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Research on absorption spectroscopy of CH_4 around 1.315 μm

Jie SHAO[1, 2], Xiaoming GAO[1, 2], Lunhua DENG[1, 2], Wei HUANG[2], Yong YANG[2],
Shixi PEI[2], Yiqian YUAN[1], Weijun ZHANG[2]

[1]Laboratory of Atmospheric Optics, Anhui Institute of Optics and Fine Mechanics,
Chinese Academy of Science, Hefei 230031, China

[2]Environmental Spectroscopy Laboratory, Anhui Institute of Optics and Fine Mechanics,
Chinese Academy of Science, Hefei 230031, China

Measurements have been made about the absorption features of CH_4 around 1.315 μm by using the second harmonic detection technique of tunable diode laser with multipass cell (white). Studies concerning the second harmonic detection technique of CH_4 around 1.65 μm have been widely reported currently, but reports about the absorption features in NIR spectra of CH_4 around 1.315 μm can scarcely be found. We have performed a detailed study about the absorption features of CH_4 around 1.315 μm and we present the results here. We give the line positions, the line intensities and self-broadening coefficients near 1.315 μm at a pressure of 0.077 torr.

Keywords: modulation spectroscopy, diode lasers, the second harmonic detection.

1. Introductions

Wavelength-modulation (WM) methodologies are frequently used for detection of species in absorption spectrometry, primarily with diode lasers due to their excellent tunability [1–3]. This experimental technique is not only widely used to monitor weak signals for the trace gas detection but can also be used to study the parameters of absorption lines [2, 4, 5].

Tunable diode laser absorption spectroscopy was used with second harmonic detection, which has the merits of high sensitivity, real-time detection, *etc*. It has become an advanced technique applied to optical sensors of polluting gases and has recently aroused wide interest. Diode lasers are characterized by low-cost, small volume, tunability, fiber-optic compatibility and can detect many characteristic qualities of different places and different gases synchronously.

Methane, the main component of natural gas, is one of the most important energy resources used in everyday life. It is very dangerous when its concentration in the atmosphere exceeds 5% [6]. The detection of concentration of CH_4, H_2O, CO_2, CO, *etc*., is always related to combustion and propulsion processes. Their concentrations are directly connected with the capability parameters of combustion and propulsion processes. So, the diagnostic method of detecting the concentration of CH_4, and H_2O in the combustion and propulsion processes has a good applicational future. A thorough investigation of the absorption spectra of CH_4 is of vital importance. There are numerous reports on the detailed absorption lines of H_2O around 1.315 μm, but those concerning CH_4 are scarce. Our research results present detailed absorption spectral lines of CH_4 around 1.315 μm obtained by using tunable diode laser absorption spectroscopy (TDLAS) with a long-path absorption cell (white). We obtain detailed spectral features of pure CH_4 in the range of 7602–7617 cm^{-1} under the low pressure condition and offer the experimental testimony to detecting CH_4 and H_2O synchronously using the same laser as gas sensors.

2. Theory

TDLAS usually scans over an isolated absorption line of the species under investigation using a single narrow laser line. To achieve the highest selectivity, the sample is made at low pressure, where the absorption lines are not substantially broadened by pressure [2, 7]. The TDLAS technique has developed into a very sensitive and general technique for monitoring most atmospheric trace species.

The intensity of monochromatic laser radiation of frequency ω transmitted through a sample cell containing an absorbing species is given by Beer's law:

$$I(\upsilon) = I_0 \exp(-\sigma L \rho) \tag{1}$$

where I_0 and I are referred to as the incident and transmitted radiation intensities, respectively, σ – the absorption cross-section of sample gases, L – the optical path length within the cell, ρ – density of absorbing species.

In order to improve the sensitivity, wavelength modulation spectroscopy with tunable diode laser sources has been used since the early 1970s [7]. When the laser is modulated around its center frequency υ_0 at a frequency ω_m, the instantaneous frequency is $\upsilon = \upsilon_0 + \delta\upsilon\cos(\omega_m t)$, where $\delta\upsilon$ is the modulation amplitude. The intensity $I(\upsilon)$ of the radiation transmitted through the absorption cell can then be expressed as a cosine Fourier series:

$$I(\upsilon, t) = \sum_{n=0}^{\infty} A_n(\upsilon)\cos(n\omega_m t). \tag{2}$$

The individual harmonic components A_n (for $n > 0$) can be measured with a lock-in amplifier and are given by:

$$A_n(\upsilon) = \frac{2}{\pi}\int_0^{\pi} I_0(\upsilon + \delta\upsilon\cos\theta)\exp\left[-\sigma(\upsilon + \delta\upsilon\cos\theta)L\rho\right]\cos(n\theta)\mathrm{d}\theta \tag{3}$$

where θ has been substituted by $\omega_m t$. In the limit of low absorbance ($\rho L\sigma \ll 1$), which is true for trace gas detection at ppb level, this equation becomes:

$$A_n(\upsilon) = \frac{2I_0}{\pi}\int_0^{\pi}\exp\left[-\sigma(\upsilon + \delta\upsilon\cos\theta)L\rho\right]\cos(n\theta)\mathrm{d}\theta. \tag{4}$$

Thus, each harmonic component is directly proportional to the species density ρ. In this case, a Taylor series expansion of $\sigma(\upsilon)$

$$A_n(\upsilon) = -\eta\frac{I_0 S\rho L 2^{1-n}}{n!}\delta^n\upsilon\left.\frac{\mathrm{d}^n\chi(\upsilon)}{\mathrm{d}\upsilon^n}\right|_{\upsilon = \upsilon_0}. \tag{5}$$

Here, the n-th harmonic component is proportional to the n-th derivative of $\chi(\upsilon)$ and the technique is known as derivative or wavelength modulation spectroscopy. At the same time, one can see that the harmonic components are directly proportional to the density ρ of the sample, so the technique can be used to detect the density of gases.

During the measurement of the absorption lines of gaseous molecules, there are three main broadening mechanisms, which are natural broadening, Doppler broadening and collision broadening. Because of the relatively narrow width of natural broadening of gaseous molecules compared to the linewidth of diode lasers, the natural broadening will not be considered in the TDLAS technique. At low pressure, Doppler broadening is of great importance. The absorption has the normalized Gaussian lineshape:

$$\chi_G(\upsilon) = \frac{1}{\gamma_D}\sqrt{\frac{\ln 2}{\pi}}\exp\left[-\ln 2\left(\frac{\upsilon - \upsilon_0}{\gamma}\right)^2\right] \tag{6}$$

where γ_D is the half-width of Doppler broadening, and

$$\gamma_D = 3.58\times 10^{-7}\times\upsilon_0\sqrt{T/M}, \tag{7}$$

(υ_0 – the central frequency of absorption line, T – the temperature in Kelvin and M – the molecular weight).

At high pressure, the collision broadening is of importance and the absorption lineshape is given by the normalized Lorentzian function.

$$\chi_L(\upsilon) = \frac{1}{\pi}\frac{\gamma_L}{(\upsilon-\upsilon_0)^2+\gamma_L^2}, \tag{8}$$

$$\gamma_L = \gamma_{L,0}\frac{p}{p_0}\left(\frac{T_0}{T}\right)^{1/2}. \tag{9}$$

Here, γ_L is the half-width of collision broadening, $\gamma_{L,0}$ – the half-width of collision broadening under the standard atmospheric pressure (T_0, p_0).

The second harmonic signal of Gaussian lineshape function is:

$$S_L^2(\upsilon) = -\eta\frac{I_0 S\rho L\gamma_L}{2\pi}\left\{\frac{\gamma_L^2-3(\upsilon-\upsilon_0)^2}{\left[(\upsilon-\upsilon_0)^2+\gamma_L^2\right]^3}\right\}\delta^2\upsilon \tag{10}$$

The second harmonic signal of Lorentzian lineshape function is:

$$S_G^2(\upsilon) = -\eta\frac{I_0 S\rho L}{2\gamma_L^5}\ln 2\exp\left[-\ln 2\left(\frac{\upsilon-\upsilon_0}{\gamma_D}\right)^2\right]\left[\gamma_D^2-2\ln 2(\upsilon-\upsilon_0)^2\right]\delta^2\upsilon. \tag{11}$$

When the Doppler linewidth is comparable to Lorentizian linewidth, the absorption lineshape is the convolution of a Lorentizian and a Gaussian lineshape function.

3. Experimental apparatus

The experimental apparatus used in this work is shown schematically in Fig. 1. For this experiment the NEL 13563TG DFB laser has been adopted as the source. The current and temperature were controlled by a laser-controller (TDS3724B), which performed the scan of the emission wavelength by the driving current with a low frequency sawtooth signal or by scanning the driving temperature. After splitting, a small portion of light from diode laser was sent to a wavemeter (WA-1500 NIR, Buleigh) through optic coupler for wavelength monitoring, the majority of light transmitted the mutilpass cell through coupling system and then was detected by a detector (New Foucs). The signal from detector was sent to a lock-in and demodulated to extract the second harmonic signals. A DAQ was used to acquire the harmonic signal from the lock-in. A GPIB card was used with the computer to control the laser

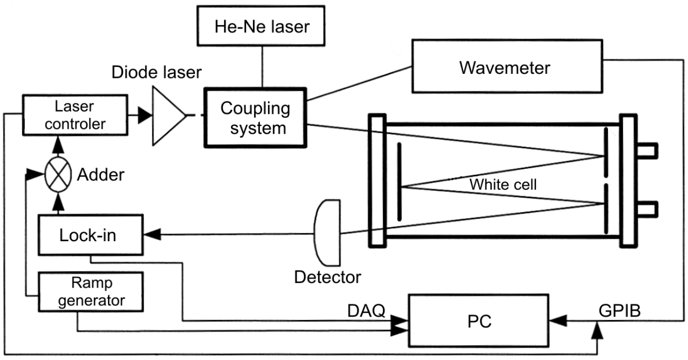

Fig. 1. Schematic diagram of experimental set up.

controller and read the wavenumber from the wavemeter. The mutilpass cell is white-type geometry with an 8 m base path length and can achieve total path length of 46–1159 m.

4. Results and discussion

As an example, a record of the low-pressure (0.077 torr) Doppler broadened CH_4 at 7605.54656 cm^{-1} is presented in Fig. 2 together with the residual of the multispectrum nonlinear least-squares fitting to the Gauss lineshape model. Figure 2, illustrates the absorption spectra with the peak at 7605.54656 cm^{-1} of CH_4 within a current scan

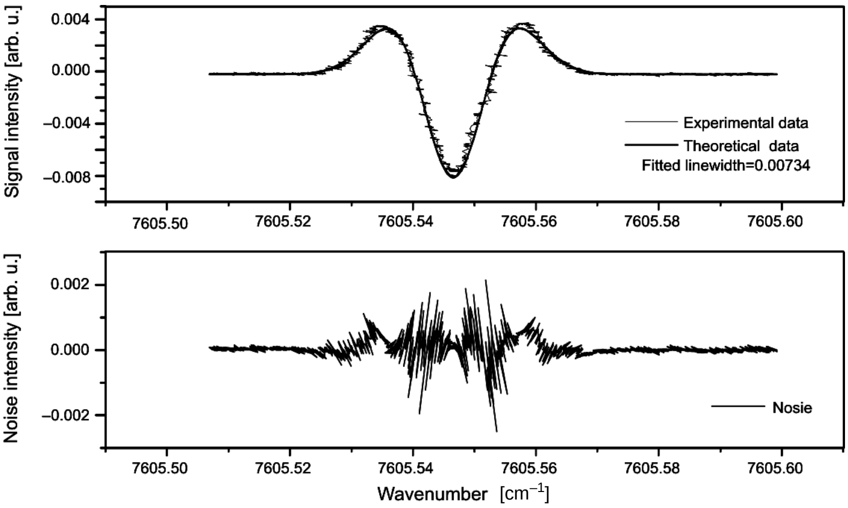

Fig. 2. Absorption line observed by WM spectroscopy and the 2nd harmonic detection technique for the gas pressure of 0.077 torr and the lock-in time constant of 3 ms.

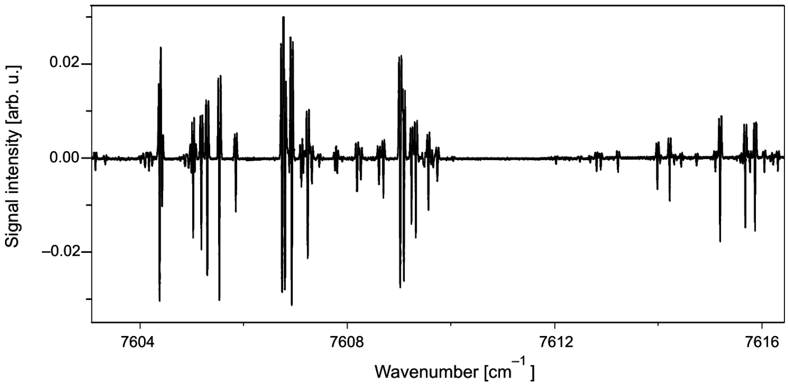

Fig. 3. Signal measured spectral absorbance of pure CH_4 by WM and the 2nd harmonic detection technique. The cell pressure was 0.183 torr, optical length was 602.68 m.

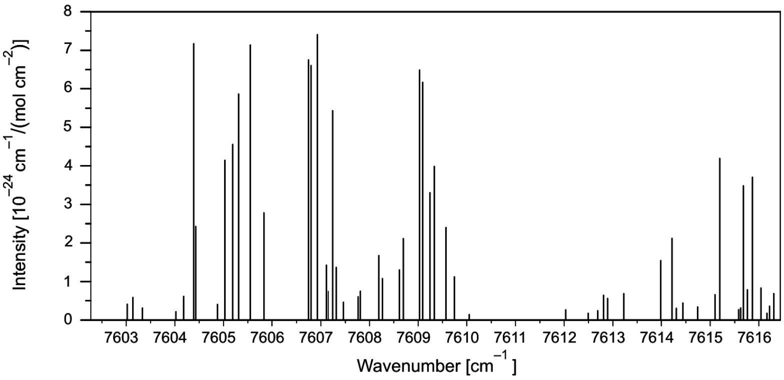

Fig. 4. Position of spectral line and the intensity of CH_4 obtained by means of WM spectroscopy and the 2nd harmonic detection technique.

cycle. The dashed line represents the signal detected by the second harmonic. The solid one is the fitted signal by using wavelength modulation theory and non-linear least square fit. During the wavelength scan period we keep the temperature and center current of diode laser at 27°C and 70 mA, respectively, with the optical path of 602.68 m. The modulation frequency and modulation amplitude of lock-in are 1.78 kHz and 40 mV, respectively. The calculated SNR is about 4, and the corresponding absorption is 3.04×10^{-6}.

In our experiment, many CH_4 absorption lines have been detected by TDLAS. There are tens of absorption lines found in the 7602–7617 cm^{-1} range. Their wavenumbers and line intensities have been obtained from the measured wavenumbers by comparing to the reference signal of CO_2 absorption lines. The experimental data obtained are given in Fig. 3. The figure shows a plot of the 7602–7617 cm^{-1} spectral region as recorded with a sample pressure of 0.183 torr 99.99% pure CH_4 and the

T a b l e. Measured spectra positions, line intensities and self-broadening coefficients.

υ_0 [cm^{-1}]	γ $\left[\frac{\text{cm}^{-1}}{\text{atom}}\right]$	S $\left[\frac{10^{-24}\text{cm}^{-1}}{\text{molecule cm}^{-2}}\right]$	υ_0 [cm^{-1}]	γ $\left[\frac{\text{cm}^{-1}}{\text{atom}}\right]$	S $\left[\frac{10^{-24}\text{cm}^{-1}}{\text{molecule cm}^{-2}}\right]$
7616.30823	0.0935	0.68722	7608.69333	0.0935	2.1149
7616.21899	0.086	0.36156	7608.61201	0.081	1.30052
7616.16785	0.1103	0.17546	7608.26387	0.0906	1.0783
7616.04058	0.0916	0.82679	7608.19158	0.0972	1.67222
7615.8682	0.0926	3.70461	7607.80772	0.0887	0.74957
7615.76383	0.0843	0.78359	7607.76435	0.0869	0.60894
7615.67942	0.0897	3.48489	7607.46179	0.0852	0.46218
7615.62926	0.081	0.31503	7607.31072	0.0946	1.36449
7615.58369	0.1079	0.26851	7607.23456	0.0835	5.43573
7615.19508	0.0906	4.19546	7607.15516	0.103	0.74725
7615.1001	0.0916	0.65845	7607.11161	0.0818	1.42358
7614.7461	0.0878	0.33764	7606.92962	0.0826	7.40904
7614.44372	0.1055	0.44043	7606.79983	0.0899	6.60335
7614.30691	0.086	0.30361	7606.7456	0.0891	6.75237
7614.21794	0.0869	2.12389	7605.82555	0.0937	2.78395
7613.98524	0.1032	1.5422	7605.54656	0.0858	7.13808
7613.22406	0.0843	0.68996	7605.30244	0.0869	5.86014
7612.89102	0.1103	0.55632	7605.1854	0.087	4.56018
7612.80917	0.0852	0.64493	7605.02354	0.0843	4.14414
7612.68826	0.1009	0.24269	7604.87095	0.1103	0.40445
7612.48967	0.1103	0.17324	7604.42824	0.0906	2.43399
7612.03015	0.0835	0.26596	7604.38354	0.089	7.16733
7610.04437	0.081	0.14325	7604.17621	0.0987	0.60945
7609.74015	0.0987	1.12264	7604.01654	0.1106	0.21694
7609.57035	0.0935	2.40103	7603.33169	0.111	0.30887
7609.32545	0.0818	3.9895	7603.14217	0.1036	0.58733
7609.2413	0.0966	3.30624	7603.01675	0.1025	0.4151
7609.32545	0.093	3.9895	7602.12196	0.11	0.17546
7609.2413	0.086	3.30624	7602.00962	0.0887	0.1306
7609.09212	0.0946	6.16403	7600.75121	0.0946	0.31503
7609.02441	0.0926	6.48563	7600.40276	0.0852	0.36156

absorption path of 602.68 m. The spectra positions and relative intensity are illustrated in Fig. 4.

The experimental data for the line intensity and self-broadening of CH_4 near 1.315 μm are compiled in the Table.

5. Conclusions

We obtained detailed spectral features of pure CH_4 in 7602–7617 cm^{-1} region at room temperature by using NIR TDLAS technique, which gives the experimental basis for detecting CH_4 and H_2O synchronously by just using a laser. We give line intensity and self-broadening coefficient of unknown lines from the experimental data. At the same time, we give nearly tens of strong absorption lines of CH_4, which points out the direction of investigating the gas sensor of CH_4 within the region.

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