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First assignment of the $5\nu_4$ and $\nu_2+4\nu_4$ band systems of $^{12}\text{CH}_4$ in the 6287-6550 cm^{-1} region.

A.V. Nikitin^{1,2}, X. Thomas¹, L. Régalia¹, L. Daumont¹, P. Von der Heyden¹, V.I.G. Tyuterev¹,
L. Wang³, S. Kassir³, A. Campargue³

- ^{1.} *Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 6089, Université de Reims, U.F.R. Sciences, B.P. 1039, 51687 Reims Cedex 2, France*
- ^{2.} *Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, Russian Academy of Sciences, 1, Akademicheskoy Avenue, 634055 Tomsk, Russian Federation*
- ^{3.} *Laboratoire de Spectrométrie Physique (associated with CNRS, UMR 5588), Université Joseph Fourier de Grenoble, B. 87, 38402 Saint-Martin-d'Hères Cedex, France.*

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Correspondence should be addressed to:

ANDREI Nikitin

Institute of Atmospheric Optics

Russian Academy of Sciences

1 av. Akademicheskii,

634055 Tomsk, Russia

E-mail: avn@lts.iao.ru

Tel. 7-382-2-49-17-94 Fax: 7-382-2-49-20-86

Abstract

This paper reports the first assignment of rovibrational transitions of the $5\nu_4$ and $\nu_2+4\nu_4$ band systems of $^{12}\text{CH}_4$ in the $6287\text{-}6550\text{ cm}^{-1}$ region which is usually referred to as part of the $1.6\text{ }\mu\text{m}$ methane transparency window. The analysis was based on two line lists previously obtained in Grenoble by Cavity Ring Down Spectroscopy at $T=297\text{ K}$ and 79 K completed by three long path Fourier Transform Spectra recorded in Reims ($L=1603\text{ m}$, $P=1\text{-}34\text{ mbar}$). In order to determine the dipole transition moment parameters and quantify the intensity borrowing due to the resonance interactions, we had to include in the fit of the effective Hamiltonian model some lines of the stronger $\nu_1+3\nu_4$ and $\nu_2+4\nu_4$ bands. For this purpose, intensities of 179 additional lines were retrieved from FTS spectra above 6550 cm^{-1} though the analysis of these higher bands is not complete. About 1955 experimental line positions and 1462 line intensities were fitted with RMS standard deviations of 0.003 cm^{-1} and 13.4% , respectively. A line list of 8027 calculated and observed transitions which are considered as dominant was constructed for $^{12}\text{CH}_4$ in the $6287\text{-}6550\text{ cm}^{-1}$ region. This is the first high-resolution analysis and modeling of 5-quanta band systems of $^{12}\text{CH}_4$.

1. Introduction

The precise knowledge of the methane absorption in the study of planetary systems, and especially of Titan (Saturn's largest satellite whose atmosphere is mainly composed of nitrogen and methane at temperatures ranging between 70 K and 200 K), is of great importance because it gives access to the determination of the physical properties of these objects [1-3]. The full interpretation of the Titan data returned by the ground-based and space observations is severely limited by the lack of precise knowledge of the methane absorption which dominates the spectrum in the near infrared.

Despite many years of experimental and theoretical studies [4-20], the infrared methane spectrum is still insufficiently understood. In particular, the line-by-line analyses based on the expansion of an effective Hamiltonian and dipole moment, were able to provide precise data reductions only up to 4800 cm^{-1} [10,13,14]. This is because the number of strongly interacting near-degenerate vibration levels increases very rapidly with energy due to the high symmetry of the methane molecule. On the other hand direct variational predictions of methane ro-vibrational lines using *ab initio* potential energy and dipole moment surfaces [15-17] are not at present sufficiently accurate for the assignment of experimental spectra and a calculation of high- J rotational transitions is not yet possible.

Considering the weakness of the absorption of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$, the $6287\text{-}6550\text{ cm}^{-1}$ region studied in this work can be used to detect other planetary species such as CH_3D and CO. A description of the methane absorbance in transparency windows represents a particular difficulty for the theoretical approach because it requires an extrapolation to high- J transitions and because intensities of these weak transitions are extremely sensitive to numerous resonance interactions which are still poorly defined. As already presented in [20], the CH_3D isotopologue contributes significant absorption in the region, complicating any analysis of laboratory spectra using natural methane samples.

Theoretically speaking, in terms of the resonance polyad structure of methane vibration states, the considered spectral range corresponds to the lowest frequency bands of the icosad which are very weak bands in interaction. The complexity of the vibrational structure is illustrated in **Fig. 1**. This scheme shows the vibrational levels $5\nu_4$, $\nu_2+4\nu_4$, $\nu_1+3\nu_4$ splitted into 26 vibrational sublevels. The $5\nu_4$ vibrational system has eight sublevels of A_1 , E, $3F_1$, $3F_2$ symmetry types, the $\nu_2+4\nu_4$ system has 14 sublevels ($2A_1$, $2A_2$, 4E, $3F_1$, $3F_2$) and the $\nu_1+3\nu_4$ system has 4 sublevels (A_1 , F_1 , $2F_2$). The symmetry notations correspond to irreducible representations of the T_d point group [7,19]. The $n\nu_4$ bending overtone levels are the lowest

energy levels of the different vibrational polyads of methane and separate progressively from the remaining part of the polyad due to the high anharmonicity in the ν_4 mode.

Rovibrational transitions from the vibration ground state (GS) to icosad sub-levels form the corresponding absorption band systems. An accurate characterization of these weak absorption features and of their dependence with the temperature is mandatory for the interpretation of various optical measurements at large optical paths. As already stressed, this is particularly important for a remote sounding of the Titan surface [1-3].

Until recently, the only line list available in the literature for the considered transparency window was constructed by Brown from spectra recorded at room temperature by Fourier Transform Spectroscopy (FTS) with path lengths up to 97 meters [5]. In absence of theoretical modeling, this FTS list, adopted in the HITRAN 2004 database [36], was limited to empirical line positions and intensities at room temperature without rovibrational assignments. Another limitation was the lack of sensitivity resulting in relatively high intensity cut off (about 4×10^{-26} cm/molecule).

A considerable improvement has been recently achieved by some of us using two spectra recorded by Cavity Ring Down Spectroscopy (CRDS) at room temperature and at 79 K [20,21]. For the 6289-6526 cm^{-1} region, two lists of 6868 and 4555 transitions with intensities as weak as 1×10^{-29} cm/molecule were constructed from the recordings at 297 and 79 K, respectively. The empirical lower state energy and lower state J'' values were derived from the variation of their line intensities at 297 and 79 K. Although a complete assignment was not provided, the low- J quantum numbers from Ref. [20] provides the temperature dependence of the line intensities and a considerable help in the line identification. In order to complete the review of the previous observations in our region of interest, the results obtained by Deng *et al* [22] in the 6607-6625 cm^{-1} section should be mentioned. These authors used direct absorption with a tunable diode laser and a White cell with a 973 m path length to detect 288 lines with intensities down to 1.4×10^{-27} cm/molecule.

The forthcoming analysis is based on the CRDS line lists of Ref. [20] completed with new long path FTS spectra recorded at 290 K in Reims with a 1603 m pathlength and pressures of 1, 7 and 34 mbar. The paper is structured as follows. In Sections 2 and 3 the experimental setup and recordings of long-path FTS and CRDS spectra are outlined. Section 4 is devoted to the assignment, line position and intensity modelling of the $5\nu_4$ and $\nu_2+4\nu_4$ band systems. We argue about the necessity to consider the coupling with the $\nu_1+3\nu_4$ band to correctly reproduce the measured intensities. Section 5 presents the construction of a synthetic

$^{12}\text{CH}_4$ line list that combines both experimental data and predicted lines. The advantages and shortcomings of the calculated line list as well as possible applications of new data are discussed in the concluding Section 6.

2. Long path FTS spectra and calibration

Several long path spectra of methane at “natural” abundance were recorded in Reims in the 3800 - 8100 cm^{-1} spectral region. The overview of the spectrum in the investigated region is presented in Fig. 2 for three pressure values. As seen in Fig.1, the weak absorption features under study are surrounded by the strongly absorbing regions of the tetradecad and icosad. The prominent 30012-00001 CO_2 band near 6350 cm^{-1} used for calibration purpose falls in the centre of the transparency window.

The spectra were recorded with the Connes' type FTS built in the GSMA laboratory as described in Refs. [23-27]. This spectrometer has been used to perform several high resolution spectroscopic studies of various molecules [28-33]. The maximum optical path difference of 3 meters corresponds to a non-apodized resolution of 0.0017 cm^{-1} . With the recent fitting of this spectrometer to the 50-meter base long White type cell [25], spectra with an absorption path length of 1.6 km can be recorded [34]. The methane spectra were recorded at 1.34, 6.66 and 33.13 mbar (referred to as spectra (a), (b) and (c) respectively in Fig. 2) with a temperature of 290 K. The iris diameter at the entrance of the spectrometer was 3.5 mm.

The pressures were measured with a MKS Baratron capacitance manometer with an uncertainty of 0.01 %. The temperatures were obtained and controlled continuously during the recordings by platinum-resistance thermometers with an uncertainty of 1K. All the spectra were recorded with the following optical setup: a SiO_2 beam splitter, two InGaAs detectors with lenses and windows in BaF_2 . The whole path between the long 50-m White cell and our spectrometer was maintained under vacuum.

For the wavenumber calibration of the spectra (a) and (b), we introduced in the optical path before the entry of the interferometer a cell with a small pressure of CO_2 . The CO_2 pressure was about 1.5 and 20 mbar for the (a) and (b) spectra, respectively. The wavenumber calibration was carried out in two steps. First, the low pressure spectrum (a) was calibrated using 56 lines of CO_2 by Miller and Brown [35] with a standard deviation of $2.18 \times 10^{-4} \text{ cm}^{-1}$. Then medium and high pressure spectra (b) and (c) were calibrated using 22 relatively strong isolated methane transitions of (a) in the region 6300-6700 cm^{-1} with corresponding standard deviations of $2.08 \times 10^{-4} \text{ cm}^{-1}$ and $2.55 \times 10^{-4} \text{ cm}^{-1}$.

Note that the positions in the HITRAN2008 line list [5,36] for 20 of 22 CH_4 transitions

used at this step of the calibration are lower than ours by $5 \times 10^{-4} \text{ cm}^{-1}$. On the contrary the line positions in the recent CRDS line list [20] are in average higher than ours by $6.5 \times 10^{-4} \text{ cm}^{-1}$ for this calibration sample. This comparison was only carried out in the $6400\text{-}6507 \text{ cm}^{-1}$ range where lines were strong enough and mostly free of CH_3D lines. It was found that the intensities from FTS was 10% lower than CRDS intensities. So the FTS intensities were adjusted by a factor of 1.1.

3. Cavity Ring Down Spectroscopy.

Spectra at room temperature

As presented in Ref. [37], the CW-CRDS spectra at room temperature (RT) were recorded over the whole methane transparency window ($6165\text{-}6750 \text{ cm}^{-1}$) with the fibered distributed feedback diodes (DFB) laser CW-CRDS spectrometer developed in Grenoble. The present analysis considers only the $6275\text{-}6525 \text{ cm}^{-1}$ section of the recordings. The reader is referred to Refs. [37-39] for the description of the experimental apparatus. The $6275\text{-}6525 \text{ cm}^{-1}$ region was continuously covered with the help of 10 fibered DFB lasers and about 60 minutes were needed to complete a temperature scan of one DFB laser. The corresponding noise equivalent absorption is on the order of $5 \times 10^{-10} \text{ cm}^{-1}$ [37].

Spectra at 80 K

The cryogenic cell specifically developed for CW-CRDS at low temperature has been described in Refs. [11,12,40]. It is based on an original design (see Fig. 1 of Ref. [40]) which dispenses with an external vacuum jacket by exploiting the fact that a low pressure sample constitutes itself a good thermal insulation. A Mode by Mode CRDS acquisition scheme was preferred instead of the usual piezoelectric actuator that modulates the optical cavity length in standard CW-CRDS [40]. Using mirrors with 99.992% reflectivity, a noise equivalent absorption of $3 \times 10^{-10} \text{ cm}^{-1}$ was obtained.

The gas temperature in the cryogenic cell was calculated to be 82.6 K from the Doppler profile of several dozen lines [40], in good agreement with the rotational temperature (79.3 K) evaluated from the intensity distribution of the $3\nu_2$ band of CH_3D [20]. During the scanning, the pressure, measured by a capacitance gauge and the ringdown cell temperature were monitored. The room temperature value was $297 \pm 2 \text{ K}$ and most of the RT spectra were recorded at 3.3 and 13 mbar, as presented in Ref. [37]. The LNT spectra were recorded at 1.3, 6.5 and 13 mbar.

Each 35 cm^{-1} wide RT spectrum recorded with one DFB laser was calibrated independently on the basis of the wavelength values provided by the Michelson-type

wavemeter. The wavemeter accuracy being limited to $3 \times 10^{-3} \text{ cm}^{-1}$, the absolute calibration was obtained by using reference line positions of methane obtained either from the HITRAN database [36] or from the FTS spectrum. The precision of the obtained wavenumber calibration estimated from the dispersion of the wavenumber differences is $1 \times 10^{-3} \text{ cm}^{-1}$. Each 80 K spectrum was then calibrated by statistically matching the line positions to those of the corresponding RT spectrum.

Fig. 3 shows a comparison of the CW-CRDS spectra at RT and 80 K near 6494 cm^{-1} . The achieved sensitivity reveals the considerable spectral congestion of the spectra and the dramatic change induced by cooling. The multiline fitting procedure used to derive the line intensities and the construction of the line lists at RT and 80 K have been described in Refs. [20,21].

4. Line position and line intensity modelling

The theoretical analysis was performed within the global effective Hamiltonian approach using the polyad vibration extrapolation scheme reviewed in [7]. The formalism of irreducible tensor operators developed in a series of works by the Dijon group and collaborators [7, 19 and references therein] allows fully account for molecular symmetry properties. The major advantage of this method is that all the terms and corresponding constants obtained in the previous analyses of the lower polyads (GS in microwave and THz regions, dyad in the $1100\text{-}1800 \text{ cm}^{-1}$ region, pentad in the $2300\text{-}3300 \text{ cm}^{-1}$ region, octad in the $3500\text{-}4700 \text{ cm}^{-1}$ region, tetradecad in the $4800\text{-}6200 \text{ cm}^{-1}$ region) are directly involved in the icosad calculations. The version of the rovibrational tensors coupling corresponds to that defined in our previous **work** [41] and the line positions and intensities **analyses** were performed using the MIRS software described in [42].

The polyad structure of the methane molecule is essentially governed by the quasi coincidence of the stretching fundamental frequencies with the first overtones of the bending frequencies $\nu_1(A_1) \approx \nu_3(F_2) \approx 2\nu_2(E) \approx 2\nu_4(F_2)$. The polyads P_n are defined by an integer n expressed in terms of the principal vibrational quantum numbers as $n=2(\nu_1+\nu_3)+\nu_2+\nu_4$. Reduced vibrational energy diagram of the methane molecule is plotted in Fig. 1. The partially transformed ro-vibrational hamiltonian adapted to the polyad structure of the CH_4 molecule is expressed as:

$$H = H_{\{GS\}} + H_{\{Dyad\}} + H_{\{Pentad\}} + H_{\{Octad\}} + H_{\{Tetradecad\}} + H_{\{Icosad\}}$$

where the subsequent terms correspond to the successive polyads with increasing vibrational energies. Each group contains a series of terms identified by rotational, vibrational and

symmetry indices [7] according to the general nomenclature $t_{n_1 n_2 n_3 n_4 m_1 m_2 m_3 m_4}^{\Omega_r(K,kC)} T_{n_1 n_2 n_3 n_4 m_1 m_2 m_3 m_4}^{\Omega_r(K,kC)}$, where T designated a tensor operator and t the corresponding adjustable parameters.

As a preliminary approach, the $5\nu_4$ band system and the lower sub bands of $\nu_2+4\nu_4$ can be considered “separately” from all the other icosad bands, except for $\nu_1+3\nu_4$. This is because the ratio of the specific polyad interaction terms to the energy gap between $n\nu_4$ and other states gradually decreases with the polyad number [7]. This approximation does not mean that the corresponding upper vibration states are treated as isolated ones: within the polyad extrapolation scheme, the $\{5\nu_4, (\nu_2+4\nu_4)\}$ coupling comes from operators specific to the dyad and the $\{5\nu_4, (\nu_2+4\nu_4), (\nu_1+3\nu_4)\}$ couplings come from the operators specific to the pentad. Note that we were able to achieve a satisfactory fit of the line positions in our spectral range without including higher-order resonance terms specific to the icosad part of the Hamiltonian.

Although the vibration extrapolation scheme provides a systematic way to expand the effective Hamiltonian and dipole moment, it is well-known that the accuracy of extrapolations from lower to higher polyads is not sufficient for a direct assignment of complicated rovibrational methane spectra. Moreover, despite considerable progress in previous methane analyses [4,7,8,9,13,14] not all coupling parameters of lower polyads are well determined. In particular, the assignments and parameter determinations of the tetradecad are not yet fully completed. For this reason in the present work, we used a limited model dedicated to the assignment of the lowest states of the icosad. As an initial iteration, the octad $^{12}\text{CH}_4$ model of [13] was used, with an addition of 132 parameters [18] specific to the tetradecad. Finally only four new diagonal vibration operators specific to the $\nu_1+3\nu_4$ system of the icosad were included in our model. **We have proceeded then by successive iterations including rovibrational extrapolations to $5\nu_4$, $\nu_2+4\nu_4$ and $\nu_1+3\nu_4$ bands, combination differences determination for observed lines and parameter fitting involving low J values.** The simultaneous use of cold ($T= 80\text{K}$) and room temperature spectra as well as the discrimination of CH_3D transitions from the line list of [20] have considerably facilitated the assignment which however proved to be very laborious. We were able finally to assign and include in the fit 1955 lines up to $J = 15$.

In order to stabilize the lower order parameter optimization, the experimentally known energy levels [13] of the dyad up to $J=19$, of the pentad up to $J=16$ and of the octad up to $J=12$ were also included in the fit. This limited model is not suitable for the description of the tetradecad, especially for its middle part between 5475 and 5750 cm^{-1} . In spite of this imperfection, our model describes satisfactorily the lowest $5\nu_4$ and $\nu_2+4\nu_4$ icosad band

systems and permitted us to make reliable assignments to most of the relatively intense $^{12}\text{CH}_4$ transitions in the 6287-6550 cm^{-1} region.

Detailed statistics of the fit of line positions and intensities are given in Tables 1 and 2 for the $5\nu_4$ and $\nu_2+4\nu_4$ band systems, respectively, ranked by upper state vibration sub-levels.

The maximum upper-state rotational quantum number included in the fit of line positions and line intensities is $J = 15$.

The $5\nu_4$ vibration sublevels included in Table 1 are the first accurate experimental determination of $^{12}\text{CH}_4$ levels with a total vibrational excitation $V=5$. Note that the theoretical predictions of these sub-levels from the best published *ab initio* potential function [17] lead to up to 20 cm^{-1} discrepancies compared to our $J=0$ values. These new information can be useful for a further improvement of potential energy surfaces and theoretical models.

Among the limitations of our analysis, we mention that some higher J values could be perturbed by other icosad states lying above 6800 cm^{-1} not considered in this work. In addition, the experimental room temperature spectrum could include hot bands which are completely unknown in this range.

Even if the $5\nu_4/\nu_2+4\nu_4$ and $5\nu_4/\nu_1+3\nu_4$ resonance couplings are relatively small, the resulting intensity borrowings are sufficient to greatly perturb the intensities of the $5\nu_4$ system because the $5\nu_4$ band is much weaker than the nearby $\nu_2+4\nu_4$ and $\nu_1+3\nu_4$ bands. The $\nu_1+3\nu_4$ band system being the strongest in the 6300-6800 cm^{-1} region, it was necessary to fit selected line intensities of this band as well, though it is beyond the range of our calculated line list described in the next section. We have thus taken these couplings into account for a realistic intensity modelling of $5\nu_4$ and $\nu_2+4\nu_4$. The fitted values of the vibrational effective dipole transition moment parameters of the $\{5\nu_4, \nu_2+4\nu_4, \nu_1+3\nu_4\}$ interacting system are listed in Table 3. These values was defined from simulation least-square fit of 9 vibrational and 18 (from 22) rotational $R_1(1,F_1)$ dipole moment parameters of the $\{5\nu_4, \nu_2+4\nu_4, \nu_1+3\nu_4\}$ interacting system.

5. Methane line list between 6287 and 6550 cm^{-1}

A major difficulty of the analysis results from the very high density of rovibrational transitions. The superposition of five-quanta excited bands of a five atom tetrahedral molecule leads to a very high density of lines (about 25 lines/ cm^{-1} in the CRDS spectrum at room temperature [20, 21]). The spectral resolution of nearly coincident transitions is frequently hampered by the Doppler broadening leading to some uncertainties in purely empirical line parameter determination. The theoretical calculations described above are particularly

valuable in those situations as they may allow identifying the various components contributing to a blended line. This is the case when the number of nearby calculated lines is higher than the number of components obtained from the empirical line list (see **Fig. 4** for instance). Thanks to this additional theoretical information we re-determined experimental line parameters at about 30 blended absorption features using a profile fitting routine. The primary aim of such modification was not a systematic improvement of the empirical line list [20] but to extend the assignments. According to the improved calibration we also lowered all empirically determined line positions of Ref. [20] by 0.00065 cm^{-1} . We shall refer to the obtained modified line list as the “corrected” empirical CRDS list.

The experimental methane spectrum in the $6287\text{-}6550 \text{ cm}^{-1}$ region contains contributions of the $^{12}\text{CH}_4$, CH_3D and $^{13}\text{CH}_4$ isotopologues. A detailed theoretical analyses of the CH_3D [43, **add 3v2**] and $^{13}\text{CH}_4$ [44, **add Lulin**] isotopologues is not complete in the region and a rigorous extrapolation is not yet possible. The determination of the CH_3D lines in the CRDS list of methane was performed in Ref. [20] on the basis of a FTS spectrum of CH_3D recorded separately. CH_3D has been found to contribute to the total absorbance by as much as 25 % in some spectral intervals of the room temperature spectrum [20, 21]. A rough estimation for the $^{13}\text{CH}_4$ spectrum can be obtained by shifting the $^{12}\text{CH}_4$ line positions down to 37 cm^{-1} for $5\nu_4$ and 29 cm^{-1} for $\nu_2+4\nu_4$ [45] and by scaling the absorbance according to the $^{13}\text{C}/^{12}\text{C}$ abundance ratio (1.1 %).

Both pure empirical and theoretical line lists have their own advantages. For some applications, the knowledge of fully assigned upper state transition is preferable (see Conclusion). The theoretical list provides this assignment and helps resolving some ambiguities for closely lying transitions, but it is limited to the $^{12}\text{CH}_4$ main isotopologue and does not account for hot bands and very high J transitions.

The positions in the calculated line list are less precise and the accuracy of calculations is not “homogeneous”. As the coupling with other icosad bands is not fully implemented in the model, the error of calculations increases with rotation quantum numbers. We considered various cut-off in J for the line list generation. For $T = 80 \text{ K}$, our calculations are in a very good agreement with the observed CRDS data and the $J = 10$ cut-off is sufficient to characterise more than 99% of the observed $^{12}\text{CH}_4$ absorbance at room temperature. For the room temperature spectra, the integrated intensity of all predicted lines in the $6350\text{-}6500 \text{ cm}^{-1}$ region is $1.2 \times 10^{-23} \text{ cm/molecule}$, while integrated intensities of transitions with $J_{upper} = 15$ and 16 are 8.7×10^{-26} and 4.4×10^{-26} , respectively. Then, the total intensity contribution of $J = 15$ and $J = 16$ lines is 0.7% and 0.3%, correspondingly. For this reason, a $J_{upper} = 15$ cut-off was

chosen for the calculated line list at room temperature. Though the RMS deviation for the total of 1955 transitions included in the fit was 0.003 cm^{-1} , the predicted positions of some $\nu_2+4\nu_4$ lines with $J > 12$ and intensities less than 4×10^{-27} could be shifted by up to 0.1 cm^{-1} compared to the observations [20].

Depending on the spectral interval, various bands and isotopologues can provide major contributions at different temperatures. The $6287\text{-}6550 \text{ cm}^{-1}$ region was divided in four sections (L1-L4) limited as indicated in **Fig. 5**:

(a) List L1: $6287\text{-}6350 \text{ cm}^{-1}$.

In this spectral interval, there are many lines which do not belong to the $5\nu_4$, $\nu_2+4\nu_4$ band systems. Moreover, the contribution of CH_3D is strong [20, 21] in this region that considerably complicates the assignment and theoretical modeling of $^{12}\text{CH}_4$ lines. This is why we prefer the experimental CRDS list at room temperature [20] with the corrections described above and some identifications added.

(b) List L2: $6350\text{-}6500 \text{ cm}^{-1}$.

As most of the lines of in this spectral interval belong to the $5\nu_4$ and $\nu_2+4\nu_4$ band systems of $^{12}\text{CH}_4$, theoretical predictions are rather complete and we provide the results of our calculations. An advantage of predicted transitions is related to very high density of $5\nu_4$ lines, thus one observed absorption feature could result of a superposition of several calculated lines with different assignments. This is important for correct extrapolations to other temperature and pressure conditions. Rare calculated high- J transitions of $\nu_1+3\nu_4$ falling in this interval with a total intensity contribution of $2.3 \times 10^{-25} \text{ cm/molecule}$ were removed because the assignment of the corresponding experimental lines is not yet available, being beyond the scope of the present paper. For completeness we added about 67 unassigned experimental lines from Ref. [20] with total intensity contribution 2.9×10^{-25} which probably belong to high- J transitions of $\nu_1+3\nu_4$ band of $^{12}\text{CH}_4$ or to $^{13}\text{CH}_4$.

(c) List L3: $6500\text{-}6525 \text{ cm}^{-1}$.

Similarly to L1, we provide a corrected experimental CRDS list [20] with some identifications added. In this range and in the following L4 range, a large fraction of lines doesn't belong to $5\nu_4$ and $\nu_2+4\nu_4$ and could not be assigned.

(d) List L4: $6525\text{-}6550 \text{ cm}^{-1}$.

The upper limit of the line list attached to Ref. 20, being 6525 cm^{-1} , we used the FTS line list from Reims measurements with a $2 \times 10^{-28} \text{ cm/molecule}$ intensity cut-off. The line

intensities were obtained by a line profile fitting Spectro-Plot routine. This range could also contain some CH₃D and ¹³CH₄ lines which are not yet assigned.

As for L1, the two last intervals based on experimental determinations contain also high-*J* lines which are perturbed by resonance interactions with upper icosad bands and are difficult to predict precisely.

The global ¹²CH₄ line list in the 6287-6550 cm⁻¹ region is given in Electronic Supplementary Materials: Appendix A. Table 4 gives a sample of the line list.

As complementary information, we also give in Appendices B and C some experimental FTS transitions in the 6256-6287 and 6550-6788 cm⁻¹ regions, respectively, used for the construction of our theoretical model. These complementary lists B and C (in the same format as Appendix A) are not complete: they contain only 179 assigned lines used to stabilize the determination of model interaction parameters; the upper range includes also some $\nu_1+3\nu_4$ lines. Though this band is beyond the scope of the present work, this was necessary to describe an intensity borrowing for the $5\nu_4$, $\nu_2+4\nu_4$ band systems under study (see above). In the 6717- 6788 cm⁻¹ region, for the assignments of these lines, we used the empirical low *J* values determined in Ref. [46]. These auxiliary line lists are separated from the principal one (A) because they only contain needed selected lines and a systematic measurements of all lines in these ranges were not a purpose of this work. All the line intensities are given at 296 K since the 6 K difference between the different experimental spectra leads to intensity corrections that are below the experimental accuracy of the FTS measurements.

The isotopic number given in the first column of the line list may be wrong because some experimental lines could be blended or belong to isotopologues of methane (see notes of Table 4 for more details).

The good agreement between the experimental spectra and the calculations is illustrated in **Figs. 6-8**. Fig. 6 shows a comparison with the FTS spectrum while Fig. 7 and 8 show a comparison with the CRDS spectrum and line list at 80 K and 296 K, respectively.

6. Conclusion

The major aim of this study was the first assignment of the $5\nu_4$ and $\nu_2+4\nu_4$ band systems and a contribution to the construction of a ¹²CH₄ line list in the 1.6 μm methane transparency window for astrophysical and planetary applications. This task was very challenging as it

represents the first rather complete high-resolution analysis and modeling of 5-quanta band systems in $^{12}\text{CH}_4$. We were able to assign 1955 rovibrational transitions belonging to 26 sub-bands of $^{12}\text{CH}_4$ corresponding to the $5\nu_4$, $\nu_2+4\nu_4$ and $\nu_1+3\nu_4$ band systems. All these line positions and 1462 line intensities were included in the fit using the model described above with RMS standard deviations of 0.003 cm^{-1} and 13.4%, respectively. This resulted in a predicted line list (L2) for the **6350-6500** cm^{-1} region that contained more than 5000 transitions up to $J = 15$. The use of low temperature CRDS spectra at $T=79\text{ K}$ was very useful for the assignment and modeling as this allowed much easier identification of low- J transitions at the first step of the analysis. In Ref. [20], the so called “two temperature method” was used to determine the empirical values of the lower state rotational number from the ratio of the line intensities measured at room temperature and at 80 K. In **Fig. 9**, we present the histogram of the differences between the approximate empirical determinations of low- J values attached to the room temperature line list of Ref. [20] and the J values theoretically determined in this study. This comparison was obtained from an automatic association of the lines whose calculated and measured centers coincide within $5\times 10^{-3}\text{ cm}^{-1}$. About 87 % of the rounded empirical J values of the lower state are found to coincide with their theoretical values, illustrating the reliability of the two temperature method.

The use of new long-path FTS spectra provided complementary information particularly for the calibration and for lines beyond the interval reported in Ref. [20]. This information helped for the theoretical determination of the intensity borrowing due to the resonance coupling with higher lying icosad bands.

The line list given in the Electronic Appendix A in the $6287\text{-}6500\text{ cm}^{-1}$ region contains predicted transitions for $5\nu_4/\nu_2+4\nu_4$ band systems completed with experimental CRDS transitions from [20] **(see Fig. 5)** which were not assignable to these bands. It contains (obs.-calc.) values for positions and intensities for all cases where experimental line parameters were possible to extract from observations.

The reason for such mixed format of our line list is the following. On the one hand it would be desirable for applications that the list would be as complete as possible and contain all available information. On the other hand a full assignment when available would be useful in the future to include pressure broadening and shift parameters as well. The m quantum number appearing in the upper state assignment is involved in various models for the broadening coefficient interpolation [47-53]. Though the N_2 , O_2 and self broadening

coefficients were not yet measured for the $5\nu_4 / \nu_2+4\nu_4$ bands one could use for their modelling in a first approximation the results of [47-53] relative to the lower polyads.

Suitability for using the empirical line list [20] or our combined line list given in Appendix A depends on required applications. The predicted line list is not recommended for applications which are very sensitive to line position precisions at relatively high temperatures, where high J transitions and also hot bands are involved. On the contrary for low resolution and/or low temperature applications, for example in typical measurements conditions in Titan atmosphere, our synthetic $^{12}\text{CH}_4$ line list in the 6350-6500 cm^{-1} region could be preferable because it contains more information on upper state assignments that can be useful for line shift and broadening models. It should be completed by isotopic lines from other sources when available. For example, CH_3D lines can be taken from Refs. [20, 21].

This work allowed a first accurate determination from experimental spectra of 8 vibrational sublevels given in Table 2 that can be used for a validation and improvement of the methane potential function. The effective Hamiltonian model employed in this work was designed to partly describe the lower edge bands $5\nu_4 / \nu_2+4\nu_4$ of the $^{12}\text{CH}_4$ icosad in the 6287-6550 cm^{-1} range. This “pragmatic” model is undoubtedly an approximation because we did not have all needed information on a huge bulk of remaining assigned isocad levels extending to higher energies up to 7600 cm^{-1} . We thus do not claim that this model could serve for a global modelling of all lower polyads (particularly of all octad and tetradecad transitions). In order to build a global effective Hamiltonian model relying on successive vibration polyad extrapolations [7], one should first considerably improve the tetradecad analysis [8] which is far from being completed.

One of “weak points” of our limited model is a poor description of the $\nu_1+3\nu_4$ sub-bands, which are in fact beyond the scope of this study, but are just above the studied $5\nu_4 / \nu_2+4\nu_4$ band systems. The higher- J $\nu_2+4\nu_4$ levels which are close to the $\nu_1+3\nu_4$ levels can be perturbed by resonance interactions; the $\nu_1+3\nu_4$ levels are in turn perturbed by other higher energy icosad states and so on. For a realistic description of these successive bands a full rovibrational assignment and analysis of the entire icosad system would be necessary. We hope that the present study constitutes a first step towards this extremely challenging goal.

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Table 1: Detailed fit statistics for the 5v₄ band system.

Vibrational sublevels and ranking number	Calculated Vibration Energy	Number of fitted line positions	St.Dev (10 ⁻³ cm ⁻¹)	Number of fitted line intensities	St.Dev (%)
F ₂ 1	6377.526	192	2.59	144	13.0
A ₁ 1	6405.965	76	2.50	54	14.1
F ₁ 1	6429.239	213	2.35	161	13.2
F ₂ 2	6450.059	270	2.39	207	12.7
E 1	6507.389	113	2.27	85	13.4
F ₂ 3	6507.553	182	2.13	129	13.7
F ₁ 2	6529.777	181	2.42	137	13.5
F ₂ 4	6539.180	204	2.61	158	13.6
Total		1441	2.40	1075	13.4

Note:

The different columns are: the vibrational sub-level / symmetry type, the corresponding band origin ($J=0$), the number of fitted rovibrational line positions, the corresponding RMS standard deviation, the number of fitted intensities and the corresponding RMS standard deviation.

Table 2: Detailed fit statistics for the $\nu_2+4\nu_4$ band system

Vibrational sublevel and ranking number for $J=0$ in the icosad	Number of fitted line positions	St. Dev (10^{-3} cm^{-1})	Number of fitted line intensities	St. Dev (%)
E 2	27	4.4	20	13.7
A ₁ 2	18	3.9	14	14.4
F ₁ 5	28	4.0	20	13.6
F ₁ 3	67	4.0	50	13.7
E 5	42	4.1	30	13.7
A ₁ 3	12	4.0	8	13.4
F ₁ 4	45	3.7	33	13.5
A ₂ 1	10	3.8	7	13.7
E 3	30	4.3	23	14.2
F ₂ 7	54	3.7	40	12.7
F ₂ 5	44	4.5	33	14.1
A ₂ 2	21	3.6	16	13.4
E 4	34	3.9	25	13.7
F ₂ 6	69	3.9	53	12.7
Total	501	4.0	372	13.6

Note:

The different columns are: the vibrational sub-level / symmetry type, the corresponding band origin ($J=0$), the number of fitted rovibrational line positions, the corresponding RMS standard deviation, the number of fitted intensities and the corresponding RMS standard deviation.

Table 3.

Principal dipole transition moment parameters for the $\{5\nu_4 / \nu_2+4\nu_4 / \nu_1+3\nu_4\}$ interacting band system

Vibrational Dipole Transition Moment Parameters	Value (in 10^{-6} Debye)
$\nu_1+3\nu_4$ (F ₂ 9)	280
$\nu_1+3\nu_4$ (F ₂ 8)	30
$\nu_2+4\nu_4$ (F ₂ 7)	-48
$\nu_2+4\nu_4$ (F ₂ 5)	27
$\nu_2+4\nu_4$ (F ₂ 6)	97
$5\nu_4$ (F ₂ 2)	-8.8
$5\nu_4$ (F ₂ 1)	27
$5\nu_4$ (F ₂ 4)	12
$5\nu_4$ (F ₂ 3)	6.3

**Table 4: Sample extracted from the line list attached as Electronic Supplementary data
Calculated and observed methane transitions in the 6287-6550 cm⁻¹ region.**

Iso	Sc	ν_0 cm ⁻¹	$S^\circ(296K)$ cm/molec	Rotational assignment		Obs- calc 10 ⁻³ cm ⁻¹	$\frac{S^\circ_{\text{obs}}}{S^\circ_{\text{cal}}}$ %	Vibrational assignment Upper	E'' cm ⁻¹
				Lower state	Upper state				
61		6349.43005	4.43e-29						
61		6349.53345	9.00e-28	9 ^a					
61		6349.56265	2.89e-26	0 9 A ₂ 1	5 8 A ₁ 8	0.77	-5.5	0005 F ₂	470.872
60		6349.58485	5.88e-28						
60		6349.61845	2.47e-28						
61		6349.64025	7.61e-28						
61		6349.66795	2.64e-27	0 8 F ₁ 2	5 7 F ₂ 18	-0.56	-3.4	0005 F ₂	376.804
61		6349.73955	9.67e-27	0 8 F ₁ 1	5 7 F ₂ 18	-1.10	-7.3	0005 F ₂	376.733
60		6349.77865	8.98e-28						
61		6349.81595	3.20e-28						
61		6349.89725	6.61e-28						
61		6349.92855	8.34e-28						
61		6349.96545	2.21e-28						
61	PR	6350.07866	2.24e-26	0 6 F ₂ 2	5 5 F ₁ 10	-1.59	-0.0	0005 F ₂	219.936
61	PR	6350.10037	1.96e-27	0 6 F ₂ 1	5 5 F ₁ 10	-1.17	26.3	0005 F ₂	219.915
61	PR	6350.12762	1.15e-28	0 14 F ₁ 1	5 13 F ₂ 61			0005 F ₁	1095.632
61	PR	6350.18216	2.04e-28	0 11 F ₂ 2	5 12 F ₁ 5			0005 F ₂	689.876

Notes: *in this table, the columns are:*

1. ISO: isotopologues: 61 for ¹²CH₄ and 60 might be ¹²CH₄, CH₃D or ¹³CH₄. In the L1, L3 and L4 ranges, the lines marked with ISO = 61 could include some contributions from blended lines of other isotopologues (except for CH₃D in case of L1,L3).
2. Sc: means type of source: PR means predictions, R means Reims FTS origin, blank corresponds to the CRDS data of Ref. [20].
3. ν_0 : line positions; except for PR type calculated lines, these are experimental data.
4. $S^\circ(296K)$: line intensities; except for PR type calculated lines, these are experimental data.
5. Lower rovibrational assignment are given by the vibrational polyad number P, the rotational quantum number J, the rovibrational symmetry type S (Td irreducible representation) and the ranking vibration sublevel number α .
6. Upper rovibrational assignment in the same format.
7. Fo-Fc is the difference between observed and calculated line position included in the fit in 10⁻³ cm⁻¹ units. These values appear for assigned lines only.
8. Io-Ic % is the relative difference between observed and calculated intensities included in the fit. These values appear for assigned lines if their intensity was included in the fit.
9. The vibrational band assignment: contains the principal vibrational quanta ($\nu_1, \nu_2, \nu_3, \nu_4$) and vibrational symmetry type Sv (Td irreducible representation).
10. $E'' = E_{\text{low}}$: lower energy value when available [in cm-1].

^aIn case where only J_lower is given, this is determined empirically from a Boltzman populations at two temperatures [20]

Figure Captions

Fig. 1

Scheme of vibrational level patterns of methane polyads (a), and of vibration sublevels of the lower icosad edge (b) corresponding to rovibrational bands analyzed in this work. At the right hand side panel, the principal vibration quantum numbers, symmetry types (T_d irreps) of vibration sublevels and vibrational ranking numbers within the icosad are given.

Fig. 2

Overview of the FTS Reims spectra ($L=1603$ m, $T = 289.6$ K) at three methane pressures (a) 1 mbar (b) 7 mbar (c) 34 mbar. The CO_2 band near 6350 cm^{-1} was used for calibration purpose.

Fig. 3

Comparison of the CW-CRDS spectrum of methane recorded at room temperature (upper panel) and 80 K (lower panel) near 6494 cm^{-1} . The sample pressure was 1.3 mbar. Note the considerable change of the line intensities depending on the low energy value of the transition.

Fig. 4

Examples explaining corrections required to improve the experimental CRDS line list accounting for our assignments. (a) calculated line list of $^{12}CH_4$, (b): CRDS line list of Ref. [20], (c) CRDS spectrum $T=296$ K, (d) CRDS spectrum $T=80$ K. One CH_3D transition is marked with a star (*) on the panel (b). Assignment notation: *Lower rovibrational assignment are given by the vibrational polyad number $P(GS=0)$, the rotational quantum number J , the rovibrational symmetry type S (T_d irreducible representation) and the ranking vibration sublevel number α . Upper rovibrational assignment in the same format but vibrational polyad number $P(Icosad=5)$.*

Fig. 5.

Overview of the line lists provided as Supplementary Material. The line list is divided in four sections which were constructed differently: L1 and L3 are based on the room temperature line list of Ref. 20, L2 is the calculated line list obtained in this work from the theoretical model and L4 is based of the present FTS measurements.

Fig. 6

Comparison of the spectrum of methane at 296 K near 6460 cm^{-1} :

Upper panel: calculated line list of $^{12}CH_4$

Lower panel: FTS spectrum 33mbar

The CH_3D transitions with intensities larger than 1×10^{-26} cm/molecule are marked with a star

Fig. 7

Comparison of the spectrum of methane at 80 K near 6400 cm^{-1} :

Upper panel: CRDS spectrum ($P= 1.3$ mbar)

Middle panel: CRDS line list of Ref. [20]

Lower panel: calculated line list of $^{12}CH_4$

The CH_3D transitions with intensities larger than 1×10^{-26} cm/molecule are marked with a star (*) on the two upper panels.

Fig. 8

Comparison of the spectrum of methane at 296 K near 6440 cm^{-1} :

Upper panel: CRDS spectrum ($P= 13\text{ mbar}$)

Middle panel: CRDS line list of Ref. [20]

Lower panel: calculated line list of $^{12}\text{CH}_4$

Fig. 9

Histogram of the differences between the J values and the corresponding empirical values obtained in Ref. [20] from the temperature dependence of their line intensities.

The comparison applies to the 836 lines whose calculated and measured line centres coincide within $5\times 10^{-3}\text{ cm}^{-1}$.

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