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Accurate determination of low state rotational quantum numbers ($J < 4$) from planar-jet and liquid nitrogen cell absorption spectra of methane near 1.4 micron.

Ondřej Votava*, Milan Mašát, and Petr Pracna

J. Heyroský Institute of Physical Chemistry, ASCR, Dolejškova 3, Prague 8, Czech Republic

**corresponding author, email: votava@jh-inst.cas.cz*

Samir Kassi and Alain Campargue

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

Summary

An improved procedure for accurate determination of empirical lower state rotational quantum numbers from molecular absorption spectra is demonstrated for methane. We combine the high resolution absorption spectra of methane in the 7070-7300 cm^{-1} frequency range obtained in liquid nitrogen cooled cryogenic cell ($T=81\text{K}$) and in supersonic planar jet expansion ($T_r=25\text{K}$). Empirical lower state energies of 59 transitions are determined from the ratio of the absolute absorption line strengths at 25 and 81K. The procedure relies on realistic description of rotational state populations in the supersonic jet expansion where non-equilibrium nuclear spin isomer distributions are generated due to the rapid cooling. The accuracy of the experimental determination of the lower state energies with $J \leq 3$ is found to considerably improve the results of the same approach applied to spectra at 296 and 81K. The 59 transitions with determined lower J values provide a good starting point for the theoretical interpretation of the highly congested icosad region of methane. In particular, the centres of nine vibrational bands are estimated from the transitions with $J=0$ lower state rotational quantum number.

1. Introduction

Absorption spectra of methane in the near-infrared spectral region provide a challenge for current state of the art theory. Despite intense theoretical and experimental efforts in recent years,¹ only very limited spectral assignments are at present available for excitation energies above 6000 cm^{-1} . The reason for this unfavourable state of affairs is the extreme spectral congestion in this overtone region caused by anharmonic couplings between stretching and bending modes, that leads to complicated polyad structure.² The rovibrational structure within these bands is further complicated by Coriolis type interactions. Indeed, very few distinct bands are discernible in this part of spectrum indicating that these transitions are strongly interacting and their rotational structures are mutually perturbed.

Due to approximate relations between methane stretching and bending vibrational frequencies $\nu_1 \cong \nu_3 \cong 2\nu_2 \cong 2\nu_4$, the vibrational spectrum exhibits a well defined polyad structure. Each polyad is characterized by a polyad number $P = 2(\nu_1 + \nu_3) + \nu_2 + \nu_4$, where ν_n are the normal mode vibrational quantum numbers. The number of interacting vibrational levels $N(P)$ within a given polyad increases as P^3 for large P values.² It is customary to name the polyads in the form “ $N(P)$ -ad” where $N(P)$ is expressed through the corresponding Greek prefix. Existing detailed analysis of the high resolution spectra extends up to the octad ($P=3$)³ and progresses are currently being achieved in the tetradecad ($P=4$) region dominated by the $2\nu_3$ band at 6004 cm^{-1} . The icosad ($P=5$) remains at present mostly unassigned, with the exception of part of the intense $\nu_2 + 2\nu_3$.^{2,4} This polyad spans the spectral range 6400 to 7600 cm^{-1} and contains 20 vibrational levels and 134 sub-levels.² Due to this high density of states in interaction, standard iterative techniques of spectral analysis cannot be applied, because no regular rotational progressions can be identified even for the lowest rotational states.

Experimental schemes that simplify the spectra and provide additional information that would guide the theoretical analysis are therefore highly desirable. Lowering the sample temperature reduces the number of thermally populated states and consequently leads to a drastic reduction of the rotational congestion of the observed spectra. Another advantage of cooling is that the Doppler widths of the transitions are decreased and therefore the line blending due to accidental overlaps is also reduced.

If spectra are measured at several different temperatures, it is possible to determine empirically the lower state energies from the corresponding line intensity temperature dependence. Following

the previous works of Refs. 5-8 we have recently applied this method to methane in the 1.30-1.70 μm region⁹⁻¹³ The absorption spectrum at 81K was recorded in Grenoble by direct absorption spectroscopy using a cryogenic cell and a series of distributed feedback (DFB) diode lasers.⁹ The investigated region from (5860-7680 cm^{-1}) covers the high energy part of the tetradecad and the whole icosad. By using intensities values at 81K retrieved from our spectra and the intensity values at 296K listed in the HITRAN database,¹ we could derive the lower state energy values for most of the transitions detected in the tetradecad⁹ and in the 7351-7655 cm^{-1} part of the icosad.¹² The analysis of the icosad region¹² was limited to the 7351-7655 cm^{-1} range including the $2\nu_2+\nu_3$ band near 7510 cm^{-1} . The results relative to the whole icosad (12780 transitions at 81K) is reported in a separate contribution.¹³

The method relies on unambiguous association of transitions observed in both the room temperature (RT) and liquid nitrogen temperature (LNT) spectra on the basis of the coincidence of their line positions and on accurate measurements of the respective line intensities. The procedure is obviously limited to the transitions observed both at LNT and RT. Furthermore, the reliability of the J determination degrades for both the $J = 0-2$ values and the higher J values (> 9) which correspond to the weak transitions in the RT and LNT spectra, respectively. This limitation was found particularly marked for the low J values transitions of the icosad as the important spectral congestion of the room temperature spectra results in larger uncertainties on the RT intensity values. Yet, the lowest rotational transitions are crucial for the unambiguous determination of the vibrational band origins and to provide initial estimates of the spectroscopic constants.

In the present work, we focus on these low J rotational energy levels by applying the two temperatures method to intensity values measured at LNT and from spectra of methane cooled in a supersonic jet expansion. The investigated region (7070-7300 cm^{-1}) corresponds to the most congested part of the icosad, where no lower state energy has been determined so far. As the temperatures achieved in a supersonic jet expansion are significantly lower than LNT, it leads to a further simplification of the absorption spectra. Fig. 1 illustrates the dramatic change of the appearance of the spectrum from room temperature to supersonic jet conditions. As a result of the temperature reduction, a more accurate determination is expected for the first energy levels. This approach is then complementary to that based on the LNT and RT temperatures which is fully operative for higher energy levels. Nevertheless, the application of the two temperature method to jet cooled spectra requires taking into account the existence of three nuclear spin varieties of methane which are not in thermal equilibrium in the expansion. This specificity will be considered

in details in the next section.

2. Line strength temperature dependence in the jet and cell spectra

The absorption line strength, $S(T)$ of a given spectral transition is proportional to the lower state population in the lower state N_i , provided the population in the upper state can be neglected. Under thermal equilibrium, the lower state population is given by the Boltzmann distribution function:

$$N_i = N_0 \frac{g_i e^{\frac{-E_i}{k_B T}}}{Q(T)} \quad (1)$$

where N_0 is the total concentration, g_i is the degeneracy factor of the state i , k_B is the Boltzmann constant and the partition function, $Q(T)$, is defined as:

$$Q(T) = \sum_i g_i e^{\frac{-E_i}{k_B T}} \quad (2)$$

The ratio of the intensities of a given spectral line at two temperatures, T_1 and T_2 , denoted in the rest of the paper as $R(T_1, T_2)$ is thus expressed as:

$$R(T_1, T_2) \equiv \frac{S_N(T_1)}{S_N(T_2)} = \frac{Q(T_2)}{Q(T_1)} e^{\frac{E_i}{k_B} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)} \quad (3)$$

In the temperature range relevant for the present study, the vibrational contribution to the partition function can be omitted and only the rotational part has to be considered. Rotational partition function can either be evaluated numerically using Eq. 2, or approximated by analytical formula valid at high temperature, yielding:¹⁴

$$\frac{Q(T_2)}{Q(T_1)} = \left(\frac{T_2}{T_1} \right)^{\frac{3}{2}} \quad (4)$$

Validity of this analytical approximation is however limited to temperatures that fulfil the $k_B T \gg B_0$ condition, where B_0 is the ground state rotational constant ($B_0 = 5.241 \text{ cm}^{-1}$). At temperatures relevant for the jet spectra, significant deviations of the exact partition functions from this analytical approximation are observed below $\sim 30\text{K}$ for methane, as indicated in the left panel of Fig. 2. The rotational state energies in the ground vibrational state used for the numerical evaluation of the partition functions have been taken from current HITRAN database.¹

The evaluation of the partition function for the jet cooled sample is further complicated by the existence of three nuclear-spin isomers due to the spin of the hydrogen nuclei. They are commonly labelled as para, ortho, and meta for the total nuclear spin quantum number $I = 0, 1, \text{ and } 2$

respectively. Due to symmetry constraints, only F_1 and F_2 symmetry, A symmetry, and E symmetry rotational states are possible for ortho, meta, and para isomers, respectively. For illustration, the structure of the methane rotational levels up to $J=5$ is summarized in Fig. 3.

The nuclear-spin isomers of methane do not thermally equilibrate during the fast supersonic cooling.^{4,15-17} Consequently the ensemble of jet-cooled methane molecules is not in thermal equilibrium but consists of three nuclear spin sub-ensembles. Each of those sub-ensembles is in thermal equilibrium with the buffer gas 'bath', but equilibrium is not established between the nuclear spin isomers. As a result, the high-temperature ortho:meta:para concentration ratios of 9:5:2 are preserved in the rapid cooling process. At the $T \rightarrow 0\text{K}$ limit, the lowest rotational states for each nuclear spin isomer are reached: $J=0$, $J=1$ and $J=2$ for meta, ortho, and para respectively. Therefore under jet conditions, separate partition functions must be evaluated for each nuclear spin isomer:

$$Q_{\text{ortho}}(T) = \frac{16}{9} \sum_{\text{ortho}} g_i e^{\frac{-E_i}{k_B T}} \quad (5a)$$

$$Q_{\text{meta}}(T) = \frac{16}{5} \sum_{\text{meta}} g_i e^{\frac{-E_i}{k_B T}} \quad (5b)$$

$$Q_{\text{para}}(T) = \frac{16}{2} \sum_{\text{para}} g_i e^{\frac{-E_i}{k_B T}} \quad (5c)$$

where the summations are over all ortho, meta, and para states respectively, and the partition functions are normalized to yield the correct high temperature limit, $Q_{\text{ortho}}(T) = Q_{\text{meta}}(T) = Q_{\text{para}}(T) = Q(T)$, as shown in the right panel of Fig. 2. Thus, the intensity ratios $R(T_1, T_2)$ as predicted from Eq. 3 for given rotational state, depend not only on the lower state energy but also on its nuclear-spin isomer.

Predicted intensity ratios for conditions relevant to this study, $R(25\text{K}, 81\text{K})$, are summarized in Table 1 and compared to their values at equilibrium. The deviations of the spin-conserved predictions from the equilibrium situation are also illustrated in Fig. 4 where the intensity ratios $R(T_1, T_2)$ are plotted as a function of T_1 , while T_2 is held at a value of $T_2 = 81\text{K}$ - the temperature of LN cooled spectra. The left-hand panel presents calculations for equilibrium ensemble while the spin-conserved ensemble predictions are presented in the right-hand panel. Clearly to take the full advantage of the very low temperatures attainable in the jet for accurate determination of empirical lower state energies in methane, it is necessary to include correctly the nuclear-spin conservation in the supersonic jet cooling process. After the forthcoming description of the experimental set up, the results of the lower state energy determination based on the above discussion, will be presented.

3. Experiment

3.1. LNT experiment

The LNT spectra were recorded at Grenoble University by differential absorption spectroscopy using a cryogenic cell. Briefly, the cell is based on an original design with no external vacuum jacket, the low pressure CH₄ sample constituting 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 (see Ref. 9). The absorption path length is 141.8 cm and the gas pressure is continuously measured during the recordings (MKS Baratron, 10 Torr range). The whole investigated region was recorded with a sample pressure of 9.35 Torr pressure (at LNT). A series of 11 DFB fibered laser diodes was used as light sources allowing for a continuous coverage of the 7070-7332 cm⁻¹ range. The DFB laser diode was tuned over about 35 cm⁻¹ by a slow temperature scan from -10 to 60 °C within about 11 minutes. The individual spectra were linearised using an etalon signal (FSR = 1 GHz) and calibrated independently by matching the CH₄ line positions to the HITRAN line positions (at 296K).¹ The standard deviation error of the differences between our line positions and HITRAN values was minimized leading to *rms* values on the order of 1×10⁻³ cm⁻¹. The steady state was achieved about one hour after the filling of the cryostat with liquid nitrogen. A gas temperature value of 81±1K was determined from the Doppler profile of several tens of well isolated lines (Ref. 9). This temperature value is what we refer to as “liquid nitrogen temperature” (LNT). More details about the spectra acquisition and the cell design can be found in Ref. 9. Note that the temperature gradient over the 1 cm distance between the ends of the cryostat and the optical windows was found to have a negligible impact on the observed line profile.

3.2. Jet experiment

The planar jet experiment used to obtain the spectra of supersonically cooled methane has been built at the J. Heyrovsky Institute in Prague and is briefly described in this section. The experiment layout is schematically shown in Fig. 5. Custom designed pulsed jet source with slit nozzle configuration is used to produce the supersonic expansion. The solenoid actuated pulsed valve is modified from the original design of Lovejoy and Nesbitt.¹⁸ The valve produces short ($\Delta t \leq 1$ ms), high intensity gas pulses at repetition rate up to 10Hz. Supersonic molecular beam is formed by a slit orifice of dimensions 40mm x 0.1mm, defined by a pair of precision machined stainless steel jaws. The widths of the slit is determined by a thin spacer inserted between the jaws during assembly. The long slit configuration permits high sensitivity direct absorption measurements with sub-Doppler spectral resolution. Co-expansion of He carrier gas and methane has been used in the present experiments. The expansion temperature decreases with decreasing methane fraction in the

expansion.¹⁹ Best compromise between the cooling efficiency and absorption intensity has been found for 80% He and 20% methane at total stagnation pressure of 400 Torr. Both methane and He were 99.96% pure and were used without further purification.

High resolution diode laser spectrometer is used to record the spectra. Extended cavity diode laser in Littmann configuration with anti-reflection coated laser diode is used as radiation source tunable between 7070 cm^{-1} and 7300 cm^{-1} . The laser output power is 3mW and the bandwidths is typically 1MHz, negligible compared to the residual Doppler widths of the observed spectral transitions in the molecular beam ($\sim 150\text{MHz}$). A beam splitter deflects about 10% of the laser beam to a Michelson wavemeter for wavelength measurement, while the transmitted beam is utilized for molecular absorption detection.

Dual beam absorption spectrometer arrangement is used to reduce the laser amplitude noise. The laser beam is split into reference and signal beams with a 50% beam splitter. The signal beam passes into the vacuum chamber to cross the molecular beam, while the reference beam is sent directly to the detector. To maximize the common mode rejection in this dual beam arrangement we use custom auto-balanced differential dual beam photodetector derived from the design of Hobbs.²⁰ To determine the absolute absorbances, it is necessary to measure not only the intensity change, ΔI , due to absorption in the jet but also the total laser intensity I_0 . The autobalanced photodetector is therefore designed to provide two output signals: into differential signal ΔI which is proportional to the instantaneous difference between the photo-current in signal and reference photodetectors, and the I_0 signal proportional to the total photo-current on the signal detector only. Details of the detector design will be published in a separate paper,²¹ briefly the detector employs a feedback loop that balances the gain in the reference detector to match exactly the measured intensity of the signal beam. Time scale of this auto-balancing servo loop is $\Delta\tau \sim 1\text{s}$. Using a bipolar transistor current splitter circuit, this gain control is placed outside the signal path, and thus permits very effective noise cancellation between the reference and signal intensities is possible in the differential signal. The transient absorption signal from the pulsed supersonic beam appears on a time scale short compared to the servo loop time constant ($\tau_{\text{abs}} \sim 1\text{ms}$), and thus it is detected as a net signal on the differential output of the photo detector. The total laser intensity is determined from the total photocurrent through the signal photodiode. The noise equivalent absorption with double path through the molecular beam is currently $2.5 \times 10^{-6} \text{cm}^{-1}$.

The differential signal ΔI and total intensity I_0 are amplified with independent transimpedance amplifiers with gains that differ by a factor of 10 to compensate for different magnitudes of ΔI and I_0 . Using this arrangement both I_0 and ΔI are determined from the same photodetector, permitting

reliable absolute absorption measurements.

The spectra are frequency calibrated according to time stamped wavemeter readings. The precision of a single wavemeter measurement (0.008cm^{-1}) is improved by a least-square fit of all the wavemeter measurements recorded during the spectral scan. As the wavemeter is referenced to a polarization stabilized He-Ne laser, its long-term stability is limited only by the residual frequency drift of the He-Ne laser ($\sim 3 \times 10^{-4}\text{cm}^{-1}$) - negligible compared to the wavemeter precision. However, the absolute frequency calibration depends on both the exact He-Ne laser frequency and the difference in air index of refraction between the He-Ne (633 nm) and the diode laser (1380 nm) wavelengths. Therefore, the absolute wavemeter calibration is determined using a series of absorption lines of jet-cooled H_2O measured through the tuning range of the laser in a separate calibration experiment with H_2O seeded in He buffer gas. Estimated accuracy of the absolute frequency measurement, based on repeated measurements of selected H_2O transitions is better than $3 \times 10^{-3}\text{cm}^{-1}$.

4. Results

4.1. Jet temperature and absolute line intensities

The dataset presented in this proof of principle study consist of 59 spectral transitions in the $7070\text{-}7300\text{cm}^{-1}$ spectral range, We have originally selected 50 strongest transitions of the 81K spectra and recorded the corresponding jet transitions in a series of short scans, each 0.2 cm^{-1} long. Some of the selected transitions were not observed in the jet spectra due to their low intensities at jet temperatures, however the data set includes a number of low- J lines that accidentally fall into the scanned windows. The strong transition at 7135.456 cm^{-1} was chosen as reference line. By measuring its absorption intensity repeatedly through the experiments, we verified that the jet conditions did not change significantly. Consistent *relative* line intensities were obtained by this procedure. The error on these relative values is estimated to be about 15% of the measured value, mainly limited by the drift in the jet conditions rather than by the line fitting error. The selected set of lines is listed in Table 2.

The temperature in a supersonic jet depends sensitively on the expansion conditions. The temperature was determined from the measured residual Doppler width. Spectral lines were fitted by a Gaussian line shape and the translational expansion temperature was calculated from the full widths at half maximum, $\Delta\nu$, and the line centre frequency, ν_0 :

$$T = \frac{M c^2}{8 R \ln(2)} \cdot \left(\frac{\Delta\nu}{\nu_0} \right)^2 \quad (6)$$

where M is the methane molar mass, $M=16$ g/mole, R is the gas constant and c is the speed of light. Since contributions from both the laser line width and pressure broadening are more than two orders of magnitude smaller than the Doppler width, they were neglected. Fig. 6 shows a representative spectral line with overlaid best fit. All lines with signal-to-noise ratio exceeding 5 were used to determine the average temperature value in the jet. A value of 25(2)K was obtained, the error corresponding to one standard deviation over the entire data set.

Determination of the rotational temperature based on this Doppler profile analysis relies on the equilibrium between the translational and rotational degrees of freedom in the jet. Such equilibrium is achieved via collisional relaxation during the expansion. The rate of this rotational relaxation is proportional to the frequency of two-body collisions during the expansion. One very important aspect of the slit expansion geometry is that the molecular densities decrease only as $1/\text{distance}$ downstream. This leads to typically an order of magnitude higher collisional rates compared to equivalent pinhole jet at given stagnation pressure and consequently to higher total number of rotation relaxing collisions.²² Much closer translation-rotation equilibrium is therefore typically established in the planar jet expansion. It has been shown, that rotational relaxation efficiency is primarily dependent on the kinetic parameters such as the masses and moments of inertia of the collisional partners rather than on the details of their interaction potentials.²³

We have tested the level of translation-rotation equilibrium using H_2O as a chromophore molecule. It has both the mass and moments of inertia comparable to those of methane and exhibits a strong overtone absorption band within the tuning range of the laser diode used for methane detection. Under the experimental conditions equivalent to the methane expansion (using He buffer gas and stagnation pressures in the range 100 to 400Torr) we determined both the translational temperature T_t from the absorption line Doppler widths and the rotational temperature T_R from the Boltzmann analysis of rotational line intensities. Under those conditions the H_2O translational temperatures were found to be systematically $\sim 2\text{K}$ lower than the corresponding rotational temperature. It is therefore reasonable to expect that the translation - rotation equilibrium for the He - CH_4 expansion will be similar to the He - H_2O system. The measured translational temperatures therefore represent a lower limit of the methane rotational temperature, it is however reasonable to expect that the true rotational temperature does not differ by more than $\sim 2\text{K}$ from this value.

In order to apply the two temperature method, accurate *absolute* line strengths, $S(T)$, are needed both at LNT and in the jet conditions. Following the nomenclature of Ref. 10 those line strengths are related to the measured integrated absorbance $I(T)$:

$$I_{\nu_0}(T) = S_{\nu_0}(T) \cdot N_0 \cdot l \quad (7)$$

where l is the absorption path length and N_0 is the molecular concentration in the laser beam volume. While the molecular concentrations are readily determined from the pressure and temperature of the gas cell experiment, the situation is rather more complicated in the jet experiment. Molecular density in the supersonic expansion depends on stagnation conditions (p_0 , T_0 , methane/He mixing ratio), as well as on the jet geometry. Furthermore, both density and temperature of the expanding gas decrease with the distance from the jet orifice and therefore the sampled concentration depends also on the exact position of the laser beam with respect to the gas jet. The absolute concentration of methane in the jet has been therefore determined experimentally by using as reference a strong and well isolated spectral line identified in the LNT spectrum and extrapolating its intensity at 25K. The absorption line at 7135.456 cm^{-1} has been selected for this purpose. The analysis of the 81K/296K intensities¹³ indicates that the corresponding lower state is probably the rotationless state, $J=0$. This is further confirmed by the fact that this line is one of the strongest lines observed in the jet spectrum and is separated from other lines of comparable intensity by more than $2B$. It is then reasonable to consider this line as a $R(0)$ transition of a dominant band of the region. Note that this assignment will be firmly confirmed by the consistency of the lower state determinations presented below. On the basis of the line strength ratio $S(25\text{K})/S(81\text{K}) = 4.37$ calculated by the theory described above for the $J=0$ lower state and on the $S(81\text{K})$ value determined from the LNT spectra,¹³ the methane concentration in the jet was deduced from the measured integrated absorbance, $I(T)$, (Eq. 7). We obtained a value of $N_0 = 0.9(2) \times 10^{16}$ molecules/cm³. This value agrees within a factor of two with the value 1.97×10^{16} molecules/cm³ predicted for planar jet by approximate theory.²²

4.2. Determination of the lower state energies

The ability to associate the lines corresponding to the same transition in the spectra measured at different temperatures is crucial and has been pointed as a limitation of the two temperature method in the treatment of the 81K/296K spectra.^{10,12,13} This is the consequence of frequent line blending in particular in the room temperature spectrum. Due to the significant simplification of the spectra, this is no longer an issue with the jet spectrum. A comparison of the measured spectra from cold cell and supersonic jet is presented in Fig. 7. Clearly, a significant number of transitions observed in the cold cell spectra vanish in the jet spectrum due to the important rotational cooling.

In addition, line widths are narrower in the jet. As a result, virtually no accidental line overlaps are observed in the jet spectrum which makes line position and intensity measurements, straightforward. While the 81K spectra exhibit a certain level of congestion, unambiguous line-by-line matching with the lines observed in the jet spectra is possible for almost all transitions observed in the jet spectrum. Contrary to the analysis of the 81K and 296K spectra, accidental coincidences in the 81K and jet spectra are practically non-existent. This is an important advantage in terms of reliability and accuracy of the determined lower state energies.

In absence of any experimental error, all measured $R(T_1, T_2)$ intensity ratios relative to spectral lines that originate from the same rotational level would have specific values given by Eq. 3. Therefore only discrete values of R would be observed. This quantized character of the R values is clearly demonstrated in the present data set, as shown in Fig. 8. Here the experimentally determined intensity ratios are plotted in the order of increasing values. The step character of the plot is indication of the quantization, each step corresponding to specific lower rotational state. Moreover, those experimental values of R agree well with the theoretical predictions, indicated by horizontal lines in the right-hand side of the figure. The residual slope within each step reflects the experimental uncertainty on the intensity ratio measurements. Based on this Fig. 8, preliminary assignments can be made for the observed spectral lines by matching the experimental values of R to the nearest theoretical prediction.

For a more quantitative analysis it is necessary to determine the empirical low state energies E_{emp} , and hence the empirical low state rotational quantum numbers J_{emp} , from the measured values of R . It follows from Eq. 3:

$$E_{emp} = \frac{\ln[R(T_1, T_2)]}{\alpha} + \frac{\ln\left[\frac{Q(T_1)}{Q(T_2)}\right]}{\alpha} \quad \text{where} \quad \alpha = \frac{1}{k_B} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (6)$$

and using analytical spherical top rotational energy dependence:

$$J_{emp} = \sqrt{\frac{1}{4} + \frac{E_{emp}}{B_0}} - \frac{1}{2}, \quad (7)$$

where B_0 is the ground state rotational constant (5.241 cm⁻¹).

To apply these relations to the jet spectra, the non-equilibrium nuclear-spin isomer populations must be taken into account. Without any prior knowledge of the nuclear-spin isomer, it is however not possible to unambiguously determine the empirical values of E_{emp} and J_{emp} from the measured intensity ratio R via Eqs. 6 and 7. This ambiguity is the result of nuclear spin dependence

of the partition function, as introduced in Eq. 5 for the non-equilibrium jet distributions. Three possible values of E_{emp} are thus calculated for each spectral line, using ortho, meta, and para partition functions respectively. Those nuclear-spin dependent E_{emp} values differ by a constant shift given by the second term in Eq. 6. Specifically, for $T_1=25\text{K}$ and $T_2=81\text{K}$, this second term yields values of -44.47 , -37.87 and -48.34 cm^{-1} for ortho, meta, and para partition functions, respectively.

For $J=0$ and $J=1$ states, the error introduced by the partition function term would be potentially most serious because the energy difference between those states is only 10.4 cm^{-1} , *i.e.* comparable to the uncertainty introduced by the difference in the partition functions. For each of those rotational levels however, only single nuclear-spin isomer exists, and thus the ambiguity is removed. For example, calculated values of J_{emp} using Eqs. 6 and 7 for a spectral line with experimental value of $R(25\text{K},81\text{K}) = 4.3$ are 0.71 , 0.09 , and 0.94 using ortho, meta, and para partition functions respectively. Rounding to the nearest integer would lead to possible assignments of $J=1$, para or meta and $J=0$, ortho. There are however no para nor meta $J=1$ states, and thus the only possible assignment for the lower state is the $J=0, A_1$ level. Likewise, a ratio value $R(25\text{K},81\text{K}) = 3.9$ would yield $J_{emp} = 0.89$, 0.41 , and 1.1 using ortho, meta, and para partition functions respectively and due to the nuclear-spin restrictions (see Fig 3), only the $J=1, F_1$ level is possible. In summary, no ambiguity arises due to the nuclear-spin partition functions in the case of $J=0$ and 1 levels.

For the $J>1$ rotational states, the energy spacing between adjacent rotational levels increases and the uncertainty introduced by the partition function has a smaller impact on the calculated J_{emp} values. Thus the rotational quantum number J can be determined with a high level of confidence. This is reflected by a small difference in predicted values of R for different spin-orbit components of a given J value, as illustrated in Fig. 4 and Table 1.

Based on the above considerations, we adopted the following general procedure to determine the empirical low state rotational quantum numbers as listed in Table 2: (i) calculate the three J_{emp} values (Eqs. 6-7) according to the three partition-function, (ii) exclude the nuclear-spin forbidden cases and (iii) average the remaining physically feasible values of J_{emp} .

The fifty nine empirical J values obtained using this "low temperature" 25K/81K analysis are compared to the recently published "high temperature" 81K/296K analysis in the same spectral region¹³ in Fig. 9 and in Table 2. The grey areas in Fig, 9 represent a ± 0.25 confidence range

around each integer value. Only 5 lines fall outside this margin in the current low temperature analysis, illustrating the high level of confidence of the obtained results. Moreover three of those outliers are assigned to the $J=4$ level, that apparently exhibit a systematic shift from the theoretical values but are highly consistent among each other. We suspect that this systematic shift may be caused by an inadequate translation-rotation equilibrium in the jet or by a larger uncertainties of the corresponding intensity values due to the weakness of those higher- J lines in the jet spectrum. Moreover of those 59 transitions analysed in the present study, 14 transitions - that is almost 25% - had to be excluded from the previous 81K/296K temperature analysis because the corresponding line was found either too weak or too blended in the RT spectrum. The current low temperature approach therefore represents a significant improvements in lower state energy determination for $J<4$ from the previous 81K/296K analysis.^{10, 12, 13}

Finally, we would like to point out that the differences in R can be potentially used to *distinguish* the nuclear-spin components for given value of J . Specifically, the predicted R values differ by about 12% for the $J=2$, E and $J=2$, F₂ components. If the experimental precision on the $R(25K, 81K)$ ratio would be better than 6 %, it would be possible to distinguish between the $J=2$, E and F₂ nuclear-spin components. The fact that no distinctive sub-steps are observed for the $J=2$ lines in the Fig. 8 indicates that our current experiment doesn't reach the required precision, but this may be accomplished with an improved experiment.

5. Discussion

In the previous analysis using room temperature and LN temperature data^{10,12,13} a good matching of the empirical rotational quantum numbers to the integer values has been obtained for $J_{emp}>3$ but the analysis proved to be less reliable for the lowest rotational states. The current low temperature analysis, on the other hand, gives good results for those low- J states. The ability to discriminate consecutive rotational levels based on the experimentally determined intensity ratios $R(T_1, T_2)$ depends on two factors: the intensity ratio contrast *i.e.* the change in R between consecutive rotational levels and the experimental errors that influence the precision of lower state energy determination. Those are the errors that affect the line intensity on one side and the errors in the temperature measurements on the other. By the nature of the supersonic jet experiment with relatively short absorption path-length, low concentrations and unsteady flow conditions, the jet data contribute to the majority of those experimental errors in the current study.

The errors in absolute methane concentration are dominated by the long term drift in expansion conditions. Even though the gas flow and stagnation pressure are controlled through the

experiment, the pulsed-valve opening characteristics are subject to slow drift over time which affects the methane concentration in the expansion. From repeated measurements of the same calibration transition we estimate this concentration drift to be typically $\sim 10\%$ for the entire data set. In addition the line-fitting error of the integrated line strengths due to the baseline noise in the direct absorption detection is currently on the order of $1 \times 10^{-24} \text{ cm} \cdot \text{molecule}^{-1}$ and thus becomes the dominant source of error for the weak transitions with $S < 1 \times 10^{-23} \text{ cm} \cdot \text{molecule}^{-1}$.

Statistical error of the translational temperature determined from the Doppler line widths is 2K (2x the standard deviation of the mean). The difference between translational and rotational temperature has not been measured, but by analogy with the expansion of H_2O seeded in He we expect it to differ by $\sim 2\text{K}$ from the translational value. Sensitivity of the observed intensity ratios to the temperature error may be assessed from Fig. 4 and Eq 3. The intensity ratios for $J''=0$ transitions are most sensitive to the temperature, and they change from 4.40 to 4.16 when the temperature is increased from 25K to 27K, approximately 5%.

The intensity ratio contrast depends on the choice of temperatures T_1 and T_2 . To illustrate how the contrast changes for the $T_1=25\text{K}/T_2=81\text{K}$ and $T_1=81\text{K}/T_2=296\text{K}$ ranges, let us consider a simplified model of a spherical top molecule at thermal equilibrium (or a molecule with a single nuclear-spin isomer). Rotational energies are given by the analytical formula, $E'' = B_0 J(J+1)$, and each rotational level has a $(2J + 1)^2$ degeneracy. The calculated population ratios $R(25\text{K}, 81\text{K})$ and $R(81\text{K}, 296\text{K})$ for such case are presented in Fig. 10 a). In agreement with Eq. 3, the predicted intensity ratios vary exponentially with E'' and the slope in the logarithmic plot of R against E'' is given by the scaling factor $\alpha = 1/k_B(1/T_1 - 1/T_2)$. Numerical values of this parameter are 0.0398 and 0.0130 cm for the low temperature (25K/81K) and high temperature (81K/296K) regime, respectively. The low temperature analysis therefore always gives better intensity ratio contrast. Obviously, the contrast increases with increasing J , as the energy spacing between adjacent rotational states increases.

The second important factor is experimental: the weakest transitions are affected by a larger uncertainty on their intensity values. Absolute line strengths are proportional to the rotational state populations. The J dependence of the rotational populations is plotted in Fig. 10 b) for 25K, 81K and 296K. The fraction of molecules with $J < 4$ represents 98% , 61% and 15% of the total population at $T = 25\text{K}$, 81K and 296K, respectively. The low- J transitions are therefore particularly weak in the room temperature spectra and frequently affected by accidental overlaps from the large number of stronger high- J lines. In contrast, the low- J states carry most of the population at low temperatures and consequently the low- J lines are strong in the jet spectra. As a result, the

experimental intensity ratios can be reliably determined for low rotational states ($J < 4$) from the jet spectra but the measurements become unreliable for higher rotational states. The considerable improvement achieved for the $J=0$ levels (see Fig. 9), clearly indicates that the uncertainty on the J values derived from the 81K/296K spectra is limited by the uncertainty on the intensity values at 296K and not at 81K.

The transitions assigned to $J=0$ are particularly interesting as they correspond to $R(0)$ lines and their corresponding wavenumber coincide with the $J=1$ level of the vibrational upper state. An estimation of the centres of the vibrational bands can be obtained by subtracting $2B$ (10.5 cm^{-1}) from the wavenumber values. The wavenumbers, estimated band centres and absolute line intensities at 81K of the nine lines assigned to $R(0)$ are listed in Table 3. As mentioned in the Introduction, to the best of our knowledge, no assignment neither rotational nor vibrational is available in the literature in the investigated spectral region. Wang and Carrington²⁴ and Bowman *et. al.*²⁵, have reported the results of a contracted basis-Lanczos calculation of the vibrational levels of methane up to 8000 cm^{-1} . A total of 39 vibrational levels were predicted between 7070 and 7300 cm^{-1} . They include 12 levels of F_2 symmetry which are likely to correspond to the strongest bands. A careful comparison did not reveal significant correlation between our band centres values and the computed values. More than the convergence error of these calculations, the insufficient accuracy of the used *ab initio* surface is probably responsible of this situation.

6. Conclusion

The combination of high resolution spectra of methane recorded with a cell cooled at 81K and in planar supersonic jet ($T_R=25\text{K}$) has proven to be a reliable method to determine the $J < 4$ lower state energies of the observed transitions, from the temperature dependence of their intensities. This low temperature approach is found complementary to that based on line intensities measured in a static absorption cell at 81K and 296K.^{10,12,13} the 81K/296K spectra are useful for the higher rotational states ($J > 3$), where the intensity ratio contrast is sufficient due to the large energy spacing between rotational levels, and line intensities are high due to sufficient thermal population. For $J < 4$ levels, the high temperature approach is however limited by (i) the large uncertainty on the experimental intensity value at 296K due to the weakness of the corresponding transitions and the strong spectral congestion and (ii) an insufficient intensity ratio contrast. While the general agreement with the 81K/296K results is good, the low temperature approach leads to more accurate low energy values for $J < 4$ as a result of improved intensity ratio contrast for all rotational states and of the quasi absence of line overlapping in the jet spectra.

Even though the nuclear-spin conservation in the supersonic jet cooling complicates the analysis, the lower J values have been unambiguously determined for the 59 transitions selected for this study. One may actually take advantage of the sensitivity of the intensity ratios to the nuclear-spin components to discriminate the symmetry species of transitions corresponding to the same lower J value. Specifically, it would require decreasing the experimental uncertainty on the absolute line intensities to a few %, which is difficult but may be achieved with an improved experiment.

The obtained results are relevant to the highly congested (at RT) region of the icosad of methane which is still resisting to a theoretical interpretation. The determination of the $J=0$ energy level of nine vibrational bands from the unambiguous assignment of nine $R(0)$ transitions, provides a good starting point for theoretical modelling of the considered polyad.

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Figure Captions:

Figure 1: Section of methane high resolution spectra in the icosad region measured at 296K and 81K in cell and 25K in supersonic jet demonstrating the significant simplification of the spectra achieved by rotational cooling.

Figure 2: Calculated partition functions for methane. a) analytical and numerical partition functions for nuclear-spin relaxed sample (cell conditions). b) nuclear-spin specific partition functions for nuclear spin non-relaxed sample (jet conditions). The 25K value corresponding to the rotational temperature in the jet experiment is indicated by arrow.

Figure 3: Diagram of the $J \leq 5$ rotational levels of $^{12}\text{CH}_4$ in the ground vibrational state. The states are sorted into T_d group symmetry species and grouped according to the nuclear spin isomers. States populated at the zero temperature limit in the jet expansion (assuming nuclear spin conservation) are marked with thick lines. Arrows indicate transitions observed in the jet spectra in the $T=0$ limit.

Figure 4: Predicted integrated intensity ratios $R(T, 81\text{K}) = S(T)/S(81\text{K})$ for $J < 4$. a) nuclear-spin equilibrium (cell conditions). b) nuclear spin un-relaxed sample (jet conditions).

Figure 5: Schematic diagram of the high resolution near-IR spectrometer coupled with a slit supersonic nozzle source. Extended cavity diode laser (ECDL) is scanned under computer control and its wavelength is monitored with a Michelson wavemeter. The laser beam is double-passed 3mm below the slit orifice (40mm x 0.1mm) of the pulsed supersonic nozzle. The solenoid actuated pulsed valve operates at 3Hz repetition rate and produces $\Delta t = 1\text{ms}$ long (FWHM) gas pulses. Gas mixture of 20% CH_4 + 80% He at total pressure of 0.5 bar is used in the present study. The transient absorption is recorded with a low noise autobalanced photodetector with high common mode rejection ratio to reduce the laser noise. A noise equivalent absorption, $\alpha_{\text{min}} \sim 2 \times 10^{-6} \text{ cm}^{-1}$ is achieved.

Figure 6: Sample Doppler profile of a selected methane spectral line recorded in the jet expansion and overlying Gaussian fit. A translational temperature of 25(2)K is determined from the Doppler broadening.

Figure 7: Comparison of the high resolution spectra of methane near 7125 cm^{-1} . Jet spectrum at 25K as determined from line Doppler broadening. Cell spectra measured in LN cooled static cell ($P=9.35 \text{ Torr}$ at 81K). The empirical J -values assignments are from the two-temperature analysis using the 25K/81K (this work) and 81K/296K (Ref. 13) method for the top and bottom assignments respectively.

Figure 8: Experimental values of the ratio of the line intensities at 25K (jet) and 81K (cell) for the selected set of 59 spectral lines between 7070 and 7300 cm^{-1} . The data-points are plotted in order of increasing value of the ratio, $R(25\text{K}, 81\text{K})$. Quantization of the R values is demonstrated by the step-like character of the plot. Theoretically predicted values of R for various methane rotational states are plotted in the right-hand side of the plot.

Figure 9: Comparison of the empirical J values determined from the analysis of the 25K/81K (left hand) and the 81K/296K (right hand) sets of line intensities. Data points outside the ± 0.25 confidence range from the expected integer values are highlighted.

Figure 10: a) Rotational level population distribution for a model spherical top ($B_0=5.24\text{cm}^{-1}$) at 25K, 81K and 296K. b) Predicted intensity ratios of model spherical top for (25K, 81K) and (81K, 296K) temperatures, *versus* the lower energies.

Textual abstract for contents page:

Methane absorption spectra in planar supersonic jet and cryogenic cell are combined to accurately determine ground state rotational quantum numbers for low-J transitions in the icosad region.

Tables:

Rotational state	nonequilibrium	equilibrium
$J=0, A_1$	4.40	5.45
$J=1, F_1$	3.65	3.50
$J=2, E$	1.80	1.45
$J=2, F_2$	1.58	1.45
$J=3, F_2$	0.45	0.38
$J=3, F_1$	0.45	0.38
$J=3, A_2$	0.36	0.38

Table 1: Predicted intensity ratios $R(T_1, T_2) = S(25\text{K, jet}) / S(81\text{K, cell})$ for $J \leq 3$.

25K Jet		81K cell		25K/81K analysis	81K/296K analysis ^a	
Center	Intensity	Center	Intensity	$R(T_1, T_2)$	J_{emp}	J_{emp}
cm ⁻¹	10 ⁻²³ cm/mol	cm ⁻¹	10 ⁻²³ cm/mol			
7076.306	9.63	7076.305	7.65	1.26	2.06	1.96
7077.810	2.83	7077.808	11.46	0.25	3.14	2.96
7100.550	0.25	7100.550	7.66	0.03	4.28	
7103.554	2.85	7103.546	12.30	0.23	3.18	3.45
7103.737	2.17	7103.729	0.74	2.93	1.07	
7106.091	44.99	7106.087	12.51	3.60	0.12	-0.5
7112.121	15.52	7112.120	11.68	1.33	2.00	1.9
7113.569	5.08	7113.570	15.74	0.32	2.96	2.87
7114.370	2.58	7114.367	8.17	0.32	2.97	2.98
7114.473	4.27	7114.471	1.29	3.31	0.88	1.94
7116.142	30.85	7116.135	8.74	3.53	0.19	
7119.954	31.02	7119.950	8.45	3.67	0.04	-0.5
7125.556	0.57	7125.558	0.54	1.07	1.99	
7125.709	12.2	7125.709	9.91	1.23	2.07	1.89
7125.861	1.27	7125.858	4.05	0.31	2.98	2.91
7126.720	8.15	7126.719	5.86	1.39	1.96	1.7
7126.812	1.74	7126.813	7.93	0.22	3.22	2.9
7126.964	5.76	7126.963	1.75	3.29	0.89	-0.2
7135.456	105.67	7135.452	28.73	3.68	0.03	-0.5
7140.939	43.96	7140.937	11.78	3.73	-0.04	-0.5
7146.240	29.53	7146.237	9.24	3.19	0.94	1.03
7154.498	2.37	7154.500	1.79	1.32	2.01	1.09
7154.585	9.36	7154.587	6.26	1.50	2.02	2.15
7154.700	6.61	7154.703	23.03	0.29	3.04	2.81
7154.801	0.53	7154.804	1.28	0.41	3.04	
7156.394	11.49	7156.393	9.25	1.24	2.07	1.74
7156.492	2.72	7156.490	0.86	3.15	0.96	
7157.847	48.81	7157.854	13.40	3.64	0.07	0.24
7158.111	10.73	7158.113	8.00	1.34	1.99	1.97
7158.929	28.76	7158.929	8.98	3.20	0.93	
7159.054	8.25	7159.057	7.18	1.15	2.14	2.1
7171.785	1.43	7171.784	1.17	1.22	2.08	1.4

7171.914	3.34	7171.915	10.66	0.31	2.98	2.91
7172.005	1.25	7172.004	4.66	0.27	3.08	2.97
7172.096	2.25	7172.097	2.95	0.76	2.49	2.31
7172.595	4.45	7172.597	3.11	1.43	2.06	1.82
7172.743	6.67	7172.746	5.11	1.30	2.02	1.89
7172.717	0.79	7172.718	4.00	0.20	3.28	2.94
7173.431	155.79	7173.435	35.65	4.37	0.11	
7176.111	2.21	7176.105	9.31	0.24	3.16	3.05
7178.110	1.63	7178.111	1.19	1.38	1.97	
7178.641	14.75	7178.639	4.53	3.26	0.9	0.99
7178.697	1.05	7178.697	3.25	0.32	2.96	2.96
7178.763	2.04	7178.762	9.63	0.21	3.24	2.9
7185.877	0.3	7185.876	9.51	0.03	4.31	3.82
7190.425	4.68	7190.430	17.81	0.26	3.10	
7195.660	2.68	7195.662	8.05	0.33	2.94	3.11
7197.032	1.85	7197.031	8.26	0.22	3.20	2.97
7209.793	0.42	7209.799	12.73	0.03	4.28	4.08
7209.940	1.64	7209.941	1.50	1.1	2.18	
7223.158	3.79	7223.162	14.90	0.25	3.12	2.59
7223.193	0.73	7223.197	2.05	0.35	3.05	
7223.279	1.69	7223.280	0.95	1.78	1.85	2.89
7245.255	1.86	7245.257	8.38	0.22	3.21	3.26
7256.735	30.36	7256.735	8.35	3.63	0.08	-0.5
7290.427	2.03	7290.426	8.43	0.24	3.15	3.11
7291.373	3.66	7291.375	14.23	0.26	3.11	3.66
7291.413	5.37	7291.414	1.51	3.55	0.17	
7291.544	4.34	7291.543	3.20	1.36	1.98	

Table 2: Observed line positions, intensities, intensity ratios, and calculated low state rotational quantum numbers for selected methane rovibronal transitions in the icosad region.

^aFrom ref. 13

$R(0)$ position (cm^{-1})	Band origin (cm^{-1})	$R(0)$ intensity at 81K (10^{-23} cm/mol.)
7106.087	7095.6	12.51
7116.135	7105.6	8.74
7119.950	7109.5	8.45
7135.452	7125.0	28.73
7140.937	7130.4	11.78
7157.854	7147.3	13.40
7173.435	7162.9	35.65
7256.735	7246.2	8.35
7291.414	7280.9	1.51

Table 3: Vibrational band origins estimated from the $R(0)$ line positions.



















