Appl. Phys. B 67, 307–315 (1998)

Applied Physics B
Lasers
and Optics

Near-infrared trace-gas sensors based on room-temperature diode lasers

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Received: 24 February 1998/Revised version: 27 April 1998

Abstract. Semiconductor lasers continue to find an increasing number of applications as tunable sources for high-resolution spectroscopy. Substantial improvements in sensitivity and detection speed have been achieved and many laser-based gas monitoring applications have been reported. In this paper the relevant characteristics of currently available semiconductor lasers with respect to spectroscopic gas analysis will be discussed. Experimental data from a CO_2 monitor designed for field applications using room-temperature diode lasers are presented. Near-infrared DFB lasers operating at 1.57 μm and around 2.0 μm have been used for CO_2 measurements. At ambient concentration levels a resolution of more than two orders of magnitude has been demonstrated at 1.57 μm, at 2 μm the precision is in the order of 0.1 ppm CO_2, and for trace analysis a detection limit of 10 ppb has been obtained. The measurements demonstrate the capability of near-infrared DFB diode lasers for the precise determination of CO_2 concentrations as required for climatological, medical, or industrial applications.

PACS: 07.65; 07.88.+y; 42.60.-v; 42.55.Px

Gases were monitored in the past almost entirely for safety and pollution control purposes. Meanwhile the sophistication of industrial processes has increased, requiring a growing use of gas analysis as a vital control tool for manufacturing processes. Gas analysers have been developed that meet the requirements for faster, more specific and precise measurements. So far the development of analytic technologies has been driven mainly by scientific questions, but increasingly these techniques are applied to a sensitive, selective and fast analysis in industry and environmental monitoring. For the variety of problems, different measurement techniques can be applied, but optical and spectroscopic techniques especially attain increasing attention for fast and selective on-line measurements. Tunable diode laser absorption spectroscopy (TDLAS) is a method of choice for in-situ trace-gas analysis, because of its high sensitivity and specificity and high spectral resolution. When semiconductor lasers were first introduced in the mid-1960s they found immediate application as much-needed tunable sources for high-resolution infrared laser absorption spectroscopy and now, more than three decades later, laser-based analysis techniques are at the threshold of routine applications in environmental monitoring and industrial process gas analysis. The most important application of TDLs to atmospheric measurements is their use in conjunction with a long-path cell to provide high-sensitivity local measurements, when a single narrow laser line scans over an isolated absorption line of the species under investigation. This type of measurement has developed into a very sensitive and general technique for monitoring most atmospheric trace species [1–3]. Modulation techniques [4, 5] have made it possible to detect absorptions below 10^{-6} for integration times of about 1 s [6]. This sensitivity, when combined with an optical pathlength through an absorbing sample of several tens of meters, translates into parts-per-billion (ppb) to parts-per-trillion (ppt) detections for many molecular species in the infrared. For many gases with near-IR absorption (overtone or combination) bands, this sensitivity corresponds to detection of sub-parts-per-million (ppm) concentrations over pathlengths of a few m [7].

Historically, most applications have been reported in the field of atmospheric research, where still better and faster instrumentation is required. Examples are the investigation of the temporal development of spatially distributed polluted air masses from airborne platforms such as balloons or aircraft and the determination of trace-gas fluxes in terrestrial ecosystems by means of the eddy correlation method. Many of these applications require instruments with higher time resolution and better sensitivities. The current great interest in carbon dioxide results from the observed rise of its atmospheric concentration and its importance for the greenhouse effect, due to its significant role in determing the heat balance of the atmosphere. The actual average ambient concentration of CO_2

is about 350 ppm, compared to about 280 ppm before the industrialization era. An increase of the average temperature by 2–3 K is expected with a doubling of the CO_2 concentration. Therefore, it is very important to quantify sources and sinks of carbon dioxide, especially the not well-known influence of seas as sinks. To perform climatological studies the resolution of the ambient CO_2 level should be in the order of 10^{-4} or about 0.1 ppm with a time resolution of 0.1 s for flux measurements or about 10 s for long-term measurements [8, 9]. In order to reach these requirements an instrument based on diode laser spectroscopy has been built up. In this paper first results of a fieldable CO_2 instrument are presented. Despite the success of TDLAS in many applications there are still problems to solve. Most of them are connected with the properties of the diode laser, which are thus the key element of TDLAS systems. The properties of these devices are considered in the next section.

1 Semiconductor lasers for spectroscopic gas analysis

A main drawback for industrial applications of laboratory prototype spectrometers is the limited suitability of the currently available lasers for continuous operation in an industrial environment. The reasons for limiting a widespread application of TDLAS in industrial process control are found in the relative complexity of current instrumentation and in the lack of high-quality, high-power diode lasers for many spectral regions of interest. Figure 1 gives an overview of different types of semiconductor lasers from the visible to the infrared region together with some absorption bands of atmospheric carbon dioxide and water vapor [10]. In the near-infrared selected wavelengths from III-V devices are widely used in communication and consumer electronics and the lasing materials are already mature and highly efficient. In contrast, because of the smaller number of applications, mid-IR diode lasers are still produced in small batches and on a much lower level of manufacturing sophistication.

Lead-salt diode lasers, made from IV-VI semiconductor materials, operate in the 3 to 30 μm spectral region and, therefore, they cover the IR fundamental band with strong absorptions for most atmospheric trace gases. They are used almost exclusively for spectroscopic applications [1, 2]. Because IV-VI lasers and their associated detectors operate at cryogenic temperatures, they are more expensive and more cumbersome to use than III-V devices. In trace gas monitoring applications, lead-salt laser instruments have routinely achieved parts-per-billion detection levels of a number of important molecular species. For many industrial applications, however, the use of lead-salt diode lasers is limited by the need for cryogenic cooling, frequent multimode emission, and power levels that are typically only several hundred μW. Lasers of this type are typically available between 3300 and 900 cm^{-1} with single-mode operation available over much of this range. Compared to GaAs lasers, lead-salt semiconductor lasers are at a relatively early stage of their development

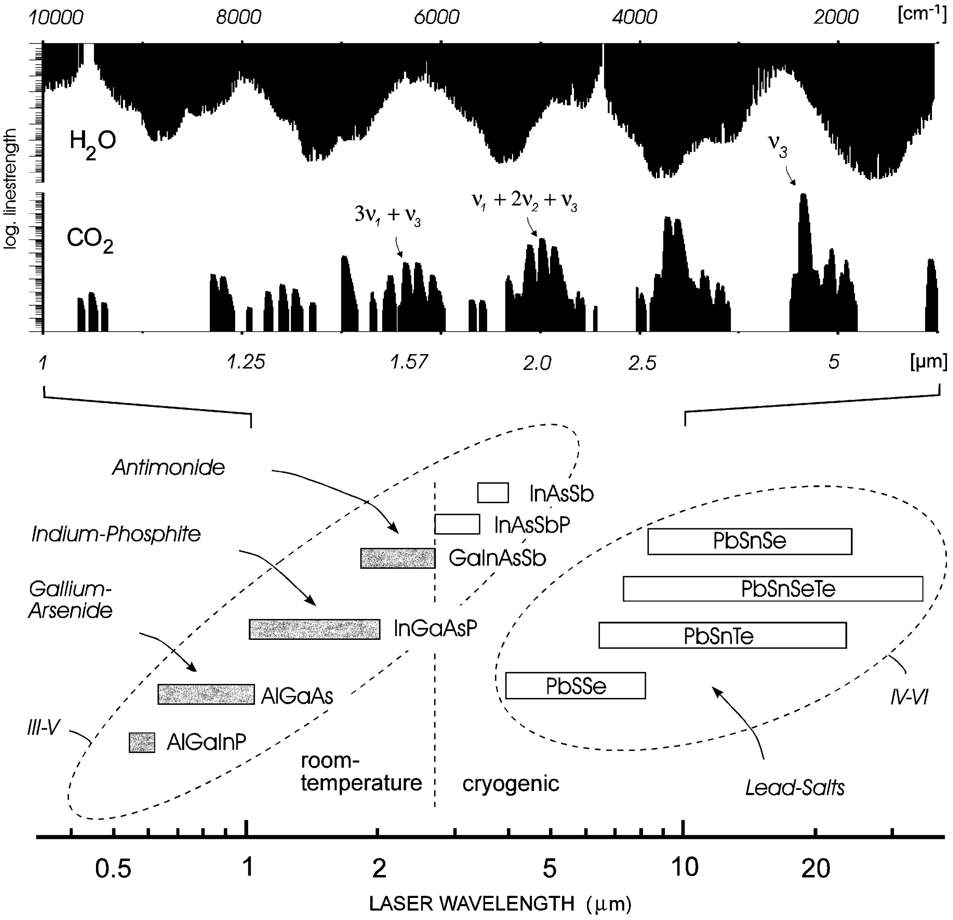

Fig. 1. Overview of the coverage of the spectral regions from the visible, near- and mid-infrared region by different semiconductor materials. The dark background indicates room-temperature cw operation, whereas above 2.8 μm cryogenic cooling is required. Also the line strength and position of H_2O (*top*) and CO_2 (*bottom*) absorption lines are displayed in the spectral range from 1 to 10 μm

due to a much smaller market. Current development is aimed at better mode quality, higher power and higher temperature operation. Distributed feedback (DFB) and distributed Bragg reflector (DBR) cavity designs use corrugated structures, either distributed along the entire cavity (DFB) or at each end (DBR). These structures act as discrete reflectors at specific wavelengths and thus give control over the laser modes and can give predominantly single-mode operation.

Gallium arsenide and indium phosphite lasers are widely available commercially. These diode lasers, made from the III-V group of semiconductor materials, emit at red and near-infrared wavelengths from about 0.63 to 1.55 μm. This includes the GaAs/AlGaAs 0.78- and 0.83-μm lasers found for example in compact disk players, as well as InGaAsP/InP 1.3–1.55 μm optical communication lasers. The technology of near-IR 1.3-μm and 1.55-μm InGaAsP/InP diode lasers developed for fiber-optic communication can be extended to fabricate lasers that emit anywhere in the wavelength interval of about 1.2–2 μm. The device structures are multiple-quantum-well DFB lasers [11, 12]. Lasers operating in this spectral region are fabricated for example at the David Sarnoff Research Center (Princeton, NJ), at Anritsu Corporation (Onna, Japan), and at the Industrial Microelectronics Center IMC (Kista, Sweden). Such lasers have been used to detect for example CO_2 and CO at 1.57 μm [13–15] and CH_4 at 1.65 μm [16, 17]. Near-IR diode lasers have the advantage of single-mode outputs at mW power and near-room-temperature operation in addition to the availability of fiber-optic technology. Of special interest for spectroscopic applications is the high modulation bandwidth up to several GHz. Together with the benefits of modulation spectroscopy they allow highly sensitive spectroscopic gas analysis and the availability of single-mode diode lasers leads to many applications based on molecular spectroscopy of overtones and combination bands. These are typically one to several orders of magnitude weaker than the IR-fundamental band. Nevertheless, many molecules of interest have near-IR absorption bands that are strong enough for detection at parts-per-million and, in some cases, even parts-per-billion levels.

Antimony containing compounds such as AlGaAsSb, InGaAsSb, and InAsSbP allow the extension to wavelengths longer than 1.8 μm for the III-V group of semiconductor materials. Room-temperature lasing from 2 to 2.4 μm has been reported from simple double heterostructure antimonide diode lasers. As the wavelength increases up to 3.7 μm, the maximum operating temperature decreases as a result of increasing optical and electrical losses. Recently III-V devices based on InAsSb/InAsSbP manufactured at the Ioffe Physico Technical Institute (St. Petersburg, Russia) have been investigated with respect to spectroscopic applications [18]. These double heterostructure devices were grown by liquid-phase epitaxy on InAs substrate and cover the spectral range from 3–4 μm at LN_2 temperatures. A detailed characterization has shown that these devices are well suited for the detection of HCHO at 3.6 μm and CH_4 at 3.26 μm and especially the single-mode power of more than 1 mW is attractive for spectroscopic trace-gas monitoring with optical multipass cells.

Representative mode maps of an antimonide laser (a) and a lead-salt diode laser (b) both cryogenic cooled to 95 K and two near-infrared InP DFB lasers (c,d) are shown in Fig. 2. Laser mode quality has an important influence on the performance of TDLAS instruments [19] and the key issue is to find a combination of base temperature and drive current at which the laser produces a strong, preferably single-mode emission, tuned to the absorption line being monitored. The problem of the change of the mode structure due to thermal cycling has been a major obstacle for a widespread use of lead-salt laser-based systems, and the properties of the lead-salt lasers presently available have to be substantially improved. A single-mode operation is required to minimize mode partition noise and to prevent absorption signals from other modes interfering with the desired signal from the spectral feature of interest. Semiconductor diode lasers oscillate essentially in several longitudinal modes because the linewidth of the gain spectrum is much broader than the separation between adjacent longitudinal modes. In conventional Fabry–Pérot type cavities fabricated by cleaving or chemical etching of the crystal facets, mode hopping between the longitudinal modes occurs. Even if the power of a specific longitudinal mode dominates, as in the case of a nearly single-longitudinal-mode oscillation, mode partition noise occurs. An analysis of noise measurements in the vicinity of mode hops and for laser multimode operation showed that $1/f$-type noise can be attributed to the presence of spurious side modes or multimode operation [20]. Consequently, higher modulation frequencies are necessary to achieve near-quantum-noise-limited performance of a spectrometer with the lead-salt lasers presently available. Therefore, the use of DFB structures is a promising direction and the successful application of NIR indium-phosphite lasers confirms the superiority of DFB devices.

Mid-infrared lasers operated at cryogenic temperatures cover the fundamental absorption bands required for ultrasensitve gas analysis, whereas near-infrared room-temperature diode lasers give access mainly to significantly weaker overtone and combination bands. This is illustrated at the top of Fig. 1, where the absorption bands of CO_2 are displayed in the spectral range from 1 to 10 μm together with water vapor, which might interfere for atmospheric measurements. The selection of the optimum operating conditions for a gas analyzer is always a trade-off between the required sensitivity and an operational system.

For many field applications the use of liquid nitrogen must be avoided, only temperature stabilization by thermoelectrical elements is acceptable. Therefore, in a recently developed fast CO_2 sensor we implemented InP DFB lasers from Sensors Unlimited Inc. (Princeton, NJ) with single-mode emission at $\lambda \leq 2$ μm together with InGaAs detectors. The selection of the absorption lines suitable for precise CO_2 measurements is determined by interferences to other gases, mainly H_2O, and the availability of laser sources. High-quality DFB diode lasers are available at the telecommunication wavelengths of 1.55 μm and 1.3 μm from different manufacturers, but there the CO_2 absorption cross section is too weak for atmospheric applications. As displayed at the top of Fig. 1, stronger absorption bands exist around 1.44, 1.57, 1.6, and around 2 μm, but then the influence of H_2O has to be taken into account. Very low water vapor absorptions at CO_2 bands are found around 1.6 μm, whereas at 1.44 μm H_2O dominates. The strongest CO_2 absorption lines in the near-infrared region can be found around 2 μm, but there also the influence of H_2O has to be considered. Based upon the HITRAN database an absorption line at 1.5723 μm (6360 cm^{-1}) has been chosen for the CO_2 measurements (at

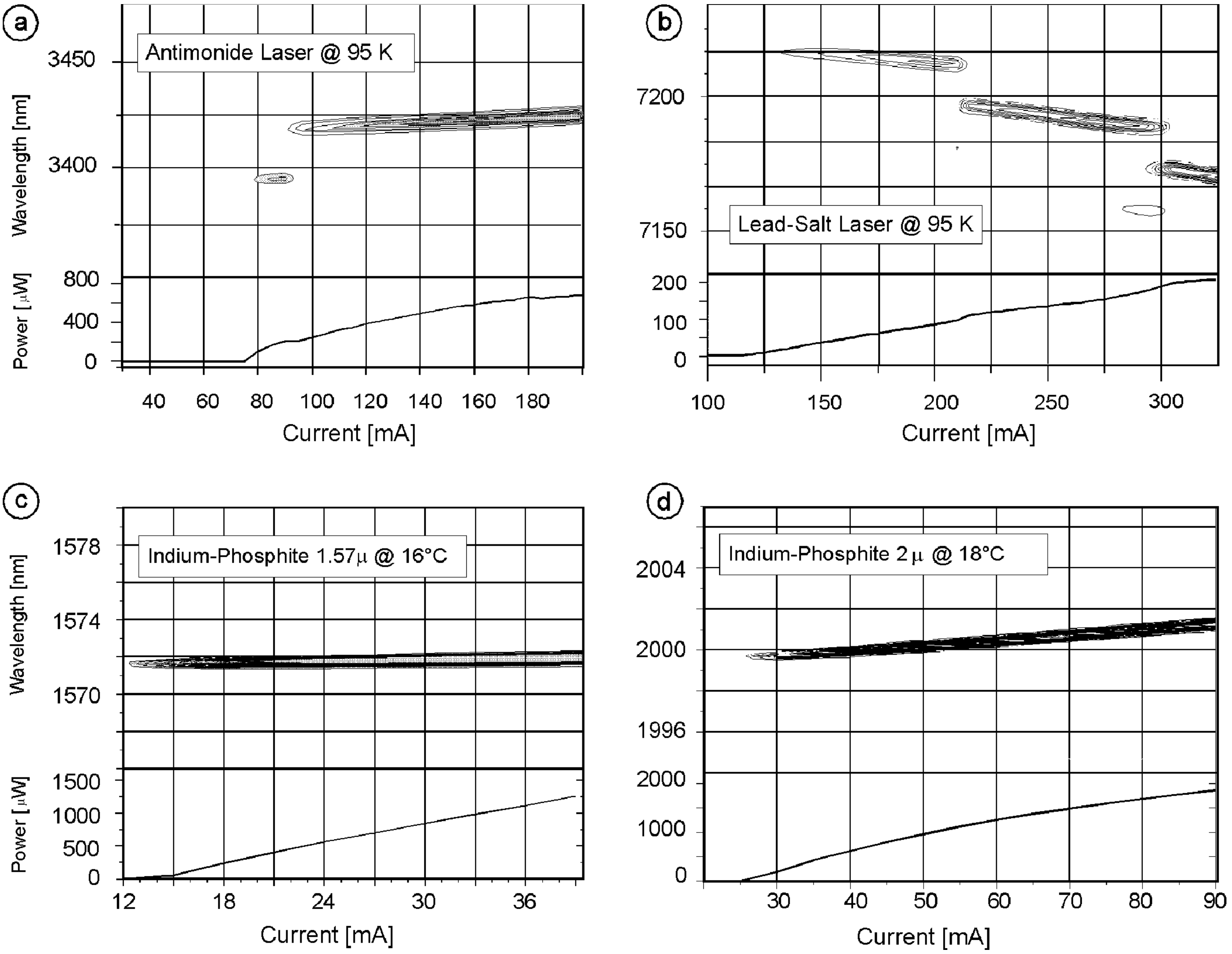

Fig. 2a–d. Mode maps with tuning characteristics and laser power for **a** a typical indium-antimonide laser near 3.4 µm and **b** a lead-salt laser at 7.2 µm, both at cryogenic temperatures, and near-infrared diode lasers operating at room temperature near **c** 1.572 µm and **d** 2.001 µm

1.6 µm no suitable DFB laser could be delivered). Since 1997 room-temperature DFB lasers at 2000/2004 nm have also been commercially available, where, at reduced pressure, strong CO_2 lines unaffected by H_2O absorptions can be found. Two near-infrared lasers, emitting in vicinity of 1573 nm (Fig. 2c) and at 2001 nm (Fig. 2d), have been characterized using an automated laser test setup [18]. Both lasers were tested in the range 10–40 °C with currents up to 4 times the threshold current I_{thr}. In Table 1 the characteristics of both lasers are listed for comparison. The specified maximum out-

Table 1. Measured parameters of two InP DFB lasers for CO_2 analysis

	Laser for 1573 nm	Laser for 2002 nm
Specified high T and high I	40 °C/45 mA	45 °C/100 mA
Threshold current I_{thr}	12 mA @ 10 °C 22 mA @ 40 °C	26 mA @ 10 °C 29 mA @ 40 °C
Maximum output power (measured at high I)	1.5 mW @ 10 °C 0.8 mW @ 40 °C	2.0 mW @ 10 °C 1.6 mW @ 40 °C
Total spectral range, 10–40 °C	1571.5–1574.4 nm	1998.3–2004.2 nm
Spectral covering at fixed T	< 0.1 nm ($< 0.4\,\mathrm{cm}^{-1}$)	1.9 nm ($4.7\,\mathrm{cm}^{-1}$)
Current tuning rate	ca. 0.003 nm/mA	0.027 nm/mA
Temperature tuning rate	0.1 nm/K	0.14 nm/K
Power change at max I @ 30 °C	35 µW/mA	12 µW/mA
Strong CO_2 lines detected	10	12
Side-mode suppression ratio	> 30 dB	> 30 dB
Beam profile (FWHM)	19° × 50°	19° × 50°

put power of 3.3 mW at 1572 nm and 5 mW at 2000 nm is not accessible due to the beam divergence. Using a lense with a small f number, about 65% of the specified power could be detected. Additionally the noise characteristics of the lasers have been investigated and show that at threshold both lasers exhibit very high and wideband noise levels (about 30 dB above the detector background). At about $1.2 \times I_{\mathrm{thr}}$ the noise level decreases, but it is still above the shot-noise limit by a factor of about 5. When higher currents are applied to the 1.57-μm laser the noise level increases due to the shot noise of the photo-current as expected, but the 2-μm laser shows a different behavior: with increasing current the noise contribution is nearly constant, but always above the shot noise. To reach the best signal-to-noise ratio (SNR) in frequency-modulation (FM) spectroscopy both lasers have to be operated at high currents. Based on these lasers a CO_2 sensor has been developed and their performance will be described in the next section.

2 A high-precision atmospheric carbon dioxide sensor

The optical layout of the instrument is shown in Fig. 3. The components are mounted on a 60 cm × 110 cm optical breadboard on top of a double 19-inch rack. The DFB laser (Sensors Unlimited) is held inside a Peltier-cooled mount which is fixed on a *xyz* stage. The laser beam is collimated by an off-axis parabola (OAP) with 10 mm diameter and 12 mm focal length. The beam is focused by a spherical mirror ($f = 1$ m) to the center of the Herriott-type measurement cell [21]. After 181 reflections, corresponding to 100 m, the beam exits the cell and is focused onto a temperature-stabilized 'extended InGaAs' detector (Sensors Unlimited) by another OAP. About 8% of the laser beam is coupled off by a beamsplitter and directed through the 28-cm reference cell onto another InGaAs detector. The whole system is pre-aligned by a visible diode laser, coupled into the setup by a pellicle beamsplitter which has to be removed during the measurements. In order to provide static as well as flux measurements at defined cell pressures, the measurement cell is equipped with a pressure sensor and on/off valves (at inlet and outlet) as well as with a needle valve at the inlet and a throttle valve at the outlet. The reference cell – filled with a high-concentration CO_2 mixture and sealed off – is connected to the measurement cell by a temperature bridge and a differential pressure sensor. With adjusted laser power and the right concentration in the reference cell the signals from both detectors have identical shape and amplitude and after system calibration using certificated gas mixtures the reference signal can be used as a secondary calibration standard. The signal processing schemes for single-tone and two-tone FM spectroscopy can be found in a recent review of advances in semiconductor-laser-based gas monitors [7].

The NIR system shown above has been applied for the detection of atmospheric CO_2. The dc current of the temperature-stabilized DFB laser is adjusted to the selected absorption line. The laser is scanned over this line by a 1-kHz ramp and additionally modulated by high frequency. In order to optimize the signal-to-noise ratio and the system stability [22] both FM techniques (single-tone and two-tone) have been implemented. Due to the limited detector bandwidth, frequencies up to 300 MHz are applied, corresponding to the linewidth of CO_2 at a pressure of 100 mbar. Some FM signals from a near-infrared InP diode laser operating around 2 μm are shown in Fig. 4 where outdoor air has been pumped through the Herriott cell and the ambient CO_2 signal of 350 ppm was recorded at 2.004 μm. From the weaker absorption lines of CO_2 and H_2O under high amplifica-

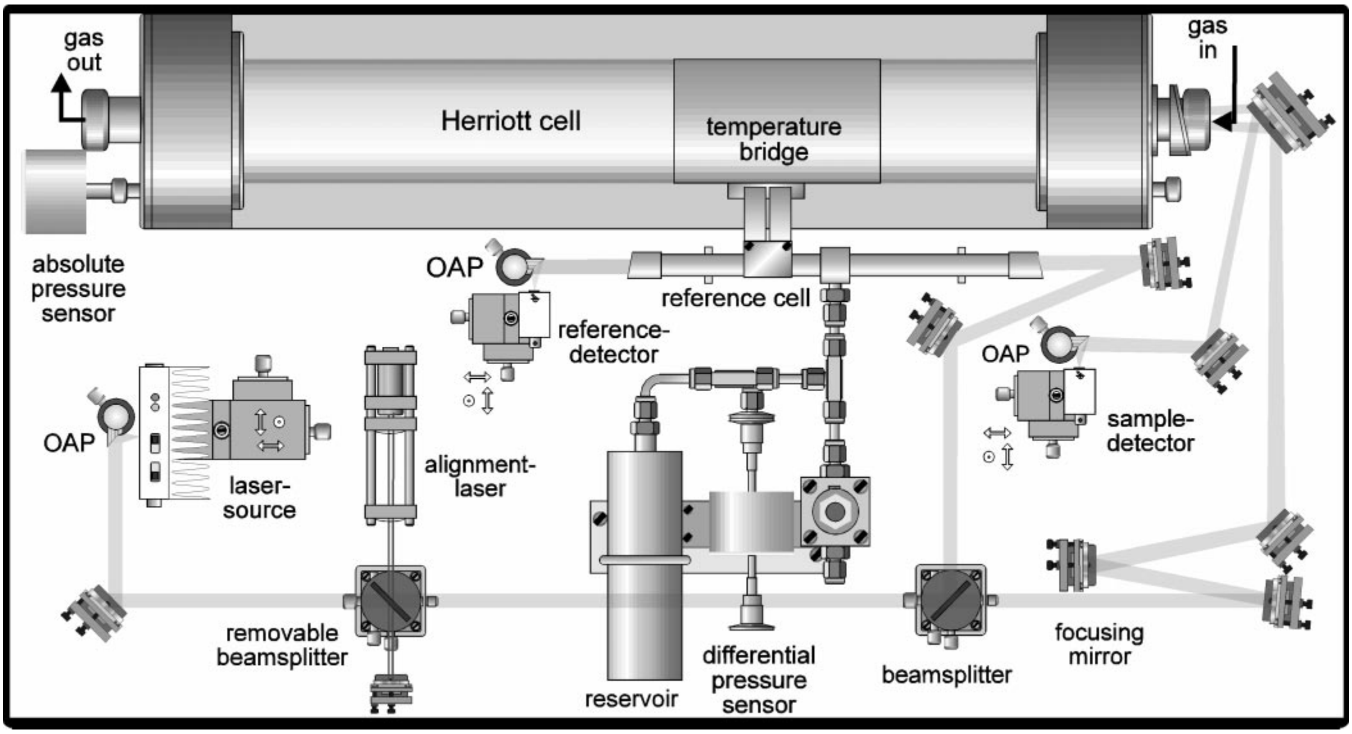

Fig. 3. Layout of the near-infrared spectrometer based on the room-temperature indium-phosphite DFB lasers from Fig. 2c,d

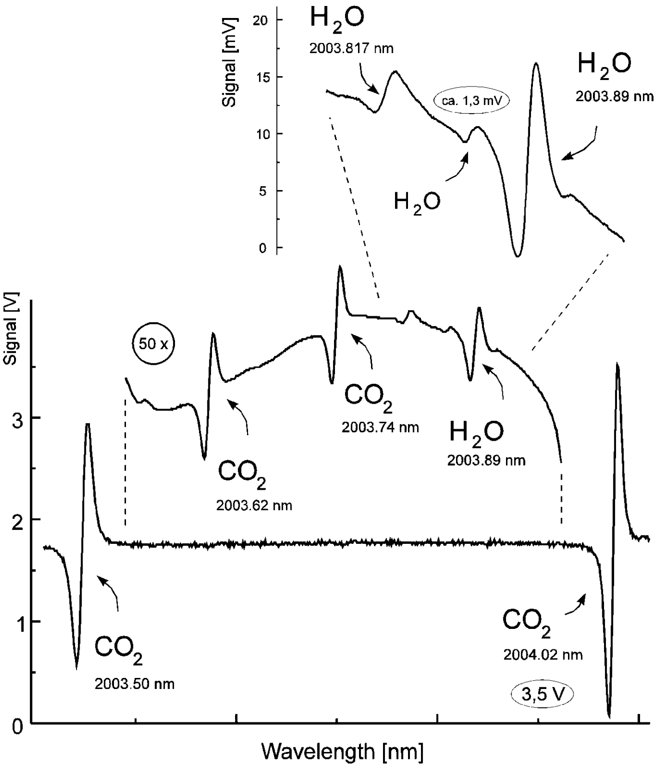

Fig. 4. Measurements of $^{12}CO_2$ in ambient air at a pressure of 100 mbar and 100 m optical pathlength

tion a precision of up to 10^{-4} has been estimated for 256 averages in less than 1 s. It is obvious that this spectral region has a significant advantage versus the 1.573-μm absorption band in the NIR, where the line strength is about 2 orders of magnitude weaker. At 2 μm the line strength is still weaker than in the fundamental band, but room-temperature operation of diode lasers is still possible for cw applications.

In order to compare both spectral regions and the system performance first the 1.57-μm laser was mounted in the CO_2 spectrometer. After the measurement cell the power of the laser reaching the detector was only 40 μW (4% of cell input power), which corresponds to a reflectivity of the cell mirrors of about 98.4%, if losses due to the imperfect beam profile are neglected. Since the wavelength range at a fixed temperature is very limited, the line identification in the 1.57-μm region was done by comparing the direct absorption signals of a gas mixture (3.38% CO_2 in synthetic air) with the calculated values from the HITRAN database. At 120 mbar and 100-m path length an absorption of 40% is expected for the strongest line at 1.5723 μm, with the next-strongest neighboring CO_2 lines weaker by a few percent. With this procedure the lines could be unequivocally identified, although a small difference in the relative intensities could be found compared to the values reported in the HITRAN database. This might be due to temperature changes during the measurement. The absorption by ambient water vapor is so small inside this wavelength interval (below 0.04%) that lines have been detected only when working with frequency modulation, but then the absolute absorption level was not available. The relative positions and amplitudes of the detected water lines confirmed the CO_2 line identification. Using the strongest absorption line of CO_2 the linearity of the FM spectrometer was checked in a dilution experiment: Two calibrated flow controllers have been used to mix N_2 gas and a 3.38% CO_2 compressed gas mixture to generate concentrations in the range 118–33 800 ppm, with N_2 as the zero level. The pressure in the cell was 120 mbar. The measured values are displayed in Fig. 5a. The exponential absorption behavior can clearly be seen. The small deviations of the measured values from the exponential curve represent the stability of the flow controllers. A linear approximation with an error below 1% is valid for concentrations below 600 ppm, corresponding to a direct absorption of 1%, and is thus suitable for ambient measurements. In the case of using a single-point calibration at 350 ppm an extrapolation of the linear operating range to 5000 ppm will result in a relative error of 4%. Since the instrument should be applied to ambient concentrations, a series of experiments using another gas mixture, specified to 358 ppm CO_2, was performed. From measurements of the SNR of several strong lines, as well as from relative amplitude ratios to weak neighboring lines and from stability tests, a 2σ reproducibility of about 2 ppm CO_2 could be determined at a measurement time of 1s within an effective electronic bandwidth of 6 Hz. These measurements have been done with a digital oscilloscope of only 8-bit resolution. Therefore, with improved signal processing a better performance is expected. Working at 90 reflections in the cell could further enhance the signal amplitude by a factor of about 2 (half absorption, but 4.5 times more power), whereas the noise on the signal would be about 20% higher, since the measurement is still dominated by the thermal noise of the detector–preamplifier combination. Therefore, a detection limit of 0.3 ppm CO_2 is feasible (1 s, 50 m, 120 mbar) corresponding to an optical density of 10^{-6} @ 1 Hz.

Line identification at 2 μm is much easier than at 1.57 μm since, within the full current range at fixed temperature, up to four strong and many weak CO_2 absorption lines together with water vapor lines can be found. Switching between N_2, CO_2 calibration gas, and ambient laboratory air in the cell allows the identification of CO_2 lines. Using a Ge etalon for frequency calibration a comparison with HITRAN data is easily done. On the other hand it should be noted that within our wavelength resolution some line positions of water show small deviations from the reported ones and additionally the isotopic distribution of H_2O has been found to be significantly different from the HITRAN value. From these measurements a SNR better than 10 000 can be estimated, when only the noise between absorption lines is considered. But this does not account for drift effects, as will be described below. Using the strong CO_2 absorption line at 2004.02 nm linearity tests have been performed at natural concentration levels in the range of 300–400 ppm. At a cell pressure of 100 mbar optimum signal amplitudes were obtained. The power reaching the detector was 100 μW. The result of the measurement is displayed in Fig. 5b. Due to the strong absorption lines an exponential absorption curve can be found at natural concentrations (the direct absorption corresponds to 35%). If the instrument is calibrated at a single point at 350 ppm and a linear approximation is used, it would result in an over- or under-estimation of 3% for the concentrations of 300 or 400 ppm, respectively. Further tests have been made to determine the stability of the instrument by Allan variance analysis [22] using a faster data acquisition and 12-bit resolution. The con-

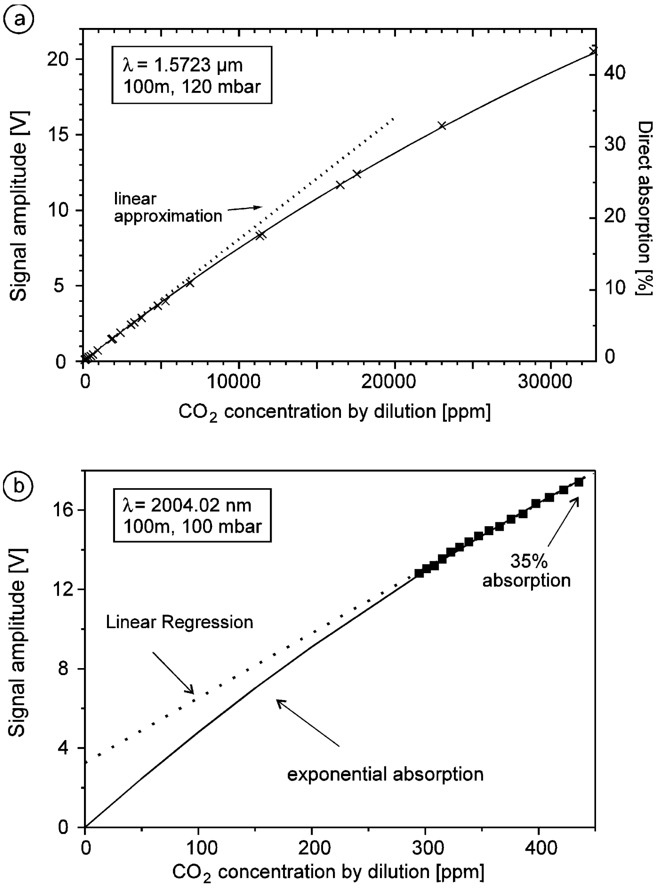

Fig. 5a,b. Nonlinear instrument response **a** to high CO_2 concentrations (at 1.57 µm). **b** to natural CO_2 concentrations (at 2 µm)

centration values have been calculated by a linear regression without further improved signal processing techniques. From the Allan plot in Fig. 6 it can be found that a standard deviation of 0.87 ppm is obtained at an integration time of 0.1 s; this corresponds to a change in optical density of 7×10^{-4}, or 1×10^{-4} normalized to 1 Hz bandwidth. Due to the white noise behavior further averaging improves the measurement reproducibility, for example at 10 s integration time a factor of 10 can be obtained in noise reduction. At longer measurement times drift effects dominate. Even without drift effects one has to take into consideration that the limited resolution of the data acquisition also will introduce deviations from the noise reduction. At 1 s averaging time the signal is very smooth and practically no noise can be identified at 12-bit resolution. But the reproducibility is only 0.3 ppm, which is worse by one order of magnitude compared to the value expected by noise considerations above. It can be assumed that temperature changes during the measurement have been below 1 K; therefore, changes in the line strength are below 0.1% [10]. This indicates that an additional noise source deteriorates the system performance, as has been found in [23] with lead-salt lasers: at strong absorption lines small laser frequency fluctuations are transferred to amplitude noise. The high current tuning rate of the 2-µm laser (Table 1) is an indication of this fact. Therefore, a reduced absorption pathlength and a very stable current controller must be applied to obtain a better SNR. To exclude temperature influences the signal of the reference detector should be used for normalizing. Futhermore, optimum signal processing strategies with matched filters will utilize the potential of the FM spectroscopy for high sensitivity measurements [24]. Further investigations into this problem are necessary. For a measurement application it implies that a concentration level of 0.1 ppm CO_2 can be detected more precisely than a 0.1-ppm concentration change on a 350-ppm signal. Therefore, an industrial application will be the determination of trace contaminations in process gas mixtures in the order of 10 ppb CO_2.

Besides ambient measurements another possible application could be isotopic ratio measurements for medical diagnosis, for example breath test [25, 26]. In the wave-

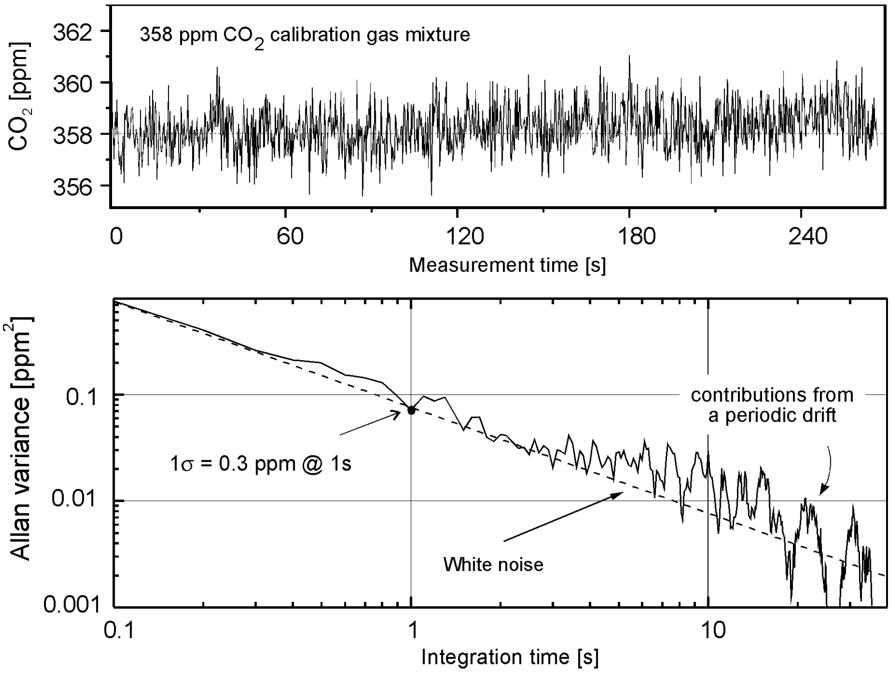

Fig. 6. Allan variance analysis of the system performance

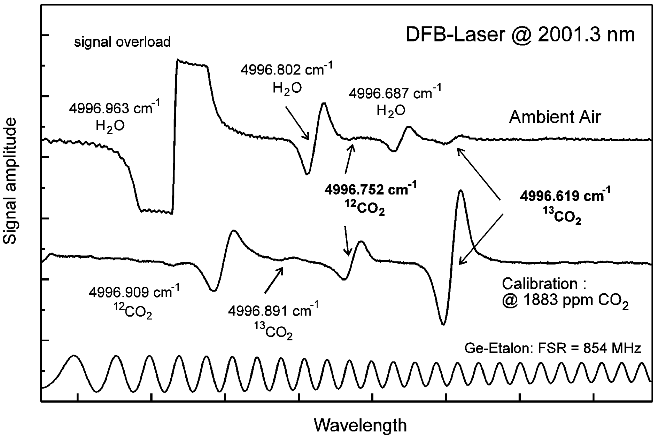

Fig. 7. Identification of $^{12}CO_2$ and $^{13}CO_2$ absorption lines around 2001.3 nm

length range accessible for the 1.57-µm laser no suitable $^{13}CO_2$ lines could be identified, the absorption strengths are too weak. Therefore, $^{13}CO_2/^{12}CO_2$ line pairs within the operation range of the tested 2-µm laser have been analysed. Lines in the vicinity of 2000.8 nm and 2001.3 nm have been identified. The latter line pair is partly influenced by water vapor as displayed in Fig. 7, but one has to consider that the CO_2 absorptions in expiration air are 20–30 times higher than the displayed ones. For medical applications the measuring instrument should be able to determine the ratio of $^{13}CO_2$ and $^{12}CO_2$ with a resolution of 0.07% [26] or at least 1% [13], whereas the absolute CO_2 concentration in human expiration air is 3%–5%, with 100% relative humidity at body temperature. A breath-test sample is typically about 1 L. The natural ratio $^{13}CO_2$: $^{12}CO_2$ is $1.095 \pm 0.003\%$. Therefore, the instrument must be able to detect both isotopes with a resolution of $< 10^{-3}$ unaffected by water vapor. The measurement of the $^{13}CO_2$ content in expiration air using the lines at 2000.8 and 2001.3 nm produces about the same signal as $^{12}CO_2$ in ambient atmospheric air masses at 2004 nm. Therefore, equivalent detection limits are expected. For a precise determination of the $^{13}C/^{12}C$ ratio, the neighboring $^{12}CO_2$ lines, which are weaker by a factor of 4, dominate the sensitivity, but even at absorption pathlengths of less than 10 m clear signals are expected. The main problem of accuracy is connected with temperature: the ratio of the line strength must be kept constant, which means here that the temperature during the analysis including calibration must be stable within 0.01 K, because the involved line strengths show opposite temperature dependencies (at 2001.3 nm the ratio of the line strengths changes from 5.4655 at 290 K to 4.081 at 300 K). A reliable measurement of the $^{13}CO_2$:$^{12}CO_2$ ratio using the 2000.8 and 2001.3 nm spectral region is not easy to perform, but is feasible using a small multipass cell. Nevertheless, the utilization of line pairs with reduced sensitivity to temperature changes is recommended.

3 Summary and conclusion

Whereas mid-infrared lasers operated at cryogenic temperatures cover the fundamental absorption bands required for ultrasensitive gas analysis, near-infrared room-temperature diode lasers give access mainly to significantly weaker overtone and combination bands. Therefore, the selection of the optimum operating conditions for a gas analyzer is always a trade-off between the required sensitivity and an operational system. Some molecular absorptions that can be used to detect carbon dioxide using mid- and near-IR diode lasers are listed in Table 2, where the detection limit in terms of volume mixing ratio [ppt] is shown based upon an absorbance sensitivity of $10^{-6}@\Delta f = 1$ Hz and 25-m optical pathlength. The absorption lines listed are not necessarily the strongest for that species nor do the wavelengths λ necessarily represent the only regions in which the species can be monitored. The detection limits must be regarded as estimates only and much depends on instrumental factors such as the quality and availability of the laser. By averaging over periods longer than 1 s or by using longer pathlengths the detection limits can be improved. Although the predicted sensitivities are based on known line strengths and the performance of a typical FM-TDLAS system, it is in the nature of field measurements that optimum performance is not always achieved. However, the 2-µm spectral region seems to be the best choice for a fieldable instrument. The experiments reported in this paper indicate that the performance of DFB diode lasers at selected wavelengths in the near-infrared spectral range is good. For the measurement of CO_2 at ambient concentration levels a resolution of more than two orders of magnitude has been demonstrated at 1.57 µm, and an enhancement by another order of magnitude is feasible after minor setup changes. At 2 µm CO_2 concentrations can be determined with a precision of about 4 orders of magnitude, if matched signal processing is applied. The reported measurements demonstrate the applicability of near-infrared DFB diode lasers to precise determination of CO_2 concentrations as required for climatological, medical, or industrial process monitoring [27].

Table 2. TDLAS detection limits for carbon dioxide in the mid- and near-infrared, calculated for a minimum detectable optical density of 10^{-6} at 30 mbar (150 mbar for < 2.7 µm), 25 m optical pathlength

CO_2 Band	Wavelength λ cm^{-1}	µm	Line strength S cm/molec	Detection limit pptv	µg/m^3
$3\nu_3$	6983.019	1.432	6.043×10^{-23}	73×10^3	144
$2\nu_1 + 2\nu_2 + \nu_3$	6359.968	1.572	1.846×10^{-23}	220×10^3	430
$\nu_1 + 4\nu_2 + \nu_3$	6240.105	1.603	1.838×10^{-23}	235×10^3	461
$2\nu_1 + \nu_3$	5109.311	1.957	4.003×10^{-23}	107×10^3	210
$\nu_1 + 2\nu_2 + \nu_3$	4989.972	2.004	1.332×10^{-21}	3.1×10^3	6.1
$\nu_1 + \nu_3$	3597.963	2.779	3.525×10^{-20}	110	0.22
ν_3	2361.466	4.235	3.524×10^{-18}	2	0.003

Acknowledgements. This research was carried out with support from the European Community under Contract ENV4-CT95-0033.

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