

High-resolution absorption spectroscopy of carbon dioxide by near infrared diode laser spectrometer between 6320 and 6335 cm^{-1}

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Introduction

NIR-diode laser spectrometers show a variety of advantages. Furthermore, due to the high spectral resolution there is no cross-sensitivity towards water vapor in the selected spectral range of 6320–6335 cm^{-1} (1578–1582 nm). Low-cost but powerful NIR tunable diode laser absorption spectroscopy (TDLAS) facilitates high resolution of weak overtone bands of gaseous molecules.^{1–3}

Carbon dioxide is of great interest in various environmental, medical or industrial issues, including monitoring of greenhouse gases emission, and analysis of breath gases. The most sensitive detection technique is tunable diode laser absorption spectroscopy^{2,3} that modulates the laser diode (LD) injected current. The LD temperature is stabilised by thermo-electric cooling (TEC) with high precision. For the most part the tuning range by injected current is very small, (less than 0.1nm), and it can cover only one absorption frequency of the gas. In addition, the temperature stability of the LD modules, (better than 0.02 degree Celsius), needs complicated configuration.

Temperature tuning can broaden the LD tuning range. R. Lewicki, *et al.*⁴ achieved a tuning range from 4982 cm^{-1} to 4993 cm^{-1} by changing the diode laser temperature that was used for carbon dioxide and ammonia detection. Hui Jia, *et al.*⁵ obtained a tuning range between 6526 cm^{-1} and 6538 cm^{-1} , which was applied to analysis of ammonia. Temperature tuning may cover several absorption lines that can be used to improve the measuring accuracy, or to detect multiple gases simultaneously. To locate the several absorption lines in the wider wavelength range; the wavelength and the amplitude wavelength response characteristics need to be accurately determined by tuning.

In this paper, a broader spectral range of 6320 to 6335 cm^{-1} with Thermally-tuned Distributed Feed Back (DFB) LD is achieved. Dynamic wavelength identification and amplitude wavelength response is achieved.

Methodology of measurement of multi-absorption lines

Dynamic wavelength identification

The laser diode radiation wavelength $\lambda(t)$ is uniquely determined by the injection current $i(t)$ and the chip temperature $T(t)$:⁶

$$\lambda(t) = F_{\lambda}(i(t), T(t)) \quad (1)$$

The depending function $F_{\lambda}()$ can be experimentally obtained. In the process of rapid-temperature tuning, there is a temperature lag $\Delta T(t)$ between the laser chip and the negative temperature coefficient (NTC) thermistor ($T_c(t)$) embedded in the laser module:

$$T(t) = T_c(t) + \Delta T(t) \quad (2)$$

The temperature lag $\Delta T(t)$ is concerned with the TEC current and the thermal inertia of the LD module. The thermal inertia of the LD module is always considered to be a first order inertial unit,⁷ and the inertial time constant t is concerned with the laser chip, NTC and Peltier, embedded in the laser module, which can be experimentally determined. Temperature lag $\Delta T(t)$ under step excitation can be represented as:

$$\Delta T(t) = 1 - \exp(-t/\tau) \quad (3)$$

With the inertia time constant t , by substituting Equation (2) and Equation (3) into Equation (1), the laser wavelength during the temperature tuning can be obtained accurately.

Amplitude wavelength response

In a broad wavelength range, the characteristics of the detector output and the LD radiation varying with the wavelength must be considered. The amplitude wavelength response function $F_A(\lambda)$ of the instrument can be determined by the measurements of absorption-free gas, (such as N_2). And the measuring signal $I(\lambda)$ can be revised as:

$$I(\lambda) = F_A(\lambda) \cdot I(\lambda) \quad (4)$$

The dynamic laser wavelength was precisely obtained by combining the injection current and the dynamic temperature of the laser chip; and the dynamic temperature of the laser chip was identified by making compensation for the NTC temperature. The measured signal amplitude is amended by the amplitude wavelength response function of the instrument. Based on the broad temperature tuning, it can cover several absorption lines for high-precision measurement or simultaneous multiple gases detection.

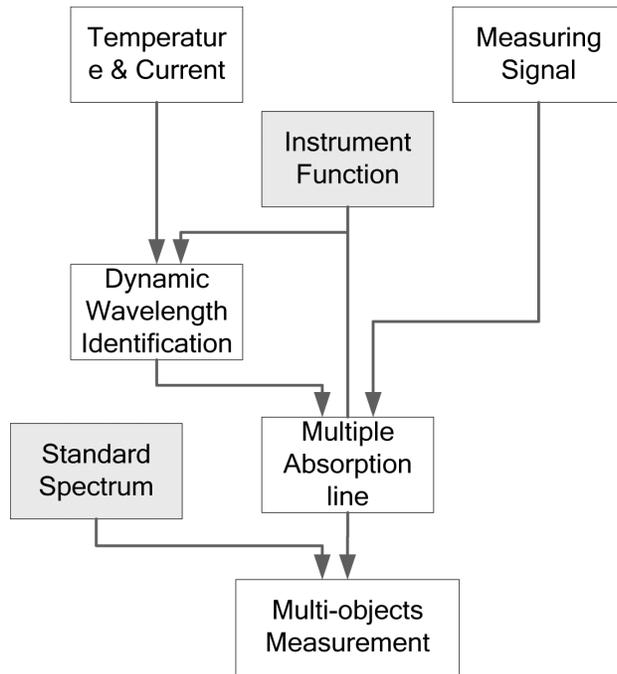


Figure 1. Procedure of multi-lines absorption spectroscopy.

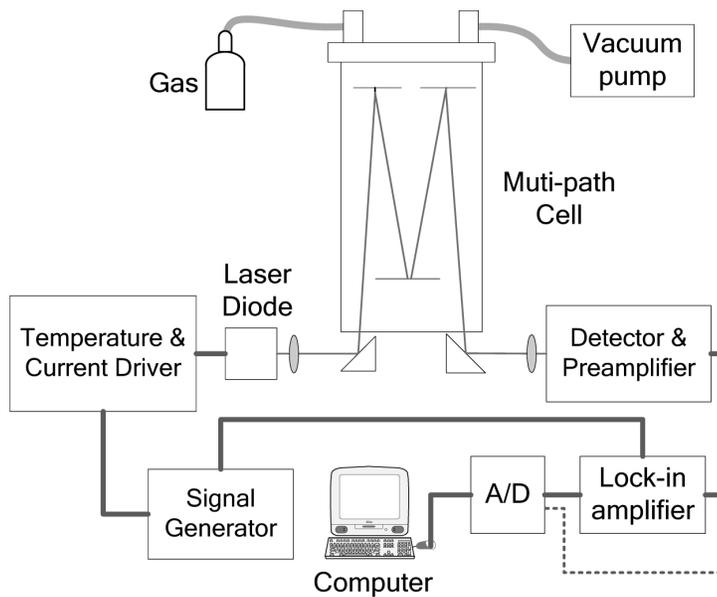


Figure 2. Sketch of experimental apparatus for the WM spectroscopy.

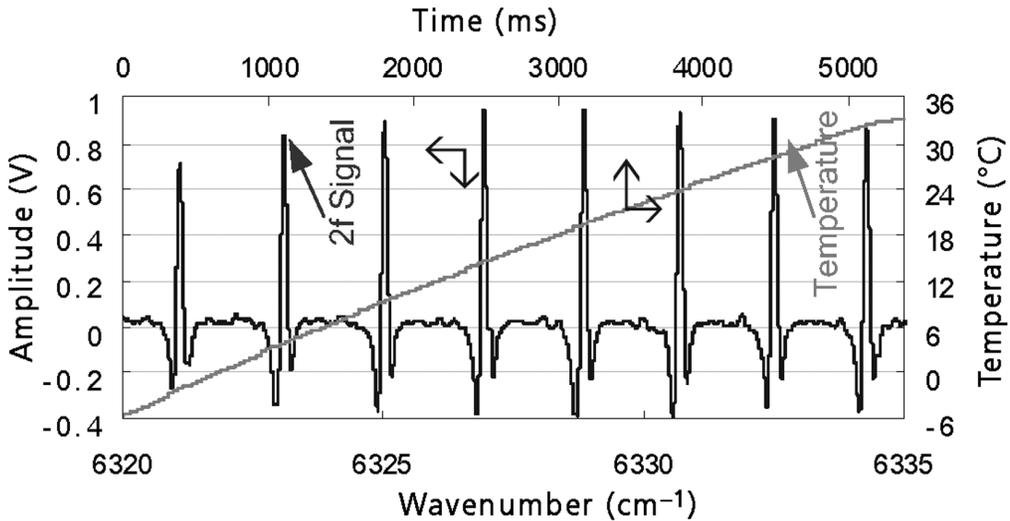


Figure 3. Measured DFB laser diode temperature (T) vs time (t) and synchronous absorption 2f-signal(S) vs wavelength (λ).

Experimental system

The current and temperature of the DFB diode laser are controlled by the laser driver. The Signal Generator provides the laser modulation signal and reference for demodulation. The optical path length of the multi-path cell is 15 m. The laser signal absorbed by the gas is converted to electrical signals by PD, pre-amplified, and sent to the lock-in amplifier for second harmonic detection. The digital signal is processed by computer after AD conversion. The signal after pre-amplification can also be AD converted directly, to get direct absorption spectra of the gas (shown in dash line in Figure 2).

Experimental results and discussion

The laser diode was operated over the temperature range of -5°C to 35°C . The current bias was injected at 20 mA and the Sinusoidal modulated at a frequency of 15 kHz and amplitude 47.5 mA_{pp} , which allows a wave number tuning range of 15 cm^{-1} (6320 cm^{-1} to 6335 cm^{-1}). Carbon dioxide was used as the test gas, for which the frequency range covered the vibrational overtone and combination band $2\nu_1 + 2\nu_2 + \nu_3$.

The direct absorption and WMS-2f signal were recorded, which covered eight absorption lines. Figure 3 shows the WMS-2f signal versus the tuning temperature, and the lapsed time, and the dynamic wave number identified.

The location and coefficient of CO_2 gas absorption lines were obtained, which were compared with HITRAN (High-resolution Transmission Molecular Absorption Database)⁸ as shown in Table 1.

The results show that the deviations of absorption peak wavelength were less than 1 pm, and the relative errors of the absorption coefficient at absorption peak were less than 1%.

Table 1. The absorption spectrum of CO₂ comparison between measured data and HITRAN.

Wavenumber (cm ⁻¹)	Hitran		Measured			
	Wavenumber (cm ⁻¹)	Absorbance [10 ⁻²³ cm ⁻¹ ·(mol·cm ⁻²) ⁻¹]	Wavenumber (cm ⁻¹)	Absorbance [10 ⁻²³ cm ⁻¹ ·(mol·cm ⁻²) ⁻¹]	Error of Wavenumber (%)	Error of Absorbance (%)
6334.464824	6334.464824	1.56	6334.465521	1.5748	1.10044e-5	0.95
6332.657732	6332.657732	1.54	6332.6579	1.5506	2.60058e-6	0.69
6330.821283	6330.821283	1.47	6330.821936	1.4748	1.03104e-5	0.33
6328.955632	6328.955632	1.37	6328.956033	1.3696	6.32996e-6	-0.03
6327.060947	6327.060947	1.26	6327.06187	1.2648	1.4583e-5	0.38
6325.137412	6325.137412	1.12	6325.139211	1.1263	2.84353e-5	0.56
6323.185225	6323.185225	0.985	6323.187824	0.9923	4.11093e-5	0.74
6321.204602	6321.204602	0.848	6321.205999	0.8476	2.21054e-5	-0.05

Conclusions

Temperature tuning of a laser diode by TEC is simple and attractive for multiple absorption lines spectroscopy. The tuning range can be enlarged to more than wave numbers of 15 cm^{-1} , for the DFB laser diode. It is a feasible and convenient system that combines the injection current and the dynamic temperature of the laser chip, which is identified by making compensation for the NTC temperature. Based on broad temperature tuning, it can cover several absorption lines for high-precision measurement or simultaneous multiple gases detection.

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