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A Trace Methane Detector Based on Mid-infrared Tunable QCL at 7.5μm*

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Abstract: In order to detect trace methane (CH_4) with non contact, the proposed manuscript describes high sensitivity trace methane detector using quantum cascaded laser (QCL) with centre wavelength at 7.5 μm, which is based on combination of Tunable Diode Laser Absorption Spectroscopy (TDLAS) and Wavelength Modulation Spectroscopy (WMS). Under room temperature, the spectrum of QCL can scan CH_4 absorption line via adjusting the injection current of QCL. Meanwhile, a compact herriott cell (40 cm long and 800 ml volume) is utilized to achieve a total optical path with 16 meters length. The aforementioned detector is applied to detect CH_4 with different concentrations, results show that the relative detection error is less than 7%, the lowest detection is 1×10^{-6}. Meanwhile, the researchers can detect other gases through replace lasers with different wavelength.

Keywords：Spectroscopy; TDLAS-WMS; Trace Methane; Quantum Cascaded Laser (QCL); Herriott Cell

1 Introduction

Compared to the traditional chemical analysis method, the detection method based on intermediate infrared absorption spectrum has advantages including convenience, efficiency and no damage to gas sample, so it has been widely used in fields such as petrochemical engineering, food safety inspection, public security, and so forth[1-3]. The lasing wavelength is intermediate infrared QCL when compared with the light source of traditional near-infrared spectroscopy. And it has high light intensity and good coherence. Moreover, we can select the lasing wavelength by adjusting the injection current to make it consistent with the spectral line of the largest absorption strength of the tested gas, so as to realize high-precision detection of hazardous gas in concentration of trace quantity [4-5].

In 2005, R. Kormann et al detected the concentration of CH_4 in the air under liquid nitrogen refrigeration by using QCL, and the lower limit of concentration in detection is 50×10^{-6} [6]. In 2012, L. Dong et al detected CH_4 with gas concentration of trace quantity by using lasing wavelength of 3.3 μm, with the minimum lower limit of detection of 10×10^{-6}[7]. In recent years, many scientific research institutions and institutions of higher learning have also tried to detect harmful gas by QCL, including Semiconductor College of Chinese Academy of Sciences, Anhui x Ray Machine Institute, Jilin University and so on. But no report on the detector of CH_4 with concentration in trace quantity by using

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continuously working intermediate infrared QCL under indoor temperature has been found yet.

In this article, we design and develop detector for CH_4 in trace quantity with high sensitivity based on the mixed TDLAS-WMS detecting techniques and in herriott air chamber with total optical distance of 16m. The QCL lasing length of 7.5 μm is used by this detector, and the strong absorption spectral line of CH_4 (1332.8 cm^{-1}) can be found by adjusting the injection current under indoor temperature. And eventually, we obtain the detection limit of CH_4 is 1×10^{-6}.

2 Selection of absorption line

Molecule of the target gas CH_4 detected by this detector has 4 natural vibrations, respectively corresponding with 4 basebands, and all of them locates in middle-infrared band [8]. Compared to the overtone bands and combined bands in near-infrared zone, molecule of CH_4 has stronger absorption at the baseband. According to the HITRAN database of 2004, and considering the molecule of CH_4 has the strongest absorption strength near wave number 1330 cm^{-1}, and also considering the experimental configuration, this detector uses this baseband as absorption band, and uses QCL with central wavelength of 7.5 μm to carry out detection of CH_4 in trace quantity. As indicated in Figure 1, we can adjust the injection current of QCL under indoor temperature during the running of the system to make the output optical wavelength sweep the absorption band of CH_4 near 1330 cm^{-1}, and finally we can get a stronger absorption line (1332.8 cm^{-1}).

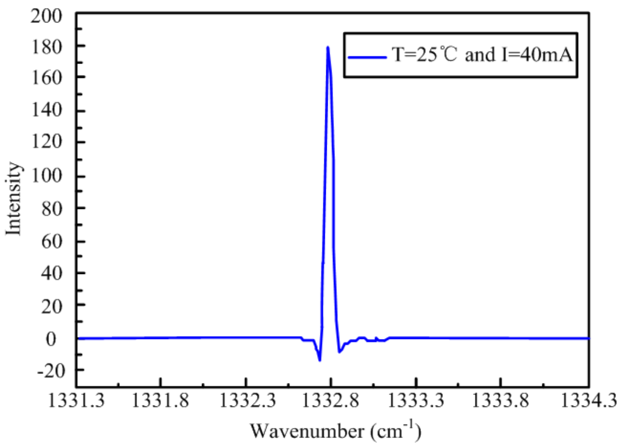

Fig. 1 QCL output wavelength at CH_4 absorption spectrum line, 1332.8 cm^{-1}

3 Deduction of formula of difference absorption method

QCL has advantages including high output energy, wide narrow line and high response speed, so the optical absorption spectrometry based on QCL has been widely used in optical gas detector for gas in trace quantity in different fields. When QCL radiation light beam with wavelength of λ passes through even gaseous medium, the beam propagation based on wavelength shall be determined by Beer-Lambert law[9-10]:

$$T_\lambda = \left(\frac{I_1}{I_0}\right)_\lambda = \exp(-sp\alpha\phi_\lambda cL) \qquad (1)$$

In the formula, I_1 and I_0 are respectively incident light intensity and emergent light intensity before and after passing through the even gaseous medium, s is the intensity of gaseous medium of gas corresponding with the specific emergent light beam, p is total air pressure, α is mole fraction of the absorbing substance, ϕ_λ is linear function, c is concentration of the detected gas, and L is the effective total optical distance of the system. ϕ_λ is generally obtained through Voigt Profile approximation with its feature of Doppler broadening. It can be derived from Formula (1) that,

$$\alpha_\lambda = -\ln\left(\frac{I_1}{I_0}\right)_\lambda = -sp\alpha\phi_\lambda cL \qquad (2)$$

In the formula, α_λ is absorptivity of the detected gas to incident beam, and $k_\lambda = sp\alpha\varphi_\lambda$, which is absorption coefficient. According to the principle above, if we want to realize effective detection of low-concentration gas, we need to increase the effective total optical distance of the system and reduce system noise as much as possible. Based on these, this detector uses gas absorbing chamber with effective optical distance of 16m, and cooperatively adopts reference gas chamber filled with calibrating gas with fixed concentration for standardization. And these measures have effectively restricted the measuring error introduced to the system by optical fluctuation and electrical noise and improved system sensitivity.

4 Configuration of detector

In order to effectively restrict the system noise and improve the lower limit of detection of the detector, this detector uses difference absorption method, that is to say, structure of single light source and double detector is used to establish the system. The overall block diagram is as shown in Figure 2.

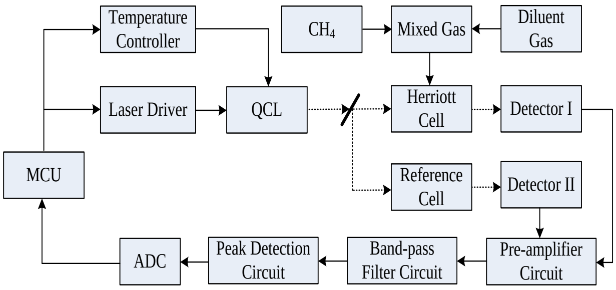

Fig. 2 The block diagram of detector

As for the light source, we use intermediate infrared QCL with central wavelength of 7.5 μm. Since the luminous surface is divergent cone, it will firstly pass through space optical structure of biconvex lens, and collimates the light on cone into parallel light with spot radius of 2mm through secondary converging. Then, it will divide the collimation light into two equal light beams through intermediate infrared 1:1 spectroscope, respectively as effective light and reference light. After this, the two beams will enter herriott gas chamber and reference gas chamber with total optical distance of 16m. The intermediate infrared laser beam output from the two gas chambers above will be focused on the liquid-nitrogen refrigerated HgCdTe infrared detector, and the output signal will be sent into lock-in amplifier for further processing after being amplified by pre-amplifier, so as to realize the detection of CH_4 with concentration in trace quantity. Since the wavelength of QCL central luminescence spectrum adopted by this sensor is 7.5 μm, we select Ge material with transmissivity above 95% to increase the transmissivity of optical devices in intermediate infrared spectrum.

5 Experiment

In the experiment, the independently designed QCL driving power and temperature controller are used to control current and temperature. During the operation, temperature controller is used to control temperature of QCL, to keep it working under 298 K. Overlay the high-frequency sine wave and a slowly changing current ramp signal to realize scanning of absorption line of QCL wave length through gas, by which we realize the adjustment of its output wave length by changing the mode of QCL injection current. Meanwhile, we can obtain CH_4 gas with different concentrations for measurement by detector through quantitative mixing of pure CH_4 and N_2 by using dynamic gas flowmeter.

5.1 Sensitivity of detector

Based on the practical condition of detector, carry out 50 times of repeated measurement experiments (1 min/time) on CH_4 gas with concentration of 1×10^{-6}, and the results are as indicated in Figure 3. The voltage at vertical axis stands for the difference between the output voltage of lock-in amplifier before and after CH_4 flows into herriott gas chamber, namely, the output voltage of lock-in amplifier corresponding with the absorbed light intensity of CH_4.

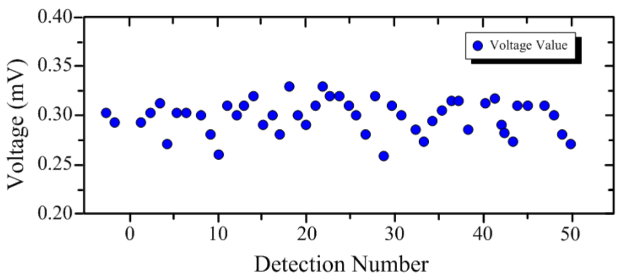

Fig. 3 50 experimental data for CH_4 concentration detection

The average value of test results of 50 experiments is 0.29 mV, and the maximum deviation is 0.03 mV. Suppose SNR (Signal to Noise Ratio) is 1, and the detection sensitivity of this sensor system is 1×10^{-6}.

5.2 Lower limit of detection of detector

The lower limit of detection of concentration of CH_4 can confirm the quality of performance of detector, and it's an important detection index of the measurement.

The experimental results of measurement of CH_4 gas with concentration of 200×10^{-6} are indicated in Figure 4.

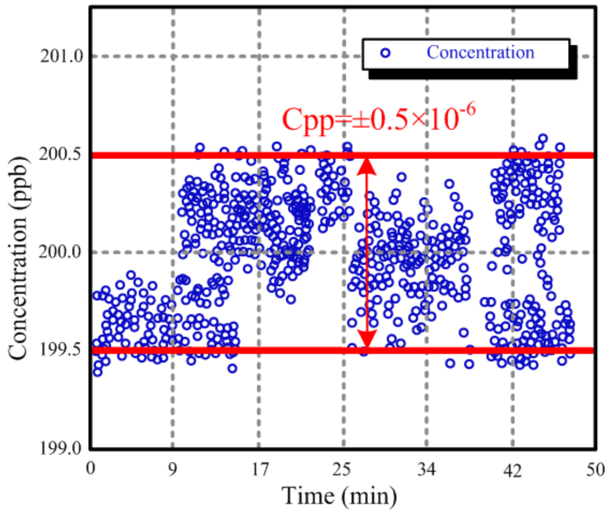

Fig.4 The experimental data under the condition of CH_4 gas concentration is 200×10^{-6}

Results indicate that the practical maximum deviation of gas concentration of CH_4 is $\pm0.5\times10^{-6}$, gas concentration difference of CH_4 is 1×10^{-6}, and lower limit of detection of concentration of CH_4 is 1×10^{-6}

5.3 Stability of detector

Carry out experiment of concentration detection of CH_4 with concentration respectively 0.1‰ and 10% for 30 hours, and the results are as shown in Figure 5.

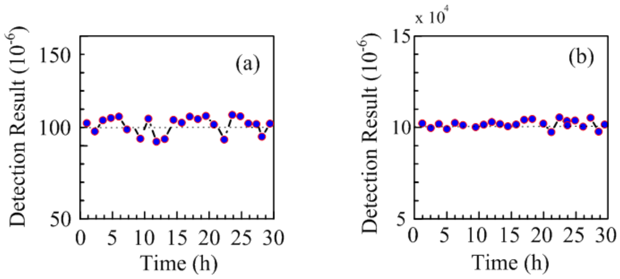

Fig. 5 Detected concentration for 24 hours on two concentration CH_4 gases, (a) 0.1‰, (b) 10%

When the gas concentration of CH_4 is 0.1‰, the result of concentration detection is 0.0912～0.1090 (‰), with relative error less than 7%. When the gas concentration of CH_4 is 10%, the result of concentration detection is 9.7～10.4 (%), with relative error less than 2.5%.

6 Conclusions

Based on detecting techniques with combination of TDLAS-WMS, QCL with central wavelength of 7.5 μm is used in this article to design and develop high-sensitivity trace detection detector. In the meantime, compact herriott gas chamber is used to make the total optical distance in detection reach 16m. In the experiment, the performance of this detector is tested and results tell that the relative error of measurement is less than 7% and lower limit of detection is 1×10^{-6}, so trace detection of CH_4 is feasible.

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