $J$ values for which $\gamma_0$ is nearly constant. An approximate formula given by Birnbaum [23] for dipole-dipole and dipole-quadrupole interactions predicts a $K$-dependence of the broadenings involving the factor $1-[K/(J+1)]^2$. This factor lead to decreasing $\gamma_0$ values as $K$ rises from 0 to $J$, especially for low $J$ values, in agreement with theoretical and experimental results. However the slopes of these decreases for a given $J$, obtained by $[K/(J+1)]^2$, are at least twice greater than those derived from the ratios $[\gamma_0(K=0,J)-\gamma_0(K,J))/\gamma_0(0,J)]$. Therefore this simple factor cannot accurately predict the variation of $\gamma_0$ with $K$ for the lines belonging to a same $J$ transition.

A sample of theoretical results of $\gamma_0(CH_3{}^{79}Br)$ is presented in Table 3 for the various sub-branches, the differences between these results can reach 10 to 20% for $K$ close or equal to $J$. The number and the accuracy of the experimental values [3] in each sub-branch are not sufficient to validate the theoretical dependences of the self-broadening coefficients in the various sub-branches. In view of the important scattering of the experimental data, neither the isotopic dependence nor the sub-branches dependence of the theoretical calculation can be observed. However, the global rotational $J$ and $K$ dependencies of the previous measurements [3] are in good agreement with the theoretical results.

### 3.4. Comparison with experimental data

Since no sub-branch and isotopic dependences have been observed in the measurements, the theoretical results obtained for the $^{R}R$ sub-branch of $CH_3{}^{79}Br$ have been compared in Fig. 5 to all experimental results of [3]. In view of the experimental dispersion, the calculation performed for the various sub-branches of $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$ closely reproduces the measured values. It should be noted that the curves $\gamma_0$ vs $J$ present a discontinuity for $J = K$, especially for $J$ and $K$ =1 to 4, for which the calculated results appear to be very weak. Although we have no experimental data for these lines, theoretical results of $CH_3D$-$H_2$ [24] and $PH_3$-$N_2$ [25] were found to be significantly smaller for lines with $K = J$ than experimental results, the discrepancy has been explained by the assumption to consider only $\Delta K = 0$ collision-induced transitions. The figure 5 is directly comparable with Fig. 10 of [3] in which the experimental measurements have been put side by side with the results derived from empirical polynomials expansions. Both calculations match the experimental data set, the major differences between the theoretical calculation and the empirical one arise from low $J$ and $K$ transitions as well as high $J$ transitions for which no measurements have been performed. Except for low $J = K$ transitions for which the results could be underestimated, the calculations performed in this work are probably more accurate than the previous one, especially when measurements are not available. Moreover, for lines with high $J$ and $K$ values, the empirical calculation has been extrapolated using constant parameters and may not be valid, so that the theoretical calculation should be much more accurate for these lines.

The theoretical results of self-broadening coefficients calculated with $r_{c(\lim)}$ = 29 Å for each sub-branch ($^{P}P$, $^{R}R$, $^{P}R$, $^{R}P$, $^{P}Q$ and $^{R}Q$) in the $\nu_6$ band of $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$ are given as supplementary material for this paper. Note that the self-broadening coefficients included in the HITRAN [26] and GEISA [27] databases come from the results of the polynomial expansions fitting the data of [3]. The differences between the present results and those derived from the polynomials given in [3] can achieve 10%. Since the vibrational dependence of these broadening coefficients are estimated to be very small (in our calculation they depend only on the spectroscopic constants used for $CH_3Br$), the present results may be considered for any fundamental band of $CH_3Br$.

## 4. Conclusion

We have calculated self-broadening coefficients at 296 K in the $\nu_6$ band of $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$ and compared them with the previous experimental measurements [3]. The calculations were performed from a semiclassical model involving the main electrostatic interactions for the anisotropic potential. The values of the potential parameters were taken from sources available in the literature and were not adjusted to fit any data. As often occurs for strongly polar molecules, the calculations overestimate the broadening coefficients. By arbitrarily limiting the integration of the differential cross-section to impact parameters up to 29 Å, we have obtained satisfactory results and *J* and *K* dependencies in rather good agreement with measurements. Other subtle differences in the theoretical results, such as the broadening dependences with the sub-branch type or the isotopic species have been pointed out but they are not observable from the scattered experimental data.

## REFERENCES

[1] G. Graner, J. Mol. Spectrosc. 90 (1981) 394-438.

[2] E. Brunetaud, I. Kleiner, N. Lacome, J. Mol. Spectrosc. 216 (2002) 30-47.

[3] D. Jacquemart, F. Kwabia Tchana, N. Lacome, I. Kleiner, J. Quant. Spectrosc. Radiat. Transfer 105 (2007) 264-302.

[4] G. Blanquet, J. Walrand, J.C. Populaire, J.P. Bouanich, J. Quant. Spectrosc. Radiat. Transfer 53 (1995) 211-219.

[5] C.J. Tsao, B. Curnutte, J. Quant. Spectrosc. Radiat. Transfer 2 (1962) 41-91.

[6] D. Robert and J. Bonamy, J. Phys. (Paris) 40 (1979) 923.

[7] J.P. Bouanich, G. Blanquet, J. Walrand, J. Mol. Spectrosc. 161 (1993) 416-426.

[8] R.P. Leavitt, D. Korff, J. Chem. Phys. 74 (1981) 2180-2188.

[9] R.P. Leavitt, J. Chem. Phys. 72 (1980) 3472-3482.

[10] R.P. Leavitt, J. Chem. Phys. 73 (1980) 5432-5450.

[11] M. Giraud, D. Robert, L. Galatry, J. Chem. Phys. 53 (1970) 352-359.

[12] J. Bonamy, L. Bonamy, D. Robert, J. Chem. Phys. 67 (1977) 4441-4453.

[13] J.P. Bouanich, J. Quant. Spectrosc. Radiat. Transfer 47 (1992) 243-250.

[14] J.H. Dymond, E.B. Smith, The Virial Coefficients of Pure Gases and Mixtures, Oxford Univ. Press, Oxford, 1980.

[15] E. Brunetaud, I. Kleiner, N. Lacome, J. Mol. Spectrosc. 216 (2002) 30-47.

[16] S. Carocci, P. Minguzzi, M. Tonelli, A. Di Lieto, J. Mol. Spectrosc. 160 (1993) 359-370.

[17] S.V. Khristenko, A.I. Maslov, V.P. Shevelko, Molecules and their spectroscopic properties, Springer-Verlag, Berlin, 1998.

[18] C.G. Gray, K.E. Gubbins, Theory of Molecular Fluids, Oxford Univ. Press, New York, 1984.

[19] J.P. Bouanich, G. Blanquet, J. Walrand, C.P. Courtoy, J. Quant. Spectrosc. Radiat. Transfer 36 (1986) 295-306.

[20] G. Blanquet, J. Walrand, J.P. Bouanich, M. Lepère, J. Mol. Spectrosc. 206 (2001) 143-149.

[21] C. Lerot, G. Blanquet, J.P. Bouanich, J. Walrand, M. Lepère, J. Mol. Spectrosc. 230 (2005) 153-160.

[22] D. Lambot, A. Olivier, G. Blanquet, J. Walrand, J.P. Bouanich, J. Quant. Spectrosc. Radiat. Transfer 45 (1991) 145-155.

[23] G. Birnbaum, Adv. Chem. Phys. 12 (1967) 487-548.

[24] C. Lerot, J. Walrand, G. Blanquet, J.P. Bouanich, M. Lepère, J. Mol. Spectrosc. 217 (2003) 79-86.

[25] J.P. Bouanich, J. Walrand, G. Blanquet, J. Mol. Spectrosc. 232 (2005) 40-46.

[26] L.S. Rothman, I.E. Gordon, A. Barbe, D.Chris Benner, P.F. Bernath, M. Birk, L.R. Brown, V. Boudon, J.-P. Champion, K. Chance, L.H. Coudert, V. Dana, S. Fally, J.-M. Flaud, R.R. Gamache, A. Goldman, D. Jacquemart, N. Lacome, J.-Y. Mandin, S.T. Massie, S. Mikhailenko, J. Orphal, V. Perevalov, A. Perrin, C.P. Rinsland, M. Šimečková, M.A.H. Smith, S. Tashkun, J. Tennyson, R.A. Toth, A.C. Vandaele, J. Vander Auwera. The Hitran 2008 Molecular Spectroscopic Database, J. Quant. Spectrosc. Radiat. Transfer 110,533-572 (2009).

[27] N. Jacquinet-Husson, N.A. Scott, A. Chédin, L. Crépeau, R. Armanta, V. Capelle, J. Orphal, A. Coustenis, C. Boone, N. Poulet-Crovisier, A. Barbe, M. Birk, L.R. Brown, C. Camy- Peyret, C. Claveau, K. Chance, N. Christidis, C. Clerbeaux, P.F. Coheur, V. Dana, L. Daumont, M.R. Debacker-Barilly, G. Di Lonardo, J.M. Flaud, A. Goldman, A. Hamdouni, Mikhailenko, M. Hess, M.D. Hurley, D. Jacquemart, I. Kleiner, P. Köpke, J.Y. Mandin, S. Massie, V. Nemtchinov, A. Nikitin, D. Newnham, A. Perrin, V.I. Perevalov, S. Pinnock, L. Régalia-Jarlot, C.P. Rinsland, A. Rublev, F. Shreier, L. Schult, K.M. Smith, S.A. Tashkun, J.L. Teffo, R.A. Toth, Vl.G. Tyuterev, J. Vander Auwera, P. Varanasi, G. Wagner. THE

GEISA SPECTROSCOPIC DATABASE: Current and future archive for Earth and planetary atmosphere studies, J. Quant. Spectrosc. Radiat. Transfer 109,1043-1059 (2008).

**Captions of tables**

Table 1. Molecular parameters for $CH_3Br$ used in the calculations.

Table 2: Sample of calculated results for $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$ broadening coefficients $\gamma_0$ (cm$^{-1}$ atm$^{-1}$) by $CH_3Br$ in the ${}^{R}R$ sub-branch of the $\nu_6$ band with $r_{c(\lim)}$ = 29 Å.

Table 3: Sample of calculated results for $CH_3{}^{79}Br$ broadening coefficients $\gamma_0$ (cm$^{-1}$ atm$^{-1}$) in the various sub-branches of the $\nu_6$ band with $r_{c(\lim)}$ = 29 Å.

**Captions of figures**

Fig. 1. *J*-dependence of broadening coefficients $\gamma_0$ in the ${}^{R}R$ sub-branch of $CH_3{}^{79}Br$ with $K$=6. The two curves represent calculated results with no limitation of the impact parameter, the upper curve is derived from the total potential defined by Eq. (5) and the lower curve is only derived from the dipole-dipole interaction. The experimental results (solid squares) are extracted from Table 2 of [3].

Fig. 2. *J*-dependence of broadening coefficients $\gamma_0$ in the ${}^{P}P$ sub-branch of $CH_3{}^{79}Br$. The upper graph corresponds to results for $K$=1 and the lower graph to results for $K$=9. The curves, from the upper to the lower, represent calculated results obtained, respectively, with $r_{c(\lim)}$ =100, 50, 35, 29, and 25 Å. The experimental data (open squares) are extracted from Table 2 of [3] for any sub-branch with $K$=1 (upper graph) and $K$=9 (lower graph) of both isotopologues.

Fig. 3. Same legend as Fig. 1 but the calculation has been performed with a limited impact parameter $r_{c(\lim)}$ = 29 Å.

Fig. 4. *K*-dependence of broadening coefficients $\gamma_0$ of $CH_3{}^{79}Br$ in the different sub-branches for $J$= 6, 10, 20, and 40. The calculated results with $r_{c(\lim)}$ =29 Å are represented by lines and open symbols, whereas the experimental data (arising from [3] for both $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$) are represented by solid symbols. Circles are for the ${}^{R}R$ sub-branch, upside down triangles for ${}^{P}R$, diamonds for ${}^{R}P$, squares for ${}^{P}P$, triangles for ${}^{R}Q$, and stars for ${}^{P}Q$.

Fig. 5. *J*-dependence of broadening coefficients $\gamma_0$ for *K* ranging from 0 to 9. The calculation obtained for the $^{R}R$ sub-branch of $CH_3{}^{79}Br$ with $r_{c(\mathrm{lim})}$ = 29 Å is represented by lines whereas the solid squares represent all the experimental data of [3] for both isotopologues and all sub-branches.

Table 1. Molecular parameters for $CH_3Br$ used in the calculations.

| 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$^{-1}$) |
|---|---|---|---|---|---|---|
| $^{12}CH_3{}^{79}B$ | Ground | 5.180632 | 0.319160556 | 3.2932 | 4.2913 | 8.47 |
| | $\nu_6$ | 5.2101669 | 0.31802097 | 3.3060 | 4.3243 | 8.7832 |
| $^{12}CH_3{}^{81}B$ | Ground | 5.180615 | 0.317947638 | 3.2694 | 4.2640 | 8.48 |
| | $\nu_6$ | 5.2101408 | 0.3168128 | 3.2829 | 4.2961 | 8.7916 |

| Molecule | $M$(amu) | $\mu$(D) | $Q$(D.Å) | $\varepsilon/k_B$ (K) | $\sigma$(Å) | $\alpha$(Å$^3$) | $\gamma$ | $U$(eV) |
|---|---|---|---|---|---|---|---|---|
| $^{12}CH_3{}^{79}Br$ | 93.9414 | 1.82171 [a] | 3.55 [b] | 441.9 [c] | 3.939 [c] | 5.87 [b] | 0.115 [d] | 10.541 [b] |
| $^{12}CH_3{}^{81}Br$ | 95.9394 | 1.82185 [a] | 3.55 [b] | 441.9 [c] | 3.939 [c] | 5.87 [b] | 0.115 [d] | 10.541 [b] |

The spectroscopic parameters for $CH_3Br$ are taken from [15] for the ground state and from [3] for the $\nu_6$ state.
[a] [16]; [b] [17]; [c] this work; [d] [18].
<u>Note:</u> The dipole moments are in Debye (1D = $10^{-18}$ esu = $3.33564\times10^{-30}$ C m), the quadrupole moments in Debye Ångström (1D Å = $10^{-26}$ esu = $3.33564\times10^{-40}$ C m$^2$).

Table 2: Sample of calculated results for $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$ broadening coefficients $\gamma_0$ ($cm^{-1}$ $atm^{-1}$) by $CH_3Br$ in the ${}^RR$ sub-branch of the $\nu_6$ band with $r_{c(\mathrm{lim})}$ = 29 Å.

| ***J*** | ***K*** | **$\gamma_0(CH_3{}^{79}Br)$** | **$\gamma_0(CH_3{}^{81}Br)$** | ***J*** | ***K*** | **$\gamma_0(CH_3{}^{79}Br)$** | **$\gamma_0(CH_3{}^{81}Br)$** |
|---|---|---|---|---|---|---|---|
| 2 | 0 | 0.4016 | 0.4003 | 30 | 0 | 0.3858 | 0.3850 |
| 2 | 1 | 0.3727 | 0.3714 | 30 | 1 | 0.3855 | 0.3848 |
| 2 | 2 | 0.2850 | 0.2839 | 30 | 2 | 0.3852 | 0.3845 |
| | | | | 30 | 3 | 0.3846 | 0.3840 |
| 5 | 0 | 0.3610 | 0.3590 | 30 | 4 | 0.3840 | 0.3833 |
| 5 | 1 | 0.3558 | 0.3537 | 30 | 5 | 0.3831 | 0.3824 |
| 5 | 2 | 0.3448 | 0.3429 | 30 | 6 | 0.3821 | 0.3814 |
| 5 | 3 | 0.3260 | 0.3242 | 30 | 7 | 0.3808 | 0.3802 |
| 5 | 4 | 0.2937 | 0.2921 | 30 | 8 | 0.3794 | 0.3787 |
| 5 | 5 | 0.2256 | 0.2244 | 30 | 9 | 0.3778 | 0.3771 |
| | | | | 30 | 10 | 0.3759 | 0.3753 |
| 10 | 0 | 0.4144 | 0.4115 | | | | |
| 10 | 1 | 0.4125 | 0.4097 | 40 | 0 | 0.2581 | 0.2583 |
| 10 | 2 | 0.4088 | 0.4060 | 40 | 1 | 0.2580 | 0.2582 |
| 10 | 3 | 0.4032 | 0.4004 | 40 | 2 | 0.2579 | 0.2581 |
| 10 | 4 | 0.3953 | 0.3926 | 40 | 3 | 0.2577 | 0.2579 |
| 10 | 5 | 0.3847 | 0.3820 | 40 | 4 | 0.2575 | 0.2577 |
| 10 | 6 | 0.3706 | 0.3681 | 40 | 5 | 0.2572 | 0.2575 |
| 10 | 7 | 0.3519 | 0.3496 | 40 | 6 | 0.2569 | 0.2571 |
| 10 | 8 | 0.3259 | 0.3237 | 40 | 7 | 0.2565 | 0.2568 |
| 10 | 9 | 0.2868 | 0.2850 | 40 | 8 | 0.2561 | 0.2564 |
| 10 | 10 | 0.2123 | 0.2111 | 40 | 9 | 0.2557 | 0.2559 |
| | | | | 40 | 10 | 0.2552 | 0.2554 |
| 15 | 0 | 0.4737 | 0.4708 | | | | |
| 15 | 1 | 0.4726 | 0.4697 | 50 | 0 | 0.1705 | 0.1708 |
| 15 | 2 | 0.4706 | 0.4677 | 50 | 1 | 0.1705 | 0.1707 |
| 15 | 3 | 0.4676 | 0.4647 | 50 | 2 | 0.1705 | 0.1707 |
| 15 | 4 | 0.4635 | 0.4607 | 50 | 3 | 0.1704 | 0.1706 |
| 15 | 5 | 0.4582 | 0.4554 | 50 | 4 | 0.1703 | 0.1706 |
| 15 | 6 | 0.4516 | 0.4488 | 50 | 5 | 0.1702 | 0.1705 |
| 15 | 7 | 0.4434 | 0.4407 | 50 | 6 | 0.1702 | 0.1704 |
| 15 | 8 | 0.4335 | 0.4309 | 50 | 7 | 0.1701 | 0.1703 |
| 15 | 9 | 0.4215 | 0.4190 | 50 | 8 | 0.1699 | 0.1702 |
| 15 | 10 | 0.4068 | 0.4044 | 50 | 9 | 0.1698 | 0.1701 |
| | | | | 50 | 10 | 0.1697 | 0.1699 |
| 20 | 0 | 0.4816 | 0.4792 | | | | |
| 20 | 1 | 0.4810 | 0.4786 | 60 | 0 | 0.1255 | 0.1255 |
| 20 | 2 | 0.4798 | 0.4775 | 60 | 1 | 0.1254 | 0.1254 |
| 20 | 3 | 0.4782 | 0.4758 | 60 | 2 | 0.1254 | 0.1254 |
| 20 | 4 | 0.4759 | 0.4736 | 60 | 3 | 0.1254 | 0.1254 |
| 20 | 5 | 0.4731 | 0.4708 | 60 | 4 | 0.1254 | 0.1254 |
| 20 | 6 | 0.4696 | 0.4673 | 60 | 5 | 0.1253 | 0.1253 |
| 20 | 7 | 0.4653 | 0.4631 | 60 | 6 | 0.1253 | 0.1253 |
| 20 | 8 | 0.4604 | 0.4581 | 60 | 7 | 0.1253 | 0.1253 |
| 20 | 9 | 0.4545 | 0.4523 | 60 | 8 | 0.1252 | 0.1252 |
| 20 | 10 | 0.4477 | 0.4455 | 60 | 9 | 0.1252 | 0.1252 |
| | | | | 60 | 10 | 0.1252 | 0.1252 |

Table 3: Sample of calculated results for $CH_3{}^{79}Br$ broadening coefficients $\gamma_0$ ($cm^{-1}$ $atm^{-1}$) in the various sub-branches of the $\nu_6$ band with $r_{c(\lim)}$ = 29 Å.

| *J* | *K* | $\gamma_0(^RR)$ | $\gamma_0(^PR)$ | $\gamma_0(^RP)$ | $\gamma_0(^PP)$ | $\gamma_0(^RQ)$ | $\gamma_0(^PQ)$ |
|---|---|---|---|---|---|---|---|
| 2 | 0 | 0.4016 | | 0.4152 | | 0.4110 | |
| 2 | 1 | 0.3727 | 0.4007 | | 0.4179 | 0.3706 | 0.4110 |
| 2 | 2 | 0.2850 | 0.3694 | | 0.3344 | | 0.3707 |
| 5 | 0 | 0.3610 | | 0.3672 | | 0.3611 | |
| 5 | 1 | 0.3558 | 0.3615 | 0.3601 | 0.3668 | 0.3555 | 0.3611 |
| 5 | 2 | 0.3448 | 0.3572 | 0.3435 | 0.3588 | 0.3431 | 0.3555 |
| 5 | 3 | 0.3260 | 0.3473 | 0.3114 | 0.3414 | 0.3207 | 0.3431 |
| 5 | 4 | 0.2937 | 0.3296 | | 0.3086 | 0.2786 | 0.3207 |
| 5 | 5 | 0.2256 | 0.2984 | | 0.2366 | | 0.2787 |
| 10 | 0 | 0.4144 | | 0.3996 | | 0.4057 | |
| 10 | 1 | 0.4125 | 0.4146 | 0.3979 | 0.3994 | 0.4039 | 0.4057 |
| 10 | 2 | 0.4088 | 0.4130 | 0.3940 | 0.3972 | 0.4002 | 0.4039 |
| 10 | 3 | 0.4032 | 0.4097 | 0.3879 | 0.3929 | 0.3944 | 0.4002 |
| 10 | 4 | 0.3953 | 0.4044 | 0.3792 | 0.3864 | 0.3862 | 0.3944 |
| 10 | 5 | 0.3847 | 0.3969 | 0.3670 | 0.3771 | 0.3749 | 0.3861 |
| 10 | 6 | 0.3706 | 0.3867 | 0.3502 | 0.3643 | 0.3597 | 0.3749 |
| 10 | 7 | 0.3519 | 0.3731 | 0.3265 | 0.3469 | 0.3390 | 0.3597 |
| 10 | 8 | 0.3259 | 0.3549 | 0.2901 | 0.3224 | 0.3091 | 0.3389 |
| 10 | 9 | 0.2868 | 0.3295 | | 0.2850 | 0.2602 | 0.3090 |
| 10 | 10 | 0.2123 | 0.2913 | | 0.2129 | | 0.2601 |
| 15 | 0 | 0.4737 | | 0.4660 | | 0.4685 | |
| 15 | 1 | 0.4726 | 0.4737 | 0.4650 | 0.4659 | 0.4676 | 0.4685 |
| 15 | 2 | 0.4706 | 0.4728 | 0.4628 | 0.4647 | 0.4655 | 0.4676 |
| 15 | 3 | 0.4676 | 0.4709 | 0.4596 | 0.4624 | 0.4625 | 0.4655 |
| 15 | 4 | 0.4635 | 0.4681 | 0.4551 | 0.4591 | 0.4583 | 0.4624 |
| 15 | 5 | 0.4582 | 0.4641 | 0.4492 | 0.4544 | 0.4528 | 0.4582 |
| 15 | 6 | 0.4516 | 0.4589 | 0.4418 | 0.4484 | 0.4458 | 0.4528 |
| 15 | 7 | 0.4434 | 0.4524 | 0.4327 | 0.4408 | 0.4373 | 0.4458 |
| 15 | 8 | 0.4335 | 0.4444 | 0.4213 | 0.4314 | 0.4268 | 0.4372 |
| 15 | 9 | 0.4215 | 0.4347 | 0.4074 | 0.4199 | 0.4140 | 0.4268 |
| 15 | 10 | 0.4068 | 0.4229 | 0.3899 | 0.4057 | 0.3981 | 0.4139 |
| 20 | 0 | 0.4816 | | 0.4846 | | 0.4815 | |
| 20 | 1 | 0.4810 | 0.4816 | 0.4840 | 0.4846 | 0.4809 | 0.4815 |
| 20 | 2 | 0.4798 | 0.4811 | 0.4829 | 0.4839 | 0.4798 | 0.4810 |
| 20 | 3 | 0.4782 | 0.4801 | 0.4811 | 0.4827 | 0.4782 | 0.4798 |
| 20 | 4 | 0.4759 | 0.4785 | 0.4786 | 0.4807 | 0.4759 | 0.4782 |
| 20 | 5 | 0.4731 | 0.4763 | 0.4755 | 0.4782 | 0.4730 | 0.4759 |
| 20 | 6 | 0.4696 | 0.4736 | 0.4716 | 0.4749 | 0.4694 | 0.4730 |
| 20 | 7 | 0.4653 | 0.4702 | 0.4669 | 0.4710 | 0.4650 | 0.4694 |
| 20 | 8 | 0.4604 | 0.4661 | 0.4613 | 0.4662 | 0.4598 | 0.4650 |
| 20 | 9 | 0.4545 | 0.4612 | 0.4547 | 0.4605 | 0.4537 | 0.4598 |
| 20 | 10 | 0.4477 | 0.4554 | 0.4469 | 0.4537 | 0.4464 | 0.4537 |
| 30 | 0 | 0.3858 | | 0.3994 | | 0.3910 | |
| 30 | 1 | 0.3855 | 0.3858 | 0.3993 | 0.3994 | 0.3909 | 0.3910 |
| 30 | 2 | 0.3852 | 0.3857 | 0.3989 | 0.3991 | 0.3905 | 0.3909 |
| 30 | 3 | 0.3846 | 0.3854 | 0.3984 | 0.3987 | 0.3900 | 0.3905 |
| 30 | 4 | 0.3840 | 0.3850 | 0.3978 | 0.3981 | 0.3894 | 0.3900 |
| 30 | 5 | 0.3831 | 0.3843 | 0.3969 | 0.3974 | 0.3885 | 0.3894 |
| 30 | 6 | 0.3821 | 0.3836 | 0.3958 | 0.3964 | 0.3875 | 0.3885 |
| 30 | 7 | 0.3808 | 0.3826 | 0.3945 | 0.3952 | 0.3863 | 0.3875 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 30 | 8 | 0.3794 | 0.3815 | 0.3929 | 0.3938 | 0.3848 | 0.3863 |
| 30 | 9 | 0.3778 | 0.3802 | 0.3912 | 0.3922 | 0.3832 | 0.3848 |
| 30 | 10 | 0.3759 | 0.3786 | 0.3892 | 0.3904 | 0.3813 | 0.3832 |
| | | | | | | | |
| 40 | 0 | 0.2581 | | 0.2701 | | 0.2631 | |
| 40 | 1 | 0.2580 | 0.2581 | 0.2701 | 0.2700 | 0.2631 | 0.2631 |
| 40 | 2 | 0.2579 | 0.2581 | 0.2700 | 0.2699 | 0.2631 | 0.2631 |
| 40 | 3 | 0.2577 | 0.2581 | 0.2699 | 0.2698 | 0.2630 | 0.2630 |
| 40 | 4 | 0.2575 | 0.2580 | 0.2697 | 0.2696 | 0.2629 | 0.2629 |
| 40 | 5 | 0.2572 | 0.2578 | 0.2695 | 0.2694 | 0.2627 | 0.2627 |
| 40 | 6 | 0.2569 | 0.2576 | 0.2692 | 0.2691 | 0.2624 | 0.2624 |
| 40 | 7 | 0.2565 | 0.2574 | 0.2689 | 0.2687 | 0.2622 | 0.2622 |
| 40 | 8 | 0.2561 | 0.2571 | 0.2685 | 0.2683 | 0.2618 | 0.2618 |
| 40 | 9 | 0.2557 | 0.2568 | 0.2681 | 0.2678 | 0.2614 | 0.2614 |
| 40 | 10 | 0.2552 | 0.2565 | 0.2676 | 0.2673 | 0.2610 | 0.2610 |
| | | | | | | | |
| 50 | 0 | 0.1705 | | 0.1774 | | 0.1736 | |
| 50 | 1 | 0.1705 | 0.1706 | 0.1775 | 0.1774 | 0.1736 | 0.1736 |
| 50 | 2 | 0.1705 | 0.1706 | 0.1775 | 0.1774 | 0.1735 | 0.1736 |
| 50 | 3 | 0.1704 | 0.1706 | 0.1775 | 0.1773 | 0.1735 | 0.1735 |
| 50 | 4 | 0.1703 | 0.1706 | 0.1774 | 0.1772 | 0.1735 | 0.1735 |
| 50 | 5 | 0.1702 | 0.1706 | 0.1774 | 0.1772 | 0.1734 | 0.1735 |
| 50 | 6 | 0.1702 | 0.1706 | 0.1774 | 0.1771 | 0.1733 | 0.1734 |
| 50 | 7 | 0.1701 | 0.1706 | 0.1773 | 0.1770 | 0.1733 | 0.1733 |
| 50 | 8 | 0.1699 | 0.1705 | 0.1773 | 0.1769 | 0.1732 | 0.1733 |
| 50 | 9 | 0.1698 | 0.1705 | 0.1772 | 0.1767 | 0.1731 | 0.1732 |
| 50 | 10 | 0.1697 | 0.1704 | 0.1771 | 0.1766 | 0.1730 | 0.1731 |
| | | | | | | | |
| 60 | 0 | 0.1255 | | 0.1288 | | 0.1270 | |
| 60 | 1 | 0.1254 | 0.1255 | 0.1288 | 0.1288 | 0.1270 | 0.1270 |
| 60 | 2 | 0.1254 | 0.1255 | 0.1289 | 0.1288 | 0.1270 | 0.1270 |
| 60 | 3 | 0.1254 | 0.1255 | 0.1289 | 0.1287 | 0.1270 | 0.1270 |
| 60 | 4 | 0.1254 | 0.1256 | 0.1289 | 0.1287 | 0.1270 | 0.1270 |
| 60 | 5 | 0.1253 | 0.1256 | 0.1289 | 0.1287 | 0.1270 | 0.1270 |
| 60 | 6 | 0.1253 | 0.1256 | 0.1289 | 0.1287 | 0.1270 | 0.1270 |
| 60 | 7 | 0.1253 | 0.1256 | 0.1289 | 0.1286 | 0.1270 | 0.1270 |
| 60 | 8 | 0.1252 | 0.1256 | 0.1289 | 0.1286 | 0.1269 | 0.1270 |
| 60 | 9 | 0.1252 | 0.1256 | 0.1289 | 0.1285 | 0.1269 | 0.1269 |
| 60 | 10 | 0.1252 | 0.1256 | 0.1289 | 0.1285 | 0.1269 | 0.1269 |

Fig. 1. $J$-dependence of broadening coefficients $\gamma_0$ in the $^{R}R$ sub-branch of $CH_3{}^{79}Br$ with $K$=6. The two curves represent calculated results with no limitation of the impact parameter, the upper curve is derived from the total potential defined by Eq. (5) and the lower curve is only derived from the dipole-dipole interaction. The experimental results (solid squares) are extracted from Table 2 of [3].

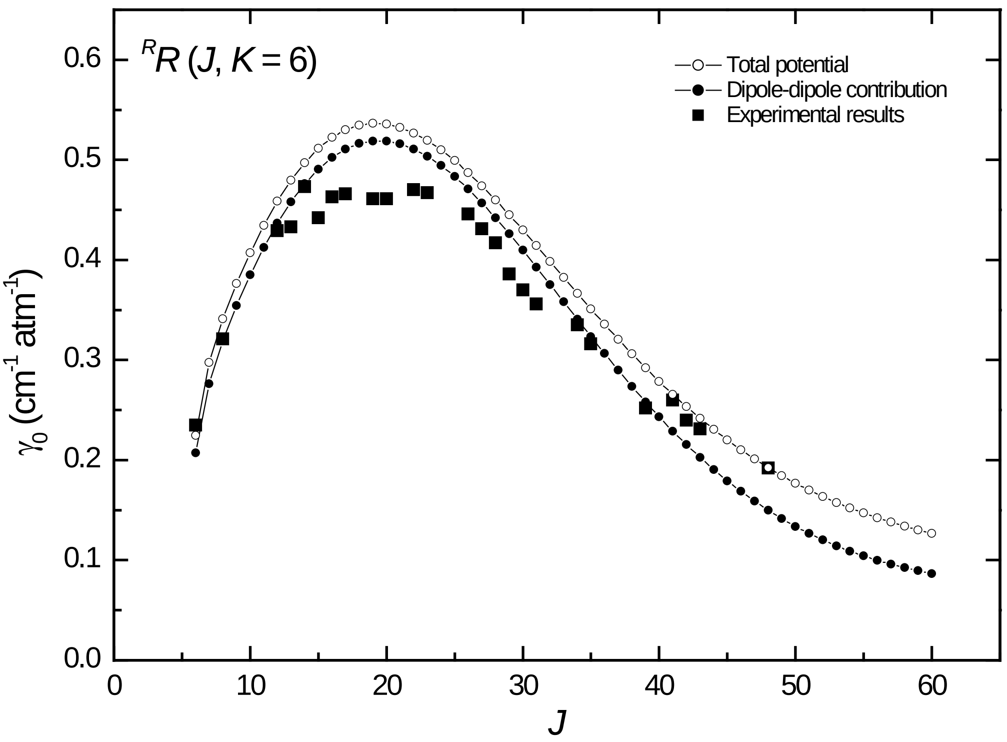


Fig. 2. . $J$-dependence of broadening coefficients $\gamma_0$ in the ${}^{P}P$ sub-branch of $CH_3{}^{79}Br$. The upper graph corresponds to results for $K$=1 and the lower graph to results for $K$=9. The curves, from the upper to the lower, represent calculated results obtained, respectively, with $r_{c(lim)}$ =100, 50, 35, 29, and 25 Å. The experimental data (open squares) are extracted from Table 2 of [3] for any sub-branch with $K$=1 (upper graph) and $K$=9 (lower graph) of both isotopologues.

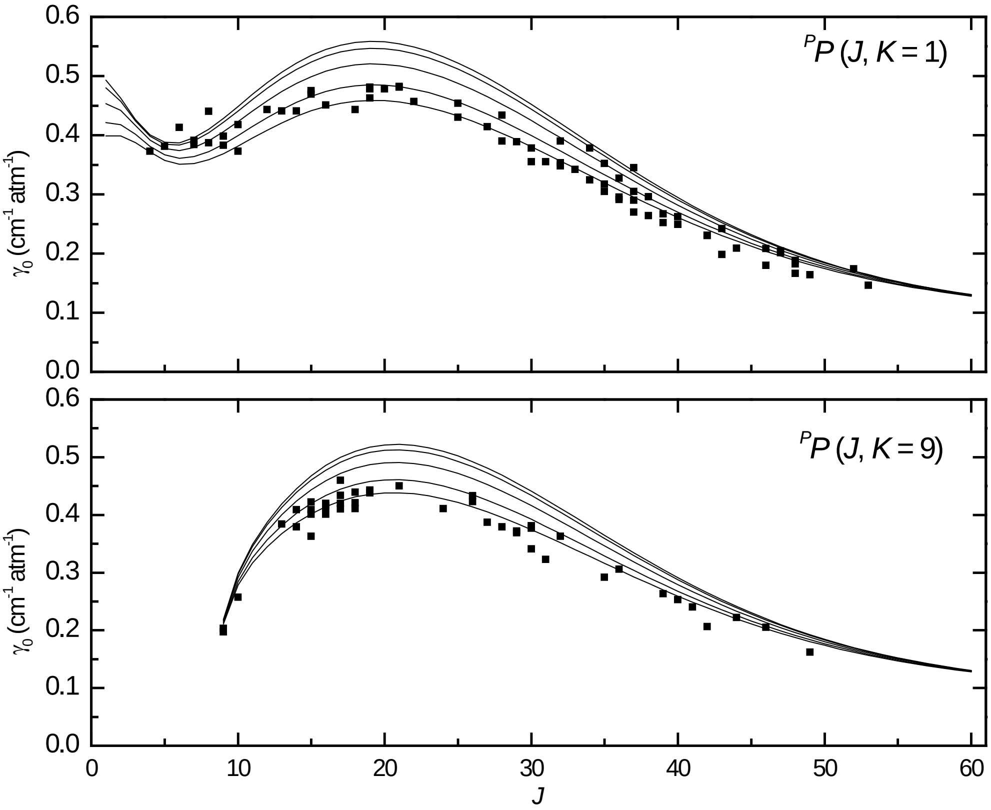


Fig. 3. Same legend as Fig. 1 but the calculation has been performed with a limited impact parameter $r_{c(\lim)}$ =29 Å.

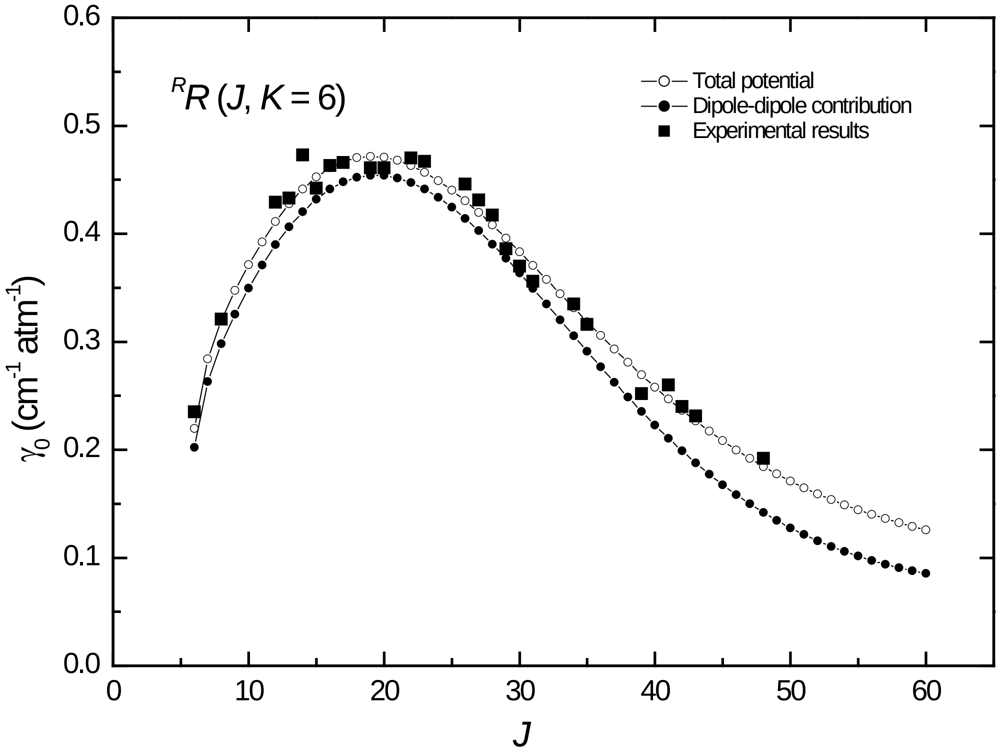


Fig. 4. *K*-dependence of broadening coefficients $\gamma_0$ of $CH_3{}^{79}Br$ in the different sub-branches for *J*= 6, 10, 20, and 40. The calculated results with $r_{c(\lim)}$ =29 Å are represented by lines and open symbols, whereas the experimental data (arising from [3] for both $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$) are represented by solid symbols. Circles are for the ${}^RR$ sub-branch, upside down triangles for ${}^PR$, diamonds for ${}^RP$, squares for ${}^PP$, triangles for ${}^RQ$, and stars for ${}^PQ$.

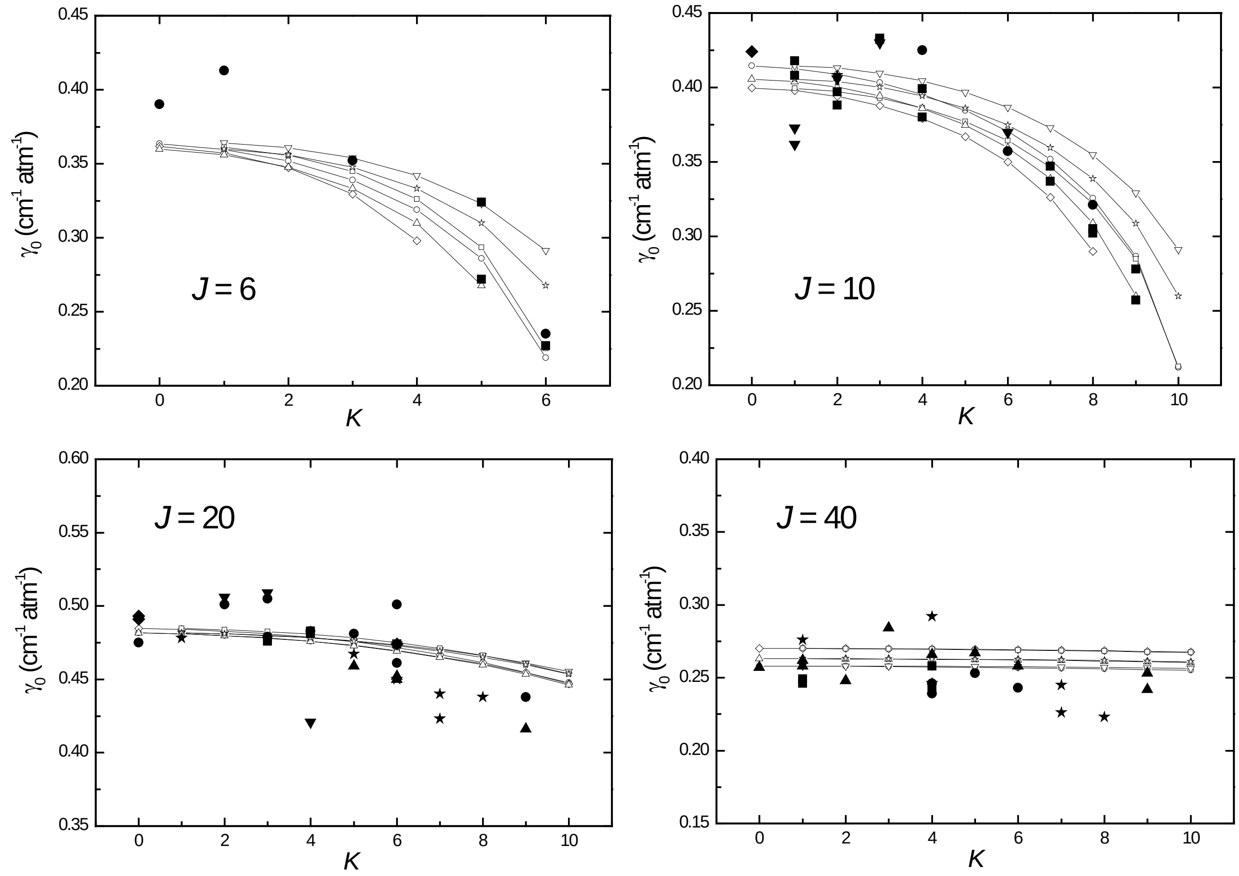
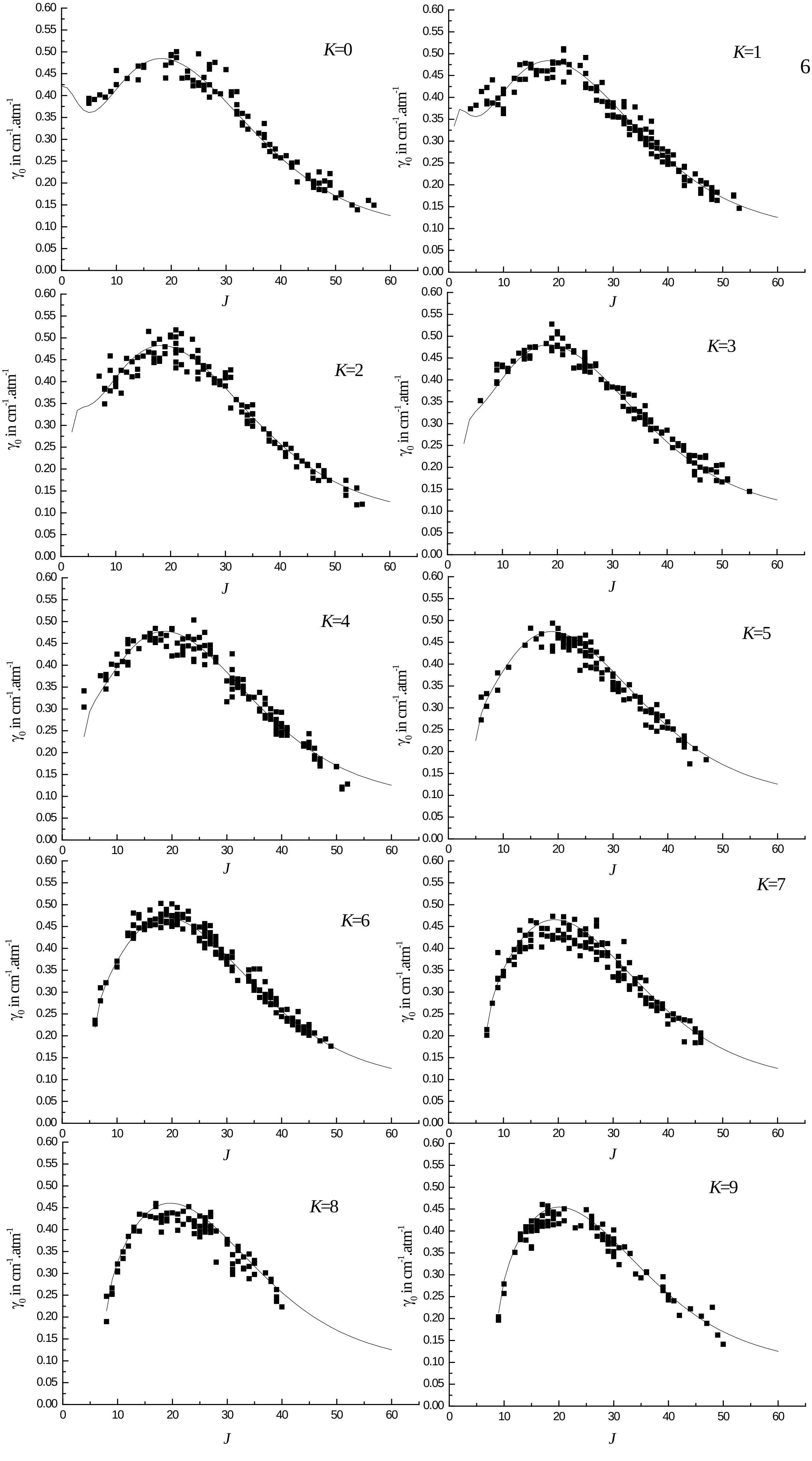


Fig. 5. $J$-dependence of broadening coefficients $\gamma_0$ for $K$ ranging from 0 to 9. The calculation obtained for the $^{R}R$ sub-branch of $CH_3{}^{79}Br$ with $r_{c(lim)}$ = 29 Å is represented by lines whereas the solid squares represent all the experimental data of [3] for both isotopologues and all sub-branches

6


K=0
K=1
K=2
K=3
K=4
K=5
K=6
K=7
K=8
K=9
γ0 in cm-1.atm-1
J
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0
10
20
30
40
50
60