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first published in:
Remote Sensing and Modeling of Ecosystems for Sustainability / Wei Gao, David R. Shaw (eds.), Proceedings of SPIE, Vol. 5544 (2004), pp. 47-54
ISBN: 0-8194-5482-6
DOI:10.1117/12.559551

Postprint published at the institutional repository of Potsdam University:
In: Postprints der Universität Potsdam :
Mathematisch-Naturwissenschaftliche Reihe ; 21
http://opus.kobv.de/ubp/volltexte/2006/1014/
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Mathematisch-Naturwissenschaftliche Reihe ; 21

NIR-Diode Laser Spectroscopy for Isotope-Selective Sensing of Soil-Respired Carbon Dioxide[1]

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ABSTRACT

The performance of a home-built tunable diode laser (TDL) spectrometer has been optimized regarding multi-line detection of carbon dioxide in natural gases. In the regime of the $(30^01)_{III} \leftarrow (000)$ band of $^{12}CO_2$ around 1.6 µm, the dominating isotope species $^{12}CO_2$, $^{13}CO_2$, and $^{12}C^{18}O^{16}O$ were detected simultaneously. In contrast to most established techniques, selective measurements are performed without any sample preparation. This is possible since the CO_2 detection is free of interference from water, ubiquitous in natural gases. Detection limits in the range of a few ppmv were obtained for each species utilizing wavelength modulation (WM) spectroscopy with balanced detection in a long-path absorption cell set-up. Linear calibration plots cover a dynamic range of four orders of magnitude, allowing for quantitative CO_2 detection in various samples, like soil and breath gas. High isotopic resolution enables the excellent selectivity, sensitivity, and stability of the chosen analytical concept. The obtained isotopic resolution of typically ± 1.0 ‰ and ± 1.5 ‰ (for 3 vol. % and 0.7 vol. % of CO_2, respectively) offers a promising analytical tool for isotope-ratio determination of carbon dioxide in soil gas. Preliminary experiments on soil respiration for the first time combine the on-line quantification of the overall carbon dioxide content with an optode sensor and isotopic determination (TDL system) of natural gas species.

Keywords: Tunable diode laser (TDL); carbon dioxide; isotope ratios; soil gas

1. INTRODUCTION

The behaviour of natural systems has always stimulated human curiosity. Rather simple explanations of atmospheric or geological phenomena and events were soon replaced by sophisticated theories of the transport and metamorphosis of matter and energy in all environmental compartments. Especially, the outstanding kinetic and thermodynamic features of living systems have always been and still are of great fascination. Progress in the understanding of the complex inter-relationships within natural systems is coupled to the invention of new concepts and new techniques. Apart from purely geochemical topics, the stable isotopes' ratios of the elements of life (carbon, hydrogen, oxygen, sulphur, nitrogen, etc.) were identified as carriers of the key information. Current research on isotope effects ranges from the molecular scale (e.g., photosynthetic dark reactions) up to modelling the whole earth climate. Particularly, the isotope ratio of carbon dioxide plays a fundamental role, since CO_2 represents a link between biotic and abiotic domains and can be used as a molecular probe in a variety of processes, e.g. soil organic carbon turn-over.[1,2] Isotope ratios usually are expressed in terms of the so-called δ ("del") notation in per mille relative to a standard material (equation 1). Concerning the $^{13}C/^{12}C$-ratio, material from the Pee Dee Belemnite (PDB) formation in South Carolina serves as a standard.

$$\delta^{13}C = \left(\frac{(^{13}C/^{12}C)_{\text{sample}}}{(^{13}C/^{12}C)_{\text{PDB}}} - 1 \right) \cdot 1000 \tag{1}$$

Typical $\delta^{13}C$ ratios of natural materials cover the range of ca. –50 ‰ to +10 ‰. Positive values relative to PDB are restricted to marine carbonate materials. Organic soil components and plant materials are usually depleted in the heavier isotope. Fractionation due to transport or biochemical transformation is commonly limited to a $\delta^{13}C$ variation of a few per mille. Any analytical technique of value is obliged to resolve such variations.

Isotope-ratio mass-spectrometry (IRMS) dominates the field of isotope selective measurements, due to unrivaled resolution (better than ± 0.2 ‰) and stability.[3] While advantageous in terms of real-time measurement capability and simpler instrumentation, optical techniques often do not reach the analytical specifications of IRMS. Important exceptions have been demonstrated by usage of infrared lasers and high-resolution FTIR (Fourier-transform-infrared)

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[1]

spectroscopy.[4,5] A first isotope selective in-situ study of atmosphere-ecosystem exchange of carbon dioxide has been conducted by Bowling et al.[6] As a consequence of the far weaker absorption bands in the near infrared (NIR) spectral region, only few groups met the demands of isotope selective measurements of CO_2 on the $\delta^{13}C$ scale. Very high precision (± 0.3 ‰) has been obtained from analysis of the lines at 2.0 µm with a concentration of 2 % CO_2 in N_2.[7,8] Chaux and Lavorel, at 1.6 µm in pure CO_2 under reduced pressure, obtained a precision of ± 4 ‰.[9] In a very recent study we could demonstrate a superior set up at the very same wavelength, already allowing a precision of ± 1 ‰ at a concentration level of 3 vol. %.[10]

In this paper we demonstrate the performance of a further improved tunable diode laser (TDL) spectrometer, working around 1.6 µm, concerning simultaneous multi-line detection of carbon dioxide. The TDL spectrometer has been evaluated for isotope-ratio determination of carbon dioxide in soil gas (typically 1.000 – 20.000 ppmv CO_2). The stability and precision of the experimental set-up is examined by replicate measurements and evaluation of the limits of detection (LOD). First results regarding the analysis of real-world soil gas samples are presented.

2. APPARATUS AND EXPERIMENTAL TECHNIQUES

The TDL spectrometer is part of a soil gas measurement unit including a soil chamber with gas reservoir and an optode with a fibre-optical chemical sensor (FOCS) detector for overall (i.e. not isotope-resolved) CO_2 detection (Figure 1). The TDL spectrometer set up has been described in detail elsewhere.[10] Only a brief summary of main features is given here. The spectrometer is based on a temperature stabilized external-cavity-diode-laser (ECDL; TEC 500 Sacher Lasertechnik, Marburg, Germany) with a maximum output power of 8 mW and an emission line width of $< 1\cdot10^{-4}$ cm^{-1}. Fine tuning of the laser is achieved by piezoelectrically controlled setting of the cavity. The set-up is made up by a dual-beam concept with electronically auto-balanced receiving and harmonic wave analysis via lock-in amplification. A triangularly shaped piezo-voltage, responsible for repetitive wavelength scanning is superimposed by an oscillating voltage (modulation frequency $f = 800$ Hz, typical modulation amplitude $\delta\nu = 0.02$ cm^{-1}), introducing higher harmonic components to the transmitted light and allowing for noise-reduced detection. A Herriott-type multi-pass-cell (MPC1000S; Scienca Industria Tecnologia, Florence, Italy; tube length 1.12 m; Volume 8.25 l), equipped with two confocal gold mirrors (reflectivity at 1.6 µm > 98.2 %) with a total light path of 100.9 m, was used as the measurement chamber. Though wavelength modulation (WM) spectroscopy in principle represents a zero-baseline technique, optical interference fringes usually form sinusoidal background signals to be removed by background subtraction. Overall, a measurement cycle, including evacuation, background measurement, sample gas purging, and sample measurement is conducted within 4 minutes.

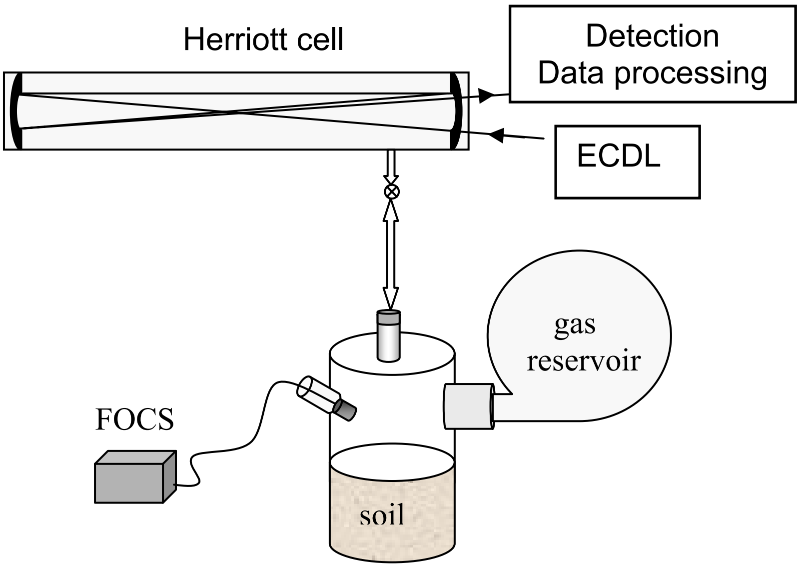

Fig. 1 Schematic depiction of the soil gas measurement unit including a soil chamber with gas reservoir, the TDL spectrometer for isotopic ratio determination,[10] and optode with fibre-optical chemical sensors (FOCS) for permanent CO_2 monitoring in the headspace.[11]

Gas mixtures (from Messer-Griesheim, Darmstadt, Germany) were used as concentration standards without further preparation. Soil gas samples were obtained from glass flasks (1000 cm^3), equipped with flexible gas-tight containers (Plastigas® Linde), allowing for variation of the total volume between 1000 and 3500 cm^3. Soil gas samples were directly injected into the MPC by hypodermic needles through a Teflon septum, to be exchanged after 20 injections. For permanent CO_2 monitoring, the FOCS detector (for details of measurement concept, see [12]) is installed at the soil chamber via a gas-tight port.[11] Soil samples (500 g) were taken at locations in the vicinity of the chemistry institute (oak forest, wheat field, meadow) and introduced to the soil chamber after addition of 50 cm^3 of water.

3. SPECTROSCOPIC BACKGROUND AND DATA ANALYSIS

Conventional absorption spectroscopy has to deal with the problem that small transmission alterations are to be distinguished from a usually large background signal. As indicated in the simulated absorption spectrum of CO_2 around 6,228.55 cm^{-1} (top panel in figure 2), the small absorption cross-sections $\sigma(\nu)$ in the NIR give rise to absorption coefficients of as low as 10^{-7} to 10^{-8} cm^{-1} even for concentrations approaching 20-fold atmospheric level (6,900 ppmv). WM techniques provide a powerful means for background reduction, since they discriminate signals strongly by curvature.[13-15] Narrower signals are enhanced, while broader features suffer considerable attenuation. In principle, derivatives of the original absorption profile are to be recorded and analyzed. The transmitted light intensity received by the photo diodes in general can be expressed as a Fourier series. If additional modulation of wavelength (or frequency) is applied, i.e., if the emission wavelength is “wobbled” around the absorption line, Fourier components of higher orders are invocated. The Fourier component amplitudes $A_{nf}(\nu_L)$, measured by a lock-in amplifier at the harmonics of f, are each proportional to the absorber concentration. As evident from the spectra measured at a concentration of 6,900 ppmv of carbon dioxide (Figure 2, middle and bottom panels), the nth harmonic spectrum resembles the nth derivative of the corresponding absorption line. Higher harmonic signals display better noise suppression, but suffer from a decrease in signal intensity. As a best compromise, 2nd harmonic spectra have been analyzed throughout this study. From signal-to-noise ratios (SNR), the least detectable absorbance is estimated to $2\cdot10^{-6}$. This value, based on a SNR of 1 at 1 Hz noise-bandwidth, is in good agreement with the results of other groups with similar experimental setups.[16-18]

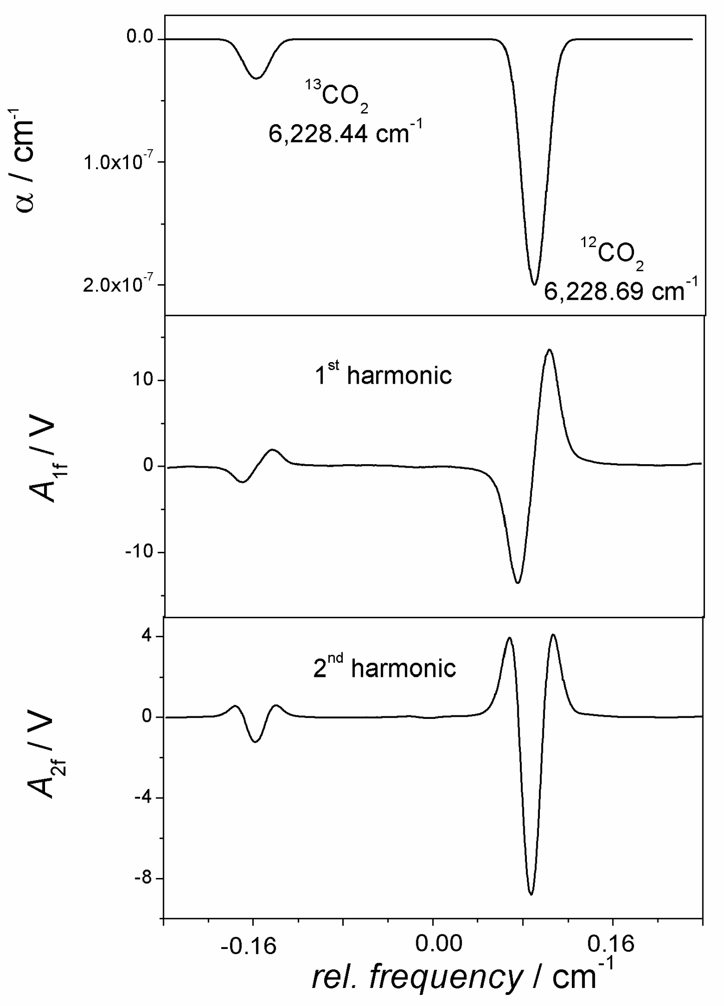

Fig.2 Absorption spectra of CO_2 around 6,228.55 cm^{-1} (6900 ppmv in N_2 at a total pressure of 60 mbar) Top panel: Simulation with a Voigt line shape profile. Middle and bottom panels: 1st and 2nd harmonic amplitude (A_{nf}) detection of the $^{12}CO_2$ $R(0)$ and the $^{13}CO_2$ $P(16)$ lines (single-scan spectra, background corrected; frequency scale centered at 6,228.55 cm^{-1}; modulation frequency f_m = 800 Hz; lock-in time-constant 100 ms with detection bandwidth of 2.5 Hz, modulation voltage U_{osc} 25 mV corresponding to modulation amplitude $\delta\nu$ = 0.0275 cm^{-1}; note different ordinate scales).

The spectral window around 6,228.55 cm^{-1} provides important experimental advantages: (i) Below atmospheric pressure, the main absorption lines $^{12}CO_2$ $R(0)$ and $^{13}CO_2$ $P(16)$ are resolved. (ii) No cross-sensitivity towards water vapor is expected (HITRAN data base search). Further measurements with real-world (i.e. "wet") samples confirmed this assumption. (iii) The intensity ratio of the two main lines at 6,228.69 ($^{12}CO_2$) and 6,228.44 cm^{-1} ($^{13}CO_2$) has been calculated as 8.55/1.00 (based on line strengths), and is thus remarkably shifted from the ratio of natural abundances (88.99/1.00).

From HITRAN data, further absorption lines are expected in the spectral region under investigation. Only one weak feature at 6,228.61 cm^{-1} ($^{12}CO_2$ $R(57)$), though partially overlapping with the $R(0)$ line, is resolved at the pressure of 60 mbar. Contrarily, the $^{12}CO_2$ $R(38)$ and the $^{13}CO_2$ $P(18)$ lines cannot be resolved from the main lines. As a consequence of overlapping absorption, rather than considering total peak areas, the following quantitative analysis is based on evaluation of signal intensities at the line centers.

4. EVALUATION OF SPECTROMETER SPECIFICATIONS

4.1. Sensitivity

Conditions for optimized sensitivity have to compromise between the highest signal strength possible and minimal pressure broadening of the signal. As a main consequence, the interplay of signal strength and line width defines an optimal pressure range of $50 < p < 150$ mbar. For our cell, the corresponding sample volumes are of the order of $400 < V_s < 1{,}200$ cm^3 (at atmospheric pressure). The choice of pressure conditions has to consider sample accessibility and abundance as well. Considering analysis of natural systems, we have chosen 60 mbar (V_s ca. 500 cm^3) as default pressure.

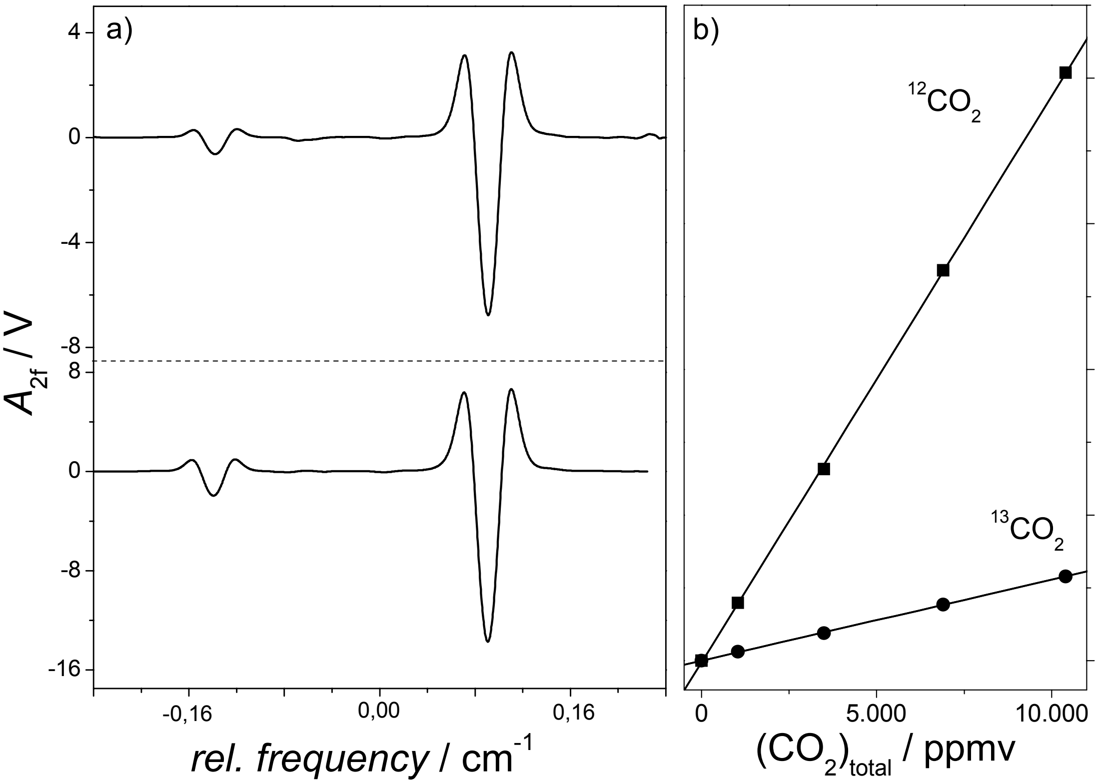

Fig. 3 a) Exemplary 2nd harmonic spectra of the $^{12}CO_2$ $R(0)$ and the $^{13}CO_2$ $P(16)$ lines for concentrations of 3,500 (upper line) and 6,900 ppmv (bottom line); pressure $p = 60$ mbar; wavenumber scale centered at 6,228.55 cm^{-1}; b) 2*f*-amplitudes (absolute values) for $^{12}CO_2$ and $^{13}CO_2$ in line center versus total concentration; symbols: experimental data; lines: linear fits.

Due to the broad tuning range of the ECDL, a variety of species can be determined quantitatively and simultaneously. However, simultaneous multi-species detection has to take into account individual sensitivities. For $^{12}CO_2$ and $^{13}CO_2$ monitoring, a suitable line pair derives from the $R(0)$ and the $P(16)$ transitions, respectively (Figure 3a). From calibration plots, detection limits of LOD = 20 and 1 ppmv for $^{12}CO_2$ and $^{13}CO_2$ were obtained (Figure 3b). Thereby, for the ^{13}C-line a relative percentage of 1.106 is assumed (PDB standard). The chosen line pair yields the maximum sensitivity for $^{13}CO_2$ detection around 1.6 μm, while only a moderate ^{12}C line is monitored. The sensitivity achieved is expected to be sufficient for precise ^{12}C/^{13}C isotope-ratio determinations in soil gases (see Chapter 5). Besides that, the linear calibration plots offer a broad dynamic range, covering a concentration range of four orders of magnitude. Approaching concentrations higher than ca. 10 vol. %, deviation from linearity is expected. The simultaneous detection of a very weak $^{12}C^{16}O_2$ and a moderate $^{12}C^{18}O^{16}O$ line will be subject to only brief discussion. As detection limits, 900 and 7 ppmv are obtained for $^{12}C^{16}O_2$ and $^{12}C^{18}O^{16}O$ from linear plots of the line center amplitudes. For the latter molecule, a relative percentage of 0.395 (according to PDB standard) is assumed. As evidend from measurements of breath gas samples, water does not interfere with the investigated carbon dioxide lines. This is important for both breath and soil gas analysis, where humidity usually reaches saturation. Regarding ^{16}O/^{18}O isotope-ratio determination, the achieved sensitivity is expected to be sufficient only for pure CO_2, whereas the smaller concentrations in human breath (30,000 to 50,000 ppmv) still demand improved baseline stability. Presently, the LOD are dominated by the residual baseline noise, introduced by statistically moving interference fringes in the optical path, which cannot completely be eliminated by background subtraction. Being stable only for short periods of time, also the overall experimental reproduction, i.e. the stability of the TDL spectrometer, is limited by the extent of the fringes.

4.2. Stability of the spectrometer

The overall precision of the spectrometer is determined by the reproducibility of the measurements. Limited baseline stability is directly converted to uncertainty in amplitude analysis. Especially the weaker ^{13}C line is affected. The uncertainty of the weaker line amplitude dominates the experimental error in isotope ratio determination.

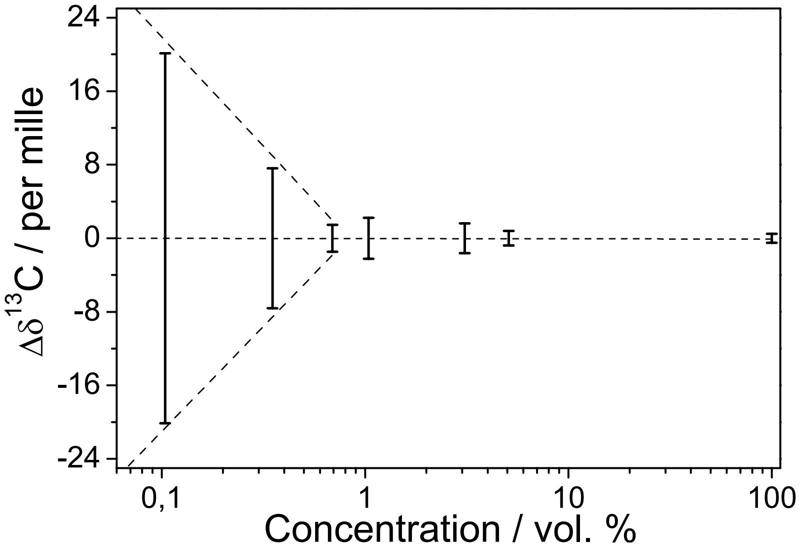

Fig. 4 Experimental precision of the spectrometer in dependence on carbon dioxide concentration; precision is evaluated from the standard deviation of the isotope ratio obtained from each of the ten replicate measurements.

As expected, the obtained precision (taken from the standard deviation of isotope-ratio determination) shows a marked concentration dependence (Figure 4). Below ca. 6,000 ppmv a steep increase of experimental uncertainty is obvious. At atmospheric concentration levels (ca. 350 ppmv) no meaningful isotope ratios are obtained, i.e. error intervals of larger than ± 100 ‰ occur. It would mean nothing less than to reach the shot-noise limit, to also allow for ultra-sensitive measurements at ambient CO_2 concentrations. The concentrations typically observed in soil gas compartments, however, reach values up to 2 vol. % (20,000 ppmv). The experimental precision obtained for this concentration regime is already greatly unaffected by imperfect background subtraction (baseline fluctuation). No significant improvement of resolution, even at very high concentrations, is observed, reaching an almost constant error interval of ± 0.5 ‰ with pure carbon dioxide. This limitation is found to be induced by scan-to-scan variation in laser power. Nevertheless, the obtained specifications provide an optimum isotope resolution at 1.6 μm, sufficient for sensitive analysis of soil respired gases.

5. EVALUATION OF ^{12}C/^{13}C ISOTOPIC RATIOS OF SOIL RESPIRED CO$_2$

Under aerated conditions, soil organic matter is efficiently transformed to carbon dioxide by microbiologic metabolisms. Besides other factors (e.g., quality of organic matter input), the amount of CO_2 respired at the soil-atmosphere interface depends on gas transport. During a feasibility study with incubation of two forest and wheat field soils, overall CO_2 concentrations of around 5,400 and 2,600 ppmv were obtained after 24 h in a closed chamber system.[10] Limited resolution prevented the discussion of isotope effects at that time. With an improved experimental concept, time-resolved determination of the overall respired CO_2 is now combined with isotope selective measurements. As a first approach towards on-line monitoring of the isotopic signature of natural gases, the gas exchange of soils with a synthetic atmosphere is studied in closed chambers with an attached gas reservoir of variable volume (for details see experimental section). The chamber is equipped with 500 g of natural soil (10 weight % rel. humidity) and incubated with synthetic air (20 vol. % O_2) in a thermostated room at 292 ± 1 K. Figure 5 summarizes the results, obtained by on-line monitoring of carbon dioxide respired from a meadow soil.

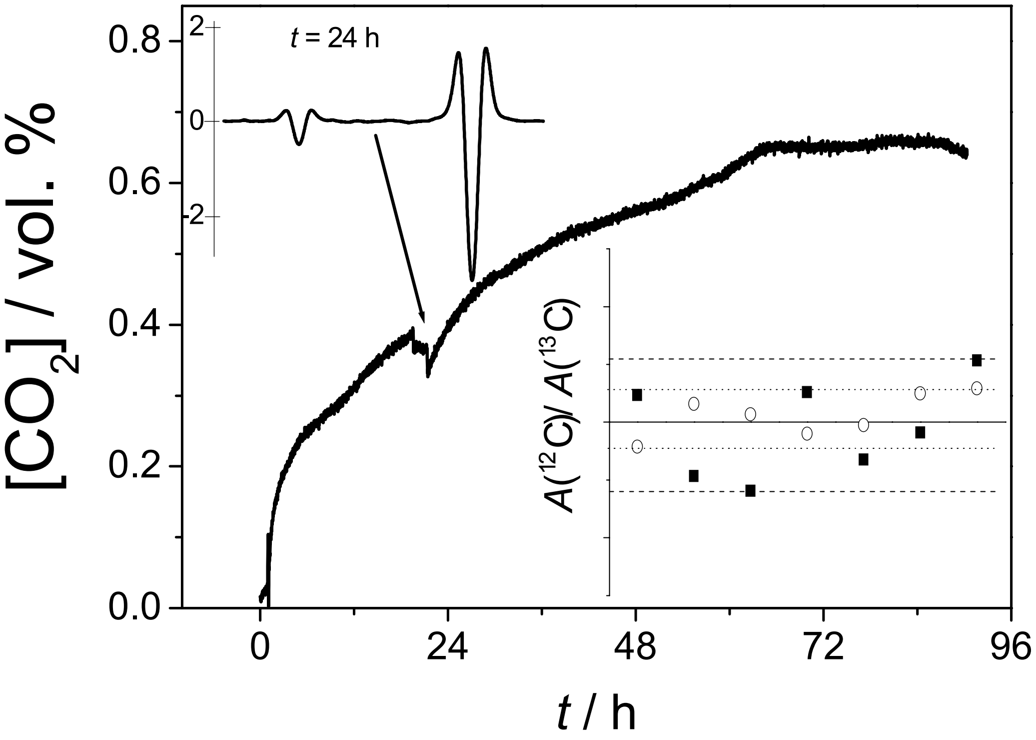

Fig. 5 On-line determination of carbon dioxide in the gaseous phase of a soil chamber system (500 g meadow soil) with FOCS detector,[11] and representative results from isotope-selective TDL spectrometry (discontinuity at t = 24 h due to sampling procedure). Left inset: Isotope-selective TDL spectrum obtained at t = 24 h (2nd harmonic spectra as in Fig. 3a with A_{2f} amplitude in V,). Right inset: Relative resolution of TDL measurements at t = 24 h (filled symbols) and t = 70 h (open symbols) obtained from seven repetitions; full line: mean value; broken and dotted lines: respective standard deviations for t =24 h and t = 70 h.

As expected, a steep increase of CO_2 concentration is obvious within the first ten hours of incubation. Leveling of the concentration-time dependency at later periods is observed and a constant concentration of ca. 6,500 ppmv is reached after three days. The concentration in the gas room allows isotope-selective measurements with TDL spectrometry. The left inset of Figure 5 represents a TDL spectrum obtained from a gas sample withdrawn after 24 h of incubation. Overall concentration determination, based on the calibration plots discussed above, validates the data obtained from the microoptode system. The precision of the measured isotope ratio is given for two samples of different concentration (sampled at *t* = 24 h and 70 h, respectively). As expected, the overall experimental error interval, $\Delta\delta^{13}C$, decreases from ± 5.0 ‰ for the lower to ± 2.5 ‰ for the higher CO_2 concentration. Within the limits of the spectrometer resolution (see above), the two samples exhibit the same isotope ratio. This is to be expected for one given soil. Marked effects on isotopic ratio in the respired gas are expected from soil systems fertilized with plant material of different isotope ratio. The so-called "C_3-C_4" exchange (usually maize litter in soils from wheat or rye fields) provides a tool for the study of the complex soil dynamics and has been used by soil scientists extensively throughout the past decade.[1,2] Such exchange experiments in the soil chamber are planned to validate our TDL system. Especially, the construction of a chamber system capable of on-line isotope ratio determination will be addressed.

6. CONCLUSIONS

The presented TDL spectrometer combines flexibility and versatility by allowing sensitive and isotope-selective measurements of carbon dioxide in various natural or artificial materials, with relatively undemanding and inexpensive equipment. With the very same set-up, both sensing of trace compounds (such as $^{12}C^{18}O^{16}O$) and quantitative analysis of simultaneously recorded species can be performed. For three isotope species of carbon dioxide, limits of detection in the lower ppmv range were obtained. Linear calibration plots cover a dynamic range of at least four orders of magnitude. Residual background fluctuations in the harmonic spectra prevent meaningful isotope ratio determination ($^{12}C/^{13}C$) at atmospheric concentration levels. For the higher concentrations in soil systems, very good precision in the range of ± 1.0 ‰ is provided on a routine level already at concentrations below 1.0 Vol. %. This development marks a further improvement with respect to the recently reported state of the art at 1.6 μm.[10] Preliminary experiments on soil respiration validate the results obtained with certified gas mixtures and render the chosen experimental concept a very promising tool for on-line determination of both quantity (FOCS detector) and isotopic composition (TDL system) of natural gas species.

ACKNOWLEDGEMENTS

Funding of the project by the Deutsche Forschungsgemeinschaft within the priority program SPP 1090 ("Soils as sources and sinks of CO_2") is gratefully acknowledged.

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