

Self and N2 collisional broadening of rovibrational lines in the ν 6 band of methyl iodide (12CH3I) at room temperature: The J and K dependence

Y. Attafi, A. Ben Ben Hassen, H. Aroui, F. Kwabia Tchana, L. Manceron, D.

Doizi, J. Vander Vander Auwera, A. Perrin

▶ To cite this version:

Y. Attafi, A. Ben Ben Hassen, H. Aroui, F. Kwabia Tchana, L. Manceron, et al.. Self and N2 collisional broadening of rovibrational lines in the $\nu 6$ band of methyl iodide (12CH3I) at room temperature: The J and K dependence. Journal of Quantitative Spectroscopy and Radiative Transfer, 2019, 231, pp.1-8. 10.1016/j.jqsrt.2019.04.017 . hal-02340436

HAL Id: hal-02340436 https://hal.science/hal-02340436

Submitted on 30 Oct 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Self and N₂ collisional broadening of rovibrational lines in the v₆ band of methyl iodide (¹²CH₃I) at room temperature: The J and K dependence

Y. Attafi,^{a,b} A. Ben Hassen,^b H. Aroui,^b F. Kwabia Tchana,^{a*} L. Manceron,^{c,d} D. Doizi,^e J. Vander Auwera,^f A. Perrin^g

- ^a Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR CNRS 7583, Université Paris Est Créteil et Université Paris Diderot, Institut Pierre Simon Laplace, 61 avenue du Général de Gaulle, F-94010 Créteil Cedex, France.
- ^b Laboratoire de Spectroscopie et Dynamique Moléculaire, Université de Tunis, Ecole Nationale Supérieure d'Ingénieurs de Tunis, 5 Av Taha Hussein, 1008 Tunis, Tunisia.
- ^c Ligne AILES, Synchrotron SOLEIL, L'Orme des Merisiers, St-Aubin BP48, F-91192 Gifsur-Yvette Cedex, France.
- ^d Sorbonne Université, CNRS, MONARIS, UMR 8233, 4 place Jussieu, F-75005 Paris, France
- ^e DEN-Service d'Etude du Comportement des Radionucléides (SECR), CEA, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France
- ^f Service de Chimie Quantique et Photophysique, C.P. 160/09, Université Libre de Bruxelles, 50 avenue F.D. Roosevelt, B-1050 Brussels, Belgium.
- ^g Laboratoire de Météorologie Dynamique/IPSL, UMR CNRS 8539, Ecole Polytechnique, Université Paris-Saclay, RD36, F-91128 PALAISEAU Cedex, France.

Nb of figures: 8

Nb of Tables: 4

*Corresponding author: Fridolin Kwabia Tchana, fridolin.kwabia@lisa.u-pec.fr

Abstract

Following our recent study devoted to measurements of intensities of rovibrational lines in the v_6 band of methyl iodide (¹²CH₃I) centered at 892.918 cm⁻¹, room temperature infrared spectra of methyl iodide diluted in nitrogen at fourteen total pressures between 20 and 300 hPa have been recorded using the Fourier transform spectrometer Bruker IF125HR located at the LISA facility in Créteil. Three hundred and forty six N₂-broadening coefficients of methyl iodide rovibrational lines have been measured in the 824–951 cm⁻¹ spectral range using mono-spectrum non-linear least squares fitting of Voigt profiles. Pressure-induced line shifts were not needed to fit the spectra to the noise level and line mixing effects could be neglected. Six hundred and eight self-broadening coefficients have also been measured in the same spectral range using the pure methyl iodide spectra recorded in our previous work. The measured self-broadening coefficients range from 0.1460 to 0.3786 $\mbox{cm}^{-1}\mbox{atm}^{-1}$ and the $N_{2}\mbox{-}$ broadening coefficients range from 0.0723 to 0.1481 cm⁻¹atm⁻¹ at 295 K. The average accuracy on the measured self- and N₂-broadening coefficients was estimated to 3%. Comparisons with measurements reported in the literature for the v₅ band of CH₃I shows a satisfactory agreement with average differences of 7% and 4% for the self- and N₂-broadening coefficients, respectively. The J and K rotational dependences of these coefficients have been observed and using an empirical polynomial expansion, the rotational K dependence was modeled. On average, the empirical expression reproduces the measured self- and N₂broadening coefficients to within 3% and 4%, respectively. The data obtained in the present work represent a significant contribution to the determination of broadening coefficients of CH₃I and complement the list of line positions and intensities generated in our previous work, thus providing useful spectroscopic information for atmospheric remote sensing and industrial detection of CH₃I.

Keywords: methyl iodide; CH₃I; high-resolution Fourier transform spectroscopy; selfand N₂-broadening coefficients; J and K dependence

1. Introduction

Remote sensing is a valuable tool for detecting and monitoring the composition of the Earth's atmosphere as well as for probing the molecular content of interstellar clouds or the atmospheres of solar and extra-solar objects [1-8]. The successful analysis of atmospheric and astrophysical spectra and the reliability of the retrieved concentrations and temperature profiles however strongly depend on the accuracy of available spectroscopic parameters, such as the positions, intensities, and pressure broadening and shifting coefficients of spectral lines. Spectroscopic information measured in laboratories is collected into a number of databases, such as HITRAN [9] and GEISA [10], continuously updated in terms of accuracy of the line parameters, molecular species and spectral coverage.

Methyl iodide (CH₃I), the molecule of interest in the present work, is essentially absent from common spectroscopic databases, despite its atmospheric importance. Indeed, CH₃I is emitted in the atmosphere by marine algae and photolyzed with a lifetime of the order of a week. It is a source of I atoms involved in the ozone destruction cycles in the upper troposphere and in the lower stratosphere [11]. Methyl iodide is also of nuclear interest. In nuclear power plants, it is mainly produced in the containment by the reaction of iodine with organic coatings of the enclosure under ionizing radiation. In the case of a severe nuclear accident, iodine fission products represent the major part of the released radioactivity and are of high concern due to the affinity of iodine with the thyroid. It is therefore crucial to monitor the release of iodine compounds into the atmosphere, as part of the nuclear safety and radio-protection. To the best of our knowledge, there is up to now no infrared detection of these species in the atmosphere from a satellite instrument. The rather strong v₆ band of CH₃I, located at 892.918 cm⁻¹, coinciding with the 11 µm transparency window in the atmosphere [12–14], could be a good candidate for such detection.

To prepare for this possible future detection, we recently carried out detailed studies concerning the line positions and intensities of the strong v_6 band [15,16], which resulted in a list of line positions and intensities of CH₃I at 11 µm. This molecule was the subject of numerous microwave and infrared studies focused on the ground and various excited states, and several combination bands (see [15,16 and references therein] for an exhaustive review on the spectroscopic parameters of CH₃I). To the best of our knowledge, only two studies dealt with the measurement of line broadening coefficients [17,18]. Self-broadening

parameters of 6 hyperfine components of the $(J = 10 \rightarrow 9, Kl = 9)$ rotational transitions in the $v_6 = 1$ excited vibrational state were accurately measured using Doppler-free doubleresonance spectroscopy [17], and room temperature self-, N₂- and O₂-broadening coefficients were measured for over 100 lines in five *Q*-branches of the v₅ perpendicular band at 7 µm using diode laser absorption spectroscopy [18].

The measurements reported here provide the first extensive data set that can be used for modelling pressure broadening coefficients of CH_3I . This work focuses on the self and N_2 collisional broadening of rovibrational lines in the v_6 band of CH_3I at room temperature. The self-broadening coefficients have been measured using the pure methyl iodide spectra recorded in our previous work [16]. The N_2 collisional broadening coefficients were retrieved from fourteen high resolution Fourier transform spectra recorded at a temperature of 295 K. An empirical model was then developed to reproduce within experimental accuracy the large set of measured broadening coefficients covering various *J* and *K* values.

Section 2 details the experimental setup and conditions used to record the spectra. The measurements of self and N_2 broadening coefficients are described in Section 3. The empirical model developed to calculate self and N_2 collisional broadening parameters of CH₃I and comparisons of the present measurements with literature data are described in Section 4. Conclusions and remark are provided in Section 5.

2. Experimental details

Fourteen absorption spectra of methyl iodide diluted in nitrogen have been recorded in the range from 500 to 1450 cm⁻¹ using the high-resolution Bruker IFS125HR FTS located at the LISA facility in Créteil (France). The instrument was equipped with a silicon carbide Globar source, a KBr/Ge beamsplitter and a liquid nitrogen cooled HgCdTe (MCT) detector. An optical filter with a bandpass of $500 - 1450 \text{ cm}^{-1}$ was used to improve the signal-to-noise ratio. The FTS was continuously evacuated below 3×10^{-4} hPa by a turbomolecular pump to minimize absorption by atmospheric gases. The diameter of the entrance aperture of the spectrometer was set to 2 mm to maximize the intensity of infrared radiation falling onto the MCT detector without saturation or loss of spectral resolution. Interferograms were recorded with a 40 kHz scanner frequency and a maximum optical path difference (MOPD) of 150 cm. According to the Bruker definition (resolution = 0.9/MOPD), this corresponds to a resolution of 0.006 cm⁻¹. The N₂ and CH₃I samples were purchased from Sigma Aldrich with stated purities of 99.99% and 99%, respectively. No further sample purifications were done. The absorption cell has a base path length of 20 cm and was adjusted for 28 transits in the present experiment, yielding an absorption path length of 564.9 \pm 1.1 cm. The path length value takes into account the distance between the surface of the field mirror and the windows of the cell (2 × 2.45 cm). The spectra were recorded at a stabilized room temperature of 295 \pm 1 K. The sample pressure in the cell was measured using calibrated MKS Baratron capacitance manometers models 628D (2 and 10 Torr full scale) and 627D (100 and 1000 Torr full scale), characterized by a stated reading accuracy of 0.12%. Considering the uncertainty arising from small variations of the pressure during the recording of the interferograms (~ 0.35%), we estimated the measurement uncertainty on the pressure to be equal to 0.5%.

The following procedure was used for the measurements. A background spectrum was first recorded at a resolution of 0.01 cm^{-1} while the cell was being continuously evacuated. The cell was then filled with CH₃I at a given pressure, followed by the perturbing gas leading to a series of 14 total pressures. One CH₃I/N₂ spectrum was recorded for each CH₃I filling. Transmittance spectra were finally generated from the ratio of the sample spectra with the background spectrum. The fourteen pressures chosen and the number of interferograms recorded and averaged to yield the corresponding spectra are listed in Table 1. For the Fourier transform, a Mertz-phase correction with a 1 cm⁻¹ phase resolution, a zero-filling factor of 2 and no apodization (boxcar option) were applied to the averaged interferograms. The root mean square (RMS) S/N in the ratioed spectra is around 300. The spectra were calibrated by matching the measured positions of about 30 lines of residual CO₂ observed therein to reference wavenumbers available in HITRAN2016 [9] with a RMS deviation of 0.00028 cm⁻¹.

3. Retrieval of the broadening coefficients and uncertainty analysis

3.1. Retrieval of self-broadening coefficients

The self-broadening parameters of rovibrational lines of methyl iodide were retrieved during our line intensities study, from simultaneous fits of the pure methyl iodide spectra recorded in our previous work [16] using a multi-spectrum least squares fitting algorithm, developed in Brussels [19,20]. This program adjusts spectroscopic (e.g. line positions, intensities and widths) and spectrum-specific (e.g. baseline) parameters to best-fit of synthetic spectra to the observed spectra using a Levenberg-Marquardt non-linear least squares fitting procedure. The self-shift coefficients of all the lines were set to zero and were not needed to fit the spectra to the noise level. Line intensities and self-broadening coefficients were therefore retrieved simultaneously. Details on these measurements can be found in our previous work [16] where the self-broadening coefficients were not reported. Taking into account the lines with an absorption between 20 and 80%, we reported in the present work 608 self-broadening coefficients. As example, the results obtained for a few transitions are provided in Table 2. The whole set of measurements is given as supplementary material. The measured self-broadening coefficients range from 0.1460 to $0.3786 \text{ cm}^{-1} \text{atm}^{-1}$ at 295 K.

The self-shift coefficients of all the lines were set to zero

3.2. Retrieval of nitrogen-broadening coefficients and uncertainty analysis

The CH₃I/N₂ collisional half widths were measured using a mono-spectrum non-linear least squares fitting program, already used and described in previous works [21-26]. Briefly, the measurements involved the adjustment of a calculated spectrum to the observed spectrum using a non-linear least squares fitting procedure. Each calculated spectrum was computed as the convolution of a monochromatic transmission spectrum with an instrument line shape function, which included the effects of the finite maximum optical path difference and of the finite source aperture diameter of the interferometer [27]. In the present work, no deviation from this instrument line shape model was observed using the nominal aperture diameter of 2 mm. The background in each spectrum was represented by a polynomial expansion up to the second order (a constant or an affine function was however found sufficient in most cases), and the profile of the lines was modeled using a Voigt function with Gaussian width always held fixed to the value calculated for the Doppler broadening. Pressure-induced line shifts were not needed to fit the spectra to the noise level and line mixing effects could be neglected. The measurements were carried out on small spectral intervals, ranging from 0.1 to 0.5 cm^{-1} and containing one to several lines. An example of the fitting procedure is shown in Fig. 1. The absence of signatures out of the spectral noise in the residuals suggests that the Voigt profile is adequate to fit the observed lines.

Although the spectra of the CH_3I/N_2 mixtures have been recorded with at most 1.3 % of CH_3I , we subtracted the self-broadening contributions to deduce reliable N_2 -broadening coefficients according to the equation:

$$\gamma_{C} = \gamma_{N_{2}} \times \boldsymbol{P}_{N_{2}} = \gamma_{C,total} - \gamma_{self} \times \boldsymbol{P}_{CH_{3}I}$$
⁽¹⁾

where γ_c is the N₂-collisional halfwidth, $\gamma_{c,total}$ is the total collisional halfwidth, and P_{CH3I} and P_{N_2} are the CH₃I and N₂ partial pressures, respectively. γ_{N_2} is the N₂-broadening coefficient and γ_{self} is the self-broadening coefficient. Evolution with pressure of the N₂collisional halfwidth γ_c for the ^RR(9,3,A_2), ^RR(25,3,A_1) and ^RR(34,6,A_1) lines in the v₆ band of CH₃I perturbed by N₂ is shown in Fig. 2. The fitted straight lines show the linear dependence of the collisional halfwidths with pressure. The N₂-broadening coefficients (in cm⁻¹atm⁻¹) can be derived from the slopes of these lines.

Examination of the residuals of the fits shows that they are generally less than 1% (see Figure 1). However, to estimate the accuracy of the measured broadening coefficients requires considering the uncertainties on the physical parameters, contributions from possible systematic errors [28] as well as the uncertainties derived from the fits, taken as the standard deviation. The various sources of error considered in the present work and their associated uncertainties expressed relative to the broadening coefficients are given in Fig. 3 for 3 selected lines, representative of the 346 measured lines, i.e. $^{R}(34,6)$, $^{R}(25,3)$ and $^{R}R(9,3)$. Figure 3 shows that systematic errors are the main sources of error. The dominant contributions to systematic errors arise from the location of the full-scale photometric level, channeling, as well as electronic and detector nonlinearities [28]. The reported estimate of 2% is an arbitrary, but conservative value. For each transition, we then calculated an overall uncertainty based on the uncertainty of the individual experimental parameters, i.e. ε_{si} (sample purity), ε_t (temperature), ε_p (pressure), ε_{pl} (pathlength), ε_{fit} (standard deviation from fit) and ε_{sys} (systematic errors), assuming that these uncertainties are uncorrelated:

$$\varepsilon = \sqrt{\varepsilon_{si}^2 + \varepsilon_t^2 + \varepsilon_p^2 + \varepsilon_{pl}^2 + \varepsilon_{fit}^2 + \varepsilon_{sys}^2}$$
(2)

Using this equation and the experimental relative uncertainties involved, the estimated overall uncertainty (estimated accuracy) for each of the 346 N₂-broadening coefficients measured was calculated. On average, the estimated accuracy on the reported N₂-broadening coefficients is equal to 3%. In our analysis, we did not apply any temperature corrections to the measured

broadening coefficients. Hence, the N₂-broadening coefficients listed in the supplementary material correspond to the temperature of 295 ± 1 K at which the spectra were recorded. The measured N₂-broadening coefficients range from 0.0723 to 0.1481 cm⁻¹atm⁻¹ at 295 K. A few transitions are collected in Table 2, together with their absolute uncertainty.

4. Calculated self and N₂ collisional broadening parameters and discussion

4.1. Empirical model

We have fitted the measured self- and N₂-broadening coefficients by an empirical polynomial expression as previously done for CH₃Br [25,29], CH₃F [30] and CH₃Cl [31-33]. Such a work requires a great amount of accurate measurements. For methyl iodide, this is the first time that an empirical model is used to adjust the measured broadening coefficients. Each set of broadening coefficients characterized by the same *J* value was fitted by the following polynomial expansion :

$$\gamma_J(K) = a_J^0 + a_J^2 K^2$$
(3)

Examples of these fits are given in Fig. 4 for transitions with J = 6, 10, 35 and 40. As has been observed in numerous studies dealing with C_{3v} -symmetry molecules [25,29-33], the broadening coefficients decrease with K. This decrease is more significant at low J than at high J values. The best-fit coefficients a_I^0 and a_I^2 were determined through a least-squares fit of the experimental broadening coefficients. They are listed in Table 3. The calculated selfand N₂-broadening coefficients (γ_{calc}) corresponding to the measured values (γ_{mea}) are presented in Table 2, together with the differences between the measured and calculated values. A statistical analysis of these differences (Table 4) shows that the fit is very good because at least 87% of the broadening coefficients fall within 7% of the measured values. On average, the empirical expression reproduces the measured self and N2 broadening coefficients to within 3% and 4%, respectively. The latter range corresponds to the measurement uncertainty of the broadening coefficients. Figure 5 is plots of the J-dependence of the self broadening coefficients measured and calculated for all studied K values in the v_6 band of CH₃I, while Figure 6 shows the J-dependence of the N₂ broadening coefficients measured and calculated. Both figures show that the self and N₂ broadening coefficients increase then decrease as J increases, exhibiting maxima around J = 22 and 4, respectively.

4.2. Comparison with previous work

In our previous study on line positions [15], the hyperfine structure had to be accounted for during the analysis and energy level calculation. For the line intensity measurements, we had carefully selected the transitions for which the hyperfine structure is not observable: this means that the hyperfine splitting is smaller than the Doppler line width [16]. In the present work, the experimental conditions do not allow differentiating the hyperfine components. Therefore, we did not compare our self-broadening coefficients with

hyperfine components. Therefore, we did not compare our self-broadening coefficients with those of Belli *et al.* [17]. We therefore compared the self-broadening coefficients measured in this work with the only data available in the literature, i.e. the self-broadening coefficients reported for the v₅ fundamental band of CH₃I [18]. Figure 7 compares the present results for the ${}^{P}Q(J, 2)$ transitions in the v₆ band and the measurements reported in Ref. [18] for the same transitions in the v₅ band. The self-broadening coefficients reported for the v₅ band are larger (the average difference is about 7%) and their rotational dependence is different. A similar comparison of N₂-broadening coefficients (Fig. 8) shows an overall good agreement with the results of Ref. [18], with an average difference of about 4%. The latter comparison tend to indicate the absence of a vibrational dependence of the N₂ broadening coefficients, similarly to what was observed for CH₃X (X = Br, F) [25,29-30].

5. Conclusion

Mono-spectrum analyses of high-resolution Fourier transform spectra of methyl iodide diluted in nitrogen at total pressures in the range 20 – 300 hPa resulted in the determination of N₂-broadening coefficients for rovibrational lines in the v₆ band of methyl iodide, at room temperature. Self-broadening coefficients have also been measured at room temperature using multi-spectrum analyses of high-resolution Fourier transform spectra of pure methyl iodide recorded in one of our previous work [16]. In both analyses, pressure-induced line shifts were not needed to fit the spectra down to the noise level and line mixing effects could be neglected. Self and N₂ broadening coefficients have been obtained for large sets of J and K values, for which clear J and K dependences have been observed. The N₂ broadening coefficients measured in the present work agree well with measurements reported in the literature for the v₅ band of methyl iodide, while some discrepancies are observed for the selfbroadening coefficients. Empirical polynomial expression have been used to model the rotational K dependence of the broadening coefficients, leading to accurate coefficients constants $(a_J^0 \text{ and } a_J^2)$ for methyl iodide. The data obtained in the present work and given as supplementary material, represent a significant contribution to the determination of broadening coefficients of methyl iodide and thus completes the list of line positions and intensities generated in our previous work [16], useful for atmospheric remote sensing and industrial detection of methyl iodide. It will be necessary to complete them with experimental determination of broadening coefficients at temperatures observed in the Earth's atmosphere.

ACKNOWLEDGEMENTS

The DECA-PF project is sponsored by the French government `Investments for the future' program through the grant ANR-11-RSNR-0003 supervised by the French National Research Agency (ANR) under the `Research in Nuclear Safety and Radioprotection' (RSNR) research initiative.

References

- [1] Demaison J, Sarka K, Cohen EA. Spectroscopy from Space. NATO Science Series. Dordrecht: Kluwer Academic Publisher; 2001.
- [2] Niro F, Hase F, Camy-Peyret C, Payan S, Hartmann JM. Spectra calculations in central and wing regions of CO₂ IR bands between 10 and 20 μm. II: Atmospheric solar occultation spectra. J Quant Spectrosc Radiat Transf 2005;90:43–59.
- [3] Hay KG, Wright S, Duxbury G, Langford N. In-flight measurements of ambient methane, nitrous oxide and water using a quantum cascade laser based spectrometer. Appl Phys B 2008;90:329–37.
- [4] Duxbury G, Langford N, Hay K, Tasinato N. Quantum cascade laser spectroscopy: diagnostics to non-linear optics. J Mod Opt 2009;56:2034–48.
- [5] McNaughton D, Robertson EG, Thompson CD, Chimdi T, Bane MK, Appadoo D. Overview of High-Resolution Infrared Measurement and Analysis for Atmospheric Monitoring of Halocarbons. Anal Chem 2010;82:7958–64.
- [6] Brown AT, Chipperfield MP, Boone C, Wilson C, Walker KA, Bernath PF. Trends in atmospheric halogen containing gases since 2004. J Quant Spectrosc Radiat Transf 2011;112:2552–66.
- [7] Swain MR, Vasisht G, Tinetti G. The presence of methane in the atmosphere of an extrasolar planet. Nature 2008;452:329–31.
- [8] Tinetti G, Vidal-Madjar A, Liang MC, Beaulieu JP, Yung Y, Carey S, et al. Water vapour in the atmosphere of a transiting extrasolar planet. Nature 2007;448:169–71.
- [9] Gordon IE, Rothman LS, Hill C, Kochanov RV, Tana Y, Bernath PF, BirkM, Boudon V, Campargue A, Chance KV, Drouin BJ, Flaud JM, Gamache RR, Hodges JT, Jacquemart D, Perevalov VI, Perrin A, Shine KP, Smith MA, Tennyson J, Toon GC, Tran H, Tyuterev VG, Barbe A, Császár AG, Devi VM, Furtenbacher T, Harrison JJ, Hartmann JM, Jolly A, Johnson TJ, Karman T, Kleiner I, Kyuberis AA, Loos J, Lyulin OM, Massie ST, Mikhailenko SN, Moazzen-Ahmadi N, Müller HSP, Naumenko OV, Nikitin AV, Polyansky OL, Rey M, Rotger M, Sharpe SW, Sung K, Starikova E, Tashkun SA, Vander Auwera J, Wagner G, Wilzewski J, Wcisło P, Yuh S, Zak EJ. The HITRAN 2016 molecular spectroscopic database. J Quant Spectrosc Radiat Transf 2017;203:3-69.

- [10] Jacquinet-Husson N, Armante R, Scott NA, Chédin A, Crépeau L, Boutammine C, Bouhdaoui A, Crevoisier C, Capelle V, Boonne C, Poulet-Crovisier N, Barbe A, Benner DC, Boudon V, Brown LR, Buldyreva J, Campargue A, Coudert LH, Devi VM, Down MJ, Drouin BJ, Fayt A, Fittschen C, Flaud JM, Gamache RR, Harrison JJ, Hill C, Hodnebrog Ø, Hu SM, Jacquemart D, Jolly A, Jiménez E, Lavrentieva N, Liu AW, Lodi L, Lyulin OM, Massie ST, Mikhailenko S, Müller HSP, Naumenko OV, Nikitin A, Nielsen CJ, Orphal J, Perevalov V, Perrin A, Polovtseva E, Predoi-Cross A, Rotger M, Ruth AA, Shanshan Y, Sung K, Tashkun S, Tennyson J, Tyuterev VG, Vander Auwera J, Voronin B, Makie A. The 2009 edition of the GEISA spectroscopic database. J Mol Spectrosc 2016;327:31-72.
- [11] Bell N, Hsu L, Jacob DJ, Schultz MG, Blake DR, Butler JH, King DB, Lobert JM, Maier-Reimer E. Methyl iodide: Atmospheric budget and use as a tracer of marine convection in global models. J Geophys Res 2002;107(D17):4340.
- [12] Bernath P. Atmospheric Chemistry Experiment: Spectroscopy From Orbit. Opt Photonics News 2005;16(4):24–7.
- [13] Fischer H. The MIPAS experiment aboard ENVISAT: Remote sensing of atmospheric composition. In: Perrin A, Ben Sari-Zizi N, Demaison J, editors. Remote Sensing of the Atmosphere for Environmental Security, Dordrecht: Springer; 2006, p. 41–55.
- [14] Clerbaux C, Boynard A, Clarisse L, George M, Hadji-Lazaro J, Herbin H, et al. Monitoring of atmospheric composition using the thermal infrared IASI/MetOp sounder. Atmos Chem Phys 2009;9:6041–54.
- [15] Perrin A, Haykal I, Kwabia-Tchana F, Manceron L, Doizi D, Ducros G. New analysis of the v₆ and 2v₃ bands of methyl iodide (CH₃I). J Mol Spectrosc 2016;324:28–35.
- [16] Kwabia Tchana F, Attafi Y, Manceron L, Doizi D, Vander Auwera J, Perrin A. Line intensities for the v_6 and $2v_3$ bands of methyl iodide (12 CH₃I). J Quant Spectrosc Radiat Transf 2019;222-223:130–7.
- [17] Belli S, Buffa G, Di Lieto A, Minguzzi P, Tarrini O, Tonelli M. Hyperfine level dependence of the pressure broadening of CH_3I rotational transitions in the $v_6 = 1$ vibrational state. J Mol Spectrosc 2000;201:314–18.

- [18] Hoffman KJ, Davies PB. Pressure broadening coefficients of v₅ fundamental band lines of CH₃I at 7 μm measured by diode laser absorption spectroscopy. J Mol Spectrosc 2008;252:101–07.
- [19] Tudorie M, Foldes T, Vandaele AC, Vander Auwera J. CO₂ Pressure broadening and shift coefficients for the 1-0 band of HCl and DCl. J Quant Spectrosc Radiat Transf 2012;113:1092–101.
- [20] Daneshvar L, Foldes T, Buldyreva J, Vander Auwera J. Infrared absorption by pure CO₂ near 3340 cm⁻¹: measurements and analysis of collisional coefficients and linemixing effects at subatmospheric pressures. J Quant Spectrosc Radiat Transf 2014;149:258–74.
- [21] Kwabia Tchana F, Jacquemart D, Lacome N, Kleiner I, Orphal J. Absolute line intensities in methyl bromide: the 7-μm region. J Mol Spectrosc 2006;235:132-43.
- [22] Kwabia Tchana F, Ngom M, Perrin A, Flaud JM, Lafferty WJ, Ndiaye SA, Ngom El
 A. Absolute line intensities for oxirane from 1420 to 1560 cm⁻¹. J Mol Spectrosc 2013;292:1-4.
- [23] Ngom M, Flaud JM, Kwabia Tchana F, Lafferty WJ, Landsheere X, Perrin A, Ngom El A. Absolute line intensities for the v₃ band of oxirane (C₂H₄O). Canadian Journal of Physics 2013;91(11):906-09.
- [24] Kwabia Tchana F, Flaud JM, Lafferty WJ, Ngom. Absolute line intensities for oxirane in the 11.4 µm spectral region. Mol Phys 2014;112:1633-38.
- [25] Boussetta Z, Kwabia Tchana F, Aroui H. Self- and N₂-broadening of CH_3Br rovibrational lines in the v₂ band: The J and K dependence. J Mol Spectrosc 2015;308/309:33-40.
- [26] Ben Hassen A, Galalou S, Kwabia Tchana F, Dhib M, Aroui H. Self-and N₂-collisional broadening coefficients of ethylene in the 1800–2350 cm⁻¹ spectral region. J Mol Spectrosc 2016;326:73-80.
- [27] Dana V, Mandin JY. New improvements in the determination of line parameters from FTS data. J Quant Spectrosc Radiat Transf 1992;48:725-31.
- [28] Ballard J, Knight RJ, Vander Auwera J, Herman M, Di Lonardo G, Masciarelli G, Nicolaisen FM, Beukes JA, Christensen LK, McPheat R, Duxbury G, Freckleton R,

Shine KP. An intercomparison of laboratory measurements of absorption crosssections and integrated absorption intensities for HCFC-22. J Quant Spectrosc Radiat Transf 2000;66:109-28.

- [29] Jacquemart D, Kwabia Tchana F, Lacome N, Kleiner I. A complete set of line parameters for CH₃Br in the 10-µm spectral region. J Quant Spectrosc Radiat Transf 2007;105:264–302.
- [30] Jacquemart D, Guinet M. Line parameters measurements and modeling for the v_6 band of CH₃F: generation of a complete line list for atmospheric databases. J Quant Spectrosc Radiat Transf 2016;185:58–69.
- [31] Barbouchi Ramchani A, Jacquemart D, Dhib M, Aroui H. Line positions, intensities and self-broadening coefficients for the v_5 band of methyl chloride. J Quant Spectrosc Radiat Transf 2013;120:1–15.
- [32] Bray C, Jacquemart D, Lacome N, Guinet M, Cuisset A, Eliet S, Hindle F, Mouret G, Rohart F, Buldyreva J. Self-broadening coefficients of methyl chloride transitions at room temperature. J Quant Spectrosc Radiat Transf 2013;116:88–100.
- [33] Barbouchi Ramchani A, Jacquemart D. Line intensities and self-broadening coefficients for the v₂ band of methyl chloride. J Mol Spectrosc 2016;326:81–6.

Figure 1

The upper panel presents a small part of the spectrum of the v_6 band of CH₃I perturbed by N₂ (spectrum 4 in Table 1; open circles) overlaid by the corresponding best-fit calculated spectrum (solid line) obtained with a source aperture diameter of 2 mm, a maximum optical path difference of 150 cm and a Voigt profile. The lower panel shows the percent differences between the observed and calculated spectra.



Evolution with pressure of the N₂-collisional halfwidth of the ^RR(9,3,A₂), ^RR(25,3,A₁) and ^RR(34,6,A₁) lines in the v₆ band of CH₃I perturbed by N₂. The slope of the best-fit lines represent the N₂-broadening coefficients γ_{N_2} . The displayed error bars are twice the uncertainties of measurement.



Comparison between various sources of relative uncertainty on the measured N₂-broadening coefficients of 3 selected lines: ${}^{R}R(34,6)$, ${}^{R}R(25,3)$ and ${}^{R}R(9,3)$.



Shared description of the comparable broadening coefficients (measured and calculated by Eq. (3)) for sets of measurements corresponding to J = 6, 10, 35 and 40. The green up triangles (\blacktriangle) and black squares (\blacksquare) represent the measured N₂- and self-broadening coefficients, respectively, and the blue down triangles (\P and red squares (\blacksquare) are the corresponding calculated N₂- and self-broadening coefficients, respectively.



J-dependence of the measured and calculated self-broadening coefficients for all studied K values in the v₆ band of CH₃I.



J-dependence of the measured and calculated N_2 -broadening coefficients for all studied *K* values in the v_6 band of CH_3I .



Comparison of room temperature self-broadening coefficients measured in this work for ${}^{P}Q(J, 2)$ transitions in the v₆ band of CH₃I with results reported by Hoffman and Davies [18] for the v₅ band.



Comparison of room temperature N₂-broadening coefficients measured in this work for ${}^{P}Q(J, 4)$ transitions in the v₆ band of CH₃I with results obtained by Hoffman and Davies [18] for the v₅ band.

