Line parameters measurements and modeling for the ν_6 band of CH_3I: A complete line list for atmospheric databases

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Abstract

The present work is dedicated to the ν_6 band of $^{12}CH_3I$ with the aim of generating a complete line list for databases. High resolution Fourier transform spectra have been recorded in MONARIS and a multispectrum fitting procedure using Voigt profile has been applied to retrieve line positions, intensities, and self-broadening coefficients for around 1200 transitions of the ν_6 band between 854 and 963 cm^{-1}. Rotational dependences of transition dipole moment squared and self-widths have been studied and empirically modeled. Line positions are retrieved with accuracy equal to 4.10^{-4} cm^{-1}. The accuracy of line intensities and self-widths measurements is estimated between 5 and 10 %. Theoretical estimates of CH_3I self-broadening coefficients for large ranges of rotational quantum numbers ($0 \leq J \leq 70$, $0 \leq K \leq 20$) are also provided in the frame of a semi-classical approach with exact trajectories and of a semi-empirical method including a correction factor to the Anderson-type line-width expression. Comparisons of our results with the data previously published in the literature are presented and discussed. A complete line list of 5787 transitions is generated. Available as supplementary material, this line list can be used for spectroscopic databases and atmospheric or industrial detection of CH_3I.

1. Introduction

Halogenoid methyl molecules (CH_3X where X is an halogen) contribute to the destruction of the ozone layer [1,2]. Methyl iodide is the most abundant iodine-containing compound, emitted primarily by the oceans [3]. This molecule is also known as a tracer for radioactive pollution of nuclear power plants. Whereas spectroscopic line lists of CH_3Cl molecule have been present in atmospheric databases HITRAN [4] and GEISA [5] for decades, CH_3Br has been included only recently in the HITRAN 2008 [6] and GEISA 2009 [7] editions with line lists in the 7- and 10-µm spectral regions. A line list for CH_3F [8] around 8.5µm exists and should be included in the next HITRAN and GEISA editions. As for CH_3I, this molecule appears only in HITRAN and GEISA databases through cross-sections files: at 3 temperatures between 500 and 6900 cm^{-1} from Ref. [9] in HITRAN database [4] and at room temperature between 7473 and 7497 cm^{-1} from Ref. [10] in GEISA database [5]. No line parameter is available for CH_3I in these databases. Recent studies [11,12] have been performed in order to generate complete line lists for its detection. In the most recent work [13] measurements of line intensities are presented but no line list is given.

Most of the previous works on CH_3I concern analysis of rovibrational levels taking into account interactions between them. A non exhaustive list of spectroscopic works is available for the six fundamental bands of $^{12}CH_3I$: ν_1 [14], ν_2 [15,16], ν_3 [17], ν_4 [18], ν_5 [15,16,19,20] and ν_6 [11-13,21-24]. Many of these works describe interactions between close levels to model the rovibrational structure of the transitions. Some of them study the hyperfine structure [11,25] observed for CH_3I due to the large value of the ^{127}I nuclear quadrupole hyperfine constant.

As for experimental line intensity studies, recent measurements for 270 lines in the ν_5 and $\nu_3 + \nu_6$ bands issued from high resolution Fourier transform spectra analyzed by a single-spectrum fitting procedure with CH_3I pressures ranging from 0.270 to 2.433 mbar have been published by Boughdiri *et al*. [20]. Measurements for 840 lines in the ν_6 band have been reported by Kwabia Tchana *et al*. [13] using high resolution Fourier transform technique and multispectrum fitting procedure with CH_3I pressures ranging from 3.4 to 28.7 hPa.

A few studies concern line broadening parameters [25,26]. Using a double resonance technique for accurate determination of the broadening parameters of hyperfine components, Belli and coworkers [25] have investigated the hyperfine *F*-dependence (6 components) of the self-broadened CH_3I transition ($J = 10 \rightarrow 9$, $Kl = 9$) in the $\nu_5 = 1$ vibrational state. Hoffman and Davies [26] have measured self- (3 series of transitions ${}^{P}Q_2$, ${}^{P}Q_4$, ${}^{P}Q_6$) as well as N_2- and

O_2- (5 series of transitions ${}^{P}Q_2$, ${}^{P}Q_4$, ${}^{P}Q_5$, ${}^{P}Q_6$, ${}^{R}Q_3$) broadening coefficients for transitions in the ν_5 band using tunable diode laser absorption spectroscopy. From the theoretical point of view, to the best of our knowledge, solely the Anderson-type semi-classical calculations by Messer and Roberts [27] have been published.

The goal of the present work is to generate a complete line list around 9.5 μm for the ν_6 perpendicular band of $^{12}CH_3I$ based on the analysis by multispectrum fitting of high resolution Fourier transform spectra recorded at various pressures of methyl iodide. In particular, we consider deducing the transition dipole moments squared from the measured line intensities and their modeling. The empirical expression used previously for other CH_3X molecules [8,28-33] has been applied to model the *J*- and *K*- rotational dependences of self-broadening coefficients for the first time in CH_3I molecule. Moreover, theoretical estimates of CH_3I line-widths are provided by a semi-classical [34] and a semi-empirical [35] approaches for wide ranges of rotational quantum numbers ($0 \le J \le 70$, $0 \le K \le 20$) typically requested by spectroscopic databases.

The experimental conditions of the recorded spectra are presented in Section 2. Section 3 is dedicated to measurements and their analysis using empirical models for line intensities and self-widths. The main features of semi-classical and semi-empirical calculations are described in Section 4. Comparison between our results and those from the literature is discussed in Section 5. The details on the generation of a line list are given in Section 6. The final section summarizes the main conclusions of the present work.

2. Experimental spectra

Four Fourier transform spectra have been recorded at room temperature with pressures of CH_3I ranging from 1 to 10 mbar using the Bruker IFS 120 HR interferometer of MONARIS laboratory. The interferometer was equipped with a KBr beam splitter, a MCT photovoltaic detector, and a globar source. A stainless cell of (68.8 ± 0.1) cm path length was used to record all spectra without any optical filter. The cell was equipped with KBr windows. For the two lowest pressures a Bruker resolution equal to 0.002 cm^{-1} has been used (corresponding to an optical maximum path length of 450 cm), whereas a lower resolution of 0.004 cm^{-1} has been chosen for the other two. The experimental conditions (pressure, temperature, spectral resolution) are summarized in Table 1. For all recorded spectra, the nominal value of the radius of the beam inside the interferometer is equal to 0.575 mm and

the focal distance of collimation is equal to 418 mm. These values have been used in order to take into account the optical weighting (see Section 3 and Eq. 1).

(Table 1)

The commercial gas sample of methyl iodide, furnished by Sigma-Aldrich, with a more than 99% announced stated purity was used. Since no accurate purity had been given by Sigma-Aldrich, no correction has been performed. The pressure of CH_3I inside the cell has been measured using a 10 mbar full scale Baratron gauge with an accuracy of 0.25%.

The introduction of an accurate quantity of gas in the cell was complicated by the fact that CH_3I was sticking to the walls of the cell leading to a non linear decreasing of pressure with time (decreasing less and less fast with time). For that reason, the evolution of the gas with time was studied and, in order to minimize the variation of pressure during recordings, we started the recordings only 1-2 hours after introduction of gas when pressure was almost stable. Variations of pressure values during the recording (around 20 hours for each pressure) were less than 1%. Average pressure values are given in Table 1 for four experimental spectra.

The recorded interferograms have been Fourier trans-formed using the procedure included in the Bruker software OPUS Package [36], selecting a Mertz phase error correction. The spectra have not been numerically apodized. The signal-to-noise ratio (peak to peak) depends on the spectral resolution used. Spectra 1 and 2 recorded with a 0.002 cm^{-1} Bruker resolution have signal-to-noise ratios around 30 at 850 cm^{-1}, 70 at 890 cm^{-1} and 125 after 960 cm^{-1}. Spectra 3 and 4 recorded with a 0.004 cm^{-1} Bruker resolution have signal-to-noise ratios around 50 at 850 cm^{-1}, 120 at 890 cm^{-1} and 200 after 960 cm^{-1}. Figure 1 illustrates the structure of the ν_6 band between 936 and 958 cm^{-1} in spectrum 3 recorded with a pressure around 5 mbar (see Table 1). As one can see from Fig. 1, a very weak multiplicative channel, due to the cell windows, has been observed in experimental spectra (maximum peak-to-peak amplitude about 2%). The period of the channel (about 0.6 cm^{-1}) being much larger than the adjusted spectral domains (around $30\text{-}60\times10^{-3}$ cm^{-1}), this channel can easily and accurately be adjusted by a continuous background modeled with a polynomial function of order 1. No anomalous signature was found in the residuals of the fit. Note that the $2\nu_3$ band around 10 µm is too weak in our experimental conditions to be accurately measured.

(Fig. 1)

3. Measurements and empirical analysis

A multispectrum fitting procedure [37] has been applied to adjust simultaneously 4 experimental spectra of CH_3I (spectra 1-4, see Table 1 for experimental conditions), constraining the adjustment of a transition by using the same set of line parameters for the calculation of this transition observed under various experimental conditions. Calculated line positions from Ref. [12] have been used as initial positions for the fit and assignments of Ref. [12] have been used to calculate the energy of the lower state of the transitions based on spectroscopic parameters of Ref. [16]. As a final result line position, line intensity and self-broadening coefficient have been retrieved for around 1200 transitions of the ν_6 band. A sample of the measurements is given in Table 2. Line intensities $S_{obs}(T_0)$ have been retrieved in cm^{-1} (molecule $cm^{-2})^{-1}$ at T_0 = 296 K in natural abundance. For self-broadening coefficients no temperature dependence has been taken into account. The complete set of measurements can be found in supplementary material. The RMS of the fitted line parameters are given in Table 2 and associated supplementary material for line intensities and self-broadening coefficients and should not be confounded with accuracies. Accuracies have been estimated to be equal to $0.4.10^{-3}$ cm^{-1} for positions, and around 5-10% for intensities and widths. They accounts for the uncertainties in wavenumber calibration, concentration (1%), path length (0.1%), temperature (≤0.2%), thermal emission (≤1%), and signal-to-noise ratio (depending on spectral region, see Section 2). We also take into account the errors due to the "noise of operator", i.e. various operator's choices for each fitted spectral range: length of the considered frequency region, number of transitions included, fixing or letting free the parameters of unknown/weak transitions, ... Finally, since in the ν_6 band of CH_3I most spectral lines are overlapped, many weak transitions are not assigned, and the hyperfine structure becomes to be resolved under our experimental conditions, supplemental errors up to 5% evaluated from our fits are added for line intensities and self-broadening coefficients.

(Table 2)

Line intensities and line-widths are strongly correlated. An error in one parameter can be compensated by the fit of the other one leading to regular fit residuals but erroneous parameters. Multispectrum fitting of several experimental spectra recorded with various pressures of CH_3I is the best way to retrieve accurate line parameters. In this work 4 experimental spectra with pressures of CH_3I ranging from 1 to 10 mbar have been simultaneously adjusted to retrieve line positions, intensities and self-broadening coefficients.

Because of low pressures probed in this work, the CH_3I shift coefficients have been taken equal to zero. An example of the multispectrum fitting procedure for a spectral range containing 3 transitions is presented in Fig. 2. A Voigt profile has been used without observing any significant signature on residuals. One can also observe in low pressure spectra of Fig. 2 the well reproduced wings of the sinus cardinal apparatus function that almost disappear for the spectrum at 10 mbar. For this fit, the residuals do not exceed 1.5%.

For each spectrum, the apparatus function $f(\sigma)$ has been calculated performing numerically the Fourier Transform of the product of the boxcar function due to finite optical path difference Δ_{max} and the optical weighting P_{opt} due to the size of the beam source inside the interferometer [37].

$$f(\sigma) = TF\left[\Pi_{\Delta_{\max}}(\Delta).P_{opt}(\Delta) \right], \tag{1}$$

where the boxcar function $\Pi_{\Delta_{\max}}(\Delta) = 1$ for $0 \le \Delta \le \Delta_{\max}$ and $\Pi_{\Delta_{\max}}(\Delta) = 0$ for $\Delta > \Delta_{\max}$, and the optical weighting $P_{opt}(\Delta) = \left| \mathrm{sinc}\left(\frac{\sigma_0 \Omega \Delta}{2} \right) \right|$ with $\Omega = \pi \frac{R^2}{f^2}$. R is the beam radius in mm inside the interferometer, f (in mm) is the focal distance used to focus the source on the entrance diaphragm. σ_0 is the wavenumber of the studied transitions in cm^{-1} and Δ is the optical path difference in cm.

(Fig. 2)

Concerning wavenumber calibration, small traces of CO_2 present in the interferometer chamber allowed us to observe transitions of the intense ν_3 band of CO_2 around 2300 cm^{-1}. Wavenumbers from HITRAN 2016 [4] coming from the work of Zak *et al*. [38] have been used as etalons. The quantity $\varepsilon = (\sigma_{\mathrm{HITRAN}} - \sigma_{\mathrm{this\ work}})/\sigma_{\mathrm{HITRAN}}$ has been retrieved for 35 transitions in each spectrum. Wavenumbers calibration is equivalent for all spectra and the mean value $< \varepsilon > = (-2.2 \pm 0.3(\mathrm{SD})) \times 10^{-7}$ has been retained for the four experimental spectra. An error of 0.3×10^{-7} on mean value $< \varepsilon >$ leads to an error of 0.4×10^{-4} cm^{-1} at 1000 cm^{-1}. Taking into account the accuracy of CO_2 line positions in HITRAN2016 [4] (equal to 10^{-4} cm^{-1}) and the SD of the mean value $< \varepsilon >$, the accuracy of line positions measurements is equal to 0.4×10^{-3} cm^{-1}.

Methyl iodide is affected by hyperfine structure and some hyperfine components resolved in our lowest pressure spectrum have been studied. Such components have been marked by a star at the end of the assignment columns in Table 2 (and associated supplementary material), meaning that the observed transition corresponds to an unknown quantity of hyperfine components. In such conditions, retrieved line intensity is useless and not considered (not present in Table 2 and associated supplementary material). However, the self-broadening coefficient is much less affected by the number of components forming the fitted bunch of transitions. Analysis of such transitions is of importance since it allowed us to reach self-broadening parameters for small J values, and consequently to obtain a better model for the self-widths.

For all transitions with K = 3, 6, 9 ... the two components $A_1 \rightarrow A_2$ and $A_2 \rightarrow A_1$ are not resolved and have been fitted together (the rotational quantum numbers of the lower state of the transitions are simply noted as J and K hereafter). For such transitions, the symmetry A is given (see Table 2 and associated supplementary material). Among the 1225 transitions studied in this work, 236 transitions correspond to hyperfine components marked with a star.
Note also that for 31 other transitions (not marked with a star) the line intensity parameter is not given. It corresponds to weak transitions for which the line intensity seemed erroneous whereas the self-widths looked consistent with our other measurements.

Transition dipole moments squared R^2 (in Debye²) have been calculated from retrieved line intensities $S_{obs}(T_0)$ using following equation including Hönl-London factor H_{JK} [39]:

$$R^2 = S_{obs}(T_0)\frac{3hc}{8\pi^3 I_a}\frac{4\pi\varepsilon_0 Z_{tot}(T_0)\exp\left(hcE''/k_B T_0\right)}{g_s\sigma_0\left(1-\exp\left(-hc\sigma_0/k_B T_0\right)\right)H_{JK}}, \qquad (2)$$

with
$$H_{JK} = \begin{cases} \dfrac{(J-K\Delta K)(J-K\Delta K-1)}{4J} & \text{for } \Delta J = -1 \\ \dfrac{(2J+1)(J(J+1)-K(K+\Delta K))}{4J(J+1)} & \text{for } \Delta J = 0, \\ \dfrac{(J+K\Delta K+2)(J+K\Delta K+1)}{4(J+1)} & \text{for } \Delta J = +1 \end{cases} \qquad (3)$$

where ΔK = −1, 1, 0 for the P, R and Q sub-branches respectively; h is the Planck's constant equal to 6.6260755×10^{-27}erg.s (1 erg $=10^{-7}$ J); c is the vacuum velocity of light equal to

2.99792458 10^{10} cm s^{-1}; σ_0 is the transition wavenumber in cm^{-1}; E" is the energy of the lower state in cm^{-1} which has been calculated using spectroscopic parameters of Ref. [16]. I_a is the natural abundance of $^{12}CH_3I$ equal to 98.9%. k_B is the Boltzmann's constant equal to 1.380658 $\times 10^{-16}$erg.K^{-1}; g_s is the statistical weight of the lower level due to nuclear spins from H and I atoms ($g_s = g_I \times g_H$). For all levels $g_I = 6$. g_H depends on the rotational level, and is equal to 8 for K = 0, 3, 6, 9, … and equal to 4 for others K values. The total partition function Z_{tot} used in Eq. (2) has been taken from Ref. [13] using identical statistical weights.

(Fig. 3)

(Fig. 4)

The transition dipole moments squared R^2 obtained using Eqs. (2-3) have been plotted versus m ($m = -J, J, J+1$ for the P-, Q-, R-branch respectively) in Fig. 3 separately for each K value. As observed in Fig. 3, no significant K- or sub-branch dependences are detected. By plotting all transition dipole moment squared in Fig. 4, small m dependence has been observed and modeled using Herman-Wallis factor H(m) to deduce vibrational transition dipole moment squared R_0^2:

$$R^2 = R_0^2 H(m) = R_0^2 (1 + A \times m) \quad (4)$$

Values of R_0^2 = 0.00401(2) D^2 and $A = -5.9(6)\times 10^{-4}$ have been obtained with between parentheses 1SD in the last unit of the digit: such notation will be used hereafter meaning in the present case R_0^2 = (0.00401 ± 0.00002) D^2 and $A = (-5.9 \pm 0.6)\times 10^{-4}$. Statistics on comparison between the measured and calculated (using Eq. (4) and R_0^2 and A parameters obtained in this work) line intensities are given in Table 3.

(Table 3)

For self-broadening coefficients, a strong J- and K- rotational dependence has been observed and modeled for the first time in CH_3I molecule using similar empirical model as

used for CH_3Cl [29-32], CH_3Br [28] and CH_3F [8]. No significant sub-branches dependence was observed. The observed self-broadening coefficients have been modeled as following:

$$\gamma_J(K) = a_J^0 + a_J^2 K^2 . \quad (5)$$

The zero-order coefficients a_J^0 correspond to the self-broadening coefficients for K = 0 transitions whereas the a_J^2 parameter allows modeling the K-rotational dependence. For high J values, the a_J^2 parameters getting closer to zero lead to difficulties to retrieve accurate parameters. Such a model requires a large amount of measurements at various J and K values to retrieve the reliable polynomial parameters a_J^0 and a_J^2 for each J value.

(Fig. 5)

Figure 5 shows an example of the observed and modeled K-rotational dependence for 4 values of J (J = 5, 12, 20, 27). The a_J^0 and a_J^2 coefficients obtained for J values ranging from J = 1 to 69 are given in Table 4 and have been plotted in Fig. 6 versus J for each K values. One can notice that as for CH_3F [8], CH_3Cl [29-32] and CH_3Br [28] the a_J^0 and a_J^2 parameters are smoothly J dependent. In the present work, a set of smoothed parameters (with some interpolations and slight extrapolations) has been manually obtained. This set of smoothed a_J^0 and a_J^2 parameters is given in Table 4 and plotted in Fig. 6 (red line).

(Table 4)

(Fig. 6)

This set of parameters allows generating self-broadening coefficients for any transitions with J up to 80 and K up to 15, using extrapolations for K= 13-15, and from J = 50-70 (depending on K values) to J = 80. The measured and modeled air-widths (using smoothed a_J^0 and a_J^2 parameters of Table 3 and Eq. (1)) have been plotted versus J separately for each K value in Fig. 7 and shows that the model reproduces quite well the rotational dependence of the measured self-broadening widths. Statistics of this comparison are given in Table 3.

4. Theoretical approaches to self-broadening coefficients

4.1. Semi-classical calculations

The collisional line-widths related to the transitions $i\ (J_i,K_i) \rightarrow f\ (J_f,K_f)$ were computed by the following traditional expression [40]

$$\gamma_{if} = \frac{n\bar{\mathrm{v}}}{2\pi c}\int_0^\infty 2\pi b db\left\langle 1-\mathrm{e}^{-\mathrm{Re}\,S_2}\right\rangle_{J_2} \qquad (6)$$

where n is the number density of perturbing particles, $\bar{\mathrm{v}}$ is the mean thermal velocity, b is the impact parameter further replaced by the distance of the closest approach r_c, and S_2 are the second-order contributions to the scattering matrix. We did not employ the modified formula [41]

$$\gamma_{if} = \frac{n\bar{\mathrm{v}}}{2\pi c}\int_0^\infty 2\pi b db(1-\mathrm{e}^{-\mathrm{Re}\langle S_2\rangle_{J_2}}) \qquad (7)$$

(performing the average $\langle\ldots\rangle_{J2}$ on the perturber's rotational states J_2 as the cumulant average in order to insure a correct application of the cumulant expansion) since our previous studies on a similar CH_3Cl-CH_3Cl system [30] demonstrated unrealistic J- and K-dependences obtained with this formula.

The trajectories of the relative translational motion were computed as exact ones [42], and the isotropic potential V_{iso} governing these trajectories was taken in the Lennard-Jones form with the parameters ε = 232.86 K, σ = 3.6367 Å [43]. It is noteworthy that this very recent potential is two times shallower than the potential proposed by Campbell *et al*. [44] (ε = 467 K, σ = 4.50 Å) and is by 37% less deep than the potential we used for the similar CH_3Cl-CH_3Cl system (ε = 368.4 K, σ = 3.584 Å [45]). By choosing it we expected avoiding the artificial cut-off on the maximal intermolecular distance necessary for self-perturbed CH_3Br [46] and CH_3Cl [30] line-widths to match the experimental data near the maximum of broadening.

In the anisotropic potential, basing on our previous experience with CH_3Cl, we considered solely the long-range electrostatic terms. As CH_3I molecule has a quite high value of the dipole moment (μ = 1.6413 D [47]), the interactions between the active and perturbing molecules are dominated by the electrostatic dipole-dipole contribution. However, in contrast with the CH_3Cl self-perturbation case considered by us previously [30], the CH_3I quadrupole moment (Q = 10.70 DÅ [48]) is much bigger than that of CH_3Cl (Q = 1.23 DÅ [49]) and both

dipole-quadrupole and quadrupole-quadrupole terms contribute significantly to the line broadening.

The dipole-dipole, dipole-quadrupole and quadrupole-quadrupole components of the potential were used to calculate the corresponding resonance functions $f_{l_1 l_2 l}^{k_1 k_2}$ determining three contributions $S_{2,i2}$, $S_{2,f2}$, $S_{2,f2i2}$ to the second-order scattering matrix term S_2:

$$S_{2,i2} = \frac{2r_c^2}{\eta^2 \bar{v}^2} \sum_{\substack{l_1 l_2 l \\ k_1 k_2}} [(2l_1+1)(2l_2+1)]^{-1} \sum_{\substack{J_i' K_i' \\ J_2' K_2'}} \left(C^{J_i' - K_i'}_{J_i - K_i \, l_1 k_1} \right)^2 \left(C^{J_2' - K_2'}_{J_2 - K_2 l_2 k_2} \right)^2 f_{l_1 l_2 l}^{k_1 k_2} \, , \tag{8}$$

$$S_{2,f2i2} = -\frac{2r_c^2}{\eta^2 \bar{v}^2} \sum_{\substack{l_1 l_2 l \\ k_2}} (-1)^{\rho + l_2 + l} [(2l_1+1)(2l_2+1)]^{-1} D(J_i J_f K_i K_f ; \rho l_1) \sum_{J_2' K_2'} \left(C^{J_2' K_2'}_{J_2 K_2 l_2 k_2} \right)^2 f_{l_1 l_2 l}^{0 k_2} \, , \tag{9}$$

The functions $f_{l_1 l_2 l}^{k_1 k_2}$ have the same form as those given in Ref. [50] for CH_3X-Y_2 but with the second superscript (zero) of the radial potential components replaced by k_2. The coefficients $D(J_i J_f K_i K_f ; \rho l_1) = (-1)^{J_i + J_f} 2[(2J_i+1)(2J_f+1)]^{1/2} \left(C^{J_i K_i}_{J_i K_i l_1 0} \right) \left(C^{J_f K_f}_{J_f K_f l_1 0} \right) W(J_i J_f J_i J_f ; \rho l_1)$, besides the Clebsch-Gordan coefficients $C^{lm}_{l_1 m_1 l_2 m_2}$, depend on the Racah coefficients $W(J_i J_f J_i J_f ; \rho l_1)$, and their analytical expressions change from one sub-branch ($^{R,P}P$, $^{R,P}Q$, $^{R,P}R$) to another.

Before going to massive computations of line-broadening coefficients we evaluated the number of effectively populated rotational levels (see Table 5 for the rotational constants values). The rotational partition function Q_r = 6075.431 was found to be converged with J_{max} = 106 and K_{max} = 22. Further trial computations of line-width J-dependences for K = 0 and K = 20 with all three electrostatic contributions showed that even J_{max} = 90 ensures the results converged within 4 significant digits, and this seems reasonable for comparison with experimental values. The convergence with respect to the resonance parameter was obtained even for $k_{c\ max}$ = 20 but in our calculations we kept $k_{c\ max}$ = 25. The intermolecular distances were taken into account up to their very high values and the line-widths were found to be nearly converged (within ≈1%) with the maximal value of 35 Å.

(Table 5)

4.2. Semi-empirical calculations

The semi-empirical approach [35] is a variant of impact theory extended by the use of empirical data to determine some fitting model parameters. It enables a realistic prediction of line-broadening and line-shifting parameters via introducing effective correction factors to the

interruption functions. As it was proposed in [35] the efficiency function can be represented in the form

$$P_l\ (\omega) = P_l^A(\omega) C_l(\omega)\,, \tag{10}$$

where $P_l^A(\omega)$ is the efficiency function of Anderson theory and $C_l(\omega)$ is a correction factor.

It was found that the correction factor in the case of CH_3I-CH_3I calculations is sufficiently described by a *J*-dependent efficiency function:

$$P_l\left(\omega_{ii'}\right) = P_l^A\left(\omega_{ii'}\right)\left[c_1/(c_2\sqrt{J_i}+1)\right] \tag{11}$$

where c_1 and c_2 are fitting parameters. The form of the correction factor is determined from the analysis of the rotational dependence of line-widths. The use of the correcting factor in Eq. (11) allows one to correctly describe the line broadening behavior at high values of quantum numbers *J*.

The model parameters determined for the ${}^RQ$-branch (Table 6) were used with some small modifications for line-widths in the ${}^RP$- and ${}^RR$-branches and then used for ${}^PQ$-, ${}^PP$- and ${}^PR$-branches without change.

(Table 6)

5. Comparison with literature

Comparisons with calculated line positions and from line list published in Ref. [12] are presented in Table 3. . A systematic shift of $0.8(2)\times10^{-3}$ cm^{-1} is observed between our measurements and calculations from Ref. [12] whereas a better consistency is observed with measured line positions of Ref. [13] (see Table 3). Note that the line positions retrieved for the hyperfine components (marked by stars in Table 2) have not been retained since the calculation of Ref. [12] did not take into account the hyperfine structure. No comparison is presented for the line intensities since the relative intensities given in Ref. [12] are strongly overestimated up to a factor of 1000 depending on transitions.

In the very recent work of Kwabia-Tchana *et al*. [13], a similar multispectrum procedure was used to retrieve line positions, intensities, and self-broadening coefficients from spectra of pure CH_3I with pressures ranging from 3.4 to 28.7 hPa. At these pressures the self-widths become quite important. However, no self-broadening coefficients were published in Ref. [13]. Comparisons of the line intensities measured our work and in Ref. [13] are

presented in Figs. 3 and 4 using transition dipole moment squared. Despite quite a strong dispersion, a good consistency is observed between our line intensities and those of Ref. [13]. For the ν_6 band, the vibrational transition dipole moment squared derived from measurements in Ref. [13] is equal to 0.00378 D^2, being 5-6% lower than our R_0^2 value. Note that the accuracy of the measured line intensities in Ref. [13] is equal to 3%, probably underestimated in view of the dispersion of R^2 values (see our Figs. 3-4) that have been calculated from the present measurements and those of Ref. [13]. The average discrepancy between the line intensities of Ref. [13] and those of our work is equal to 2% with 1SD = 11%. As for the line positions, the agreement is much better since the average difference between the line positions of Ref. [13] and those of the present work is equal to $0.13(5)\times10^{-3}$ cm^{-1}; a less favorable comparison is stated with the results of Ref. [12]. The dispersion is also 4 times less when compared to that of Ref. [13]. Detailed statistics of comparisons of line positions and intensities from this work and those of Ref. [13] can be found in Table 3.

The measurements of self-broadening coefficients by Hoffman and Davies [26] obtained for the ν_5 band of CH_3I at 7 μm are plotted in Fig. 7 (blue triangles). As solely 3 series of transitions ${}^{P}Q_2$, ${}^{P}Q_4$, and ${}^{P}Q_6$ were studied in Ref. [26], comparisons are available only for K = 2, 4 and 6. A good consistency between our measurements and those of Ref. [26] is observed except for K=2 where the J-rotational dependence from Ref. [26] increases slower.

(Fig. 7)

Calculations of CH_3I self-broadening coefficients have been done for all six sub-branches ${}^{R}R$, ${}^{P}R$, ${}^{R}Q$, ${}^{P}Q$, ${}^{R}P$ and ${}^{P}P$ of the ν_6 band. Comparison between measurements and various models can be visualized in Fig. 8 for the ${}^{R}R$-sub-branch case. For the other sub-branches the figures are quite similar and are not given. As can be seen from this figure, the semi-empirical (SE) results generally match the experimental points better than the semi-classical (SC) calculations. One can easily understand this from the use of the empirically-fitted model parameters in the SE approach. The SC computations however are not very far from the measurements and, contrary to the case of CH_3Cl self-broadening [30], without any artificial cut-off on the maximal value of the intermolecular distance. The difference with

CH_3Cl can be attributed to quite a shallow isotropic potential employed for CH_3I in comparison with that for CH_3Cl.

To get an idea about the performances of our empirical modeling and our theoretical approaches to predict the line-broadening at high *K*-values inaccessible experimentally, we plotted the *J*-dependences for all considered *K* in different panels of Fig. 9. The general trends of *J*-dependences for fixed *K*-values are quite similar for all three approaches, and the self-broadening coefficients range globally between 0.20 and 0.45 $cm^{-1}atm^{-1}$. For *K*=0 the empirical model and the semi-empirical approach give very similar results since based on fits to experimental values; the semi-classical calculations (traditionally) underestimate the broadening at very small *J*. The asymptotic high-*J* behaviors predicted by SC and SE calculations are nearly the same:

(Fig. 8)

(Fig. 9)

Measurements performed for CH_3Cl molecule in submillimeter/terahertz region (0.2 − 1.4 THz) and at 3 μm [30], showed no significant vibrational dependence. For CH_3I, self-broadening coefficients by Hoffman and Davies [26] (obtained for the ν_5 band of CH_3I at 7 μm) are in good agreement with the present measurements around 10 μm. It means that the vibrational dependence is weak and the results obtained in the present work for the ν_6 band may be safely used for other bands.

6. Complete line list

Complete line list meaning requires for each transition the assignment, the lower state energy, the line position, intensity, the self- and N_2-broadening coefficients and temperature dependence exponents as listed in HITRAN [4] and GEISA [5] databases. From our reduced set of measurements, models are used in order to generate a complete line list.

As shown by the statistics of comparisons in Table 3, the various models (this work and Refs. [12,13]) are quite satisfactory to reproduce measurements within sufficient accuracies for first atmospheric detection using line parameters instead of absorption cross-sections data. The line list of the ν_6 band has been built in HITRAN format [4,51] using the complete calculation of line positions and assignments available from Ref. [12]. A constant correction of -0.8×10^{-3} cm^{-1} has been applied for all line positions in order to be in better agreement with measurements of the present work and those of Ref. [13]. The line list of

positions and assignments from Ref. [12] has been used despite a better agreement with published line positions of Ref. [13] because no complete calculations was available from Ref. [12] For most of atmospheric instruments using lower resolution than 0.01 cm^{-1}, line positions of Ref. [12] (with no hyperfine structure) will be enough to accurately model atmospheric spectra. The assignments of the transitions are given in two fields for both upper and lower states. For the vibrational fields, a text notation is given: "NU6" for the upper state and "GROUND" for the lower state (see for example CH_3Cl notation described in HITRAN 2004 [51]). For the rotational fields, the *J* and *K* quantum numbers as well as the symmetry *A* / *E* are given using HITRAN format (see Ref. [51]). The line intensities in cm^{-1} (molecule $cm^{-2})^{-1}$ at 296 K for natural abundance of CH_3I 98.9% have been calculated using Eqs. (2-4) and R_0^2 and *A* parameters obtained in this work (see Section 3). For the self-broadening coefficients, the empirical model developed in Section 3 and the SE and SC models presented in Section 4 are quite consistent within 10-20%. The empirical model has been used for all transitions of the line list since it reproduces better the whole set of experimental measurements. Note that less than 5% transitions in the present line list have *J*- and *K*-rotational quantum numbers corresponding to extrapolations of the empirical model. If extended (*K* up to 20) or missing in our measurements sets of rotational quantum numbers are required, we recommend the use of semi-empirically computed self-broadening coefficients which provide better (with respect to the SC computations) agreement with measurements and consider all six sub-branches individually. Forthcoming measurements of N_2-broadening and/or air-broadening for transitions of the ν_6 band are in preparation, as well as theoretical calculations. However in the meantime, it has been decided to use the N_2-broadening coefficients of CH_3Br [28] multiplied by 0.9 in order to estimate the air-broadening coefficients. The air-broadening coefficients of the present line list will be updated in our forthcoming paper. The energies of the lower state (ground state) of the transitions have been calculated using spectroscopic parameters of Table 1 and Eq. (3) of Ref. [16]. The final line list contains line parameters for a total of 5787 transitions belonging to the ν_6 band and ranging between 762 and 1025 cm^{-1} with line intensities ranging from $0.5.10^{-23}$ to 10^{-21} cm^{-1}(molecule $cm^{-2})^{-1}$. A cutoff of 10^{-23} cm^{-1} (molecule $cm^{-2})^{-1}$ has been used except for *K*= 3, 6, 9, 12, 15 transitions which have two components $A_1 \rightarrow A_2$ and $A_2 \rightarrow A_1$ present in our line list and for which the cutoff has been divided by 2.

HITRAN accuracy codes [51] have been used in the line list. The code 4 has been used for line positions (between 0.1×10^{-3} cm^{-1} and 1×10^{-3} cm^{-1}), the code 5 for line intensities

(between 5 and 10%), the code 5 for air-broadening coefficients (between 5 and 10%), the code 5 for the self-broadening coefficients (between 5 and 10%), and the code 2 for temperature dependence of the widths and air-shifting coefficients (average or estimate).

A sample of this list is presented in Table 7 between 910 and 912 cm^{-1} and the complete line list of 5787 transitions is available as supplementary material. Note that molecule number 50 has been arbitrary chosen in Table 7 and associated supplementary material. This line list should be useful for atmospheric or industrial detection of CH_3I. For atmospheric measurements, new generation of instruments as future IASI-NG satellite instrument (Infrared Atmospheric Sounding Interferometer New Generation), may be able to detect CH_3I. As for industrial detection, cavity ring down spectroscopy is probably the best way to detect with good accuracy small quantity of CH_3I in industrial environment.

(Table 7)

7. Conclusion

The present study is based on analysis of high resolution Fourier transform spectra and measurements of line positions, intensities and self-broadening coefficients of ν_6 transitions of $^{12}CH_3I$ at room temperature. Based on a large set of measurements obtained for various *J* and *K* values, empirical models have been used to predict line intensities and self-broadening coefficients. In addition of the empirical treatment of the self-broadening coefficients, semi-classical and semi-empirical calculations showing a good consistency have been performed. A forthcoming work will focus on N_2-broadening coefficients to replace approximations performed in this work concerning this line parameter. A complete list in HITRAN format has been generated for 5787 transitions of the ν_6 band. This line list is available as supplementary material for atmospheric detection of CH_3I in the 9.5 µm spectral region.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version

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