

Intracavity spectroscopy of methane and silane within 1.06 μm range

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We present analysis of the absorption spectra of CH_4 and SiH_4 in the spectral range near 1 μm . The spectra have been recorded with an intracavity neodymium-glass-laser-based spectrometer. The energy levels have been determined.

The molecules of CH_4 and SiH_4 are actively used in modern technologies connected with production of ultra-pure materials. Therefore their spectra are necessary for diagnostics of molecules participating in chemical reactions and for monitoring the chemical processes themselves. The absorption spectrum of methane is one of the main sources of information on the atmospheres of many planets. Methane is one of the main atmospheric gases of such planets as Jupiter, Uranium, Neptune, Saturn (and its satellites), it occupies the second position on concentration after H_2 among the elements of the Solar system. Structure of highly excited states of spherical top molecules, to which type methane and silane belong, is also interesting from the theoretical point of view.

At present large number of studies are being devoted to the methane absorption spectra. A lot of information is available on the parameters of spectral lines of this molecule, such as positions, intensities, halfwidths, lower energy levels, broadening coefficients induced by air, selfbroadening coefficients, as well as shift coefficients.

A review of the modern studies of methane absorption spectra has been published in Ref. 1. The spectral range up to 6200 cm^{-1} is most thoroughly investigated. The region higher than 6000 cm^{-1} is not yet investigated in that many details, the spectra were recorded with low accuracy and resolution. The region near 1 μm where absorption lines of methane are fewer in number and the spectrum consists of separate nonoverlapping lines belonging to the $3\nu_3$ band, which may be used for measuring both concentration and temperature of methane and its isotopic species, attracts a strong interest.

$^{12}\text{CH}_4$

Investigations of rotational structure of the $3\nu_3$ band of methane as well as measurements of the $R(0)\dots R(7)$ line positions, intensities, and halfwidths in the $9050\text{--}9130\text{ cm}^{-1}$ range have been published in Refs. 2 to 6. Lines corresponding to transitions between energy states with higher values of the rotational

quantum number J could not be recorded due to low sensitivity of spectrometers. Most complete spectrum of methane in the $9000\text{--}9165\text{ cm}^{-1}$ range is presented in Ref. 5. The spectrum was recorded using Fourier-transform spectrometer; the identification of the $3\nu_3$ ($\nu_0 = 9045\text{ cm}^{-1}$) band was performed, two new bands: $2\nu_2 + 2\nu_3$ ($\nu_0 = 9018\text{ cm}^{-1}$) and the band centered at $\nu_0 = 9049\text{ cm}^{-1}$ were recorded as well.

In this study the absorption spectrum of methane molecule was recorded using an intracavity neodymium-glass-laser-based spectrometer. This spectrometer allows one to investigate absorption spectra with a spectral resolution of 0.05 cm^{-1} and a sensitivity to absorption of $3\cdot 10^{-8}\text{ cm}^{-1}$. Since we used industrial methane without preliminary drying, the water vapor absorption lines observed in the recorded spectrum were used as reference lines.⁶

More than 300 absorption lines are observed in the spectrum of $^{12}\text{CH}_4$ (at a pressure of 2 and 12 kPa) within the region from 9100 to 9520 cm^{-1} . In the low frequency $9000\text{--}9170\text{ cm}^{-1}$ range the absorption of methane is determined, mainly, by the $3\nu_3$ band, with strong enough lines belonging to other bands of CH_4 being observed between the J -multiplets of the band under study. Intense Q -branch of the $3\nu_3$ band is located in the 9050 cm^{-1} region. Similar in structure group of lines, though less intense, that belong to Q -branch of the $2\nu_2 + 2\nu_3$ band, is observed near 9025 cm^{-1} . P -branch of the $3\nu_3$ band overlaps considerably with the $2\nu_2 + 2\nu_3$ band. R -branch of the $3\nu_3$ band is distinctly traced up to $J = 10$. Intensities of the lines belonging to R -branch of the $3\nu_3$ band decrease sharply as the rotational quantum number increases, and at $J = 11$ the lines appear to be on the noise level.

Large number of strong absorption lines of methane with uncertain structure belonging to the bands centered beyond the high frequency edge of laser radiation was recorded in the high frequency part of the obtained spectrum – $\nu > 9300\text{ cm}^{-1}$. Using the literature data on bands centers it has been found that the following bands due to transitions from the ground vibrational state: $2\nu_1 + \nu_2 + \nu_3$, $2\nu_1 + \nu_3 + \nu_4$, $2\nu_1 + \nu_2 + 2\nu_4$, $3\nu_1 + \nu_4$, $3\nu_1 + \nu_2$ are located in the $9500\text{--}12000\text{ cm}^{-1}$ region.

In Ref. 7 (the study performed with a low resolution and sensitivity) the lines of the $2\nu_1 + \nu_2 + \nu_3$, $2\nu_1 + \nu_3 + \nu_4$ absorption bands centered near 10000 cm^{-1} and extending down to 9400 cm^{-1} were also recorded.

Analysis of the $^{12}\text{CH}_4$ spectrum allowed us to identify lines of the R -branch of the $3\nu_3$ band up to $J = 10$, and lines of the Q -branch up to $J = 8$. The line positions are presented in Table 1. The band centered at 9049 cm^{-1} with R -branch multiplets traced up to $J = 8$ is superimposed with the $3\nu_3$ band. The energy structure of rotational levels of the corresponding states is presented in Fig. 1. Energy levels of the (0030) vibrational state as well as vibrational state with $E_v = 9049\text{ cm}^{-1}$ have classical tetrahedral structure for low values of the rotational quantum number J .

Table 1. Absorption spectrum of methane in 9039–9168 cm^{-1} region

Frequency, cm^{-1}	$3\nu_3$		ν^*	Frequency, cm^{-1}	$3\nu_3$			ν^*
	$Q(J)$	$R(J)$	$R(J)$		$Q(J)$	$P(J)$	$R(J)$	
9039.75				9120.33		6		
9039.86				9120.54		6		
9040.21				9121.30		6		
9040.33				9121.48		6		
9040.38				9121.55		6		
9040.54				9123.40				
9041.16				9123.51				
				9125.11				
9041.42				9125.30				
				9125.50				
9041.52				9126.95				
				9127.08				6
9041.68				9127.46				6
				9127.77				6
9041.86				9127.95				6
				9128.18				6
9042.05				9130.19		7		
9042.25				9130.59		7		
9042.37	5			9130.98		7		
9042.47				9131.35		7		
9042.66				9132.03		7		
9042.83	5			9132.30		7		
9043.33	5			9132.41		7		
9043.52	5			9148.36				7
9043.73	4			9138.48				7
9044.00	4			9138.70				7
9044.45	4			9139.38				7
9044.67	3			9139.62				7
9045.03	3			9139.76				7
9045.42	3			9139.89				7
9045.58	2			9140.88				7
9045.84	2			9141.07				
9046.34	1			9141.27		8		
9057.77		0		9141.57		8		
9060.93			0	9141.85		8		
9068.57		1		9142.01		8		
9071.44			1	9142.88		8		
9079.16			2	9143.74		8		
9079.25			2	9144.18		8		
9082.24			2	9149.78				8
9082.31			2	9149.92				8
9089.38		3		9150.85				8
9089.66		3		9151.73				8

Table 1 (continued)

Frequency, cm^{-1}	$3\nu_3$		ν^*	Frequency, cm^{-1}	$3\nu_3$		ν^*
	$Q(J)$	$R(J)$	$R(J)$		$Q(J)$	$P(J)$	$R(J)$
9089.84			3	9151.85			9
9093.42				9152.55			9
9093.56				9152.70			9
9093.67				9152.82			9
9099.71				9153.99			9
9100.20		4		9154.23			9
9100.32		4		9154.45			9
9100.47		4		9154.74			9
9104.44			4	9154.99			9
9104.68			4	9155.56			9
9104.83			4	9156.05			9
9105.02			4	9156.88			9
9110.01				9157.40			9
9110.12		5		9161.76			10
9110.77		5		9162.10			10
9110.95		5		9162.42			10
9112.52				9162.67			10
9112.77				9162.93			10
9113.43				9163.39			10
9113.64				9163.77			10
9114.33				9164.47			10
9114.61				9164.76			10
9114.80				9165.50			10
9115.06				9166.13			10
9115.73			5	9166.63			10
9116.08			5	9166.86			10
9116.38			5	9167.41			10
9116.48			5	9168.07			10
9120.14		6		9168.36			10

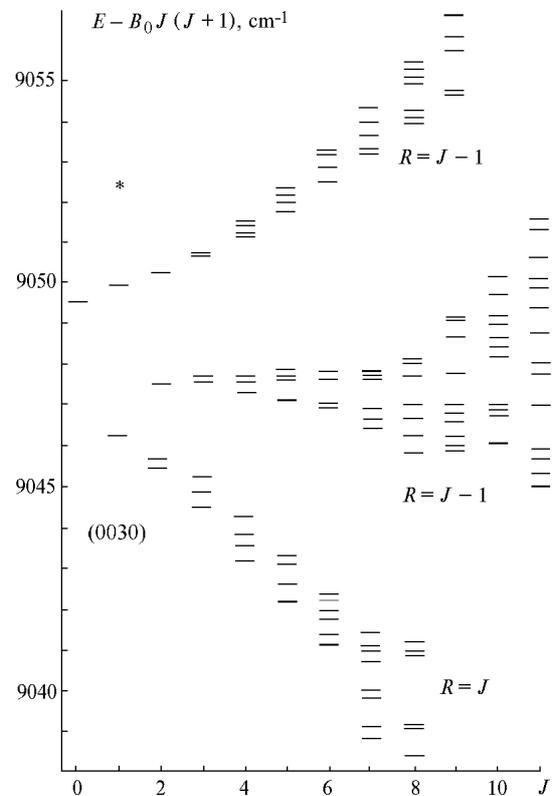


Fig. 1. Rotational energy levels structure of the (0030) and (*) states of $^{12}\text{CH}_4$.

Table 2. Energy levels of the (0030) state of $^{12}\text{CH}_4$

J	E_Q, cm^{-1}	E_R, cm^{-1}
7	9041.57	9041.55
7	9041.23	9041.29
7	9041.13	9041.10
7	9040.87	9040.82
7	9040.10	9040.13
7	9039.92	9039.92
7	9039.24	9039.25
7	9039.00	9039.00
8	9039.35	9039.38
8	9039.25	9039.27
8	9041.36	9041.37
8	9041.17	9041.17
8	9041.02	9040.98

The structure of energy levels of the (0030) state (Table 2) at the values of rotational quantum number $J > 7$ is strongly perturbed. This perturbation is due to the resonance interaction of the (0030) state with the state having vibrational energy $E_v = 9049 \text{ cm}^{-1}$. The $R = J + 1$ levels of this state at high values of J start to overlap with the $R = J - 1$ levels of the (0030) state. In addition to lines of the band centered at 9049 cm^{-1} weaker lines which may be explained as belonging to "forbidden" transitions are observed between the R -branch lines of the $3\nu_3$ band.

$^{13}\text{CH}_4$

The $3\nu_3$ band of the $^{13}\text{CH}_4$ is used in analysis of atmospheres of the Solar system planets. Laboratory investigations of methane- ^{13}C allowed one to estimate a content of this isotope in the Jupiter atmosphere. The structure of the $3\nu_3$ band has been only poorly investigated so far. Seventeen lines of $^{13}\text{CH}_4$ belonging to the $R(1)\dots R(6)$ multiplets of the $3\nu_3$ band were recorded in Ref. 8. Low sensitivity of the spectrometer hampered recording of lines corresponding to transitions between states with higher values of the rotational quantum number.

Table 3. R -branch line positions of the $3\nu_3$ band of $^{13}\text{CH}_4$

J	Frequency, cm^{-1}	J	Frequency, cm^{-1}
1	9042.02	7	9105.69
2	9052.79	7	9106.13
3	9063.42	7	9106.31
3	9063.52	7	9106.81
4	9073.99	7	9107.12
4	9074.22	7	9107.54
4	9074.29	8	9116.78
5	9084.69	8	9117.09
5	9084.82	8	9117.48
5	9084.96	8	9117.66
5	9085.16	8	9118.89
6	9094.97	8	9119.04
6	9095.16	8	9119.20
6	9095.36	8	9119.35
6	9095.61	8	9120.00
6	9095.96		
6	9096.16		

Absorption spectrum of the $^{13}\text{CH}_4$ was recorded in the $9200\text{--}9500 \text{ cm}^{-1}$ region at pressures of 95 and 200 Torr. Multiplets of the R -branch of the $3\nu_3$ band with values of rotational quantum number as high as 8 were recorded in the spectrum of methane isotope. Line positions with rotational identification are presented in Table 3. The energy levels of the subsystem of levels with $R = J - 1$ of the (0030) state of $^{13}\text{CH}_4$ up to $J = 8$ were determined by adding the corresponding values of the ground state energy levels.⁹ Thus obtained energy levels have typical tetrahedral structure and are not subjected to strong perturbations observed in the case of the (0030) state of $^{12}\text{CH}_4$.

SiH_4

Rovibrational spectra of silane (SiH_4) molecule are of interest for investigation of the local mode approach in studying the characteristic features of the energy levels yielding spectra of high-symmetry molecules, rovibrational interaction of highly excited states. Knowledge of the energy levels structure, thermodynamical properties of the molecule is necessary in developing chemical technologies of new generation.

When analyzing the absorption spectra using the local mode approach, one considers the states ($n000$) where $n = 1, 2, 3, \dots$. At present the states with n up to 7 are well studied and the absorption lines have been identified up to spectral range of 14500 cm^{-1} (see Refs. 10 and 11). At the same time states with simultaneously excited valent and bending vibrations are significantly poorer investigated with the available data on the low lying states ($n100$) only.¹²

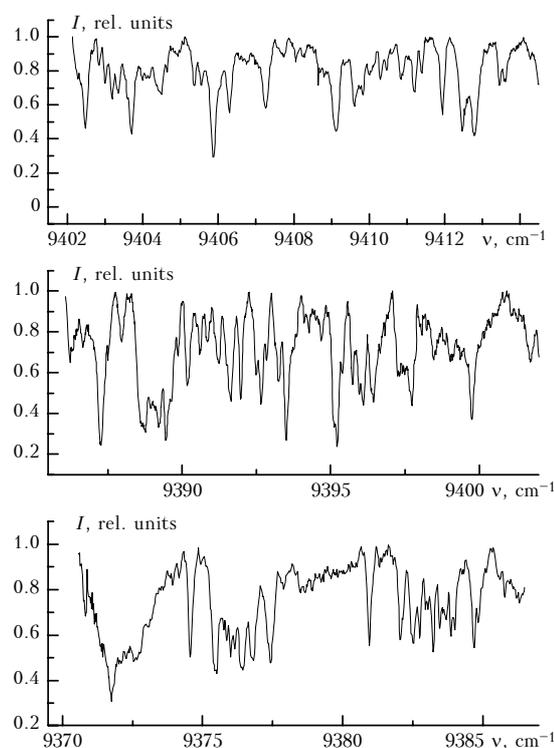
**Fig. 2.** Absorption spectrum of silane within $1.06 \mu\text{m}$ range.

Table 4. Fragment of absorption spectrum of SiH₄

Frequency, cm ⁻¹	
9402.48	9409.13
9402.84	9409.61
9403.01	9409.83
9403.19	9410.31
9403.34	9410.47
9403.70	9410.85
9404.64	9411.20
9405.38	9411.40
9405.55	9411.95
9405.87	9412.48
9406.30	9412.79
9407.26	9413.46
9408.06	9413.60

Absorption spectrum of the SiH₄ was recorded using an intracavity laser spectrometer within 1.06 μm range at a pressure of 2 Torr and temperature of 300 K (Fig. 2 and Table 4). Absorption lines in the analyzed region are located between the well investigated (4000)–(0000) and (5000)–(0000) bands centered at 8347 and 10267 cm⁻¹, respectively. The estimations show that the spectrum in this region is generated by the superposition of the transitions between the states: (1111: A₁), (2200: A₁, E, F₁, 2F₂) and (3100: A₁, E, F₁, 2F₂) at high values of the rotational quantum number *J*. The identification of this spectrum

is considerably complicated by the lack of information on low lying levels of these states with low *J* values.

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