High Resolution and High Sensitivity Measurement of Methane at 1.51 μm *

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The high-resolution absorption spectrum of CH_4 at 1.51 μm is observed by direct absorption spectroscopy technique with a White absorption cell. Multi-peak fitting technique is adopted to reveal line positions and line intensities of CH_4 from 6608 cm^{-1} to 6625 cm^{-1}. Special attention is paid on the determination of the line positions, and the accuracy is better than ± 0.002 cm^{-1}. A minimum measurable absorption of 2.1×10^{-8} (3σ) has been achieved based on the measured direct absorption spectroscopy.

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As the main component of natural gas, methane is one of the most important energy resources. When the concentration of CH_4 in the atmosphere exceeds 5%, it will has a danger of explosion;[1] so it is also a dangerous gas. Under some conditions such as combustion process, the concentrations of CH_4 are generally used as the diagnostic factor. Because of its important role in life, many researchers have focused their attention on the high resolution spectra[2−6] or the concentration detection[7,8] of methane. During the methane concentration detection and other diagnostic application, the parameters such as the intensity and pressure broadening coefficient of the absorption lines are of great importance.[9−12]

In the near-infrared (NIR) spectral region, the absorptions of methane due to its combination rovibrational bands. Some investigations have been performed on line parameters measurement of methane in the near-infrared (NIR) region.[11,12] The line parameters of methane at 1.51 μm have been studied by Brown[13] and the results are used by the HITRAN database.[14] In our experiments, we found that the parameters of methane given in HITRAN database at 1.51 μm do not represent the real materials. Therefore we are motivated to have a detailed research on the absorption spectrum of CH_4 at 1.51 μm using direct absorption spectroscopy detection technique together with a long-path absorption cell (White). We obtain the detailed spectral features of pure CH_4 from 6608 cm^{-1} to 6625 cm^{-1} under laboratory condition. The acquired high resolution and high sensitivity absorption spectrum have made the retrieval of accuracy spectral parameters possible.

The experimental apparatus has been introduced before[9,10] and is schematically shown in Fig. 1. The absorption cell is White-type with the base path length of 7.726 m. The total optical path length ranges from 46.356 m to 1158.9 m according to the relationship $7.726 \times 2 \times (4 \times n - 1)$, where n is an integer ranging from 1 to 19. The pressure in the absorption cell is determined by the combination of a 1000-Torr capacitance manometer and an oil pressure gauge (for low pressure) or a mercury pressure gauge (for high pressure). During the experiments, the cell was filled with the natural abundance methane gas of 99.99% purity. A monochromatic-frequency distributed feedback (DFB) diode laser with the tuning range from 6608 cm^{-1} to 6625 cm^{-1} was used. It has the typical linewidth of about 2 MHz which can be neglected as compared to the molecular absorption line width. A laser controller (TDS3724B, LightWave) is used to control the injection current of the diode laser. The diode laser controller is linked to a personal computer (PC) via a GPIB (General Purpose Interface Bus) interface. The temperature and injection current ramps of the diode laser are communicated to the controller from custom logic routines in the PC via the GPIB interface. A laser beam splitter is used to split the laser beam. Most of the power is directed through the cell for absorption spectrum measurement. The residual power is directed to a wavemeter (WA-1500 NIR, Buleigh) for monitoring the frequency. The transmitted laser intensity from the White cell was captured by an InGaAs photodiode. A PC-based data acquisition board (DAQ) is used to acquire data.

The line positions of pure methane gas have been determined at 1.51 μm in laboratory with two methods. The first method was used to determine the positions of strong lines. In this method, the injection temperature of the diode laser increased from

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10°C to 44°C with 1°C increment. For each temperature point, the injection current of the laser varies from 30 mA to 100 mA with 0.03 mA increment. The transmitted intensity of the laser is recorded together with the corresponding wavelength at each current value. The wavelength is monitored using a wavemeter. For lines with intensity greater than $4.0\times10^{-26}\,\mathrm{cm^{-1}/(molecule\,cm^{-2})}$, their line positions are determined using this method and the accuracy is better than $\pm0.0015\,\mathrm{cm^{-1}}$.

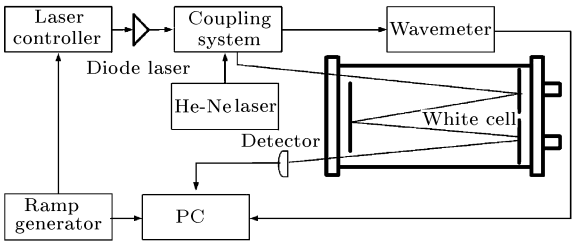


Fig. 1. Schematic representation of experimental setup for the high resolution measurement.

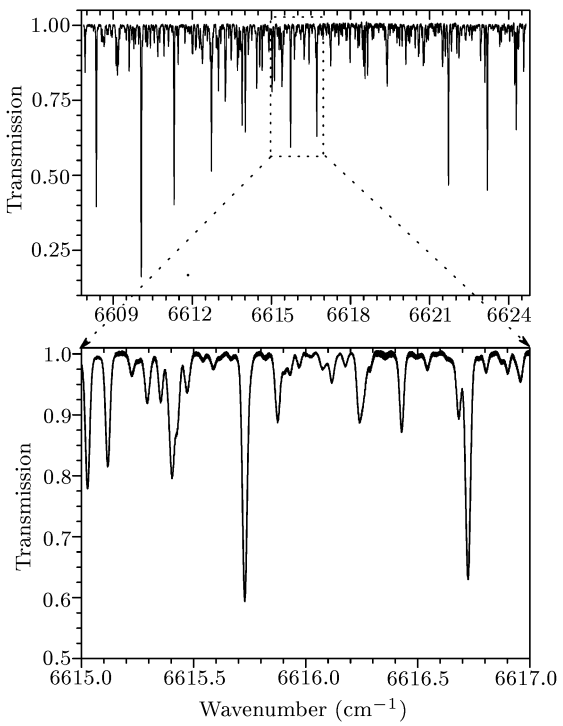


Fig. 2. Measured direct absorption spectrum of pure methane at room temperature. The path length and the pressure are 973.476 m and 18.87 Torr, respectively.

However, though the above method can gain relatively accurate line position, it has bad signal-to-noise ratio and is ineffectual to determine the positions of weak lines. For weak lines, the second method has been used to determine their positions. In this method, a 0.6-Hz injection current tuning is used to scan the DFB diode over a frequency range of about $1\,\mathrm{cm^{-1}}$ repeatedly and the data are averaged to gain an adequate signal-to-noise ratio. The tuning rate of the frequency is calibrated at the same temperature with a wavemeter measured at the same injection current ramp amplitude and sweep rate. The strong-line positions measured using the first method have been used to amend the small error of the weak-line positions occurring from the non-linearity tuning of the diode laser. Thus the positions of weak lines can be determined and the accuracy is better than $\pm0.002\,\mathrm{cm^{-1}}$.

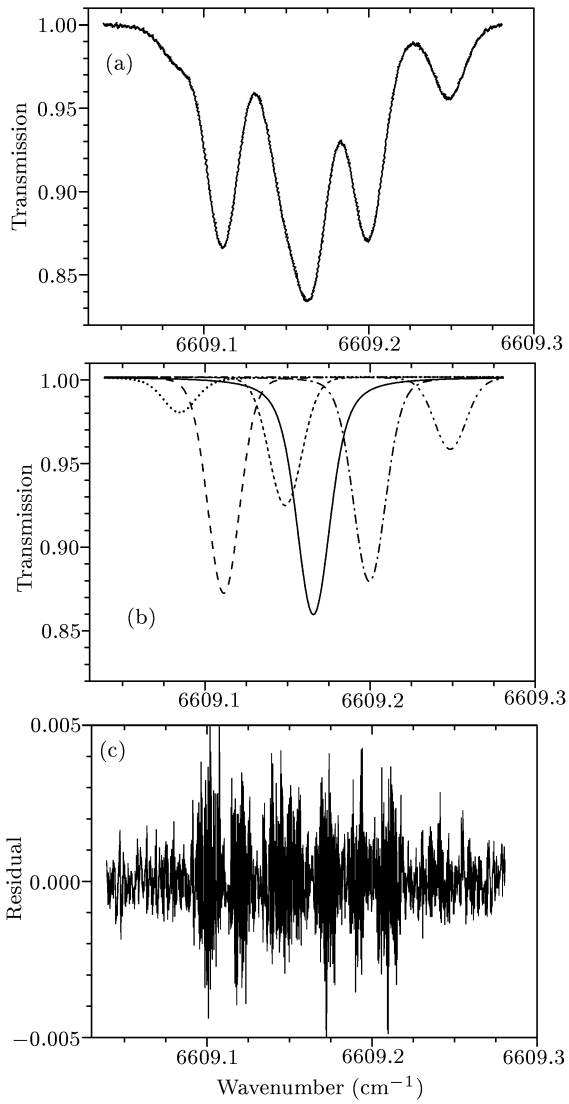


Fig. 3. Overlapped direct absorption spectrum (a) and its fitted lines (b) using a Voigt line shape; (c) the residual. The pressure and the optical path are 18.81 Torr and 973.476 m, respectively.

There are more than 320 absorption lines have been investigated during the spectral region from $6608\,\mathrm{cm^{-1}}$ to $6625\,\mathrm{cm^{-1}}$. The measured high resolution absorption spectrum of methane is shown in Fig. 2. The figure shows the connected spectrum of

several single frequency scan. For data shown in the figure, the optical length and the pressure in cell are 973.476 m and 18.87 Torr, respectively. The enlarge panel shows the detail of the measured spectrum.

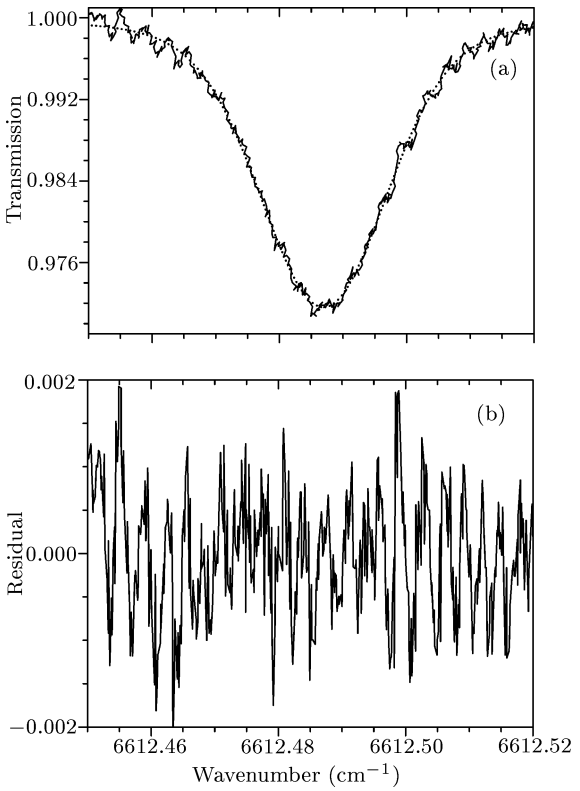


Fig. 4. (a) The absorption spectrum (at 6612.486 cm^{-1}) of CH_4 observed by direct absorption detection technique and its fitted line to a Voigt line shape; (b) the residual. The pressure and the optical path are 15.2 Torr and 973.476 m, respectively.

This kind of overlapped absorption spectrum must be properly fitted to obtain accurate line parameters. The multi-peak fitting technique has been used in our data fitting process. An example of the measured direct absorption spectrum and its multi-peak fitting results are shown in Fig. 3. The direct absorption spectrum shown Fig. 3(a) is obtained from CH_4 with 99.99% purity. The absorption optical path length and pressure are 973.476 m and 18.81 Torr, respectively. The measured spectrum is fitted to a Voigt line shape and the fitted lines are shown in Fig. 3(b). It can be seen that six lines overlap within the narrow spectral region. During the Voigt line-shape fit process, the Gaussian width is fixed at the Doppler line width and the Lorentizian line width varies to reach the best fit. The residual in Fig. 3(c) shows that the multi-peak fitting can distinguish the single absorption line from the overlapped spectrum satisfactorily.

The detection sensitivity has also been studied experimentally. The absorption spectrum for peak 6612.486 cm^{-1} at room temperature is shown in Fig. 4. The pressure and the optical path length are 15.2 m and 973.476 m, respectively. The measured absorption line shape is fitted to the Voigt line shape using a nonlinear least-squares fit process and the line intensity is determined to be 1.20×10^{-26} cm^{-1}/(molecule cm^{-2}). Figure 4(b) shows the fringes arising from the White cell. The SNR, which is the ratio of the peak amplitude of the fitted signal to its rms deviation, is about 41.4 with the absorption at line centre corresponding to 2.87×10^{-7}. Thus, the minimum measurable absorption would then be 2.1×10^{-8} (3σ).

In summary, the high-resolution absorption spectrum of CH_4 has been studied at room temperature from 6608 cm^{-1} to 6625 cm^{-1} with a tunable diode laser spectrometer associated with a multi-pass cell. The results are helpful for further improvement of reliable retrievals of the concentration of this minor constituent in the atmosphere. Multi-peak fitting technique has been successfully used to resolve the seriously overlapped absorption spectrum to reveal the line parameters. When the optical path length and the pressure are 973.476 m and 15.2 Torr, the minimum measurable absorption for the line of 6612.486 cm^{-1} is about 2.1×10^{-8} (3σ).

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