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# **Empirical low energy values for methane transitions in the 5852-6181 cm<sup>-1</sup> region by absorption spectroscopy at 81 K.**

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### *Abstract*

The high resolution absorption spectrum of methane has been recorded at liquid nitrogen temperature by direct absorption spectroscopy between 1.62 and 1.71  $\mu\text{m}$  (5852–6181  $\text{cm}^{-1}$ ) using a newly developed cryogenic cell and a series of distributed feedback (DFB) laser diodes. The minimum value of the measured line intensities is on the order of  $3 \times 10^{-26}$   $\text{cm}/\text{molecule}$ . The investigated spectral range corresponds to the high energy part of the tetradecad dominated by the  $2\nu_3$  band for which a theoretical treatment is not yet available. The positions and strengths at 81 K of 2187 transitions were obtained from the spectrum analysis. From the values of the line strength at liquid nitrogen and room temperatures, the low energy values of 845 transitions could be determined. The obtained results are discussed in relation with the previous work of Margolis and compared to the line list provided by the HITRAN database.

## 1. INTRODUCTION

Methane is a strong window effect gas whose increasing concentration participates to the global warming of the Earth atmosphere. Methane absorption has an even stronger impact on the radiative budget of the atmospheres of the giant outer planets and of Saturn's satellite Titan. The knowledge of the methane absorption spectrum in conditions similar to those existing on these planets is then a prerequisite for the modelling of their structure and climate. Despite important experimental and theoretical efforts [1], the highly congested absorption spectrum of methane above  $6000\text{ cm}^{-1}$  is still resisting to a satisfactory interpretation. Empirical line-by-line spectroscopic parameters as included in HITRAN [2] or GEISA [3] databases are far from fulfilling the needs as for most of the transitions, rovibrational assignments or at least the energy of the transitions lower levels are not provided. Consequently, line intensities cannot be computed at different temperatures which makes the available line lists of limited use in planetology.

An alternative to the theoretical interpretation is an empirical determination of the lower state energy from the temperature dependence of the line intensities. Two spectra recorded at different temperatures are sufficient to deduce the low energy level of a transition from the ratio of the line strengths values. This method has been applied to methane in a few previous investigations. For instance, Pierre *et al.* [4] used two spectra recorded at 295 and 149 K by Fourier Transform Spectroscopy (FTS) to determine lower state quantum numbers in the region of the  $3\nu_3$  band near  $9000\text{ cm}^{-1}$ , Tsukamoto *et al.* [5] could assign 215 transitions with respect to  $J''$  among the 269 transitions of the  $3\nu_1+\nu_3$  that they recorded at 77 K. Of particular relevance for the present study is the investigation by Margolis of the  $5500\text{-}6150\text{ cm}^{-1}$  spectral region by FTS at room [6] and reduced [7] temperatures. Using spectra recorded at 180-220 K with a 0.8 m long cryogenic cell, he could derive the lower energy value,  $E''$  of 1600 transitions. Except for the theoretically assigned lines of the strong  $2\nu_3$  band, the low energy values adopted in the 1996 version of the HITRAN database are the theoretical ground state values corresponding to the rounded  $J$  values obtained by Margolis [7].

Thanks to the 10 Torr vapor pressure of methane available at liquid nitrogen temperature (LNT), absorption spectra can be recorded in the laboratory at temperature conditions approaching those existing for instance on Titan. We have recently developed a new cryogenic cell dedicated to the methane absorption spectroscopy at LNT [8]. Selected spectral regions were chosen for a continuous recording of the absorption spectrum during the cell cool-down to 77 K. We showed that the measurement of the Doppler linewidth is an

accurate method for an *in situ* determination of the gas temperature. Compared to the traditional method based on the determination of the rotational temperature, it has the advantage of not requiring any rotational assignment. By analyzing a  $30\text{ cm}^{-1}$  section of our spectra, we also checked that the temperature dependence of the line intensities can be used for an unambiguous discrimination of the angular momentum  $J$  of the lower state of the observed transitions. In the present contribution, we applied the same method to the  $5850\text{--}6200\text{ cm}^{-1}$  spectrum from which 2187 line strengths at LNT could be derived. This spectral range is dominated by the  $2\nu_3$  band near  $6005\text{ cm}^{-1}$  and corresponds to the high energy part of the tetradecad for which a theoretical treatment is not yet available

After the description of the experimental set up (section 2), the construction of the LNT line list will be presented in section 3. Section 4 is devoted to the determination of the low energy values which are compared to Margolis' results in section 5.

## 2. EXPERIMENT

The cryogenic cell used in the present study was described in details in Ref. 8. It is based on an original design which differs from the cryogenic cells described in the literature by the absence of an external vacuum jacket. Our simple design dispenses with the evacuated volume by exploiting the fact that we want to perform high resolution spectroscopy with a low pressure sample, which itself may constitute a good thermal insulation. We eliminated the internal pair of windows such that the sample fills both the inside of the cryostat and the thermal insulation volume. The cryostat is suspended inside the sample volume through its liquid nitrogen filling tube, which eliminates stresses normally present in a double-jacket cell configuration. The external stainless steel cylinder is 1.4 m long, with a 6.3 cm diameter, while the cryostat is made of two co-axial tubes joined at the ends by two rings. The distance between the windows and the cryostat ends is 1 cm. For pressures below 10 Torr, heat transfer is slow and insufficient to cool significantly the external walls, even after several hours of operation. 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 14 InGaAsP distributed feedback (DFB) fibered diode lasers allowing a continuous coverage of the  $5852\text{--}6181\text{ cm}^{-1}$  ( $1.62\text{--}1.70\text{ }\mu\text{m}$ ) spectral range except for an inaccessible  $8.8\text{ cm}^{-1}$  gap between  $6124.0$  and  $6132.8\text{ cm}^{-1}$  (see Ref. [8] for details about the spectra acquisition). Each complete diode laser 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 °C swept this window over the whole DFB tuning range of about  $30\text{ cm}^{-1}$  within 12 minutes. These  $30\text{ cm}^{-1}$  wide spectra were calibrated independently by matching the  $\text{CH}_4$  line positions measured by FTS at room temperature [2] as adopted in the HITRAN database. The standard deviation error of the differences between our line positions and HITRAN values was minimized leading to *rms* values less than  $10^{-3}\text{ cm}^{-1}$ .

A typical noise equivalent absorption of  $2\times 10^{-6}\text{ cm}^{-1}$  was achieved, corresponding to a detectivity limit on the order of  $3\times 10^{-26}\text{ cm/molecule}$  for the line intensities at LNT at a 10 Torr pressure.

In our previous contribution [8], we showed that the measurement of the Doppler line broadening is a very precise way to measure the gas temperature in a cooled cell. From a line profile analysis of several tens of absorption lines, a temperature value of  $81\pm 1\text{ K}$  was determined, the error bar corresponding to one standard deviation. In the forthcoming analysis, we will refer to this value as the “liquid nitrogen temperature” (LNT).

### 3. LINE INTENSITY RETRIEVAL

At LNT, the depletion of the population corresponding to high  $J$  rotational levels leads to a drastic reduction of the rotational congestion. As illustrated in Fig. 1, the change may be so strong that the spectrum may become hardly recognizable compared to the room temperature (RT) spectrum. In addition, the Doppler linewidth is a factor of 2 narrower, which allows the resolution of a number of multiplets (Fig. 2) and helps for the line intensity retrieval.

Most of our spectra were recorded at a pressure of 9.35 Torr (at 81 K). A few additional recordings were performed with lower pressure values in order to avoid saturation of the strongest lines. The self broadening coefficient of methane at low temperature has recently been reported for the  $2\nu_3$  band [9]. Its value, which is expected to be mostly independent of the vibrational band, is on the order of  $0.21\text{ cm}^{-1}/\text{atm}$  (Half Width at Half Maximum) at 80 K *i.e.* about  $2.8\times 10^{-3}\text{ cm}^{-1}$  HWHM at 10.0 Torr. This value is smaller but significant compared to the Doppler width (HWHM  $4.8\times 10^{-3}\text{ cm}^{-1}$  at 80 K). The DFB line width (1-5 MHz) is much smaller than the Doppler broadening [150 MHz (HWHM) at LNT] and is then negligible. In our analysis, the line profile was then assumed to be a Voigt function of the wavenumber.

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

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

Where:

$\frac{I_0(\nu)}{I(\nu)}$  is the ratio of the incident intensity to the transmitted intensity,

$l$  is the absorption pathlength in cm

$\nu$  is the wavenumber in cm<sup>-1</sup>

$\alpha(\nu)$  is the absorption coefficient in cm<sup>-1</sup>

$N$  is the molecular concentration in molecule/cm<sup>3</sup> which can be obtained from the pressure value:  $P = NkT$ .

Because of the large number of observed transitions (about 8 lines/cm<sup>-1</sup>), lines were frequently blended. 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. The line centre, the integrated absorbance, the HWHM of the Gaussian and Lorentzian components and the baseline (assumed to be a second order polynomial function of the wavenumber) were determined by using the *fityk* program. This freely accessible software (<http://www.unipress.waw.pl/fityk/>) is an interactive least square multi-line fitting program based on the Levenberg–Marquardt algorithm. Depending on the line overlapping and signal to noise ratio in the considered spectral section, some of the fitted parameters were constrained. In particular, the Gaussian width was often fixed to its theoretical value.

**Fig. 3** shows a comparison between the measured and fitted spectra. Because of the high signal to noise ratio of the spectra, the *rms* of the residuals of the simulation could be decreased to a small value (*rms*~ 2×10<sup>-4</sup>). This *rms* value corresponds to a minimum line strength value of 3×10<sup>-26</sup> 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 could reproduce the observed line profile.

The most complete line list was obtained by gathering the line lists corresponding to the different DFB laser diodes, each extending over about 30 cm<sup>-1</sup>. The values of the centre and strengths of the lines corresponding to the overlapping regions were averaged. The obtained global line list was further checked and cleaned from spurious lines or irreproducible spectral

features close to the noise level. The final list consists of 2187 lines with intensity values ranging from  $3 \times 10^{-26}$  to  $2 \times 10^{-21}$  cm/molecule for methane in natural abundance at 81 K.

An overview comparison of our LNT spectrum with the spectrum (at 296 K) provided in the HITRAN2004 database is presented in Fig. 4. In the studied region, the HITRAN2004 list includes 1300 lines with strength above a cut off value fixed to a  $4 \times 10^{-24}$  cm/molecule

Above  $4800 \text{ cm}^{-1}$ , the empirical line-by-line spectroscopic parameters provided by the present version of the HITRAN database were obtained by Brown at room temperature by high resolution Fourier Transform Spectroscopy (FTS) with path lengths up to 433 meters [10], except for the  $5500\text{-}6184 \text{ cm}^{-1}$  region. In this region which includes our region of interest, the parameters come from a previous investigation by Margolis [6]. He retrieved the line positions and strengths of methane from a FTS spectrum recorded at RT with path length limited to 1.5 meter [6]. This is the reason why the intensity cut off in our region ( $4 \times 10^{-24}$  cm/molecule) is 100 times larger than in the nearby spectral regions investigated by L. Brown (see Fig. 1 of Ref. [8]). As discussed below, this insufficient sensitivity of the available line list at room temperature limited the amount of transitions for which the lower state energy could be determined.

#### 4. DETERMINATION OF THE LOWER STATE ENERGY

The low energy value,  $E''$ ,  $E'' \approx B_0 J''(J''+1)$ , 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 is true independently of any rovibrational assignment as long as individual line intensities can be accurately determined. A typical example is presented in Fig. 5 which shows two groups of lines exhibiting very different temperature dependence.

The temperature dependence of the line strength can be expressed as follows:

$$S_{\nu_0}(T) = S_{\nu_0}(T_0) \frac{Q(T_0)}{Q(T)} \exp \left[ -E'' \left( \frac{1}{kT} - \frac{1}{kT_0} \right) \right] \quad (2)$$

where  $T_0$  is a reference temperature (296 K for instance) and  $Q(T)$  is the internal partition function. The extremely weak stimulated emission term from the upper level of the transition is negligible. Since the energies of the excited vibrational states are high compared to the considered thermal energies, the vibrational contribution to the partition function is also negligible and only the rotational partition sum has to be considered:

$$\frac{Q(T_0)}{Q(T)} = \left( \frac{T_0}{T} \right)^{3/2} \quad (3)$$



The lower energy of the considered transition can then be deduced from the variation of the line strength:

$$\ln \left( \frac{S_{v_0}(T)T^{3/2}}{S_{v_0}(T_0)T_0^{3/2}} \right) = -E'' \left[ \frac{1}{kT_0} - \frac{1}{kT} \right] \quad (4)$$

This relation was applied to the 845 transitions of our LNT line list coinciding with the HITRAN line list at 296 K. The coinciding lines are highlighted on the overview spectrum of Fig. 4. From these empirical determinations of the  $E''$  values, the low  $J''$  value was calculated as the positive root of the  $E''=B_0J''(J''+1)$  equation (with  $B_0=5.24 \text{ cm}^{-1}$ ). We present in Fig. 6 a scattered graph of the obtained  $J''$  values versus the line centre. We note with satisfaction that a high number of empirical  $J''$  values are concentrated around integer values. The corresponding histogram, presented on Fig. 7 shows that 80 % of the obtained  $J''$  values fall in a  $\pm 0.25$  interval around integer values. This high percentage validates the method. From the histogram, it is clear that the reliability of the  $J''$  determination degrades for both the  $J''=0-2$  values and the higher  $J''$  values ( $>9$ ). This is a consequence of the increased uncertainty on the line strength values due to the weakness of the transitions with low or high  $J''$  value in the LNT and RT spectra respectively. A significant proportion of non integer  $J''$  values are due to an inaccurate determination of the RT value of the line strength. As a consequence of the larger Doppler broadening and higher rotational congestion, blended lines are more frequent in the RT spectrum which hampers an accurate determination of some line strengths. Such problematic situations are illustrated in Fig. 3 which includes a comparison of the LNT spectrum with the HITRAN stick spectrum at 296 K.

The list of the 845 transitions with  $J''$  determination is provided as Supplementary Material. This list includes the LNT line strength, the corresponding RT line strength as provided by HITRAN, our  $J''$  value, HITRAN  $J''$  value when available and a specific note for problematic lines. A small part of this line list is reproduced in Table 1.

## 5. COMPARISON WITH MARGOLIS' RESULTS

In 1990, Margolis applied the same procedure to determine empirical low energy values from the variation of the line strength between room temperature and 200 K. In our spectral region, he could derive low energy values for 1126 of the 1300 absorption lines that he measured above an intensity cut off of  $4 \times 10^{-24} \text{ cm/molecule}$  at RT. A small part of the obtained line list is included in Ref. [7] with the corresponding empirical  $J''$  values. In the 1996 version of the HITRAN database, except for the assigned lines of the  $2\nu_3$  band, the low

energy values are the theoretical ground state values corresponding to the rounded  $J$  values as obtained by Margolis. Transitions for which  $E''$  could not be determined by Margolis are provided with 333.3333 or 555.5555  $\text{cm}^{-1}$  lower energy values (no ground state level has these values). In the 2004 version of the HITRAN database [2], the line centre and line strength were transferred unchanged from the 1996 linelist but the rotational assignments and  $E''$  information were erroneously converted in the new format of the database. Consequently, the forthcoming discussion will use the HITRAN 1996 line list.

The statistical comparison of our results with HITRAN 1996 is presented in Fig. 8. 766 transitions with lower state  $J''$  values determined can be compared. The difference between our values and Margolis values is plotted versus  $J''$  on Fig. 9. Overall, the  $J''$  values coincide for 69 % of the considered transitions and the difference is  $\pm 1$  for 23 %. We note a clear dissymmetry in the distribution of the differences, our values being more frequently lower than Margolis's value. The reduced temperature value in Margolis experiment was about 200 K measured from the rotational distribution of the  $2\nu_3$  band. By using a much lower reduced temperature, the dynamics of the line strengths ratio is considerably enhanced: for a transition from a  $J=0$  level, a temperature reduction down to 200 K leads to an increase of the strength by a factor of 1.8 while this factor is 7.0 for a 81 K reduced temperature. For a  $J=9$  level, the line intensity is lowered by only a factor of 1.7 for a 200 K reduced temperature but by a factor of 63 for an 81 K temperature. This is why we believe that our  $J$  determination is in general more reliable for  $J$  values up to 9 or 10. As a test, we constructed a histogram similar to that of Fig. 7 for the transitions listed by Margolis in Ref. [7]. The percentage of the  $J$  values falling in a  $\pm 0.25$  interval around integer values is 64 % and 79 % for Margolis results and our results, respectively. In addition, our spectrum benefited from the reduced Doppler broadening which allowed retrieving reliable line intensities for a number of transitions that Margolis could not measure at 200 K. We could determine for the first time the lower energy values for 79 of such transitions. We checked that the high majority of the 361 additional lines provided with  $E''$  values in HITRAN corresponded to high  $J$  values in agreement with their disappearance in our 80 K spectrum.

It is interesting to test to which extent the HITRAN 1996 line list can be used to predict the  $\text{CH}_4$  spectrum at 81 K. The line strengths at 81 K can be calculated from the low energy values provided in the HITRAN 1996 database and directly compared to our values. Probably more illustrative is the comparison of a "low resolution" spectrum at 81 K simulated by affecting to each transition a broad profile representing the apparatus function of a low resolution spectrograph. The spectra calculated for a pressure value of 10 Torr are displayed

on Fig. 10 together with their difference. The overall agreement is good but significant deviations are noted in the regions of the  $Q$  branch and around  $6100\text{ cm}^{-1}$  for instance. All over the investigated region, our absorption is larger than HITRAN absorption. On average, our observations add 9.6 % of the total absorption in the region which corresponds to an average value of  $3.3 \times 10^{-5}\text{ cm}^{-1}$ . We have examined in more details the discrepancies around  $6100\text{ cm}^{-1}$ . Fig. 11 shows that part of the deviations are due (i) to transitions which are given with the arbitrary  $555.555\text{ cm}^{-1}$  low energy level in HITRAN and are then predicted with negligible intensity at 81 K while they correspond in fact to a low  $J$  values and (ii) to erroneous theoretical assignments as in the region of the  $R(9)$  manifold near  $6106\text{ cm}^{-1}$ . Note that the 1342 transitions for which we could not calculate the  $E''$  value, represent 5.8 % of the total absorption at 81 K.

## 6. CONCLUSION

Using a newly designed cryogenic cell coupled with a series of DFB lasers, the absorption spectrum of methane at 81 K was recorded by direct absorption spectroscopy between  $5852$  and  $6181\text{ cm}^{-1}$ . The typical achieved noise equivalent absorption is  $2 \times 10^{-6}\text{ cm}^{-1}$  corresponding to a detectivity limit on the order of  $3 \times 10^{-26}\text{ cm/molecule}$  for the line intensities. Empirical  $J$  values of the lower level of 845 transitions were obtained from the temperature variation of the absolute line strengths between RT and LNT. For the RT line strengths, we adopted the values measured by Margolis [6] as included in the HITRAN database [2]. Compared to Margolis results [7] which are based on a reduced temperature spectrum recorded at about 200 K, we believe that our 81 K spectrum has the advantage to provide more accurate determination for transitions corresponding to low  $J$  values. New or different empirical  $J$  values were determined for 79 and 247 transitions respectively. This is particularly important for the infrared observations of planets or satellites with low atmospheric temperature such as Titan ( $T \sim 90\text{ K}$ ).

In addition to these 845 transitions, about 1350 transitions were measured in our LNT spectrum. Their lower state energy could not be determined as the corresponding RT line strength value is missing in the HITRAN database. This is a consequence of the relatively high intensity cut off of the  $\text{CH}_4$  HITRAN line list in the considered region ( $4 \times 10^{-24}\text{ cm/molecule}$ ). We hope that the next update of the HITRAN database will lower the intensity cut off to the same value than in the surrounding spectral regions ( $4 \times 10^{-26}\text{ cm/molecule}$ ), allowing for a  $E''$  determination for most of our transitions observed at LNT. Another suitable improvement of the present HITRAN database concerns the multiplets unresolved at RT

whose line strength determination may benefit from the measurement of well resolved components at LNT.

In several planetary atmospheres, methane absorption may overlap the absorption bands of other species. This is why a precise characterization of the methane spectrum in the low opacity windows is of particular interest. Spectroscopy techniques with higher sensitivity than direct absorption will be necessary to detect the very weak absorption lines which have an impact over atmospheric path length. We are planning to couple the cryogenic cell used in the present work with the CW-Cavity Ring Down Spectroscopy technique which proved to be a very powerful tool to characterize the CH<sub>4</sub> absorption spectrum at RT in the 1.55  $\mu$ m transparency window [10].

We hope that the obtained results will help for a theoretical modeling of the considered region and will contribute to a better characterization of methane absorption in different spectral regions which are of primordial importance in planetology.

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**Fig. 1.**

A section of the methane absorption spectrum near  $5998\text{ cm}^{-1}$  showing a considerable variation of the line intensities from room temperature (upper panel) to liquid nitrogen temperature (lower panel). The spectra were recorded at 9.30 (RT) and 9.35 (LNT) Torr respectively.

**Fig. 2.**

An example of resolution of multiplets allowed by the reduction of the Doppler line width at 81 K.

**Fig. 3.**

Simulation of the  $\text{CH}_4$  spectrum recorded at LNT and comparison with the HITRAN database (296 K). The selected spectral regions were chosen to illustrate the difficulties for a line by line correspondence of the RT and LNT transitions.

From top to bottom:

- (a) Stick spectrum as provided by the HITRAN database at RT (296 K),
- (b) Experimental spectrum at LNT,
- (c) Simulated spectrum resulting from the line fitting procedure,
- (d) Residuals between the simulated and experimental spectra

The left hand and right hand spectra were recorded at 9.34 and 7.32 Torr respectively

**Fig. 4.**

Overview of the scattered spectrum of methane between  $5850$  and  $6180\text{ cm}^{-1}$  recorded at liquid nitrogen temperature (this work) and as provided in the HITRAN database at 296 K. Black dots highlight the 845 transitions used for the lower energy determination.

**Fig. 5.**

Temperature evolution of the methane absorption spectrum near  $6096\text{ cm}^{-1}$ . The intensity variation allows to discriminate two groups of lines: the three stronger lines in the 81 K spectrum arise from a  $J = 3$  level while the others correspond to  $J = 8$ .

**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 K and 296 K between  $5852$  and  $6181\text{ cm}^{-1}$ .

**Fig. 7.**

Histogram of the lower  $J$  values with a step interval of 0.5. 80 % of the obtained  $J''$  values fall in a  $\pm 0.25$  interval around integer values.

**Fig. 8.**

Statistics of the spectroscopic information retrieved in this work compared to the HITRAN database.

**Fig. 9.**

Difference between the lower  $J$  values determined in this work with the values provided by the HITRAN database. The percentages corresponding to 0,  $\pm 1$  and  $-2$  are indicated on the right hand.

**Fig. 10.**

Comparison of the “low resolution” spectrum at 81 K simulated by affecting to each transition a broad Gaussian profile (FWHM  $5\text{ cm}^{-1}$ ). The spectra were simulated for a 10.0 Torr pressure using our list of measured transitions at 81K (upper panel) and the HITRAN 1996 line list calculated for the same temperature (medium panel). The difference between the two spectra is displayed on the lower panel with an amplification factor of 10.

**Fig. 11.**

Comparison of the absorption spectrum of methane recorded at 81 K with the stick spectrum calculated at the same temperature from the HITRAN 1996 database. The two strong lines marked by a star (\*) are given with the arbitrary  $555.555\text{ cm}^{-1}$  low energy level in HITRAN 1996 and are then predicted with negligible intensity at 81 K while they correspond in fact to a low  $J$  values. In its 2004 version, the HITRAN database doesn't provide lower state energy levels for most of the transitions of the region and the spectrum cannot be calculated at 81 K. In both HITRAN1996 and HITRAN2004 versions, the two lines marked by a cross (+) are erroneously assigned as components of the  $R(9)$  manifold while they correspond to  $J''=4$ .

<i>Line center (cm<sup>-1</sup>)</i>	This work ( <i>T</i> = 81 K)			HITRAN ( <i>T</i> = 296 K)	
	<i>Line intensity</i> (10 <sup>-24</sup> cm/mol)	<i>E''</i> (cm <sup>-1</sup> )	<i>J<sub>low</sub></i>	<i>Line intensity</i> (10 <sup>-24</sup> cm/mol)	<i>J<sub>low</sub></i>
5922.9319	0.45	385.3878	8.09	9.32	<sup>a</sup>
5923.5253	0.85	296.0169	7.03	5.57	7
5923.5835	1.69	223.3637	6.05	4.32	5
5923.6052	1.80	224.8878	6.07	4.68	6
5923.7274	1.36	388.7834	8.13	29.40	8
5924.6277	2.73	202.4621	5.74	5.32	5
5924.9461	0.09	481.7432	9.10	6.49	8
5924.9603	0.63	393.6638	8.18	14.60	9
5924.9900	0.09	537.7280	9.64	13.50	10
5925.0968	3.63	227.3043	6.11	9.76	6
5925.8624	0.39	381.3083	8.05	7.66	8
5925.8815	0.82	379.7792	8.03	15.80	9
5926.4662	42.40	298.2627	7.06	285.00	7
5926.4838	41.70	298.8449	7.07	282.00	7
5926.5754	67.60	299.7730	7.08	463.00	7
5926.6250	39.50	300.7311	7.09	274.00	7
5926.6479	27.60	296.8502	7.04	182.00	7
5926.6782	39.20	299.2831	7.07	267.00	7
5928.1577	0.27	407.0264	8.33	7.42	<sup>a</sup>
5928.7439	4.06	229.9263	6.14	11.30	7
5928.8588	3.51	229.0414	6.13	9.64	7
5929.1206	0.39	455.7426	8.84	20.20	9
5929.5838	0.26	478.2047	9.07	18.10	9
5929.9622	0.70	469.0947	8.97	42.90	9
5930.5238	1.07	304.4751	7.14	7.82	<sup>a</sup>
5930.5948	0.98	301.2358	7.10	6.82	<sup>a</sup>
5933.1492	0.21	389.0478	8.13	4.64	7
5933.1803	3.45	225.6060	6.08	9.07	6
5933.2691	0.24	483.4388	9.12	17.90	9
5933.2958	13.70	159.0849	5.03	15.30	5
5933.5227	0.09	543.8973	9.70	14.10	<sup>a</sup>
5933.7167	0.62	475.7358	9.04	40.90	9
5934.0415	0.22	480.3107	9.09	15.60	9
5934.0708	8.26	161.0181	5.07	9.44	5
5934.6266	11.60	158.0803	5.02	12.80	5
5935.0487	5.86	135.8952	4.62	4.84	3
5936.5353	0.16	467.5260	8.96	9.44	10
5937.8348	0.31	387.8304	8.12	6.61	<sup>a</sup>
5938.0573	88.70	227.5185	6.11	239.00	6
5938.0660	132.00	228.3529	6.12	360.00	6
5938.0945	227.00	224.8141	6.07	590.00	6
5938.1675	135.00	225.1407	6.07	352.00	6
5938.1896	136.00	223.6343	6.05	348.00	6
5938.2085	217.00	226.5516	6.09	578.00	6
5938.6221	0.93	306.2055	7.16	6.90	8
5938.6581	0.56	311.3686	7.22	4.48	7
5945.6878	0.35	478.2164	9.07	24.20	9

**Table 1.**

Empirical low energy and *J* values for methane transitions near 5930 cm<sup>-1</sup> region by absorption spectroscopy at 81 K. Comparison with HITRAN 1996 database. This Table is a small section of the list of 845 transitions attached as Supplementary Material

<sup>a</sup> Transitions for which *E''* could not be determined are provided with 333.3333 or 555.5555 cm<sup>-1</sup> lower energy values (no ground state level has these values) in HITRAN 1996.



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Grenoble, 10 September 2008

Here are our answers to the two reviewer's suggestions:

*Reviewer #1: The article is recommended for the publication. This is an interesting work.*

*Comments:*

*(1) Abbreviation DFB, RT, HWHM have been used without decoding.*

**Our answer:** The signification of these abbreviations has been added in the text

*(2) Table 1. In last column of table symbol 'a' have been used, in text symbol have been used '\*'.*

**Our answer:** Correction done. Thank you

*(3) Page 9 and 10. Hitran 1996 and 2004 discussion and pictures 10,11. Hitran 2004 really has wrong identification in the tetradecade region. HITRAN 2004 lines in region 6100-6110cm<sup>-1</sup> have reasonable WvNm, Intens, Lower Energy Levels (Lower J could be found from lower energy for little J). Maybe it is better for pictures 10, 11 use Hitran 2004 because identification doesn't used for construction pictures 10, 11. In any case because errors of Hitran1996 and Hitran2004 are different it is better in the end of paragraph 5 don't use abbreviation Hitran but HitranNNNN. If authors can't use Hitran 2004 it's better add to picture 11 title that these errors have been corrected in Hitran2004.*

**Our answer:** We have added on the plot of Figs 10 and 11 that HITRAN 1996 was used (it was already written in the captions). In fact, HITRAN 2004 cannot be used as most of the lower state energy values of HITRAN1996 have been lost and replaced by a “-1” value. For instance in the 6100-6110 cm<sup>-1</sup> section mentioned by the reviewer, 27 lines are provided by HITRAN2004 but only 8 are given with lower state energy while HITRAN1996 provides the lower state energy for all of them. So we cannot follow the referee's suggestion “*Maybe it is better for pictures 10, 11 use Hitran 2004 because identification doesn't used for construction pictures 10, 11.*” as the lower state energy *ie* the *J* assignment is required to calculate the line intensities at low temperature. This comment has been added in the caption of Fig. 11.

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Supplementary Material attached to the paper "Empirical low energy values for methane transitions in the 5852-6181 cm<sup>-1</sup> region by absorption spectroscopy at 80 K." by

Bo Gao, Samir Kassi , and Alain Campargue.

List of the 845 CH<sub>4</sub> transitions measured at 81 K by direct absorption spectroscopy between 5852 and 6181 cm<sup>-1</sup>.

The corresponding line strength at 296 K and J" values as provided by HITRAN (1996 version) are given for comparison (see Text).

**Figure**

Fig.1

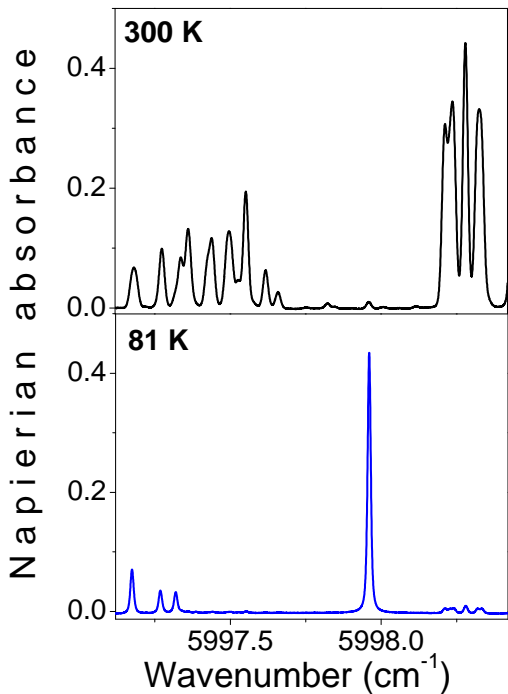


Fig. 2

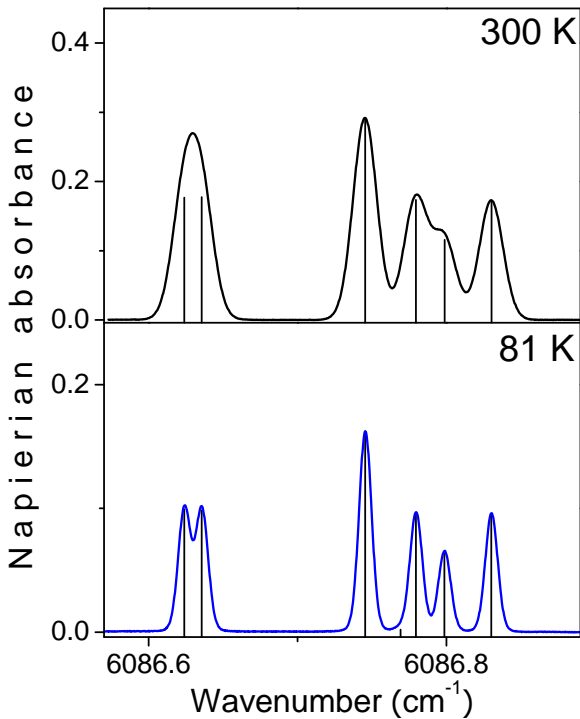


Fig. 3

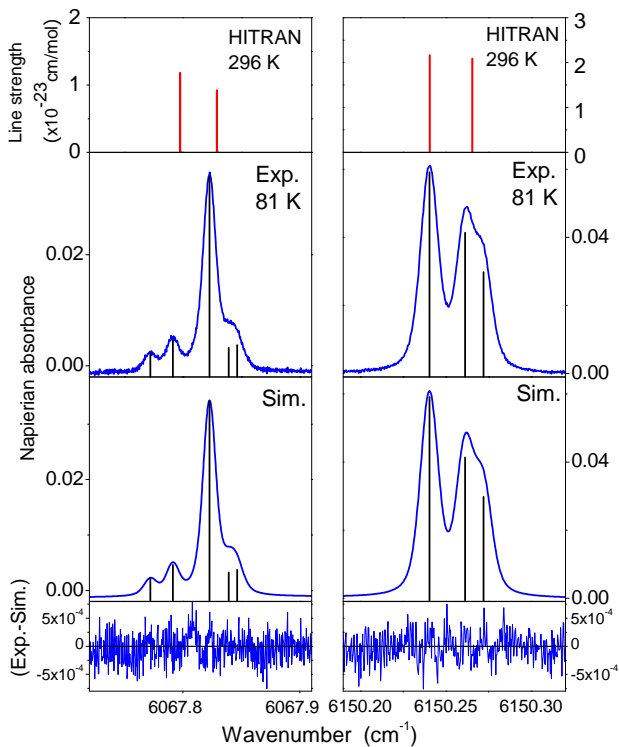


Fig. 4

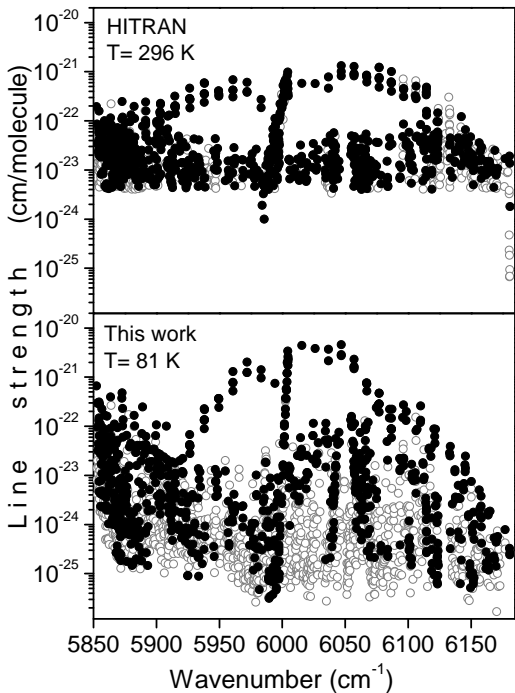


Fig. 5

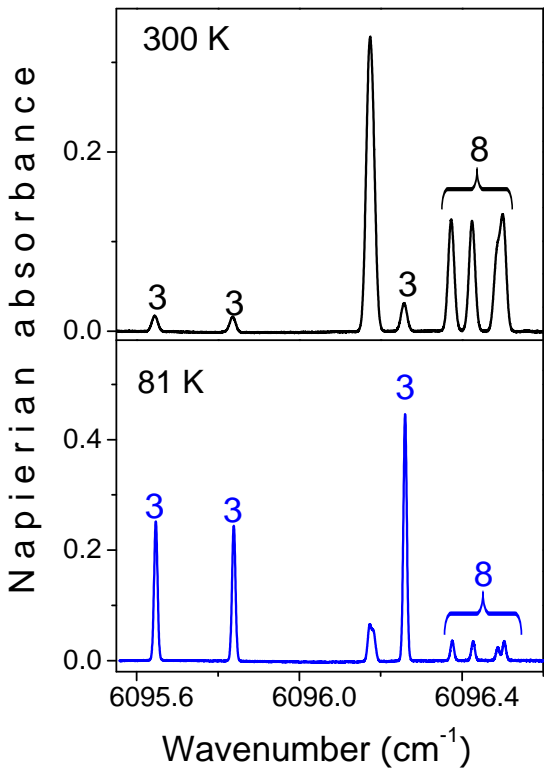


Fig. 6

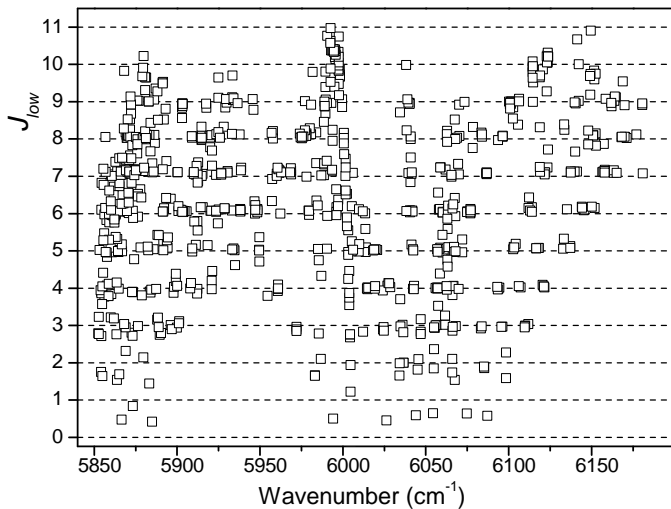
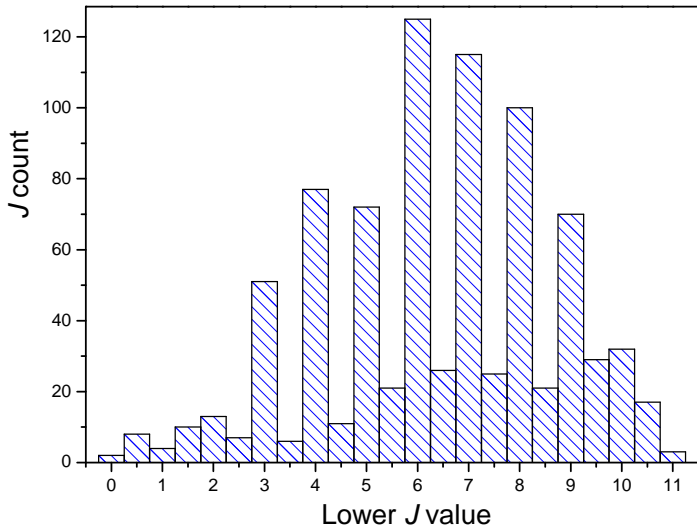




Fig. 7



	95 no <i>J</i>	360 <i>J</i> HITRAN only	HITRAN 96 (1300 lines)
	79 new <i>J</i>	766 <i>J</i> comparison 68% agreement	
This work (2187 lines)	1342 not yet <i>J</i>		

Fig. 9

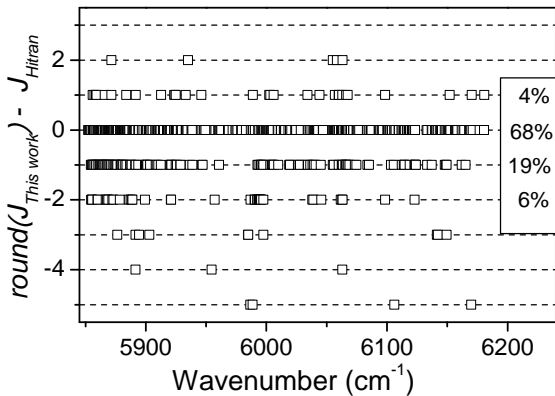


Fig. 10

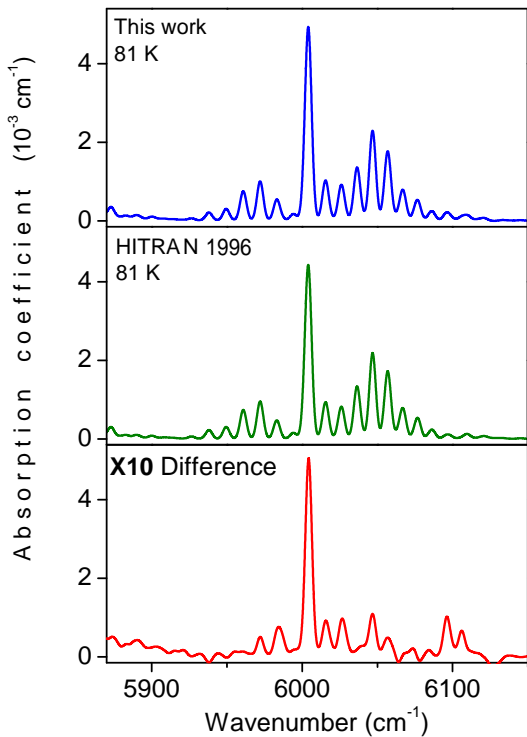
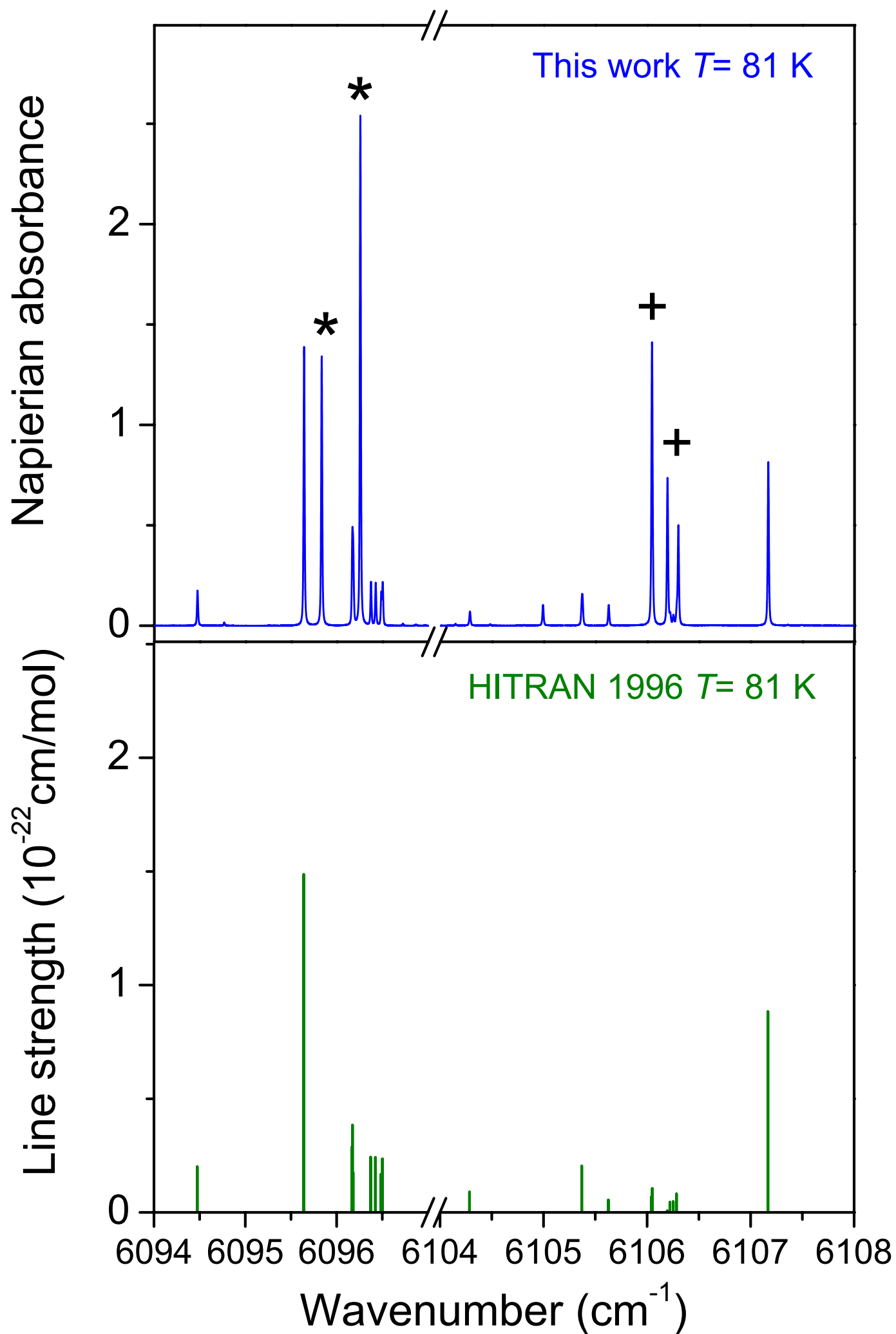


Fig 11



**Supplementary Material**

[Click here to download Supplementary Material: sup\\_mat\\_final line list simplified formatted.txt](#)