Journal of Quantitative Spectroscopy & Radiative Transfer ■ (■■■■) ■■■–■■■

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Semi-empirical calculations of line-shape parameters and their temperature dependences for parallel bands of monodeuterated methane perturbed by nitrogen

J. Buldyreva [a,*], N.N. Lavrentieva [b], A.S. Dudaryonok [b]

[a] Institut UTINAM, UMR 6213 CNRS, Université Bourgogne Franche-Comté, 16 Route de Gray, 25030 Besançon cedex, France
[b] V.E. Zuev Institute of Atmospheric Optics, Siberian Branch of the Russian Academy of Sciences, 1 Akademishian Zuev square, 634021 Tomsk, Russia

ARTICLE INFO

Article history:
Received 15 January 2017
Received in revised form
24 February 2017
Accepted 24 February 2017

Keywords:
Monodeuterated methane
N_2-broadening coefficients
N_2-induced shifts
J- and *K*-dependences
Temperature dependence
Semi-empirical calculation
Outer planets
Planetary atmosphere

ABSTRACT

Theoretical nitrogen-pressure broadening and shift coefficients as well as their temperature-dependence characteristics for $^{12}CH_3D$ (*J*, *K*) lines in the parallel ($\Delta K=0$) ν_3 band are calculated by a semi-empirical approach based on analytical Anderson-type expressions corrected to account for the real curved trajectories. The parameters of the correction factor are adjusted on some recent experimental data for room-temperature line-broadening coefficients, and the unknown CH_3D polarizability in the excited vibrational state is determined from a few measurements of room-temperature line-shifts. After validation by comparison with a set of measured values from the literature, this approach is employed for massive calculations of line-shape parameters for enlarged ranges of rotational quantum numbers ($0 \le J \le 70$, $0 \le K \le 20$) requested by atmospheric/astrophysical applications and spectroscopic databases. The temperature-dependence characteristics are obtained for the range 200–400 K recommended for HITRAN. Given the negligible vibrational dependence of CH_3D line-widths, our calculated broadening coefficients and their temperature-dependence exponents can be also used for other CH_3D-N_2 parallel bands.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The important role of monodeuterated methane CH_3D along with the parent methane molecule CH_4 is widely recognized for physical and chemical processes occurring in the terrestrial atmosphere. Namely, they are known as greenhouse gases released by natural (wetlands, ocean) and anthropogenic (fossil fuel extraction) sources. They are also present in atmospheres of giant planets and their moons, in particular, those of Saturn, Jupiter [1–3], Uranus [4–6] and Titan [7–9] as well as in comets [10,11].

Despite a low abundance of about 5×10^{-4}, CH_3D occupies a privileged place with respect to other CH_4 isotopologues because of the possibility of D/H ratio determination which gives access to the past and present thermodynamic and kinetic processes, chemical reactions and evolution of planetary atmospheres, i.e. enables the development and validation of models for the origin and evolution of the Solar system. The D/H measurements from relative CH_3D/CH_4 line intensities are feasible owing to the fact that the isotopic substitution H→D changes significantly the stretching frequency ν_2, so that the second overtone $3\nu_2$ shifts to the 1.58 μm transparency window where CH_4 absorption is extremely weak [12]. In such a way, the $3\nu_2$ CH_3D band has been used for determination of D/H ratios for Uranus [13], Neptune [14] and Titan [8,15]. As CH_3D strongly absorbs in CH_4 transparency windows, reliable modeling (radiative transfer, climate changes, etc.) of CH_4 reach atmospheres requires moreover a precise knowledge of its other line-shape parameters such as pressure-broadening and -shift coefficients as well as their temperature dependences for main atmospheric perturbers N_2, O_2, H_2, He, etc.

The case of perturbation by nitrogen appears as the most important for remote sensing of planetary atmospheres, so that it benefited from a considerable attention of experimentalists and theoreticians. From the viewpoint of pressure-broadening and -shift parameters, the data were generally published for room temperature, only few works reported low-temperature measurements and calculations allowing evaluation of temperature dependences. So, N_2-broadening coefficients at 296 K were retrieved with Voigt-profile (VP) model by Devi et al. [16] for seventeen $^{12}CH_3D$ lines in the P-, Q- and R-branches of the parallel ($\Delta K= 0$) ν_3 band (near 7.6 μm); similar measurements were performed by the same authors [17] for 24 ^{R}P and ^{P}P lines in the perpendicular

* Corresponding author.
E-mail address: jeanna.buldyreva@univ-fcomte.fr (J. Buldyreva).

http://dx.doi.org/10.1016/j.jqsrt.2017.02.014
0022-4073/© 2017 Elsevier Ltd. All rights reserved.

Please cite this article as: Buldyreva J, et al. Semi-empirical calculations of line-shape parameters and their temperature dependences for parallel bands of monodeuterated methane.... J Quant Spectrosc Radiat Transfer (2017), http://dx.doi.org/10.1016/j.jqsrt.2017.02.014

($\Delta K = \pm 1$) ν_6 band (at 8.6 μm). The ν_6 fundamental was also investigated at 296 K by Lacome et al. [18] who retrieved VP collisional widths for ten ^{P}P and ^{R}P lines. One of early experimental works by Chudamani and Varanasi [19] on the parallel ν_2 band region (around 4.7 μm) provided CH_3D-N_2 broadening coefficients extracted with VP model for five P-branch lines P(5,2), P(5,3), P(7,2), P(7,3), P(8,3) at 94, 100, 146, 150, 197, 200, 248, 300 K and the deduced temperature-dependence exponents. Three lines P(4,2,E), P(5,3,A), P(7,3,A) in the fundamental ν_3 band for 131, 228, 295 K and four lines ^{P}P(6,1,E), ^{R}P(5,0,A+), ^{P}P(5,1,E), ^{P}P(4,2,E) in the ν_6 band for 123, 188, 295 K to get VP-broadening coefficients and their temperature exponents were analyzed later by the same authors [20]. Line-shape models going beyond the traditional Voigt profile were employed by Blanquet and collaborators [21] who analyzed 33 lines recorded at 296 K in the R- and P-branches of the ν_3 band with Rautian profile and showed that this strong-collision model accounting for collisional narrowing yields naturally significantly larger broadening coefficients.

Further CH_3D-N_2 line-shape studies privileged simultaneous analysis of spectra recorded at various pressures in order to reduce errors in parameters' determination. For instance, a very detailed room-temperature (294 K) study of N_2-pressure-broadening and -shift coefficients with a multispectrum fitting technique [22] was done for 217 lines in the P-, Q- and R-branches ($0 \le K \le 6$ and $J \le 14$, $J \le 13$ and $J \le 12$, respectively) in the $3\nu_2$ band presenting a particular interest in planetology. The authors also demonstrated the negligible vibrational dependence of CH_3D-N_2 broadening coefficients in the A1-type bands from comparison of ν_2, ν_3, ν_6 and $3\nu_2$ P-line data. Devi et al. [23–25] extended multispectrum line-shape analysis to the $\nu_3/\nu_5/\nu_6$ triad bands with a report on broadening, shifting and line-mixing coefficients at 296 K for hundreds of lines. For the ν_2 band at the same temperature, measurements of N_2-broadening and N_2-shift coefficients extracted by a multispectrum approach for 368 lines were published by Predoi-Cross and coauthors [26]. The need of spectroscopic databases such as HITRAN [27] and GEISA [28] for temperature-dependence characteristics of both CH_3D-N_2 line-broadening and shifting initiated very recently a series of measurements and multispectrum analyses of the bands from the $\nu_3/\nu_5/\nu_6$ triad in the temperature range 79–296 K [29,30]. The reference-temperature (296 K) line-broadening and line-shift coefficients as well as the corresponding temperature exponents and temperature-dependence shift parameters were deduced for 184 transitions ($0 \le J \le 22$, $K \le 14$) in the ν_3 band, 205 transitions ($0 \le J \le 17$, $K \le 11$) in the ν_5 band [30] and about 400 transitions ($0 \le J \le 19$, $K \le 16$) in the ν_6 band [29].

From the theoretical point of view, N_2-broadening of CH_3D lines have been evaluated first [31] with the use of the Anderson-Tsao-Curnutte theory, accounting for the dipole and octupole moments of CH_3D and the quadrupole moment of N_2. The authors reported the room-temperature (300 K) line-widths for the transitions K=0–10, J=0–20 in the pure rotational band and the (averaged over K) temperature exponents up to J=25 for the range 100–300 K. Their estimates of line broadening were about 13% lower with respect to later measurements by Lacome et al. [18]. Much lower results (by 40 to 60%) were obtained for the ν_3 band [21] with the same electrostatic potential as in [31] but with an improved semi-classical treatment based on an exponential representation of the scattering operator and including the influence of the isotropic potential in the trajectory model. Since adding induction and dispersion forces did not furnish satisfactory results [21], the atom-atom interactions of Lennard-Jones form were used later to complete the electrostatic terms for the ν_2 band studies [26]; to account for these short-range terms, the authors approximated CH_3D by a "linear" molecule "$_3$HCD" with three H atoms projected on the molecular symmetry axis. Moreover, the isotropic potential was adjusted on a m-n Lennard-Jones potential form. All these improvements allowed the authors getting a 6.4% agreement with their measurements for J below 14 (except for $K=J$ or $K=J-1$). A semi-classical approach based on the exponential form of the scattering operator, a rigorous treatment of the active molecule as a symmetric top, an intermolecular potential comprising both long- and short- range interaction and exact classical trajectories was used in the recent woks [29,30] to evaluate theoretically the line-broadening coefficients and the temperature exponents in the ν_3, ν_5 and ν_6 bands. While comparing very favorably with measurements at $K \le 7$, this approach seemed to overestimate the broadening for high values of K and J.

As the theoretical estimates are of crucial importance for lines with high values of rotational quantum numbers which are inaccessible experimentally, in the present paper we apply an alternative semi-empirical (SE) method [32] for calculating CH_3D-N_2 line-broadening and line-shift parameters with their temperature dependences. This method employs analytical Anderson-type linewidth and line-shift expressions corrected by a few-parameter empirical factor to account for the real trajectory curvature, vibrational effects, and corrections to the scattering matrix. Once the model parameters are determined on some experimental linewidths, extensive and reliable computations can be performed for wide ranges of J and K requested by spectroscopic databases and atmospheric/astrophysical applications. The next section describes briefly the theoretical background of our approach and provides some details of correction-factor parameterization for the particular CH_3D-N_2 case. Presentation of our results and their comparison with available in the literature experimental and theoretical data are given in Section 3. The final section summarizes concluding remarks and perspectives.

2. Theoretical background and details of calculations for CH_3D-N_2

The semi-empirical method [32] employed in the present work was initially proposed for molecular systems with quite strong electrostatic interactions (H_2O-N_2, CO_2-N_2, etc.), to which the An-

Table 1
Semi-empirical fitting parameters deduced from experimental values of room-temperature R-branch CH_3D-N_2 broadening coefficients [30] for K=0–12 and extrapolated, on the basis of K=0–12 trend, for K=13–20.

K	c_1	c_2	c_3	c_4
0	1.0	0	0	0
1	1.15	0	−20	7
2	1.5	0.001	−65	8
3	1.6	0.002	−90	9
4	2.1	0.003	−100	10
5	2.25	0.004	−107	11
6	2.3	0.005	−105	12
7–20	2.3	−0.008+0.002 K	−105	6+K

Table 2
CH_3D and N_2 molecular parameters used in calculations: dipole moments μ, quadrupole moments Q, octupole moments Ω, mean ground-state polarizabilities α and polarizability anisotropies γ.

Molecule	μ (D)	Q (D Å)	Ω (D Å^2)	α (Å^3)	γ
CH_3D	0.0057 [38]	0	3.10 [43]	2.59 [44]	0
N_2	0	−1.3 [42]	0	1.74 [44]	0.137 [45]

Please cite this article as: Buldyreva J, et al. Semi-empirical calculations of line-shape parameters and their temperature dependences for parallel bands of monodeuterated methane.... J Quant Spectrosc Radiat Transfer (2017), http://dx.doi.org/10.1016/j.jqsrt.2017.02.014

Download English Version:

https://daneshyari.com/en/article/7846492

Download Persian Version:

https://daneshyari.com/article/7846492

Daneshyari.com