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**Temperature dependence of the absorption spectrum of CH₄ by high resolution spectroscopy at 81 K:
(II) The icosad region (1.49-1.30 μm).**

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Abstract

The high resolution absorption spectrum of methane has been recorded at liquid nitrogen temperature by direct absorption spectroscopy between 6717 and 7351 cm^{-1} ($1.49 - 1.36\text{ }\mu\text{m}$) using a cryogenic cell and a series of Distributed Feed Back (DFB) diode lasers. The investigated spectral region corresponds to the very congested low energy part of the icosad for which the HITRAN database provides neither rovibrational assignments nor the lower state energies. The positions and strengths at 81 K of 9389 transitions were obtained from the spectrum analysis. The minimum value of the measured line intensities (at 81 K) is on the order of $10^{-26}\text{ cm/molecule}$. From the variation of the line strength between 81 K and 296 K , the low energy values of a total of 4646 transitions were determined. They represent 79.4% and 68.4% of the total absorbance in the region at 81 and 296 K , respectively, and include 28 transitions assigned to the $\nu_2+4\nu_4$ band near 6765 cm^{-1} . The reliability of the method based on the association of lines with coinciding centers in the 81K and 296 K spectra is discussed. The results of the present analysis have been combined with previously analyzed high energy part of the icosad dominated by the $\nu_2+2\nu_3$ band near 7510 cm^{-1} . The line list for the whole icosad ($6717\text{-}7655\text{ cm}^{-1}$) consists of 12865 transitions at 81 K .

1. INTRODUCTION

This work continues our systematic study of the highly congested near infrared spectrum (1.71-1.26 μm) of CH_4 by direct absorption spectroscopy at low temperature [1-4]. The main purpose of this project is to determine the low energy levels of the observed transitions from the variation of their intensities between 296 and 81 K. Indeed, in absence of a satisfactory theoretical modelling, this approach is the most efficient approach to determine the Boltzmann factor which rules the temperature dependence of the line strengths. From the obtained energy values, it is possible to extrapolate the absorption of methane in a wide range of temperature conditions, for example, those relevant to conditions existing in the atmosphere of the giant outer planets and of Saturn's satellite, Titan.

Fig. 1 shows an overview of the methane spectrum at 296 K as provided by the HITRAN database [5] for the 5700-7700 cm^{-1} region (1.75-1.30 μm). The present contribution is devoted to the analysis of the 6717-7351 cm^{-1} region corresponding to the low energy part of the icosad. It completes our preceding studies of the high energy parts of the tetradecad (5852-6181 cm^{-1}) [2, 4] and icosad (7351-7655 cm^{-1}) [3] dominated by the $2\nu_3$ and $\nu_2+2\nu_3$ band, respectively. At room temperature, the spectrum in the icosad region is particularly congested as a result of the numerous rovibrational interactions between the 20 vibrational levels (134 sublevels) constituting this vibrational polyad. Only 76 transitions of the $\nu_2+2\nu_3$ band near 7510 cm^{-1} are provided with J assignment in the HITRAN database [5]. Below 7400 cm^{-1} , neither rotational nor vibrational assignments are given in the HITRAN line list of the icosad. In the region presently investigated (6717-7351 cm^{-1}), the HITRAN database provides empirical spectroscopic parameters of 12250 transitions obtained by L. Brown at room temperature (296 \pm 4 K) by high resolution Fourier Transform Spectroscopy (FTS) with path lengths up to 97 meters [6]. As the lower state energies of the listed transitions are unknown, the line intensities cannot be extrapolated at different temperatures and the line list is of limited use in planetology. Note that in her original paper [6], L. Brown provided J assignments for 13 transitions of the R branch of the $\nu_2+4\nu_4$ band near 6765 cm^{-1} . To the best of our knowledge, these are the only rovibrational assignments available in the literature in the investigated region.

From spectra recorded at two temperatures, the lower state energies can be empirically determined from the variation of the measured line intensities. Following the same approach as in Refs. [2-4], we used the HITRAN line intensities at 296 K and the intensities at 81 K

retrieved from spectra recorded using a cryogenic cell and a series of distributed feedback (DFB) diode lasers.

The two temperature method relies on unambiguous association of transitions on the basis of matching their line positions measured in both the room temperature (RT) and liquid nitrogen temperature (LNT) spectra. In the present case, the discrimination of the “identical” transitions in the RT and LNT spectra is made difficult by the considerable congestion of the RT spectrum (about 20 lines/cm⁻¹!) along with the dramatic change of the line intensities due to the cooling down to LNT. As a rule, the lines are generally blended which affects the quality of the retrieval of both the line positions and strengths.

The rest of this report is organized as follows: The experimental set up and line list construction are presented in Section 2 while the determination of the low energy values is presented in Section 3. In Section 4, we consider in details the impact of the choice of the criterion used to associate the RT and LNT intensities on the quality of the obtained results.

2. EXPERIMENT AND CONSTRUCTION OF THE LINE LIST AT 81 K

The reader is referred to Ref. [1] for the detailed description of the experimental set up and of the data acquisition system. Briefly, the 1.418 m long cryogenic cell is based on an original design without external vacuum jacket. Spectra were recorded by differential absorption spectroscopy using 23 DFB fibered laser diodes allowing a continuous coverage of the 6717-7351 cm⁻¹ region except for a small gap between 6958.2 and 6962.1 cm⁻¹. Each complete laser diode spectrum (about 35 cm⁻¹) was obtained by a temperature scan from -10 to 60 °C. These 35 cm⁻¹-wide spectra were linearized using an etalon signal (BK7 glass, 10 cm length), and calibrated independently by matching the observed spectral line positions to the HITRAN line positions at 296 K. 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.

During the spectrum acquisition, the gas pressure was continuously measured by a capacitance gauge (MKS Baratron, 10 Torr range). The spectra were recorded at a pressure of either 7.36 or 9.35 Torr. A temperature value of 81±1 K was determined from the Doppler profile of several tens of well isolated lines [1]. This value is what we refer to as “liquid nitrogen temperature” (LNT).

The methane spectrum at room temperature was also recorded with the same experimental set up, for comparison. Fig. 2 shows a part of the recorded spectra at RT and

LNT. The reduction of the rotational congestion by cooling is not apparent at the scale of this Figure. This is due to the fact that the peak depths in the LNT spectra are increased as (i) the Doppler line widths are reduced by a factor of about 2 at LNT and (ii) for a given pressure, the molecular concentration is about four times larger at LNT than at RT. A comparison in an expanded spectral section around 7280 cm^{-1} is presented Fig. 3. The variation of the line intensities leads to a very different appearance of the RT and LNT spectra.

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} (cm^{-2} /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: $P = Nk_B T$.

Assuming that the pressure self broadening at 81 K of the vibrational bands contributing to our spectrum is similar to that of the ν_3 and $2\nu_3$ bands ($0.20 \text{ cm}^{-1}/\text{atm}$ [7]), it leads to a value of $2.6 \times 10^{-3} \text{ cm}^{-1}$ (HWHM) at 10.0 Torr. This value being about half that of the Doppler broadening (HWHM $5.8 \times 10^{-3} \text{ cm}^{-1}$), a Voigt function of the wavenumber was adopted as line profile. The first step of the spectrum analysis consisted in the manual determination of the spectral sections of overlapping or nearby transitions that could be fitted independently. An interactive multi-line fitting program was used to reproduce the spectrum. The local baseline (assumed to be a cubic function of the wavenumber) and the three parameters of each Voigt profile (line centre, integrated absorbance, HWHM of the Lorentzian component) were fitted. The HWHM of the Gaussian component was fixed to its theoretical value for $^{12}\text{CH}_4$. In the case of blended lines or lines with low signal to noise ratios, the Lorentzian HWHM was also constrained to the average value obtained from nearby isolated lines. Fig. 4 shows an example of comparison between the measured and fitted spectra. Some significant differences between the observed and simulated spectra are still noted. It is not clear whether these differences are due to the small sections of warm gas lying between the ends of the cold jacket and the cell windows or if they indicate that a more sophisticated velocity dependent profile should be used instead of the chosen Voigt profile.

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

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 spectral sections corresponding to the overlapping of two successive DFB lasers, the centre and strengths of the lines were averaged. The final dataset consists of 9389 lines with intensity values ranging from about 1×10^{-26} to $3.6 \times 10^{-22} \text{ cm/molecule}$ for methane in natural abundance at 81 K.

3. DETERMINATION OF THE LOWER STATE ENERGY

Taking into account the partition function, the lower energy of a given transition was calculated from the line strengths at two temperatures (see Ref. [2] for more details):

$$\ln \left(\frac{S_{\nu_0}(T)T^{3/2}}{S_{\nu_0}(T_0)T_0^{3/2}} \right) = E \left[\frac{1}{kT_0} - \frac{1}{kT} \right] \quad (2)$$

where T_0 and T are the RT and LNT, respectively. As mentioned above, the line strengths provided by HITRAN at 296 K [5] were adopted for the RT values. An overview comparison of our LNT line list and the HITRAN line list at 296 K is presented on the scattered plots of Fig. 5 for the entire icosad.

Considering the congestion of the spectrum, matching the lines corresponding to the same transition in the RT and LNT spectra is the crucial step of the procedure (see next Section). On the basis of the claimed uncertainties on the RT and LNT line positions (± 0.0015 [6] and $\pm 0.001 \text{ cm}^{-1}$ respectively), we considered as identical the RT and LNT lines when the difference, δ , of their centres was less than 0.002 cm^{-1} . 3780 transitions were associated according to this criterion. They are highlighted on Fig. 5.

Using Eq. 2, the low energy values, E , were determined and the corresponding empirical J values were obtained from $J_{emp} = \sqrt{\frac{1}{4} + \frac{E}{B_0}} - \frac{1}{2}$ where $B_0 = 5.214 \text{ cm}^{-1}$ is the methane ground state rotational constant. The above expression based on a simple rigid rotor approximation is sufficient as the splitting of the tetrahedral multiplets remains small in our range of J values (for instance 0.5 cm^{-1} at $J=12$).

As an example, Fig. 6 gives the rounded J values obtained for the RT and LNT spectra in a spectral region around 7125 cm^{-1} . The obtained J values are plotted as a function of the line intensities at RT and LNT in Fig. 7. The marked dissymmetry of the RT and LNT panels

reflects the considerable intensity variation of the transitions corresponding to the low and high J values: by cooling down to 81 K, the line intensity from a $J=0$ level is increased by a factor of 7, while that from a $J=5$ level is unchanged and that from a $J=10$ level is decreased by a factor 240. The propensity of the J values to be close to integer values is particularly apparent for the strongest lines but degrades for the weakest transitions. This is why on the J values histograms presented in Fig. 8, the alternation between integer and half-integer J values is less pronounced for the number of lines than for the sum of their intensities: the fraction of J values falling in a ± 0.25 interval around integer values is 62.5 % while the corresponding fractions in terms of intensities are 74.5 and 73.1 % at LNT and RT, respectively.

The complete list, provided as Supplementary Material, includes the line strengths at 81 K, the corresponding values at 296 K as provided by HITRAN and the derived E and J values. A sample of this line list is reproduced in Table 1 as an example. For the convenience of the user, the results of our analysis of the higher part of the icosad (3473 lines) [3] have been joined with the present results. It leads to a total number of 12865 transitions for the entire icosad region ($6717\text{-}7655\text{ cm}^{-1}$) at 81 K.

The band near 6765 cm^{-1}

In the RT spectrum (see Fig. 2 of Ref. [6]), a band with a Q branch near 6765 cm^{-1} is clearly apparent in the low energy part of the icosad. It was assigned to $\nu_2+4\nu_4$ in Ref. [6] but according to the theoretical calculations of Ref. [9] an assignment to $\nu_1+3\nu_4$ is possible. At RT, this band is partly obscured by the rotational structure of some stronger bands of the icosad centred at higher energy. It becomes much clearer in the 81 K spectrum as the intensities of most of the transitions of the other bands are strongly decreased by cooling (see Fig. 9). In her original paper [6], L. Brown obtained the J assignment of a sequence of 13 transitions of the R branch by comparison of their intensities with those of the ν_3 band. Our empirical J values confirm 11 of these J values while a different value is obtained for the two others. By considering the positions, relative intensities and empirical J values, we could reliably extend the J assignments to 28 transitions of the P , Q and R branches (see Table 2 including the comparison with Ref. [6]). It is worth noting that the empirical J values of the assigned lines are very close to integer values which illustrates the high reliability of the method in a region where the congestion is not high. We hope that the obtained assignments together with the empirical J values of the other lines of the region will help for the theoretical interpretation of this band.

4. DISCUSSION

The two temperature method is a “blind” method as it uses the line centre matching as only criterion to associate RT and LNT lines. Application of this technique to the considered region of the icosad is made particularly difficult by the congestion of the spectrum (15 and 19 lines per cm^{-1} at LNT and RT, respectively), the large dynamic range on the intensity values (4 decades) and the absence of regular spectral structure. In this section, we examine the reliability of the method by considering (i) the “unmatched” lines left without RT or LNT partner for which the low energy derivation was not possible and (ii) the role of the accidental coincidences leading to erroneous lower state energies.

Both issues are related to the choice of the maximum value for the difference, δ , between the RT and LNT line positions. The difference between the centre values in the RT and LNT spectra may be either due to the quality of the wavenumber calibration and/or due to the precision of the line centre determination. According to Ref. [6], the RT positions of isolated lines are good to $\pm 0.0015 \text{ cm}^{-1}$ in the HITRAN line list. As mentioned above, we used a statistical matching of the HITRAN positions with our line centres at LNT to calibrate each individual spectrum corresponding to one DFB laser diode. The comparison of the calibration of the overlapping regions corresponding to successive DFB lasers scans indicates that our calibration error is on the order of 0.001 cm^{-1} at maximum. In other words, we believe that most of the deviations between the RT and LNT positions are due to errors in the line profile fitting. Obviously, larger errors are expected for the weak lines both for their centre and strength values. Errors on the line centres may hamper matching the RT and LNT lines while errors on the intensities lead to inaccurate lower energy values.

The $\delta_{Max} = 0.002 \text{ cm}^{-1}$ value chosen above is rather conservative: it corresponds to less than one fifth and one tenth of the Doppler broadening at 81 K (FWHM $11.6 \times 10^{-3} \text{ cm}^{-1}$) and 296 K (FWHM $22.2 \times 10^{-3} \text{ cm}^{-1}$), respectively. A careful examination of the line lists and spectra shows that the $\delta < 0.002 \text{ cm}^{-1}$ criterion is too strict and that additional pairs of lines correspond undoubtedly to the same transitions and should be associated. We decided to increase δ_{Max} up to 0.003 cm^{-1} which allowed 866 additional J determinations representing 11 % of the total absorbance at 81 K. However, in the J values histogram limited to the lines with $0.002 < \delta < 0.003 \text{ cm}^{-1}$, integer values are not clearly dominant. It indicates that relaxing the coincidence criterion up to 0.003 cm^{-1} leads to larger uncertainties on the intensity values or to the accidental association of lines corresponding to different transitions.

In order to estimate the impact of these line pairs corresponding to different transitions, associated as a result of an accidental coincidence of their positions, we applied the two temperature method (with $\delta_{Max}=0.002\text{ cm}^{-1}$), to the HITRAN line list at RT and our LNT list *with line positions shifted by 0.100 cm^{-1}* . Because this applied shift is much larger than the line width, all the coincidences are at this point accidental and we checked that the obtained results are mostly independent of the shift value. Excluding coincidences between strong lines at LNT and weak lines at RT which lead to unrealistic negative values for the lower state energy, only 6.6 % of the lines of the LNT dataset found a RT partner within $\delta < 0.002\text{ cm}^{-1}$. As expected, the histogram of the derived J values (Fig. 10) shows a random distribution where integer J values are not favored. The associated lines bring only 2.5 % of the total absorbance at LNT which should be compared to a 68.6 % value for the unshifted dataset (see the comparison presented in Fig. 10). In other words, accidental coincidences within a $\pm 0.001\text{ cm}^{-1}$ interval lead to erroneous lower energy determination for transitions representing only 2.5 % of the total absorbance. (Obviously, this percentage is proportional to the tolerance amplitude, δ_{Max}). In regard of this small fraction of absorption due to the accidental coincidences, we conclude that the 11 % additional absorbance obtained above by associating lines with $0.002 < \delta < 0.003\text{ cm}^{-1}$ must be mostly attributed to transitions which should indeed be associated in spite of larger errors on their line positions. This is why we have included (and specifically marked) the low energy and J values corresponding to $0.002 < \delta < 0.003\text{ cm}^{-1}$ in the line list attached as Supplementary Material. Although less accurate, these 866 additional lower state energy determinations will help to better account for the temperature variation of the methane absorbance in this region.

As demonstrated in Fig. 8, 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. Yet, the lowest rotational transitions are the most valuable for the unambiguous determination of the vibrational band origins and to provide initial estimates of the spectroscopic constants. We have recently applied the two temperature method to our LNT intensities combined to absolute line intensities of methane cooled down to 25 K in a planar supersonic expansion [9]. The lower energy values of 59 transitions ranging between 7070 and 7300 cm^{-1} were determined. Even though the general agreement with the 81K/296K determinations is good, the 25K/81K approach leads to much more accurate low energy values for $J < 4$ levels. This is a result of the virtually no overlapping in the jet spectra and of a higher intensity ratio contrast between the $J=0-3$ levels. In particular,

the centers of nine vibrational bands of the icosad could be estimated from the wavenumber of nine transitions unambiguously assigned as $R(0)$ lines.

Considering the 4 orders of magnitude dynamic range on the intensity values in the LNT line list and the natural abundance of the $^{13}\text{CH}_4$ isotopologue (1.1×10^{-2}), no doubt that some of the listed transitions are due to $^{13}\text{CH}_4$. Note that the ground state energy levels of the $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ isotopologues are very close as reflected by their nearly identical rotational constant, B_0 . The above treatment using the two temperature method is therefore valid for the two species. This is however no longer the case for the CH_3D species which is as symmetric top species with a different rotational structure. Nevertheless, its natural abundance being 6.1×10^{-4} , all the CH_3D lines present in our line list are very weak and the CH_3D contribution has only a marginal impact on the total absorbance in the region.

5. CONCLUSION

A list of 9389 transitions has been constructed from the spectrum of methane recorded between 6717 and 7351 cm^{-1} by direct absorption spectroscopy at 81 K . On the basis of line positions coincidence ($\delta < 0.003 \text{ cm}^{-1}$), intensities corresponding to the same transition in the LNT and RT line lists were associated. The corresponding empirical lower state energy could be determined for 4646 transitions. Those associated transitions represent 79.4% and 68.4% of the total absorbance at LNT and RT, respectively. The impact of accidental coincidences has been estimated to be about 3% of the total absorbance. In other words, most of the temperature dependence of the methane absorption in the considered region is accounted for using the obtained lower state energies. Considering that practically no rovibrational assignments nor lower state energies were previously available in the literature in the considered region, this work represents a significant advance of the knowledge of the icosad of methane. The complete line list relative to the whole icosad region ($6717\text{-}7655 \text{ cm}^{-1}$) at 81 K is provided as Supplementary Material. It includes extended J assignments of the rotational structure of the $\nu_2+4\nu_4$ (or $\nu_1+3\nu_4$) band near 6765 cm^{-1} which should constitute a good starting point for the theoretical interpretation of this band.

The lower state energy could not be determined for about a half of the transitions observed at LNT since no line position coincidences were found in the HITRAN line list at 296 K . These transitions are mostly weak transitions and represent about 21% of the absorbance at LNT. They will be nevertheless valuable for the analysis of the spectra of methane on Titan as the temperature conditions ($T \sim 90 \text{ K}$) of Titan's atmosphere is close to that of our recordings.

The present work completes the study of the two high absorbing regions surrounding the low opacity window at 1.58 μm (see Fig. 1). Our direct absorption spectroscopy experiment at 81 K provided a sufficient sensitivity ($\alpha_{min}\sim 10^{-6} \text{ cm}^{-1}$) to characterize the high energy region of the tetradecad [2, 4] and the icosad (this work and [3]). In the 6181-6717 cm^{-1} gap between these two regions, a higher sensitivity is required. We have recently been able to combine the CW-Cavity Ring Down Spectroscopy (CW-CRDS) technique with the cryogenic cell used for the present measurements [11]. The achieved sensitivity at both RT [10] and LNT [11] ($\alpha_{min}\sim 3\times 10^{-10} \text{ cm}^{-1}$) lowers by more than three orders of magnitude that of the present recordings. It will allow for an accurate characterization of the 1.58 μm transparency window of particular interest in planetology. By joining the results obtained by CW-CRDS and direct absorption spectroscopy, the temperature dependence of methane absorption over the wide 1.26-1.71 μm range will be accounted for.

Acknowledgements

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Figure captions

Fig. 1.

Overview spectrum of the HITRAN line list for methane at 296 K. The spectral regions covered by our previous analysis [2-4] of the 81 K spectrum are indicated.

Fig. 2.

Section of the methane spectrum recorded at liquid nitrogen and room temperature in the 7050-7200 cm^{-1} of the icosad. The RT and LNT spectra were recorded at 11.8 and 9.35 Torr respectively.

Fig. 3.

Comparison between the LNT and RT methane spectra illustrating the considerable change by cooling down to 81 K.

Fig. 4.

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

From top to bottom:

- (a) Experimental spectrum at LNT ($P = 9.36$ Torr),
- (b) Simulated spectrum resulting from the multi line fitting procedure
- (c) Residuals between the simulated and experimental spectra.

Fig. 5.

Overview of the scattered spectrum of methane between 6717 and 7351 cm^{-1} as provided in the HITRAN database at 296 K (upper panel) and recorded at liquid nitrogen temperature (lower panel). The full circles (in blue) highlight the 3780 transitions whose line positions at RT and LNT match within 0.002 cm^{-1} , for which it was therefore possible to derive the lower energy values. The higher part of the icosad analyzed in Ref. [3] is plotted in gray for completeness.

Fig. 6.

Empirical lower J assignments shown for transitions near 7125 cm^{-1} in a section of methane spectra at room temperature (upper panel) and liquid nitrogen temperature (lower panel).

Fig. 7.

Empirical lower J values *versus* the line intensities at 296 K [5] (upper panel) and LNT (lower panel). The empirical J values were obtained from the strengths of the methane transitions at 81 K and 296 K between 6717 and 7351 cm^{-1} by associating transitions with line centers differing by less than 0.002 cm^{-1} .

Fig. 8.

Upper panel: Histogram of the obtained J values with a step interval of 0.5.

Lower panels: The sum of line intensities corresponding to each histogram interval for both the RT and LNT.

Note that the fraction of 62.5 % of the J values falling within the ± 0.25 interval around integer values, corresponds to a fraction of 74.5 % of the absorbance at 81 K.

Fig. 9.

The $\nu_2+4\nu_4$ (or $\nu_1+3\nu_4$) band near 6765 cm^{-1} .

From top to bottom:

- stick spectrum of CH_4 as provided by the HITRAN database at 296 K
- experimental spectrum recorded at 81 K
- expanded region of the experimental spectrum in the region of the R branch
- expanded region showing the $R(2)$ and $R(3)$ manifolds. The empirical J values obtained from the two temperature method are indicated.

Fig. 10.

Estimation of the impact of the accidental coincidences on the results of the two temperature method applied to the 81 K and 296 K methane spectra between 6717 and 7351 cm^{-1} .

Upper panel: Histogram of the empirical J values and corresponding percentage of lines and absorbance at LNT. The maximum difference between the RT and LNT line centers was fixed to 0.002 cm^{-1} .

Lower panel: Same as above but with a shift of 0.1 cm^{-1} is applied to the RT line positions. All the coincidences are accidental. The accidentally matched lines represent only 2.5 % of the total absorbance.

This work (81 K)		HITRAN (296K)		E_{low} (cm^{-1})	J_{low}
<i>Line center</i> (cm^{-1})	<i>Line intensity</i> (cm/mol)	<i>Line center</i> (cm^{-1})	<i>Line intensity</i> (cm/mol)		
6865.0450	1.97E-25	6865.0456	2.77E-25	177.1625	5.34
6865.2414	3.40E-24	6865.2412	2.38E-24	123.0509	4.37
6865.2732	3.31E-26	6865.2733	2.16E-25	295.9747	7.03
6865.3762	1.23E-25	6865.3757	8.86E-25	303.7382	7.13
6865.4187	3.41E-25	6865.4189	3.73E-25	157.6360	5.01
6865.9467	3.93E-26	6865.9484	3.72E-25	324.8941	7.39
6866.0181	2.40E-25	6866.0184	7.52E-26	60.7276	2.94
6866.1567	4.44E-26				
6866.3825	5.98E-25	6866.3821	3.36E-25	106.0742	4.03
6866.5182	3.66E-25	6866.5179	4.77E-25	171.1447	5.24
6866.6216	6.78E-26				
6866.6335	3.47E-26				
6866.8122	5.48E-26	6866.8143	6.27E-26	161.1506	5.07*
6866.8729	4.06E-26	6866.8717	5.25E-26	170.6450	5.23
6866.9758	8.51E-26				
6867.0042	8.56E-26				
6867.1064	1.00E-24	6867.1088	1.98E-25	25.0632	1.74*
6867.1467	7.31E-26	6867.1487	7.53E-26	152.9511	4.93
6867.2587	3.75E-26	6867.2576	1.25E-25	244.2271	6.35
6867.2975	1.08E-25				
6867.3283	5.75E-25	6867.3286	2.08E-25	71.9633	3.24
6867.3744	4.99E-26				
6867.6287	2.61E-24	6867.6280	6.05E-25	37.3447	2.22
6867.6870	1.74E-25				
6867.8355	4.65E-26	6867.8349	1.88E-25	258.9808	6.55
6868.0619	1.15E-25	6868.0618	1.21E-25	154.3484	4.95
6868.2598	8.06E-25	6868.2605	2.68E-25	65.3783	3.07
6868.3667	1.34E-24	6868.3685	2.54E-25	21.7620	1.60
6868.6302	1.91E-24	6868.6309	6.44E-25	66.4007	3.09
6868.6559	2.30E-25	6868.6539	1.05E-24	268.4287	6.67
6868.7127	4.31E-26	6868.7157	1.36E-25	239.9565	6.29*
6868.7859	4.54E-24	6868.7861	1.53E-24	66.4126	3.10
6868.9547	1.76E-25	6868.9537	1.28E-25	126.1018	4.43
6869.0154	3.83E-25	6869.0143	2.84E-25	127.4839	4.46
6869.0997	4.26E-26	6869.1009	1.76E-25	260.5728	6.57
6869.1512	1.01E-25	6869.1486	1.28E-25	169.0253	5.20*

Table 1.

Wavenumbers and line strengths of the methane transitions recorded at 81 K near 6867 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 ($\delta < 0.002\text{ cm}^{-1}$). This Table is a small section of the list of 12865 transitions attached as Supplementary Material. The “*” symbols in the last column mark the lines whose RT and LNT line centres differ by $0.002 < \delta < 0.003\text{ cm}^{-1}$.

This work (81 K)		HITRAN (296K)				
<i>Line center</i> (cm^{-1})	<i>Line intensity</i> (cm/mol)	<i>Line center</i> (cm^{-1})	<i>Line intensity</i> (cm/mol)	J_{low}	<i>Assignment</i> <i>of the $\nu_2+4\nu_4$ band</i>	
					<i>This work</i>	<i>Ref. [6]</i>
6728.8452	1.04E-24	6728.8468	2.79E-24	6.10		
6736.6079	1.63E-24	6736.6078	1.92E-24	5.10		
6736.7038	1.13E-24	6736.7033	1.21E-24	4.98		
6737.1241	1.27E-24	6737.1247	4.24E-25	3.07		
6737.2585	1.32E-24	6737.2585	7.49E-25	4.04		
6740.4543	1.90E-24	6740.4522	1.25E-24	4.28*		
6742.5923	4.49E-24	6742.5937	2.95E-24	4.27		
6743.7758	2.24E-24	6743.7754	7.57E-25	3.10	P3	
6744.0622	7.00E-24	6744.0611	2.24E-24	2.99	P3	
6744.4541	3.52E-24	6744.4540	1.10E-24	2.93	P3	
6746.1845	1.03E-24	6746.1836	1.17E-24	5.06		
6748.6063	2.47E-24	6748.6064	1.61E-24	4.26		
6748.9879	3.82E-24	6748.9881	5.79E-25	0.55		
6752.0704	5.34E-24	6752.0719	1.06E-24	1.77	P2	
6752.3695	3.51E-24	6752.3718	6.71E-25	1.63*	P2	
6753.5140	1.94E-24	6753.5132	1.20E-24	4.18		
6754.6543	2.81E-24	6754.6542	8.71E-25	2.92		
6756.1120	2.11E-24	6756.1120	1.32E-24	4.19		
6757.0174	1.05E-24	6757.0171	2.77E-24	6.08		
6758.7129	3.09E-24	6758.7127	4.73E-25	0.61	P1	
6759.0517	2.07E-24	6759.0514	2.47E-24	5.12		
6760.4943	2.05E-24	6760.4941	2.35E-24	5.07		
6760.8282	8.01E-24	6760.8280	4.46E-24	4.01		
6761.4740	4.65E-24	6761.4742	2.46E-24	3.92		
6762.2658	6.95E-24	6762.2657	2.20E-24	2.97		
6762.9543	1.34E-24	6762.9533	1.41E-24	4.95		
6763.0989	3.09E-24	6763.0988	1.75E-24	4.03		
6763.2473	7.96E-24	6763.2471	2.55E-24	2.99	Q3	
6763.4586	3.53E-24	6763.4583	1.98E-24	4.02		
6763.8363	7.71E-24	6763.8355	1.45E-24	1.57	Q2	
6763.9584	1.05E-23	6763.9587	2.01E-24	1.62	Q2	
6764.4301	1.02E-23	6764.4302	1.63E-24	0.87	Q1	
6764.5597	1.46E-23	6764.5595	4.72E-24	3.01		
6765.3167	1.32E-24	6765.3166	3.52E-24	6.10		
6766.4225	1.06E-24	6766.4228	2.20E-25	1.90		
6766.8224	1.02E-24	6766.8227	3.29E-25	3.00		
6768.2157	1.04E-24	6768.2144	1.02E-24	4.86		
6768.6440	3.42E-24	6768.6442	1.88E-24	3.99		
6768.8597	3.05E-24	6768.8614	8.77E-25	2.75		
6770.1569	2.32E-23	6770.1570	3.13E-24	0	R0	R0
6771.7828	1.18E-24	6771.7825	1.47E-24	5.18		
6775.2015	1.80E-23	6775.2019	2.96E-24	1.01	R1	R1
6776.5285	2.38E-24	6776.5286	7.66E-25	3.00		
6776.9207	1.97E-24	6776.9207	1.14E-24	4.08		
6779.7315	6.60E-24	6779.7304	1.05E-24	0.85		R2
6779.8531	1.87E-23	6779.8533	3.89E-24	1.90	R2	R2
6780.3529	5.73E-24	6780.3530	1.22E-24	1.97	R2	
6781.7825	3.78E-24	6781.7825	5.99E-25	0.82		
6783.9795	2.41E-23	6783.9796	7.94E-24	3.05	R3	R3
6784.1940	1.27E-23	6784.1942	4.07E-24	2.99	R3	R3
6784.4959	1.34E-23	6784.4961	4.32E-24	3.00	R3	R3
6785.9547	1.46E-24	6785.9546	5.00E-25	3.13		
6786.5696	8.76E-24	6786.5698	2.82E-24	3.00		R4
6787.5687	7.50E-24	6787.5689	4.25E-24	4.04	R4	R4
6788.1825	1.43E-24	6788.1834	3.30E-25	2.20		

6788.5379	7.88E-24	6788.5382	4.37E-24	4.00	R4	R4
6788.7653	8.65E-24	6788.7655	4.87E-24	4.03	R4	R4
6788.8143	1.78E-24	6788.8152	3.97E-25	2.11		
6788.8533	5.11E-24	6788.8535	2.92E-24	4.05	R4	R4
6789.8712	1.21E-24	6789.8714	1.43E-24	5.11		
6789.9947	5.82E-24	6789.9945	3.26E-24	4.02		
6790.0118	1.01E-24	6790.0113	2.92E-25	2.76		
6790.3123	2.27E-24	6790.3122	2.63E-24	5.08	R5	
6792.4357	3.62E-24	6792.4354	4.58E-24	5.20	R5	
6792.9396	1.31E-24	6792.9388	9.12E-25	4.36		
6793.0378	2.22E-24	6793.0387	2.49E-24	5.04	R5	
6795.1915	2.02E-24	6795.1916	5.52E-24	6.12	R6	
6795.4673	1.15E-24	6795.4667	1.36E-24	5.11		
6796.0399	2.30E-24	6796.0401	6.21E-24	6.11	R6	
6796.2765	1.12E-24	6796.2767	3.04E-24	6.12	R6	
6796.8311	1.85E-24	6796.8307	3.45E-24	5.68	R6	
6796.8687	1.15E-24	6796.8683	6.59E-25	4.06		

Table 2.

Wavenumbers and line strengths of the methane transitions recorded at 81 K in the region of the $\nu_2+4\nu_4$ (or $\nu_1+3\nu_4$) band near 6765 cm^{-1} , limited to the lines with intensity larger than $10^{-24}\text{ cm/molecule}$. The complete line list is provided as Supplementary Material. The low energy E and J values were obtained for the transitions whose centres coincide with the HITRAN line positions at 296 K ($\delta < 0.002\text{ cm}^{-1}$). The two J_{emp} values marked with “*” correspond to RT and LNT line centres differing by $0.002 < \delta < 0.003\text{ cm}^{-1}$.

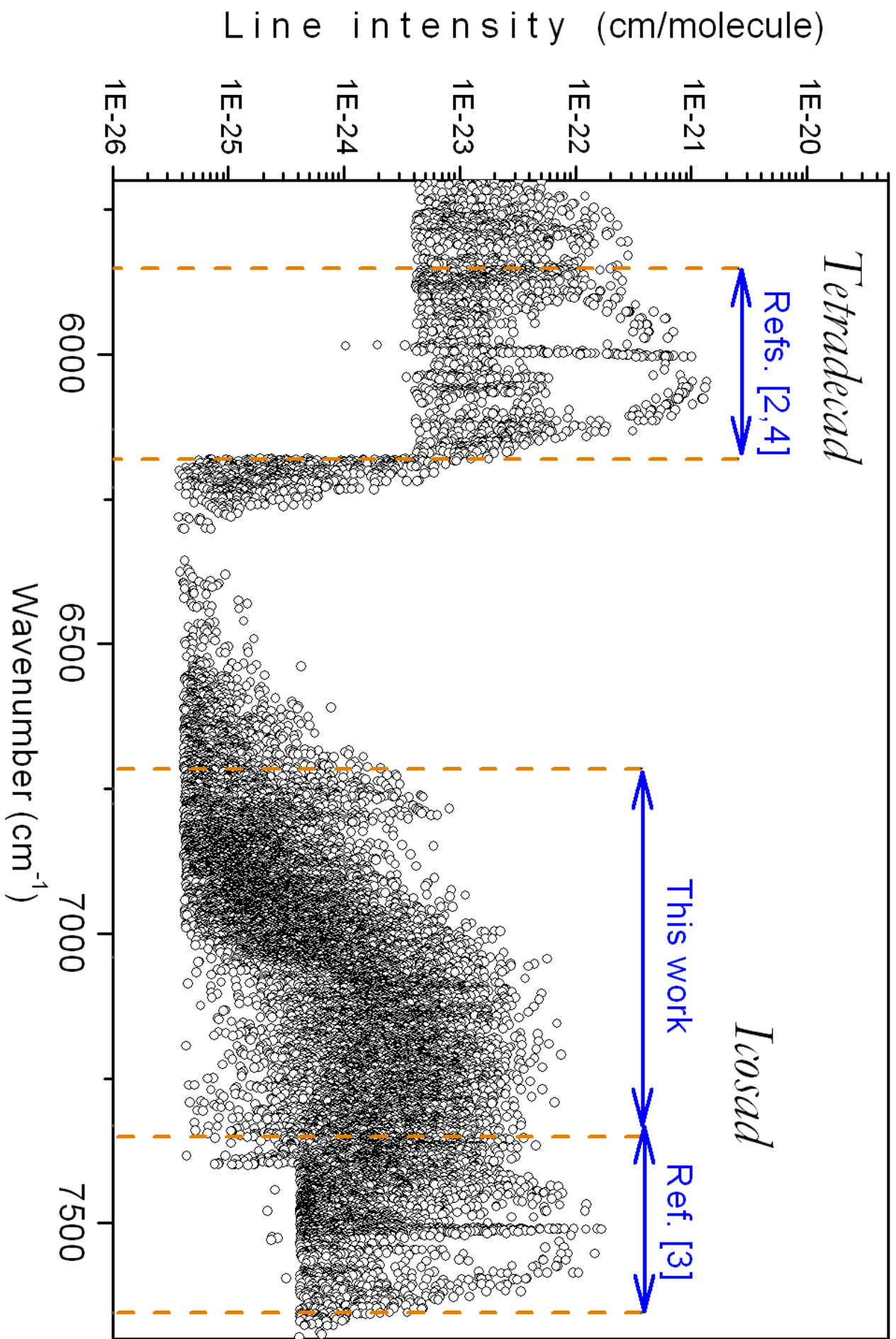
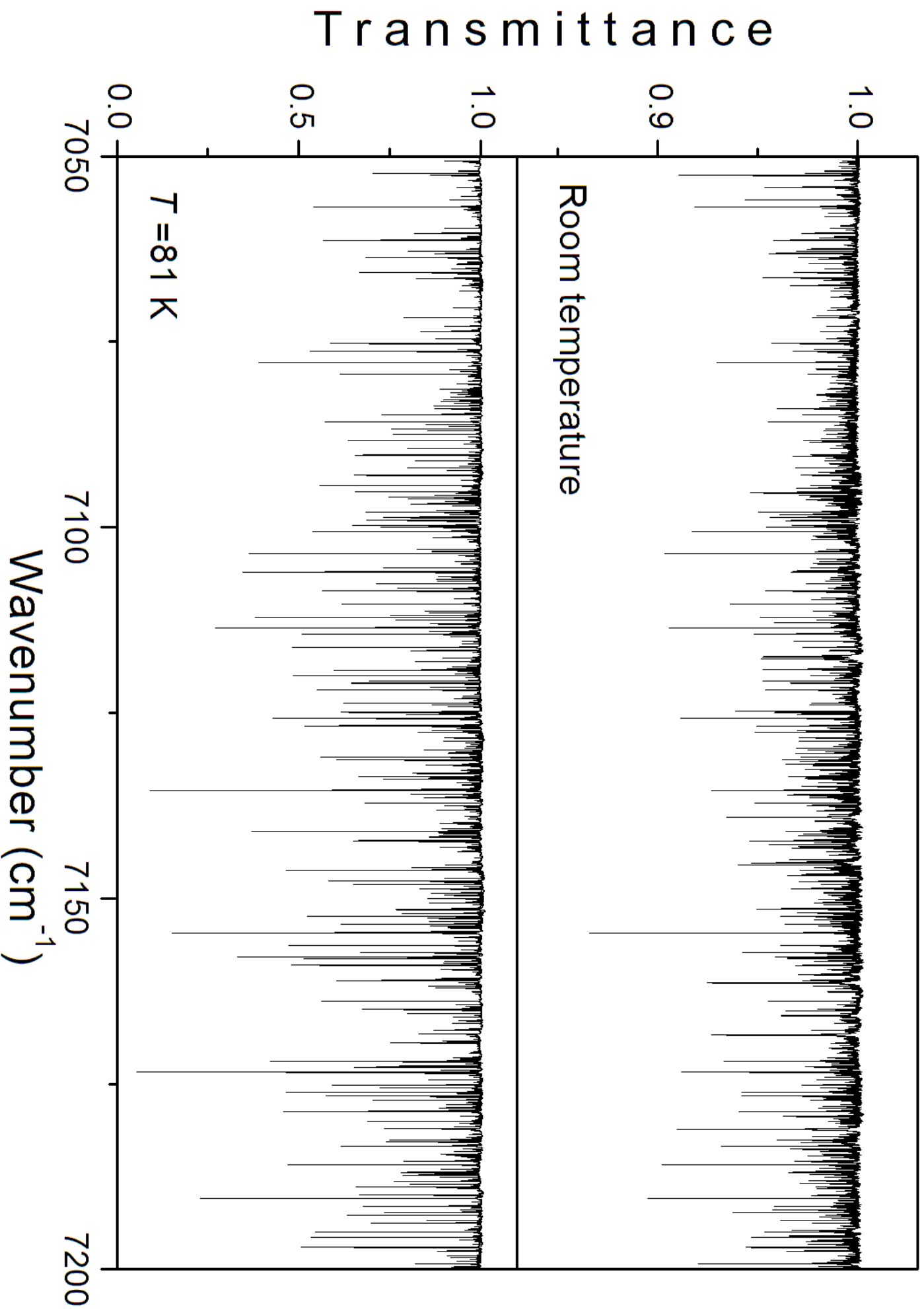


Fig. 1

Fig. 2



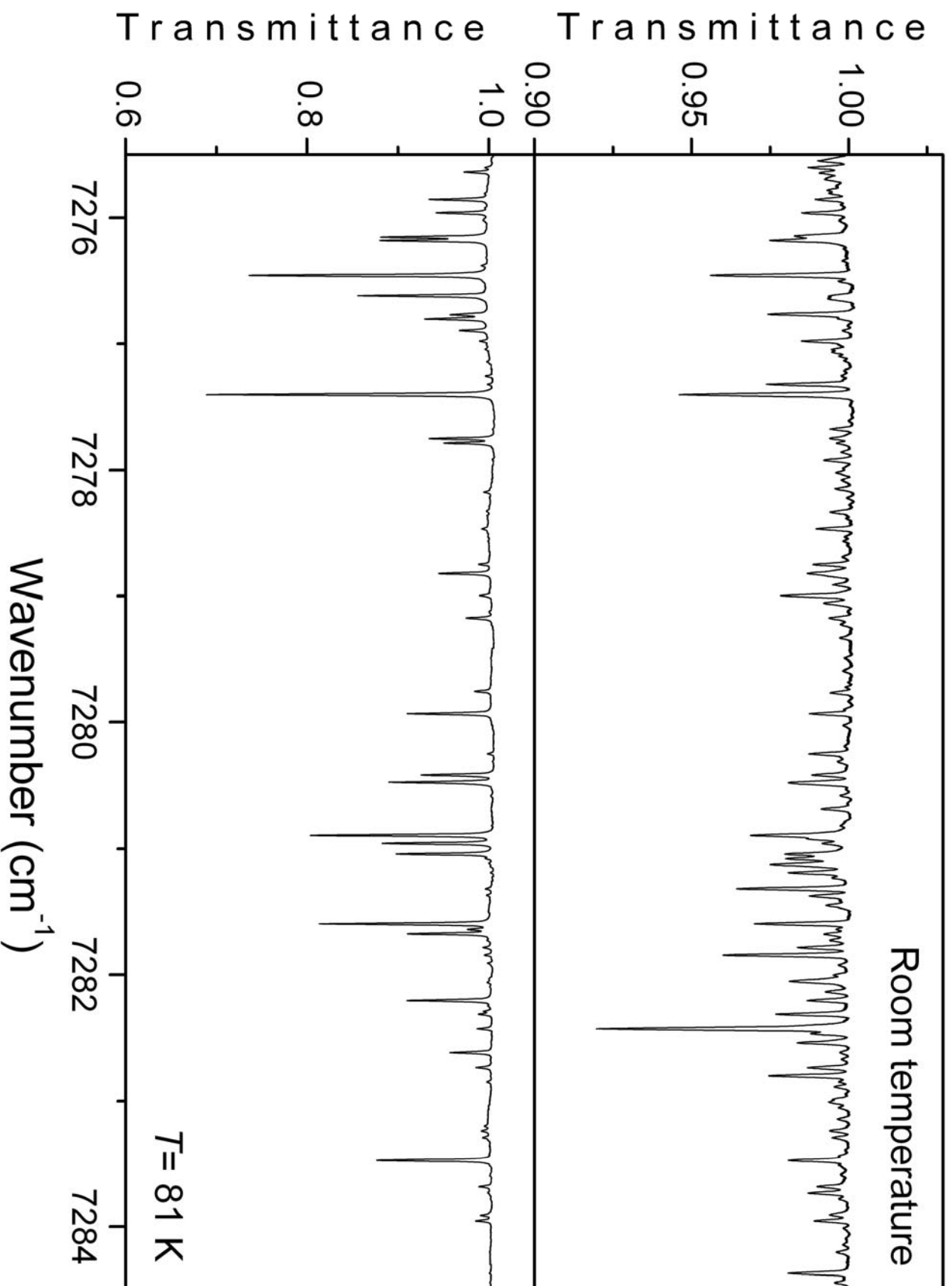


Fig. 3

Fig. 4

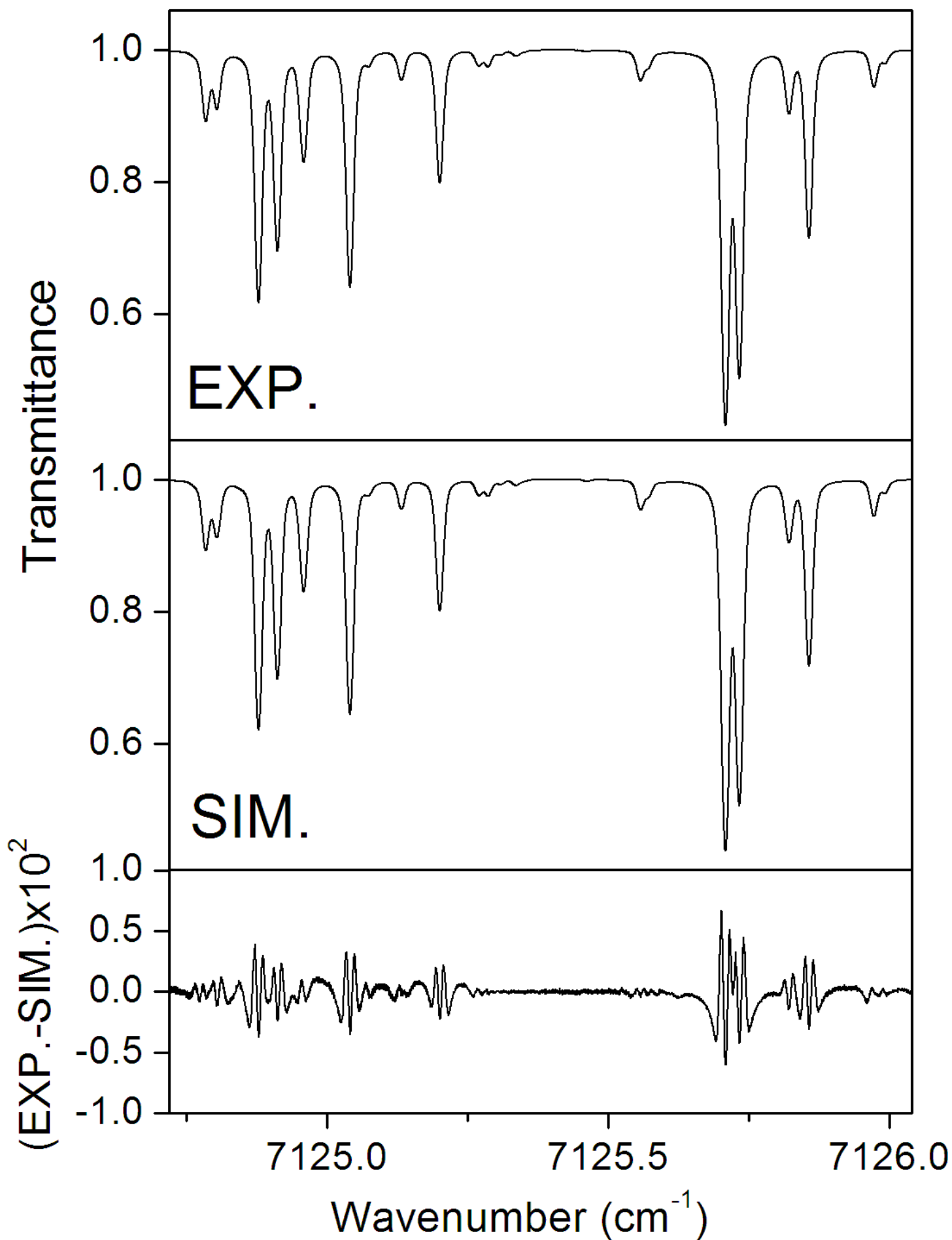


Fig. 5

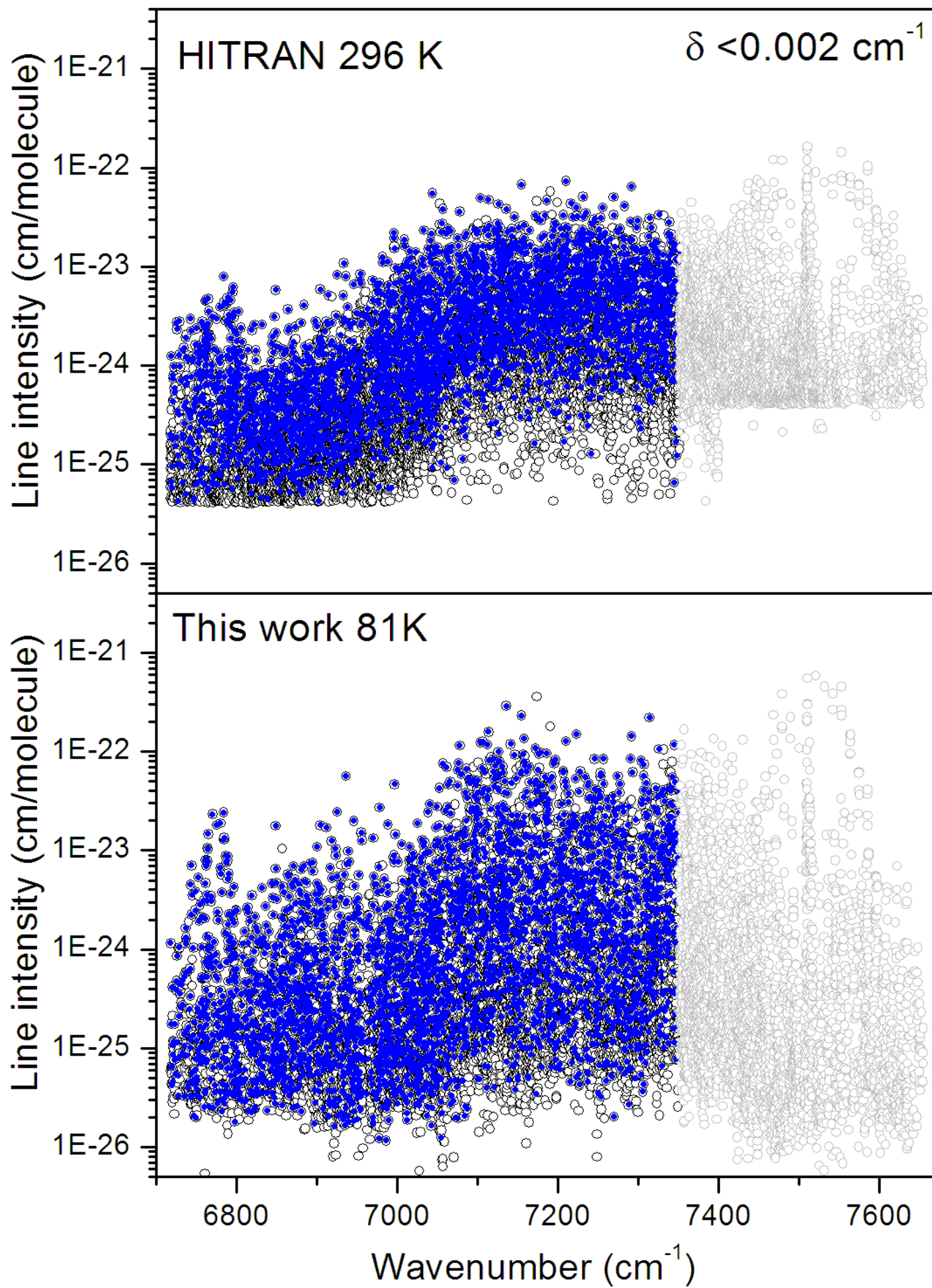
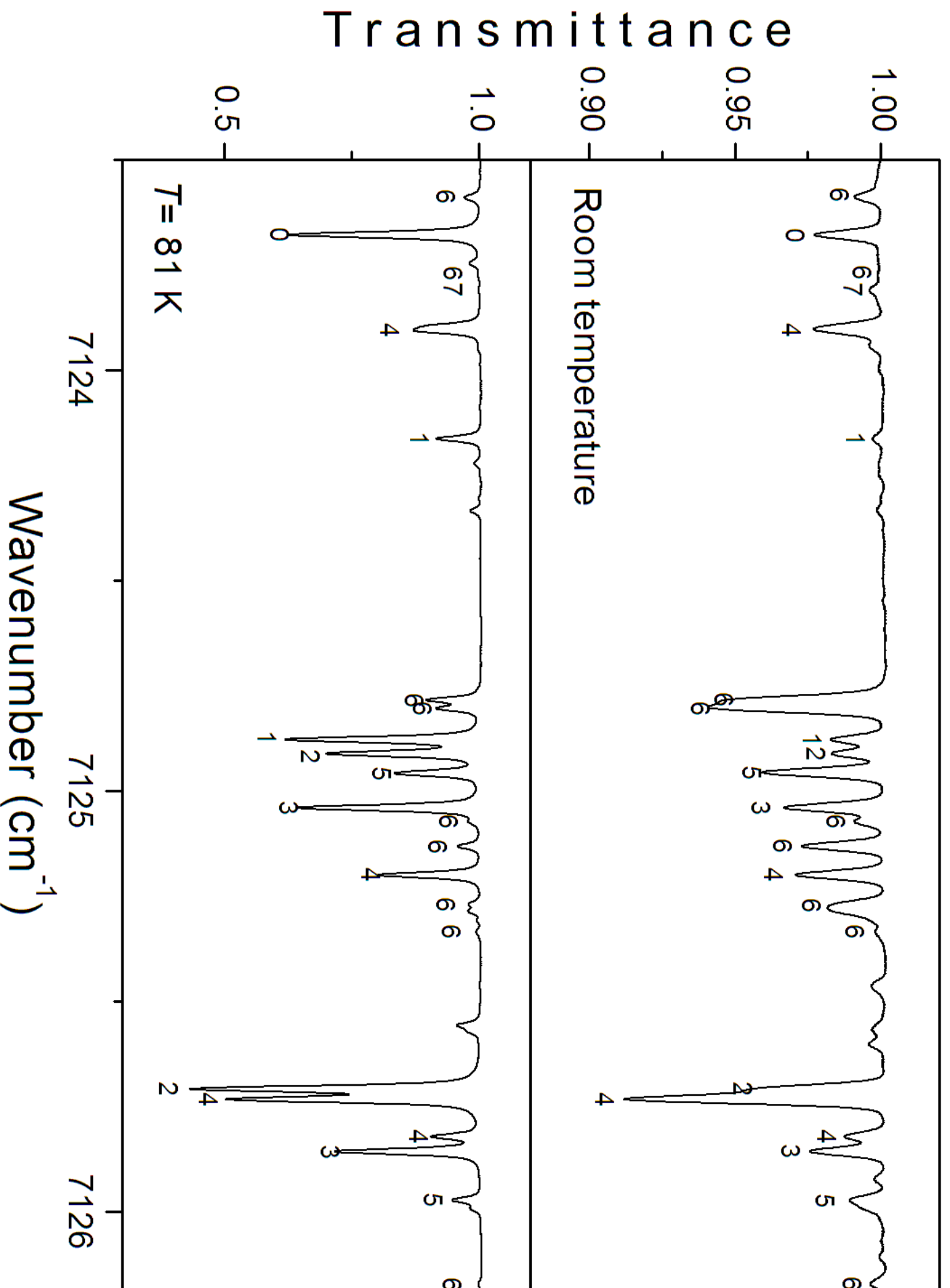


Fig. 6



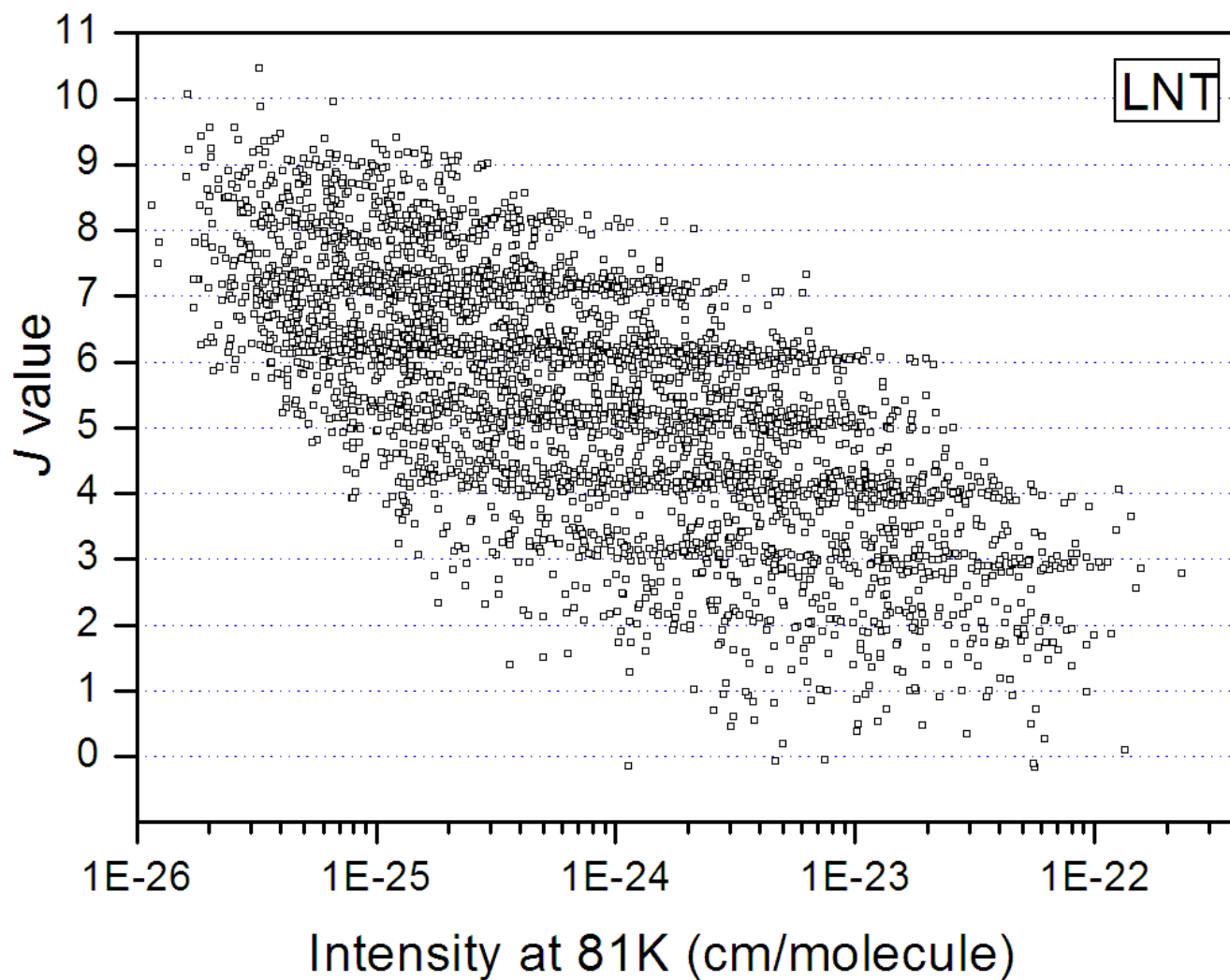
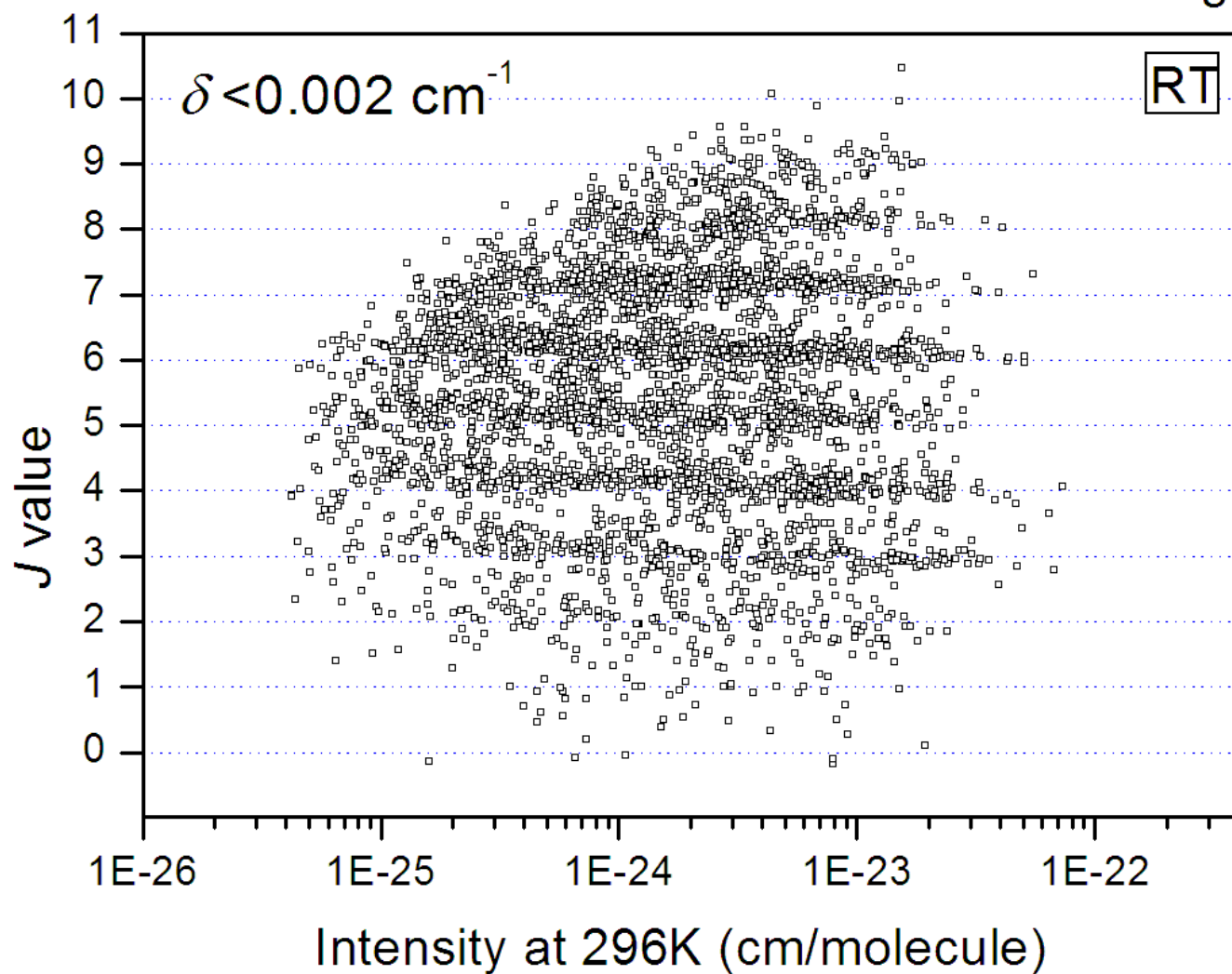


Fig. 8

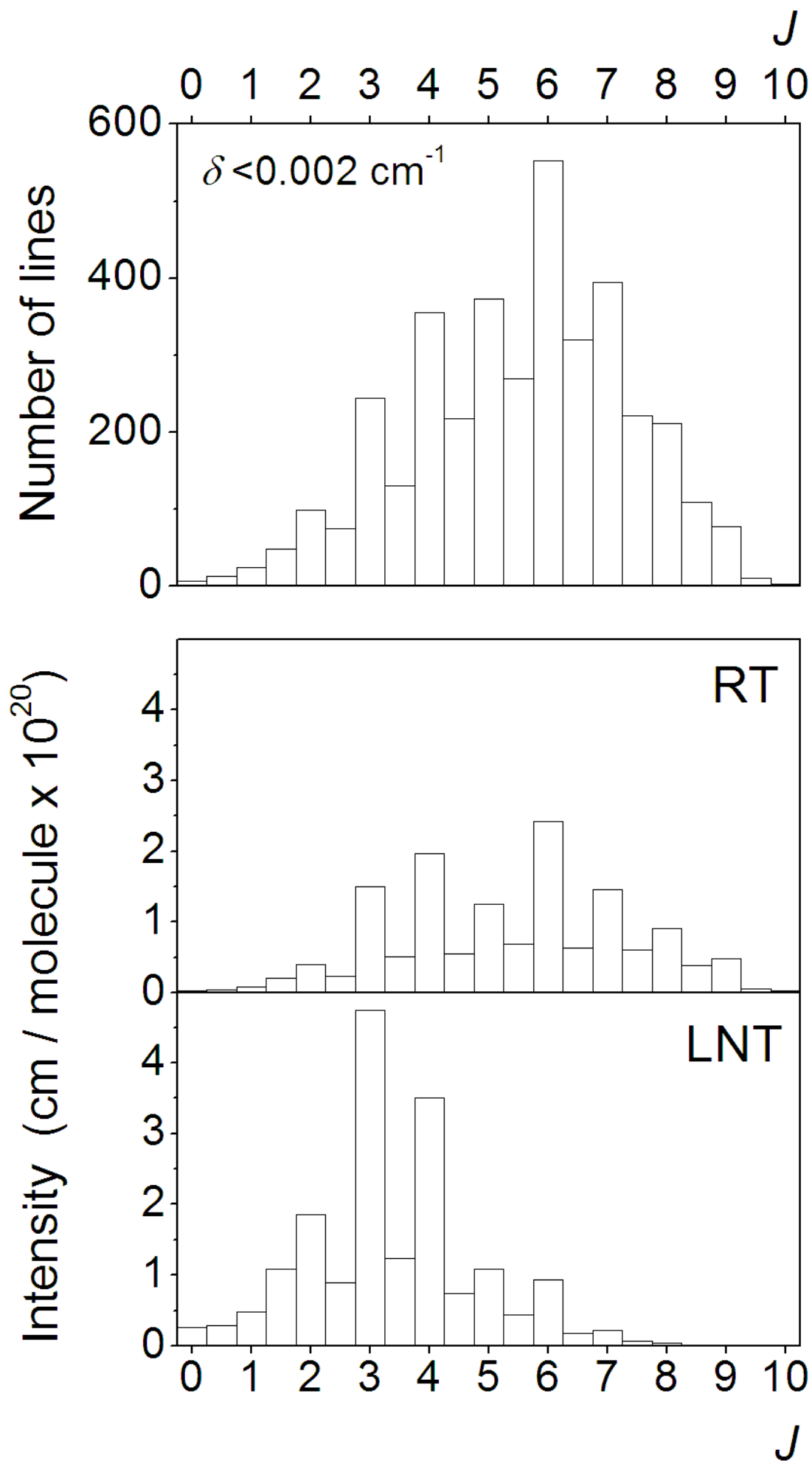


Fig.9

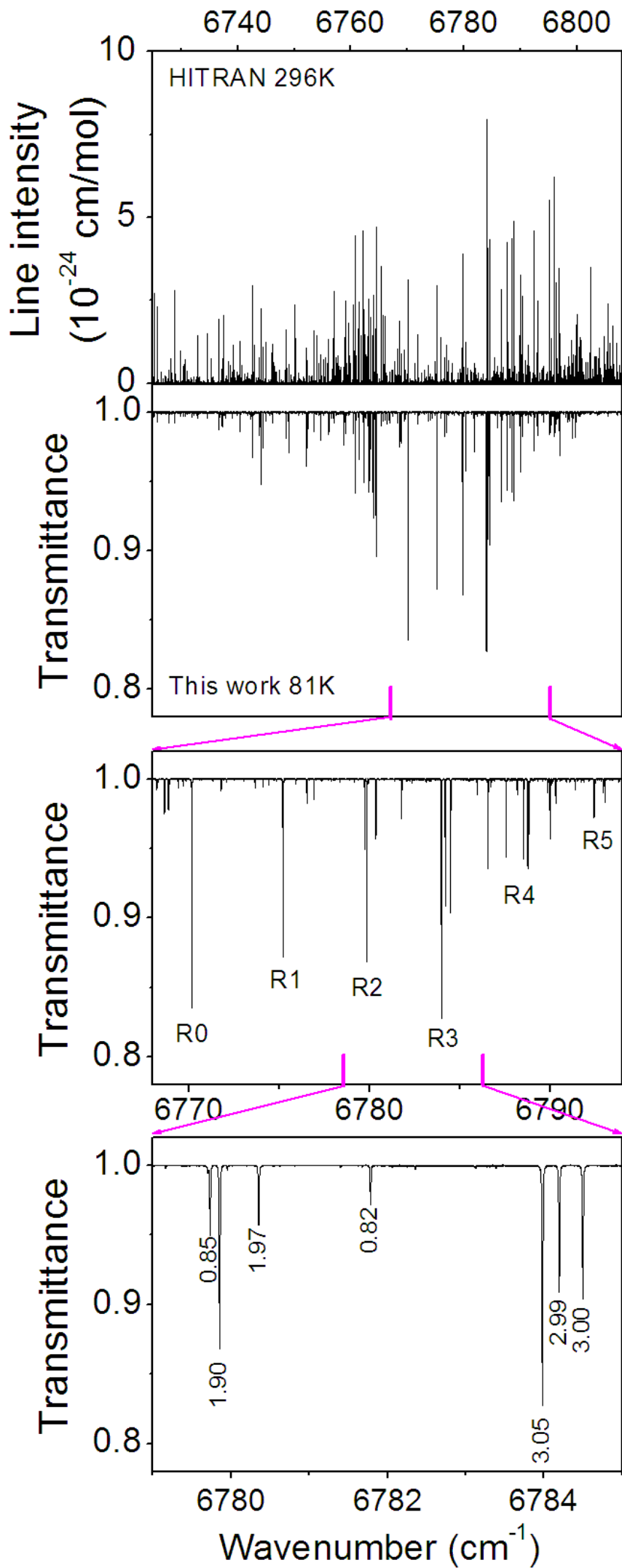
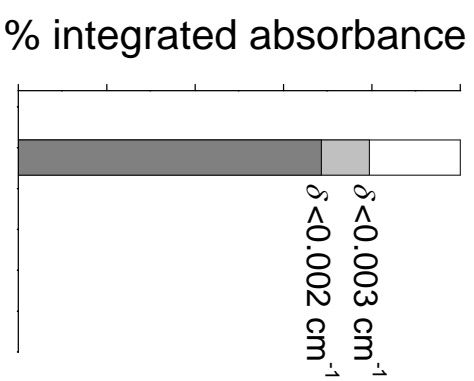
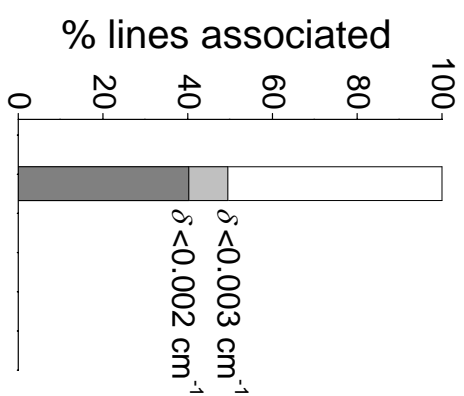
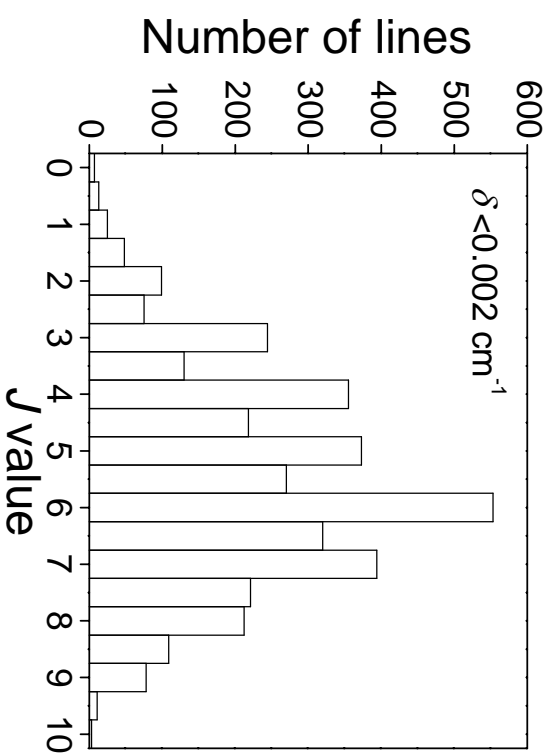
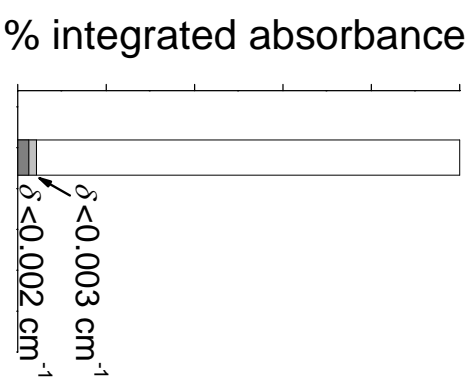
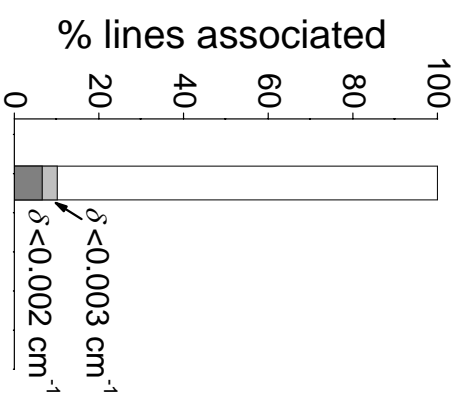
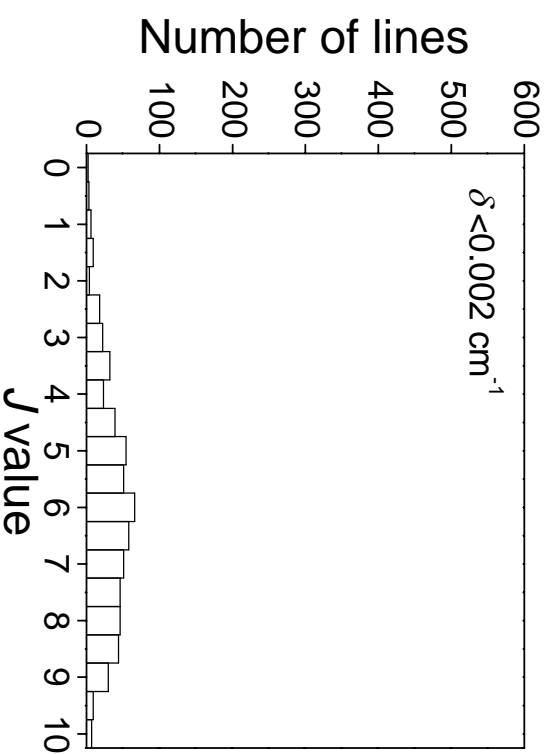


Fig.10



If LNT line positions are shifted by 0.1 cm^{-1}



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