Relative line intensity measurement in absorption spectra using a tunable diode laser at 1.6 μm: application to the determination of $^{13}$CO$_2$/12CO$_2$ isotope ratio

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Abstract. The measurement of relative intensities in CO$_2$ combination bands spectrum is performed using wavelength modulation spectroscopy (WMS) and a DFB (distributed feedback) diode laser operating at 1.6 μm. The diode laser is stabilized with an external Fabry–Pérot interferometer and absorption spectroscopy is performed in a multipass gas cell. A spectrum containing spectral lines of both $^{13}$CO$_2$ and $^{12}$CO$_2$ isotopic species is recorded. The variation of laser power during frequency scanning and the line shape are taken into account to accurately extract line intensities from experimental data. The isotopic concentration ratio is deduced from the intensity ratio. Both ratios are measured with an accuracy of about 0.5% in pure CO$_2$.

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During last years there has been considerable interest in using tunable diode lasers for different applications such as pollutant detection [1, 2], petroleum prospecting [3] or medical diagnostics [4]. For example, optical gas detectors based on a tunable diode laser absorption spectrometer (TDLAS) are employed for monitoring trace gases [5].

The present work is devoted to the measurement of relative absorption intensities using such lasers. The experiments have been conducted in a CO$_2$ sample at low pressure. One application could be the determination of the concentration ratio of the stable isotopic species $^{13}$CO$_2$ and $^{12}$CO$_2$, of interest in breath analysis.

Previous studies using stable isotopic tracers primarily rely on two techniques: mass spectrometry [6–9] and non-dispersive infrared spectroscopy [10, 11]. The first one provides high precision, but the instruments are cumbersome to use and very expensive. The second one has proven its ability in human breath testing. An alternative could be an infrared spectroscopic technique that uses a single-mode tunable diode laser.

Since operation at room temperature in the 1–2 μm range is easy, direct measurement of isotopic ratio is possible [12–15]. Such a diode laser does not need a cryogenic cooling system as required by a lead-salt diode laser [16]. Furthermore, the optical components for this wavelength range (detectors, mirrors, beamsplitters, windows, etc.) are cheap. These diode lasers have a wide spectral-range tunability in combination with high spectral resolution, and therefore are suitable for spectroscopy of the combination bands of CO$_2$. Using a single diode laser, this method allows the simultaneous detection of $^{13}$CO$_2$ and $^{12}$CO$_2$ species, which present numerous absorption lines in the infrared region. However, the main drawback consists in measuring weak absorption lines in comparison with lines of fundamental bands.

The main goal of the present work was to estimate the achievable accuracy in intensity and isotope ratio measurements using a simple and cheap experimental setup.

1 Experimental setup

The experimental setup used to measure line intensity ratio is illustrated schematically in Fig. 1. The light source is an InGaAs/InP distributed feedback (DFB) diode laser (Anritsu Corporation). Its wavenumber scanning characteristics are 0.27 cm$^{-1}$/°C and 0.01 cm$^{-1}$/mA rates. The diode laser operates at 1.6 μm with a threshold current of about 35 mA at 25 °C and an output power of about 6 mW at a 100 mA current.

The wavelength of the diode is first determined by the temperature (35 °C) and the average current (100 mA). Temperature and laser current stabilizations are provided by a commercial driver (ILX LDC 3722 B). The temperature control is obtained through a Peltier device with an accuracy of 0.01 °C at the operating temperature. Fine tuning is achieved by varying the laser current. The laser current is varied and modulated by the signals received from outputs of a lock-in-1 (signal, home-made) and a lock-in-2 (frequency modulation, EGG 5209) amplifier, respectively.

The first measurements have shown an important frequency jitter of the diode laser at low frequencies. Therefore, the frequency has been stabilized with a reference interferometer (FP1 confocal Fabry–Pérot interferometer, 8 cm long). A piezo actuator (PZT) provides frequency tuning by chang-
Fig. 1. Experimental setup. See text for details

ing the interferometer length. The output of the DFB diode laser passes through an optical isolator (40 db) to avoid the optical feedback scattering of the cell.

To achieve optical alignment, a reference He-Ne laser is used. The red beam can be introduced into the optical path by inserting a sliding mirror (SM).

A study based on line intensity measurement in the 1.6 µm spectral region (3ν₁ + ν₃ combination band) was carried out on R(16) (13CO₂, 6253.8987 cm⁻¹) and R(40) (12CO₂, 6253.7297 cm⁻¹) absorption lines. This couple of lines allows measurement with a single-frequency scan. At this wavelength, the absorption is weak. Therefore, a better signal-to-noise ratio is obtained with a White-type multi-pass gas cell [17] whose path is adjusted to 32 m. The laser light transmitted through the cell is detected with a low-noise InGaAs photodetector (EGG C30642) followed by a preamplifier (D1).

The spectrometer operates in the wavelength modulation spectroscopy (WMS) mode [18–20]. The 5 kHz sine wave inner reference signal of the lock-in-2 amplifier is applied to the laser current to produce a wavelength modulation. The output signal of the lock-in-2 amplifier is a derivative-like line shape during a frequency sweep. The peak-to-peak modulation amplitude is fixed at about twice the full width of the absorption line, limited in the experiment by the Doppler line width. The carrier frequency is slowly tuned by sending a voltage to the PZT actuator of FP1 (output from the computer acquisition card). The lock-in-2 amplifier, with a 300 ms time constant, detects the first-harmonic output signal (D1).

Simultaneously with the absorption signal (output of the lock-in-2 amplifier), the transmission signal of an 8-cm-long frequency marker (output of the preamplifier D3) is monitored and stored by a digital oscilloscope (Tektronix TDS 420) (Fig. 2a). Both signals are transmitted to a computer by means of an IEEE communication. Afterwards, the gas is evacuated and the baseline is recorded and subtracted from the absorption signal [21] (Fig. 2b). Since the power variation is always the same for identical frequency scans, it is recorded only once, and updated from time to time. This power recording (Fig. 2a) is used during the fitting procedure described further.

Fig. 2. a Laser power and interference fringes from the Fabry–Pérot interferometer as a function of the laser wavenumber. b Absorption signal after subtraction of the baseline. The large line is due to 12CO₂, the weak is assigned to 13CO₂.