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## Experimental low energy values of CH<sub>4</sub> transitions near 1.33 μm by absorption spectroscopy at 81 K

Ella Sciamma-O'Brien<sup>a</sup>, Samir Kassi<sup>a</sup>, Bo Gao<sup>a,b</sup>, Alain Campargue<sup>a,\*</sup><sup>a</sup> Laboratoire de Spectrométrie Physique (associated with CNRS, UMR 5588), Université Joseph Fourier de Grenoble, B.P. 87, 38402 Saint-Martin-d'Hères Cedex, France<sup>b</sup> Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China

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### ABSTRACT

The high resolution absorption spectrum of methane has been recorded at liquid nitrogen temperature by direct absorption spectroscopy between 1.36 and 1.30 μm (7351–7655 cm<sup>-1</sup>) using a cryogenic cell and a series of distributed feed back (DFB) diode lasers. The investigated spectral range corresponds to the high energy part of the icosad dominated by the ν<sub>2</sub>+2ν<sub>3</sub> band near 7510 cm<sup>-1</sup>. The positions and strengths at 81 K of 3473 transitions were obtained from the spectrum analysis. The minimum value of the measured line intensities (at 81 K) is on the order of 10<sup>-26</sup> cm/molecule, i.e. significantly lower than the intensity cut off of the HITRAN database in the region (4 × 10<sup>-25</sup> cm/molecule at 296 K). From the variation of the line strength between 81 and 296 K, the low energy values of 1273 transitions could be determined. They represent 69% and 81% of the absorbance in the region at 296 and 81 K, respectively. The obtained results are discussed in relation with the few rovibrational assignments previously reported in the region.

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### 1. Introduction

It is necessary to know the low energy levels of methane absorption transitions to be able to calculate the line strengths in temperature conditions of the giant outer planets and of Saturn's satellite, Titan. However, despite important experimental and theoretical efforts [1], the highly congested absorption spectrum of methane above 6000 cm<sup>-1</sup> has yet to be satisfactorily interpreted. The HITRAN [2] or GEISA [3] databases only provide empirical line-by-line spectroscopic parameters at room temperature (RT) without rovibrational assignments for most of the transitions above 5500 cm<sup>-1</sup> such that line intensities cannot be computed at different temperatures. This makes the available line lists of limited use in planetology. In the tetradecad region (5500–6150 cm<sup>-1</sup>), the HITRAN database in its 1996 version did include the low energy values obtained by Margolis from two spectra recorded by Fourier transform spectroscopy (FTS) at room [4] and reduced [5] temperatures. Using spectra recorded at 180–220 K with a 0.8 m long cryogenic cell, Margolis derived the lower energy value, *E*, of 1600 transitions, from the temperature dependence of the line intensities.

The use of a much lower temperature is made possible by the 10 Torr vapor pressure of methane available at liquid nitrogen temperature (LNT). It is then possible to characterize the transitions at temperature conditions approaching those existing, for instance, on Titan. In a recent contribution [6], we applied this two temperature method to the

\* Corresponding author. Tel.: +33 476514319; fax: +33 4 76 63 54 95.

E-mail address: [Alain.Campargue@ujf-grenoble.fr](mailto:Alain.Campargue@ujf-grenoble.fr) (A. Campargue).

5850–6200  $\text{cm}^{-1}$  region using the HITRAN line strengths at RT and the line strengths retrieved from spectra that we recently recorded at LNT with a new cryogenic cell and a series of distributed feed back DFB laser diodes. In this region, the HITRAN database (which reproduces Margolis's line strengths at RT) provides with 1300 transitions while we could measure 2187 transitions at LNT. Using the wavenumber agreement as criterion to associate the RT and LNT line strengths, the low  $J$  values of 845 transitions were determined. 1342 transitions measured in our LNT spectrum were left without lower state energy determination because the corresponding RT line strength values are missing in the HITRAN database. This is mainly due to the high intensity cut off of the  $\text{CH}_4$  HITRAN line list in the considered region ( $4 \times 10^{-24}$  cm/molecule) compared to our detectivity limit at LNT on the order of  $3 \times 10^{-26}$  cm/molecule [6].

In the study presented here, we followed the same procedure to determine the lower state energy of the transitions observed in our LNT spectrum between 7351 and 7655  $\text{cm}^{-1}$ . This region corresponds to the high energy section of the icosad dominated by the  $\nu_2+2\nu_3$  band near 7510  $\text{cm}^{-1}$ . The congestion of the spectrum is significantly higher here than in the tetradecad region (the density of transitions is roughly doubled in our LNT spectra) which adds to the difficulty of retrieving accurate line strengths. The complexity of the spectrum may also explain the fact that, while substantial progress is being made in the theoretical treatment of the tetradecad region, it remains at its very beginnings for the icosad region.

Up to date, the most significant advance in this region has been achieved by Hippler and Quack [7,8] who reported the first assignments of the  $\nu_2+2\nu_3$  combination band by high-resolution FTS at RT and CW—cavity ring down spectroscopy (CRDS) in slit jet expansions. An isolated band analysis was presented for low  $J$  values ( $J = 0-4$ ) but strong perturbations prevented a detailed assignment of higher rotational levels. The list of 21 transitions assigned in this previous study will be considered below for comparison with our results.

For completeness, we mention the methane spectrum in the 3800–9100  $\text{cm}^{-1}$  at LNT reported by McKellar [9] although the medium spectral resolution (0.14  $\text{cm}^{-1}$ ) of these recordings prevented the resolution of individual lines.

After the description of the experimental set up (Section 2), the construction of the LNT line list will be presented in Section 3. The determination of the low energy values is presented in Section 4 and the obtained results are discussed in Section 5.

## 2. Experiment

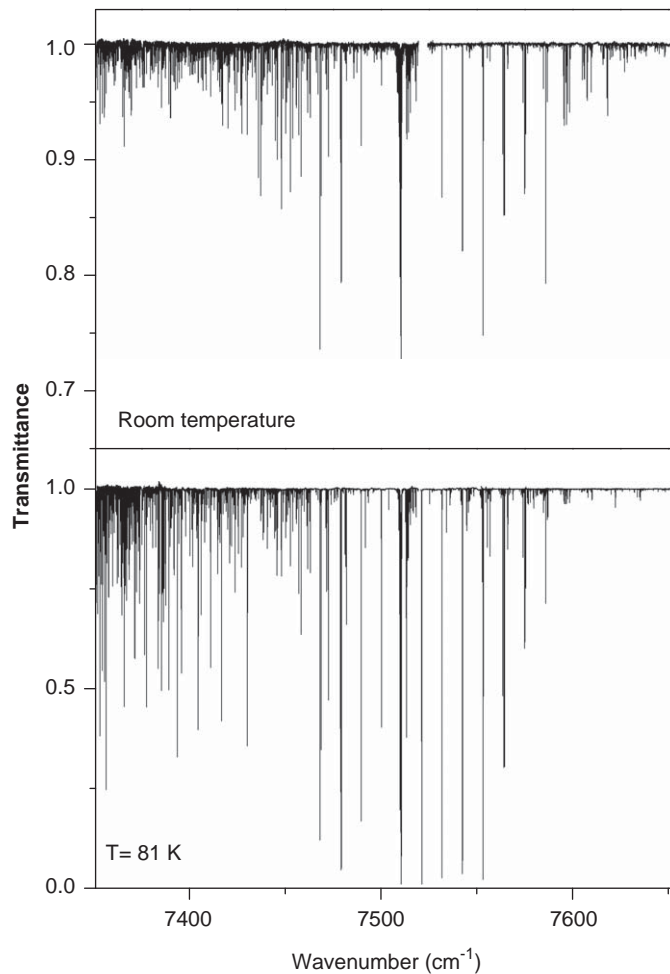
We have recently developed a new cryogenic cell dedicated to the methane absorption spectroscopy at LNT [10]. It is based on an original design which dispenses with the external vacuum jacket by exploiting the fact that a low pressure sample may constitute by itself a good thermal insulation. In the absence of an internal pair of windows, the gas sample fills both the inside of the cryostat and the thermal insulation volume. The external stainless steel cylinder is 1.418 m long, with a 6.3 cm diameter, while the inner diameter of the cryostat, made of two co-axial tubes, is 1 cm. During the spectrum acquisition, the gas pressure was continuously measured by a capacitance gauge (MKS Baratron, 10 Torr range).

Spectra were recorded by direct absorption spectroscopy using a series of nine DFB fibered laser diodes allowing a continuous coverage of the 7351 to 7655  $\text{cm}^{-1}$  spectral range, except for an inaccessible 2  $\text{cm}^{-1}$  gap between 7518.4 and 7520.4  $\text{cm}^{-1}$ . Each complete laser diode spectrum consisted of the dynamic averaging and concatenation of several thousands 1  $\text{cm}^{-1}$ -wide spectra obtained by a fast current ramping with a 10 MHz spectral resolution. A slow temperature scan from  $-10$  to  $60^\circ\text{C}$  swept this spectral window over the whole DFB tuning range of about 35  $\text{cm}^{-1}$  within 12 min. These 35  $\text{cm}^{-1}$ -wide spectra were linearized using an etalon signal and calibrated independently by matching the observed spectral line positions to the HITRAN line positions measured by FTS at RT [2]. The standard deviation error of the differences between our line positions and HITRAN values was minimized leading to *rms* values on the order of  $10^{-3}$   $\text{cm}^{-1}$ .

More details about the spectra acquisition and the cell design can be found in Ref. [10]. This reference includes a movie showing the evolution of the spectrum in a section of the tetradecad region, during the cell cool-down to 77 K. In that experiment, the gas temperature value was continuously determined from the measured Doppler width of a well isolated line. This method gives a very precise *in situ* measurement of the gas temperature in a cooled cell. About one hour after the filling of the cryostat with liquid nitrogen, the steady state was achieved. A temperature value of  $81 \pm 1$  K was determined from the Doppler profile of several tens of well isolated lines, the error bar corresponding to one standard deviation. This temperature value is what we refer to as “LNT”.

In our study of the icosad region of methane, we also recorded the methane spectrum at RT with the same experimental set up, for comparison. Fig. 1 shows the overview of the recorded spectra at RT and LNT. Except for the reduction of the rotational extension of the  $\nu_2+2\nu_3$  combination band, the reduction of the rotational congestion is not visually apparent on these spectra. This is due to the fact that similar sample pressures (about 10 Torr) were used for the two recordings. The molecular concentration was then about four times larger for the low temperature spectrum. The increase of the peak depth (by a factor of about 2) due to the line narrowing at low temperature, also contributes to the apparent congestion of the low temperature spectrum, independently of the variation of the line intensities during the cooling.

Fig. 2 shows a similar comparison in a limited spectral section around 7360  $\text{cm}^{-1}$ . The cooling induces such a strong change on this section of the spectrum that the LNT spectrum becomes hardly recognizable compared to the RT spectrum. The stick spectrum corresponding to the HITRAN line list (at 296 K) is included in this figure. Apart from a few water lines present as an impurity in our sample, our RT spectrum coincides with the HITRAN line list and our noise level corresponds roughly to the HITRAN intensity cut off in this region. This is the reason why we did not use our RT spectrum for line intensity retrieval and adopted the HITRAN intensity values at 296 K.



**Fig. 1.** Overview comparison of the spectra of methane recorded at liquid nitrogen temperature (lower panel) and room temperature (upper panel) in the high energy region of the icosad ( $7350\text{--}7650\text{ cm}^{-1}$ ). The room temperature and liquid nitrogen temperature spectra were recorded at 11.8 and 9.7 Torr, respectively. Note the change in the ordinate scale.

A typical value of  $10^{-6}\text{ cm}^{-1}$  was estimated for the noise equivalent absorption in the LNT spectrum. It corresponds to a minimum value on the order of  $10^{-26}\text{ cm/molecule}$  for the line intensities at 10 Torr pressure.

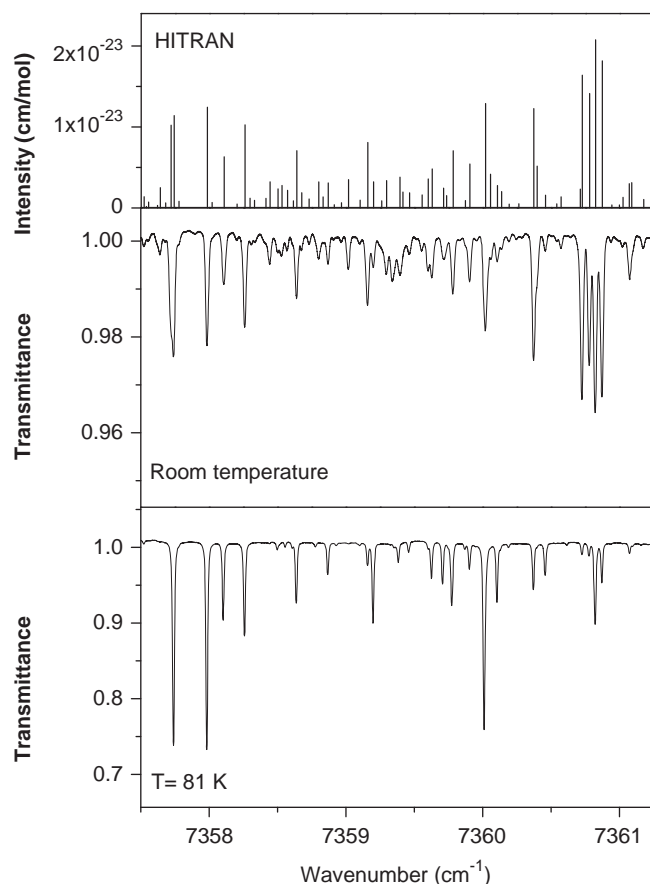
### 3. Line intensity retrieval

Most of the 81 K spectra were recorded at a pressure of either 7.36 or 9.35 Torr. A few additional recordings were performed with a pressure value of 0.51 Torr in order to avoid saturation of the strongest lines of the  $\nu_2+2\nu_3$  band. From the measurements and review of literature data presented in Ref. [11], the pressure self broadening of the  $\nu_3$  and  $2\nu_3$  bands at 81 K has a value on the order of  $0.20\text{ cm}^{-1}/\text{atm}$  (HWHM). Assuming the same value for the vibrational bands contributing to our spectrum, it leads to a  $2.8 \times 10^{-3}\text{ cm}^{-1}$  HWHM at 10.0 Torr which is small but significant compared to the Doppler width (HWHM  $5.8 \times 10^{-3}\text{ cm}^{-1}$  at 81 K). We therefore adopted a Voigt function of the wavenumber for the line profile. Note that the DFB line width (1–5 MHz) is much smaller than the Doppler broadening [175 MHz (HWHM) at LNT] and therefore negligible.

The line strength  $S_{\nu_0}$  (cm/molecule) of a rovibrational transition centred at  $\nu_0$ , was obtained from the integrated line absorbance,  $I_{\nu_0}$  ( $\text{cm}^{-2}/\text{molecule}$ ), expressed as

$$I_{\nu_0}(T) = \int_{\text{line}} \alpha_{\nu} \cdot l d\nu = \int_{\text{line}} \ln \left[ \frac{I_0(\nu)}{I(\nu)} \right] d\nu = S_{\nu_0}(T)Nl \quad (1)$$

where  $I_0(\nu)/I(\nu)$  is the ratio of the incident intensity to the transmitted intensity,  $l$  the absorption pathlength in cm,  $\nu$  the wavenumber in  $\text{cm}^{-1}$ ,  $\alpha(\nu)$  the absorption coefficient in  $\text{cm}^{-1}$  and  $N$  the molecular concentration in  $\text{molecule}/\text{cm}^3$  obtained from the measured pressure value:  $P = NkT$ .



**Fig. 2.** The absorption spectra of methane recorded at room temperature (middle panel) and liquid nitrogen temperature (lower panel) near  $7360\text{ cm}^{-1}$ . The stick spectrum of  $\text{CH}_4$  as provided by the HITRAN database at 296 K is displayed on the upper panel for comparison.

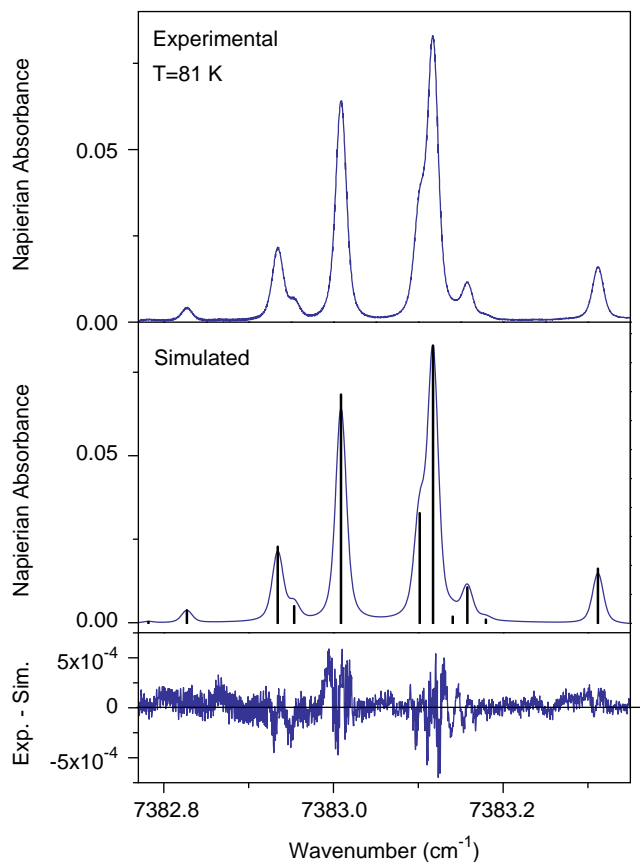
Because of the large number of observed transitions (about  $12\text{ lines/cm}^{-1}$ ), lines were frequently blended together. The first (manual) step of the spectrum analysis consisted in the determination of the spectral sections of overlapping or nearby transitions that could be treated independently. For each of these spectral sections, the local baseline was assumed to be a cubic function of the wavenumber and spectral lines were fitted with a Voigt function having four parameters, (line centre, integrated absorbance, HWHM of the Gaussian and Lorentzian components) that were determined using the *fityk* program. This freely accessible software (<http://www.unipress.waw.pl/fityk/>) is an interactive least square multiline fitting program based on the Levenberg–Marquardt algorithm. For each diode, up to 20 well isolated lines were fitted without fixing any of the four Voigt function parameters. An average value of the Gaussian and Lorentzian components of the Voigt profile was then obtained for each diode. In the case of blended overlapping lines or low signal to noise ratios, these two parameters could then be constrained to their average values.

Fig. 3 shows an example of comparison between the measured and fitted spectra. Because of the high signal to noise ratio of the spectra, a typical value of  $1 \times 10^{-4}$  was achieved for the *rms* deviation of the experimental and simulated absorbances. This *rms* value corresponds to a minimum line strength value of  $10^{-26}\text{ cm/molecule}$ . Some significant differences between the observed and simulated spectra were nevertheless noted for some lines. It is not clear whether these differences are experimental and are due to the small sections of warm gas lying between the ends of the cold jacket and the cell windows or if they are analytical and a more sophisticated velocity dependent profile might better reproduce the observed line profile.

The complete LNT line list was obtained by gathering the line lists corresponding to the different DFB laser diodes, each extending over about  $35\text{ cm}^{-1}$ . In the case where the coverage of two diodes overlapped, the centre and strengths of the lines corresponding to these overlapping regions were averaged. The final line list consists of 3473 lines with intensity values ranging from  $1 \times 10^{-26}$  to  $5.9 \times 10^{-22}\text{ cm/molecule}$  for methane in natural abundance at 81 K.

#### 4. Determination of the lower state energy

Independently of any rovibrational assignment, the low energy value,  $E$ ,  $E \approx B_0J(J+1)$  and then the value of the angular momentum  $J$  can be deduced from the strength values of a given transition recorded at two temperatures. This method has



**Fig. 3.** An example of simulation of the CH<sub>4</sub> spectrum recorded at LNT. From top to bottom: (a) experimental spectrum at LNT ( $P = 9.38$  Torr), (b) simulated spectrum resulting from the line fitting procedure (see Text) and (c) residuals between the simulated and experimental spectra.

been successfully applied to methane in a number of studies [12,13] including Margolis' studies [4,5] and our recent study of the tetradecad region [6].

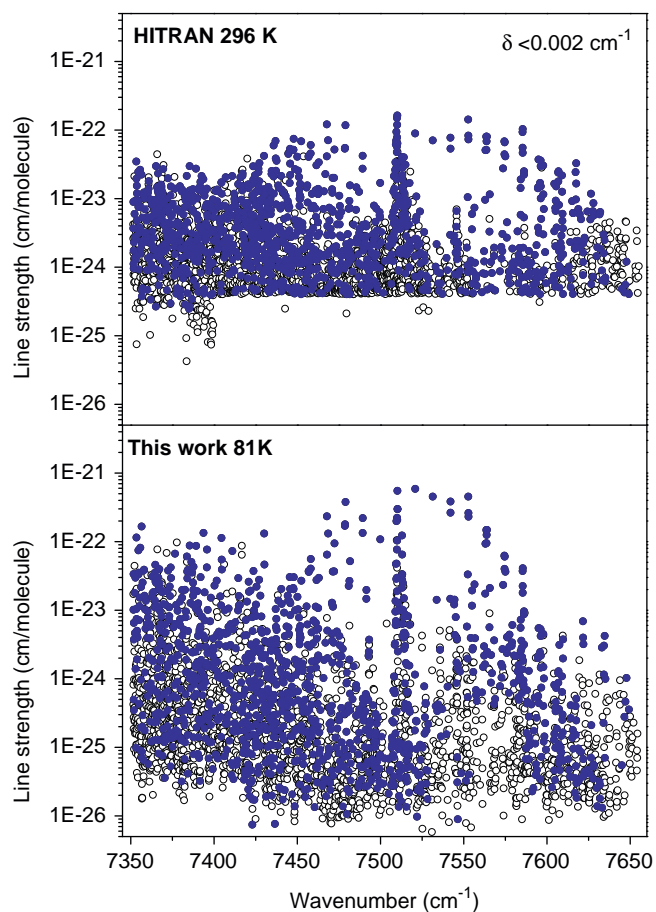
Taking into account the partition function, the lower energy of a particular transition can be deduced from the variation of its line strength (see Ref. [6] for more details):

$$\ln\left(\frac{S_{v_0}(T)T^{3/2}}{S_{v_0}(T_0)T_0^{3/2}}\right) = -E\left[\frac{1}{kT_0} - \frac{1}{kT}\right] \quad (2)$$

where  $T_0$  and  $T$  are the RT and the LNT, respectively. As mentioned above, in our analysis, we adopted HITRAN values for the RT line strengths. An overview comparison of our LNT line list and the HITRAN line list (at 296 K) is presented on the scattered plots of Fig. 4. In the icosad range (6300–8000 cm<sup>-1</sup>) including our region, the empirical line-by-line spectroscopic parameters provided by the HITRAN database were obtained by L. Brown at RT (296 ± 4 K) by high resolution FTS with path lengths up to 97 m [14]. The intensity cut off of the HITRAN line list was fixed to a value of  $4 \times 10^{-26}$  cm/molecule, except in our region above 7400 cm<sup>-1</sup> including the relatively strong  $\nu_2 + \nu_3$  band, where this value was increased to  $4 \times 10^{-25}$  cm/molecule (see Fig. 1 of Ref. [8]).

The determination of the lower state energy relies on the association of RT and LNT line strength values on the basis of coinciding line positions. Considering the congestion of the spectrum, this step is crucial (see below). If we consider as identical, the RT and LNT transitions with line centres differing by less than 0.002 cm<sup>-1</sup>, 1273 transitions are found in both our LNT line list and the HITRAN line list at 296 K. The matching lines are highlighted on the overview spectrum of Fig. 4.

Using Eq. (2), the  $E$  values were empirically determined and the corresponding  $J$  values were calculated as the positive root of the  $E = B_0(J+1)$  equation (with  $B_0 = 5.24$  cm<sup>-1</sup>). Fig. 5 gives the rounded  $J$  values obtained for the RT and LNT spectra in a spectral region around 7425 cm<sup>-1</sup>. We present in Fig. 6 a scattered graph of the obtained  $J$  values as a function of the line centre. The corresponding histogram, presented in Fig. 7 shows that 74% of the  $J$  values fall in a ±0.25 interval around integer values. This value approaches the 80% value achieved in the tetradecad region [6] illustrating the reliability of the method in a region where the spectral congestion is significantly higher.



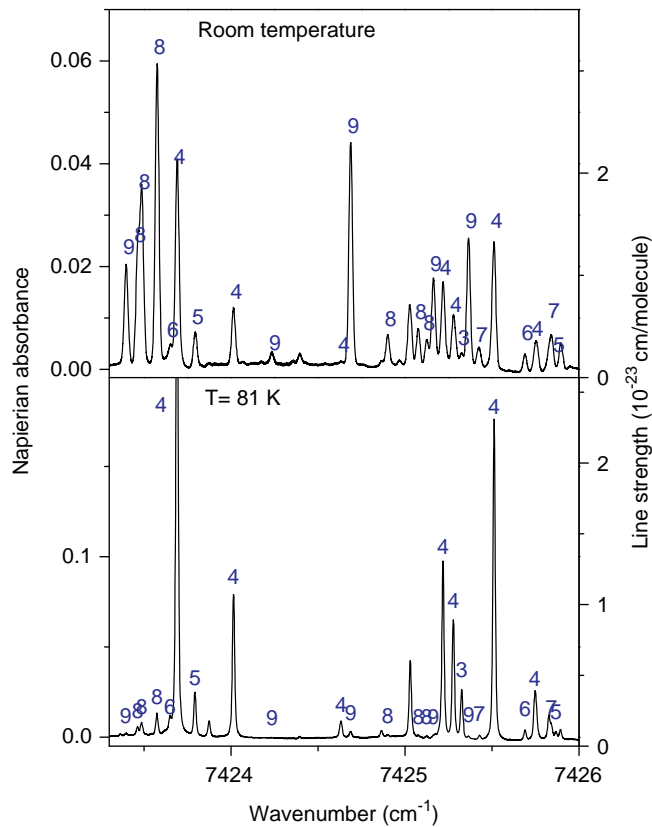
**Fig. 4.** Overview of the scattered spectrum of methane between 7350 and 7655  $\text{cm}^{-1}$  recorded at liquid nitrogen temperature (this work) and as provided in the HITRAN database at 296 K. The full circles (in blue) highlight the 1273 transitions whose line positions at RT and LNT matched ( $\delta < 0.002 \text{ cm}^{-1}$ ) and for which it was therefore possible to derive the lower energy values. The open circles correspond to the non-associated/non matching lines.

The complete list of the 3473 transitions is provided as Supplementary Material. This list includes the LNT line strength, the corresponding RT line strength as provided by HITRAN and the  $E$  and  $J$  values when available. A sample of this line list is reproduced in Table 1 as an example.

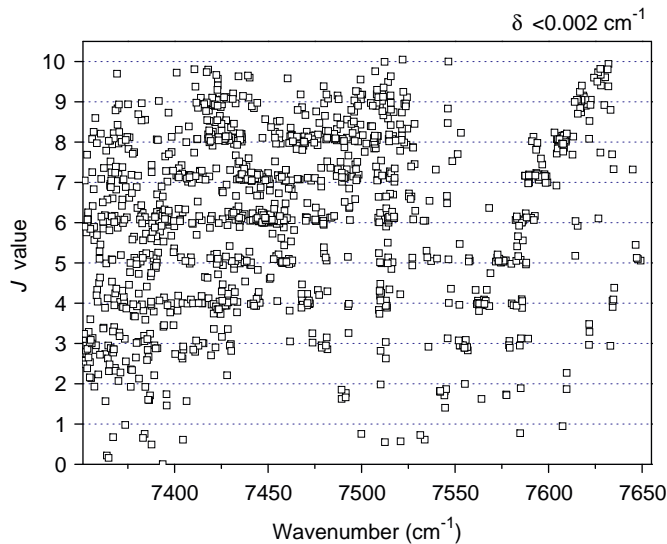
## 5. Discussion

The wavenumber agreement is the only criterion used to associate the transitions observed in the RT and LNT spectra. The obtained results are then directly affected by the uncertainties on the wavenumber values resulting from the calibration of our spectra and from the precision on the line centre determinations. The achieved precision depends on the line profile fitting and may be limited by the high congestion and the intensity dynamics of the measured transitions. According to Ref. [14], the positions of isolated lines are good to  $\pm 0.0015 \text{ cm}^{-1}$  in the HITRAN line list. Due to the larger Doppler broadening and higher rotational congestion, blended lines are more frequent in the RT spectrum which increases the uncertainty on the determination of their centres and strengths. Problematic situations were encountered in the tetradecad region (see Ref. [6]) and are expected to be more frequent in the region studied here. The LNT spectrum is not free of strongly blended absorption features whose profile fitting as a sum of individual lines can sometimes be partly arbitrary. In particular, larger errors are expected for the weak lines for both their strength and centre values. From the histogram of Fig. 5, it is clear that the reliability of the  $J$  determination degrades for both the  $J = 0-2$  values and the higher  $J$  values ( $>9$ ) which correspond to the weakest transitions in the RT and LNT spectra, respectively.

The maximum value of the difference between the RT and LNT positions must be chosen large enough to associate the maximum number of identical transitions and small enough to minimize the number of accidental coincidences. The total



**Fig. 5.** Comparison and lower  $J$  values of the transitions of methane recorded at room temperature (upper panel) and liquid nitrogen temperature (lower panel) near  $7425\text{ cm}^{-1}$ .



**Fig. 6.** Scattered graph of the lower  $J$  values versus the line centres. The  $J$  values were obtained from the strengths of the methane transitions at 81 and 296 K between  $7350$  and  $7655\text{ cm}^{-1}$  by associating transitions with line centres differing by less than  $0.002\text{ cm}^{-1}$ .

number of  $J$  determinations and the percentage of “integer” values can then be used as criteria to fix the optimum tolerance interval of the line centres difference. In order to show that the value of  $0.002\text{ cm}^{-1}$  chosen above is a good compromise, we have plotted on Fig. 8 the  $J$  histograms corresponding to  $\delta < 0.001\text{ cm}^{-1}$ ,  $0.001 < \delta < 0.002\text{ cm}^{-1}$  and  $0.002 < \delta < 0.003\text{ cm}^{-1}$



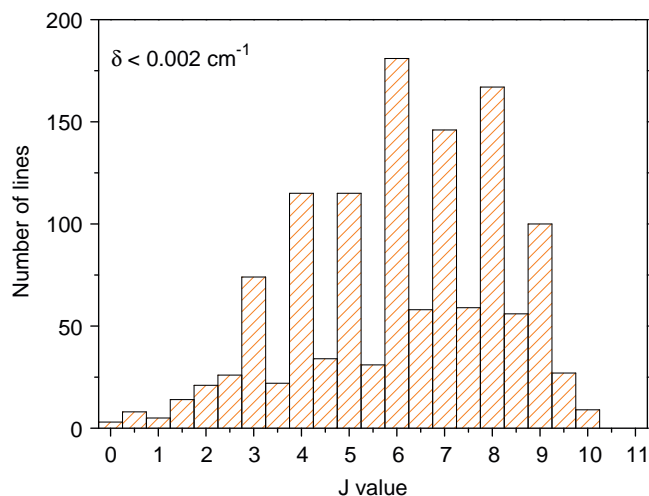


Fig. 7. Histogram of the lower  $J$  values with a step interval of 0.5. 74% of the obtained  $J$  values fall in a  $\pm 0.25$  interval around integer values.

( $\delta$  is the absolute value of the RT and LNT line centres difference). The percentage of “integer” values of  $J$  is on the same order for  $\delta < 0.001 \text{ cm}^{-1}$  (79%) and for  $\delta < 0.002 \text{ cm}^{-1}$  (74%) (see Fig. 7) but the number of  $J$  determinations is significantly smaller indicating that the  $0.001 \text{ cm}^{-1}$  value is too small and that a fraction of identical lines were missed. This is confirmed by the second histogram ( $0.001 < \delta < 0.002 \text{ cm}^{-1}$ ) which exhibits a clear alternation corresponding to integer and half integer  $J$  values. At the opposite, the third histogram limited to the lines with  $0.002 < \delta < 0.003 \text{ cm}^{-1}$ , doesn't show a clear alternation, indicating that relaxing the coincidence criterion up to  $0.003 \text{ cm}^{-1}$  leads to either larger uncertainties on the obtained  $J$  values or to the accidental association of lines corresponding to different transitions.

As shown in Fig. 8, the 1273 transitions with  $J$  determination ( $\delta < 0.002 \text{ cm}^{-1}$ ) represent about one third of the total number of lines in both our line list and HITRAN line list (3473 and 3406 lines, respectively). This relatively low percentage is partly due to the high number of very weak lines detected in the LNT spectrum. It is also limited by the fact that the intensity of most of the lines corresponding to high  $J$  values fall below our detection limit in the LNT spectrum. For instance, the intensity of a transition from a  $J = 10$  level decreases by a factor of 240 when cooling down to 81 K. More meaningful are the fractions of the integrated strengths corresponding to these 1273 transitions. They represent 81% and 69% of the total absorbance at LNT ( $1.66 \times 10^{-20} \text{ cm/molecule}$ ) and at RT, ( $1.46 \times 10^{-20} \text{ cm/molecule}$ ), respectively. These percentages indicate that our line list accounts for most of the temperature variation of the absorbance in the considered region.

As mentioned above the histogram of Fig. 8 corresponding to the lines with  $0.002 < \delta < 0.003 \text{ cm}^{-1}$ , doesn't show a clear propensity for integer  $J$  values. Nevertheless the  $\delta < 0.002 \text{ cm}^{-1}$  criterion is conservative in regards to the uncertainties on the RT and LNT line positions ( $\pm 0.0015$  [14] and  $\pm 0.001 \text{ cm}^{-1}$ , respectively). A careful analysis of the additional lines fulfilling the  $0.002 < \delta < 0.003 \text{ cm}^{-1}$  relation (in particular the strongest ones) has shown that in many cases, the “non integer” values obtained for  $J$  are due to uncertainties on the line strengths and not to accidental coincidences of different transitions. This is why we have included (and specifically marked) in the line list attached as Supplementary Material the  $J$  values corresponding to  $0.002 < \delta < 0.003 \text{ cm}^{-1}$ . Although less reliable, we believe that the  $J$  values of these 266 additional lines representing 2.0% of the integrated absorbance, will be useful to better account for the temperature variation of the methane absorbance in this region.

Previous rovibrational analyses of the methane spectrum in our spectral region are scarce. Lower state energies of only 77 transitions, all belonging to the  $\nu_2+2\nu_3$  combination band, are provided by the HITRAN database [2]. They correspond to different components of the  $P(1)-P(7)$ ,  $Q(1)-Q(4)$  and  $R(0)-R(9)$  transitions and the sum of their strengths at RT is  $3.92 \times 10^{-21} \text{ cm/molecule}$ . Hippler and Quack [8] obtained a complete rovibrational assignment for 21 of these transitions by high-resolution FTS at RT and CRDS in a supersonic slit jet expansion. An isolated band analysis was possible at low  $J$  values ( $J < 4$ ) but strong interactions, in particular of Coriolis type, prevented the extension of the modelling to higher  $J$  values. As a result of the analysis, the origin ( $7510.3378 \text{ cm}^{-1}$ ) and the integrated band strength ( $9.8 \times 10^{-21} \text{ cm/molecule}$ ) of the  $\nu_2+2\nu_3$  band were reported [8]. We note that this last value is equivalent to the sum of the RT intensities of all the lines lying over the spectral extension of the  $\nu_2+2\nu_3$  band ( $7430-7650 \text{ cm}^{-1}$ ) but three times larger than the sum of the lines of the 77 transitions assigned in HITRAN. It may be a consequence of the strong coupling between the six sub-vibrational components of the  $\nu_2+2\nu_3$  band and the nearby rovibrational states, leading to an important line fractionation and dilution of the band strength over many transitions.



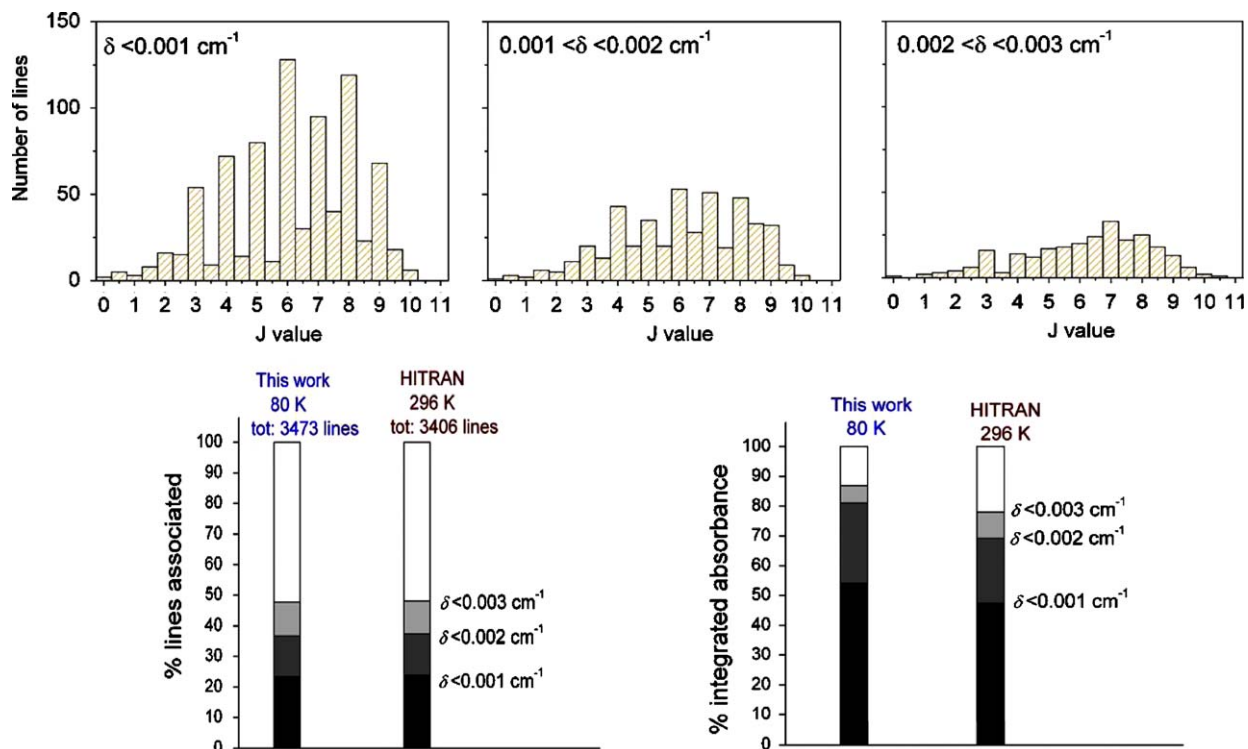
**Table 1**Wavenumbers and strengths of the absorption lines of methane recorded at 81 K near 7394 cm<sup>-1</sup>.

Line centre (cm <sup>-1</sup> )		Line intensity (10 <sup>-24</sup> cm/mol)		<i>E</i> (cm <sup>-1</sup> )	<i>J</i> <sub>low</sub>
This work <i>T</i> = 81 K	HITRAN <i>T</i> = 296 K	This work <i>T</i> = 81 K	HITRAN <i>T</i> = 296 K		
7393.0458	7393.0444	0.577	3.28	285.42	6.90
7393.0673	7393.0664	0.809	1.85	214.66	5.92
7393.1357	7393.1328	1.2	0.458	76.16	3.35*
7393.3561	7393.3589	0.584	2.29	256.75	6.52*
7393.3859		0.172			
7393.5194		0.115			
7393.5299	7393.5278	0.602	3.00	275.08	6.76*
7393.5485		0.347			
7393.5559	7393.5552	4.32	12.4	232.15	6.17
7393.6639	7393.6641	134	19.2	0.02	0.00
7393.6965	7393.6963	0.749	3.34	266.47	6.65
7393.8178		0.516			
7393.8282		0.636			
7393.8917	7393.8911	1.07	3.32	238.26	6.26
7393.9850	7393.9824	0.192	0.318	189.78	5.54*
7394.0421	7394.0415	1.03	0.41	79.00	3.41
7394.0985	7394.0977	0.264	0.434	189.27	5.53
7394.1081		0.793			
7394.2834	7394.2842	0.188	0.482	223.41	6.05
7394.3506	7394.3506	18.2	11.00	111.66	4.14
7394.3754	7394.3740	7.11	2.88	80.64	3.45
7394.5024		0.302			
7394.5846	7394.5874	0.144	1.1	308.50	7.19*
7394.6506		3.68			
7394.6620	7394.6611	3.9	12.8	242.90	6.33
7394.8037		0.104			
7394.8166		0.252			
7394.8354	7394.8340	1.60	4.24	226.19	6.09
7394.8571	7394.8560	0.887	2.49	230.52	6.15
7394.9062		0.106			
7394.9180		1.86			
7394.9785	7394.9775	0.134	1.67	346.16	7.64
7395.0104	7395.0107	2.92	7.55	224.27	6.06
7395.1509		4.12			
7395.1906	7395.1929	4.79	2.84	110.11	4.11*
7395.2653	7395.2647	1.70	4.31	222.92	6.04
7395.3328	7395.3301	0.773	3.1	258.15	6.54*
7395.3546		0.12			
7395.4284	7395.4287	0.302	2.55	316.06	7.28
7395.5230		0.287			
7395.6982	7395.6982	42.1	8.31	24.96	1.74
7395.7695	7395.7705	76.6	14.00	18.82	1.46
7395.8078		0.51			
7395.9047		0.164			
7395.9721		0.826			
7396.0559	7396.0562	2.36	5.86	221.24	6.02
7396.0774	7396.0767	1.51	3.94	225.06	6.07
7396.1650	7396.1660	0.25	1.61	294.93	7.02
7396.2251	7396.2246	10.1	5.41	285.42	3.95

The low energy *E* and *J* values were obtained for the transitions whose centres coincide with the HITRAN line positions at 296 K. This Table is a small section of the list of 3473 transitions attached as Supplementary Material. The *J*<sub>low</sub> values marked by \* in the last column have a higher uncertainty (see Text).

We have performed a systematic comparison of our *J* values determined from the temperature dependence of the line intensities with the assignments provided by HITRAN and obtained by Hippler and Quack. Compared to HITRAN, we noted a perfect agreement for all the *R* and *P* lines except for (i) two components presented as belonging to the *P*(7) manifold in HITRAN and that we have assigned to a *J* = 8 lower level (see Fig. 9) and for (ii) the very weak line at 7512.2218 cm<sup>-1</sup> assigned as a *Q*(4) transition in HITRAN and that disappears in our LNT spectrum indicating that it arises from a level with higher *J* value.

The discussion of the assignments of the *Q* branch is complicated by the density of overlapping lines in the RT spectrum (see Fig. 10). At RT, the *Q*(1) line is superimposed with at least one line which vanishes at low temperature. This overlapping explains the difference between the HITRAN position of the *Q*(1) transition (7510.2939 cm<sup>-1</sup>) and the LNT and jet [8] values



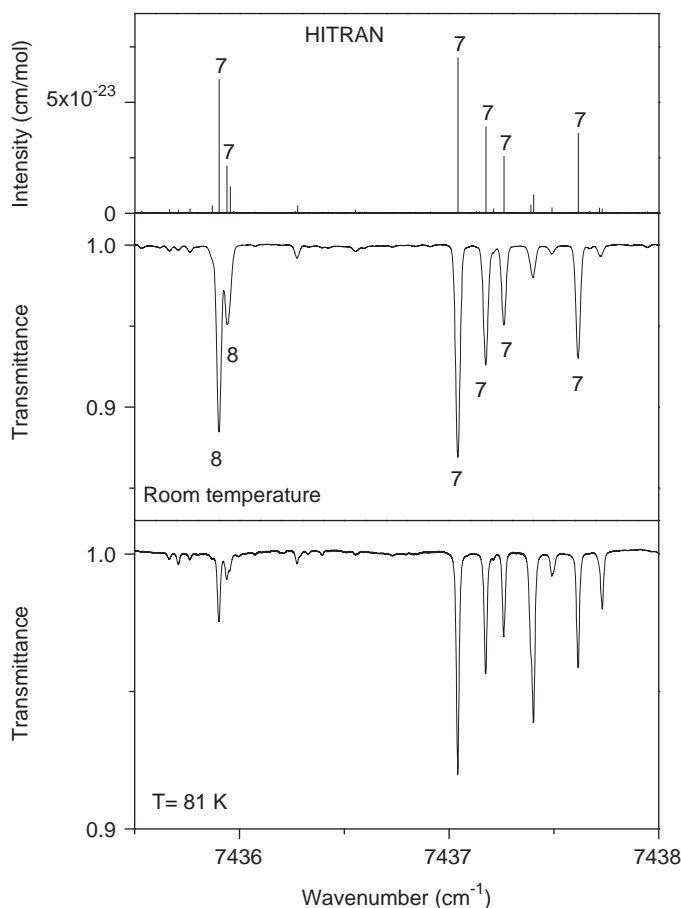
**Fig. 8.** Histograms of the lower  $J$  values obtained by associating transitions according to different criteria on the line centres difference,  $\delta$ , at RT (HITRAN) and LNT (This work):  $\delta < 0.001$ ,  $0.001 < \delta < 0.002$  and  $0.002 < \delta < 0.003 \text{ cm}^{-1}$  (upper panel) and percentages of lines (left hand) and absorbance (right hand) corresponding to  $\delta < 0.001$ ,  $\delta < 0.002$  and  $\delta < 0.003 \text{ cm}^{-1}$  (lower panel).

(7510.2869 and  $7510.2873 \text{ cm}^{-1}$ , respectively). The same situation is noted for the  $Q(4)$  transition at  $7509.774 \text{ cm}^{-1}$  which is larger by  $0.006 \text{ cm}^{-1}$  compared to both the RT and jet values.

From the comparison with Hippler and Quack's results [8], we note a few discrepancies. (i) The higher frequency  $R(3)$  component is given at  $7552.9779 \text{ cm}^{-1}$ , exactly  $0.1 \text{ cm}^{-1}$  above the LNT and HITRAN values, indicating a misprint error which is transferred to the obtained term value [8]. (ii) The  $E$  and  $F2$  components of the  $R(2)$  line were not resolved in the CRDS jet spectra [8] while they are clearly distinguished in the LNT spectrum and included in the HITRAN database. In agreement with the HITRAN value ( $0.0160 \text{ cm}^{-1}$ ), we measured a wavenumber separation of  $0.0168 \text{ cm}^{-1}$  which is larger than both the Doppler broadening at 81 K ( $0.0118 \text{ cm}^{-1}$  FWHM) and the spectral resolution achieved in the jet CRDS spectrum ( $0.0098 \text{ cm}^{-1}$ ) [8]. (iii) The line at  $7510.1912 \text{ cm}^{-1}$  is given as a  $Q(2)$  transition in HITRAN but was assigned to  $Q^{(0)}(3)A_2$  by Hippler and Quack. This last assignment is strongly supported by the band analysis presented in Ref. [8]. According to the temperature variation of the intensity of this line which differs from that of the nearby  $Q(3)$  transition (see Fig. 10), we obtained a lower  $J$  value of 2 in agreement with HITRAN but our result may be affected by large uncertainties on the RT line strength due to the congestion of the  $Q$  branch head. The same reason probably explains the deviations observed between our  $J$  values and some of the eight  $Q(J)$  assignments obtained by Hippler and Quack (see Supplementary Material).

## 6. Conclusion

The spectrum of methane at 81 K was recorded by direct absorption spectroscopy between  $7351\text{--}7655 \text{ cm}^{-1}$  using a specifically dedicated cryogenic cell coupled with a series of DFB laser diodes. The investigated spectral range corresponds to the high energy part of the icosad dominated by the  $\nu_2+2\nu_3$  band. The minimum value of the measured line intensities (at 81 K) was on the order of  $10^{-26} \text{ cm/molecule}$  i.e. a factor of 40 lower than the intensity cut off of the HITRAN database in the considered region ( $4 \times 10^{-25} \text{ cm/molecule}$  at 296 K). The positions and strengths at 81 K of 3473 transitions were obtained from the spectrum analysis. On the basis of line positions coincidence, strengths corresponding to the same transition in the LNT and RT line lists were associated and  $J$  values of the lower level of 1273 transitions could be determined from the variation of the line strength between 81 and 296 K. A value of  $0.002 \text{ cm}^{-1}$  was adopted as best compromise for the tolerance interval of the difference between the RT and LNT line positions. This value is about one sixth



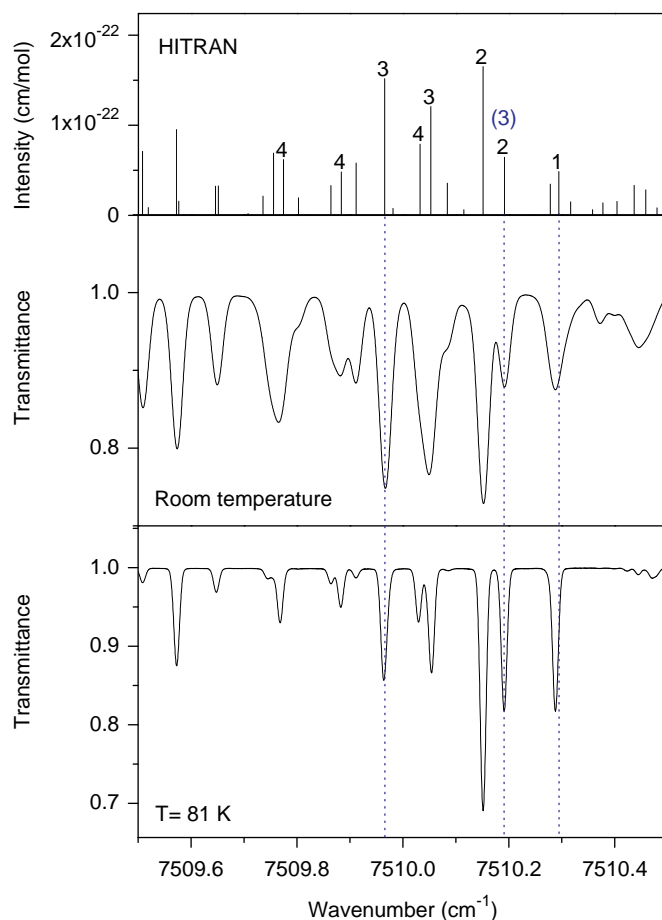
**Fig. 9.** The absorption spectra of methane in the region of the  $P(7)$  manifold at room temperature (middle panel) and liquid nitrogen temperature (lower panel). The stick spectrum of  $\text{CH}_4$  as provided by the HITRAN database at 296 K is displayed on the upper panel with the  $J$  assignment provided by HITRAN. The intensity of the doublet near  $7435.8 \text{ cm}^{-1}$  shows a different variation than the  $P(7)$  components around  $7437.2 \text{ cm}^{-1}$ , indicating that its lower  $J$  value is higher (we obtained a  $J = 8$  value).

of the Doppler broadening (FWHM) at 81 K and on the same order than the uncertainty of the line positions provided in HITRAN [14]. Relaxing the coincidence criterion to higher values (up to  $0.003 \text{ cm}^{-1}$ ) leads to the determination of less reliable  $J$  values that do not show any propensity to be close to integer values. Nevertheless, it may be an effective way to account for the temperature variation of a higher fraction of the absorbance in the region.

Part of the large deviations between RT and LNT line positions is due to the difficulty to correctly account for the highly congested spectrum as a sum of individual line profiles. This problem is more serious at RT than at LNT as the line Doppler profile is twice as large and the spectrum is more congested. The precision on the RT and LNT spectroscopic parameters may be improved by a simultaneous fitting of the RT and LNT spectra. An iterative multispectrum procedure could consist in successively determining the lower  $J$  values of the strongest lines, fixing the temperature dependence of these line intensities to their theoretical values (Eq. (2)), determining the lower  $J$  values of the medium lines from the (obs.–calc.) residuals and so on. The power of such multispectra treatment would be even more efficient by using a series of spectra recorded at intermediate temperatures.

The obtained results represent a significant advance in the knowledge of the temperature dependence of the methane absorbance, in a region where very few lower state energies were previously determined. The 1273 transitions with  $J$  determination ( $\delta < 0.002 \text{ cm}^{-1}$ ) represent 69% and 81% of the absorbance at 296 and 81 K, respectively. In other words, most of the temperature variation of the absorption in the region is accounted for in the attached line list.

In addition to these 1273 transitions, 2200 mostly weak transitions were measured in our LNT spectrum. Their lower state energy could not be determined since no line position coincidences were found in the HITRAN line list. This is mainly due to the high intensity cut off of the HITRAN line list in the considered region ( $4 \times 10^{-25} \text{ cm/molecule}$ ) which left many LNT lines without RT partners. The spectroscopic parameters of these 2200 LNT transitions are included (without a  $J$  value)



**Fig. 10.** The absorption spectra of methane recorded at room temperature (middle panel) and liquid nitrogen temperature (lower panel) in the region of the head of the Q branch of the  $\nu_2+2\nu_3$  band. The stick spectrum and lower J values as provided by the HITRAN database at 296 K are displayed on the upper panel. The J assignments obtained in Ref. [8] coincide with HITRAN except for one line assigned as Q(2) in HITRAN and Q(3) in Ref. [8] (see Text for details).

in the line list attached as Supplementary Material. They may be valuable for a spectrum simulation in temperature conditions approaching those existing on Titan ( $T \sim 90$  K).

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [10.1016/j.jqsrt.2009.02.004](https://doi.org/10.1016/j.jqsrt.2009.02.004).

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