Empirical line parameters of methane in the 1.63–1.48 μm transparency window by high sensitivity Cavity Ring Down Spectroscopy

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ARTICLE INFO

Article history:
Received 4 April 2010
In final form 10 May 2010
Available online 31 May 2010

Keywords:
Methane
CH₄
CH₃D
Titan
CRDS
HITRAN

ABSTRACT

The positions and intensities of methane in the 1.58 μm transparency window have been measured by high sensitivity Cavity Ring Down Spectroscopy at room temperature. The achieved sensitivity allowed measuring intensities as small as 3 × 10⁻²⁹ cm/molecule i.e. three orders of magnitude smaller than the intensity cut off of the HITRAN line list of methane. The complete list contains a total of 16,149 transitions between 6165 and 6750 cm⁻¹. Their intensity values vary over six orders of magnitude from 1.6 × 10⁻²⁶ to 2.5 × 10⁻²³ cm/molecule. Transitions due to CH₃D in “natural” abundance in our methane sample were identified using a new spectrum of CH₃D recorded separately with a Fourier Transform spectrometer. From simulations of the CH₃D and methane spectra at low resolution, the CH₃D isotopologue has been found to contribute by up to 30% of the absorption near 1.58 μm. © 2010 Elsevier B.V. All rights reserved.

1. Introduction

Methane is present in a large variety of astronomical objects including Titan, giant outer planets and comets. In view of applications to planetary science, the knowledge of the absorption spectrum of methane at very high sensitivity is required in particular in the spectral windows of low opacity. While the ¹³CH₄ infrared absorption spectrum can be theoretically modelled above 2 μm, the near infrared spectrum is not yet understood and lists of empirical line parameters provide an alternative solution. The difficulties encountered in the theoretical treatment are a consequence of the extreme spectral congestion in the near infrared region caused by anharmonic couplings between stretching and bending modes that leads to complicated polyad structure [1]. Due to approximate relations between the vibrational frequencies, υ₁ ≈ υ₅ ≈ 2υ₂ ≈ 2υ₆, each polyad is characterized by a polyad number P = 2υ₁ + υ₅ + υ₂ + υ₆, where υᵢ are the normal mode vibrational quantum numbers. The present report is devoted to the 1.63–1.48 μm transparency window lying between the tetradecad (P = 4) region dominated by the 2υ₃ band at 6004 cm⁻¹ and the icosad (P = 5) region. Theoretical calculations (see Ref. [2] for instance) show that the lowest bands of the icosad which are very weak (in particular 5υ₄) fall in our region and are then partly responsible of the residual absorption. Due to the high density of states in interaction – the icosad contains 20 vibrational levels and 134 sub-levels [1] – standard iterative techniques of spectral analysis cannot be applied because no regular rotational progressions can be identified even for the lowest rotational states. In consequence, above 5000 cm⁻¹ the HITRAN08 database [3] provides empirical line by line spectroscopic parameters without rovibrational assignments. The upper panel of Fig. 1 shows the HITRAN line list between 5800 and 7000 cm⁻¹. In the tetradecad region (5500–6150 cm⁻¹), the HITRAN database in its last version [3] reproduces the empirical line positions and intensities obtained by Margolis 20 years ago [4,5]. Note that in HITRAN08, some of the Margolis intensities [4,5] of the 2υ₃ transitions were slightly changed using the results obtained by Frankenberg et al. [6]. Above 6180 cm⁻¹, the spectroscopic parameters obtained by Brown by Fourier Transform Spectroscopy (FTS) with path lengths up to 97 m [7] were adopted. As illustrated in Fig. 1, the intensity cut off in the tetradecad region is relatively high (about 4 × 10⁻²⁴ cm/molecule) i.e. two orders of magnitude higher than above 6180 cm⁻¹. The characterization of the tetradecad has been recently improved by a line list constructed in relation with the “Greenhouse Gases Observing Satellite” (GOSAT) project [8]. The GOSAT line list [9], also presented in Fig. 1, has a 4 × 10⁻²⁶ cm/molecule intensity cut off which is equivalent to the HITRAN intensity cut off above 6180 cm⁻¹.

The HITRAN08 line list for methane includes also the 3υ₂ band of CH₃D of importance for planetary applications (see Fig. 1). The line positions and line intensities were obtained by Lutz et al. [10] and Boussin et al. [11], respectively, from FTS spectra of a CH₃D sample with a sample purity of 96.8%. The HITRAN line intensities being scaled according to the relative abundance of CH₃D in methane (6.15 × 10⁻⁴ [3]), it leads to intensity values ranging
between $1.4 \times 10^{-28}$ and $2.5 \times 10^{-26}$ cm$^{-2}$ molecule$^{-1}$, much below the $4 \times 10^{-26}$ cm$^{-2}$ molecule$^{-1}$ cut off corresponding to the main isotopologue. This CH$_3$D band at 6430 cm$^{-1}$ has been used to determine the D/H ratio on Titan for instance [12,13]. The CH$_3$D absorption is then observed superimposed to the absorption of the main isotopologue which is poorly characterized. This is the reason why the analysis of the planetary atmospheres [12–15] uses Saturn spectrum as an intermediary spectrum of methane. In a very recent contribution [16], the Cavity Ring Down Spectroscopy technique was used to characterize at high sensitivity the methane absorption spectrum in the region of this $3v_2$ band of CH$_3$D (6289–6526 cm$^{-1}$). This technique allows increasing by more than 3 orders of magnitude the sensitivity achieved in the region of interest, the results obtained by Deng et al. [17] in the 6607–6625 cm$^{-1}$ section should be mentioned. These authors used direct absorption with a tunable diode laser and a White cell with a 973 m path length to detect 288 lines with intensities down to $1.4 \times 10^{-27}$ cm$^{-2}$ molecule$^{-1}$ (see Fig. 1 upper panel).

The rest of this report is organized as follows: after a brief description of the CW-CRDS spectrometer, we will present in Section 2 the line list construction which was a laborious task considering the congestion and blending of the spectrum. In Section 3, we will compare our line parameters to those provided in the HITRAN database. Section 4 will be devoted to the identification of the CH$_3$D lines by comparison with a spectrum of CH$_3$D recorded separately by Fourier Transform Spectroscopy and to the estimation of the importance of the CH$_3$D contribution from low resolution simulations.

2. Experiment and line list construction

Some of the presently analyzed spectra are those recorded in Ref. [18] but additional recordings were performed extending the spectral coverage and the pressure conditions. The CW-CRDS spectra were obtained with our “standard” fibered DFB laser CW-CRDS spectrometer described in Refs. [18–20]. The 6165.7–6749.5 cm$^{-1}$ region was continuously covered with the help of 27 fibered DFB lasers. The DFB typical tuning range is about 35 cm$^{-1}$ by temperature variation from −5 to 60 °C. The stainless steel ringdown cell (l = 1.42 m, φ = 10 mm) is fitted by a pair of super mirrors with a typical ring down time on the order of τ ~ 60 μs. About 100 ringdown events were averaged for each spectral data point and 70 min were needed to complete a temperature scan of one DFB laser. The corresponding noise equivalent absorption is on the order of $5 \times 10^{-10}$ cm$^{-1}$ [18].

The methane sample was purchased from Air Liquide (stated purity >99.995%). During the recordings, the pressure measured by a capacitance gauge and the ringdown cell temperature were monitored. The temperature value was 297 ± 2 K. Most of the spectra were recorded at 2.5 and 10.0 Torr but lower values down to 0.25 Torr were used near the borders of the investigated region where absorption is stronger.

Each 35 cm$^{-1}$ wide spectrum recorded with one DFB laser was calibrated independently on the basis of the wavelength values provided by the Michelson-type wavemeter (Burleigh WA-1650, 60 MHz resolution and 100 MHz accuracy). The wavemeter accuracy being limited to $3 \times 10^{-3}$ cm$^{-1}$, the absolute calibration was obtained by a statistical matching of the line positions to those listed in the HITRAN database [3]. Very recently, a high sensitivity FTS spectrum was recorded in Reims (non-apodized resolution of 0.0017 cm$^{-1}$, l = 1603 m, P = 1 and 5 Torr) [21]. The Reims spectrum could be accurately calibrated against the 30012–00001 band of $^{12}$CO$_2$ (added in small quantity) near 6348 cm$^{-1}$ [3] which appears superimposed to the methane spectrum. We decided to use this calibrated spectrum to refine the calibration of the CRDS spectra. The comparison with the HITRAN line positions shows a systematic shift of $1.1 \times 10^{-3}$ cm$^{-1}$ on average compared to Reims spectra, Reims values (and then our values) being larger than HITRAN values. The use of Reims spectrum instead of HITRAN data has also the advantage to solve a significant shift between Margolis [4,5] and Brown [7] calibrations around 6180 cm$^{-1}$. The precision of the obtained wavenumber calibration estimated from the dispersion of the wavenumber differences is on the order of $1 \times 10^{-4}$ cm$^{-1}$.

The overview of the CW-CRDS spectra over the whole transparency window is shown in the upper panel of Fig. 2. Four successive enlargements illustrate the high dynamics on the intensity scale of...
the recordings and the impressive congestion of the methane spectrum in the considered transparency window. Absorption coefficients differing by more than four orders of magnitude can be measured from a single CW-CRDS spectrum. Note that, over most of the region, spectral sections free of absorption lines are extremely scarce and the absorption is larger than the noise level.

The line intensity, \( S_m \) (cm/molecule), of a rovibrational transition centred at \( \nu_0 \), was obtained from the integrated absorption coefficient, \( A_m \) (cm\(^{-2}\)/molecule):

\[
A_m(T) = \int \alpha(v)\, dv = S_m(T)N
\]

where, \( \nu \) is the wavenumber in cm\(^{-1}\), \( \alpha(\nu) \) is the absorption coefficient in cm\(^{-1}\), and \( N \) is the molecular concentration in molecule/cm\(^3\) obtained from the measured pressure and temperature values: \( P = NkT \) (\( k \) is the Boltzmann constant).

An interactive multi-line fitting program was used to reproduce the spectrum [22]. A Voigt function of the wavenumber was adopted for the line profile as the pressure self broadening has a significant contribution. As isolated lines are exceptions, the first step of the analysis consisted in the manual determination of the spectral sections of overlapping or nearby transitions that could be fitted independently. The local baseline (assumed to be a cubic function of the wavenumber) and the three parameters of each Voigt profile (line center, integrated absorption coefficient, HWHM of the Lorentzian component) were fitted. The HWHM of the Gaussian component was fixed to its theoretical value for \( ^{12}\text{CH}_4 \).

As a rule, in the case of blended lines or lines with low signal to noise ratios, the Lorentzian HWHM was also constrained to the average value obtained from nearby isolated lines.

It is worth underlining the difficulties of the line profile fitting due to the high density and systematic overlapping of the lines. The average density of lines is 27.7 lines per cm\(^{-1}\). Fig. 3 shows a comparison between the measured and fitted spectra. Some significant differences are noted. They are probably due in part to line

![Fig. 2. Four successive enlargements of the CW-CRDS spectrum of methane in the 6165–6750 cm\(^{-1}\) region revealing a highly congested structure. The pressure was 1.0 Torr. The open circles mark the lines included in the HITRAN database and correspond to the right hand intensity scale.](image)

![Fig. 3. An example of spectrum reproduction of the CH\(_4\) spectrum illustrating the difficulty of the line by line simulation: in the displayed region, 79 lines had to be simultaneously adjusted to reproduce the observed spectrum. Upper panel: experimental spectrum (\( P = 9.83 \) Torr), middle panel: simulated spectrum resulting from the line fitting procedure (a Voigt profile was affected to each line), lower panel: residuals between the simulated and experimental spectra.](image)
mixing effects [23] which were neglected. Some spectral sections required simultaneous profile fitting of up to 100 lines. (This is indeed the case of the fit illustrated in Fig. 3 where 79 lines were simultaneously treated.) In such situations, one must recognize a certain level of subjectivity in the obtained results, the number of components required to reproduce a broad absorption feature being sometimes ambiguous in particular for the weakest lines in the wings of strong lines with intensities larger by three or four orders of magnitude. As a rule, in these ambiguous cases, we preferred to relax the constraints on the Lorentzian width and even on the Gaussian width instead of adding several weak components. These difficulties were encountered because of the sensitivity of the recordings and are mostly limited to the dense background of the weakest lines.

The complete line list provided as Supplementary material was obtained by gathering the line lists corresponding to the different DFB laser diodes. A few H2O lines present as an impurity in the sample were identified in the high energy part of the investigated region and then deleted. The final CH4 dataset including the spectroscopic parameters of 6868 lines obtained in Ref. [16] for the 6289–6526 cm–1 region, consists in 16,149 entries for the whole 6165–6750 cm–1 region (see lower panel of Fig. 1). Their intensity values vary over six orders of magnitude from 1.6 × 10–29 to 2.5 × 10–23 cm/molecule for methane in “natural” abundance at 297 K.

3. Comparison with the HITRAN line list

3.1. Sensitivity

The detailed comparison of our line list with HITRAN08 list provided very interesting information. Fig. 1 shows that CRDS has allowed lowering by more than three orders of magnitude the detectivity threshold in the lowest opacity region near 6400 cm–1. The gain in sensitivity is also illustrated in Fig. 2 where the open circles mark the lines included in the HITRAN database. In order to estimate the relative importance of the newly observed transitions on the absorbance in the region, we have simulated a “low resolution CW-CRDS spectrum” by affecting a 10 cm–1 wide (FWHM) normalized Gaussian profile to each line of our list. The resulting absorption coefficient obtained as the product of the obtained simulation by the molecular density (at 1.0 Torr and 296 K) is displayed in Fig. 4 (in logarithmic scale) and compared to a “low resolution HITRAN spectrum” obtained in the same way. The spectra displayed in Fig. 4 shows that the absorption is always larger than 1 × 10–9 cm–1. Of course, the relative impact of the new observations is particularly marked in the 6310–6350 cm–1 region where no transitions are listed in HITRAN. Conversely, we note an excellent overall agreement near the low and high energy limits of the investigated region, the transitions newly detected in those regions having a negligible impact compared to the stronger transitions included in HITRAN. We have also included in Fig. 4, the low resolution simulation obtained with the GOSAT line list[9] below 6180 cm–1. The very good agreement between the GOSAT and HITRAN simulations shows that the numerous additional lines with intensities in the 4 × 10–30–4 × 10–24 cm/molecule range in the GOSAT list add a negligible contribution to the overall absorption.

3.2. Line positions

In order to find automatically the HITRAN lines in coincidence with a CRDS observation, we have used a program which associates a CRDS line and a HITRAN line when both their line centers differ by less than 5 × 10–3 cm–1 and their intensities differ by less than 20%. The second condition aims to reduce the number of accidental coincidences. The differences of the line centers displayed in Fig. 5 clearly shows the 1.1 × 10–2 cm–1 underestimation of HITRAN values compared to our values. This reflects the above mentioned difference of calibration between the Reims spectra[21] adopted as reference and HITRAN. Of importance, is the observation that the series of lines showing an average (CRDS–HITRAN) difference of −1.8 × 10–3 cm–1 between 6320 and 6500 cm–1 are due to CH3D (see Fig. 5). As mentioned above, these CH3D line positions recently included in the HITRAN database[3] were obtained in Ref. [10]. The relative positions error between the CH4 and CH3D transitions pro-

![Fig. 4. Comparison of the 'low resolution' absorption spectrum of methane ($P = 1.0$ Torr) simulated from the CW-CRDS line list (red) and from the HITRAN database (grey). The spectra were obtained by affecting a normalized Gaussian profile (FWHM = $10.0$ cm$^{-1}$) to each line. The GOSAT simulation (blue) displayed below 6200 cm$^{-1}$ is in close coincidence with HITRAN simulation. Note the logarithmic scale adopted for the absorption coefficient. (For interpretation of color mentioned in this figure the reader is referred to the web version of the article.)](image-url)
intensities.

automatic association program and fixed to 1.0

the same transition in the CRDS and HITRAN lists, we used the same

3.3. Line intensities

provided in HITRAN is then on the order of 0.003 cm$^{-1}$. This value

agrees well with the claimed uncertainty of the original data used

for HITRAN: Brown [7] used CO 2–0 and 3–0 bands as standards to

calibrate her CH$_4$ spectra but quoted 'generic' absolute accuracies

of 0.0007 cm$^{-1}$ at 5000 cm$^{-1}$ to 0.0015 cm$^{-1}$ at 7000 cm$^{-1}$ because

of the congestion of lines; no calibration standards were used by

Lutz et al. [10] which estimated to 0.005 cm$^{-1}$ the absolute accu-

racy of their CH$_3$D spectra.

3.3. Line intensities

In order to associate one by one the lines corresponding to the

same transition in the CRDS and HITRAN lists, we used the same

automatic association program and fixed to 1.0 × 10$^{-3}$ cm$^{-1}$ the

maximum line centers differences (after correction of the

1.1 × 10$^{-3}$ cm$^{-1}$ calibration shift). The obtained ratios of the CRDS

and HITRAN intensities are plotted in Fig. 6 versus the line

intensities.

A very good overall agreement is noted for the CH$_4$ intensity

values (average value very close to 1). The large discrepancies ob-

served for some strong lines below 6180 cm$^{-1}$ are due to transitions

for which a multiplet structure was used in the CRDS line

profile fitting while they appear as single lines in the HITRAN line

list. The comparison for the CH$_3$D intensities evidences a system-

atic underestimation of the CRDS values, our values being on average

18% smaller than HITRAN values. This discrepancy is

significantly higher than the 8% value given by Boussin et al. [11]

for the uncertainty of their CH$_3$D intensities.

Our search of the origin of this disagreement was puzzling.

First, we compared our CH$_3$D intensity values to those mea-

sured from the long path absorption spectrum of methane re-

corded in Reims and found a very good agreement between these

two measurements performed with methane in "natural" abundance.

Second, we checked Boussin's intensity values obtained with

CH$_3$D sample (96.8% purity) by comparison to the FTS spec-

trum of an enriched CH$_3$D sample (99% stated purity) recently re-

corded in Hefei (see Ref. [16] and next section). We found a very good

coincidence between these two measurements performed with a

highly enriched CH$_3$D sample.

The conflict between the sets of intensity results retrieved from

“natural gas” or enriched CH$_3$D is only apparent. The CH$_3$D HITRAN

intensity values are scaled according to the CH$_3$D relative abun-

dance in methane. The 6.15 × 10$^{-4}$ value adopted in HITRAN for

the CH$_3$D/CH$_4$ abundance results from the D/H relative abundance

(1.5576 × 10$^{-4}$) of the Vienna Standard Mean Ocean Water

(VSMOW) [24]. This value differs significantly from the CH$_3$D/CH$_4$

relative abundance in natural gas as that used for the CRDS and

Reims recordings. More precisely, the 18% difference evidenced be-

tween the CRDS and HITRAN intensity values of CH$_3$D coincides

exactly to the known δD$_{28}$ depletion of CH$_3$D in natural gas com-

pared to the VSMOW value (see Fig. 1 of Ref. [25], for instance).

As mentioned in the Section 1 (Fig. 1), Deng et al. have recorded

the methane spectrum in the 6607–6625 cm$^{-1}$ section by direct

absorption spectroscopy using a DFB laser source of the same type

as used for our CRDS recordings, which was coupled to a White cell

with a maximum path length of 973 m [17]. In the studied 18 cm$^{-1}$

wide interval, 288 lines were measured with intensities down to

1.4 × 10$^{-27}$ cm/molecule which improved the HITRAN line list

(67 transitions above 4 × 10$^{-26}$ cm/molecule). For comparison,

our line list provides 468 lines in the same region. The line by line

comparison of the intensity ratios presented in Fig. 7 shows a rea-

sonable agreement.

4. Identification of the CH$_3$D transitions

Considering the variation of the CH$_3$D/CH$_4$ relative abundance

in the various sources of methane on Earth [25] and in planetary

atmospheres [15], the discrimination of the CH$_3$D and CH$_4$

transitions is necessary to be able to scale their relative intensities

according to the relative abundance value.

Practically all the 3$\nu_2$ transitions of CH$_3$D included in the HI-

TRAN list could be identified in our line list between 6300 and

6520 cm$^{-1}$ [16]. The HITRAN list for CH$_3$D is limited to the transi-

tions of the 3$\nu_2$ transitions with intensity larger than

1.4 × 10$^{-29}$ cm/molecule, which is above the sensitivity of our

spectra (see Fig. 1). In order to identify further CH$_3$D transitions in

our line list, the FTS spectrum of CH$_3$D was recorded at USTC

(Hefei, China) [16]. The enriched CH$_3$D methane sample had a sta-

ted purity of 99%. The recordings were performed with unapodized

resolution of 0.015 cm$^{-1}$ and several absorption path lengths (15,

33 and 51 m) and pressure values (4.17 and 19.92 Torr) were used.

This FTS spectrum revealed a high number of lines not included in

HITRAN (see Fig. 8 of Ref. [16]). They were identified in the CRDS

spectra of methane using both positions and intensities as criteria

(see Fig. 8 for instance). Obviously, a fraction of the CH$_3$D transi-

tions were found superimposed with CH$_4$ transitions. In the line

list attached as Supplementary material, the CH$_3$D transitions are

indicated together with the CH$_4$ transitions which are believed to

be strongly blended with CH$_3$D lines. Finally, among the 16,149

CRDS transitions of methane, 1385 were attributed to CH$_3$D and
1115 transitions are believed to have an important contribution of both isotopologues. Let us underline that the CH$_3$D intensities in our list correspond to a CH$_3$D/CH$_4$ relative abundance which is about 18% smaller than HITRAN value.

In order to further quantify the CH$_3$D contribution to the methane absorption in the region, we present on Fig. 9 a comparison of the low resolution simulation of the absorption spectra of methane and CH$_3$D in “natural” abundance. The methane spectrum was calculated from the CRDS line list as described in Section 3. The CH$_3$D absorption was simulated by convolution with a 10 cm$^{-1}$ wide (FWHM) Gaussian function of the FTS absorbance normalized by the pressure (in Torr) and the absorption pathlength (in cm); the obtained result being multiplied by the HITRAN value of the CH$_3$D abundance. For comparison, the low resolution simulation of the $3_{12}$ band of CH$_3$D as provided in HITRAN is also included in Fig. 9. The obtained curves show that the CH$_3$D relative contribution is negligible outside the 6260–6530 cm$^{-1}$ interval and that it represents about 30% of the total absorption near the Q branch of the $3_{12}$ band at 6430 cm$^{-1}$ and in the lowest opacity region near 6320 cm$^{-1}$. The lack of completeness of the HITRAN database in this last region is then the most prejudicial.

In absence of a high sensitivity spectrum of the $^{13}$CH$_4$ isotopologue, the $^{12}$CH$_4$ and $^{13}$CH$_4$ transitions could not be discriminated. Nevertheless, the $^{13}$C/$^{12}$C isotopic substitution leads to much smal-
the 13CH4 relative contribution to the absorbance is expected to be
H substitution. In consequence, all over the transparency window,
er isotopic shifts of the vibrational bands [26] compared to the D/
Fig. 8. Identification of the CH3D transitions (marked with “D”) contributing to the methane absorption near 6296 cm−1. Upper panel: CW-CRDS spectrum of methane (P = 1.0 Torr). Lower panel: FTS spectrum of CH3D (99% stated purity) recorded with a sample pressure of 4.17 Torr and an absorption pathlength of 15 m.

Fig. 9. Contribution of the CH3D isotopologue to the absorption spectrum of methane between 6220 and 6600 cm−1 (P = 1.0 Torr). The ‘low resolution’ spectrum of methane was simulated from the CW-CRDS line list (red) while the CH3D simulation (blue) is a convolution of the FTS spectrum of CH3D with a normalized Gaussian profile (FWHM = 10.0 cm−1) scaled according to the HITRAN abundance. The ‘low resolution’ simulation of the 31 band of CH3D as provided in HITRAN is also displayed. (For interpretation of color mentioned in this figure the reader is referred to the web version of the article.)

on the same order of magnitude than the 1.1% relative abundance of this isotopologue.

5. Conclusion

We have completed the spectral coverage of the absorption spectrum of methane in the 1.58 μm transparency window by high sensitivity Cavity Ring Down Spectroscopy at room temperature. The achieved sensitivity (Smin ~ 3 × 10−10 cm−1) has allowed measuring line intensities as weak as 1.6 × 10−29 cm/molecule i.e. three orders of magnitude below the intensity cut off of the HITRAN line list. Overall, the line list attached as Supplementary material provides the positions and strengths of 16,149 transitions between 6165 and 6750 cm−1. The significance of these observations is illustrated by Fig. 1 and Table 1 which presents the overall comparison with previous works. On the basis of a FTS spectrum of CH3D, the CH3D transitions could be discriminated. The apparent discrepancy between the CH3D/CH4 relative intensities measured in our CRDS spectra of methane and provided in HITRAN was explained by the difference between the CH3D/CH4 abundance ratio in natural gas and the VSMOW relative abundance adopted in HITRAN. Interestingly, the CH3D abundance in our sample (about 5 × 10−4) is very close to the CH3D/CH4 abundance on Titan [12,13,27,28].

The relative contribution of the CH3D isotopologue estimated by simulation of the CH3D and methane spectra at low resolution (10 cm−1 FWHM) has shown that, in spite of its very small relative abundance, the CH3D absorption contributes to up to 30% of the absorbance in the region. Considering the large variation of the CH3D/CH4 ratios in the different planetary atmospheres [15], the accurate calculation of the transmission in the considered transparency window requires scaling the CH3D intensities according to the CH3D/CH4 relative abundance of the considered medium. For instance, the CH3D relative concentrations on Jupiter and Saturn being about 10 times less than in the Earth atmosphere [15], the CH3D contribution to the absorption near 1.58 μm will be marginal on these planets.

Considering the large variety of temperature conditions, planetary applications require also the knowledge of the temperature dependence of the methane spectra. Indeed, the methane spectrum at both high and low resolution (for instance, the overall shape of the 1.58 μm transparency window), is highly sensitive to the temperature [16,29]. We have recently used the “two temperature method” to derive the lower state energy necessary to compute the Boltzmann factors which rule the temperature dependence of the line intensities. From the ratio of the line intensities measured at room temperature and at liquid nitrogen temperature, the low energy levels of the transitions in common in the two spectra were obtained. The “two temperature method” is a robust and reliable method which was successfully applied to the high absorbing regions surrounding the presently studied transparency window at 1.58 μm [29–34]. In these regions, the spectra at 81 K were obtained by differential absorption spectroscopy using a specifically designed cryogenic cell and a series of several tens DFB diode lasers [29]. This experimental approach provided a sufficient sensitivity (Smin ~ 10−8 cm−1) in the high energy part of the tetradecad (5850–6180 cm−1) [29–31] and in the icosad region (6700–7700 cm−1) [33,34]. In the 1.58 μm transparency window corresponding to the 6180–6750 cm−1 gap, a much higher sensitivity is required. We have recently been able to combine the CW-CRDS technique with the same cryogenic cell [35]. The sensitivity achieved by CW-CRDS at 80 K and room temperature are equivalent [35] (Smin ~ 3 × 10−10 cm−1). In Ref. [16], the “two temperature method” has been applied to the CRDS spectra in the region of the the 31 band of CH3D (6289–6526 cm−1). After the present
completion of the room temperature line list over the whole transparency window, the next step will be the construction of a similar line list at 80 K in order to determine the lower state energy. By gathering, the results obtained in Refs. [16,31,33], we hope to provide in a near future a line list allowing accounting for the temperature dependence of the methane absorption over the whole 1.26–1.70 μm range.

Acknowledgements

This work is part of the ANR project “CH4@Titan” (ref: BLAN08-2_321467) which is a joint effort among four French laboratories (ICB-Dijon, GSMA-Reims, LSP-Grenoble and LESIA-Meudon) to adequately model the methane opacity. We would like to thank E. Kerstel (University of Groningen), J. Chappelaz and J. Savarino (LGGE, Grenoble) for valuable discussions relative to the CH3D/CH4 abundance. We thank the GSMA group (University of Reims) for providing us with their long path absorption spectrum of methane which was used to refine the wavenumber calibration of our spectra. The support of the Groupement de Recherche International SAMIA between CNRS (France), RFBR (Russia) and CAS (China) is acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemphys.2010.05.011.

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