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Experimental low energy values of CH₄ transitions near 1.33 μm by absorption spectroscopy at 81 K.

Ella Sciamma-O'Brien^a, Samir Kassi^a, Bo Gao^{a,b}, and Alain Campargue^{a*}

^a *Laboratoire de Spectrométrie Physique (associated with CNRS, UMR 5588), Université Joseph Fourier de Grenoble, B.P. 87, 38402 Saint-Martin-d'Hères Cedex, France.*

^b *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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* Corresponding author: Alain.Campargue@ujf-grenoble.fr

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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^{-1}) 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 $\nu_2+2\nu_3$ band near 7510 cm^{-1} . 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^{-26} $\text{cm}/\text{molecule}$ *i.e.* significantly lower than the intensity cut off of the HITRAN database in the region (4×10^{-25} $\text{cm}/\text{molecule}$ at 296 K). From the variation of the line strength between 81 K 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.

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^{-1} has yet to be satisfactorily interpreted. The HITRAN [2] or GEISA [3] databases only provide empirical line-by-line spectroscopic parameters at room temperature without rovibrational assignments for most of the transitions above 5500 cm^{-1} 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 ($5500\text{-}6150\text{ cm}^{-1}$), 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 $180\text{-}220\text{ K}$ 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. 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 $5850\text{-}6200\text{ cm}^{-1}$ region using the HITRAN line strengths at room temperature (RT) and the line strengths retrieved from spectra that we recently recorded at liquid nitrogen temperature (LNT) with a new cryogenic cell and a series of **Distributed Feed Back (DFB) lasers**. 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 CH_4 HITRAN line list in the considered region ($4\times 10^{-24}\text{ cm/molecule}$) compared to our detectivity limit at LNT on the order of $3\times 10^{-26}\text{ cm/molecule}$ [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 cm^{-1} . This region corresponds to the high energy section of the icosad dominated by the $\nu_2+2\nu_3$ band near 7510 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 [6], 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 cm^{-1} at LNT reported by McKellar [9] although the medium spectral resolution (0.14 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 cm^{-1} spectral range, except for an inaccessible 2 cm^{-1} gap between 7518.4 and 7520.4 cm^{-1} . Each complete laser diode spectrum consisted of the dynamic averaging and concatenation of several thousands 1 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 spectral window over the whole DFB tuning range of about 35 cm^{-1} within 12 minutes. These 35 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 room temperature [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} 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 $81 \pm 1 \text{ K}$ 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 “liquid nitrogen temperature” (LNT).

In our study of the icosad region of methane, we also recorded the methane spectrum at room temperature 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 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.

A typical value of 10^{-6} 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 ν_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 about 10 times smaller than the Doppler broadening [175 MHz (HWHM) at LNT] and therefore negligible.

The line strength S_{ν_0} (cm/molecule) of a rovibrational transition centred at ν_0 , was obtained from the integrated line absorbance, I_{ν_0} ($\text{cm}^{-2}/\text{molecule}$), 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,

ν 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 value: $P = NkT$.

Because of the large number of observed transitions (about 12 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 multi-line 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 1×10^{-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} 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 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 linelist consists of 3473 lines with intensity values ranging from 1×10^{-26} to 5.9×10^{-22} 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 , $E \approx B_0 J(J+1)$, 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 method has 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 ($6300\text{-}8000\text{ cm}^{-1}$) including our region, the empirical line-by-line spectroscopic parameters provided by the HITRAN database were obtained by L. Brown at room temperature ($296 \pm 4\text{ K}$) by high resolution FTS with path lengths up to 97 meters [14]. The intensity cut off of the HITRAN line list was fixed to a value of $4 \times 10^{-26}\text{ cm/molecule}$, except in our region above 7400 cm^{-1} including the relatively strong $\nu_2+2\nu_3$ band, where this value was increased to $4 \times 10^{-25}\text{ cm/molecule}$ (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^{-1} , 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 equation (2), the E values were empirically determined and the corresponding J values were calculated as the positive root of the $E = B_0 J(J+1)$ equation (with $B_0 = 5.24\text{ cm}^{-1}$). Fig. 5 gives the rounded J values obtained for the RT and LNT spectra in a spectral region around 7425 cm^{-1} . 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.

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 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 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 $0.002 < \delta < 0.003 \text{ cm}^{-1}$ (δ 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 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 cm^{-1} leads to 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 (1.66×10^{-20} cm/molecule) and at RT (1.46×10^{-20} 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 $0.002 < \delta < 0.003$ cm⁻¹, doesn't show a clear propensity for integer J values. Nevertheless the $\delta < 0.002$ cm⁻¹ criterion is conservative in regards to the uncertainties on the RT and LNT line positions (± 0.0015 [14] and ± 0.001 cm⁻¹ respectively). A careful analysis of the additional lines fulfilling the $0.002 < \delta < 0.003$ 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 $0.002 < \delta < 0.003$ 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 3.92×10^{-21} cm/molecule. Hippler and Quack obtained a complete rovibrational assignment for 21 of these transitions by high-resolution FTS at RT and CRDS in a supersonic slit jet expansion [8]. 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 analysis to higher J values. As a result of the analysis, the origin (7510.3378 cm⁻¹) and the integrated band strength (9.8×10^{-21} 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 ($7430-7650$ 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.

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 $7512.2218 \text{ cm}^{-1}$ 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 ($7510.2939 \text{ cm}^{-1}$) and the LNT and jet [8] values (7510.2869 and $7510.2873 \text{ cm}^{-1}$ respectively). The same situation is noted for the $Q(4)$ transition at 7509.774 cm^{-1} which is larger by 0.006 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 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 cm^{-1}), we measured a wavenumber separation of 0.0168 cm^{-1} which is larger than both the Doppler broadening at 81 K (0.0118 cm^{-1} FWHM) and the spectral resolution achieved in the jet CRDS spectrum (0.0098 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 lasers. 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} cm/molecule *i.e.* a factor of 40 lower than the intensity cut off of the HITRAN database in the considered region (4×10^{-25} 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 empirical J values of the lower level of 1273 transitions could be determined from the variation of the line strength between 81 K and 296 K. A value of 0.002 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 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 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 (4×10^{-25} cm/molecule) which left many LNT lines without RT partners. The spectroscopic parameters of these 2200 LNT transitions are included (without a J value) 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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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.

Fig. 2.

The absorption spectra of methane recorded at room temperature (middle panel) and liquid nitrogen temperature (lower panel) near 7360 cm^{-1} . The stick spectrum of CH_4 as provided by the HITRAN database at 296 K is displayed on the upper panel for comparison.

Fig. 3.

An example of simulation of the CH_4 spectrum recorded at LNT.

From top to bottom:

- (a) Experimental spectrum at LNT ($P = 9.38\text{ Torr}$),
- (b) Simulated spectrum resulting from the line fitting procedure (see Text),
- (c) Residuals between the simulated and experimental spectra.

Fig. 4.

Overview of the scattered spectrum of methane between 7350 and 7655 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.

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 cm^{-1} .

Fig. 6.

Scattered graph of the lower J values *versus* the line centers. The J values were obtained from the strengths of the methane transitions at 81 K and 296 K between 7350 and 7655 cm^{-1} by associating transitions with line centers differing by less than 0.002 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 ± 0.25 interval around integer values.

Fig. 8.

Upper panel: Histograms of the lower J values obtained by associating transitions according to different criteria on the line centers difference, δ , at RT (HITRAN) and LNT (This work): $\delta < 0.001\text{ cm}^{-1}$, $0.001 < \delta < 0.002\text{ cm}^{-1}$ and $0.002 < \delta < 0.003\text{ cm}^{-1}$.

Lower panel: Percentages of lines (left hand) and absorbance (right hand) corresponding to $\delta < 0.001$, $\delta < 0.002$ and $\delta < 0.003\text{ cm}^{-1}$.

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 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 cm^{-1} shows a

different variation than the $P(7)$ components around 7437.2 cm^{-1} , indicating that its lower J value is higher (we obtained a $J = 8$ 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).

<i>Line center (cm⁻¹)</i>		<i>Line intensity (10⁻²⁴ cm/mol)</i>		<i>E (cm⁻¹)</i>	<i>J_{low}</i>
<i>This work T = 81 K</i>	<i>HITRAN T = 296 K</i>	<i>This work T = 81 K</i>	<i>HITRAN T = 296 K</i>		
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

Table 1.

Wavenumbers and strengths of the absorption lines of methane recorded at 81 K near 7394 cm⁻¹. 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.

Answers to reviewer 2 of Ref. No.: JQSRT-D-08-00308

- *The authors actually measured methane spectra also at room temperature but didn't make use of it (apart from the plots). It would be good to show a fit of the entire RT spectrum fixing spectroscopic parameters to HITRAN values (ie if you compare modeled transmission of you experimental setup at RT with HITRAN values, does it exactly match your measurements or would you have to scale line intensities or other parameters?). Given different experimental setups and a 4K T uncertainty for the HITRAN RT data, how would your results change if you scale HITRAN line intensities by +/- 2%?*

Our answer: Such a comparison may be very instructive. In general, I would expect a good overall agreement as our results show that both HITRAN RT and our LNT intensity values are consistent and reliable. This is confirmed for instance by the fact that J values calculated for the transitions of the $\nu_2+2\nu_3$ band are very close to the expected integer values. Nevertheless, I anticipate a number of practical difficulties: (i) which line profile should we attach to the HITRAN RT lines? I guess that a different Voigt profile should be attached to each line and the Lorentzian component has not be included in HITRAN (ii) we will have to deal with the presence of H₂O lines superimposed to our LNT spectrum (Note that H₂O lines were also present in the spectra used by L. Brown to construct the HITRAN line list) (iii) I am not sure if the pressure conditions were accurately controlled in our RT spectra (iv) it will be a heavy task considering the number of individual spectra (corresponding each to one DFB laser). Nevertheless, we will consider such a comparison and if the obtained results are of interest, we will include them in our future contribution which will be devoted to the low energy part of the icosad (6900-7300 cm⁻¹).

- *What is the estimated uncertainty in your E determination (given error propagation of uncertainties in line strength)?*

Our answer: This is another good point which was already considered in details by Margolis in one of his original paper (see Figs.1 and 2 of Margolis JS. Empirical values of the ground-state energies for methane transitions between 5500 and 6150 cm⁻¹. Appl. Opt. 1990;29:2295–302.). In our case, the difficulty is that the uncertainty of our E determination depends not only on the uncertainty on each of our LNT line strength value but also on that of the HITRAN RT line strength values, which are unknown. The nice propensity of the obtained J values to be close to integer values gives a qualitative idea that on average the uncertainties are small enough to discriminate successive J values. It is nevertheless difficult to give a more precise answer. In order to examine this point in more details, we could also fit the line profile of our RT spectrum. In that case, the simultaneous fit of the RT and LNT spectra could help decrease the number of fitted parameters and then the uncertainty on the retrieved E values.

- *Which spectral region is being used in planetology, the 1.3, the 1.6 or the 2.3 micron region (and why?). In remote sensing of the Earth, mostly 1.6 and 2.3 is used (SCIAMACHY on ENVISAT, GOSAT) as the 1.3 micron region is more contaminated with overlapping water vapor absorptions. What is the advantage/disadvantage of the 1.3 micron region for planetology purposes?*

Our answer: For the study of Titan, the methane windows at 1.3, 1.6 and 2.3 μm are of interest since the Cassini Huygens observations cover these wavelengths where the methane absorption is weak. The advantage of the 1.3 μm region is that in this spectral window, the albedo of Titan appears particularly bright in spectroscopy. Of course, there is no problem of overlapping with water absorption.

- *Please explain all acronym/names when they first occur (eg DFB laser, Napierian Absorbance).*

Our answer: DFB has been explained, Napierian is not an acronym

Specific remarks

- Page 5, last paragraph: "our RT spectrum coincides with the" see comments above. How do you define "coincide", a more quantitative statement or a fit plot would be very useful as the line intensities at the two different temperatures are measured by different people using a different setup which might introduce additional systematic error in E" determinations.

Our answer: See above our answer to the point "estimated uncertainty in your E determination"

- Page 6, Ch. 3, First paragraph: Was the 0.21cm-1/atm measured for all lines globally?

Our answer: It was worth to clarify this sentence. The text has been amended:

"From the measurements and review of literature data presented in Ref. [11], the pressure self broadening of the ν_3 and $2\nu_3$ bands at 81 K has a value on the order of 0.20 cm⁻¹/atm (HWHM). Assuming the same value for the vibrational bands contributing to our spectrum, it leads to a 2.8×10^{-3} cm⁻¹ HWHM at 10.0 Torr which is small but significant compared to the Doppler"

End of paragraph: ". therefore negligible" ? ". and therefore negligible"

Our answer: Done

- Page 6, last paragraph: Why was a cubic function chosen as baseline? Would a linear function change results?

Our answer: We chose a cubic function as baseline to have the best possible fit for all lines. In some cases, the baseline had to be fitted with a cubic function because the base line was curved by some etaloning effect between the optical windows which introduced a low frequency sinusoidal modulation of the baseline. In cases where the baseline could have been fitted with a linear function, the multiline fitting software fityk automatically put the extra parameters in the cubic fit to negligible values, making it be close to a linear function.

- Page 7, first paragraph: Why was the Gaussian part of the Voigt profile fitted if it should be known exactly given the fixed temperature?

Our answer: This is the alternative way to proceed. We preferred to fit the Gaussian component and checked that the obtained value was close to its theoretical value. In principal the two methods should give the same results, nevertheless it seems that a slightly better profile reproduction could be achieved by fitting the Gaussian component.

- Page 9, last paragraph: "It is also limited by.below detection limit in the LNT spectrum" Does that imply that the choice of 81K is actually too low as many lines cannot be measured anymore? The choice of the temperature pairs in this kind of analysis is certainly a tradeoff between an "as big as possible" temperature difference and the aforementioned problem.

Our answer: The reviewer addresses an important point and we agree with his comment. For applications in planetology, it is more important to reliably assign transitions with low J values. This implies to decrease the low temperature value as much as possible and consequently the intensities of the high J transitions may become too weak to be detected in the LNT spectrum. This is not a serious problem as these high J transitions have a negligible impact on the spectrum of Titan or Pluton for instance. Nevertheless, the reviewer is right: if the goal was to assign the maximum number of transitions observed at RT, it would be preferable to use a higher value for the 2nd temperature but the decrease dynamics on the transitions with low J values would lead to a poorer determination of their J values. The more favorable situation would be to increase the sensitivity of the LNT spectra by using a more sensitive method allowing detecting the very weak high J transitions at LNT. We are currently implemented our cell for CRDS at LNT. We hope to lower the detection limit by 3 orders of magnitude and then detect many more lines at LNT.

- Page 11, before conclusions: "uncertainties on the RT line strength." Would it help to adapt line positions from your LNT spectra (as they are less congested) and then fit line strength at RT with fixed positions? Trying to derive line intensities from the RT spectra at least for some of these crucial Q transitions would help.

Our answer: In principle, it is a very good suggestion. In practice, it will be difficult considering the congestion of the spectrum and that a significant fraction of RT lines disappear at LNT. The proposed procedure is quite similar to that we proposed in the Conclusion.

- Figure 4: Unclear when reading only the caption. Describe blue and black dots and ideally change (and make smaller) symbols for blue (eg a cross) as overlapping points cannot be seen at all.

Our answer: The caption has been modified according to the reviewer's suggestion.

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The form of the references has been adapted according to JQSRT standard.

Dr Alain Campargue
Laboratoire de Spectrométrie Physique
UMR CNRS 5588
Université Joseph Fourier, BP 87
38402 Saint Martin d'Hères Cedex
France

Grenoble, 02/02/2009

Dear Editor,

You will find enclosed the revised manuscript *No.:* *JQSRT-D-08-00308*

*Title: " Experimental low energy values of CH₄ transitions near 1.33 μm
by absorption spectroscopy at 81 K."*

by Ella Sciamma-O'Brien , Samir Kassi , Bo Gao, and Alain Campargue

We thank the two reviewers for their positive comments and in particular Reviewer 2 for his (her) constructive criticism. The suggestions of Reviewer 2 were taken into account as far as possible (see the Answers) and the changes have been highlighted in the text of the revised version.

We hope that the amended version is now suitable for publication.

Yours sincerely,

Alain Campargue
Alain.Campargue@ujf-grenoble.fr

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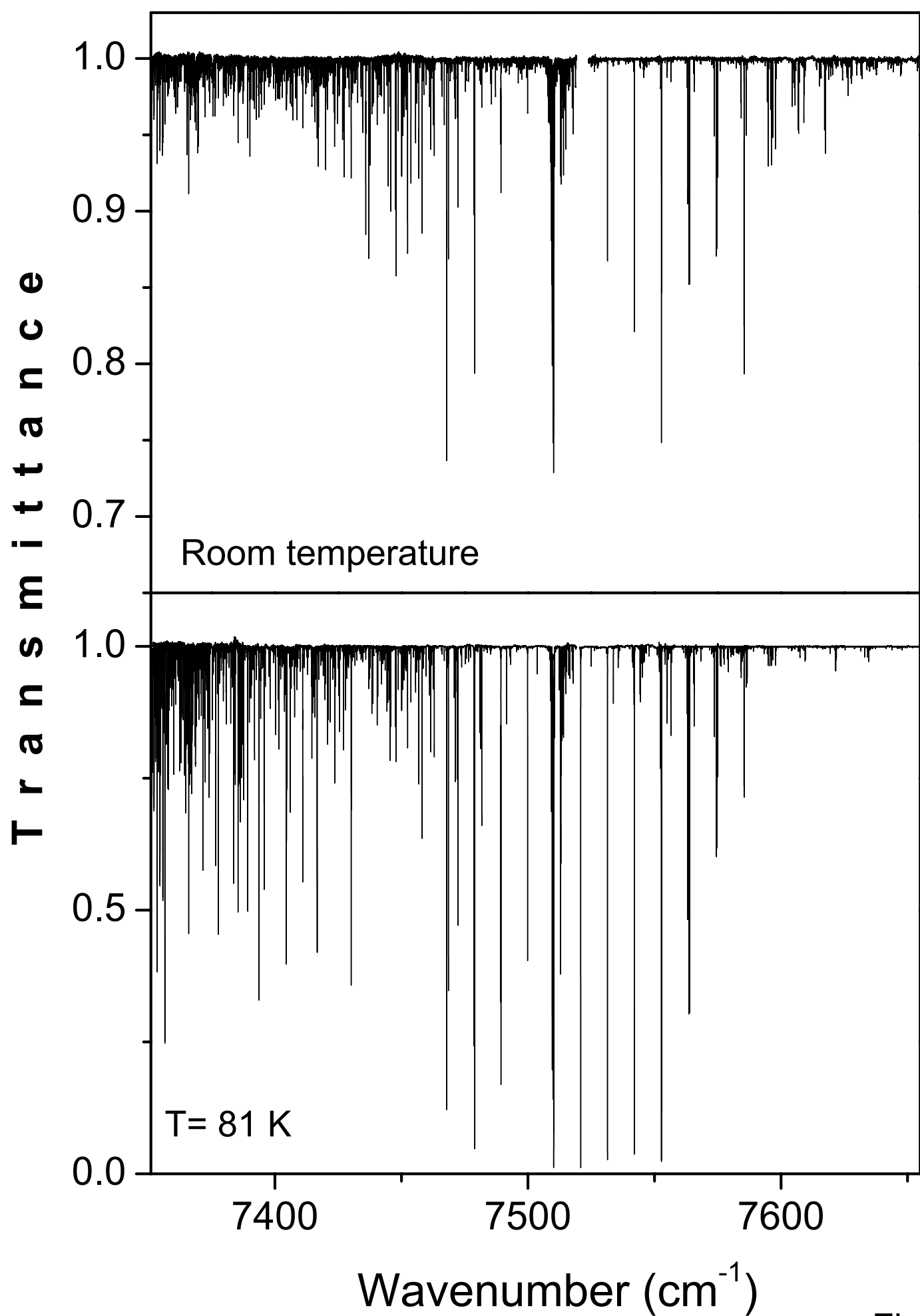


Fig. 1

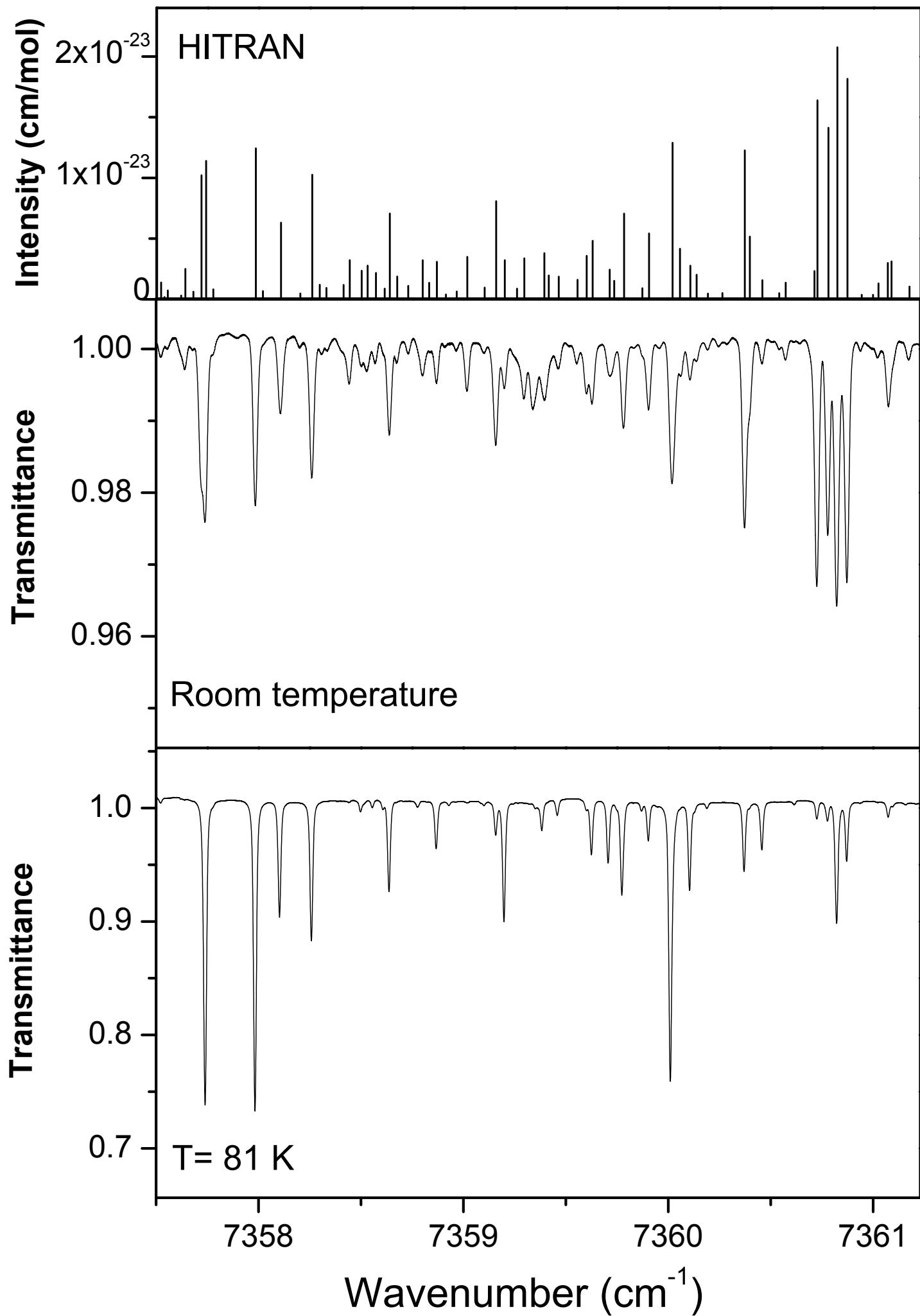


Fig. 2

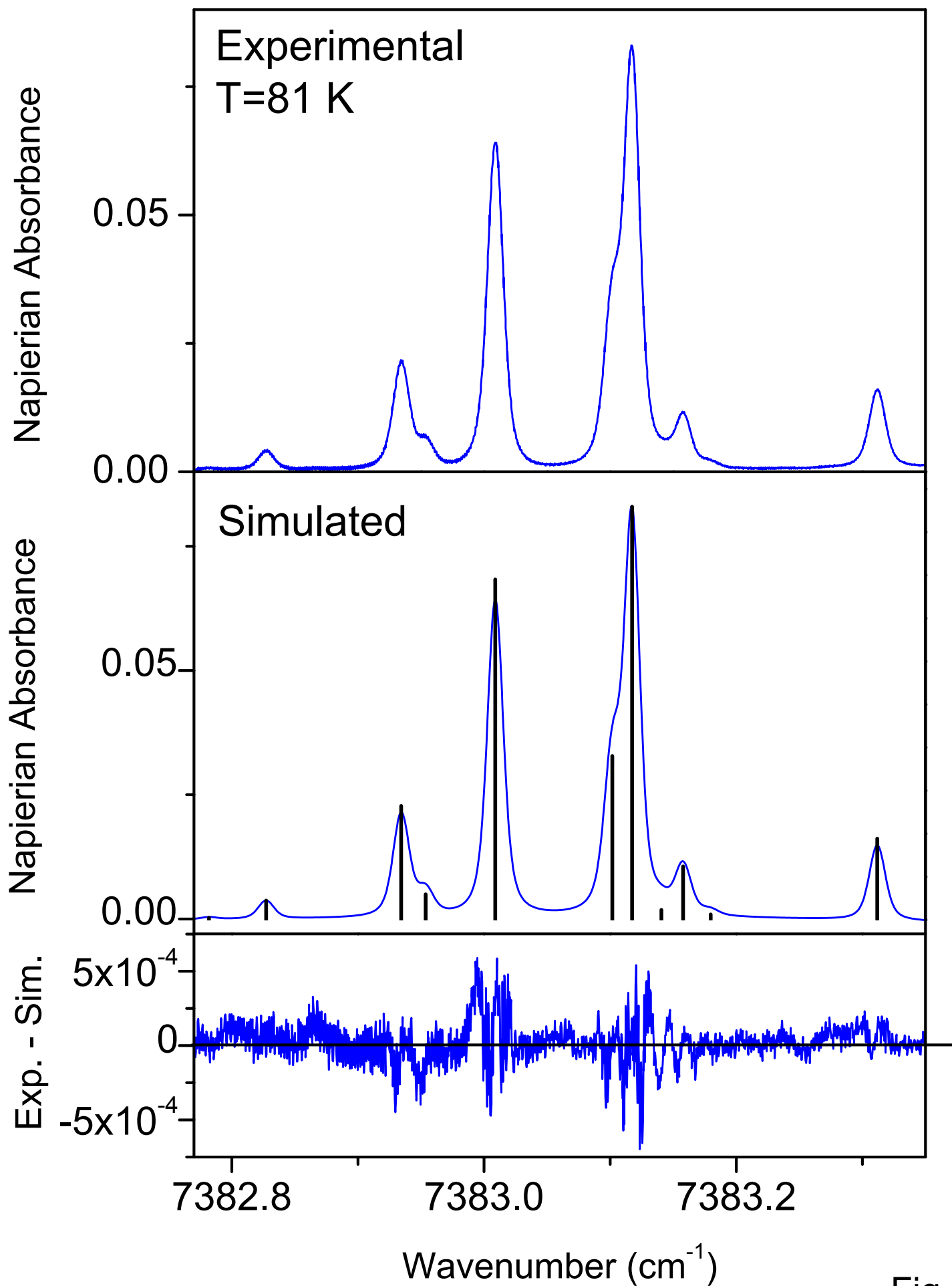


Fig. 3

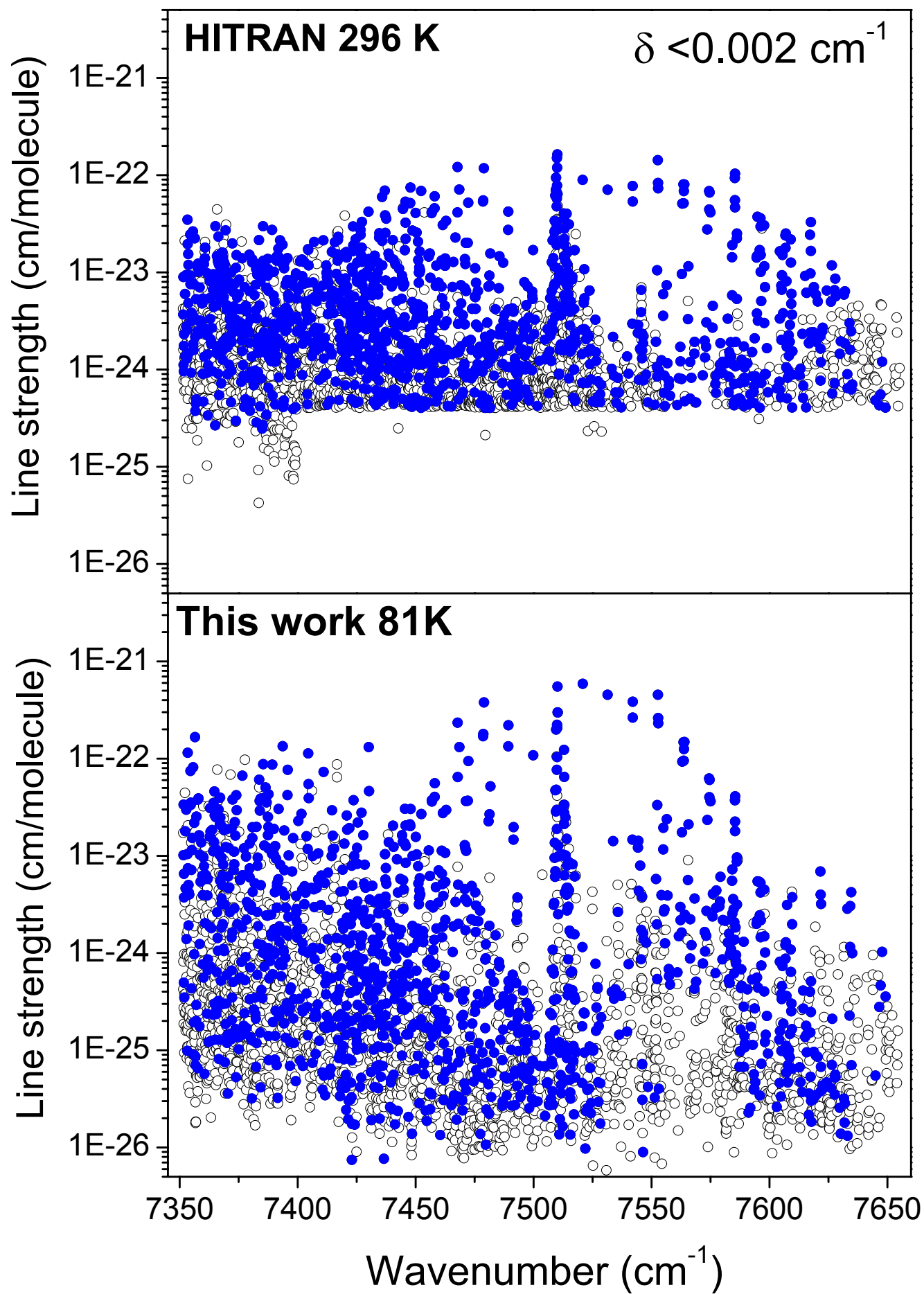


Fig. 4

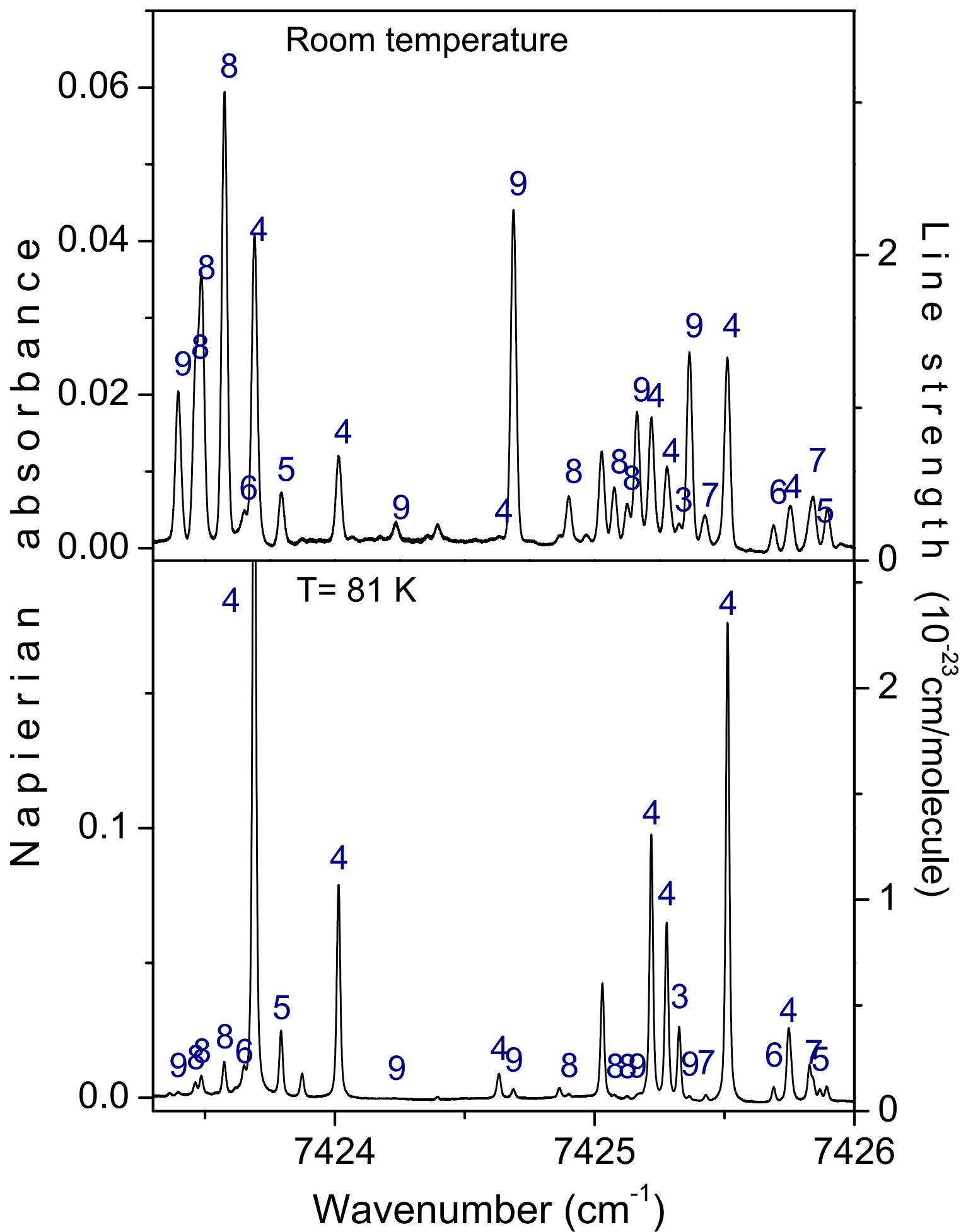


Fig. 5

$\delta < 0.002 \text{ cm}^{-1}$

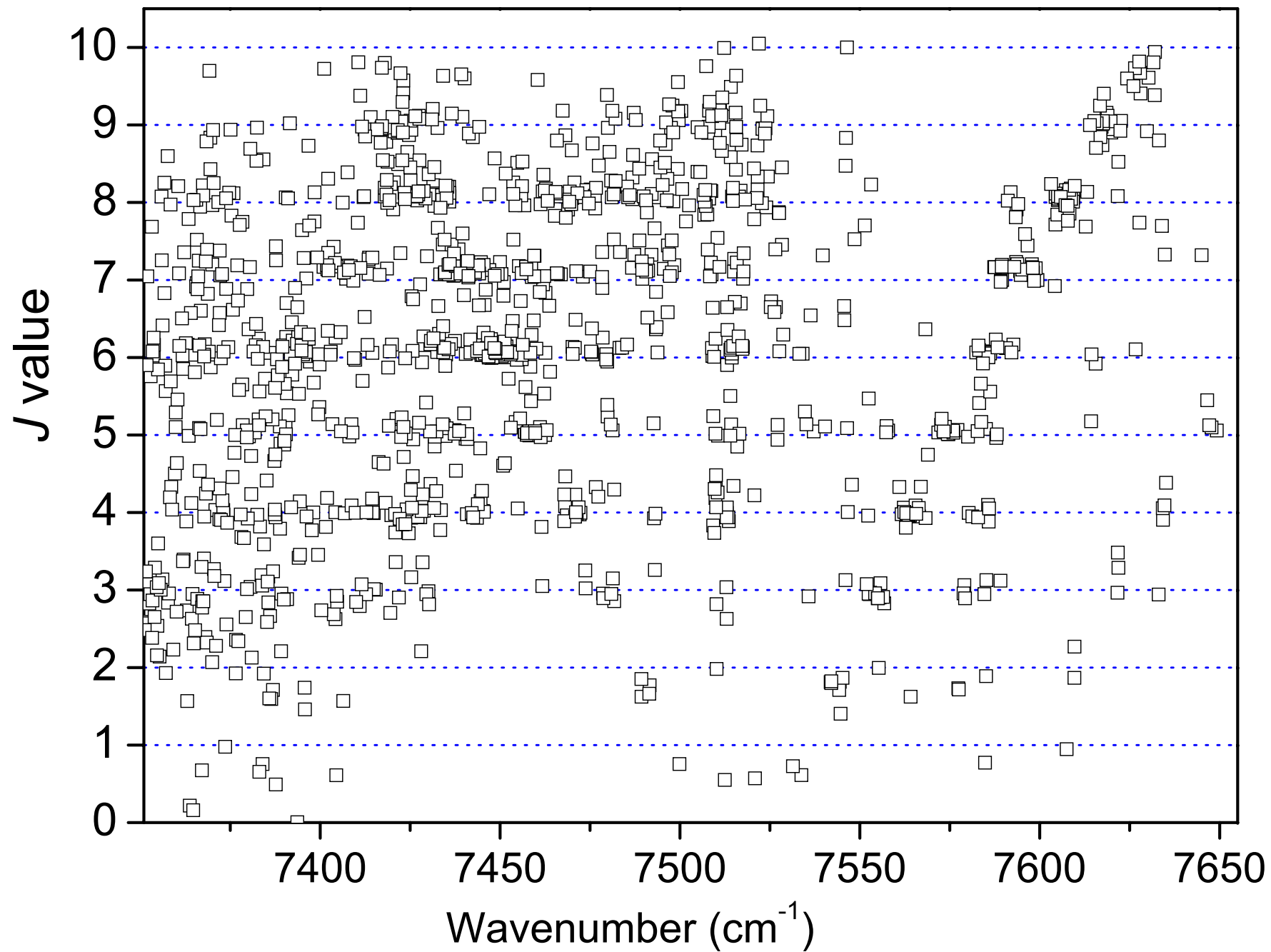


Fig. 6

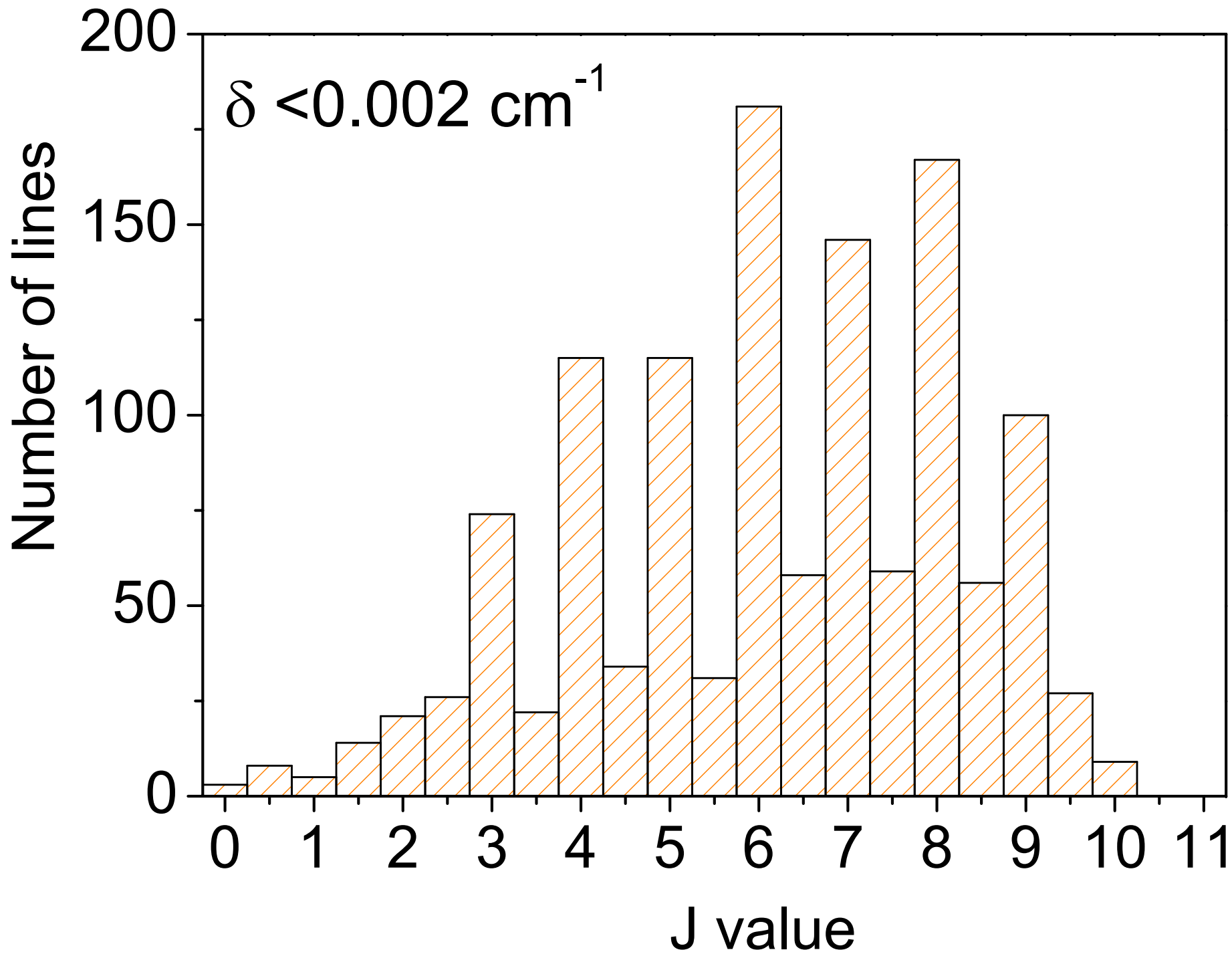


Fig. 7

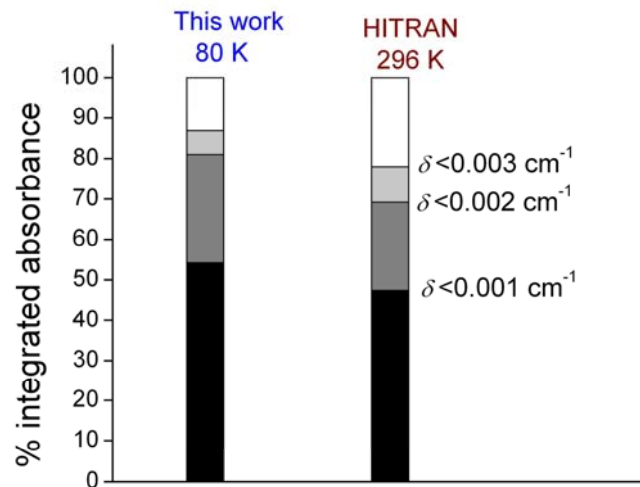
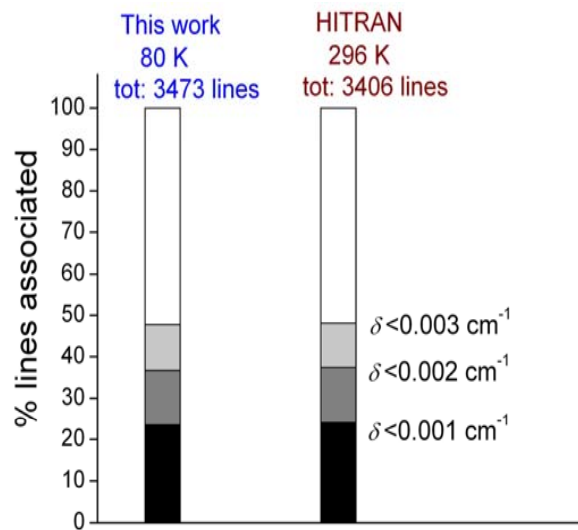
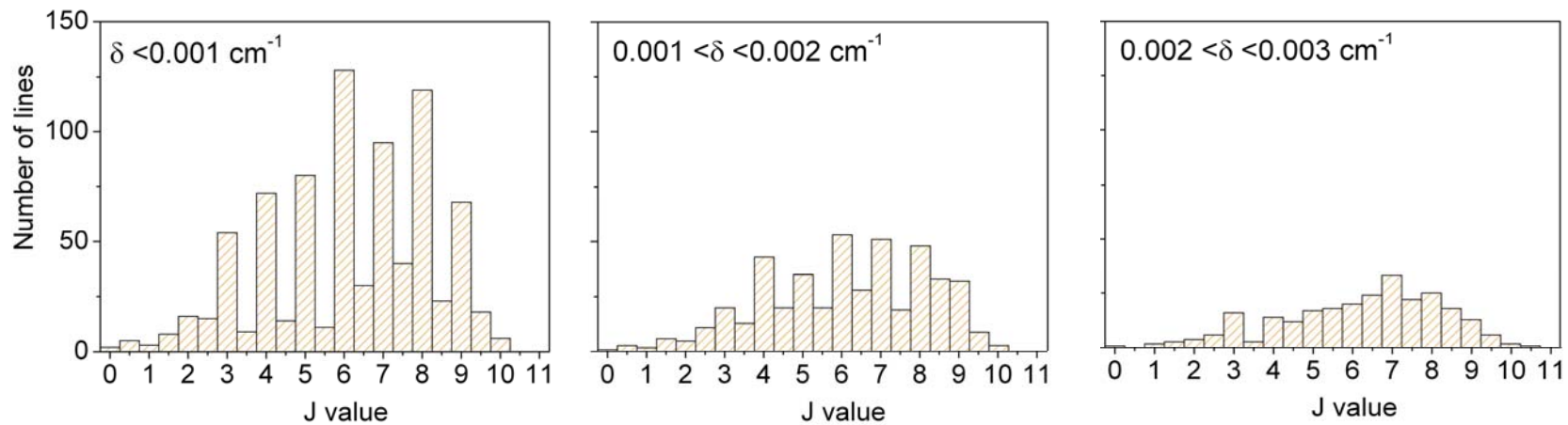


Fig. 8

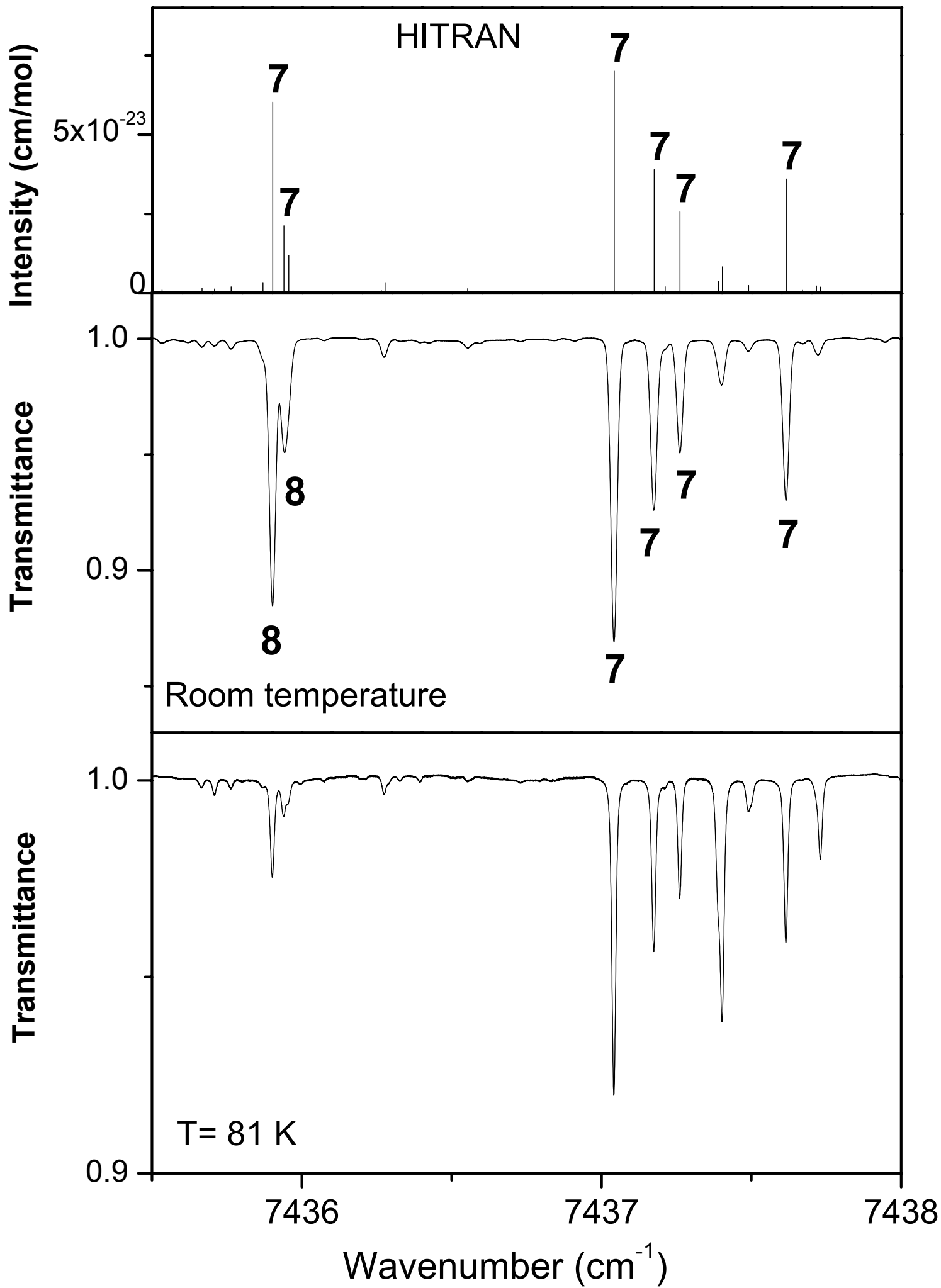


Fig. 9

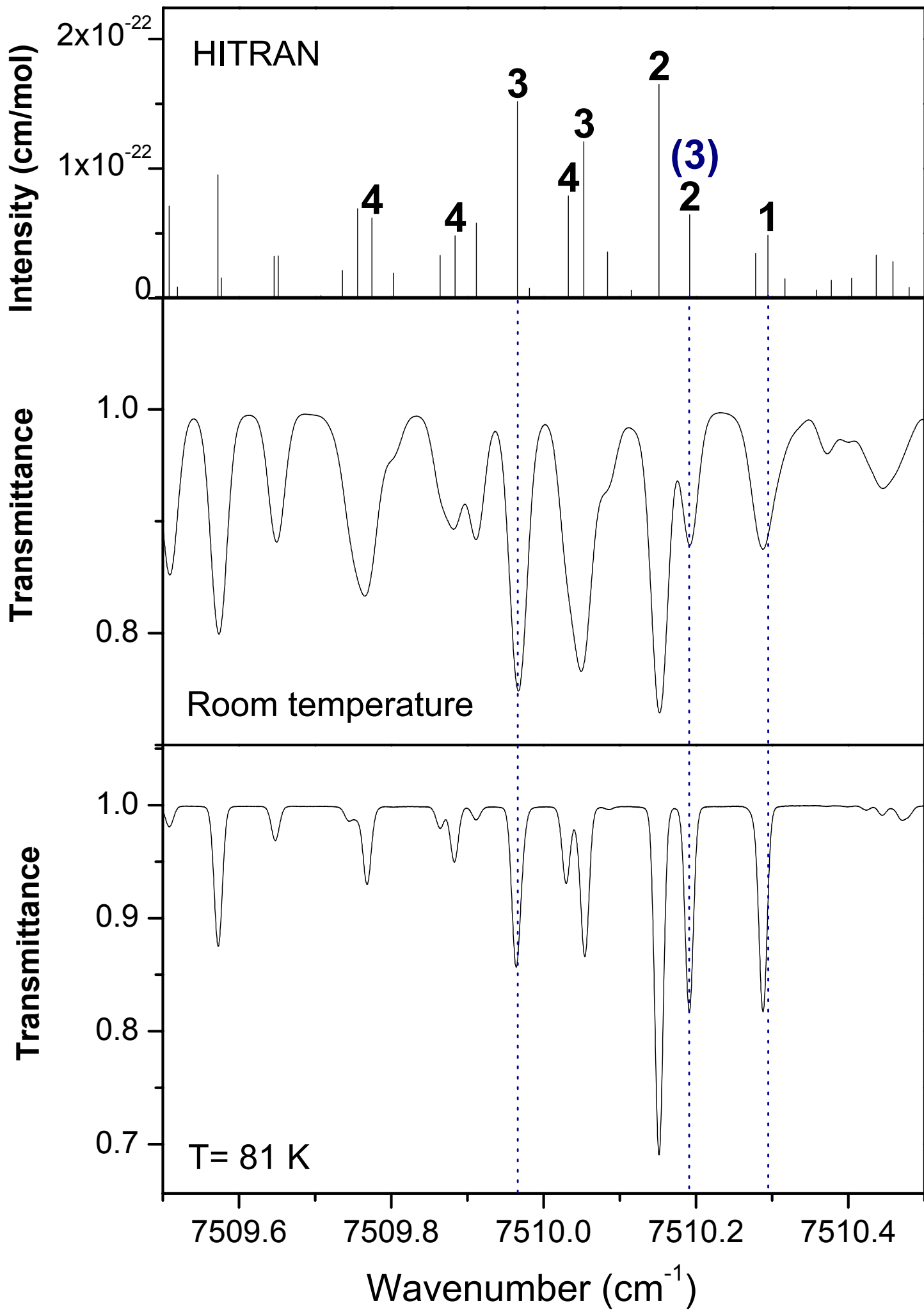


Fig. 10