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Assignment and modeling of $^{13}\text{CH}_4$ spectrum at 298 K in the lower part of the Tetradecad in the 4970–5300 cm^{-1} range

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Highlights:

1. Analyzed a high resolution $^{13}\text{CH}_4$ absorption spectrum at 298 K in the 4970-5300 cm^{-1} region.
2. Theoretically modelled 1548 line positions to an *rms* of 0.0017 cm^{-1} .
3. Successfully fit 674 experimental line intensities to an *rms* of 7%.
4. Assigned and compiled experimental and theoretical line lists at 296 K.

Keywords: methane; $^{13}\text{CH}_4$; absorption spectroscopy; spectra analyses; effective Hamiltonian; low Tetradecad; variational calculations; HITRAN

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Abstract

The absorption spectrum of the $^{13}\text{CH}_4$ methane isotopologue was recorded on a Bruker IFS-125HR Fourier transform spectrometer at 298 K in the 4970-6200 cm^{-1} range. In this paper we report the results of assignment and modelling of the line positions and intensities of $^{13}\text{CH}_4$ in the range of weaker absorption between 4970 and 5300 cm^{-1} , corresponding to the lower part of Tetradecad, dominated by the $4\nu_4$ band system near 5180 cm^{-1} . The empirical list in this spectral range contains 1642 lines. Using an effective Hamiltonian initially derived from the analyses of cold Fourier transform (4970-5853 cm^{-1}) and laser direct absorption (5853-6200 cm^{-1}) spectra of the $^{13}\text{CH}_4$, we assigned 1600 lines belonging to four bands of the Tetradecad up to $J_{\text{max}}=16$. The 1548 line positions were fitted with an *rms* deviation of 1.7×10^{-3} cm^{-1} . Measured line intensities were modeled for 674 transitions using the effective dipole transition moments to an *rms* deviation of about 7 %. The new data were used for the simultaneous global fit of the $^{13}\text{CH}_4$ Hamiltonian parameters for the {Ground state / Dyad / Pentad / Octad / Tetradecad} system and the dipole moment parameters for the {Ground state - Tetradecad} system.

1. Introduction

Methane is one of the ubiquitous species in diverse celestial objects in the wide temperatures from comets, planets, exoplanets and their systems. Exact knowledge of the methane spectroscopy is crucial in the study of planetary atmospheric systems [1-4], since its spectral characteristics are used to determine their physical and chemical properties as well as their evolutionary tracts when it is combined with the isotopic data. Detailed spectroscopy characterization on the methane at higher temperatures (up to 1500 K) provides useful information needed to interpret the atmospheres of exoplanets and brown dwarfs [5-9], for which the ^{13}C -enriched methane also provide additional complementary information as well. Among them, the temperature dependence of its line intensities is urgently needed for accurate atmosphere opacity calculations as part of the atmospheric remote sensing of both cold and hot planets.

Additionally, methane is a greenhouse gas for the Earth's atmosphere [10], hence requiring accurate measurements of temperatures and concentrations to understand climate change in the Earth's atmosphere [11-15]. However, it is not only the main isotopologue of methane ($^{12}\text{CH}_4$) that is of scientific interest, but also its other isotopic species, including $^{13}\text{CH}_4$. In particular, knowledge of the relative content of the methane isotopic ratio ($^{13}\text{C}/^{12}\text{C}$) and its temporal variations in different parts of the atmosphere will help to determine whether the increase of atmospheric methane is due to natural causes or anthropogenic factor [12,13,15].

Analyses of high-resolution methane spectra have been the subject of numerous studies for $^{12}\text{CH}_4$ [16-31] and for other isotopologues [32-39] (and references therein). Ro-vibrational interactions in spherical top molecules split some degenerate levels in sub-levels, giving rise to complicated spectral patterns due to near coincidences of vibrational frequencies. The infrared spectra of both $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ are partitioned in several spectral ranges corresponding to the polyads of strongly coupled bands and sub-bands as reviewed in [40]. This includes Dyad (2 bands), Pentad (5 bands, 9 sub-bands), Octad (8 bands, 24 sub-bands), Tetradecad (14 bands, 60 sub-bands) and so on.

The analyses of the $^{13}\text{CH}_4$ bands up to the Octad range (below 4740 cm^{-1}) have been reported in the previous works [32,33,38,39] and incorporated in the spectroscopy databases [41-43] partly accessible via the European VAMDC portal [44]. $^{13}\text{CH}_4$ lines in the upper part of Tetradecad were previously recorded and identified from the natural methane spectra recorded with the support of the GOSAT mission [45]. The identification of $^{13}\text{CH}_4$ lines was achieved for several hundred strong lines using isotopic shift predictions [46].

In our previous studies during the last a few years we have identified and assigned all the 60 sub-bands of the Tetradecad in cold conditions from the combined analyses of the JPL FTS spectra recorded at 80 K in the $4970\text{--}5850\text{ cm}^{-1}$ [47,48] and the laser direct absorption spectra (DAS) at 80 K recorded in Grenoble [49] between 5853 and 6201 cm^{-1} . The analyses up the upper part of $^{13}\text{CH}_4$ Tetradecad was also accomplished using DAS spectra at 296 K, and the corresponding line parameters have been included in the HITRAN2016 [50]. However, experimentally based room-temperature data for the lower Tetradecad range of $^{13}\text{CH}_4$ are not yet available in the existing spectroscopic databases [41-43,51]. To our knowledge, the only currently available line lists of $^{13}\text{CH}_4$ at 296 K in this spectral interval were based on *ab initio* variational predictions [52,53] accessible via TheoReTS information system [54].

To fill this gap in this work, we focus on the ro-vibrational assignment of high-resolution room-temperature $^{13}\text{CH}_4$ spectrum of the lower part of the Tetradecad: $4970\text{--}5300\text{ cm}^{-1}$. In **Fig. 1**, a comparison of the $^{13}\text{CH}_4$ Tetradecad line lists available in the HITRAN2020 [42] to the principal isotopologue of methane is shown, where the contribution of this work is highlighted in blue.

Fig. 1. An overview of the $^{13}\text{CH}_4$ line lists (in red) and $^{12}\text{CH}_4$ line lists (in black) available in the HITRAN2020 [42]. Newly added line parameters for $^{13}\text{CH}_4$ from this work are highlighted in blue.

2. Acquisition of the $^{13}\text{CH}_4$ spectra at JPL

A couple of $^{13}\text{CH}_4$ spectra were recorded at 298 K for a gas sample of ^{13}C -enriched methane (^{13}C , 99%) in a broad spectral range ($4970\text{--}6200\text{ cm}^{-1}$) covering the entire Tetradecad. For this, a cryogenic Herriott cell [55] was employed, which is vacuum-coupled to a Fourier transform spectrometer, Bruker IFS-125HR, at the Jet Propulsion Laboratory. The Herriott cell is composed of the cell body, two spherical mirrors and end caps, all of which is in one single piece. The detailed information of its optical dimensions, performance, and the JPL-unique design can be found in our previous work [55]. The first spectrum was obtained at a Doppler-limited spectral resolution, 0.0056 cm^{-1} (unappodized) with a sample pressure of 5.12 Torr, which provided decent optical density for the weak transitions in high J-manifolds. The second spectrum was obtained with a sample pressure of 21.76 Torr at a lowered resolution (0.056 cm^{-1}), solely for an inspection of a possible zero offset of the cell system, which turned out to be less than 0.3% across the band. Thus, the first spectrum was adopted and analysed in this work, from which their line positions were determined through peak-find in a precision of 0.0003 cm^{-1} . Instrumental configuration and experimental conditions are presented in **Table 1**.

Table 1. Instrumental set up and experimental conditions

Optical filter band pass	4600 - 6250 cm ⁻¹
Spectral region analysed	¹³ CH ₄ in the 4970 – 5300 cm ⁻¹
Aperture diameter	1.15 mm
IR source	Tungsten lamp
Focal length	418 mm
Beam splitter	CaF ₂
Cell path	20.94 m
Windows (Cell, Coupler box)	CaF ₂
Detector	InSb (LN ₂ -cooled)
Sample (purity, enrichment)	¹³ C-enriched (¹³ C, 99%) from CIL
FTS chamber Pressure	Evacuated to be ~0.015 Torr (0.02 hPa)

The spectrum has covered the entire Tetradekad region of ¹³CH₄ (**Fig. 2**), offering the best consistent analysis for the bands. In this work, we have focused on the lower part of its panning from 4970 to 5300 cm⁻¹.

Fig. 2. An overview of the entire ¹³CH₄ spectrum recorded at 298 K (*Left panel*) and the region analyzed in this work between 4970 and 5300 cm⁻¹ (*Right panel*).

3. Rovibrational assignment and modeling

The harmonic frequency ratios for the construction of methane polyads, the scheme of vibrational levels and sublevels of the Tetradekad, as well as theoretical methods of vibrational-rotational analysis of methane spectra have been described in detail in the previous papers [47-49]. Here we will remind only the general approach applied for the analyses of methane spectra in our works.

Initially, to analyze the spectra of ¹³C-enriched methane we have used theoretical calculations [52,53] based on potential energy surface (PES) and *ab initio* dipole moment surfaces (DMS) reported by Nikitin, Rey and Tyuterev [56-58]. A part of parameters of the non-empirical effective Hamiltonian (EH), obtained from *ab initio* PES via high order Contact Transformation (CT) method by the MOL_CT code [59,60] has been adjusted during the modeling of the experimental data. These include ro-vibrational transitions up to Octad [32-34,39], and Tetradekad [47-49]; the latter obtained from analysis of cold Fourier [47,48] and DAS spectra [49]. Such mixed (*ab initio*/CT/empirical) approach described in detail in [59,60] permitted to obtain the EH model with the coupling terms between ro-vibrational states, deduced from the potential energy surface. In purely empirical models, these coupling terms responsible for the resonance perturbations and intensity transfers are poorly determined [61,62]. An alternative numerical method of similar transformations was suggested in [63].

Finally, from the cold spectra analysis we have obtained the effective Hamiltonian that describes 7077 observed transitions of the whole Tetradekad with an *rms* of 1.35×10⁻³ cm⁻¹ and the final model of the effective dipole transition moment that reproduces the set of 4025 selected line intensities of the whole Tetradekad with an *rms* deviation of 8.9%.

As an initial step for the spectrum assignment we used the line list constructed as follows: first, we fitted the Tetradekad lines up to *J*=10. Their positions were well known from the

analysis of cold spectra [47-49] while the line intensities were recalculated to 298 K. At the next step this data set was supplemented by the transitions up to $J=15$ predicted using our empirically optimized models of the effective Hamiltonian and the dipole transition moment [48].

The treatment of experimental spectrum, its visualization and comparison with the simulated one, as well as graphical identifications of lines were carried out using the freely available SpectraPlot [64] program. Theoretical modeling of observed line positions and intensities, followed by direct spectra calculations were carried out with the use of the MIRS software [65,66] dedicated for spectroscopy of polyatomic molecules in the representation of irreducible tensor operators.

In total, for the 4970-5300 cm^{-1} region, an empirical list including 1642 lines was created. Among them, 1600 assigned observed transitions belong to the $4\nu_4$, $\nu_2+3\nu_4$, $\nu_3+2\nu_4$, and $\nu_1+2\nu_4$ band systems, as illustrated on the upper panel of **Fig. 3**.

Fig. 3. *Upper panel:* An overview of the assigned transitions in the $^{13}\text{CH}_4$ spectrum recorded at 298 K between 4970 and 5300 cm^{-1} . *Lower panel:* Fit residuals in % for line intensities in the $^{13}\text{CH}_4$ lower part of the Tetradecad region. Different colors are used to indicate different band systems contributing to the spectrum.

4. Data fit statistics

The detailed statistics of assigned transitions are summarized in **Table 2**, the fit residuals for the line positions and intensities are given in **the Figs. 3 and 4**.

Table 2 is partitioned in two panels: the part. In the first (A) part of **Table 2**, the results of the line positions and intensity fits of the $4\nu_4$ band systems, located in the analyzed regions, are summarized. We assigned 1110 ro-vibrational transitions belonging to seven sub-bands with the origins in the range 5093-5210 cm^{-1} . However, a large part of the observed line belongs to the sub-bands, for which the origins lie above 5300 cm^{-1} . The second part (B) shadowed in grey includes the information about three band systems located above 5300 cm^{-1} : 379 transitions were assigned to the $\nu_2+3\nu_4$ band, 54 and 5 transitions to the $\nu_3+2\nu_4$, and $\nu_1+2\nu_4$ bands, respectively.

As mentioned above, for the assignment and fit of the observed data we used the effective Hamiltonian that have been early obtained for the Tetradecad from the analyses of the cold FTS and DAS spectra. It contained 4195 parameters, including 10 parameters for the Ground state, 62 for the Dyad, 382 for the Pentad, 1202 for the Octad and 2539 parameters for the Tetradecad. In total, only 897 (21%) effective Hamiltonian parameters were adjusted to model 12659 observed transitions covering Dyad, Pentad, Octad regions [32-34,39], and the lower part of Tetradecad assigned in this work, as well as hot transitions from Tetradecad to Dyad [67]. Among them, 58, 216, 322 and 301 parameters specific to the Dyad, Pentad, Octad and Tetradecad, respectively, were fitted. The other ones were held fixed to their initial values predicted from the PES using MOL_CT code [59,60]. This set of parameters including empirically refined ones permitted us to describe 861 line positions of the Dyad with a root mean square (*rms*) deviation of $0.4 \times 10^{-3} \text{ cm}^{-1}$, 3085 transitions of Pentad with an *rms* = $0.9 \times 10^{-3} \text{ cm}^{-1}$, 7085 transitions of Octad with an *rms* = $1.2 \times 10^{-3} \text{ cm}^{-1}$ and 1548 observed transitions of the $^{13}\text{CH}_4$ Tetradecad with an *rms* deviation of $1.7 \times 10^{-3} \text{ cm}^{-1}$. The fit residuals for the line positions are shown in **Fig 4**. An *rms* deviation for 80 hot Tetradecad-Dyad transitions [67] is $1.2 \times 10^{-3} \text{ cm}^{-1}$.

Fig. 4. Fit residuals for line position in the $^{13}\text{CH}_4$ lower part of the Tetradecad region. Different colors are used to indicate the different band systems contributing to the spectrum.

Because of weak intensities of the Tetradecad bands in the investigated spectral range that led to relatively low signal-to-noise ratio, only 674 measured line intensities were selected to derive the parameters of the effective dipole transition moment operator. The obtained set of parameters allowed us to reproduce these line intensities with an *rms* deviation of 6.8%. Detailed statistics of the intensity fit for the two frequency ranges are given in **Table 2**, and the fit residuals are given in the lower panel of the **Fig. 3**.

Table 2. An overview of the rovibrational assignments of the $^{13}\text{CH}_4$ transitions obtained at 298 K between 4970 and 5300 cm^{-1} region and their corresponding line position and intensity fit statistics.

Band	Upper sublevel	Sub-band centre (cm^{-1})	Positions			Intensities	
			Nb. data	J_{\min}, J_{\max}	<i>RMS</i> (10^{-3} cm^{-1})	Nb. data	<i>RMS</i> (%)
(A) analysis of sub-bands located in the spectral range under investigation: 4970-							
4v₄	A ₁ 1 ^a	5093.2	43	3 , 11	1.5	17	7.9
	F ₂ 1 ^b	5114.375	313	0 , 14	1.5	166	5.9
	E 1 ^c	5137.79	218	1 , 13	1.7	106	7.1
	F ₂ 2 ^b	5180.681	193	0 , 14	1.9	101	6.1
	E 2 ^c	5198.22	79	1 , 13	1.6	35	7.1
	F ₁	5199.937	220	1 , 14	2.1	90	7.2
	A ₁ 2 ^a	5209.6	44	5 , 12	1.8	18	6.1
(B) preliminary analysis of sub-bands having origins located in the upper wavenumber range > 5300 cm^{-1}							
v₂+3v₄	F ₂ 1 ^d	5348.6	69	3 , 12	1.8	17	8.7
	F ₁ 1 ^e	5367.6	89	4 , 15	1.6	27	6.9
	E	5401.9	47	5 , 14	2.0	16	9.6
	F ₂ 2 ^d	5406.5	34	5 , 15	2.1	6	3.9
	F ₁ 2 ^e	5414.2	39	5 , 13	1.8	14	9.1
	F ₂ 3 ^d	5421.7	79	4 , 14	1.6	28	8.1
	F ₁ 3 ^e	5439.5	22	7 , 13	1.9	8	7.3
v₁+2v₄	F ₂	5503.7	1	11 , 11	1.0		
	E	5515.6	4	10 , 15	0.3		
v₃+2v₄	A ₁	5582.9	13	13 , 15	5.6	6	2.4
	F ₂ 2 ^f	5589.8	10	13 , 14	3.9	7	6.0
	F ₁ 1 ^g	5590.3	15	13 , 15	3.1	3	6.4
	E	5591.4	8	13 , 15	3.8	4	3.6
	F ₁ 2 ^g	5600.2	2	13 , 13	5.1	1	11.0
	F ₂ 3 ^f	5602.5	6	13 , 15	3.1	4	2.8

Total	1548	1.7	674	6.8
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Notes:

The vibrational sublevels are enumerated here for each band for a given symmetry type. The ranking numbers within the Tetradecad[49,50] are the following:

^a $N=1$ and $N=2$ for A_1 1 and A_1 2; ^b $N=1$ and $N=2$ for F_2 1 and F_2 2; ^c $N=1$ and $N=2$ for E 1 and E 2; ^d $N=3$, $N=4$ and $N=5$ for F_2 1, F_2 2 and F_2 3; ^e $N=2$, $N=3$, and $N=4$ for F_1 1, F_1 2 and F_1 3; ^f $N=8$ and $N=9$ for F_2 2 and F_2 3; ^g $N=5$ and $N=6$ for F_1 1 and F_1 2.

5. Line lists

Using the determined parameters of the effective Hamiltonian and of the effective dipole transition moment we have computed a list of 6809 transitions of the lower part of the $^{13}\text{CH}_4$ Tetradecad in the $4970\text{--}5300\text{ cm}^{-1}$ region. The intensity cut off was fixed to 1×10^{-27} cm/molecule with $J_{\text{max}} = 16$ at $T=296\text{ K}$.

A synthetic spectrum of the bands simulated from this list shows a good agreement with the experimental spectrum, as illustrated in **Fig. 5** for the whole analyzed range as well as for a small range around 5165 cm^{-1} in **Fig 6**. In the Electronic Supplements we provide two sets of the line lists. One set is for the experimental line list that includes our assignments for 1642 lines, where the line positions and intensities included in the corresponding fits are flagged by the ‘+’ sign. The second set of the line list contains all the calculated transitions with the cut-offs mentioned above. The corresponding examples of the file formats are given in **Tables 3 and 4**, respectively.

A comparison with TheoReTS [54] line list for $^{13}\text{CH}_4$, illustrated in **Figs. 5 and 7**, demonstrates the excellent quality of the *ab initio* calculations for this molecule [52,53].

Fig. 5. An overview comparison between the experimental spectrum of $^{13}\text{CH}_4$ at 298 K (*lower panel*) with simulation based on the effective Hamiltonian/Dipole moment models (*middle panel*) and TheoReTS (*upper panel*) in the $4970\text{--}5300\text{ cm}^{-1}$ region of the $^{13}\text{CH}_4$ Tetradecad.

Fig. 6. A comparison between the experimental spectrum of $^{13}\text{CH}_4$ at 298 K (*lower panel*) with simulation based on the effective Hamiltonian/Dipole moment models (*middle panel*) in the $5162\text{--}5167\text{ cm}^{-1}$. Residuals between observed and calculated spectra are demonstrated on the *upper panel*.

Fig. 7. The same comparison as in Fig 5 in two small ranges: around 5102 cm^{-1} (*left panel*) and 5202 cm^{-1} (*right panel*).

Table 3. A sample of the Electronic Supplement data for the observed $^{13}\text{CH}_4$ transitions at 298 K along with their quantum assignments in the $4970\text{--}5300\text{ cm}^{-1}$ region.

ν_0 cm^{-1}	S, Intensities at 298 K cm/molec	Rotational Assignments		Vibrational assignments		E lower cm^{-1}	Obs-Calc	
		Low. state	Up. State	Low. state	Up. state		for pos. $\times 10^{-3}\text{ cm}^{-1}$	for int. in %
4970.1391 +	2.289E-25 +	0 9 A1 1	4 8 A2 3	0000 A1	0004 F2	470.8530	3.9039	9.70
4970.6138	6.663E-26	0 10 E 1	4 9 E 7	0000 A1	0004 A1	575.0782		

4971.0567 +	9.747E-26	0 9 F1 2	4 8 F2 8	0000 A1	0004 F2	470.8273	-2.0636	
4971.3869 +	3.967E-26	0 12 E 1	4 12 E 5	0000 A1	0004 F2	814.6873	-1.8398	
4971.7494 +	8.259E-26	0 9 E 1	4 8 E 5	0000 A1	0004 E	470.8210	-0.9810	
4971.7648 +	1.294E-24 +	0 7 F1 2	4 6 F2 1	0000 A1	0004 F2	293.1920	0.3260	-2.40
4972.2288 +	5.527E-25 +	0 7 E 1	4 6 E 1	0000 A1	0004 F2	293.1840	1.1571	0.79
4972.7304	5.127E-26	0 10 A1 1	4 9 A2 4	0000 A1	0004 A1	575.2499		
4973.7230 +	1.972E-25 +	0 7 F1 2	4 6 F2 2	0000 A1	0004 F2	293.1923	2.4925	-9.52
4973.9976 +	1.353E-24 +	0 7 F2 2	4 6 F1 1	0000 A1	0004 F2	293.1780	-0.0408	-1.34

Notes: the columns are the following:

1. ν_0 : measured line positions.
2. S (298 K): measured line intensities in $\text{cm}^{-1}/(\text{molecule cm}^{-2})$ at 298 K
3. Lower state rovibrational assignment are given by the vibrational polyad number P , the rotational quantum number J , the rovibrational symmetry type C (T_d irreducible representation) and the rovibrational ranking index N .
4. Upper state rovibrational assignments in the same format
5. Lower vibrational band assignments in terms of the principal vibrational quanta ($\nu_1, \nu_2, \nu_3, \nu_4$) and vibrational symmetry type C_V (T_d irreducible representation)
6. Upper vibrational band assignments in the same format
7. E lower: lower state energies [in cm^{-1}]
8. Difference between measured and calculated line position included in the fit in 10^{-3} cm^{-1} units
9. $(S_0 - S_c)/S_0$ in % is the relative difference between measured and calculated intensities included in the fit. These values appear for assigned lines if their measured intensities were included in the fit.

Table 4. A sample of the Electronic Supplement data for the calculated line list of the $^{13}\text{CH}_4$ methane transitions at 296 K for the 4970–5300 cm^{-1} region.

ν_0 cm^{-1}	S, Intensity at 296 K cm/molec	Rotational assignment		V n	Vibrational assignment		E lower cm^{-1}
		Low. state	Up. state		Low. state	Up. state	
4970.1017	2.186e-26	0 10 F2 1	4 9 F1 10	V 58	0000 A1	0004 A1	575.0796
4970.1352	1.969e-25	0 9 A1 1	4 8 A2 3	V 57	0000 A1	0004 F2	470.8530
4970.5327	3.393e-27	0 14 F1 2	4 13 F2 26	V 60	0000 A1	0004 F2	1095.9211
4970.6175	2.029e-26	0 10 E 1	4 9 E 7	V 58	0000 A1	0004 A1	575.0782
4970.6752	1.036e-27	0 12 F2 2	4 12 F1 6	V 57	0000 A1	0004 F2	815.0466
4970.8168	5.895e-27	0 12 F2 1	4 12 F16	V 57	0000 A1	0004 F2	814.9050
4970.8441	2.318e-27	0 12 A1 2	4 12 A2 2	V 57	0000 A1	0004 F2	815.1822
4970.9371	1.225e-26	0 11 A2 1	4 10 A1 6	V 54	0000 A1	0004 A1	689.8947
4970.9630	2.572e-27	0 14 E 2	4 13 E 17	V 60	0000 A1	0004 F2	1095.9467
4971.0090	3.009e-26	0 9 F1 3	4 8 F2 8	V 55	0000 A1	0004 E	470.8770

Notes: in this table, the columns are:

1. ν_0 : calculated line positions.
2. S (296 K): calculated line intensities in $\text{cm}^{-1}/(\text{molecule cm}^{-2})$ at 296 K
3. Lower state rovibrational assignments are given by the vibrational polyad number P , the rotational quantum number J , the rovibrational symmetry type C (T_d irreducible representation) and the rovibrational ranking index N .
4. Upper state rovibrational assignments in the same format
5. V n is the number of vibrational sub band in the MIRS [49,50] labeling
6. Lower vibrational band assignments in terms of the principal vibrational quanta ($\nu_1, \nu_2, \nu_3, \nu_4$) and vibrational symmetry type C_V (T_d irreducible representation)
7. Upper vibrational band assignments in the same format
8. E lower: lower state energies [in cm^{-1}]

6. Conclusion

The main goal of this study was the assignment of high-resolution FTS spectrum of ^{13}C -enriched methane in the range of $4970\text{-}5300\text{ cm}^{-1}$ at 298 K. This spectral range corresponds to the lower part of the $^{13}\text{CH}_4$ Tetradekad. The initial assignment was made using effective Hamiltonian and the effective dipole transition moment derived in our previous work on $^{13}\text{CH}_4$ spectra analyses at 80 K. The new analysis allowed us to assign 1600 lines belonging to four bands $4\nu_4$, $\nu_2+3\nu_4$, $\nu_3+2\nu_4$, and $\nu_1+2\nu_4$ of the Tetradekad, which include 22 sub-bands up to $J_{\text{max}}=16$.

The 1548 line positions were fitted with an *rms* deviation of $1.7\times 10^{-3}\text{ cm}^{-1}$. The set of 674 selected line intensities was fitted with an *rms* deviation of 7%. This new data was used for the simultaneous fit of the $^{13}\text{CH}_4$ Hamiltonian parameters for the {Ground state /Dyad / Pentad / Octad / Tetradekad} system and the dipole moment parameters for the {Ground state - Tetradekad} system. A line list that contains 6809 calculated transitions up to $J = 16$ for the $4970\text{-}5300\text{ cm}^{-1}$ region was created.

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References:

1. Sromovsky LA, Fry PM, Boudon V, Campargue A, Nikitin A. Comparison of line-by-line and band models of near-IR methane absorption applied to outer planet atmospheres. *Icarus* 2012;218:1–23.
2. De Bergh C, Courtin R, Bézard B, Coustenis A, Lellouch E, Hirtzig M, Rannou P, Drossart P, Campargue A, Kassi S, Wang L, Boudon V, Nikitin A, Tyuterev VIG. Applications of a new set of methane line parameters to the modeling of Titan's spectrum in the 1.58 μm window. *Plan Space Science* 2012;61:85–98.
3. Hirtzig M, Bézard B, Lellouch E, Coustenis A, De Bergh C, Drossart P, Campargue A, Boudon V, Tyuterev V, Rannou P, Cours T, Kassi S, Nikitin A, Mondelain D, Rodriguez S, Le Mouélic S. Titan's surface and atmosphere from Cassini/VIMS data with updated methane opacity. *Icarus* 2013;226:470–86.
4. Tinetti G, Encrenaz T, Coustenis A. Spectroscopy of planetary atmospheres in our Galaxy. *Astron Astrophys Rev* 2013;21:63.
5. Burrows AS. Highlights in the study of exoplanet atmospheres. *Nature* 2014;513:345–50.
6. Bernath PF. Molecular opacities for exoplanets. *Phil Trans R Soc. A* 2014;372:20130087.
7. Rey M, Nikitin AV, Tyuterev VG. Accurate theoretical methane line lists in the infrared up to 3000 K and quasi-continuum absorption/emission modeling for astrophysical applications. *Astroph J* 2017;847(2):aa8909. DOI: 10.3847/1538-4357/aa8909
8. Wong A, Bernath PF, Rey M, Nikitin AV, Tyuterev VG. Atlas of experimental and theoretical high-temperature methane cross sections from $T = 295$ to 1000 K in the near-infrared. *Astroph J, Suppl Series* 2019;240(1):4, DOI: 10.3847/1538-4365/aaed39
9. Yurchenko SN, Owens A, Kefala K, Tennyson J. ExoMol line lists – LVII. High accuracy ro-vibrational line list for methane (CH_4). *MNRAS* 2024;528:3719–29. <https://doi.org/10.1093/mnras/stae148>
10. Khalil M. Non- CO_2 greenhouse gases in the atmosphere. *Ann Rev Energy Envir* 1999;24:645–61.
11. Dlugokencky EJ, Masarie KA, Lang PM, Tans PP. Continuing decline in the growth rate of atmospheric methane. *Nature* 1998;393:447–50.
12. Dlugokencky EJ, Nisbet EG, Fisher RE, Lowry D. Global atmospheric methane: Budget, changes, and dangers. *Philos Trans R Soc London, Ser A.*, 369;2011:2058–72.
13. Kirschke S, et al. Three decades of global methane sources and sinks. *Nat Geosci* 2013;6:813–23.
14. Nisbet EG, Dlugokencky EJ, Bousquet P. Methane on the rise – Again. *Science* 2014;343:493–5.
15. Nisbet EG, Dlugokencky EJ, Manning MR, Lowry D, Fisher RE, et al. Rising atmospheric methane: 2007–2014 growth and isotopic shift. *Global Biogeochem. Cycles* 2016;30:1356–70.
16. Boudon V, Pirali O, Roy P, Brubach BJ, Manceron L, et al. The high-resolution far-infrared spectrum of methane at the SOLEIL synchrotron. *J Quant SpectroscRadiatTransfer* 2010;111:1117–29.

17. Daumont L, Nikitin AV, Thomas X, Régalia L, Von der Heyden P, Tyuterev VIG, Rey M, Boudon V, Wenger C, Loëte M, Brown LR. New assignments in the 2 μm transparency window of the $^{12}\text{CH}_4$ Octad band system. *J Quant Spectrosc Radiat Transfer* 2013;116:101–9.
18. Nikitin AV, Boudon V, Wenger Ch, Albert S, Brown LR, Bauerecker S, Quack M. High resolution spectroscopy and the first global analysis of the Tetradecad region of methane $^{12}\text{CH}_4$. *Phys Chem Chem Phys* 2013;15:10071–93.
19. Campargue A, Leshchishina O, Wang L, Mondelain D, S. Kassi, The WKLMC empirical line lists (5852–7919 cm^{-1}) for methane between 80 K and 296 K: "final" lists for atmospheric and planetary applications. *J Molec Spectrosc* 2013;291:16–22.
20. Devi VM, Benner DC, Smith MAH, Mantz AW, Sung K, Crawford TJ, Predoi-Cross A. Self- and air-broadened line shape parameters in the $\nu_2+\nu_3$ band of $^{12}\text{CH}_4$: 4500–4630 cm^{-1} . *J Quant Spectrosc Radiat Transfer* 2015;152:149–65.
21. Rey M, Nikitin AV, Tyuterev VIG. Convergence of normal mode variational calculations of methane spectra: Theoretical line list in the icosad range computed from potential energy and dipole moment surfaces. *J Quant Spectrosc Radiat Transfer* 2015;164:207–20.
22. Amyay B, Louviot M, Pirali O, Georges R, Vander Auwera J, Boudon V. Global analysis of the high temperature infrared emission spectrum of $^{12}\text{CH}_4$ in the dyad (ν_2/ν_4) region. *J Chem Phys* 2016;144:024312.
23. Rey M, Nikitin AV, Tyuterev VG, Ab initio variational predictions for understanding highly congested spectra: Rovibrational assignment of 108 new methane sub-bands in the icosad range (6280–7800 cm^{-1}). *Phys Chem Chem Phys* 2016;16:176–89.
24. Ghysels M, Vasilchenko S, Mondelain D, Béguier S, Kassi S., Campargue A., Laser absorption spectroscopy of methane at 1000 K near 1.7 μm : A validation test of the spectroscopic databases. *J Quant Spectrosc Radiat Transfer* 2018;215:59–70.
25. Nikitin AV, Thomas X, Daumont L, Rey M, Sung K, Toon GC, et al. Assignment and modelling of $^{12}\text{CH}_4$ spectra in the 5550–5695, 5718–5725 and 5792–5814 cm^{-1} regions. *J Quant Spectrosc Radiat Transfer* 2018;219:323–32.
26. Foltynowicz A, Rutkowski L, Silander I, Johansson A, Silva de Oliveira V, Axner O, Soboń G, Martynkien T, Mergo P, Lehmann K. Measurement and assignment of double-resonance transitions to the 8900–9100 cm^{-1} levels of methane. *Phys Rev Lett* 2021;103:022810.
27. Malarich N, Yun D, Sung K, Egbert S, Coburn S, Drouin B, Rieker G. Dual frequency comb absorption spectroscopy of CH_4 up to 1000 Kelvin from 6770 to 7570 cm^{-1} . *J Quant Spectrosc Radiat Transfer* 2021;272:107812.
28. Germann M, Hjältén A, Boudon V, Richard C, Krzempek K, Hudzikowski A, Głuszek A, Soboń G, Foltynowicz A. A methane line list with sub-MHz accuracy in the 1250 to 1380 cm^{-1} range from optical frequency comb Fourier transform spectroscopy. *J Quant Spectrosc Radiat Transfer* 2022;288:108252.
29. Rodina AA, Nikitin AV, Manceron L, Thomas X, Daumont L, Rey M, Sung K, et al. Improved line list of $^{12}\text{CH}_4$ in the 4100–4300 cm^{-1} region. *J Quant Spectrosc Radiat Transfer* 2022;279:108021.
30. Dudas E, Vispoel B, Gamache RR, Rey M, Tyuterev VG, Nikitin AV, Kassi S, Suas-David N, Georges R. Non-LTE spectroscopy of the tetradecad region of methane recorded in a hypersonic flow. *Icarus* 2023;394:115421.

31. Campargue A, Karlovets EV, Vasilchenko SS, Turbet M. The high resolution absorption spectrum of methane in the 10 800–14 000 cm^{-1} region: literature review, new results and perspectives. *Phys Chem Chem Phys* 2023;25:32778–99.
32. Champion J-P, Hilico JC, Brown LR. The vibrational ground state of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$. *J Mol Spectrosc* 1989;133(2):244–55.
33. Niederer HM, Albert S, Bauerecker S, Boudon V, Champion JP, Quack M. Global analysis of the infrared spectrum of $^{13}\text{CH}_4$: Lines in the region 0 to 3200 cm^{-1} . *Chimia* 2008;62:273–76.
34. Nikitin A, Champion JP, Tyuterev VIG, Brown L, Mellau G, Lock M. The infrared spectrum of CH_3D between 900 and 3200 cm^{-1} : extended assignment and modeling. *J Molec Struct* 2000;517:1–24.
35. Nikitin AV, Brown LR, Féjard L, Champion JP, Tyuterev VIG. Analysis of the CH_3DNonad in the region 2000–3300 cm^{-1} . *J Mol Spectrosc* 2002;216:225–51.
36. Nikitin AV, Champion JP, Brown LR. Preliminary analysis of CH_3D from 3250 to 3700 cm^{-1} . *J Mol Spectrosc* 2006;240:14–25.
37. Nikitin AV, Brown LR, Sung K, Rey M, Tyuterev VIG, Smith MAH, Mantz AW. Preliminary modeling of CH_3D from 4000 to 4550 cm^{-1} . *J Quant Spectrosc Radiat Transfer* 2013;114:1–12.
38. Brown LR, Nikitin AV, Sung K, Rey M, Tashkun SA, Tyuterev VIG, Crawford TJ, Smith MAH, Mantz AW. Measurements and modelling of cold $^{13}\text{CH}_4$ spectra in the 3750–4700 cm^{-1} region. *J Quant Spectrosc Radiat Transfer* 2016;174:88–100.
39. Niederer HM, Wang X-G, Carrington T, Albert S, Bauerecker S, Boudon V, Quack M. Analysis of the rovibrational spectrum of $^{13}\text{CH}_4$ in the Octad range. *J Mol Spectrosc* 2013;291:33–47.
40. Brown LR, Sung K, Benner DC, Devi VM, Boudon V, Gabard T, Wenger C, Campargue A, Leshchishina O, Kassi S, Mondelain D, Wang L, Daumont L, Régalia L, Rey M, Thomas X, Tyuterev VIG, Lyulin OM, Nikitin AV. Methane line parameters in the HITRAN2012 database. *J Quant Spectrosc Radiat Transfer* 2013;130:201–19.
41. Ba YA, Wenger Ch, Surleau R, Boudon V, Rotger M, Daumont et al. MeCaSDa and ECaSDa: Methane and ethene calculated spectroscopic databases for the virtual atomic and molecular data centre. *J Quant Spectrosc Radiat Transfer* 2013;130:62–8.
42. Gordon IE, et al. The HITRAN2020 molecular spectroscopic database. *J Quant Spectrosc Radiat Transfer* 2022;277:107949. DOI: 10.1016/j.jqsrt.2021.107949
43. Delahaye T, Armante R, Scott NA, et al. The 2020 edition of the GEISA spectroscopic database. *J Molec Spectrosc* 2021;380:111510.
44. Rixon G, Dubernet ML, Piskunov N, Walton N, Mason N, Le Sidaner P, et al. VAMDC - The Virtual Atomic and Molecular Data Centre - A new way to disseminate atomic and molecular data - VAMDC level 1 release. *AIP Conf Proc* 2011;1344:107–15. DOI: 10.1063/1.3585810
45. Nikitin AV, Lyulin OM, Mikhailenko SN, Perevalov VI, Filipov NN, Grigoriev IM, et al. GOSAT-2009 methane spectra line list in the 5550–6236 cm^{-1} range. *J Quant Spectrosc Radiat Transfer* 2010;111:2211–24.

46. Nikitin AV, Mikhailenko S, Morino I, Yokota T, Kumazawa R, Watanabe T. Isotopic substitution shifts in methane and vibrational band assignment in the 5560–6200 cm^{-1} region. *J Quant Spectrosc Radiat Transf* 2009;110:964–73.
47. Starikova E, Sung K, Nikitin AV, Rey M, Mantz A, Smith MAH. The $^{13}\text{CH}_4$ absorption spectrum at 80 K: Assignment and modeling of the lower part of the Tetradekad in the 4970–5470 cm^{-1} spectral range. *J. Quant. Spectrosc. Radiat. Transfer*. 2018;206:306–12.
48. Starikova E, Sung K, Nikitin AV, Rey M. Assignment and modeling of the $^{13}\text{CH}_4$ cold absorption spectrum in the 5471–5852 cm^{-1} spectral range. *J. Quant. Spectrosc. Radiat. Transfer*. 2019;235:278–86.
49. Starikova E, Nikitin AV, Rey M, Tashkun SA, Mondelain D, Kassi S, Campargue A, Tyuterev V. Assignment and modeling of the absorption spectrum of $^{13}\text{CH}_4$ at 80K in the region of the $2\nu_3$ band (5853-6201 cm^{-1}). *J. Quant. Spectrosc. Radiat. Transfer*. 2016;177:170–80.
50. Gordon IE, Rothman LS, Hill C, Kochanov RV, Tan Y, Bernath PF, et al. The HITRAN2016 molecular spectroscopic database. *J Quant Spectrosc Radiat Transfer* 2017;203:3–69. <https://doi.org/10.1016/j.jqsrt.2017.06.038>
51. Tyuterev VIG, Babikov YL, Tashkun SA, Perevalov VI, Nikitin A, Champion JP, et al T.D.S. spectroscopic databank for spherical tops. *J Quant Spectrosc Radiat Transfer* 1994;52:459–80.
52. Rey M, Nikitin AV, Tyuterev VG. Predictions for methane spectra from potential energy and dipole moment surfaces: Isotopic shifts and comparative study of $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$. *J Molec Spectrosc* 2013;291:85–97. DOI: 10.1016/j.jms.2013.04.003
53. Rey M, Nikitin AV, Bezard B, Rannou P, Coustenis A, Tyuterev VG. New accurate theoretical line lists of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ in the 0–13400 cm^{-1} range: Application to the modeling of methane absorption in Titan's atmosphere. *Icarus* 2018;303:114–30. DOI: 10.1016/j.icarus.2017.12.045
54. Rey M, Nikitin AV, Babikov Y, Tyuterev VIG, TheoReTS – An information system for theoretical spectra based on variational predictions from molecular potential energy and dipole moment surfaces. *J Molec Spectrosc* 2016;327:138–58.
55. Mantz AW, Sung K, Brown LR, Crawford TJ, Smith MAH, Devi VM, Benner DC. A cryogenic Herriott cell vacuum-coupled to a Bruker IFS-125HR. *J Mol Spectrosc* 2014;304:12–24.
56. Nikitin AV, Rey M, Tyuterev VIG. Rotational and vibrational energy levels of methane calculated from a new potential energy surface. *Chem Phys Lett* 2011;501:179–86.
57. Nikitin AV, Rey M, Tyuterev VIG. First fully ab initio potential energy surface of methane with a spectroscopic accuracy. *J Chem Phys* 2016;145:114309.
58. Nikitin AV, Rey M, Tyuterev VIG. Accurate line intensities of methane from first-principles calculations. *J Quant Spectrosc Radiat Transfer* 2017;200:90–99.
59. Tyuterev VIG, Tashkun SA, Rey M, Kochanov RV, Nikitin AV, Delahaye T. Accurate spectroscopic models for methane polyads derived from a potential energy surface using high-order contact transformations. *J Phys Chem A* 2013;117:13779–805.

60. Tyuterev VG, Tashkun S, Rey M, Nikitin A. High-order contact transformations of molecular Hamiltonians: general approach, fast computational algorithm and convergence of ro-vibrational polyad models. *Molec Phys* 2022;120:e2096140.
61. Tyuterev VIG, Champion J-P, Pierre G, Perevalov VI. Parameters of reduced Hamiltonian and invariant parameters of interacting E and F2 fundamentals of tetrahedral molecules: ν_2 and ν_4 bands of $^{12}\text{CH}_4$ and $^{28}\text{SiH}_4$. *J Mol Spectrosc* 1986;120:49–78.
62. Perevalov VI, Tyuterev VIG, Zhilinskii BI. Ambiguity of spectroscopic parameters in the case of accidental vibration-rotation resonances in tetrahedral molecules. r2 J and r2J2 terms for E/F2 interacting states. *Chem Phys Lett* 1984;104:455–61.
63. Rey M, Novel methodology for systematically constructing global effective models from ab initio-based surfaces: A new insight into high-resolution molecular spectra analysis. *J Chem Phys* 2022;292:108349.
64. Nikitin AV, Kochanov RV. Visualization and identification of spectra by the SpectraPlot program. *Atmos Ocean Opt* 2011;24:931–41.
65. Nikitin AV, Champion JP, Tyuterev VIG. The MIRS computer package for modeling the rovibrational spectra of polyatomic molecules. *J Quant Spectrosc Radiat Transf* 2003;82:239–49.
66. Nikitin AV, Rey M, Champion JP, Tyuterev VIG. Extension of the MIRS computer package for modeling of molecular spectra: from effective to full ab initio ro-vibrational Hamiltonians in irreducible tensor form. *J Quant Spectrosc Radiat Transf* 2012;113:1034–42.
67. Chizhmakova I, Nikitin AV, Martínez RZ, Paredes-Roibás D, Bermejo D, Starikova E, Tyuterev VIG. Modelling of the $2\nu_1-\nu_1$ and ν_1 band transitions of $^{13}\text{CH}_4$ using high resolution Raman spectroscopy measurements. *J Quant Spectrosc Radiat Transfer* 2021;270:107682.