Simulation and Analysis of CH₄ Concentration Measurement Based on QCL-TDLAS

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Abstract. Tunable diode laser absorption spectroscopy (TDLAS) is a kind of gas concentration measurement technology with high precision widely used in the detection of methane (CH₄). Compared with the near-infrared absorption band, CH₄ molecule has greater absorption intensity in the range of mid-infrared absorption band. Therefore, the TDLAS performance can be greatly improved when the mid-infrared quantum cascade laser (QCL) is adopted as light source when detecting CH₄ concentration. As an important parameter, the effect of modulation factor on the second harmonic signal was analyzed, and the optimal value of modulation factor was obtained to be 2.2 by simulation. In addition, both the TDLAS measurements of CH₄ concentration in the range of near-infrared and mid-infrared were simulated and analyzed under normal temperature/pressure and troposphere environment respectively. The results show that the sensitivity of the detection of CH₄ gas in the mid-infrared band of 7.6 μm is greatly improved relative to the absorption band of 1.6 μm in the near-infrared.

1. Introduction

CH₄ is a kind of gas with extremely high combustion efficiency. It exists in a large amount in nature and is widely used in production and life. CH₄ is flammable and extremely explosive in the air, and its explosion limit is 5%~15% at normal temperature and pressure [1]. Simultaneously, CH₄ is one of the greenhouse gases at the top of the troposphere that is second only to CO₂ in triggering the greenhouse effect, and the greenhouse effect of CH₄ is much greater than that of CO₂ [2,3]. Therefore, it is particularly important to monitor the concentration of CH₄ gas in real time. Tunable diode laser absorption spectroscopy (TDLAS) has the advantages of high accuracy, high sensitivity, and non-contact compared with traditional detection methods [4], whose measurement methods include direct absorption method and wavelength modulation method [5]. The second harmonic method in the wavelength modulation method is used to invert the concentration of the gas to be measured by extracting and analyzing the second harmonic in the gas absorption signal, which can effectively reduce the interference of the background signal to the experiment and improve the accuracy of the experimental measurement [6, 7]. Currently, near-infrared Distributed Feedback Laser (DFB) is used as the main light source to measure CH₄ concentration. However, the absorption intensity of CH₄ molecules in the near-infrared band is too weak, which makes it difficult to meet the measurement requirements of CH₄ concentration. The absorption intensity of CH₄ in the mid-infrared band (7~8 μm) is dozens of times greater than that in the near-infrared band. Therefore, the absorption spectrum in the
mid-infrared band is used to measure the concentration of CH₄ to greatly improve the measurement accuracy. With the gradual commercialization of quantum cascade laser (QCL), mid-far infrared QCL laser system (3.6~19 μm) has been developed [8]. It is expected that with the increasing maturity of QCL laser technology, the high-precision gas detection technology based on QCL-TDLAS will have broad application prospects in the fields of atmospheric pollution and hazardous gas monitoring in the future.

MATLAB software was used in the simulation analysis of CH₄ concentration measurement in TDLAS system in this article. The relation between amplitude and width of the second harmonic signal and modulation coefficients were analyzed. Simultaneously, the concentration of CH₄ gas in the QCL-TDLAS system and the DFB-TDLAS system under normal temperature/pressure and the troposphere environment were simulated respectively.

2. Theory method

In order to reduce the interference of environmental noise on the measurement, a high-frequency sine wave with a frequency of ω is used to measure the wavelength of the modulated laser during the TDLAS gas concentration measurement. And the emission frequency of the laser is [9-11]:

\[
ν(𝑡) = \bar{ν} + acos(ω𝑡),
\]

where the ‘ν’ is the average scanning frequency and the ‘a’ is the modulation amplitude.

Since the measurement of the concentration of trace CH₄ is discussed in this paper, the absorption rate \(α(ν) < 10\%\). Beer-Lambert's law is approximated by first-order Taylor series, and the results are as follows [12,13]:

\[
\frac{I_t}{I_0} = \exp[-α( \bar{ν} + acos(ω𝑡))] ≈ 1 - α( \bar{ν} + acos(ω𝑡)) = 1 + \sum_{n=0}^{∞} H_k( \bar{ν}, a)cos(kω𝑡) \tag{2}
\]

In the formula, ‘\(I_t\)’ is the incident light intensity (mW), ‘\(I_0\)’ is the transmitted light intensity (mW), ‘\(α\)’ is the absorption rate, ‘\(H_k( \bar{ν}, a)\)’ is the amplitude of each harmonic signal of the absorption signal, and the expression is [14 ,15]:

\[
\begin{align*}
H_0( \bar{ν}, a) &= -\frac{P \times S(T) \times X}{2π} \int_{-π}^{π} \phi( -\bar{ν} + acosθ) dθ \\
H_k( \bar{ν}, a) &= -\frac{P \times S(T) \times X}{π} \int_{-π}^{π} \phi( -\bar{ν} + acosθ) coskθ dθ \tag{3}
\end{align*}
\]

In the formula, ‘\(P\)’ is the gas pressure (atm), ‘\(S(T)\)’ is the line strength (cm²atm⁻¹), ‘\(X\)’ is the concentration of the gas to be measured in the gas chamber, ‘\(L\)’ is the optical path length (cm), ‘\(\phi(ν)\)’ is the linear function of the gas (cm).

The second harmonic component of the transmitted light signal passing through the gas absorption pool can be measured by the lock-in amplifier. Among them, the figure of the first, second, third and fourth harmonic signals is as follows:

![Figure 1. Schematic diagram of each harmonic of the absorbed signal](image-url)
It can be seen from formula (3) that the amplitude of the second harmonic signal with a larger signal amplitude at the absorption center wavelength is proportional to the concentration of the gas to be measured, so it can be used to invert the gas concentration.

3. Results and discussion

3.1 Simulation analysis of modulation coefficient

Define the modulation factor ‘m’:

\[ m = \frac{\alpha}{\Delta \nu} \]  

(4)

Where ‘\( \alpha \)’ is the modulation amplitude of the high-frequency sine wave, and ‘\( \Delta \nu \)’ is the half-height and half-width value of the gas absorption peak.

MATLAB simulation software is used to simulate the absorption of the second harmonic component of the absorption line of \( \text{CH}_4 \) gas with a concentration of 1 ppm in the QCL-TDLAS system at normal temperature/pressure. The parameters are shown in Table 1.

**Table 1. Simulation parameters of \( \text{CH}_4 \) concentration measurement in QCL-TDLAS system.**

| Experimental parameters       | Value | Unit |
|------------------------------|-------|------|
| Temperature (\( T \))        | 296   | K    |
| Pressure (\( P \))           | 1     | atm  |
| Concentration (\( X \))      | \( 10^{-6} \) | /    |
| Absorption line (\( \nu_0 \))| 1318.827 | cm\(^{-1} \) |
| Optical path length (\( L \)) | 20    | cm   |

The values of different modulation coefficients (‘m’) are taken as the figure of the second harmonic of \( \text{CH}_4 \) molecular absorption spectrum. As shown in Figure 2, different modulation coefficients have a greater impact on the second harmonic of the same gas absorption line. As shown in Figure 3, the amplitude of the second harmonic of \( \text{CH}_4 \) increases first and then decreases with the increase of ‘m’. It reaches the maximum when ‘m’ is equal to 2.2. In addition, the width of the second harmonic signal is also affected by ‘m’. As shown in Figure 4, the width of the second harmonic signal shows a monotonous increase with the increase of ‘m’. It is very important for the selection of ‘m’ in the process of wavelength modulation for experimental measurements. When selecting ‘m’, not only the influence of the amplitude of the second harmonic signal is considered to obtain a larger signal-to-noise ratio, but also the influence of the width of the second harmonic signal is considered to avoid interference of adjacent absorption signals. Considering comprehensively, the modulation factor ‘m=2.2’ was selected for simulation analysis during the TDLAS measurement process.

![Figure 2. Signal diagram of the second harmonic under different modulation coefficients](image-url)
3.2 CH₄ concentration measurement simulation analysis at normal temperature/pressure

The MATLAB simulation model is used to simulate the absorption of the second harmonic signals of different CH₄ concentrations which center wavelength are 6046.964 cm⁻¹ and 1318.827 cm⁻¹ in the DFB-TDLAS system and the QCL-TDLAS system in normal temperature/pressure (296 K, 101 kPa) environment. The parameters of line strength, self-broadening, air-broadening, and temperature coefficient were found from the HITRAN database. As shown in Figure 5, the amplitude of the second harmonic of the absorption signal of CH₄ gas increases monotonously with the increase of gas concentration in DFB-TDLAS system and QCL-TDLAS system in the normal temperature/pressure environment, and the sensitivity of the QCL-TDLAS system increases by about 31 times.

### Table 2. Simulation parameters of CH₄ concentration measurement

|                     | DFB-TDLAS system | QCL-TDLAS system |
|---------------------|------------------|------------------|
| **Experimental parameters** | **Value** | **Unit** | **Value** | **Unit** |
| Center frequency of absorption line (ν₀) | 6046.964 | cm⁻¹ | 1316.827 | cm⁻¹ |
| Spectral line intensity in normal temperature/pressure environment (S(T)) | 0.0362 | cm²·atm⁻¹ | 1.0474 | cm²·atm⁻¹ |
| Spectral line intensity in the environment at the top of the troposphere (S(T)) | 0.0684 | cm²·atm⁻¹ | 2.1641 | cm²·atm⁻¹ |
| Self width (r) | 0.079 | cm⁻¹·atm⁻¹ | 0.081 | cm⁻¹·atm⁻¹ |
### 3.3 Simulation analysis of CH$_4$ concentration measurement at the top of the troposphere

![Second harmonic amplitude-concentration graph in DFB-TDLAS and QCL-TDLAS systems under tropospheric top environment](image)

The second harmonic signal absorbed by different concentrations of CH$_4$ is also simulated in DFB-TDLAS system and QCL-TDLAS system at the environment of the top of the troposphere (-53°C 150hPa). As shown in Figure 6, in the environment at the top of the troposphere, the amplitude of the second harmonic of the CH$_4$ gas absorption signal of the DFB-TDLAS and QCL-TDLAS systems all increase monotonously with the increase of gas concentration, and the sensitivity of the QCL-TDLAS system in the top of the troposphere is increased by about 36 times compared with DFB-TDLAS.

### 4 Conclusion

The relation between modulation coefficient '$m$' and second harmonic signal was studied. In addition, the second harmonic method was used to simulate the measurement process of trace CH$_4$ gas concentration at normal temperature/pressure and the top of the troposphere environment. The results show that the signal-to-noise ratio of the second harmonic is largest and the interference of adjacent absorption signals is weaker when the modulation coefficient is 2.2. The performance of QCL-TDLAS is much better than that of DFB-TDLAS both in normal temperature/pressure and top of troposphere environment.

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