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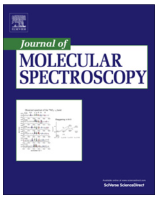

Calculated line broadening parameters for methane perturbed by diatomic molecules

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ABSTRACT

We report semiclassical line broadening calculations for methane perturbed by diatomic molecules: nitrogen, N_2, oxygen, O_2 and hydrogen, H_2, at room temperature. For this, we have developed a symmetrized version of the Robert and Bonamy theory. The interaction potential was built from electrostatic (octopole and hexadecapole for methane, quadrupole for the diatomic molecules) and atom–atom contributions. The relative (classical) trajectories of the molecules were computed in the frame of the usual parabolic model, through analytical formula. High orders of developments had to be used for the short range molecular interactions in the case of N_2 and O_2. For H_2, a lower order of development was found to be convenient. We have compared our calculations to some of the available experimental data for hydrogen and oxygen. For nitrogen, we have already reported some comparisons to measurements [T. Gabard, V. Boudon, J. Quant. Spectrosc. Radiat. Transfer 111 (2010) 1328–1343]. Thus, we report here new extensive calculations for the dyad (near 1300 cm^{-1}) and the pentad (near 3000 cm^{-1}) spectral regions.

1. Introduction

Methane is one of the major greenhouse gases on Earth. It is also found, for example, on other planetary atmospheres in the solar system. For the purpose of remote sensing or radiative transfer modeling, the absorption spectrum of methane must be known with great accuracy. Thus, many efforts are devoted to individual line-by-line medeling of methane in spectral regions that extend up to the visible. Recently, many results have been reported regarding line positions and intensities for various vibrational bands of methane [1–11]. Regarding line shape parameters and line broadenings, the literature dealing with theory is more sparse. On the contrary, the subject of infrared line shape studies for methane is extensively documented from an experimental point of view. Some of the most recent works dealt with measurements in the first five polyads of methane (ground vibrational state, dyad near 1300 cm^{-1}, pentad near 3000 cm^{-1}, octad near 4300 cm^{-1} and tetradecad near 6000 cm^{-1}) [12–30]. A review of earlier experimental studies may be found in Ref. [31]. Theoretical and/or experimental works on line-mixing (collisional interferences between spectral lines) have also been reported [32–42]. We note that the temperature dependencies of line shape parameters and/or line-mixing parameters could be determined in some of these studies.

This paper reports new results on collisional broadening coefficient calculations for methane perturbed by diatomic molecules. It extends our previous work on methane perturbed by nitrogen [43] to other perturbing species. We also did extended line broadening predictions for the methane–nitrogen couple. For this molecular pair, we are in a process of refining the interaction potential using recent ab initio results. We will describe the present status of these developments.

2. Theory

The mathematical background and the practical implementation of the calculations have been described in details in Ref. [43]. The main features of the theory are outlined below.

1. The theory is semiclassical. The internal degrees of freedom of the molecules are treated quantum mechanically. The ones describing the relative motions of the molecules are treated classically.
2. For what concerns methane, the theory is properly symmetrized according to the tetrahedral formalism [44–46], consistent with the theory used for infrared line position and intensity calculations.
3. The line broadening coefficient is obtained as an average over the rotational populations of the perturbing species and over the impact parameters of the collisions of the interruption function,

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$$\gamma_{fi} = \frac{1}{2\pi c} L \frac{T_0}{TP_0} \bar{v} \sum_{\{2\}} \rho_{\{2\}} \times \int_{r_{c_0}}^{\infty} 2\pi\, r_c\, dr_c \left(\frac{v'_c}{\bar{v}}\right)^2 \left[1 - \exp\left(-S_{2,fi,\{2\}}(r_c, \bar{v})\right)\right] \quad (1)$$

In this equation *i* and *f* are short notations that represent the sets of labels for the initial and final states of the transition. *c* is the speed of light. $L = 2.6867775 \times 10^{19}\ \mathrm{cm}^{-3}$ is Loschmidt's number. *T* is the temperature. T_0 and P_0 are the temperature and pressure at STP conditions. The calculation are done at the mean thermal relative velocity $\bar{v}$ for a given temperature *T*,

$$\bar{v} = \left(\frac{8K_BT}{\pi\mu}\right)^{1/2} \quad (2)$$

where μ is the reduced mass of the molecular couple. {2} represents all the labels for a given A_2 perturber quantum state and $\rho_{\{2\}}$ is the population factor for such a state,

$$\rho_{\{2\}} \equiv \rho(J_2) = \frac{S_{A_2}(J_2)(2J_2+1)}{Z_{R,A_2}(T)} \times \exp\left(-E_{A_2}(J_2)/K_BT\right) \quad (3)$$

The $S_{A_2}(J_2)$ are the rotational statistical weights,

$$S_{A_2}(J_2) = \alpha_{A_2} + \beta_{A_2}(-1)^{J_2} \quad (4)$$

$Z_{R,A_2}(T)$ is the rotational partition function. The rotational energies are given by

$$E_{A_2}(J_2)/hc = B_{0,A_2}J_2(J_2+1) - D_{0,A_2}J_2^2(J_2+1)^2 \quad (5)$$

where *h* is Planck's constant. In Eq. (1), r_c is the distance between the centers of mass of the molecules at the time of closest approach for a given impact parameter. v'_c is the apparent relative velocity at that time. r_{c_0} is the minimum value of r_c, i.e. the one at the classical turning point of the relative trajectory governed by the isotropic interaction potential.

4. The interruption function is expressed in terms of a development of the *S* scattering operator truncated to order two. $S_{2,fi,\{2\}}$ contains, schematically, sums of probabilities of collisions that induce changes of quantum states from the lower state *i* and the upper state *f* of the considered methane line [43].
5. The interaction potential contains long range electrostatic contributions and short range ones calculated as a sum of atom–atom terms. The potential is thus an analytical combinations of angular and radial functions. The angular functions are combinations of Wigner functions depending on the Euler angles relative to molecule 1 (methane) and molecule 2 (diatomic perturber). The tensorial ranks of the functions are such that $l_1 \leqslant 6, l_2 \leqslant 6$ and $l_1 + l_2 \leqslant 6$. The radial functions for the short range interaction are developed into powers of 1/*R* where *R* is the distance between the centers of mass of the two molecules. The number of terms is limited according to a given value of $q_{\max}$ that defines the order of development for these functions. The resulting radial functions are given by

$$V_{|m|}^{l_1,\Gamma_1,l_2}(R) = {}_{|m|}f^{l_1,l_2} \frac{F^{l_1,l_2}}{R^{l_1+l_2+1}} + \sum_{q=q_{\min}}^{q_{\max}} \left[{}_{|m|}d_q^{l_1,l_2} \frac{D_q^{l_1,l_2}}{R^{12+q}} - {}_{|m|}e_q^{l_1,l_2} \frac{E_q^{l_1,l_2}}{R^{6+q}} \right] \quad (6)$$

Γ_1 is the symmetry label of the associated angular operator relative to methane. *m* is the projection number on the intermolecular axis. The *f*, *d* and *e* are numerical factors. The *F* depend on the multipolar moments of the molecules. The *D* and *E* are polynomials depending on the atom–atom interaction parameters and on some geometrical parameters of the two molecules. Detailed expressions for the above factors are not given here but may be found in the supplementary material of Ref. [43].

6. Owing to the complexity of the implementation of the theory for line broadening calculations in the case of methane, we choosed as a first step to use a simple model for the relative trajectories. These ones are limited to second order in time *t* (parabolic approximation), since this is only when $t \approx 0$ that the autocorrelation function of the dipole moment takes significant values. In this framework, the Fourier transforms resulting from the interaction representation of the interaction potential are derived analytically using a symbolic computation software. We note, however, that recent works by Gamache, Lamouroux et al. [47–50], by Buldyreva et al. [51–54], by Bray et al. [55,56], by Guinet et al. [57] and by Rozario et al. [58] indicate that major improvements can be obtained in the calculations through the use of "exact" trajectories. These ones are obtained by solving the classical equations of motion governed by the isotropic part of the interaction potential. As a consequence, the Fourier transforms mentioned above have to be calculated through numerical integration. We did not implement this procedure up to now mainly due to technical limitations. Indeed, the energy spectrum of methane contains a large amount of individual states, due to rovibrational interactions and vibrational resonances. Also, large sets of lines have to be considered in practical calculations. Thus, times of computation happen to be very long, even in the simple framework of the parabolic trajectory model. Nevertheless, we hope to be able to implement the exact trajectory model in our calculations in the near future.
7. For the practical implementation of the calculations, we have used a scripting language that allows to fully automate the generation of the necessary source codes. This technique appeared to be particularly suitable. For a given perturber, it can be necessary to include many terms in the potential to ensure proper convergence of the calculations, which leads to a large amount of Fourier transforms. For example, in the case of N_2, calculations were done using more than 840 Fourier transforms. In addition, the implementation is modular. This may allow, for example, to consider various perturbers for methane.

Since the implementation of the calculations is essentially the same as the one described in Ref. [43], we do not give here further details. We will only mention the few points that need particular attention for the present study.

For the different perturbers, the values for the molecular parameters and the ones concerning the interaction potentials are given in Table 1. The values in the table and other data given below were mostly taken from Refs. [31,49,59–61]. We write the atomic Lennard–Jones potentials as

$$V(r) = 4\epsilon\left(\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6}\right) \equiv \frac{d}{r^{12}} - \frac{e}{r^6} \quad (7)$$

Hetero-atomic parameters were obtained from mono-atomic ones using

$$\epsilon_{ij} = \sqrt{\epsilon_{ii} \times \epsilon_{jj}} \text{ and } \sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (8)$$

where the indices *i* and *j* stand for C, N, O or H. We believe that the combinations rules of Eq. (8) are the most commonly used. We note also that the values of the atom–atom parameters may greatly differ