

# Field Laser Applications in Industry and Research

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### **Online - Abstracts**

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# INDEX

<b>INDUSTRY SESSION.....</b>	<b>1</b>
VERTILAS - Recent developments and prospects of long-wavelength VCSELs for TDLS applications.....	2
NANOPLUS - Remote gas sensing with long wavelength DFB laser diodes.....	3
LASER 2000 - Tunable lasers for infrared and terahertz spectroscopy.....	4
HAMAMATSU - Quantum cascade lasers for FLAIR.....	5
ALPES LASERS - Advanced quantum cascade lasers for spectroscopic applications.....	6
DAYLIGHT SOLUTIONS - Applied spectroscopic results using broadly tunable miniaturized external cavity quantum cascade lasers for the mid-infrared.....	7
TIGER OPTICS - Developments & industrial applications using continuous-wave cavity ring-down spectroscopy.....	8
AERODYNE RESEARCH - Compact quantum cascade laser instrument for rapid, high sensitivity measurements of atmospheric trace gases: ammonia detection at 10.3 $\mu\text{m}$ .....	9
PICARRO - Real time ultra-trace monitoring of ethylene production via cavity ring down spectroscopy (CRDS) for preclimacteric fruit in ozone treated regular and controlled atmospheres.....	10
SOUTHWEST SCIENCES - VCSEL-based trace gas monitoring with industrial applications.....	11
LOS GATOS - Recent advances in instrumentation based on cavity enhanced absorption spectroscopy.....	12
NOVAWAVE - Mid-infrared trace gas sensing with difference frequency generation lasers.....	13
NORSK - New developments in laser spectroscopy at Norsk Elektro Optikk A/S.....	14
TDL SENSORS - Transferring tunable diode-laser gas measurement technology from the laboratory to industrial environments.....	15
LOCCIONI - Laser boiler test: an industrial application.....	16
NEOPLAS CONTROL - On further developments of the Q-MACS technology for online process control and trace gas measurements in research and industry.....	17
SIEMENS - Industrialization trends of tunable diode-laser spectroscopy.....	18
<b>APPLIED SPECTROSCOPY.....</b>	<b>19</b>
Laser based diagnostics from our cultural heritage to human health.....	20
Developing intrinsic spectroscopic standards for quantitative gas analysis.....	21
Widely tunable external cavity quantum cascade lasers for high resolution spectroscopy and chemical sensing.....	22
Stark-enhanced diode-laser spectroscopy of formaldehyde using a modified Herriott-type multipass cell.....	23
Fiber-laser-based NICE-OHMS and trace gas detection.....	24
Diode laser based photoacoustic detection of carbon dioxide and oxygen using micromechanical cantilever pressure transducer.....	25
Potentials and limits of mid-infrared laser spectroscopy for the detection of explosives.....	26
Applications of new sources of mid-infrared radiation in sensitive spectroscopy.....	27
Application of fused CWFM-lidar and TDLS approaches to open-path range-resolved gas leaks detection.....	28
Beyond the limitations of conventional mid-IR DFG lasers for trace gas sensing in industry and research.....	29
TraceScout - an advanced sensor system for in-line monitoring of special gases in semiconductor industry.....	30
Recent advances and applications of semiconductor laser based gas sensor technology.....	31
Ultra-broadband difference-frequency generation in waveguide PPLN crystal in the mid-infrared.....	32
Use of optical feedback CEAS for atmospheric detection.....	33
Pressure broadening and shift measurements of ammonia lines with a selection of broadening gases.....	34
Cavity enhanced absorption methods for trace gas detection.....	35
Method for improving the sensitivity in a fiber coupled diode-laser spectrometer by selective predistortion.....	36
Potential of NICE-OHMS for ultra-sensitive atmospheric spectroscopy.....	37
Phase-shift off-axis cavity-enhanced absorption spectrometer for nitrogen dioxide.....	38
New, automated, software-based selection of optimized absorption lines for TDLAS-based concentration measurements.....	39
Compact, high-sensitivity water vapor absorption spectrometer using new 2.6 $\mu\text{m}$ room-temperature DFB diode-lasers.....	40
Application of 940 nm high power DFB lasers in high resolution spectroscopy using a robust and compact sensor unit.....	41
Laser micro-profilometry for applications in the cultural heritage field.....	42
Design and noise properties of free-running kHz-linewidth broadly-tunable single-frequency external-cavity VCSELs.....	43
Control and synchronization of polarization dynamics by optical feedback.....	44
Tunable diode-laser spectroscopy for industrial process applications.....	45
<b>MEDICINE, LIFESCIENCE AND AGRICULTURE.....</b>	<b>46</b>
Laser applications in life science, sensitive chemical sensing in biology and agriculture.....	47
Tissue imaging with non linear laser microscopy.....	48
Breath diagnostics using laser spectroscopy.....	49
Agricultural trace-gas emissions determination using open-path lasers and inverse dispersion analysis.....	50
Application of supercontinuum lasers to confocal microscopy.....	51
QCL-based detection of UV-induced nitric oxide formation from aqueous solutions.....	52
Development of a CO <sub>2</sub> triggered alveolar air sampler.....	53
An ultra-sensitive, six-species trace gas analyzer for continuously monitoring concentrated animal feeding operations.....	54
Gassification process monitoring by photoacoustic diode-laser spectroscopy.....	55
<b>ENVIRONMENTAL SCIENCE AND BIOGEOCHEMISTRY.....</b>	<b>56</b>
Infrared laser applications to field measurements of trace gas sources and fluxes in environmental research.....	57
Biosphere – Atmosphere exchange: an overview.....	58
High resolution measurements of absolute water transpiration rates from plant leaves via 1.37 $\mu\text{m}$ tunable diode-laser absorption spectroscopy.....	59
Evanescent field sensors for monitoring of diluted CO <sub>2</sub> during sequestration in aquifers and for detection of explosives.....	60
Applications of integrated cavity output spectroscopy in environment science.....	61
Measurements of atmospheric CH <sub>4</sub> and N <sub>2</sub> O with a new-design long-path room-temperature quantum cascade laser spectrometer.....	62
Kinetic study of the degradation of aromatic hydrocarbons by simultaneous detection of OH and HO <sub>2</sub> radicals by laser photolysis coupled to LIF and cw-CRDS.....	63
Cavity ringdown analyzer for carbon dioxide and methane atmospheric inversion measurements.....	64
A case study for dispersion models: methane emission from the landfill of Florence.....	65
A near-infrared sensor for the near-ground measurement of atmospheric CO <sub>2</sub> : Intercomparison with Lidar and other sensors.....	66

A compact laser instrument based on difference-frequency generation for trace gas detection of VOCs .....	67
NO detection using double lock-in detection technique with a quantum cascade laser .....	68
<b>PLASMA AND COMBUSTION DIAGNOSTICS .....</b>	<b>69</b>
On recent progress in diagnostics of molecular plasmas using mid infrared diode-lasers in research and industry.....	70
Advanced near infrared diode-laser based in-situ sensors for full-scale technical combustion processes .....	71
Measuring toxic heavy metals in combustion - challenges and approaches.....	72
Spatially-resolved flame thermometry at kHz repetition-rates using diode-lasers.....	73
Detection of HCl in combustion chamber using 1.74 $\mu$ m DFB laser-diode .....	74
Detection of O <sub>2</sub> (a <sup>1</sup> $\Delta_g$ ) molecules in inductively coupled O <sub>2</sub> plasma.....	75
Trace gas detection using a novel cantilever-based photoacoustic spectrometer with multiplexed optical fibre-coupled diode-lasers and fibre amplification.....	76
In-situ monitoring of silicon plasma etching using a quantum cascade laser arrangement.....	78
Sensors network system for in-line analysis and disposal of CO <sub>2</sub> laser steels cutting fumes.....	79
Laser-diode sensor for the measurement of temperature under different pressure conditions.....	80
Time resolved absorption spectroscopic studies on the kinetics of a pulsed DC discharge using quantum cascade lasers.....	81
Molecular oxygen sensor based upon direct absorption and a vertical-cavity surface-emitting laser at 765 nm.....	82
<b>AIRBORNE ATMOSPHERIC RESEARCH.....</b>	<b>83</b>
Airborne atmospheric research in Europe : CARIBIC and HALO.....	84
Airborne measurements of HCHO, CO and CH <sub>4</sub> using cw quantum cascade laser spectroscopy.....	85
Airborne measurements of atmospheric trace species using diode-laser absorption spectroscopy.....	86
Mission to Mars and the Earth's stratosphere: laser applications to planetary and atmospheric research .....	87
Demonstration of a ultra sensitive airborne difference frequency spectrometer: performance characterization and ambient measurements of Formaldehyde .....	88
A pulsed QC-laser based dual-spectrometer instrument for fast response, high accuracy, high precision airborne measurements of CO <sub>2</sub> , CO, CH <sub>4</sub> and N <sub>2</sub> O.....	89
In-flights performances of a tunable diode-laser spectrometer for airborne measurement of carbon monoxide during tropical campaign90	90
Development of a small balloon-borne instrument for the study of water vapor in the upper troposphere and lower stratosphere .....	91
Argus: A compact, dual channel, mid-IR tunable diode laser spectrometer for use on multiple airborne platforms.....	92
Airborne in-situ trace gas measurements during HOOVER with the three laser quantum cascade laser absorption spectrometer TRISTAR .....	93
Performance and design of TRISTAR: A compact three laser quantum cascade laser spectroscopy instrument for airborne measurements .....	94
Airborne Measurements of CO and NH <sub>3</sub> during ICARTT 2004 using TDLAS.....	95
CO <sub>2</sub> laser-based trace gas ethylene detector for airborne measurements over Texas.....	96
TDLAS: an instrument based on near-infrared diode-laser technology for the in-situ monitoring of the Martian atmosphere.....	97
MILD: a laser altimeter transmitter for Mercury planetary orbiter.....	98
Flight testing and laboratory calibrations of the HIAPER VCSEL hygrometer.....	99
<b>ISOTOPES.....</b>	<b>100</b>
Advances and challenges in stable isotope infrared spectrometry.....	101
The Harvard integrated cavity output spectroscopy (ICOS) isotope instrument.....	102
Continuous Measurement of CO <sub>2</sub> Isotopic Ratios by Infrared Spectroscopy using FTIR and QCL Instruments.....	103
Long-path absorption spectrometers for determining $\delta^{13}C$ in CO <sub>2</sub> at field sites .....	104
Tunable diode-laser spectrometer for atmospheric measurement of the isotopic ratio <sup>13</sup> CO <sub>2</sub> / <sup>12</sup> CO <sub>2</sub> .....	105
Simultaneous measurements of multiple gas species and the <sup>13</sup> C/ <sup>12</sup> C isotope ratio in CO <sub>2</sub> from a wood-based combustion emission by laser absorption spectroscopy.....	106
<sup>12</sup> CO <sub>2</sub> / <sup>13</sup> CO <sub>2</sub> ratio measurement by off-axis cavity-enhanced absorption spectroscopy .....	107
A theoretical analysis of marijuana grow house detection by TDLAS using the H <sub>2</sub> <sup>18</sup> O/H <sub>2</sub> <sup>16</sup> O isotope ratio.....	108
Long-term continuous monitoring of atmospheric CO <sub>2</sub> stable isotopic ratios using a 4.3 $\mu$ m pulsed QCL .....	109
Cryogenic free QCLAS for simultaneous and continuous mixing ratio measurements of CO <sub>2</sub> isotopologues in ambient air.....	110
<b>Analytical Index.....</b>	<b>111</b>
<b>Notes.....</b>	<b>115</b>

# **INDUSTRY SESSION**

# VERTILAS - Recent developments and prospects of long-wavelength VCSELs for TDLS applications

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Owing to fundamental technological challenges, the development of long-wavelength VCSELs with emission wavelengths beyond 1.3  $\mu\text{m}$  has been significantly delayed in comparison to their short wavelength counterparts or DFB lasers. In the past few years, however, the emergence of novel device concepts has led to a tremendous progress for this type of laser. Since then, the performance has been steadily improved and revealed long-wavelength VCSELs as a competitive light source for exiting systems or even enabling technology for new applications and markets. The unique device features include high current tuning rates, wide tuning ranges, extended modulation capabilities and cost effective production including on wafer testability.

With its Buried Tunnel Junction (BTJ)-VCSEL technology, VERTILAS has been pioneering the commercialization of long-wavelength VCSELs for optical sensing and communication. These lasers are based on mature InP-based material systems. By tailoring the layer thicknesses and compositions, near infrared emission wavelengths from 1.3 to 2  $\mu\text{m}$  are currently available. Continuous ageing tests show a very good long term stability with failure rates of less than 1 % in 10 years.

While VCSELs for TDLS are well established with emission wavelengths up to 2  $\mu\text{m}$ , there is also substantial interest in combining the advantages of VCSELs with gas detection at longer wavelengths such as 2.33  $\mu\text{m}$  for carbon monoxide. VERTILAS is being involved in the development of such lasers and several important milestones have already been achieved.

An optimized active region design based on strained quantum wells exhibits very good material quality even for an emission around 2.3  $\mu\text{m}$ . This novel active region has been implemented in the proven BTJ-design. Fig. 1 shows the output characteristics of a VCSEL emitting around 2.3  $\mu\text{m}$ .

While these wavelength regime represents a limit for InP-based VCSELs, even longer wavelengths will be achieved with GaSb-based VCSELs. For these devices we discuss the current development status and the prospects regarding performance and commercialization.

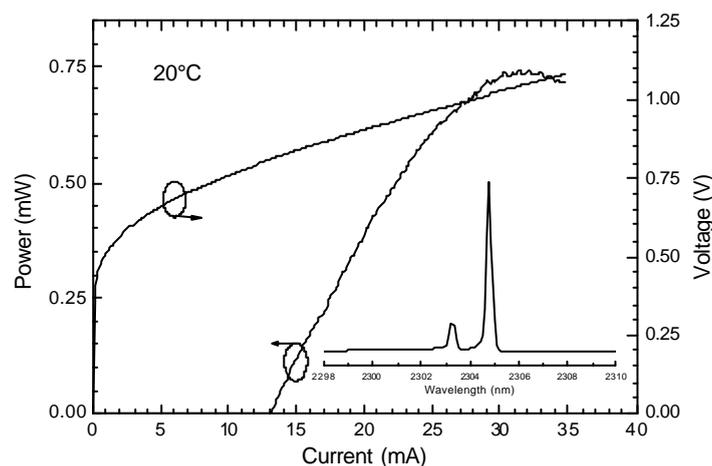


Fig. 1 Light-current curve and emission spectrum of 2.3  $\mu\text{m}$  VCSEL

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- [2] M. Ortsiefer, G. Böhm, M. Grau, K. Windhorn, E. Rönneberg, J. Rosskopf, R. Shau, O. Dier, and M.-C. Amann, *Electron. Lett.*, **42**, 640-641 (2006)

## NANOPLUS - Remote gas sensing with long wavelength DFB laser diodes

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Strong interest in remote gas sensing systems has emerged in the last few years.

A key element remote of modern gas sensing systems are distributed feedback laser diodes, which are used to scan over absorption lines of the gas species to be detected and the degree of absorption serves as a precise monitor for the amount of the specific gas molecules under investigation. With gas sensors based on tunable diode laser spectroscopy sophisticated detection limits can be achieved. Typical sensitivities for these detection systems lie the range of ppm to ppb [1]. However, there is an ever growing need for even higher sensitivities and at the same time increased spectral selectivity.

One obstacle limiting the sensitivity of currently available conventional laser-based gas sensors is the fact that they are mostly equipped with laser diodes emitting in the near infra red spectral range at wavelengths which are typically below 2.3  $\mu\text{m}$ , where the absorption of many molecules is inherently lower than at higher wavelengths. As an example the absorbance of water at 2756 nm wavelength is by a factor of 15 higher as compared to the prominent absorption line at 1368 nm.

Hence, there is a demand for lasers which are able to address these stronger absorption features located above 2.3  $\mu\text{m}$  wavelength.

Recently DFB lasers with emission wavelengths as long as 2.8  $\mu\text{m}$  were successfully fabricated using the technology of lateral metal Bragg gratings incorporated in the laser structure [2]. The emission spectrum of such a laser diode at room temperature is characterized by a high side mode suppression ratio  $\alpha > 30$  dB which ensures a high spectral selectivity. These diodes offer a large potential for applications in novel gas sensors ensuring higher detection limits than currently available laser based gas detection systems operating at lower wavelengths. These diodes are applied in sensor systems for such different fields as environmental monitoring, process control or medical analytics, where a high level of precision is required. For instance, NASA will use nanoplus DFB laser diodes emitting at about 2.7  $\mu\text{m}$  wavelength for their 2009 Mars Mission to search for water vapor and carbon dioxide on Mars. The high spectral brilliance of these diodes even enables a discrimination between different gas isotopes, which exhibit slightly different absorption lines. This demonstrates the high potential of these laser diodes in a wide variety of remote gas sensing applications.

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## LASER 2000 - Tunable lasers for infrared and terahertz spectroscopy

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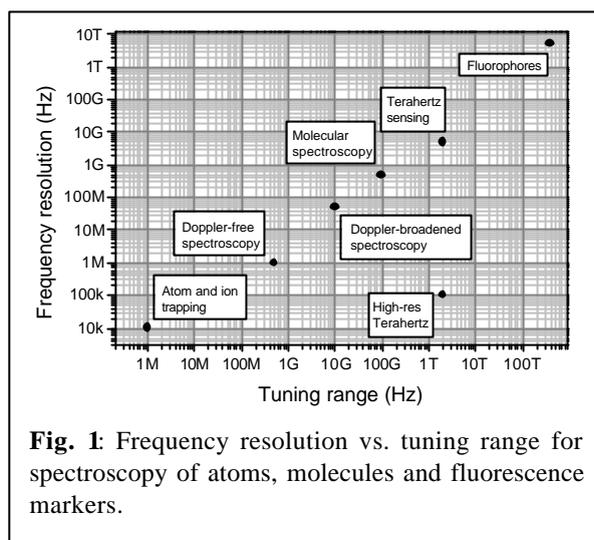
Tunable laser spectroscopy covers a broad range of applications, with vastly diverse demands on the utilized laser source. Between precise manipulation of atoms and ions in quantum-optical experiments on one side, and wide-range excitation of fluorophores on the other, both the required frequency tuning span and the appropriate frequency resolution vary over more than eight decades (Fig. 1). Tunable external-cavity diode lasers (ECDLs), Distributed Feedback (DFB) diodes, and femtosecond fiber lasers complement one another for different applications.

Frequency control on the 10 kHz scale is mandatory for precision spectroscopy, e.g. in ion trapping experiments. On the laser side, this calls for high-bandwidth frequency stabilization. We realized a PID regulator with 10 MHz bandwidth and demonstrated frequency locking of ECDLs and DFB lasers to transmission fringes of a high-finesse Fabry-Perot resonator. The laser linewidth was measured simultaneously with a delayed self-heterodyne beat setup. The beat signal FWHM ( $\approx 2$  times the laser linewidth), was 1 .. 1.5 kHz for both ECDLs and DFB lasers. This represents a linewidth reduction by 2 .. 3 orders of magnitude, compared to non-stabilized lasers.

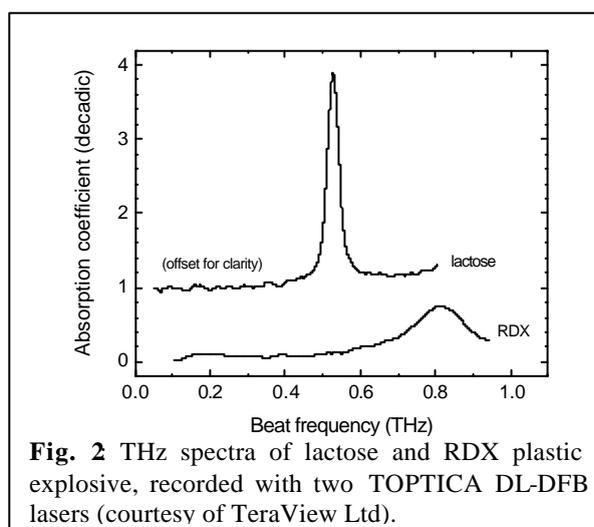
Molecular absorption lines are about 1000 times broader than atomic resonance transitions. Scan ranges of  $\sim 100$  GHz are thus required to sweep the laser frequency across several molecular transitions. Thermally tuned DFB lasers meet this demand; continuous frequency shifts up to 1400 GHz have been demonstrated with near-infrared DFB diodes (e.g. 780 nm, 895 nm). Commercially available DFB lasers now cover the complete wavelength range between 760 nm and 2800 nm and hence, the absorption bands of a multitude of relevant trace gases.

The Terahertz (THz) spectral range refers to far-IR wavelengths between 30  $\mu\text{m}$  and 1 mm. Tunable CW THz radiation is obtained by difference frequency mixing of two lasers of adjacent wavelengths on a semiconductor photomixer. Here, too, DFB lasers are ideally suited due to their high output power and wide tuning range. Accurate stabilization of the DFB frequency with interferometric locking schemes, further helps achieve an exact control of the THz frequency, e.g. for precise detection and quantification of hazardous gases (Fig. 2).

Wavelength tuning over several 100 nm is feasible with femtosecond fiber lasers: The emission spectrum of Er: fiber lasers is broadened in highly nonlinear fibers, wavelength-shifted by pulse dispersion control, and frequency doubled to generate laser radiation tunable from blue to infrared wavelengths. This laser finds applications in biophysical and biomedical research (chromophore excitation).



**Fig. 1:** Frequency resolution vs. tuning range for spectroscopy of atoms, molecules and fluorescence markers.



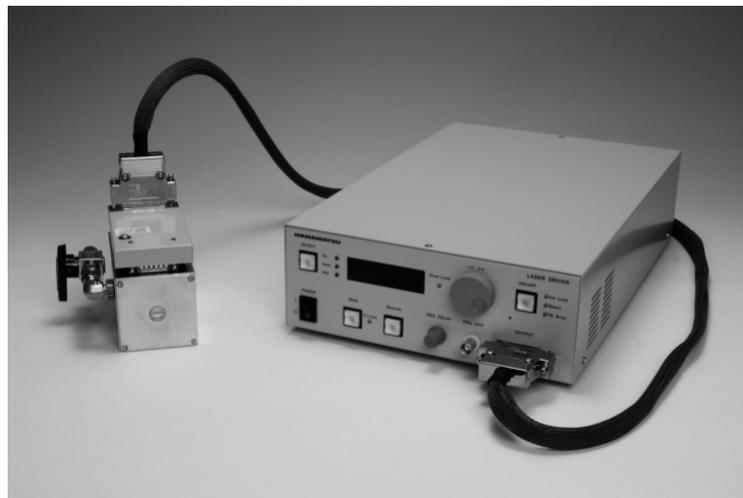
**Fig. 2** THz spectra of lactose and RDX plastic explosive, recorded with two TOPTICA DL-DFB lasers (courtesy of TeraView Ltd).

## HAMAMATSU - Quantum cascade lasers for FLAIR

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The quantum cascade laser (QCL) is the only semiconductor laser that is accessible to the mid-infrared region with its narrow line width, robustness and single-mode operation. It is a promising mid-infrared laser source for industrial laser-based optical sensors. A QCL-based absorption spectrometer offers advantages not only for high sensitivity but also high selectivity, non-destructivity, compactness, portability and real-time monitoring. Many applications to environmental gas monitoring and emission gas measurement have been already demonstrated by means of various sensing techniques: direct absorption spectroscopy using a multi-pass cell, cavity ring-down spectroscopy, photoacoustic spectroscopy, etc. Developments of sensing techniques using the QCL will cultivate its market. In fact, potential new applications such as detection of explosives and medical diagnostics like breath analysis have been suggested. The market shows signs of growing.

HAMAMATSU has been developing QCLs. TE-cooled pulsed QCLs in the range from around 4  $\mu\text{m}$  to 10  $\mu\text{m}$  are on the market. We succeeded in CW operation at room temperature at a wavelength of 7.8  $\mu\text{m}$ . HAMAMATSU also developed TE-cooling laser head modules, fast pulse drivers and related equipments including MCT detectors. The commercially available QCLs and the current status of development will be mentioned in the talk. In addition, measurements of various gases in the laboratory using our devices and equipments will be presented and discussed.



**HAMAMATSU**

# ALPES LASERS - Advanced quantum cascade lasers for spectroscopic applications

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Quantum cascade (QC) distributed-feedback (DFB) lasers operating in continuous wave (cw) with narrow linewidths (<3.5 MHz) became a technology of choice for many chemical sensing applications, ranging from industrial process control to environmental science and medical diagnostics. The relatively small temperature-tuning range of a single device usually limits the possibilities of gas analysis. This is particularly true for complex mixtures with multiple absorption lines or in mixtures with very broad lines (typically those with a liquid phase matrix).

We studied possibilities of monolithic integration of several lasers emitting at different wavelengths - a device ideal for construction of a multi-channel laser spectrometer. A bound-to-continuum active region consisting of 35 periods<sup>[1]</sup> was optimized for an emission maximum at 1270 cm<sup>-1</sup> (7.87 microns). It exhibits a broad gain-span with a full-width at half maximum in the range of 250 cm<sup>-1</sup>.

The structure has been grown using molecular beam epitaxy (MBE). Twenty-four different gratings have been wet chemical etched into the chip. The upper cladding has been grown on the top of the gratings has been grown using MOVPE. The laser ridges have been shaped using a standard lithography process. After cleaving into 1.5 mm-long laser bars, a high reflection coating with a reflectivity of  $R \approx 97\%$ , was evaporated on the back facet.

The devices operate in cw-mode, up to the of +60°C at the gain maximum and up to +35 °C the edge of the gain-span. The output powers measured at 0°C range from 40 mW at the edge to 80 mW at the center of the gain. Each of the single devices exhibit a single mode emission with a tuning range of several wavenumbers and a tuning coefficient  $b$  of  $-8.88 \cdot 10^{-5} \text{ K}^{-1}$  (see fig.1).

Using the broad gain peak of the bound-to-continuum and 25 different DFB gratings, we were able to achieve a single mode emission at wavelengths ranging from 7.7 to 8.3 μm (7.6 % of the central wavelength) in a single processing run, on one piece of material. The results show the usability of the approach for the monolithic integration of high-performance DFB lasers emitting at different wavelengths. These devices currently undergo ageing tests and they accumulated over 5000 hours of uninterrupted operation at 90 % of the maximum emission power at ambient temperature. So far they exhibit no sign of degradation. As such they appear to be viable as a key component of multi-channel laser spectrometers.

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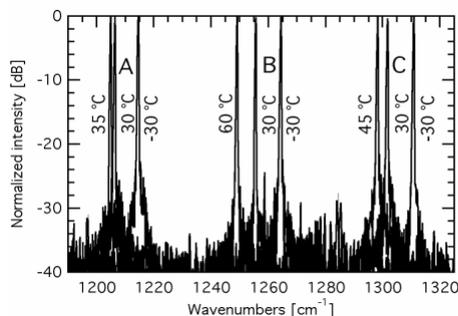


Fig. 1: High resolution single mode cw spectra of samples A, B and C show operation with a side-mode suppression ratio >25 dB. Depicted are the spectra at 1.1 x threshold, at +30 °C, and at the extremes of single laser tuning range achieved by the variation of temperature tuning. The corresponding single tuning ranges for samples A, B and C are 10, 15 and 12 cm<sup>-1</sup>,

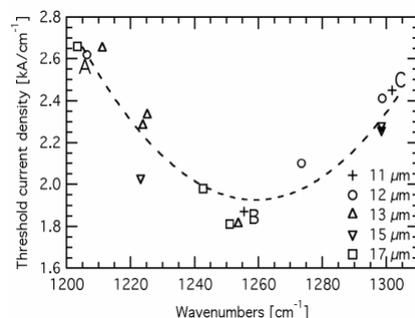


Fig. 2: Threshold current density in cw operation at +30 °C versus wavenumbers (at 1.1 x threshold current). The dashed lines serve as guide for the eye. The threshold current densities increase from the 1.87 kA/cm<sup>2</sup> (sample B) to 2.62 kA/cm<sup>2</sup> (sample A) and 2.45 kA/cm<sup>2</sup> (sample C).



## **TIGER OPTICS - Developments & industrial applications using continuous-wave cavity ring-down spectroscopy**

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Continuous-wave cavity ring-down spectroscopy (CW-CRDS) is now in use in a range of industries for the sensitive detection of a different trace gas species, including water vapour, methane, carbon monoxide and formaldehyde, as well as for trace measurements of corrosive and toxic gases including hydrogen bromide and ammonia. It has also now been applied in a range of matrix gases, including those that are corrosive and those that have the potential for spectral interference with the target species. The developments that have been carried out to achieve this will be outlined, and examples of the industrial applications, covering single sensors and multi-species and multi-head sensors will be presented.

One limitation of the current sensor technology is that it uses mirrors that are highly reflective over a very restricted spectral range, and this generally limits a given sensor to the measurement of one gaseous species, as it is not practical to obtain mirrors that have the required reflectivity over a large spectral range. We present the development of a new type of ring-down cavity that uses reflective optics that can be used from the ultraviolet to the infrared spectral regions. Potential new industrial applications will also be outlined.

# AERODYNE RESEARCH - Compact quantum cascade laser instrument for rapid, high sensitivity measurements of atmospheric trace gases: ammonia detection at 10.3 mm

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We have developed a new compact instrument for sensitive, rapid and continuous measurement of trace gases in air, with the focus here on ammonia. This instrument takes advantage of recent technology in quantum cascade (QC) lasers and infrared detectors, which allows high sensitivity to ammonia (~0.2 parts per billion  $\text{NH}_3$  in 1 s) without cryogenic liquids. One may substitute a QC laser operating at a different wavelength to measure other gases. The instrument operates continuously, requiring little operator attention, and web-based remote access is provided for instrument control, calibration and data retrieval. The instrument design includes a thermoelectrically (TE) cooled pulsed QC laser operating at  $967 \text{ cm}^{-1}$ , a low volume multi-pass cell offering 76 meter absorption path length and a TE cooled detector. Integrated software for laser control and data analysis using direct absorption provides quantitative trace gas measurements without calibration gases. The instrument may be applied to field measurements of gases of environmental concern including methane and nitrous oxide.

The instrument described in this presentation is a compact design, with optics and the electronics mounted together in a single 19" rack mountable enclosure weighing less than 25 kg. The optics include three paths, the main one through the long (76 meter) absorption cell, and two reference paths. One reference path is used to normalize laser output fluctuations. The second passes through a reference gas cell for locking the laser wavelength. A sample of recent data is shown in Figure 1, wherein we ran the instrument for 12 hours measuring the output of a permeation tube added to laboratory room air. An Allan variance plot is shown in the lower panel of Figure 1, which shows the variance as a function of averaging time. The  $\text{NH}_3$  concentration noise (standard deviation) with 1 second averaging is 0.22 ppb. The minimum in the Allan plot indicates the ultimate noise limit (0.019 ppb), at the longest useful averaging time of 100 seconds.

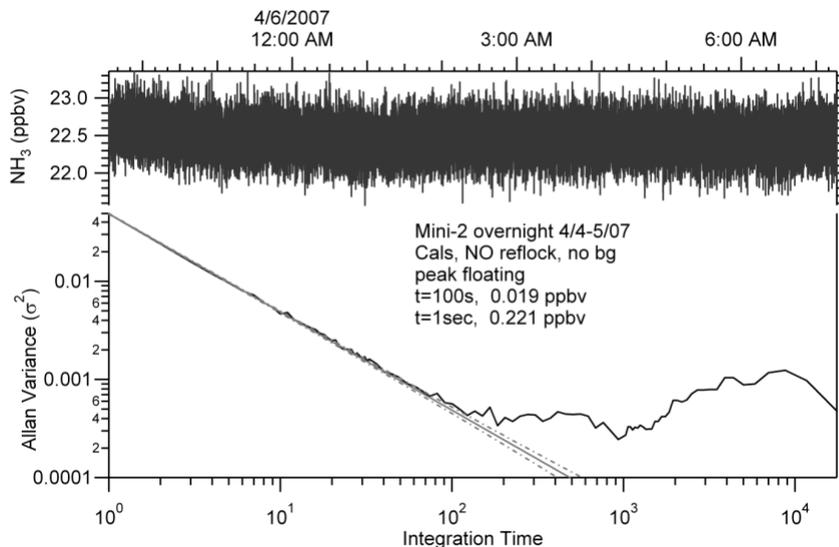


Figure 1: Upper trace: Sample of data, 12 hours continuous measurement of ammonia in "zero-air". Lower Trace: Allan variance for the data sample, showing noise in 1 second of 0.22 ppb, and a minimum noise of 0.02 ppb with 100 seconds averaging.

## **PICARRO - Real time ultra-trace monitoring of ethylene production via cavity ring down spectroscopy (CRDS) for preclimacteric fruit in ozone treated regular and controlled atmospheres**

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Ethylene production in preclimacteric fruit is a well known precursor to ripening. Preservation of fruit in regular and controlled atmospheres demands careful control of ethylene levels. The factors that influence ripening and ethylene production include, but are not limited to, time of harvest, storage temperature, atmospheric composition, as well as the presence of other ethylene-producing commodities that may be in close proximity. A particularly challenging problem is cross-ripening, in which early ripening of a few pieces of fruit can cause the premature ripening of the entire group. For this reason, it is important to monitor the ethylene production early on in the ripening process, where the ethylene levels in a storage container can be in the low parts-per-billion levels.

Cavity Ring-Down Spectroscopy (CRDS) is a laser-based, all-optical technique capable of parts-per-billion sensitivity. A high finesse optical cavity coupled to a high precision wavelength monitor enable the CRDS analyzer to have a spectral resolution 1000 times better than a Fourier Transform Infrared Spectrometer (FTIR), thus allowing CRDS to distinguish individual absorption features. We have utilized the high sensitivity of a commercial Cavity Ring Down Spectroscopy (CRDS) to monitor, in real-time, ethylene production at the parts-per-billion level in regular and controlled atmospheres of preclimacteric fruit. In addition, we have explored the effects of adding ozone to moderate ethylene levels in both laboratory and field tests. While it has been demonstrated that the use of ozone within storage facilities can reduce decay, with this research we have observed the mitigating effects of ozone on ethylene concentrations within the storage container.

## **SOUTHWEST SCIENCES - VCSEL-based trace gas monitoring with industrial applications**

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Single frequency, tunable and room temperature operating diode lasers have a wide array of gas sensing applications. Compared to readily available edge-emitting DFB devices, recently available VCSEL (Vertical Cavity Surface Emitting Laser) devices offer characteristics that are favorable for industrial monitoring applications. Simpler device fabrication and wafer-level device testing result in lower per laser cost. Low threshold and operating currents enable portable, battery-operated instruments. Wide wavelength tuning available by bias current tuning allows monitoring of several spectral lines which can offer wider dynamic range and sometimes multiple species detection. I will describe some of the active trace gas sensing applications at Southwest Sciences that utilize VCSEL lasers. Some of them has led to industrial applications. These include airborne trace moisture sensing and moisture contaminant detection in wafer processing, methane detection for environmental monitoring and natural gas leak detection, and oxygen detection for combustion monitoring in scramjet engine.

## **LOS GATOS - Recent advances in instrumentation based on cavity enhanced absorption spectroscopy**

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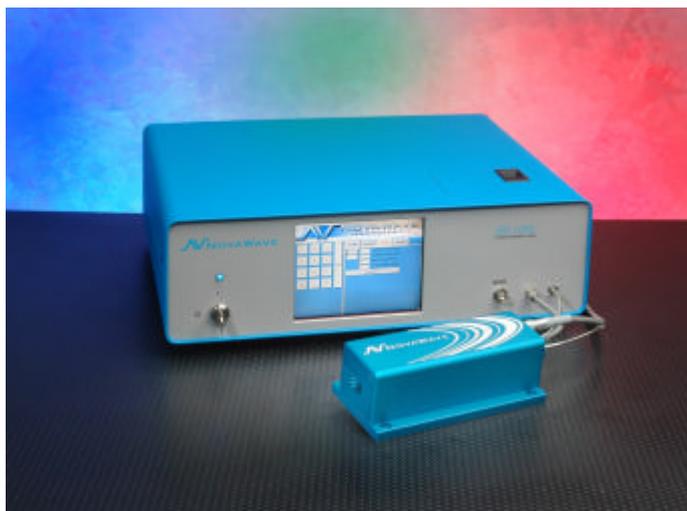
Novel instruments based on cavity enhanced absorption spectroscopy techniques have been developed and deployed for a wide range of applications. These commercial instruments operate autonomously and report measurements with high sensitivity, accuracy, and specificity in real time. We present an overview of measurements recorded by a variety of near-IR and mid-IR laser-based analyzers operating in the field and in the laboratory for applications including process control in chemical refineries, atmospheric trace gas monitoring, isotope hydrology, combustion diagnostics and fundamental spectroscopy.

## NOVAWAVE - Mid-infrared trace gas sensing with difference frequency generation lasers

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The advantages of monitoring chemical species via their associated fundamental rovibrational bands in the middle-infrared is well established, and numerous studies have demonstrated the requisite selectivity and sensitivity for monitoring greenhouse gases, industrial pollutants, and combustion precursors, intermediates, and products. In particular, the O-H, N-H, and C-H stretch region between 3-4 microns and the C-O and N-O stretch region between 4-4.6 microns are particularly important as they offer the ability to monitor key gases such as CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O, which are largely regarded as the most important greenhouse gases. Over the last two decades, Difference Frequency Generation (DFG)-based lasers have been developed at many laboratories, providing a direct, non-cryogenic solution to accessing these important spectral regions. Recently, NovaWave has leveraged these developments together with novel telecom-derived fiber and diode technologies to develop the world's first commercial DFG middle infrared laser system, providing a turnkey, truly single frequency tunable laser source that is suitable for many trace gas sensing applications.

The advantages of DFG technology include single frequency, room temperature operation, mode-hop free frequency tunability over a broad range, the ability to employ mature and reliable commercial-off-the-shelf (COTS) subcomponents, and nearly perfect transverse beam quality, which is particularly favorable for multipass absorption spectroscopy. NovaWave has recently developed several types of DFG laser systems and integrated these sources with single pass absorption cells, traditional Herriot-type multipass cells, and CRDS and ICOS cells to comprise different types of sensor systems. As the absorption intensities in the mid-IR are typically 10-10,000 times stronger than those in the near-infrared, absorption pathlengths ranging from tens of cm to several meters are often sufficient to achieve desired sensitivity levels, NovaWave is focusing on providing robust fieldable sensor systems for autonomous sensing applications based on sensor platforms that are as simple as possible. Results will be presented that demonstrate the generality and sensitivity of several of the above platforms, with emphasis on monitoring greenhouse gas species using simple and robust direct absorption approaches.



Iris-1000, the World's first commercially available, room temperature, DFG-based infrared laser system operating at 3.3  $\mu\text{m}$

## **NORSK - New developments in laser spectroscopy at Norsk Elektro Optikk A/S**

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Gas Analysers based on tuneable diode laser (TDL) absorption spectroscopy in the near infrared were introduced to the market more than 10 years ago and have now been widely accepted in the industry for applications where other techniques have failed to operate satisfactorily. The majority of the applications so far have been for emission control of pollutants such as HF, HCl and NH<sub>3</sub> where an in situ TDL measurement is superior to most other spectroscopic techniques both with respect to sensitivity, accuracy and reliability. The TDL technique has also become widely accepted in the chemical and petrochemical industry by providing in-process measurements of gases such as O<sub>2</sub> in hazardous and/or poisonous atmospheres. More recently the technique has been introduced into the mass production industry where reliable and fast measurements of critical parameters can improve both product quality and yield.

TDL absorption spectroscopy became feasible when reliable, tuneable laser diodes became available as a direct spin-off from the development of light sources for optical fibre communication. The wavelength range for these devices has been extended out to 2700 nm, allowing more gases such as CO and CO<sub>2</sub> to be measured in the low ppm/ppb range. The fundamental and thus strongest absorption bands for most gases are, however, in the mid infrared (4-12 μm). During the last 10 years several research groups both in the US and Europe has made great efforts to develop tuneable radiation sources in the mid infrared, and devices operating continuously (CW) at room temperature are now becoming available for spectroscopic applications.

I will start with a presentation of our most recent work in the NIR that will include a description of several new challenging applications as well a brief presentation of a new product for detection of H<sub>2</sub>S from oil and gas installations for personnel safety. Exploitation of new oil and gas fields has in some areas in the World been delayed or stopped due to very high H<sub>2</sub>S levels.

With the promising performance of Quantum Cascade lasers and other tuneable sources in the mid infrared high sensitive and robust instruments for industrial environments can soon be realised and I will report from our work in this area. I will also try to make some comments to the future of single line spectroscopy in the mid infrared in general.

## **TDL SENSORS - Transferring tunable diode-laser gas measurement technology from the laboratory to industrial environments**

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In recent years tunable diode laser (TDL) gas monitoring has gained wider acceptance as a proven, reliable technique for making sensitive and specific gas measurements. Gas-phase concentration measurements of species such as oxygen, carbon monoxide, ammonia, hydrogen chloride, hydrogen fluoride, carbon dioxide, and methane can be made using the TDL instrumentation. New methods have been developed to improve the basic TDL gas sensor performance in order to improve the limits of detection and the range of species that can be monitored.

The commercial challenge faced by manufacturers is to successfully transfer laboratory demonstrated TDL techniques to hostile industrial environments. High dust loads, varying alignment, and changing environmental temperatures are just some examples of the conditions that a TDL gas sensor must be able to operate under. In addition, there is now also the requirement for TDL gas sensors to have certification such as ATEX, TUV, and MCERTS in order to achieve sales into a growing number of applications.

Some of our experience in facing these challenges will be discussed.

## **LOCCIONI - Laser boiler test: an industrial application**

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We report on a tunable diode-laser system for the detection of CO<sub>2</sub> emissions in condensing boilers. A new diode-laser spectrometer has been specifically developed to provide a fast and reliable tool in boiler testing, where the carbon dioxide concentration in exhaust gases is the main parameter to set the correct percentage of air and methane.

Actual systems are NDIR based, they are slow and water effect dependent. Gas treatment is needed to remove water presence and a dry measure is carried out. Laser spectroscopy allows real time measurements, good sensibility and accuracy. To increase sensitivity and reduce noise influence, the injection current is modulated with a sinusoidal wave and the second harmonic component of the signal is used to measure the concentration of the absorbing gas.

The system is equipped with a humidity sensor to compensate the water effect. Water molecules affect the shape of the carbon dioxide absorption lines and displace carbon dioxide molecules (dilution effect). The first effect always causes an error on the detected concentration, while the second represents the gap between our system measure and a dry measure with NDIR system. A custom developed LABVIEW software compensates both effects and allows automatic control by a personal computer. Field tests were performed on a production line.

## **NEOPLAS CONTROL - On further developments of the Q-MACS technology for online process control and trace gas measurements in research and industry**

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Neoplas control GmbH is a centre of competence for gas and plasma diagnostics and environmental technology. It is a spin-off of INP Greifswald (Institute of Low Temperature Plasma Physics) and was founded in 2006. Neoplas control's mission is to provide pioneering work for operations in gases and plasmas. The Q-MACS technology represents an outstanding solution for on-line process control and measurement applications.

Until recently the on-line control of plasma processes was not feasible and traces gas analysis in the ppb range rather difficult. The idea to design Q-MACS is based on the recent development and commercial availability of a new laser class, the quantum cascade laser (QCL). The Q-MACSystem is a compact and user friendly quantum cascade laser measurement and control system developed to monitor plasma processes and to detect trace gases with high sensitivity. Q-MACS combines the advantages of absorption spectroscopy in the mid infrared spectral range with the unique properties of QCL. In combination with thermo-electric cooled infrared detectors Q-MACS is well suited for scientific and industrial applications, in particular for on-line process monitoring. Q-MACS needs nearly no maintenance and due to its modular design it can be individually adapted to customer requirements inside industrial processes and for research.

The Q-MACS Basic represents the basis component of the product line. Being used as a stand alone QCL source it can be utilized for spectroscopy research purposes. The Q-MACS Basic comes with a laser head, power supply, cable connection and trigger software (Q-MACSoft 2.0) to tune the mid infrared radiation source perfectly.

The Q-MACS Trace is an adaptable steady state or portable system developed for trace gas measurements for ecological and environmental researches. It is based on the Q-MACS Basic and allows a highly sensitive gas analysis up to concentration rates of ppb using optical long path cells.

The Q-MACS Process is an open path system or is directly coupled to the measuring path via an IR-fibre and can be deployed in industrial on-line processes without using a long path cell. Directly adapted to production systems it can ensure an effective control of production processes, which have to rely on the exact allowance of tiny concentrations of different molecular compounds in plasma or gas states up to the ppb range.

The Q-MACS components category includes several system elements which are available separately. Different key components present the basis on the one hand to access the area of Mid Infrared Absorption Spectroscopy or on the other hand to improve Q-MACS or other systems.

## **SIEMENS - Industrialization trends of tunable diode-laser spectroscopy**

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The use of tunable diode-laser spectrometers recently gained more and more acceptance in the industrial environment. Coming the long way from a laboratory environment, then stepping into well defined niche markets like NH<sub>3</sub>, HCl, or HF detection, today the technology enjoys such high confidence that more and more closed-loop process optimization and safety relevant applications are being served e.g. in chemical, petrochemical, and power industry. This trend required a high level of confidence in the technology, since for these applications possible consequences of a malfunction can be dramatically. Not only inherent benefits of the technology, such as speed and low cross interferences, but also enhanced features like extended self-monitoring and self-control strategies of the analyzer enabled this trend. Several thousands of installed measuring points and more than 10 years of industrial experience proving the prognosticated long lifetimes and high availability of the laser technology were also root causes for the increased confidence in the industrial environment which lifted the technology also into sensitive application areas. In the presentation we will name some particular examples. Since analyzer self monitoring data can be made available in comprehensive analyzer management systems, a logical consequence is also the development of advanced communication strategies and up-links to data control systems e.g. for means of asset management.

# **APPLIED SPECTROSCOPY**

## Laser based diagnostics from our cultural heritage to human health

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An overview of applied laser-based diagnostics as pursued at the Lund Laser Centre is given. The fields of application range from environmental monitoring including cultural heritage assessment, to combustion diagnostics and biomedical applications. General aspects of laser-based methods are non-intrusiveness, high spectral and spatial resolution, and data production in real-time. Different applications are frequently generically very similar irrespective of the particular context, which however, decides the spatial and temporal scales as well as the size of the optics employed. Thus, volcanic plume mapping by lidar and optical mammography are two manifestations of the same principle, as is fluorescence imaging of a human bronchus by an endoscope and the scanning of a cathedral using a fluorescence lidar system. Recent applications include remote laser-induced break-down spectroscopy (LIBS) and gas monitoring in scattering media (GASMAS). In particular, a powerful method for diagnostics of human sinus cavities was developed, where free oxygen and water molecules are monitored simultaneously.

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## Developing intrinsic spectroscopic standards for quantitative gas analysis

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For over thirty years, the National Institute of Standards and Technology (NIST) has provided a traceability structure to support a large variety of domestic and international gas concentration measurements. Currently, NIST-prepared primary gravimetric gas cylinder mixtures underpin NIST gas reference standards. It will be challenging for this approach to continue to meet the expanding requirements of the next-generation industrial gas concentration standards, especially for reactive gas species. Recent advances in spectroscopic intensity measurements provide the potential for the realization of gas concentration standards based on intrinsic molecular properties, the line and band intensities for molecular absorption features. Accurate molecular absorption data coupled with precise spectroscopic measurements can be used to deliver measurements at several levels of accuracy ranging from primary NIST measurements to field-based measurements.

Our current work is focusing on demonstrating the precision and accuracy of optical methods for gas analysis and generating improved molecular absorption data. We are using a variety of approaches ranging from ultra-high resolution frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) in the near-infrared spectral region, direct laser absorption spectroscopy in the mid-infrared region, as well as broadband measurements using Fourier transform infrared (FT-IR) absorption. An overview of the laser-based methods will be presented.

FS-CRDS uses a ring-down cavity which is actively length stabilized and the probe laser is frequency locked to successive  $TEM_{00}$  resonances of the ring-down cavity. A recent comparison of the frequency-stabilized ring-down method with other more conventional unstabilized cavity ring-down approaches demonstrated that FS-CRDS method provides the lowest measurement uncertainty.<sup>1</sup> The FS-CRDS approach is being used to measure water vapor using several transitions of the  $\nu_1 + \nu_3$  combination band around 1.392  $\mu\text{m}$  and methane using four closely spaced  $2\nu_3$  transitions at approximately 1.65  $\mu\text{m}$ . The water vapor FS-CRDS measurements were directly compared to a standards-grade hygrometer and the observed systematic differences between the thermodynamic and spectroscopic measurements were dominated by background effects and uncertainties in the spectroscopic line intensity. FS-CRDS measurements of NIST  $\text{CH}_4$ -in-air standard reference materials, demonstrate that the long-term precision of the FS-CRDS measurements are comparable to the uncertainties of the gravimetrically prepared standards. It is important to note that the quality of the results is highly dependent upon the line shape model used in the data analysis. Line shape models which account for collisional effects of the line profile significantly improve the result.<sup>2</sup> Work is currently underway to produce line intensity values linked to primary gravimetric standards and with uncertainties approaching 0.25 %.

For ozone, a reactive gas, absorbance measurements at 253.6 nm are used in the ozone standard reference photometer to determine the concentration of  $\text{O}_3$  delivered by the NIST standard.<sup>3</sup> By using high resolution direct absorption measurements in the mid-infrared region, specific ro-vibrational transitions of a given chemical species can be probed, allowing greater selectivity compared to probing unresolved transitions in the UV region. Room temperature quantum cascade lasers are being used to link the  $\text{O}_3$  concentrations measurements to gravimetrically prepared  $\text{NO}$  and  $\text{NO}_2$  standards through a gas phase titration reaction and provide accurate determinations of line intensities for these species traceable to national standards.

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## Widely tunable external cavity quantum cascade lasers for high resolution spectroscopy and chemical sensing

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The development of laser spectroscopic techniques strongly relies on increasing the availability of new tunable laser sources. Quantum cascade lasers (QCLs) have proved to be robust light spectroscopic sources for mid-infrared (mid-IR) spectroscopic applications.<sup>1</sup> QCLs have recently made significant advances as effective mid-infrared spectroscopic sources for trace gas detection. Continuous wave, room-temperature QCL devices have been demonstrated and are now available for applications that require compact, high power (>50 mW), liquid-nitrogen free, mid-infrared spectroscopic sources.<sup>2</sup> This feature makes them suitable for applications which require compact, sensitive, thermoelectrically cooled spectroscopic sources. The wavelength tunability of DFB-QCL relies on thermal tuning of the refractive index by temperature or an injection current variation, which limits the frequency coverage to  $\sim 10 \div 20 \text{ cm}^{-1}$ . Therefore DFB-QCLs are typically designed for operation at a single target frequency with a practical tuning range of few wavenumbers ( $\text{cm}^{-1}$ ) and are usually used in trace gas detection and quantification of small molecules with narrow, resolved ro-vibrational lines. Such applications can also be addressed by using an external cavity configuration QCLs (EC-QCLs) with mode-hop free tuning.<sup>3</sup> The EC-QCL sources have an important advantage over DFB-QCLs, which is broadband wavelength tunability. The gain characteristics of QCL can provide sufficient amplification to achieve laser action over a much broader spectral range. Several specific QCL designs have addressed the issue of further broadening of the QCL gain curve that include: 1) a bound-to-continuum QCL design first proposed by Faist<sup>4</sup> and further developed for EC-QCL applications by Maulini et al.<sup>5</sup> and 2) a heterogeneous QC structure first demonstrated by Gmachl et al.<sup>6</sup> A luminescence spectrum of  $350 \text{ cm}^{-1}$  and a pulsed EC-QCL tuning of  $265 \text{ cm}^{-1}$  were recently achieved by combining both concepts a heterogeneous quantum cascade active region structure based on two bound-to-continuum designs emitting at  $8.4$  and  $9.6 \mu\text{m}$ .<sup>7</sup>

This presentation will describe recent progress in the development of room temperature, continuous wave, widely tunable mid-infrared EC-QCL spectroscopic sources that employ broadband QC gain chips at  $5.3 \mu\text{m}$  [Ref. 5] and  $8.5 \mu\text{m}$  [Ref. 2] and a piezo-activated cavity mode tracking system for mode hop free wavelength tuning. This technology is particularly suitable for high resolution spectroscopic applications of broadband molecular absorbers and multi species trace-gas detection. A single mode tuning range of  $155 \text{ cm}^{-1}$  and  $135 \text{ cm}^{-1}$  was achieved for  $5.3 \mu\text{m}$  and  $8.5 \mu\text{m}$  EC-QCL respectively. Several examples of QCL applications that are currently being investigated by our group will be reported. These include high resolution spectral measurements of small molecules such as Nitric Oxide (NO) at reduced pressures and the detection of broadband absorbing species with unresolved rotational structure (such as acetone, Freon 125, and ethanol) using quartz enhanced photoacoustic spectroscopy (QEPAS).<sup>8</sup>

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# Stark-enhanced diode-laser spectroscopy of formaldehyde using a modified Herriott-type multipass cell

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Diode-laser absorption spectroscopy is an established technique among analytical methods for trace gas analysis in atmospheric studies. Absorbance sensitivities (optical density) in the lower  $10^{-6}$  to lower  $10^{-7}$  have been achieved by averaging of spectral data for up to a few minutes [1,2]. Achieving of the necessary spectrometer stability time generally requires recording of background spectra by flushing of the absorption cell with zero air. The subsequent subtraction of these background spectra from the sample spectra forms the major limitation to high-sensitivity diode-laser spectroscopy, because the background is time-dependent which in turn limits the validity of the background measurements.

In addition, the flushing of the absorption cell with zero air, as well as the resulting exchange time lead to a considerable reduction of the system's duty-cycle. This is often a limiting factor for applications requiring a high time resolution such as measurements on airborne platforms, where relatively small spatial and short temporal atmospheric inhomogeneities may not be detected when performing background measurements.

The implementation of a selective sample modulation, which in our case is based on the Stark effect in molecular spectra, is a proven approach to increase the stability of laser spectrometers [3]. Therefore, we conducted experiments to apply a selective Stark-modulation to  $\text{CH}_2\text{O}$  measurements in the mid-infrared as an addition to wavelength-modulation spectroscopy. The results of different sample-modulation schemes will be presented, pointing out the very high potential of this approach. By employing a Herriott-type multipass cell [4] specifically designed for this purpose, stability times exceeding 1000 s (Fig. 1) have routinely been achieved [5]. Such long stability times allow to skip background measurements entirely, and to increase the duty-cycle to almost 100%.

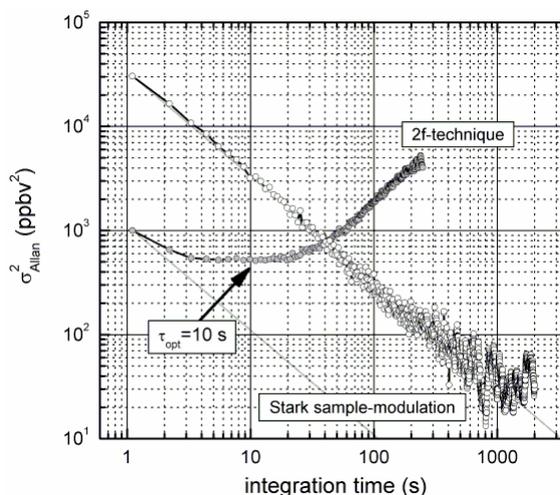


Fig. 1 Allan plot for the classical 2f-technique and the Stark sample-modulation technique.

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## Fiber-laser-based NICE-OHMS and trace gas detection

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Noise-immune cavity-enhanced optical heterodyne molecular spectroscopy is an absorption technique that combines frequency modulation (FM) for reduction of noise with cavity enhancement for increased interaction length with the sample to provide ultra high detection sensitivity [1]. The carrier of the FM triplet is locked to a mode of an external cavity by the Pound-Drever-Hall locking scheme, and the FM modulation frequency is matched to the free spectral range (FSR) of the cavity. All components of the FM triplet are thereby transmitted through the cavity with the same efficiency, wherefore the balance between the carrier and the sidebands is not disturbed by residual frequency noise of the laser with respect to the optical resonator, giving the technique a noise-immune property. In order to reduce the influence of low frequency noise and drifts, a wavelength modulation (WM) dither is optionally applied to the laser carrier by modulating the cavity piezo. The cavity transmitted light is detected with a fast photo detector and demodulated first at the FM modulation frequency and second at the WM dither frequency. Despite its high detection sensitivity, the technique has so far not been commonly used for trace gas detection, mostly due to its technical complexity.

This contribution describes the first steps taken by our group towards practical realization of a compact NICE-OHMS spectrometer for ultrasensitive trace gas detection [2]. The spectrometer is based on an erbium doped fiber laser, whose narrow linewidth (1 kHz/120 ms) simplifies the locking of the laser frequency to the cavity mode. The use of integrated-optics devices, such as a fiber-coupled electro-optic modulator, reduces further the complexity of the setup.

The spectrometer can be used in the Doppler-broadened as well as in the Doppler-free regime. The advantages and disadvantages of these modes of operation for trace gas detection, as well as the optimum conditions and dynamic range, are addressed. A general theoretical description of the NICE-OHMS signals that combines the standard FM nomenclature with the Fourier series formalism of WM is presented. The discussion is supported by experimental results obtained for detection of acetylene in ppt concentrations around 1531 nm using cavities with finesse of 1400 and 4600.

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# Diode laser based photoacoustic detection of carbon dioxide and oxygen using micromechanical cantilever pressure transducer

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Photoacoustic spectroscopy (PAS) is a sensitive method for trace gas analysis. Tunable diode laser based photoacoustic spectroscopy allows for compact, selective, and sensitive gas monitoring instruments [1-3]. In this work diode laser induced photoacoustic pressure waves were monitored with a novel sensitive micromechanical silicon cantilever pressure transducer. The sensor technique has been applied to the detection of carbon dioxide and oxygen.

The sensing technique uses a novel sensitive pressure transducer based on a micromechanical silicon cantilever. The deflections of the cantilever due to the incident pressure waves are monitored with a compact optical Michelson interferometer [4]. In this work a photoacoustic cell having 20 cm<sup>3</sup> sample gas volume and 6 cm absorption length was used. The cell was operated with static gas samples in acoustically non-resonant mode at 250 mbar total pressure. 20-100 Hz modulation frequencies were used to generate pressure pulses.

For the excitation of the photoacoustic signal of carbon dioxide a 30 mW distributed feedback (DFB) diode laser operating at 1572 nm was used. A noise equivalent detection limit of 4 parts per million (ppm) was obtained for carbon dioxide diluted in argon. By increasing the excitation power with a 1 Watt optical fiber amplifier sub-ppm detection limits for CO<sub>2</sub> were demonstrated [5]. The cantilever based PAS was also applied to the detection of oxygen. O<sub>2</sub> molecules have well-know weak absorption lines around 760 nm. 5000 ppm detection limit of O<sub>2</sub> was obtained with a relatively low-cost 0.5 mW 762 nm vertical cavity surface emitting laser (VCSEL). In addition, a 30 mW DFB laser operating at 763 nm yielded a noise equivalent detection limit of 20 ppm [6]. To date the best noise equivalent sensitivity obtained with the cantilever based technique is  $1.7 \times 10^{-10} \text{ cm}^{-1}\text{WHz}^{-1/2}$  [7].

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## Potentials and limits of mid-infrared laser spectroscopy for the detection of explosives

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An all fiber-coupled mid-IR spectrometer for the detection of explosives is presented. Explosives can be separated into two different classes: peroxide based improved explosives (e.g. TATP) mainly used by terrorists and nitro based explosives (e.g. TNT) which are frequently used by military. Both classes are detected in the gas phase under atmospheric pressure in ambient air.

A pulsed DFB-quantum cascade laser (QCL) operating at 8.05 $\mu\text{m}$  with a quasi cw-power of  $P=10\text{mW}$  is coupled into a silver halide fiber and guided to the sensor head. There the light is coupled out of the fiber, collimated and directed via an open optical path. For retro reflection a prism is used. Subsequently the radiation is again coupled into a silver halide fiber and guided to the detector. This setup provides the sensor with an absorption length of  $l=15\text{cm}$  while the sensor head can be moved and positioned near the sample. With this setup trace amounts of TATP have been detected in ambient air. Samples typically used for these measurements are metal foams that are loaded with TATP in the  $\mu\text{g}$  range. Sublimation leads to a detectable concentration in the gas phase in the vicinity of the sample.

Another task for enhancement of security is remote and stand-off detection of nitro based explosives [1]. A combination of photo-fragmentation and mid-infrared absorption spectroscopy for detection of the fragments is used for the stand-off detection of TNT [2]. For fragmentation of traces of explosives on different surfaces, a fiber amplified Er:Yb:glass microchip laser is used. Nanosecond pulses are generated at a wavelength of 1.5  $\mu\text{m}$ ,  $E=150\ \mu\text{J}$  and a repetition rate of 5 kHz. A pulsed DFB-QCL operating at 5.3 $\mu\text{m}$ , with  $P=2\text{mW}$  and a repetition rate of 250 kHz is used for the stand-off detection of the fragmentation product NO.

Different operating points of quantum cascade lasers are used for sensitive and selective absorption spectroscopy in the mid-infrared spectral region for both approaches. QCL-aided mid-infrared spectroscopy is discussed in terms of versatility for security applications.

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## **Applications of new sources of mid-infrared radiation in sensitive spectroscopy**

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High power sources of narrow bandwidth coherent mid-infrared radiation are highly desirable for a range of fundamental and applied science. Two such sources are (i) quantum cascade lasers, and (ii) those based upon difference frequency generation within waveguide structures. This contribution will detail our current research using both devices in a variety of areas from plasma chemistry to chemical reaction dynamics.

# Application of fused CWFM-lidar and TDLS approaches to open-path range-resolved gas leaks detection

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Inexpensive low-power instruments are needed to perform routine remote monitoring of atmospheric trace constituents in urban, industrial and agricultural environments to detect pollutants and chemical leakages. For open-path range-resolved gas leaks concentration measurements, the use of pulsed monostatic lidar techniques is already well established, but they exploit relatively expensive high-power pulsed laser sources. The availability of laser diodes with flexible modulation capabilities provides a sound basis for low-cost, compact, frequency-modulated range-resolving instruments. They use a frequency modulation of the CW-laser radiation and frequency-domain signal processing, including opto-electronic mixing and spectral analysis, to obtain the range-resolved measurements of optical parameters along the light path [1-2]. At the same time, the CW-FM range-resolving technique is in contrast to commonly used diode laser gas sensors based on the WM/FM spectroscopy approaches that provide real-time measurement of a wide variety of gaseous species with high sensitivity and fast time response, but they do not have ranging capabilities.

The concept of a spectroscopic CW-FM-TDL-lidar instrument for leaks monitoring combines features of conventional methods of modulation spectroscopy and existing technologies of remote sensing, together with modern techniques of optical signal transmission, reception/detection and processing.

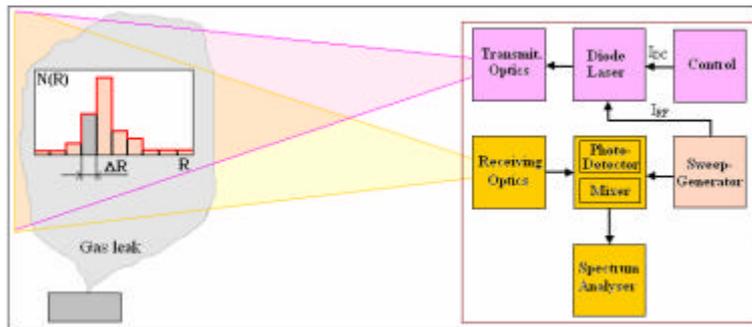


Fig. 1. Structure of range-resolving remote detector of gas leaks.

The schematics of the range resolving CW-FM TDLS remote gas leaks detector is shown in Fig. 1. The optical carrier of the laser transmitter is frequency modulated by a signal having a linear sweep of the subcarrier frequency (LFM). For laser diodes, the optical control is provided by bias current modulation, and the biasing current is selected to sweep the optical carrier frequency throughout the absorption line of the species under investigation.

To probe the absorption profile in an open path configuration, the spectroscopic CW-FM gas leaks remote detector uses aerosol backscattering. The interaction between the optical carrier and an absorption line of the target species then converts the frequency modulation of the optical carrier into an intensity modulation of the received echo-signal. For range information, the optical carrier is frequency-modulated by a subcarrier, that is, in turn, linearly frequency-modulated so the beat frequency spectrum corresponds to a range profile.

We discuss features of linear frequency modulation applied to optical remote monitoring and gas leaks detection tasks, including probing LFM-signal parameters and achievement of range resolution at CW-sounding. Mathematical treatments of range-resolving CW-FM-LD spectroscopic instrument with analysis of relations between laser and absorption line spectral parameters and development of the LF-modulated echo-signal is performed. Features of the LFM echo-signal inversion are studied for scanning of only one and both wings of the absorption line. Potential capabilities and applications of the approach for open-pass range-resolvable gas leaks detection are discussed.

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## Beyond the limitations of conventional mid-IR DFG lasers for trace gas sensing in industry and research

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Mid-IR lasers based on difference frequency generation (DFG) in periodically-poled LiNbO<sub>3</sub> (PPLN) are attractive for use in trace gas sensing since they can generate a continuous wave (CW) output at room temperature in the 2-5  $\mu\text{m}$  range where most environmental gases exhibit strong absorption lines originating from fundamental and low ro-vibrational absorption bands [1]. However, there are still various challenging issues as regards the development of mid-IR DFG lasers that relate to such technical aspects as conversion efficiency, output power and tunability as well as in such practical features as compactness, cost, reproducibility and reliability.

These limitations of conventional mid-IR DFG lasers can be addressed by using ridge PPLN waveguides fabricated by direct bonding technology [2]. The technology utilizes the bulk LN characteristics, and so has several advantages over the conventional annealed proton exchange technique, such as a high optical damage threshold, precise device design, device fabrication reproducibility. The PPLN waveguides exhibit a conversion efficiency that is about 100-times larger than that of PPLN bulk crystals in the mid-IR regions. Using a direct-bonded PPLN waveguide made of damage resistant Zn:LN, we obtained a mid-IR output of a few tens of mW in the 3- $\mu\text{m}$  range via excitation with two telecom laser diodes (LDs) combined with fiber amplifiers. The high-power output capability of the PPLN waveguides makes them suitable for use in, for instance, open path remote sensing and cavity-cell-based gas sensing for industrial and medical applications.

The wavelength range accessible by current tuning with mid-IR DFG lasers is limited by the bandwidth of the quasi-phase-matching (QPM) curve of the PPLN waveguide. For instance, the 3-dB bandwidth of a 50-mm long waveguide is about 8 nm for a 3- $\mu\text{m}$  output. The current tunable wavelengths can be extended by employing various domain engineering technologies for the PPLN waveguides. The first example utilizes apodization in the PP structure to yield an arbitrary degree of band broadening and a flat-phase response [3]. We fabricated a 3.4- $\mu\text{m}$ -band PPLN waveguide with seven times the QPM bandwidth (60 nm at 3-dB bandwidth) and one-ninth the conversion efficiency (2 %/W) of a uniform PP waveguide with the same dimension. The second example is the realization of unequally spaced multiple QPM peaks by phase modulation. We fabricated a direct-bonded waveguide with three QPM peaks, each of which had a conversion efficiency of 15 %/W. These domain engineered PPLN waveguides are advantageous for applications to multiple gas sensing and gas sensing using multiple absorption lines.

Compact and robust mid-IR DFG lasers for practical use can be realized by constructing a laser head containing a direct-bonded PPLN crystal that is fiber-coupled with pump and signal telecom LDs. We fabricated a fiber-coupled PPLN waveguide module where the PPLN waveguide was packaged together with a Peltier element and a thermistor for temperature control [4]. The use of telecom LDs is also effective to reduce the cost of the mid-IR DFG lasers. The mid-IR DFG lasers we constructed could generate a stable mW-level output without the use of fiber amplifiers and were compatible with tunable diode laser absorption spectroscopy (TDALS) by modulating the signal LD.

Mid-IR DFG lasers based on direct-bonded PPLN waveguides can address various challenging issues that have been related to conventional mid-IR DFG lasers, and are thus promising for use in trace gas sensing in industry and research.

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## **TraceScout - an advanced sensor system for in-line monitoring of special gases in semiconductor industry**

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Gas quality monitoring is currently done only for bulk gases with high throughput and high process relevance. Especially in semiconductor industry corrosive and special gases become more and more essential relevance to run complex CVD processes. With the lack of inexpensive monitoring systems these crucial process gas species cause sometimes failure on processed wafer.

The developed TraceScout-H<sub>2</sub>O sensor is based on the sensitive and robust TDLAS techniques and aims to application in gas cylinder cabinets for corrosive gases as well as for troubleshooting or final inspection after gas installation. Due to high cost and small throughput of special gases, the sensor is designed to operate in-line in a bypass or mainline setup within a wide range of flow and pressure compared to current trace gas analyzers.

The poster presents initial quality control of a series of HCl gas cylinder in industrial application. Moisture as the key impurity varies there in a significant level and is considered to be one of the highly relevant process species. After passing the evaluation, the HCl cylinders will be connected to process gas line.

Further shown are field evaluation tests of the TraceScout-multigas sensor for simultaneously monitoring of three trace gas impurities (H<sub>2</sub>O, O<sub>2</sub>, CH<sub>4</sub>). In addition to the laser diode spectrometers, tested with the sensor there are further NIR-LDS modules available for the measurement of: CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, H<sub>2</sub>S, NO, N<sub>2</sub>O, NH<sub>3</sub>, HCl, HF and HCN tested with other application. Due to its modular design, they can easily be assembled.

## Recent advances and applications of semiconductor laser based gas sensor technology

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This talk will focus on recent advances in the development of sensors based on infrared semiconductor lasers for the detection, quantification and monitoring of trace gas species at ppmv to pptv levels and their application to environmental monitoring, medical diagnostics and homeland security. Ultrasensitive chemical analysis of gases based on molecular absorption laser spectroscopy is a well-established technology [1]. The development of compact trace gas sensors based on the use of both diode lasers as well as quantum cascade (QC) [2] and interband cascade (IC) [3] lasers will be emphasized. QC and IC lasers permit the targeting strong fundamental rotational-vibrational transitions in the mid-infrared. Vibrational fundamentals are one to two orders of magnitude more intense than the overtone transitions of the near infrared.

The architecture and performance of several sensitive, selective and real-time gas sensors based on near and mid-infrared semiconductor lasers will be described. To date we have detected 13 gases ( $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{NO}$ ,  $\text{H}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{NH}_3$ ,  $\text{C}_2\text{H}_4$ ,  $\text{OCS}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{H}_2\text{CO}$  and  $\text{C}_2\text{H}_5\text{OH}$ ) [4-8]. In several cases, isotopic signatures of carbon and oxygen have also been observed. High sensitivity requires sensitivity enhancement schemes such as multipass gas absorption cells, cavity absorption enhancement, or photoacoustic absorption spectroscopy. These methods can achieve minimum detectable absorbances in the range from  $10^{-4}$  to  $10^{-5}$  for field deployable gas sensors. Examples of real world applications in atmospheric chemistry, medical diagnostics and the monitoring of air quality in spacecraft habitats will be reported. Recently the development of miniaturized, battery powered trace gas sensor nodes and the implementation of sensor networking applications has been initiated [9-10]

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# Ultra-broadband difference-frequency generation in waveguide PPLN crystal in the mid-infrared

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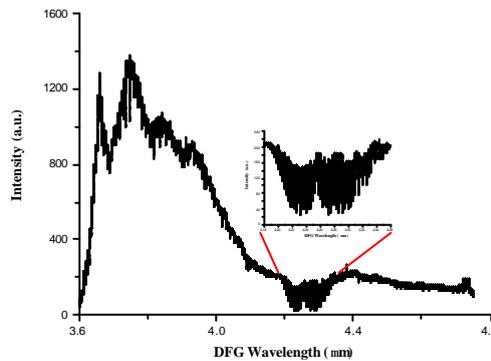
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We report on the development of a continuous-wave laser source based on difference-frequency generation (DFG) in waveguide periodic poled LiNbO<sub>3</sub> crystal (WG-PPLN) with an ultra broad phase-matched bandwidth of about 1200 nm. In the present work, a diode-pumped monolithic Nd:YAG laser was used as “signal” source, which emitted a maximum power of 1W at 1.064  $\mu\text{m}$ . A Ti:Sapphire laser tunable from 770 to 930 nm was used as “pump” source with an output power up to 1.2 W. The pump and signal beams were collinearly overlapped with a beam splitter and focused by a lens of  $f=200$  mm onto a 35-mm-long WG-PPLN crystal. The crystal, with a waveguide cross-section of 4 mm wide  $\times$  0.5 mm thick, is temperature controlled to within 0.1-K. The generated idler beam was collimated by a CaF<sub>2</sub> lens with 50 mm focus-length and directed to spectroscopic application. A liquid-nitrogen-cooled InSb detector was used for detection. The unwanted pump and signal beams were blocked by a Ge filter. With a phase-matching grating period of 22.7  $\mu\text{m}$  and the temperature of the crystal fixed at 24.5°C, a broad wavelength tuning of the DFG laser source from 3.6 to 4.8  $\mu\text{m}$  has been achieved by a single scan of the pump laser wavelength, as shown in Figure 1, the phase-matched tunable bandwidth was about 1.2  $\mu\text{m}$ . To the best of our knowledge, this is the largest phase-matchable DFG tuning bandwidth by means of a single grating period at a fixed temperature. Maximum mid-infrared DFG output power of 47  $\mu\text{W}$  was obtained by mixing a 16 mW signal and a 30 mW pump, which corresponds to a power conversion efficiency of 10%/W.



## Use of optical feedback CEAS for atmospheric detection

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Optical Feedback Cavity Enhanced Absorption Spectroscopy (OF-CEAS)<sup>1,2</sup> is an exciting new technique which exploits the line narrowing effect of self-feedback into a diode laser, to lock directly to the modes of an external CEAS cavity. This allows a substantial intensity of light to build up into each mode as the laser wavelength is swept across the range of interest, giving a considerable signal-to-noise enhancement for an absorption spectroscopy experiment. We seek to apply this technique to atmospheric detection, taking advantage of the fact that the optical locking can bring superior sensitivity compared to traditional CEAS techniques, whilst this setup is easier to realise experimentally than electronically-locked systems such as NICE-OHMS.

A V-shaped optical cavity is employed, configured to ensure that only the cavity-resonant light is reflected back along the original light path and into the laser. This optical feedback achieves a substantial narrowing in the spectral width of the laser output and allows the laser to lock to the resonant frequencies of the external cavity. We then measure the maxima of successive TEM<sub>00</sub> modes as the laser is swept across them with a simple current ramp. The frequency locking allows us to observe these modes with substantial signal enhancement, and without phase noise, giving an improved-sensitivity CEAS spectrum.

An electronic error-signal loop, designed and optimised in this laboratory, feeds a signal derived from the symmetry of the external cavity modes to a piezoelectric transducer attached to a pre-cavity mirror. Small adjustments are made to the laser-cavity distance in this way, so as to maintain all TEM<sub>00</sub> modes in phase across the laser scan. Further calibration is avoided by moving the laser briefly below-threshold during a scan and measuring the ring-down time. An additional advantage of this technique is that the spacing of the cavity modes provides a ready calibration of the frequency scale for the resulting spectrum.

We will present our work applying the OF-CEAS technique to trace detection of atmospheric species of interest, using a fully enclosed stainless steel cell designed and produced in this laboratory. We will demonstrate our measurements on aerial water and carbon dioxide absorptions around 1596 nm, and indicate our future aims for sensitive OF-CEAS detection.

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## Pressure broadening and shift measurements of ammonia lines with a selection of broadening gases

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Trace gases within the atmosphere can have a disproportionate influence and can therefore lead to modifications in many chemical processes. Ammonia within the atmosphere originates from a variety of sources including agricultural practices and vehicular and industrial emissions and chemically it can help neutralise airborne acids and catalyse removal of sulphur oxides. As such, there is a need for sensitive ammonia monitoring and laser absorption spectroscopy in the near infrared has been suggested as an effective monitoring solution [1]. Accurate knowledge of line parameters including intensities, pressure broadening and pressure shift coefficients are required to make quantitative measurements of ammonia in varying atmospheric and industrial conditions.

We present measurements of pressure broadening and shift coefficients for four ammonia transitions near 1500 nm that have the potential for use in environmental monitoring. Data are provided at room temperature for six broadening gases, nitrogen, oxygen, helium, argon, xenon and neon. Our data were obtained using a standard setup for cavity enhanced absorption spectroscopy (CEAS). A tuneable external cavity diode laser, operating in the 1520 nm region, was used to probe the gas in a high finesse cavity of length 70 cm. The ammonia transitions were recorded separately for a number of different pressures of the perturbing gases between 0 and 500 Torr, and their line shape and position were analysed. A spectrum analyser provided an accurate frequency scale for the data, and a reference cell of ammonia maintained at a constant pressure provided an accurate reference point for the pressure shift measurements.

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## **Cavity enhanced absorption methods for trace gas detection**

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High sensitivity and a relatively low-cost set-up make cavity based techniques, coupled with cw-diode laser sources, functional in a wide range of analytical fields. The gain in sensitivity with respect to a traditional single-pass absorption technique is brought about by the presence of two high reflectivity mirrors constituting the optical resonator.

According to these features, we show the potential of cavity enhanced absorption spectroscopy (CEAS) and cavity ring-down spectroscopy (CRDS) as powerful methods for trace gas detection with medical applications, focusing attention on quantitative measurements of volatile compounds contained in human breath and absorbing in the visible and infra-red regions, such as oxygen, carbon dioxide, and ammonia.

## Method for improving the sensitivity in a fiber coupled diode-laser spectrometer by selective predistortion

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The sensitivity obtained in Tunable Diode Laser Absorption Spectroscopy (TDLAS) is often limited by various background signals whose levels often are several orders of magnitude above that of the (theoretical) shot noise. These background signals originate from laser excess noise, nonlinearities in the laser IP curve and etalon effects. Various approaches have been developed for reducing these effects and detection limits close to the theoretical limit set by the shot noise have been obtained by several groups. The most common approach today is Wavelength Modulation Spectroscopy (WMS) in which the diode laser is modulated at a frequency  $f_0$  whereas the detection is made on one of the higher harmonics, i.e. at  $Nf_0$ . This shifts the detection signals into a higher frequency range with low laser excess noise enabling detection of relative absorptions in the order of  $10^{-5}$ . However, fiber coupled systems are often limited by etalon effects from the laser to fiber coupling, reflexes in connectors, polarization dependent losses in couplers and birefringent effects introduced by the single mode fiber, which produce background signals at  $Nf_0$  by optical wavelength selective fading that drift and through which noise is introduced, all limiting the performance of the technique.

We describe here a method for suppressing the background signals in a fiber coupled WMS/TDLAS system by measuring the baseline of the laser/fiber assembly in a separate monitor channel and actively compensate the transmitted WMS signal at the detection frequency  $Nf_0$  by selective predistortion of the modulation injection current at the  $Nf_0$  harmonic [1]. This method suppresses common mode background signals from the entire assembly including diode laser, optical fiber, fiber coupler and any other component included into the loop. It also reduces unwanted residual absorption signals from an analyte such as water trapped in the laser encapsulation. In many process applications rapidly changing transmission conditions will modulate the transmitted laser beam and if it contains signal components at  $Nf_0$  this will create background signals that cannot be removed by any detection scheme at the receiver side. Therefore it is clear that the main advantage realized by this predistortion scheme is that unwanted signal components at the detected harmonic are removed before the laser beam enters the measurement channel. Several examples will be given of using this method in the gas analyzer LDS6 from Siemens Laser Analytics.

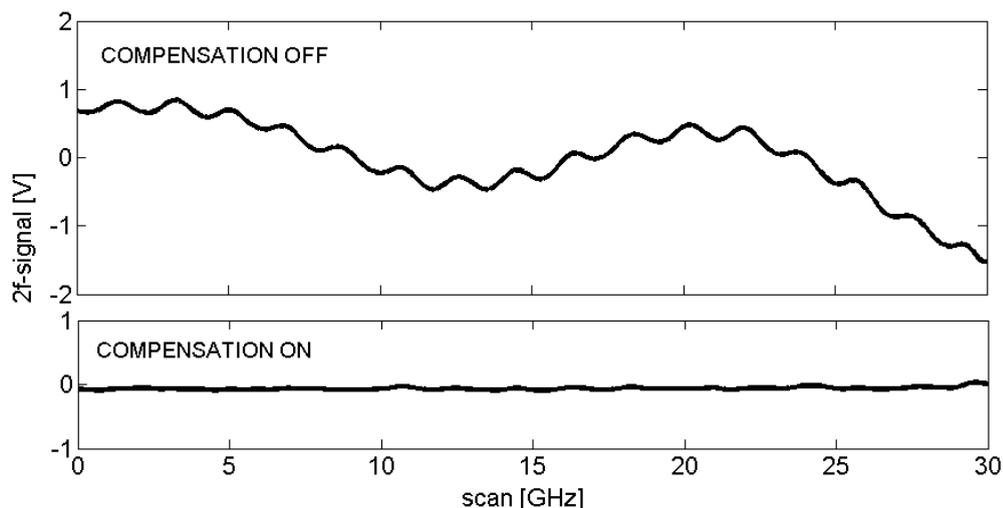


Figure 1. Second harmonic background signal without and with active predistortion compensation.

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## Potential of NICE-OHMS for ultra-sensitive atmospheric spectroscopy

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Noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (or NICE-OHMS) is an ultra-sensitive absorption spectroscopy technique. It combines the widely known methods of cavity-enhanced spectroscopy and frequency modulation spectroscopy to obtain both a large signal enhancement and a low noise signal. NICE-OHMS was initially developed for the study of very narrow saturated absorptions of interest as frequency standards, and an impressive sensitivity of  $1 \times 10^{-14} \text{ cm}^{-1}$  (with 1 s averaging) was reported for detection of these transitions [1]. The technique has since been extended for the detection of broadened absorptions, such as those found at atmospheric pressures, and detection of both Doppler and pressure broadened transitions have been reported with sensitivities of  $6.9 \times 10^{-11} \text{ cm}^{-1} \text{ Hz}^{-1/2}$  and  $8 \times 10^{-10} \text{ cm}^{-1}$  [2,3].

With such a high sensitivity NICE-OHMS has considerable potential for use in the detection of very small absorptions, such as those found for trace species in the atmosphere. However, its experimental complexity has meant few studies in the pressure broadened regime have been undertaken. In this talk, we will provide an overview of the technique and present our work on a NICE-OHMS apparatus for the detection of HO<sub>2</sub> near 1500 nm. We discuss the advantages and limitations of NICE-OHMS in the pressure broadened regime and investigate its potential for use in atmospheric sensing.

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## **Phase-shift off-axis cavity-enhanced absorption spectrometer for nitrogen dioxide**

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Phase sensitive, off-axis cavity-enhanced absorption spectroscopy techniques with a rectangular pulse current modulated violet diode laser (~404 nm) were applied to measurement of nitrogen dioxide (NO<sub>2</sub>) in diluted standard mixture and laboratory air. An optical cell of an NO<sub>2</sub> detector was bounded by two plano-concave mirrors with a diameter of 7.75 mm and reflectivity of 0.999, separated by a distance of 43 cm. The phase shift measurements due to Rayleigh scattering extinction were used for calibration of the detector. NO<sub>2</sub> sensitivities were extracted from synchronous measurements of either the cavity output light intensity or the phase shift induced by the cavity. NO<sub>2</sub> noise equivalent detection limit (S/N=1) of 1 – 2 ppbv was demonstrated for the intensity measurements with a lock-in amplifier time constant of 1 s. From the Allan plot of the intensity measurements the NO<sub>2</sub> minimum concentration was estimated to be 0.24 ppbv in 80 s at atmospheric pressure.

Vasili L. Kasyutich, Philip A. Martin, Robert J. Holdsworth, “Phase-shift off-axis cavity-enhanced absorption spectrometer for nitrogen dioxide”, *Meas.Sci. Technol.*17, 923-931 (2006)

## New, automated, software-based selection of optimized absorption lines for TDLAS-based concentration measurements

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Tunable Diode Laser Absorption Spectroscopy (TDLAS) has become an important analytical technique in industry and basic science for highly sensitive and specific gas concentration measurements as it is reliable, fast and accurate. Using direct absorption spectroscopy TDLAS<sup>1</sup> can provide absolute concentrations without the need for a reference gas based sensor calibration. The sole requirements are accurate spectroscopic parameters of the absorber, a precise characterization of the critical TDLAS spectrometer components and a good knowledge of the main physical-chemical parameters, namely pressure, temperature and absorption path length<sup>2</sup>. This property makes TDLAS quite often the method of choice for precise in situ monitoring of gas concentrations.

However, the performance of TDLAS instruments depends severely on the appropriate choice of an absorption line. But this selection strongly depends on the specific application and subtle details on the choice of components for the instrument<sup>3</sup>. The large number of possible absorption lines which may - especially for gas matrices containing species like H<sub>2</sub>O or CO<sub>2</sub> - exceed tens of thousands, the different effects of temperature and pressure variations on the spectroscopy, spatially non-uniform absorber and temperature distribution, interference by other absorbing species, and finally technical parameters like detector or laser performance, makes a line selection often a crucial and essential but very time consuming task, which is currently to a large extent governed by the subjective decision of the instrument developer. Especially for trace species detection<sup>4</sup> the sheer number of lines to be considered in combination with the variations in the experimental parameters prohibits a systematic "manual" study by the instrument designer, so that the line selection is frequently based on coarse selection according to the highest line strengths and estimates about the nearest interfering species. Line selection thus remains somewhat arbitrary and misses out on the opportunity to optimize the total spectrometer performance.

In order to avoid these deficiencies and to be able to select an optimal subset of absorption lines with the provision of optimizing the overall spectrometer performance (and not only the peak absorption) we developed a new spectral simulation and line selection software package.

This software uses spectral data bases like HITRAN and is capable of simulating wide range absorption spectra with arbitrary species combinations (if necessary isotopically resolved) taking into account respective gas concentrations, the required line shape models, the laser line width, as well as pressure, temperature and absorption path length. In addition a special batch mode the software is capable of computing a library of spectra depending on spatial and/or temporal variations in the species concentrations, pressure or temperature. This library may then be used to compute the temporal evolution of the spectra or the total spectrum through spatially inhomogeneous matrixes and its dependence on different absorption paths.

The line selection module is built on this spectral simulation tool. Depending on the specific spectrometer application which defines a desired sensitivity, expected experimental boundary conditions, parameter windows for pressure resp. temperature fluctuations and the interesting spectral range the tool automatically selects the optimum lines on a quantitative basis of well defined selection parameters e.g. absorption strength, the temperature/pressure dependence of the absorption signal and the spectral isolation of an absorption line addition. Even further than that it is possible to account in the line selection for special laser and detector parameters (i.e. detector noise D\* and its wavelength dependence). These may significantly influence the overall spectrometer performance, so that the lines may be selected according to the expected signal to noise ratio on a given spectrometer configuration (Laser, detector, absorption line).

In the paper we will discuss the software for the case of a model line selection for a set of optimized absorption lines for concentration measurements around evaporating water droplets.

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## Compact, high-sensitivity water vapor absorption spectrometer using new 2.6 $\mu\text{m}$ room-temperature DFB diode-lasers

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The precise *in-situ* determination of  $\text{H}_2\text{O}$  concentrations is of great importance not only for basic research, i.e. to understand the biosphere-atmosphere coupling and its influence on global warming, but also for industrial applications like drying processes or semiconductor manufacturing. However, the strong water vapor adsorption on nearly all surfaces presents a severe problem for extractive  $\text{H}_2\text{O}$  measurement techniques and frequently generates significant systematic errors. Tunable Diode Laser Absorption Spectroscopy (TDLAS) is a powerful technique capable of sampling-free *in situ* measurements. Especially *direct* TDLAS is promising as it permits absolute concentration measurements without the need for frequent sensor calibration, which is quite difficult for gases like water, that are essentially impossible to store in stable calibration gas mixtures. Self-calibrating  $\text{H}_2\text{O}$ -TDL spectrometers using 1.4  $\mu\text{m}$  diode lasers have been successfully demonstrated even for complex tasks like the dynamic *in situ* determination of the water vapor supersaturation *within* ice clouds during their formation<sup>1</sup>. However, the relatively weak NIR line strengths either limit the sensitivity or require absorption paths in the multi-10 m range to achieve sub-ppm detectivities.

The emergence of room temperature cw-diode lasers at a wavelength of 2.7  $\mu\text{m}$  promises significant sensitivity improvements for  $\text{H}_2\text{O}$  absorption spectrometers owing to the approximately 20 times larger absorption strengths compared to 1.4  $\mu\text{m}$  lines. Using 2.7  $\mu\text{m}$  lasers the minimum measurable  $\text{H}_2\text{O}$  concentration at STP should approach sub-ppm levels even on a 10 cm path length, which is quite interesting i.e. for spatially resolved measurements of the water transpiration from plants even on the single leaf scale (see paper by *Hunsmann et al* this conference).

However, as the worse overall 2.7  $\mu\text{m}$  laser/detector performance and specific properties of the 2.7  $\mu\text{m}$  water lines may consume the 20-fold gain in line strength, we decided to investigate the overall capabilities of a 2.7  $\mu\text{m}$   $\text{H}_2\text{O}$  spectrometer. Special care was taken to select an optimized water line specifically for the application of spatially resolved  $\text{H}_2\text{O}$  measurements above a single plant leaf. This selection was done using a new, advanced spectral simulation and line selection software. Furthermore we realized first high resolution open-path  $\text{H}_2\text{O}$  measurements using the new 2.7  $\mu\text{m}$  DFB diode laser. This laser, which emits at 27 °C about 2 mW of single mode radiation ( $\lambda = 2763$  nm), was precisely characterized for its static (current and temperature) and especially for the nonlinear dynamic tuning properties. With a linear current modulation we found the dynamic tuning coefficient to vary by as much as 200% over the total course of the laser scan. At a modulation frequency of 139.8 Hz we achieved with 56 mA current modulation a scanning depth of about  $1\text{cm}^{-1}$  which is sufficient to cover two atmospherically broadened  $\text{H}_2\text{O}$  absorption lines. Using a static setup with a diverging laser beam and 10 cm absorption path we determined (by coadding 20 laser scans captured within 3 seconds) the absolute humidity to be 8012 ppm (=26 % rel. Hum.). A S/N ratio of 600 ( $1\sigma$ ) was achieved, which corresponds to a detection limit of 14 ppm (=0.4% rH). This detection limit was governed by strong fringing of the setup and by an absorption line not listed in the HITRAN04 database. Assuming that we approach the optical resolution of  $2 \cdot 10^{-5}$  OD<sub>e</sub> from our 1.4  $\mu\text{m}$  TDLAS at least within a factor of five we expect with the 2.6 $\mu\text{m}$  system at 10 cm absorption path an ultimate  $\text{H}_2\text{O}$  detectivity of 1 ppm. Less demanding tasks permitting absorption length in the order of 1 m should therefore yield detectivities in the order of 100 ppbV.

Finally, in preparation for spatially resolved  $\text{H}_2\text{O}$  measurements above a single plant leaf under atmospheric conditions we developed a 1D linear traversing TDLAS and scanned the inhomogeneous water distribution above different artificial  $\text{H}_2\text{O}$  sources at a horizontal resolution of 0.5 – 1 mm, which may be seen as a first step towards tomographic 2D  $\text{H}_2\text{O}$  measurements. The evaluated data, achieved accuracy and an outlook to future applications of the new system will be presented in the talk.

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# Application of 940 nm high power DFB lasers in high resolution spectroscopy using a robust and compact sensor unit

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The application of *in-situ* spectroscopic methods for concentration measurements of atmospheric constituents, e.g. water vapour, and pollutants requires the exact knowledge of line positions, strength, broadening coefficients. Moreover, precise data for broadening are prerequisite for the understanding of intermolecular collision processes<sup>1</sup>. The near infrared spectral range is interesting due to the relatively high transparency of the atmosphere, e.g. for DIAL measurements in the range around 940 nm ( $2\nu_1+\nu_3$  and  $3\nu_1$ -bands)<sup>2</sup>. The determination of line parameters in overtone and combination bands is interesting to investigate the vibrational dependence for the studied molecule.

Tuneable diode lasers operating at room temperature are available in this spectral range. For the application in DIAL systems and also for the measurements of line parameters, the emission line-width of the devices must be at least one order of magnitude smaller compared to the Doppler width of H<sub>2</sub>O lines of 0.03 cm<sup>-1</sup> at 940 nm. This can be achieved using devices with an external grating (external cavity laser) or with diode lasers with an internal grating, e.g. distributed feedback (DFB) lasers.

In this paper, results obtained with high-power DFB lasers will be presented. These lasers reach a maximal output power larger than 500 mW<sup>3</sup> and allow at a fixed temperature of 20 °C a continuous current tuning over 4.7 nm with a tuning rate of  $8 \times 10^{-2}$  cm<sup>-1</sup>/mA. The temperature-tuning rate was 0.8 cm<sup>-1</sup>/K. With measurements at 20 °C and 50 °C a full tuning range of 7.2 nm could be obtained. The side mode suppression ratio was better than 40 dB. The emission line-width of the device measured with a homodyne fibre interferometer of Mach-Zehnder type was determined to be smaller than 2 MHz, i.e.  $0.7 \times 10^{-4}$  cm<sup>-1</sup>. This value would allow even Sub-Doppler measurements.

To demonstrate the potential of the devices, individual H<sub>2</sub>O rotational-vibrational absorption lines at atmospheric pressure in natural abundance were measured. To obtain the necessary path length an integrating sphere instead of sophisticated multi-reflection cells was applied. The laser is placed without any optics in front of the entrance hole of the sphere, in another output port a photodiode is mounted. The effective path length within a 4" cell was estimated to be about 6.7 m<sup>4</sup>.

With this arrangement 15 absorption lines from the  $2\nu_1+\nu_3$  band and 6 lines from the  $3\nu_1$ -band in the spectral range from 10585.4 cm<sup>-1</sup> to 10658.4 cm<sup>-1</sup> (938.2 nm – 944.7 nm) were measured under atmospheric pressure. From the measurements, pressure broadening coefficients in the range  $0.12 \text{ cm}^{-1}/\text{atm} \leq \gamma \leq 0.23 \text{ cm}^{-1}/\text{atm}$  were determined with an experimental uncertainty below 5% for lines with a strength larger than  $10^{-22} \text{ cm}^{-1}/(\text{molecule cm}^{-2})$ . The comparison with the HITRAN data<sup>5</sup> show for the  $3\nu_1$ -band a good agreement and for the  $2\nu_1+\nu_3$ -band about 5% larger broadening coefficients.

These results illustrate the capabilities of the 940 nm DFB lasers in this non-sophisticated set-up to determine line-broadening coefficients in good agreement with the literature. Moreover, this quantitative results illustrate also the applicability of this system for the detection of H<sub>2</sub>O.

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## Laser micro-profilometry for applications in the cultural heritage field

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A quantitative morphological analysis of an artwork represents an important element for historical and artistic evaluations, diagnostic studies and conservation projects.

Digital models, carried out from 3D surface surveys, find their application for the analysis of the artwork condition, for planning and supporting restoration interventions, for assembling 3D catalogues and archives, for monitoring the various phases of the repair process, for virtual reality applications and for making no-contact molds. Moreover, the difference between high-resolution 3D surveys taken at different time makes it possible to monitor the object shape variation.

Optical techniques are widely diffused and extremely well received in the field of conservation because of their effectiveness and safety. The characteristics of being non-invasive make them particularly suitable for measuring frail and precious objects. Many optical devices for three-dimensional survey are derived from industrial metrology, but the peculiarity of each artwork does not allow for a straightforward application. Difficulties in artwork diagnostics are mainly due to the irregularity and the polychromy of surfaces as well as to the high-accuracy required to catch even the smallest details of an artwork.

In this work applications of a high-resolution laser micro-profilometer for surface survey are presented. Our laser micro-profilometer is composed of a commercial laser distance-meter, based on the conoscopic holography principle, mounted on a scanning system. The instrument has high resolution (height res.  $\sim 1 \mu\text{m}$ , transversal res.  $\sim 20 \mu\text{m}$ ) and accuracy (better than  $6 \mu\text{m}$ ), a measurement range of  $\pm 4 \text{ mm}$  with a standoff distance of about  $40 \text{ mm}$ . The maximum scanning area is  $280 \times 280 \text{ mm}^2$  and the acquisition rate ranges from 100 to 400 Hz depending on the set spatial sampling frequency.

The micro-profilometer is insensitive to color contrast, it enables measurements on surfaces with almost any reflectivity and it allows the survey of very small details working with an incident angle very close to grazing incidence. This makes it particularly well suited for cultural heritage applications, where objects are characterized by a huge variety of materials and polychromy surfaces.

We have used the micro-profilometer on a variety of artworks (paintings, statues, xylographic engravings, architectural parts, archaeological objects, etc.) and materials (wood, canvas, stone, paint, gold, bronze and other metal, gypsum, plaster, fresco, etc.), and a few examples of applications will be presented.

Concerning the measurement of a painting surface, the laser micro-profilometry allows a quantitative evaluation of flakings, wrinkles and engravings in the paint layer, marks in the preparatory layer and deformations in the support. This is not possible with the commonly used techniques like the raking light photography.

Another application of laser micro-profilometry concerns the evaluation of the effects of surface cleaning that is one of the most important and sometimes controversial stages of the conservation process. The cleaning of artworks generally results in substantial physical changes of the object surface, raising thus a series of questions regarding aesthetics, the potential loss of historical information, and the ability to control the cleaning process adequately.

Furthermore, laser micro-profilometry, providing a topographic map of the investigated region, allows a statistical surface analysis by means of the computation of parameters related to the surface roughness. This enables the evaluation of the effects of corrosion and degradation processes in outdoor artworks that are exposed to pollutants and other physical and biochemical agents. Roughness computation is quite a new application in the Cultural Heritage field where there is a lack of rules defining both measurement and analysis protocols.

# Design and noise properties of free-running kHz-linewidth broadly-tunable single-frequency external-cavity VCSELs

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Laser technology is maturing rapidly and is finding applications in areas such as high resolution spectroscopy, medicine, optical telecoms, metrology, where highly coherent tunable low noise sources are required. Single frequency tunable high-power solid-state lasers rely on intracavity filtering. A more compact design can be achieved using a simple External-cavity VCSELs (VECSELs), to develop highly coherent laser. VECSELs exhibit single-frequency operation and wide mode-hop-free tuning range. They offer cw 300 K operation at high output power with a TEM<sub>00</sub> beam. Previous works reported on single-frequency VECSELs operating at 300 K at 1 μm (GaAs-based) [1] and 2.3 μm (GaSb-based) [2], optically-pumped by a 800 nm laser diode, with threshold densities <1 kW/cm<sup>2</sup>.

Here, the GaAs-based VECSELs were formed by a 1/2 VCSEL emitting at 1μm (inset Fig. 1) - composed of a HR bottom Bragg mirror and a InGaAs strain quantum-well active layer -, a 10 to 25 mm air gap to stabilize single longitudinal mode operation, and a commercial concave mirror (99% reflectivity). A low power (120 mW) 800 nm commercial single transverse mode laser diode was used as pump. The external cavity enforces TEM<sub>00</sub> beam operation ( $M^2 < 1.2$ ) and single frequency operation (SMSR > 40 dB) up to 22 mW output without any intracavity spectral filter. VECSELs

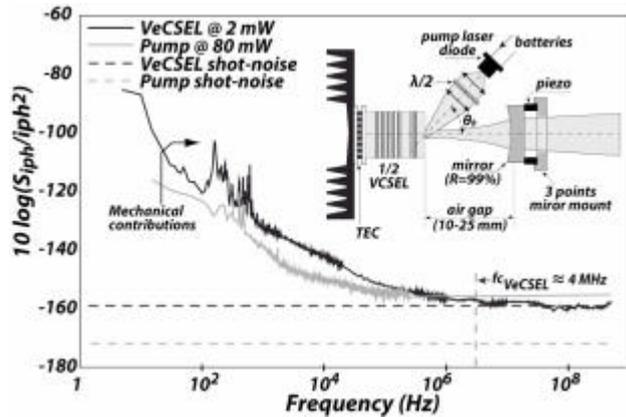


Fig 1: Pump RIN and VECSEL RIN versus RF frequency. Inset: Schematic view of the VECSEL.

were linearly polarized due to QW gain dichroism which stabilizes a linear polarization along the [110] crystal axis. A continuous tunability >40 GHz was obtained by moving the mirror with a PZT. For this purpose, the substrate back side was polished with a wedge and gold covered. The free running single frequency VECSEL was studied in terms of RIN (Relative Intensity Noise) and linewidth limitations. The RIN (fig. 1) reached the quantum limit below the VECSEL cavity cut-off frequency, in spite of a highly super-poissonian pump. The linewidth properties shown in fig. 2 are obtained with a delayed self-homodyne technique, using two fiber time delays  $\tau=5$ ms and 125ms between the two paths. The photo-detected signal is then Fourier-transformed and averaged with a high dynamic (>24 bit) 10 MHz FFT Analyser. For the longest delay (fig.2-a) the linewidth exhibits a 1.2kHz technical FM-noise induced broadening @ -3 dB for 40 ms measuring time, two order of magnitude narrower than commercial External-Cavity Laser Diodes. For the shortest delay (fig. 2) the measurements are fitted with an FFT-transformed autocorrelation function taking into account both white and 1/f FM noise contributions [3]. This treatment leads to a classical behavior for the white FM noise originated linewidth (fig. 2) with a 0.1 Hz.W slope and a 10 Hz limit at 10 mW emitted power. An optical power independent 1/f FM noise contribution ( $2.10^5$  Hz<sup>2</sup>/Hz at 1Hz) is also observed. All these parameters are 5 to 6 orders of magnitude smaller than usual values for conventional integrated semiconductor lasers [3].

This work was supported by the French ANR (MIREV).

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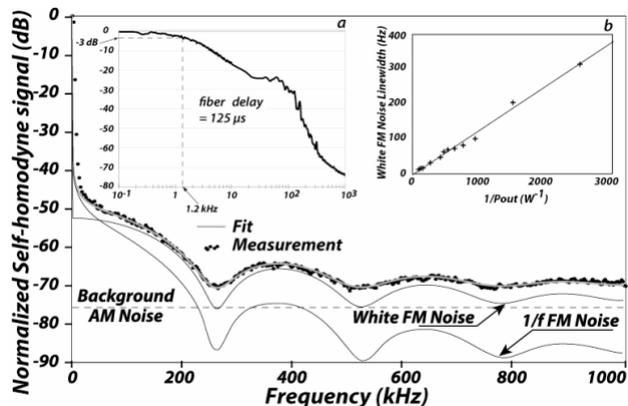


Fig 2: Fitted and measured self-homodyne signal @ 3.7mW,  $t=5$ ms. (a) : Self-homodyne signal @ 7mW,  $t=125$ ms - (b) : White FM noise linewidth versus  $1/P_{out}$

## Control and synchronization of polarization dynamics by optical feedback

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Experimental evidence of polarization selection in a quasi - isotropic CO<sub>2</sub> laser has been achieved by means of an unpolarized optical feedback<sup>(1)</sup>. Taking advantage of this possibility, we demonstrate stabilization of polarization emission and controlled fast switching between two polarization states. These results are applicable to different industrial processes including cutting which is highly sensitive to polarization. Usually, improvement of the cutting process is obtained by using circular polarized laser light obtained by insertion a reflecting phase retarder in the beam delivery path. Our method, in addition to selection and stabilization of one of two polarization states can produce a polarization balance between two orthogonal states by means of a fast switching of the optical feedback.

Controlled polarization switching plays a crucial role also in secure cryptographic communications. The quantum key distribution is satisfied by polarization encoding of the optical link. By means of polarization control a free space communication with high efficiency and key exchange rate could be implemented .

The other experimental issue here addressed is polarization synchronization between two unpolarized CO<sub>2</sub> lasers<sup>(2)</sup>. The degree of synchronization depends on the value of the coupling strength which is critically influenced by the injection angle. Polarization synchronization, in addition to secure communication, is a relevant problem in industrial applications where laser arrays are commonly used.

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## Tunable diode-laser spectroscopy for industrial process applications

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Tunable diode laser spectroscopy (TDLS) is the preferred technique for gas composition measurement in a growing number of industrial process control applications. TDLS with direct detection provides absolute measurement of a vibration-rotation gas absorption line transmission function, facilitating the extraction of gas concentration through line depth measurement. In many industrial applications TDLS with wavelength modulation is preferred as AC detection of absorption line derivatives, at frequencies where the laser noise is reduced, coupled with coherent electronic detection techniques, provide increased sensitivity and immunity to high infra-red background signals produced at high temperatures. However, significant issues remain with conventional approaches to this technique that hinder accurate concentration measurement, particularly in applications where the pressure may be varying and unknown. Through complex analysis these issues can be addressed [1-3]; however, inaccuracies in determining the instrument scaling factors (including the AM and FM characterisation of the laser) and the primary system scaling factor (which varies in relation to the unknown pressure) accumulate to determine a large error on the recovered gas concentration. Also, in conventional approaches the target AM signal (generated by interaction of FM on the laser output with a gas absorption line function) is heavily distorted by the presence of residual amplitude modulation (RAM) [1-3].

At FLAIR 2007 we will be presenting an alternative approach to TDLS with wavelength modulation that exploits the inherent phase relationship between the laser FM and AM, to recover the undistorted RAM transmission signal. It will be shown that, through appropriate analysis and signal processing, we can measure the absolute gas absorption line transmission function, enabling accurate and simultaneous measurement of gas concentration and pressure. The technique, like TDLS with direct detection, is absolute without the need for calibration, and also offers many of the practical advantages of coherent electronic detection discussed above. As such, it is better suited to stand-alone instrumentation for on-line deployment in industrial processes, where pressure drift and high temperatures are commonplace.

Measurements of the 1650.956 nm vibration-rotation absorption line shape function for 1% and 10% methane in nitrogen are compared to theoretical predictions based on HITRAN '04 data, and the excellent agreement validates this new technique.

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**MEDICINE, LIFESCIENCE AND  
AGRICULTURE**

## Laser applications in life science, sensitive chemical sensing in biology and agriculture

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Recently, continuously tunable, quantum cascade lasers and Optical Parametric Oscillators (OPOs) have been developed for the mid-infrared wavelength region. They provide continuous wave (cw) laser output at relatively high power (several hundreds of milliWatts up to Watts) and emit any desired wavelength within the infrared wavelength range from 2.5 to 5  $\mu\text{m}$ . Accurate detection of specific gases becomes into reach thanks to the infrared fingerprint absorption spectrum of molecular gases in this wavelength region, the high laser powers and the exact tuning capabilities of lasers. When the lasers are combined with sensitive spectroscopic techniques, such as photoacoustic spectroscopy and cavity ring down spectroscopy, gases can be determined extremely sensitive under atmospheric conditions.

The laser based gas sensors typically reach detection limits around 1 part per billion (volume mixing) for small molecules and possess a time resolution of only a few seconds. This has made lasers applicable for a wide variety of applications in biological and medical research. Examples will be given on bacterial infection, fruit storage, cell membrane damage, etc.

Thus far, research has mainly focused on the detection of small molecules such as NO, H<sub>2</sub>O, CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, and CH<sub>4</sub>. However, gas mixtures containing more complex molecules like alcohols, aldehydes, etc., which have a high degree of vibrational and rotational freedom, result in broad absorption spectra. Here we show a novel approach of trace gas detection of larger molecules, based upon a combination of continuous cavity ringdown (cw-CRD) spectroscopy using a cw infrared Optical Parametric Oscillator (OPO) system and supersonic planar jet.<sup>1</sup>

Last year the claim was made that plants also emit methane; this could have a considerably impact on the global methane cycle.<sup>2</sup> However, Keppler et al. could not find a clear explanation for a metabolic mechanism. In cooperation with plant physiologists we grew plants in a <sup>13</sup>CO<sub>2</sub> enriched atmosphere to give any methane produced a recognizable <sup>13</sup>CH<sub>4</sub> isotopic signature. The concentration of <sup>13</sup>CH<sub>4</sub> in the samples was determined using photoacoustic spectroscopy in combination with a cw OPO at using a strong absorption features centered at 3240.08 nm. In contrast to our expectations we could detect no significant methane emissions.<sup>3</sup>

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<sup>1</sup> Selective trace gas detection of complex molecules with a continuous wave optical parametric oscillator using a planar jet expansion A.K.Y. Ngai, H. Verbraak, S.T. Persijn, and H. Linnartz and F.J.M. Harren **Applied Physics Letters** 90 (2007) 081109

<sup>2</sup> Methane emissions from terrestrial plants under aerobic conditions F. Keppler et al. **Nature** 439 (2006) 187–191

<sup>3</sup> No evidence for substantial aerobic methane emission by terrestrial plants: a <sup>13</sup>C-labelling approach T. Dueck et al., **New Phytologist** (2007) doi:0.1111/j.1469-8137.2007.02103.x

## **Tissue imaging with non linear laser microscopy**

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Non linear laser scanning imaging techniques will be described. Multiphoton and Second Harmonic Generation Imaging application to tissue imaging will be shown together with the principle of functioning. Lifetime and spectral study will be demonstrated as powerful analysis methods to elucidate morphofunctional behaviour of different skin lesions.

Also, application of Aminolevulinic Acid as contrast medium will be shown as an effective marker for tumor border detection.

Finally, an application to brain tissue will be described. Here, the power of multiphoton technique to image intact neural network will be demonstrated as a unique tool to understand some basic functional mechanisms, as the reaction of a central nervous system to a local damage.

## Breath diagnostics using laser spectroscopy

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Monitoring emission rates and ambient concentrations of trace gases is of big interest in life sciences and several other fields. Infrared spectroscopic techniques have proven to be powerful tools for this purpose. Major activities are directed towards transportable sensors with sub-ppb sensitivities for mixtures containing several compounds. In this talk we report on our advances in extremely sensitive and specific analysis of trace gases by means of infrared laser absorption spectroscopy. Our measurements are mainly carried out by cavity leak-out spectroscopy (CALOS) which proved to be a unique and universal tool for rapid and precise medical breath testing. The CALOS technique enables rapid analysis of various VOCs, NO, CO, etc. at ppt concentrations.

Currently we are exploring this technique for the quantitative real-time detection of breath constituents; for example ethane which is considered as the most important volatile marker of free-radical induced lipid peroxidation and cell damage in the human body.

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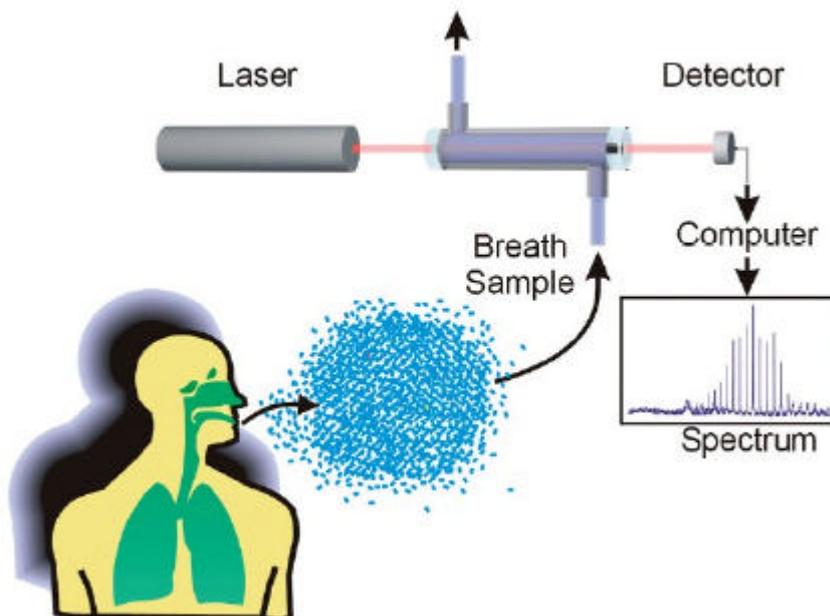


Fig: 1 Schematic of laser-assisted breath analysis.

## Agricultural trace-gas emissions determination using open-path lasers and inverse dispersion analysis

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There is concern that large confined animal feeding operations (AFOs) are significant sources of trace-gas emissions to the atmosphere, leading to air-quality and global-change issues. This concern makes it important to obtain good estimates of AFO trace-gas emissions. The gases of concern include ammonia (NH<sub>3</sub>) which is produced by conversion of urea and organic nitrogen (N) to ammonium, and methane (CH<sub>4</sub>) which is produced from enteric fermentation and anaerobic conversion of organic carbon. Evaluation of trace-gas emissions from AFOs is difficult and expensive and there is question that emissions estimates currently used may be developed from inadequate or inappropriate measurement technologies. Because of the ability of some trace-gases (particularly NH<sub>3</sub>) to react with measurement equipment, many of the early studies were somewhat inaccurate and often estimates suggested more loss of N as gaseous NH<sub>3</sub> occurred than as N entering into the production system. Indeed, the US Environmental Protection Agency, in the *National Emissions Inventory – Ammonia Emissions from Animal Husbandry*, suggests more NH<sub>3</sub> leaves swine and dairy production than N entering the systems (111 and 162%, respectively) and that 94% of feed N leaves beef feeding systems as NH<sub>3</sub> (USEPA. 2004). The purpose of this presentation is to discuss evaluation technologies which have been used and the development of a new technology for accurately determining trace-gas emissions.

In this presentation we discuss how the combination of open-path laser technology and inverse dispersion analysis presents an economical and accurate technique for calculating emissions and how it was used to calculate NH<sub>3</sub> and CH<sub>4</sub> gas emissions from swine, dairy, and beef production systems. In this technique the concentration of gas downwind of the source is measured and is then related to the emission rate. Determination of the emission rate is accomplished with an atmospheric dispersion model that describes the physical mechanism of how gas is removed and swept away from the emission source (requiring a measurement of the prevailing wind conditions). The technique is a remote, non-interference type measurement and has been verified in its accuracy using known trace-gas emissions (Flesch et al., 2007). Open-path lasers provide an ideal concentration sensor for the inverse-dispersion technique. With their long measurement path, they can provide useable measurements for a much larger range of wind directions than point sensors. And, by integrating concentration over a long atmospheric path, the path integration reduces the sensitivity of the emission calculations to the most common of dispersion model error of correctly calculating lateral dispersion (Flesch et al., 2004). We demonstrate how this technique is used in three different studies where NH<sub>3</sub> and CH<sub>4</sub> emissions are calculated from swine, dairy, and beef production AFOs. The emissions were determined from the whole farms as a single unit including housing and waste-management structures. Several measurement scenarios will be presented including studies made from the same farm during several seasons, from two farms simultaneously, and from several farms sequentially during the same season.

In summary, comparisons between our measured trace-gas emissions from AFOs and estimates used by regulatory agencies (for the same type AFOs) showed that regulatory agencies' estimates were 3 to 7 times higher than our emissions determined from non-interference, inverse dispersion analysis techniques.

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## Application of supercontinuum lasers to confocal microscopy

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Confocal fluorescence microscopy is one of the most powerful techniques in the biological sciences. Advances in microscope instrumentation are required to facilitate multiplexed fluorophore measurements and to provide a more complete characterization of the interactions of fluorophores with their local environment. We describe a confocal microscope system with continuously tunable fluorescence excitation and detection wavelengths from 450-700 nm. This system has the flexibility for optimal excitation and detection of a wide range of fluorophores and provides a new capability for multi-parameter fluorescence measurements. We use a fiber-laser pumped photonic crystal fiber to generate supercontinuum radiation for fluorescence excitation. This laser technology is a promising alternative to the more complex and expensive Ti:Sapphire based supercontinuum systems.

The multiplexing capability of the confocal microscope system is illustrated by imaging a mixture of microbeads containing three different fluorescent dyes. The beads are 0.18- $\mu\text{m}$  diameter PS-Speck beads (Molecular Probes) with excitation and emission maxima at approximately 505/515 nm, 540/560 nm, 633/660 nm. A fluorescence excitation scan is performed using 2-D confocal imaging of a 29  $\mu\text{m}$  x 29  $\mu\text{m}$  region with a 60x objective lens (Olympus PlanApo, N.A. 1.4/oil). Fig. 1a displays a composite image of the mixture of beads. The blue, green, and red beads are detected using fluorescence excitation at 508 nm, 560 nm, and 632 nm, respectively. This result demonstrates the excellent contrast that an excitation scan can provide for a mixture of fluorophores. The measured excitation spectra for the different beads are plotted in Fig. 1b.

The ability to continuously tune the excitation wavelength enables optimized excitation of fluorescent proteins. Fig. 2a shows a confocal image of a live human U2OS Osteosarcoma cell labeled with mCherry-Rad51 fluorescent protein using fluorescence excitation at 587 nm for optimal sensitivity (see spectrum in Fig. 2b). *In-situ* fluorescence excitation scans provide insight into fluorophore properties in cell environments. For example, protein aggregation and association of proteins to cellular substructures may result in subtle spectral shifts that are impossible to detect with fixed wavelength systems. Fluorescence excitation scans with the supercontinuum laser can detect these shifts.

The methodology that we present permits any fixed wavelength confocal system to be converted into a platform with diffraction limited spectrofluorometric imaging capabilities. The system is compact, economical and turn-key, without affecting the inherent functionality of the confocal microscope. High-resolution fluorescence imaging is feasible throughout the visible spectrum with relatively minor effects of chromatic aberration. Spectral imaging capabilities are sufficiently fast to track dynamic phenomena in living cells and can be improved using parallel detection arrays.

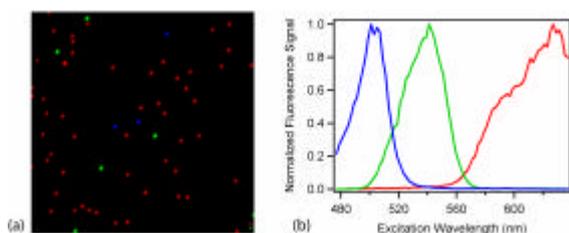


Fig. 1. (a) Confocal image of a mixture of microbeads containing three different fluorescent dyes. The blue, green, and red beads are identified by a fluorescence excitation scan. (b) Fluorescence excitation spectra of beads.

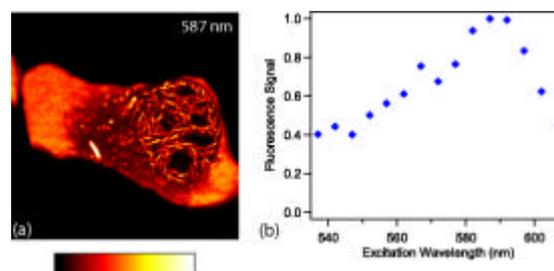


Fig. 2. (a) Confocal fluorescence image of a human U2OS Osteosarcoma cell labeled with mCherry-Rad51 fluorescent protein using optimal excitation at  $\lambda = 587$  nm. (b) Normalized fluorescence excitation spectrum of mCherry-Rad51

## QCL-based detection of UV-induced nitric oxide formation from aqueous solutions

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When exposed to intense sunlight, the human skin starts to sweat. One effect of this reaction is the cooling of the body, but human sweat consists not only of water, but of a complex mixture of a large number of substances. One of these substances is  $\text{NO}_2^-$ , from which nitric oxide is formed in the presence of UV radiation and water. The reaction pathway is theoretically predicted, but not yet experimentally proven. Within the reaction pathway from  $\text{NO}_2^-$  to NO, it is predicted that free radicals ( $\text{NO}_2$  and OH) are produced. Several other substances, e.g. ascorbic acid, vitamin E and glutathione, act as scavengers and affect the production of NO.

The aim of our presented work is to understand and to quantify the effect and interactions of scavengers on the UV induced production of NO in aqueous solutions of  $\text{NO}_2^-$ . Due to its extreme selectivity on NO, the Faraday Modulation Spectroscopy (FAMOS) technique is an excellent method for measuring NO production from aqueous solutions [1]. We used nitrogen to transport the gaseous NO from the reaction chamber to our cw-QCL based spectrometer, which is capable of detecting NO with a suitable time resolution (1 s) and an excellent sensitivity (14 ppb noise-equivalent concentration) without any cross-sensitivity to water or other molecules.

We measured the dependence of the UV induced NO production rate on the amount of ascorbic acid, glutathione and vitamin E injected into an aqueous solution of  $\text{NO}_2^-$ . Furthermore, we investigated the interactions of the different scavengers. We were able to verify the predicted reaction pathways of UV induced NO production and to quantitatively compare glutathione, vitamin e and ascorbic acid. Furthermore we observed that vitamin e suppresses the effects of ascorbic acid.

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## **Development of a CO<sub>2</sub> triggered alveolar air sampler**

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In the last years promising results revealed the potential of a noninvasive biochemical monitoring of the exhaled breath. Thanks to an almost instantaneous equilibrium between the pulmonary blood and the air in the alveoli of the lung, volatile substances in breath exhalation can provide insights of biochemical processes. Sensor-based electronic devices are expected to play the main role when specific patterns of disease markers have been defined, and a new generation of breath test instruments could, in time, become ordinary in medical screening. Despite its enormous potential, breath analysis is far from reaching a widespread use in the clinical practice. Among many reasons, the lack of effective and reproducible sampling procedures plays a primary role. Exhaled air can be sampled in two ways: mixed expiratory sampling and alveolar sampling. The former method entails the collection of the total breath, including the air contained in the upper airways which experiences no gas exchange with blood (dead space), while the latter method involves the collection of the only alveolar air discriminated by the carbon dioxide concentration. Alveolar air contains most of the chemical information on blood composition. Mixed expiratory sampling is often used due to its simplicity, but the variable individual dilution of the alveolar air with dead volume introduces a noise in the data.

In this paper, an alveolar air sampler is presented. A CO<sub>2</sub> sensor based on tunable laser diode spectroscopy was integrated in the system to measure the carbone dioxide concentration.

## **An ultra-sensitive, six-species trace gas analyzer for continuously monitoring concentrated animal feeding operations**

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There are an estimated 1.3 million livestock and poultry farms located across the United States. About 238,000 of these are considered animal feeding operations (AFOs) and the largest of these are defined as Concentrated Animal Feeding Operations (CAFOs). The rapid proliferation of CAFOs over the last few decades has raised concerns about health and environmental effects of aerial emissions from animal production and waste management systems. Concentrated Animal Feeding Operations can emit ammonia (NH<sub>3</sub>), nitrous oxide (N<sub>2</sub>O), nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), methane (CH<sub>4</sub>), volatile organic compounds (VOCs), hydrogen sulfide (H<sub>2</sub>S), and particulate matter. Extensive literature documents acute and chronic respiratory diseases and dysfunction among swine and poultry workers from possible exposure to complex mixtures of particulates, gases, and vapors within CAFOs. In addition, both nitrous oxide and methane are greenhouse gases that contribute significantly to global warming.

Efforts to regulate air emissions from agricultural sources have been confounded by a lack of accurate aerial emissions data. The Animal Feeding Operations Air Compliance Consent Agreement was recently negotiated between the United States Environmental Protection Agency (EPA) and the livestock and poultry industries. This agreement mandates that the aerial emissions from CAFOs be quantified before regulations are formulated to ensure compliance with applicable clean air provisions. The EPA and the animal agriculture clean air consortium has embarked upon a national, two-year long emission measurement study to help establish emission standards for the livestock and poultry industries.

Cavity Ring-Down Spectroscopy (CRDS) is a laser-based, all-optical technique capable of parts-per-billion sensitivity. A high finesse optical cavity coupled to a high precision wavelength monitor enable the CRDS analyzer to have a spectral resolution 1000 times better than a Fourier Transform Infrared Spectrometer (FTIR), thus allowing CRDS to distinguish individual absorption features. Picarro, Inc. has developed a CRDS gas analyzer that can measure up to six separate species using CRDS technique. If follow-up studies are deemed necessary or if EPA regulations mandate continuous monitoring or the periodic measurement of emissions from livestock and/or poultry facilities, a robust, affordable instrumentation that could measure CH<sub>4</sub>, N<sub>2</sub>O, H<sub>2</sub>S, CO<sub>2</sub> and NH<sub>3</sub> would simultaneously provide the accurate concentration measurements required to ensure compliance, as well as quantifications of important greenhouse gas contributions from CAFO's. In this work, results obtained from analyzer measurements of these five important atmospheric contaminants at a CAFO operation is shown. This work was partially supported by the USDA.

### **ACHIEVED PRECISION FOR THE ANALYZER**

Species	Achieved (5 minute)	Notes
Ammonia	0.05 ppbv	1 sigma @ zero
Hydrogen sulfide	0.4 ppbv	1 sigma @ zero
Nitrous oxide	9.6 ppbv	1 sigma @ zero
Methane	0.15 ppbv	1 sigma @ 1 ppmv

## Gassification process monitoring by photoacoustic diode-laser spectroscopy

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Resonant photoacoustic laser spectroscopy has opened a new field for fast and on line monitoring methods [1] allowing ppm sensitivity range with low power (few mW) diode lasers [2]. The selectivity of spectroscopic detection, which depends on spectral resolution, is potentially very high and gives the possibility of unambiguous detection of different species by scanning a small frequency range. With the development of high-quality NIR diode lasers characterized by broad tunability and high spectral purity, multi-gas detection can be now very efficient [3]. Fundamental ro-vibrational transitions ( $\lambda > 3 \mu\text{m}$ ) are typically accessible, up to now, only to complex and/or very expensive laser systems. The first and second overtones and combination bands wavelength region around 1.7  $\mu\text{m}$  are now covered by diode lasers, which are rapidly developing in simple, compact, economic and high performance systems. A multi-gas photoacoustic trace gas detector working with a tunable diode laser at 1.63  $\mu\text{m}$  was developed in our laboratory for simultaneous detection of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$  and  $\text{NH}_3$  [4]. These molecules play an important role in many industrial and biological processes like methane and hydrogen production from biomass gasification [5]. This process often produces secondary undesired species like  $\text{H}_2\text{S}$ ,  $\text{HCl}$ ,  $\text{NH}_3$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_6\text{H}_6$  and their concentrations in the final gas mixture strongly depend on biomass composition and on process parameters. Ethylene and acetylene, for example, have negative effects if the outsourcing gas mixture is burned in internal combustion engines, because they can induce detonation. Ammonia and hydrogen sulfide present a corrosive behaviour and are pollutant precursor producing  $\text{NO}_x$  and  $\text{SO}_x$  compounds. The monitoring of these molecules would be very important in order to improve the processes efficiency and to reduce their environmental impact. Measurements on real sample gas produced by a biomass gasification plant are presented.

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# **ENVIRONMENTAL SCIENCE AND BIOGEOCHEMISTRY**

## **Infrared laser applications to field measurements of trace gas sources and fluxes in environmental research**

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Recent advances in infrared lasers and laser technology have greatly facilitated field measurements of atmospheric trace gases to identify and quantify their sources, sinks, and fluxes in many environments. The availability of non-cryogenic mid-infrared lasers, improvements in non-cryogenic infrared detectors, and advances in detection techniques including cavity enhanced absorption methods and longer path length-smaller volume direct absorption techniques have led to a new generation of smaller, lighter, and more robust instrumentation suitable for measurements both from mobile platforms and from fixed sites at remote locations. Applications of infrared laser technology to measurements of greenhouse gas fluxes of methane and nitrous oxide from natural ecosystems, nitrogen oxides and ammonia from urban sources, and the identification of hydrocarbon sources and oxidation products formaldehyde and formic acid will be presented.

## **Biosphere – Atmosphere exchange: an overview**

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Surface-atmosphere exchange processes of a variety of substances are closely coupled and highly sensitive to climate change. They contribute to climate forcing through their effect on tropospheric chemistry and radiative flux. To predict the impact of future changes to air quality, climate and ecosystems, there is a need to understand the details of carbon and nitrogen cycling between the terrestrial and atmospheric systems. Integrated ecosystem-atmosphere processes studies are part of the international Geosphere-Biosphere Programme (IGBP) and will provide a better understanding how the interacting physical, chemical and biological processes transport and transform energy and matter through the land-atmosphere interface from the cell level to a global scale, where times scales range from diurnal to centennial, past to future.

In this overview talk, Biosphere-Atmosphere interactions are discussed with a focus on the exchange of CO<sub>2</sub>, water vapor and energy between forests and the atmosphere. The experimental design for the measurement of turbulent surface-atmosphere exchange processes and objective methods to scale-up from footprint to ecosystem fluxes are presented and discussed with respect to inhomogeneous surfaces.

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# High resolution measurements of absolute water transpiration rates from plant leaves via 1.37 $\mu\text{m}$ tunable diode-laser absorption spectroscopy

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The phytosphere as a main part of the biosphere plays a significant role for the atmospheric water fluxes and thus for the earth's climate. A more accurate understanding of the atmosphere-phytosphere coupling is needed to improve global water balance models used for climate modelling. The transpiration of plants is of particular interest and has to be investigated on the scale of single leaves, plants and complete canopies. Commonly used extractive water vapour sensors are often too slow and prone to systematic errors caused by  $\text{H}_2\text{O}$  adsorption and their need for frequent sensor calibration. Recently we developed a self-calibrating open-path  $\text{H}_2\text{O}$  TDL spectrometer (with 80m White cell) for rapid, *in situ* water vapour supersaturation measurements *within* ice clouds<sup>1</sup>.

Here we present a new solution for a much more size restricted application: The determination of the temporal dependence of the leaf-side resolved  $\text{H}_2\text{O}$  transpiration rate from a single plant leaf, for which we developed a new, calibration-free, ultra-compact, fibre-coupled, multi-point  $\text{H}_2\text{O}$  sensor. This spectrometer consists of four fibre-coupled  $8 \times 6 \times 4 \text{ cm}^3$  detection chambers containing a 15 cm absorption path. The absolute humidity of the air streams is simultaneously measured by direct TDLAS (with a frequency of 0.5 Hz averaging 100 laser scans) in all four chambers, that is, in the moistened incoming air delivered to the leaf, separately on the upper and lower leaf-surface and in the outgoing air. Sensors calibration was avoided by a highly accurate laser tuning characterisation. To further increase the sensor accuracy we realised precision line parameter measurements (strength and air broadening) with significantly improved precision compared to the HITRAN data. The high optical resolution of  $5 \cdot 10^{-5} \text{ OD}_{10}$  (Fig. left) permitted a single-digit ppm detection limit over a dynamic range of 6000 to 20000 ppm. Using the absolute  $\text{H}_2\text{O}$  difference between incoming and outgoing gas, resp. the upper and lower leaf chamber, the measured leaf-area and the metered gas-flow, we determined total absolute  $\text{H}_2\text{O}$  transpiration rates with a resolution of about  $2 \mu\text{mol}/\text{m}^2 \cdot \text{s}$ , and separately the rates for the lower and the upper leaf side (Fig. right). Further we studied the dependence of the dynamic transpiration rate of *Epipremnum pinnatum* on ambient conditions over several day and night cycles and on periodic light stimulation. Further prospects are to measure spatially resolved transpiration rates using a 1.4  $\mu\text{m}$  NIR line scan camera.

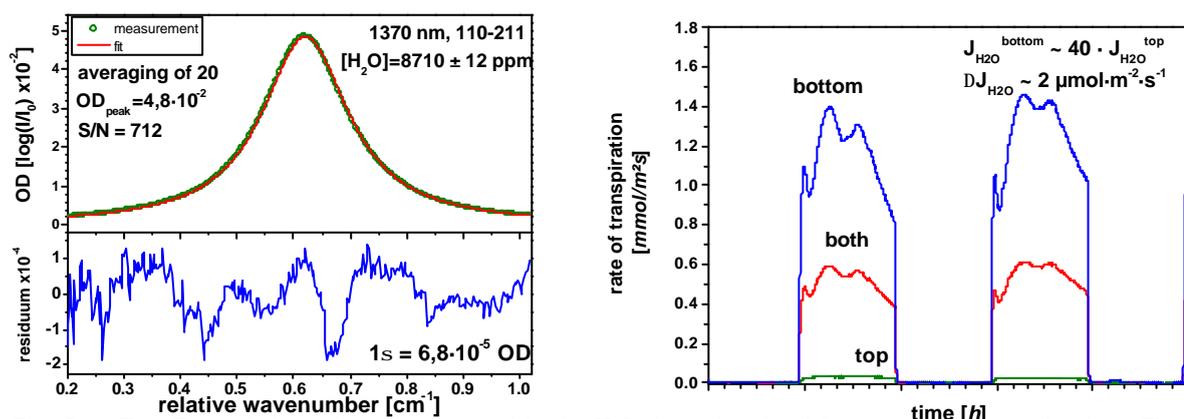


Fig.: Left: Top: Transmission and tuning corrected in situ  $\text{H}_2\text{O}$  absorption signal from one of the leaf chambers. The residual (bottom) between measurement and fit (top) indicates an optical resolution of  $7 \cdot 10^{-5} \text{ OD}_{10}$  yielding a SNR of about 700 and a detection limit of about 10 ppm. Right: Using the  $\text{H}_2\text{O}$  difference of the leaf chambers, the measured gas flow and the leaf area we derived absolute  $\text{H}_2\text{O}$  transpiration rates  $J_{\text{H}_2\text{O}}$  for the total leaf as well as for the top and bottom side with a resolution of  $2 \mu\text{mol}/\text{m}^2/\text{s}$ . The bottom side emits 40x more  $\text{H}_2\text{O}$  than the top side.

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## Evanescent field sensors for monitoring of diluted CO<sub>2</sub> during sequestration in aquifers and for detection of explosives

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Sequestration is one of the methods currently discussed to extract CO<sub>2</sub> off the carbon cycle. One possibility to store it is within deep saline aquifers. The process is tested within the European project COSINK at Ketzin, Germany. There, CO<sub>2</sub> is sequestered into a depth of 800 m. In parallel, a nationally funded project aims at monitoring the CO<sub>2</sub> concentration through observation holes during the sequestration process and afterwards to model the distribution and stability of the storage.

Simple, rugged and easy to use sensors are needed and optical technologies have the advantage that measurement is possible fast and without preparation of samples. Evanescent-field spectroscopy relies on the interaction of radiation guided within an optically thicker material and the optically thinner surrounding material when total internal reflection occurs. This means that no free optical path needs to be accessible but that the fiber-coupled sensor can be inserted directly into the borehole. First results of sensing CO<sub>2</sub> diluted in water using evanescent-field spectroscopy at  $\lambda=1570$  nm are shown. The cladding is removed from a standard optical multi-mode fiber which enables the interaction of the light within the fiber core and the surrounding medium. Changes in attenuation of the signal can be detected depending on the temperature which determines the maximum amount of CO<sub>2</sub> that can be diluted into the water.

A second very interesting application of evanescent-field spectroscopy is the detection of nitro-based explosives. These possess a very low vapour pressure and can therefore hardly be detected in the gas phase. However, if the sensing element is coated with adequate receptor molecules, the concentration is enhanced and the color change due to the building of a reddish interstitial compound can be detected using the interaction with the evanescent-field. The receptor (triphenylen ketals) is specially designed to react with TNT and shows no interference with the respective dinitro derivates. The color change due to the charge-transfer band in the spectral region between 500nm and 550 nm is reversible and fast and can be easily detected at  $\lambda=532$  nm. As a reference, the attenuation is measured as well at  $\lambda=1064$  nm. Fig. 1 shows typical data. The decay times represent the flow rate of TNT and should not be mistaken with the response time of the sensor.

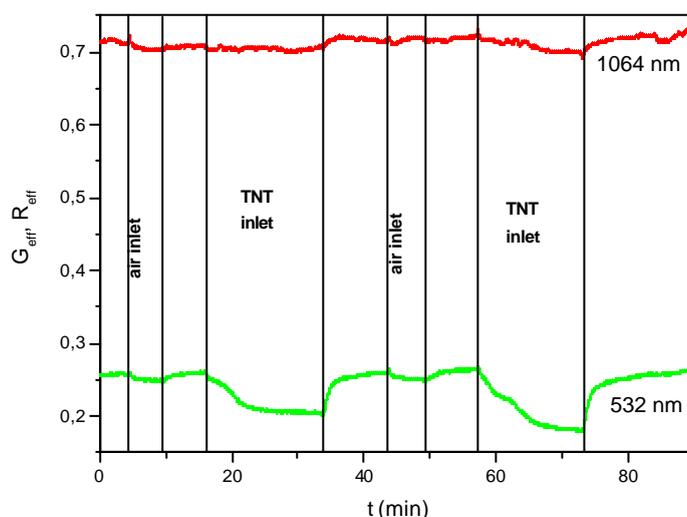


Fig.1: Sensing of TNT with an evanescent-field sensor coated with receptor molecules.

## Applications of integrated cavity output spectroscopy in environment science

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A novel spectrometer based on an improved off-axis alignment of integration cavity output spectroscopy (OA-ICOS) in conjunction with a wavelength modulation (WM) technique was developed using DFB diode lasers operating in the near infrared around 1.5  $\mu\text{m}$ . The cavity was aligned had almost no right mode structure characterizing a cavity and it ceased to be a cavity. At this way it is possible to eliminate the mode injection noise completely. Applications of this spectrometer were performed by trace gas detection of ambient  $\text{CO}_2$  and by coupling with a smog chamber for the investigation of atmospheric relevant problems. The ambient  $\text{CO}_2$  detection was performed with a 44 cm optical cavity that provided an effective absorption path length of  $\sim 68$  m at 1.573  $\mu\text{m}$  ( $6357.3\text{ cm}^{-1}$ ). Compared to OA-ICOS, the detection limit was about 14 times improved by implementation of the WM technique to OA-ICOS. A minimum detectable absorption of approximated  $3.6\text{ ppmv Hz}^{1/2}$  or  $2.3 \times 10^{-7}\text{ Hz}^{-1/2}$  per optical pass was obtained using second harmonic detection.

For the investigation of atmospheric relevant problems, the coupling between OA-ICOS using a WM technique at 1.511  $\mu\text{m}$  ( $6625\text{ cm}^{-1}$ ) and a smog chamber was demonstrated for the first time. The preliminary results of the photolysis of methyl nitrite ( $\text{CH}_3\text{ONO}$ ) were presented, which demonstrated the ability of our system for the degradation mechanisms studies of atmospheric relevant organic compounds. The photolysis products of  $\text{CH}_3\text{ONO}$  were shown in Figure.

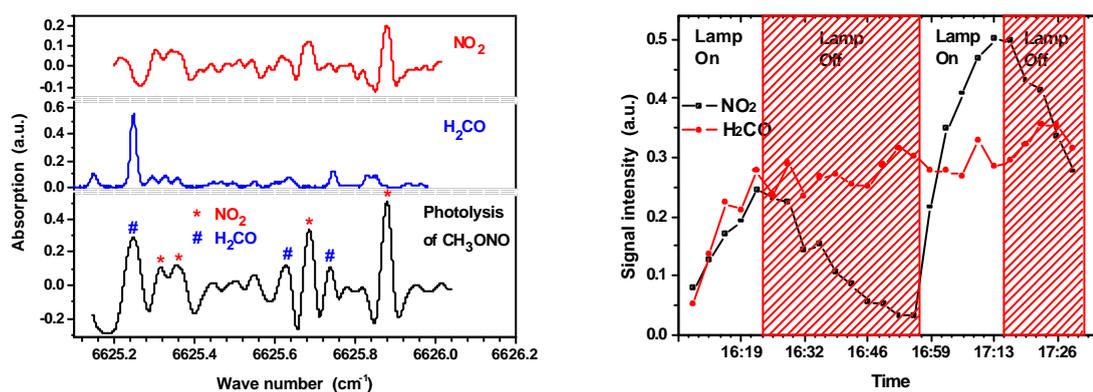


Figure (a) Characterization of the photolysis of  $\text{CH}_3\text{ONO}$ . Up panel: 2f harmonic signal of  $\text{NO}_2$ ; Middle:  $\text{H}_2\text{CO}$  absorption spectrum; Low: spectrum of the photolysis products of  $\text{CH}_3\text{ONO}$ . (b)  $\text{H}_2\text{CO}$  and  $\text{NO}_2$  absorption signal intensity at different times in the photolytic process.

# Measurements of atmospheric CH<sub>4</sub> and N<sub>2</sub>O with a new-design long-path room-temperature quantum cascade laser spectrometer

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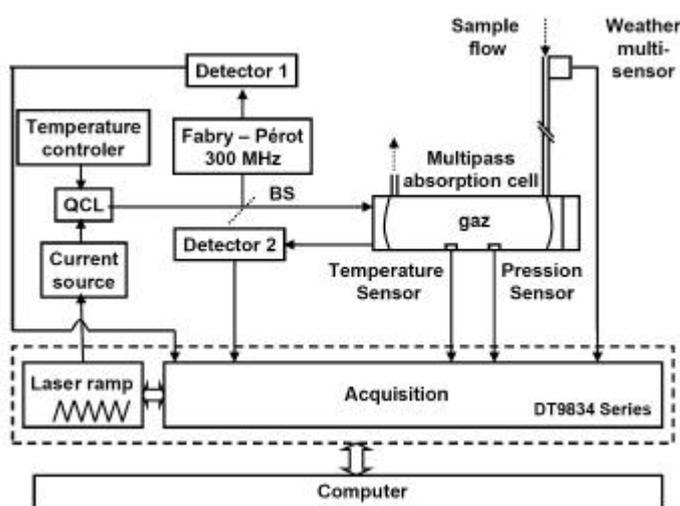
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We report in this work the development and the performances of a field deployable infrared laser sensor. This instrument is designed to measure N<sub>2</sub>O and CH<sub>4</sub> concentrations at ground level (See figure). The sensor is based a distributed feedback quantum cascade laser (QCL DFB) operating in continuous wave (cw) at room temperature (RT) from Alpes Lasers. The concentrations of the gases were determined by long path infrared diode laser absorption spectroscopy in the laboratory. The absorption cell is a new type of multiple-reflexion cell developed by C. Robert.



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The sample gas (outside the laboratory) is brought from atmospheric pressure to about 40 mbar across the inlet orifice in order to reduce the pressure broadening of the absorption lines, increasing the distinctive nature of the absorbing species spectral signature. The system operates at a gas flow of 5 L/min and the pressure inside is not actively regulated but the drift is only 1.5 mbar per 12 hours. A dust filter is at the inlet of the measurement head to protect the gas system and the mirrors of the cell from pollution. The long term stability of the instrument was evaluated using the Allan variance technique. All these results will be presented.

A preliminary evaluation of the instrument performance was realized by in situ measurements of N<sub>2</sub>O and CH<sub>4</sub> concentration variations at ground level during one day. Addition of N to the soil via mineral N fertilisers generally increases the N<sub>2</sub>O emission. The sensor has been also applied to study time response of N<sub>2</sub>O flux to a fertilizer addition in a soil sample demonstrating its good performance for this type of measurements. In the next months we will participate to measurements campaigns in collaboration with INRA (Institut National de la Recherche Agronomique).

## Kinetic study of the degradation of aromatic hydrocarbons by simultaneous detection of OH and HO<sub>2</sub> radicals by laser photolysis coupled to LIF and cw-CRDS

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Aromatic hydrocarbons are a major class of anthropogenic compounds in the troposphere and still account for up to 30% of the non-methane hydrocarbons in urban air, despite emission control measures. They react rapidly with OH radicals and have a strong influence on the urban air quality. While the initial reaction with OH is well understood and leads predominantly to adduct formation, the consecutive steps of this adduct with typical atmospheric radical scavengers like O<sub>2</sub>, NO and NO<sub>2</sub> is not fully understood. We have therefore investigated the simplest system: C<sub>6</sub>H<sub>6</sub> / OH / O<sub>2</sub> by a new experimental set-up permitting the simultaneous time resolved detection of OH and HO<sub>2</sub> radical concentrations.

We have built a new experimental set-up permitting the selective and sensitive detection of HO<sub>2</sub> radicals by coupling cw-CRDS (cavity ring down spectroscopy) in the near infrared to laser photolysis<sup>1</sup>. The quantitative detection is performed by time-resolved cw-CRDS in the 2ν<sub>1</sub> band around 1500 nm., an absolute calibration of the absorption coefficients has been obtained by measuring kinetic decays of the bimolecular self reaction. The detection limit of the actual set-up is 4×10<sup>10</sup> cm<sup>-3</sup> (single shot S/N = 1).

The detection of OH radicals is performed in the same reactor by LIF (Laser Induced Fluorescence) with an excitation at 282 nm and detection of the fluorescence at 308 nm. The reaction is initiated by excimer laser photolysis, mainly the generation of OH radicals by 248nm photolysis of HNO<sub>3</sub> in the presence of the reactants C<sub>6</sub>H<sub>6</sub> and O<sub>2</sub>.



From fitting the concentration –time profiles of both species, OH and HO<sub>2</sub>, measured at different reactant concentrations, the rate constant of the reaction (2) between the adduct and O<sub>2</sub> can be obtained. The detection of OH radicals by LIF being a relative technique, the deduction of the branching ration between (2a) and (2b) is not so straightforward. A calibration procedure using 248nm photolysis of H<sub>2</sub>O<sub>2</sub> is used in order to obtain absolute OH-concentrations



Measuring OH and HO<sub>2</sub> concentration – time profiles under the same conditions and fitting to the above mechanism (3) – (5) permits to calibrate the relative OH LIF signals with respect to the absolute HO<sub>2</sub> cw-CRDS signals.

[1] J. Thiebaud, C. Fittschen: "Near infrared cw-CRDS coupled to laser photolysis: spectroscopy and kinetics of the HO<sub>2</sub> radical", Appl. Phys. B **85**, pp.383-389 (2006)

## Cavity ringdown analyzer for carbon dioxide and methane atmospheric inversion measurements

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A network of field deployable cavity ring-down analyzers capable of performing, in a single instrument, measurements of methane, carbon dioxide, and water vapor suitable for atmospheric inversion studies has been developed by Picarro and deployed in the field. The analyzer is designed to be extremely linear, insensitive to contaminant species, require little sample preparation, and operate over a wide range of environmental conditions. A patented high precision wavelength monitor makes certain that only the spectral absorption feature of interest is being monitored, greatly reducing the analyzer's sensitivity to interfering gas species. As a result, the analyzer maintains high linearity, precision, and accuracy over changing environmental conditions with minimal calibration required. Water removal and temperature and pressure control of the sample is not needed— thus eliminating the cost associated with these additional expenditures. Precise temperature and sub-torr pressure stability also enables excellent accuracy from analyzer to analyzer and low drift over time— important considerations for a network of measurement sites. The extremely compact cell size gives the analyzer fast rise and fall times at very small flow rates translating into significantly reduced calibration gas volumes. Because the analyzers do not require frequent calibration and maintain high linearity, precision, and accuracy over changing environmental conditions, these analyzers pave the way toward reduce operating costs and further enables high-density field deployment.

The particular instruments described here are designed to measure atmospheric carbon dioxide for atmospheric inversion studies. Five of these analyzers have recently been deployed as part of the North American Carbon Program's Midcontinental Intensive regional study in the upper midwest, USA. A primary goal of this 18 month project is to increase the regional atmospheric CO<sub>2</sub> data density so that:

- 1) atmospheric inversions can derive well-constrained regional ecosystem carbon flux estimates.
- 2) the trade off between data density and accuracy of the inversion-derived flux estimates can be determined quantitatively using field observations, thus providing guidance to future observational network designs.

In this work, analyzer design and performance will be discussed. In addition, carbon dioxide measurements from this study will be shown. Data generated by a modified version of this analyzer capable of performing, in a single instrument, atmospheric inversion-quality and high-rate eddy-covariance flux measurements of CO<sub>2</sub>, H<sub>2</sub>O, and CH<sub>4</sub> will also be shown. The performance specifications for this analyzer is shown below. Work supported by the U.S. Department of Energy under Contract No. DE-FG02-03ER83751, and the Office of Science (BER)'s Terrestrial Carbon Processes Program.

### Performance Specifications

Target Gas	Precision (5 sec / 30 sec)	Max Drift
Carbon Dioxide (CO <sub>2</sub> )	200 ppbv / 80 ppbv	< 500 ppbv / month
Methane (CH <sub>4</sub> )	1 ppbv / 0.4 ppbv	3 ppbv / month
Water Vapor (H <sub>2</sub> O)	10 ppmv	

## A case study for dispersion models: methane emission from the landfill of Florence

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In order to verify a dispersion model for gaseous pollutant we have measured the atmospheric concentration of  $\text{CH}_4$  at the site of the University of Florence, located in Sesto Fiorentino, 2 km far from the landfill of Florence.

The measurements have been carried out by measuring the methane absorption, at  $1.65 \mu\text{m}$ , along the double path between two adjacent buildings, 85 m far each other (Fig. 1). The detection technique is direct absorption, so that the calibration of the measurements was straightforward.

The campaign lasted one month, continuously, the only interruptions being due to data download. Once analyzed the data, the results were associated with meteorological data, supplied by La.M.M.A. – Regione Toscana (Laboratory per la Meteorology and Environmental Modelling)

The diffusion model takes into account the percentage of methane which is captured before exiting the landfill, the wind direction and velocity, and the other atmospheric parameters. The correlation of concentration values with model predictions is shown in Fig. 2, over two days of measurements. It's worth nothing that the the measurements have been averaged over one hour, in order to meet the model time resolution.



Figure 1: location of the measurement

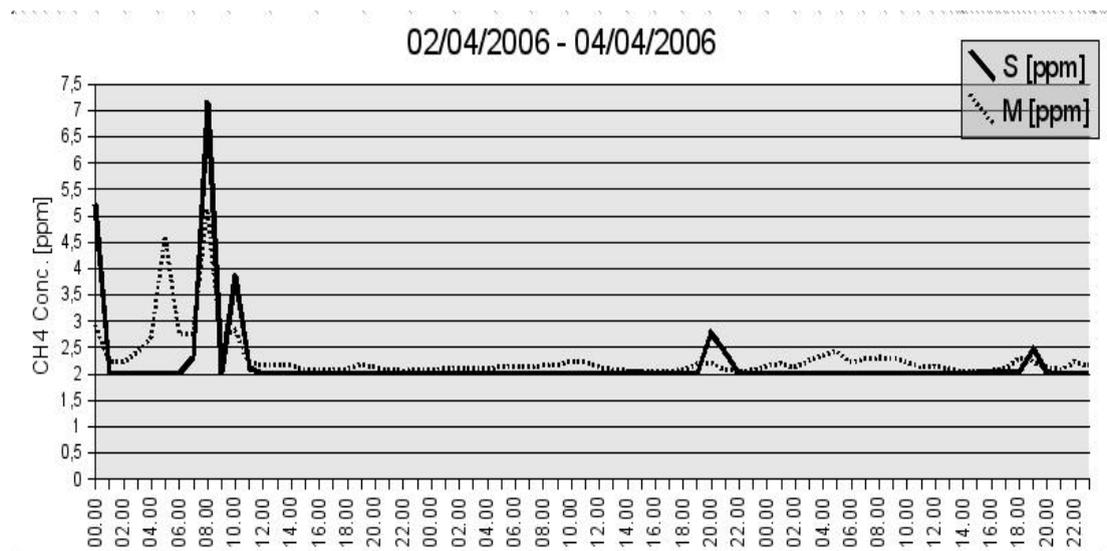


Figure 2: Correlation of model with measurements

## A near-infrared sensor for the near-ground measurement of atmospheric CO<sub>2</sub> : Intercomparison with Lidar and other sensors

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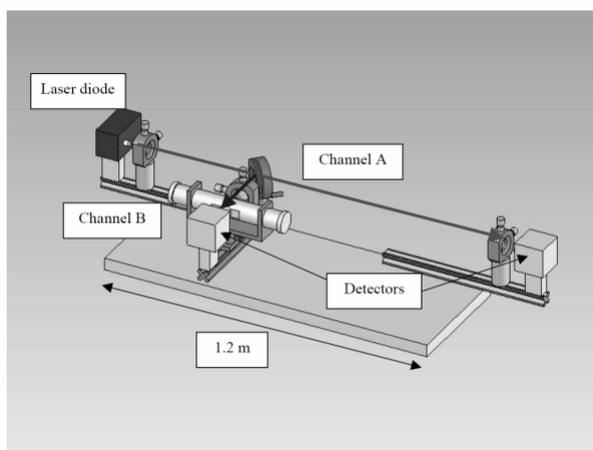
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We report in this work the development of a field deployable infrared laser spectrometer in GSMA (Reims) [1]. This instrument is designed measure CO<sub>2</sub> concentrations open to the atmosphere at ground level (See photograph). Absorption lines are selected around 2.68 μm to minimize interferences from neighboring water vapor transitions. The design of the sensor, details of the data processing technique and the evaluation of the sensors long-term stability with Allan variance method are reported. All these results will be discussed.



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To evaluate the performance of our diode laser based sensor, atmospheric carbon dioxide was measured for a period of one day with the instrument installed on the roof of our laboratory. The minimum CO<sub>2</sub> detection limit achieved was sufficient to observe carbon dioxide variation over one diurnal cycle. An improvement of our sensor has included improved stabilization of the diode laser emission. Then this sensor has been used during the CIEL campaign at the end of 2006. The obtained CO<sub>2</sub> concentrations were compared with those of a Lidar from LMD and other in situ sensors. All the results of this campaign will be presented.

In the future, we would like to obtain in-situ vertical concentration profiles of CO<sub>2</sub> in the troposphere and the lower stratosphere. For this purpose a meteorological laser sonde will be developed and operated from a weather balloon based on former experience of balloon borne sensors with telecom diode lasers.

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## A compact laser instrument based on difference-frequency generation for trace gas detection of VOCs

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In this paper, we describe the development of a compact band transportable mid-infrared laser instrument for trace gas detection of chemical species, in particular VOCs (volatile organic compounds). The laser source, widely tunable from 2.94 to 3.57  $\mu\text{m}$ , is based on continuous-wave difference-frequency generation (DFG) in a periodically poled  $\text{LiNbO}_3$  (PPLN) crystal. Two continuous-wave near-infrared lasers were used as difference-frequency mixing source: one was an external cavity diode laser (ECDL, New Focus) and the other was an erbium ( $\text{Er}^{3+}$ ) doped fiber laser (EDFL, IPG LASER GmbH). The ECDL was continuously tunable from 1040 to 1080 nm, amplified with an ytterbium doped fiber amplifier (Keopsys Inc.) up to 2 W. The EDFL, tunable from 1543 to 1601 nm with a mode-hop free frequency tuning of about  $2\text{-}3\text{ cm}^{-1}$ <sup>[1]</sup>, was designed in a master-oscillator power-amplifier (MOPA) configuration with a single mode/single frequency output power up to 1 W. Both lasers had a narrow linewidth of less than 1 MHz. Two laser beams were coupled together via a WDM (OZ Optics Ltd.), collimated and then focused with a telescope focusing system into a temperature controlled multi-channel PPLN crystal. The PPLN crystal was 50-mm long consisting of 14 channels whose poling periods range from 28.2 to 31  $\mu\text{m}$  (Deltronic, Inc.). With a pumping configuration mentioned above, infrared radiation from 2.94 to 3.57  $\mu\text{m}$  has been produced by quasi-phase-matched DFG in the PPLN by means of grating period of  $\Lambda=29.5\text{-}30.2\text{ }\mu\text{m}$  in conjunction with temperature tuning from 60 to 170 °C. DFG-based laser powers of ~0.25 mW with a linewidth of ~1 MHz were obtained at 3.29  $\mu\text{m}$  by mixing laser beams with 634 mW @ 1570.2 nm and 516 mW @ 1062.6 nm. The QPM condition was realized using  $\Lambda=29.9\text{ }\mu\text{m}$  at 121.1 °C. The corresponding DFG power conversion efficiency was ~0.62 mW/W<sup>2</sup>.

Spectroscopic characteristics of the DFG source have been evaluated using high-resolution absorption spectra of ethylene ( $\text{C}_2\text{H}_4$ ) near 3.23  $\mu\text{m}$ . Line parameters (line strength, self- and air-broadening coefficients) of the  $\nu_9$   $6_{1,5}\text{-}6_{2,4}$  transition have been determined. The experimental results were in good agreement with those given in the HITRAN database. Trace detection of benzene vapor by difference-frequency laser absorption spectroscopy near 3.28  $\mu\text{m}$  will be presented.

### Acknowledgments

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### References

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## NO detection using double lock-in detection technique with a quantum cascade laser

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We developed a distributed-feedback quantum cascade laser (Hamamatsu, L10195-5261A) which was designed for pulsed operation at 5.2  $\mu\text{m}$  on a thermo-electric cooler. We applied it to wavelength-modulation spectroscopy of NO using double lock-in technique. Current pulses of a 20-ns duration and a 500-kHz repetition rate were applied to the laser. This short duration was selected because the narrower laser linewidth is obtained with the shorter current pulses in this range. A 500-Hz sine-wave subthreshold current was added to the current pulses for wavelength modulation. This enabled double lock-in detection for high sensitivity wavelength-modulation spectroscopy even with a pulsed quantum cascade laser. A schematic diagram of the experimental setup is shown in Fig. 1. A multipass cell having a total path length of 100 m was filled with a 1000-ppm NO sample at 170 Torr. First, the output signal from a fast HgCdTe detector (Hamamatsu, P3257-30) was lock-in amplified with the reference frequency of 500 kHz. The detected signal was then lock-in amplified with the reference frequency of 500 Hz. Tuning range from 1907 to 1895  $\text{cm}^{-1}$  was obtained by changing the operation temperature of the laser from  $-40$  to  $+40$   $^{\circ}\text{C}$ . A part of the absorption spectrum thus acquired is shown in Fig. 2. We clearly observed the R8.5, R7.5 and R6.5 lines of both  $^2\Pi_{1/2}$  and  $^2\Pi_{3/2}$  components of the fundamental vibration band of NO. The  $\gamma$ -type doubling was not resolved.  $\text{H}_2\text{O}$  lines were also observed as a contamination.

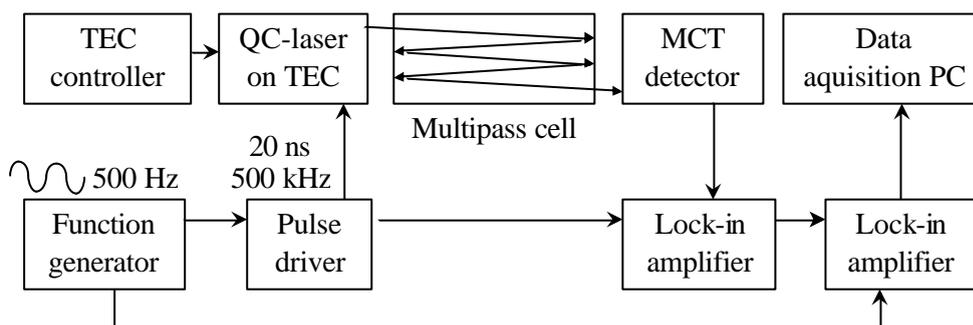


Fig. 1 Schematic diagram of the experimental setup.

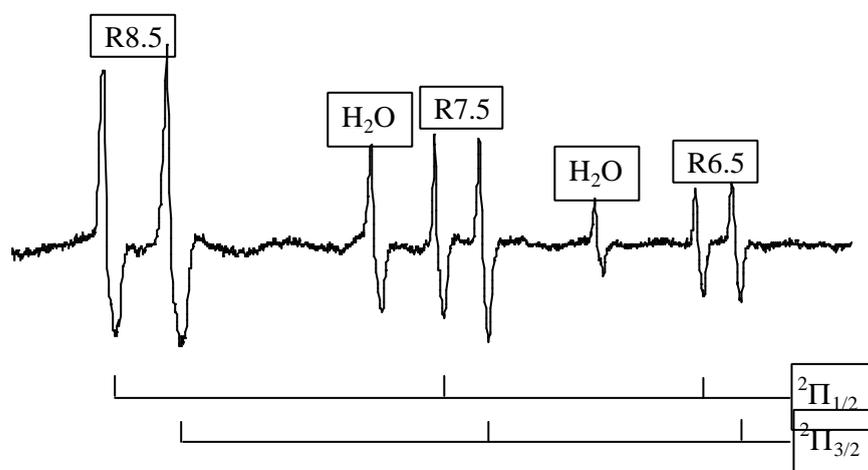


Fig. 2 Part of the absorption spectrum of NO and  $\text{H}_2\text{O}$  between 1907  $\text{cm}^{-1}$  (left) and 1898  $\text{cm}^{-1}$  (right).

# **PLASMA AND COMBUSTION DIAGNOSTICS**

## On recent progress in diagnostics of molecular plasmas using mid infrared diode-lasers in research and industry

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Within the last decade mid infrared absorption spectroscopy between 3 and 20  $\mu\text{m}$ , known as Infrared Laser Absorption Spectroscopy (IRLAS) and based on tuneable semiconductor lasers, namely lead salt diode lasers, often called tuneable diode lasers (TDL), and quantum cascade lasers (QCL) has progressed considerably as a powerful diagnostic technique for *in situ* studies of the fundamental physics and chemistry of molecular plasmas. The increasing interest in processing plasmas containing hydrocarbons, fluorocarbons, organo-silicon and boron compounds has lead to further applications of IRLAS because most of these compounds and their decomposition products are infrared active. IRLAS provides a means of determining the absolute concentrations of the ground states of stable and transient molecular species, which is of particular importance for the investigation of reaction kinetics.

Information about gas temperature and population densities can also be derived from IRLAS measurements. A variety of free radicals and molecular ions have been detected, especially using TDLs. Since plasmas with molecular feed gases are used in many applications such as thin film deposition, semiconductor processing, surface activation and cleaning, and materials and waste treatment, this has stimulated the adaptation of infrared spectroscopic techniques to industrial requirements. The recent development of QCLs offers an attractive new option for the monitoring and control of industrial plasma processes as well as for highly time-resolved studies on the kinetics of plasma processes.

The aim of the present contribution is threefold: (i) to review recent achievements in our understanding of molecular phenomena in plasmas, (ii) to report on selected studies of the spectroscopic properties and kinetic behaviour of radicals, and (iii) to describe the current status of advanced instrumentation for TDLAS in the mid infrared.

## Advanced near infrared diode-laser based in-situ sensors for full-scale technical combustion processes

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Even in the coming decades industrial combustion processes will remain to be the back bone of the world-wide energy supply. In order to keep the atmospheric damage to a minimum, it is of highest importance to realize clean and effective combustion processes and to optimize pollutant formation, conversion efficiency and plant life time. Simultaneously, for safety and economical reasons these processes have to be kept close to their optimal operation point -despite large power variations-, and problems like slagging or high temperature corrosion have to be avoided to keep the plant healthy and to reduce down times. Depending on fuel type and fuel variability this generates a strong need for innovative measurement techniques to permanently quantify educt, product and pollutant species concentrations, but also gas temperatures or gas residence times. Active control strategies also require sufficient temporal resolution and thus rapid sensor response. Furthermore sensor techniques are needed which are capable to monitor as close to the region of interest (reaction zone) as possible, in order to avoid the long gas transport times common in large technical combustion processes. Severe limitations are caused by the heterogeneity of the common analytical techniques available for industrial combustors and the systematic errors arising from the frequently used extractive gas sampling, mostly done in the relative cold flue gas. A monitoring of the combustion chemistry, i.e. the simultaneous detection and comparison of multiple combustion species is thus of only limited validity.

Diagnostic techniques for rapid, non-contact, and possibly calibration-free, *in situ* detection of multiple species and other combustion parameters (i.e. gas temperature, residence time) would therefore be highly advantageous, but were hardly achieved due to the very harsh boundary conditions in full scale combustion plants. By developing efficient strategies (i.e. using DSP based electronics) to correct the very strong optical and spectroscopic disturbances found in these large combustion chambers (up to 20m diameter, and 1000 MW thermal power) in combination with tools like an automatic beam alignment, we were able to close this gap and demonstrate numerous, robust, industry-qualifiable laser absorption sensors based on compact and inexpensive NIR telecommunication diode lasers. These sensors covered temperatures between 300 and 1800K, pressures of up to 15 bar and proved to be able to overcome very rapidly fluctuating, dust-related transmission losses of up to 99.99% or background radiation levels 10 times stronger than the laser signal. The development of self-calibrating, direct absorption strategies abandoned the need for sensors calibration thus reducing the overall cost for such sensors. With these capabilities we realized -in cooperation with industry- various, new, multi-parameter laser absorption spectrometers, which ranged from the simultaneous detection of the gas temperature and the four main species (O<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>O) in a 1000 MW<sub>th</sub> gas-fired plant, the first *in situ* CO-detection in a rotary kiln (using 2.3μm lasers)<sup>1</sup> and (using 1.5μm lasers) in the 20m-Ø combustion chamber of a 600 MW lignite-fired power plant, to a new radio-tracer free technique for a permanent online monitoring of the gas residence time distribution in high temperature processes. Recently we extended the technique to *in situ* sensors for fire suppression scenarios<sup>2</sup> and multiphase flows and demonstrated a simultaneous detection of O<sub>2</sub>, liquid phase and vapor phase H<sub>2</sub>O in dense water mist environments.

The talk will explain the principles behind direct *in situ* TDLAS, describe the disturbances found in such applications and the techniques and strategies developed to cope with such environments, and discuss several examples for *in situ* combustion sensors to show their capabilities.

1 V. Ebert, H. Teichert, P. Strauch, T. Kolb, H. Seifert, J. Wolfrum, "High Sensitivity In-Situ CO-Detection in a 3 MW<sub>th</sub> Rotary Kiln for Special Waste Incineration Using New 2.3 μm Distributed Feedback Diode Lasers", Proc. Comb. Inst. 30, 1611-1618 (2005)A. R. Awtry,

2 J. W. Fleming, and V. Ebert, "Simultaneous diode-laser-based in situ measurement of liquid water content and oxygen mole fraction in dense water mist environments," Opt. Lett. 31, 900-902 (2006)

## Measuring toxic heavy metals in combustion - challenges and approaches

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The increasing pressure on employing waste incineration for power generation makes the control of toxic heavy metal emissions into the atmosphere a high-priority concern in regard to human health and the environment. The EU Commission has defined a group of twelve metals (V, Cr, Mn, Co, Ni, Cu, As, Cd, Sb, Hg, Tl, Pb) the emissions of which have to be measured twice a year and kept below prescribed limits. In addition to this group of metals, popularly called “the European dirty dozen”, Mo and Zn are of similar concern. Biomass also contains varying amounts of heavy metal compounds, which may become released in biomass combustion processes.

The EU emission limits are a global 0.5 mg/m<sup>3</sup>n for the metals Sb+As+Pb+Cr+Co+Cu+Mn+Ni+V, a global 0.05 mg/m<sup>3</sup>n for Cd+Tl and 0.05 mg/m<sup>3</sup>n for Hg. It would be highly desirable to have instruments capable of on-line *in situ* measurements of these elements on the plant. However, the required sensitivity implied by the emission limits is a considerable challenge for spectroscopic measurements, for example. In spite of a decade of research no on-line instruments for multi-species heavy metal measurement have yet appeared on the market. At present compliance measurements of the heavy metal emissions have to be made using sampling and wet chemistry, involving considerable time delay between sampling and analysis.

This presentation will focus on heavy metal measurement approaches based on optical spectroscopy. A complete measurement of heavy metals present in stack gases would require accounting for aerosol particles, either consisting of or containing metals, metal salt vapours and elemental metals. A valid measuring technique needs to address the following issues:

- The detection limit
- Selectivity between different metals and metal compounds vs. global measurement of all metal species
- Differentiation between metal carrying particulates and vapour phase species vs. global measurement of all metal species.

In view of the multitude of metals that need to be measured and the multitude of compounds these metals may form, realisation of sensitive and selective single species measurement is already a very demanding task. Measuring global concentrations of a single metal species on-line requires evaporation of aerosol particles followed by dissociation of the metal compounds. In a technique called Excimer Laser Induced Fragmentation (ELIF) a UV laser beam dissociates metal compound molecules and generates excited metal atoms. The latter revert to the ground state emitting fluorescence radiation, the intensity of which is related to the concentration of the metal atoms in question. Another technique called Plasma Excited Atomic Resonance Line Spectroscopy (PEARLS) incorporates a thermal DC arc plasma to dissociate the compounds, whereupon the liberated metal atoms can be measured by atomic absorption spectroscopy, either using conventional spectral discharge light sources or a frequency-doubled external cavity diode laser. The merits and problems related to these two approaches will be discussed in the talk.

Spectroscopic measurement of metal salt vapours would lift the requirement for dissociation of the compounds. In some cases a single metal compound, like chloride, may be the dominating species. In such a case there is interest in being able to measure such a species, instead of measuring a multitude of compounds. Results of recent measurement of lead chloride using UV laser induced photoacoustic spectroscopy will be presented.

It seems that the main challenge in developing on-line *in situ* optical measurement of heavy metal emissions remains to be achieving the required detection limits for the compliance measurements without excessive system complexity.

## Spatially-resolved flame thermometry at kHz repetition-rates using diode-lasers

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Accurate measurements of flame temperature have been made with much faster temporal-resolution ( $< 500 \mu\text{s}$ ) and repetition-rate ( $>2 \text{ kHz}$ ) than has previously been possible with the diode-laser-induced fluorescence technique. This was done by using an optical chopper to switch rapidly between two wavelength-locked diode lasers. Experiments to determine precision and accuracy of these rapid measurements were performed in a laminar flat-flame.

Two extended-cavity diode lasers, emitting at wavelengths of 410 nm and 451 nm respectively, were used to perform temperature measurements by two-line atomic fluorescence. These lasers were used sequentially to probe the  $5^2P_{1/2}$ ?  $6^2S_{1/2}$  and  $5^2P_{3/2}$ ?  $6^2S_{1/2}$  transitions of seeded indium atoms, and the resulting fluorescence at 451 nm was detected through a pin-hole using a filtered photomultiplier tube. The ratio of the fluorescence line-strengths is related to the relative populations in the  $5^2P_{1/2}$  and  $5^2P_{3/2}$  indium energy states, and therefore to temperature.

In previous research [Hult et al. (2005)], the diode laser wavelengths were slowly scanned over the respective indium transitions. A novel method was required to achieve the substantial increase in the measurement repetition-rate reported here because the single-mode wavelength tuning rates of extended-cavity diode lasers are usually limited to a maximum of little more than 100 Hz. Instead the wavelengths of the diode lasers were locked to positions near to the peaks of the transitions, and a high-speed mechanical chopper wheel was used to switch rapidly between the two beams. The wavelength locking was done by directing weak reflections of the two laser beams through an indium hollow cathode lamp and using feedback control loops to stabilize the intensities of the transmitted beams.

The averages of the high-speed temperatures obtained in the laminar flame show good agreement with reference measurements performed at the same flow conditions, and the spread in the data corresponds to a precision of less than 2.5% (or  $\pm 40 \text{ K}$ ) for a measurement performed in  $500 \mu\text{s}$ .

J. Hult, I.S. Burns, C.F. Kaminski: "Two-line atomic fluorescence flame thermometry using diode-lasers", Proceedings of the Combustion Institute **30**, 1535-1543 (2005).

## **Detection of HCl in combustion chamber using 1.74 $\mu$ m DFB laser-diode**

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Adaptive control strategies which utilize the unique measurement capabilities afforded by laser diode absorption sensors were developed to measure and control the HCl concentration in a lot of different combustors. This paper describes the design of a laser diode sensor monitoring the HCl concentrations in combustion gases. The sensor is based on the measurement of the absorption of the particular reduced light produced by a laser diode emitting at 1.74  $\mu$ m, caused by interaction with HCl's molecules. The value of concentration is calculated from the measurement of the attenuation of the emitted laser beam. The detection process uses the double tone frequency modulation technique that allows an effective improvement of the signal to noise ratio.

The experiment, successfully conducted in a industrial combustion chamber, demonstrates the potential of laser diode absorption sensors when applied to processes of measurement and control within combustion chambers as well as to any process involving development of HCl. The experiment proves that the laser diode absorption sensors are particularly efficient in applications requiring remote and nonintrusively monitoring.

## Detection of $O_2(a^1D_g)$ molecules in inductively coupled $O_2$ plasma

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Inductively coupled oxygen plasmas are commonly used in the industry for depositing or etching of materials. Oxygen plasmas are unusual as they are electronegative plasmas, which results in a complex chemistry. We present measurements of the density of ground state  $O_2$  molecules,  $O_2(X^3\Sigma_g^-)$ , and  $O_2$  molecules in the first excited state,  $O_2(a^1\Delta_g)$ .

The  $O_2$  in the ground state was observed via transitions in the (0,0) band of the  $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$  electronic transitions around 760 nm. The detection limit was enhanced by the use of cavity enhanced absorption spectroscopy.

The  $O_2(a^1\Delta_g)$  was observed via transitions in the (0,0) band of the  $b^1\Sigma_g^+ \leftarrow a^1\Delta_g$  electronic transition around 1.9  $\mu\text{m}$ . The mid-infrared radiation was produced by difference frequency generation (DFG). In DFG the laser light of a cw Nd:Vanadate at 532 nm and a ECDL diode laser at 737 nm are mixed in a periodic poled lithium niobate (PPLN) crystal producing light around 1.9  $\mu\text{m}$ . The laser light is then directed into the ICP plasma chamber and the detection sensitivity is enhanced by using a multipass cell. The signal to noise ratio is further improved by applying wavelength modulation spectroscopy, which involves modulating the laser wavelength at relatively high (kHz) frequencies followed by demodulation of the absorption signal at the  $n^{\text{th}}$  harmonic of the modulation frequency.

## Trace gas detection using a novel cantilever-based photoacoustic spectrometer with multiplexed optical fibre-coupled diode-lasers and fibre amplification

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The operation of a novel cantilever-based photoacoustic (PA) spectrometer capable of gas detection at trace levels ( $\sim$  ppm) will be discussed. Pressure waves, resultant from diode laser-induced excitation of gaseous species of interest, cause movement of a micro-machined silicon cantilever. A compact Michelson Interferometer is used to measure the magnitude and the frequency of the cantilever movement. Simultaneous quantitative measurement of several species of interest is possible because the excitation of different analytes can be carried out at different frequencies. The cantilever movement contains several different frequency components which can be distinguished using the interferometer. Furthermore, the output from individual diode lasers can easily be combined and delivered to the sensing region using optical fibre-based technology. We will demonstrate the simultaneous frequency-divisional multiplexed detection of CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub> and CH<sub>4</sub> using four fibre-optically coupled distributed feedback diode lasers, and show how the cantilever sensitivity at different frequencies can be used to compensate for the different absorption strengths of the species of interest.

PA signals are directly proportional to the optical power incident upon the sample. In experiments carried out on single component gas samples, an Erbium-doped fibre amplifier (EDFA) has been used to increase power at the excitation region and a detection limit of 14.5 ppb was achieved for C<sub>2</sub>H<sub>2</sub> in N<sub>2</sub> at 277 mbar, using 1.17 W of radiation centred at 1534.086 nm. The best-case sensitivity (2s) of the spectrometer was  $2.2 \times 10^{-9} \text{ cm}^{-1} \text{ W Hz}^{-1/2}$ .

Investigations are currently underway into the feasibility of combining frequency-divisional multiplexing and EDFA amplification.

R.E. Lindley, A.M. Parkes, K. A. Keen, E.D. McNaghten and A.J. Orr-Ewing: "A sensitivity comparison of three photoacoustic cells containing a single microphone, a differential dual microphone or a cantilever pressure sensor", *Appl. Phys. B* **86**, 707-713, (2007).

## **Development of a Multiple Gas Analyzer using Cavity Ringdown Spectroscopy for use in Advanced Fire Detection**

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A portable cavity ringdown spectrometer was used to detect effluents from small test fires in the Fire Emulator/Detector Evaluator (FE/DE) Facility at in the Building Fire and Research Laboratory at the National Institute of Standards and Technology (NIST). The output from two fiber-coupled DFB lasers is combined and each laser detects two of the four target gases. Fire effluents were extracted from these test facilities during smouldering and flaming fires and measurements of CO, CO<sub>2</sub>, HCN, and C<sub>2</sub>H<sub>2</sub> were obtained every 25-30 seconds. In the FE/DE test, peak concentrations of the gases from smouldering paper were: 440 ppm CO, 1740 ppm CO<sub>2</sub>, 550 ppb HCN, and 461 ppb C<sub>2</sub>H<sub>2</sub>.

## In-situ monitoring of silicon plasma etching using a quantum cascade laser arrangement

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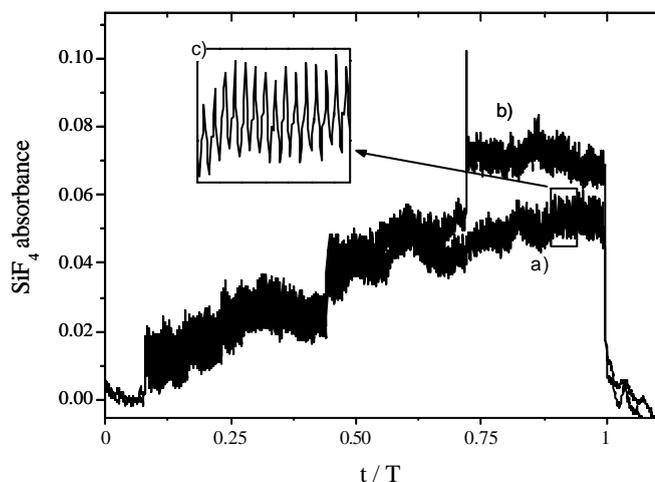
Molecular plasmas in the low as well as in the high pressure range are of increasing importance not only for fundamental research but also for plasma processing and technology. Thin-film deposition, semiconductor processing, the destruction of toxic compounds, surface cleaning and treatment are established applications of plasmas.

For the first time, in industrial etching plasmas used for semiconductor processing, concentrations of the precursor gas  $\text{NF}_3$  and of the etch product  $\text{SiF}_4$  were measured on-line and *in situ* (figure 1). For this purpose a new compact diagnostic arrangement, the Q-MACS Etch system, which is based on quantum cascade laser absorption spectroscopy and interferometry has been designed and constructed. The Q-MACS Etch system provides high sensitivity and long term stability, because additionally to the measuring channel used in the plasma chamber, a reference and a pulse normalization channel are included. For simple operation and avoiding of open optical pathways an optical coupling with a MIR fibre to the plasma reactor has been realized. Using internal reflections, provided by a retro-reflector, only one optical access window is necessary. Adapted to clean room requirements and for a low maintenance level thermoelectric cooled detectors are used on board.

With Q-MACS Etch the etch rates of  $\text{SiO}_2$  layers and of the silicon wafer were monitored. The QCL system has shown its capabilities for plasma etching endpoint detection and for mass flow controller calibration. The experiments have been performed in an industrial dual frequency capacitively coupled magnetically enhanced reactive ion etcher (MERIE), which is a plasma reactor developed for DRAM technologies.

To achieve a sufficient accuracy of concentration measurements the absorption cross sections of  $\text{NF}_3$  and  $\text{SiF}_4$  have been determined. The temperature and pressure dependence of the cross sections have been proven. In the spectral range  $1028 \pm 0.3 \text{ cm}^{-1}$  the absorption cross sections of  $\text{SiF}_4$  and  $\text{NF}_3$  have been determined to be  $\sigma = 7.7(\pm 0.7) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  and  $\sigma = 8.7(\pm 0.8) \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ , respectively.

The first application of a quantum cascade laser arrangement for monitoring of industrial etch processes has opened up a challenging new option for control of demanding semiconductor production. Focused on sensitive and fast concentration measurements of molecular key components, while ensuring compactness, robustness and long term stability, this new class of process control equipment has the potential to become implemented also into other fields of plasma technology.



**Figure 1.**  $\text{SiF}_4$  absorbance monitoring using QCLAS for: a) a complete plasma etching process; b) complete plasma etching process with injection of 2%  $\text{SiF}_4$ ; c)  $\text{SiF}_4$  concentration variation due to changes of the magnetic field. The experiments were performed with a process wafer.

## **Sensors network system for in-line analysis and disposal of CO<sub>2</sub> laser steels cutting fumes**

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During CO<sub>2</sub> laser cutting of metals, the absorbed energy by the material in the cutting zone, corresponding to the laser focus position, is converted in heat. If this heat is higher than the capacity of the base material to diffuse heat by thermal diffusion, temperature in the laser-material interaction zone will rapidly increase, so causing material melting and partial vaporization. Fumes generated by metals laser cutting are mainly constituted by particulate, which constituent particles mainly show a spherical geometry, and about 90% of them has a less than a micron diameter.

This work deals with the study of toxicity and environmental aspects connected with AISI304 e 25CrMo<sub>4</sub> steels CO<sub>2</sub> laser cutting, and with the design and development of a system for in-line sampling and analysis of emissions, to be integrated in industrial laser cutting workstations.

In a first phase of activities, fumes produced during laser cutting processes of metals were analysed, in order to determine their composition in terms of toxicity and environmental impact. Obtained results showed for both steels a very high production of air suspended particulate, and a not critical amount of gaseous products.

Being known fumes composition, a system based on a sensors network has been developed. The aim of this system is to perform in-line analysis of fumes by the evaluation during cutting processes of their composition, toxicity and environmental impact, in order to define how to dispose them avoiding possible risks for workers and environment, according to international laws and rules in the field of safety.

## **Laser-diode sensor for the measurement of temperature under different pressure conditions**

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Adaptive control strategies which utilize the unique measurement capabilities afforded by diode-laser absorption sensors were developed to measure and control the gas temperature in a lot of different combustors. This paper describes the design of a diode laser sensor monitoring the temperature in combustion gases. The sensor, which employs a multiple fixed wavelength absorption strategy, has the potential to monitor the temperature under different conditions of the environmental pressure. The sensor uses the variation in the ratio between two selected H<sub>2</sub>O absorption line strengths for temperature measurement in combustion systems. The experiment, successfully conducted in realistic combustion systems, illustrates the potential of diode-laser absorption sensors for improved measurement and control of combustion and other processes involving temperature flows. The experiment proves that the diode-laser absorption sensors are particularly efficient in applications requiring remote and nonintrusively monitoring.

## Time resolved absorption spectroscopic studies on the kinetics of a pulsed DC discharge using quantum cascade lasers

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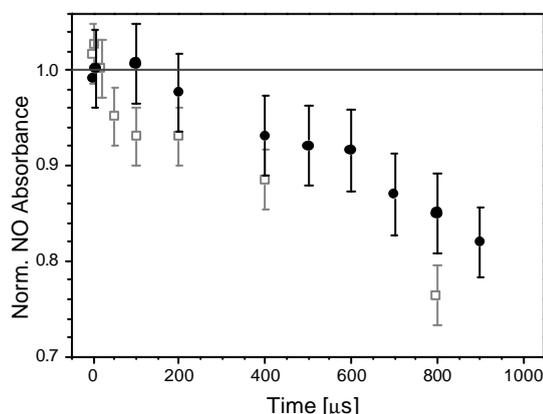
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One of the key issues when studying plasma processing for gas treatment is to make sure that no undesirable by-product results from the process. Among them, NO<sub>x</sub> are readily produced in air plasmas. Since a few years mid-infrared absorption techniques are increasingly being used for quantifying studies of phenomena related to NO<sub>x</sub> production and removal in plasmas [1]. Pulsed plasmas are preferred when intending a higher efficiency of the processes. Using cryogenic cooled lead salt lasers, a sufficient time resolution of less than a few hundred microseconds has been barely achieved for *in situ* measurements to investigate the temporal evolution of the plasma pulses.

Within the last few years a new light source in the infrared spectral range has become available: quantum cascade lasers (QCL) exhibiting high output power combined with single-frequency operation. In order to function near room temperature commercially available QCLs are usually operated in a pulsed mode with low duty cycles of a few percent. When using pulse-on times for the laser in the order of 100 ns an infrared spectrum can be gained within this period due to the inherent sweeping of the laser frequency [2]. This *intra pulse* mode of operation requires fast thermoelectrically cooled detectors to record the spectra on the nanosecond timescale.

Based on this new approach for fast *in situ* plasma diagnostics an experiment to study the time decay of NO in single discharge pulses of 1 ms duration has been designed. In the centre of interest was the kinetics of the destruction of NO in a pulsed DC discharge of a 2.66 mbar Ar/N<sub>2</sub> mixture containing 0.91% of NO. The QCLAS measurements have been performed using a compact quantum cascade laser measurement and control system (Q-MACS) [3]. Applying a delayed trigger scheme for the QCL opened up the field for time resolved studies limited only by the pulse-on time of 90 ns for the QCL.

Under low gas pressures the *intra pulse* mode for QCLs is naturally accompanied by the “rapid passage effect” [4] leading to falsified concentrations deduced from the spectra. Therefore a calibration procedure was used and evaluated to obtain values for the absorbance of NO by integrating over the absorption line at 1894.15 cm<sup>-1</sup>. Experiments during one plasma pulse have been performed for flow and static gas conditions (fig. 1). The comparison of the time evolution for these two cases, supported by experiments with successive pulses under static conditions combined with simplified model calculations enabled the analysis of the dynamics of the plasma heating which is about 70 K.



**Figure 1.** NO absorbance during one plasma pulse for static (full) and flow (open) gas conditions.

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## **Molecular oxygen sensor based upon direct absorption and a vertical-cavity surface-emitting laser at 765 nm**

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Optical sensing of molecular oxygen is of interest in monitoring and control of gas emission in industrial processes such as combustion. On-line, real time, non-extractive O<sub>2</sub> sensing across a stack, or furnace would be very advantageous for the control of combustion efficiency and the suppression of dioxin generation in incinerators. Despite the demonstration of different techniques such as direct absorption, balanced detection, wavelength-modulation spectroscopy (WMS) and cavity enhanced absorption spectroscopy for oxygen detection, only sensors based on direct absorption and WMS have been demonstrated to be suitable for harsh industrial applications. However, a detector based on direct absorption measurement is insensitive to gas pressure and flow content, whilst a sensor based upon WMS is sensitive to gas pressure, temperature, flow content and an instrument-specific parameter modulation index. Here, we describe an optical sensor based on a tunable vertical-cavity surface-emitting laser (VCSEL) tuned over a centre wavelength of 764.74 nm and a direct absorption spectroscopy technique. Measurements of the sensitivity of the detector, linearity, the effect of sample gas temperature, cross-sensitivity and stability have been carried out at the facilities of the National Physical Laboratory. Results of the tests will be reported including an analysis of the measurement accuracy of the gas temperature using an optical sensor with a VCSEL at 760.5 nm.

# **AIRBORNE ATMOSPHERIC RESEARCH**

## **Airborne atmospheric research in Europe : CARIBIC and HALO**

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In CARIBIC a well-instrumented (19 sensors) airfreight container (weight: 1.5 t) for the measurement of atmospheric trace gases and aerosol particles is utilized onboard a passenger aircraft (Airbus A340-600) of Lufthansa. Eleven institutes from six European countries are involved. Flight routes are between Germany, South America and South-east Asia, currently on a monthly basis. Besides samplers for air and aerosol, diverse instrumental techniques such as uv photometry, uv resonance fluorescence, mass spectrometry, remote sensing differential optical absorption spectrometry, laser and broad-band absorption spectrometry, optical particle counters etc. are applied. HALO (a G550 business jet from Gulfstream) is the new German research aircraft starting its operation in 2009. A multitude of different in-situ and remote sensing instruments are proposed.

The talk will give an overview on the two projects with emphasis on the laser absorption measurements applied.

## Airborne measurements of HCHO, CO and CH<sub>4</sub> using cw quantum cascade laser spectroscopy

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Recent laboratory and field studies demonstrated that replacing lead-chalcogenide tuneable diode lasers by cw operated quantum cascade lasers (QCL) results in sensitivity improvements of mid-IR TDLAS systems by a factor 2 to 3 (Kormann et al., 2005). Therefore, the MPI-C three laser TRacer In-situ Tdlas for Atmospheric Research (TRISTAR) was equipped with 3 QCL emitting at 1268.98, 2158.30, and 1759.72 cm<sup>-1</sup> to measure CH<sub>4</sub>, CO and HCHO, respectively. In October 2005 the modified TRISTAR instrument was installed on a Lear Jet 35A as part of a scientific payload to study the photochemistry over the tropical rainforest in South America during the GABRIEL campaign. A second deployment was during fall 2006 as part of the HOOVER campaign to study HO<sub>x</sub> and its precursors in the upper troposphere over Europe. This project will be continued in summer 2007 to study the influence of convection on the photochemistry of the tropopause region. The performance of the instrument during these airborne campaigns was examined for the three species and precisions for CO and CH<sub>4</sub> were measured in the field to be 0.5% and 0.8% respectively (2 $\sigma$ ). The 1 $\sigma$  detection limit for HCHO was ~500 pptv for a 2 second average, while post-flight signal averaging over a 2 minute time interval resulted in a 150 pptv detection limit.

Kormann, R., Königstedt, R., Parchatka, U., Lelieveld, J., Fischer, H.: QUALITAS: A mid-infrared spectrometer for sensitive trace gas measurements based on quantum cascade lasers in CW operation, Rev. Sci. Inst., **76**, 075102 (2005).

## **Airborne measurements of atmospheric trace species using diode-laser absorption spectroscopy**

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Measurements of atmospheric trace gases CO, CH<sub>4</sub>, N<sub>2</sub>O, and H<sub>2</sub>O(v) have been made by our group using wavelength-modulated diode laser absorption spectroscopy aboard several aircraft over the past 30 years. These measurements have contributed to the understanding of atmospheric chemistry, long range transport, and cloud and aerosol processes. They have also contributed to the validation of both computer models which describe the atmosphere and the satellite instruments which serve to provide a larger scale picture of that atmosphere. Over the 30-year period during which we have made these measurements, large advances have been made in the technology which underpins these efforts, and our instruments have evolved over that period to take advantage of those advances.

We describe the instruments used to make these measurements, including calibration, control methodology, data collection, and on-the-fly data analysis used to convert signal levels to concentrations in-flight. We also describe the process of data reduction used post-flight to remove artifact signals which may be present.

We discuss the use of our data for the purposes of source characterization, and model and satellite validation, and we give examples of the typical precision with which we can characterize different types of air masses. We also describe how we make use of other trace species measurements to aid in that characterization.

## **Mission to Mars and the Earth's stratosphere: laser applications to planetary and atmospheric research**

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Advances in semiconductor laser technology have enabled broad application of tunable laser spectroscopy to Earth and planetary applications, specifically for the *in situ* detection of gases that are atmospheric or evolved from mineral and soil samples.

Carbon, oxygen and hydrogen isotope ratios in atmospheric and evolved gases are recognized indicators of atmospheric escape, sources and sinks, and possible biogenic origin. Several examples of laser isotopic analysis will be presented, beginning with precious gem analysis, medical breath and diet diagnosis. Water isotope analysis will be shown to reveal the origin of tropical cirrus clouds in Earth's upper atmosphere and trace atmospheric transport. NASA's Mars Science Laboratory (MSL) Mission will be described with an emphasis on laser instrumentation to perform *in situ* rock analysis and to measure carbon, hydrogen and oxygen isotopes in Martian gases and soils to characterize habitability and search for life on Mars. The MSL mission goals will be contrasted with those of ExoMars, and the potential role of laser instrumentation on Europa, Titan and lunar missions described.

The research described was carried out by the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA).

## Demonstration of an ultra sensitive airborne difference frequency spectrometer: performance characterization and ambient measurements of Formaldehyde

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An airborne, mid-IR difference frequency spectrometer system (DFG) for ultra sensitive measurements of formaldehyde is presented. Airborne performance yielded sensitivities of  $\sim 20$  pptv (Absorbance  $\sim 7 \times 10^{-7}$ ). The measurement of many atmospheric trace gases require sensitive, selective and versatile instruments capable of measuring mixing ratios of less than 100-parts-per-trillion on airborne platforms. Carrying out such measurements are very challenging, as airborne platforms not only experience vibrations, and accelerations, but also undergo large swings in cabin pressures and temperatures. The DFG spectrometer, presented here, incorporates a new laser source in place of the cryogenically-cooled lead-salt tunable diode laser (TDL) [1]. The new spectrometer is significantly enhanced in terms of reduced weight and size, elimination of cryogenics and improved robustness compared to our present airborne TDL spectrometer. The DFG technology also shows potential for better sensitivity, autonomous operation and multi-species capability in the near future. Here we review our latest DFG spectrometer design and discuss the performance during three airborne field campaigns. To our knowledge, this is the first time a DFG spectrometer has been employed on an airborne platform.

The deployed airborne spectrometer is based on our laboratory prototype design [2, 3], which generates  $\sim 3.5 \mu\text{m}$  by mixing a DFB diode laser at 1562 nm and a DFB fiber laser at 1083 nm in a periodically poled LiNbO<sub>3</sub> crystal. The laboratory performance typically achieved a sensitivity of 13 pptv for 60 s averaging. In comparison to the laboratory instrument, the airborne one is enhanced in several areas, including higher mechanical stability in the transfer optics, the impinging power miss-match onto the detectors is addressed using a beam splitter with a reflectance coating, the PPLN crystal resides in an improved temperature controlled environment and finally, vibration and acceleration induced instrument background noise is minimized applying vibration damping techniques. The whole instrument ( $\sim 300$  kg), containing the DFG spectrometer, the gas handling system, the air conditioning system and the computer system, is housed in two aircraft racks occupying  $1 \times 1.5 \text{ m}^2$  floor space.

The instrument performance characteristics were assessed during three consecutive airborne field missions; MIRAGE, IMPEX, TEXAQS2006 utilizing NCARs C-130 and NOAAs P-3 airborne platforms. During a total of  $\sim 300$  mission flight hours the instrument produced scientific data 60%, 80% and 95% of the time, respectively for the different campaigns. In the beginning of the first deployment (MIRAGE), excessive cabin temperatures, large temperature variations and severe aircraft vibrations exceeded the instrument operational design range. However, by improving fiber management, fiber amplifier operation, as well as increasing the cooling capacity of the system, the performance was continuously improved throughout the campaigns. Attention to these issues improved the performance from 3 ppbv to  $\sim 20$  pptv and increased the instrument stability time from a few seconds to a minute. During TEXAQS2006 the instrument was operated semi-autonomously only requiring minimal user intervention at the beginning and end of each research flight. Fully autonomous operation is a desirable feature of the next generation instrument for advanced airborne platforms (Gulfstream G-V and UAV).

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## **A pulsed QC-laser based dual-spectrometer instrument for fast response, high accuracy, high precision airborne measurements of CO<sub>2</sub>, CO, CH<sub>4</sub> and N<sub>2</sub>O**

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CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O are the most important long-lived greenhouse gases in the earth's atmosphere. CO indirectly affects the radiative balance by reducing the oxidative capacity of the atmosphere through OH scavenging. Simultaneous measurement of these trace gases allows characterization of air parcels (e.g. tropospheric/stratospheric), determination of transport rates, and estimation of fluxes using inverse modeling techniques. As these species are long lived (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) or moderately long lived (CO), their atmospheric concentrations show only small variations, typically of a few percent, particularly above the boundary layer. Fractional accuracies and precisions on the order of 0.1% or better are thus required for these measurements to be meaningful.

The new instrument has been designed, built and tuned to meet these requirements. The instrument encompasses two quantum-cascade laser (QCL) based spectrometers: a single pass dual cell based spectrometer for CO<sub>2</sub>, and a dual laser, astigmatic mirror multipass cell based spectrometer for CO, CH<sub>4</sub> and N<sub>2</sub>O. The spectrometers use thermo-electric cooled (TEC), pulsed (1 MHz) DFB QC-lasers operated with short electrical pulses (~12 ns FWHM), and at low currents above threshold in order to minimize spectral chirping and ensure single mode operation. Direct absorption spectra are obtained by modulating (3-10 kHz) the QCL temperature with a sub-threshold current ramp. In both spectrometers, QCL beams are split into sample and reference beams. Real-time normalization of sample spectra by reference spectra eliminates the effect of pulse-to-pulse variations. The normalized spectra are real-time averaged and non-linearly fitted to retrieve mixing ratios at 1 Hz. The laser pulses are detected with dual LN<sub>2</sub>-cooled InSb (CO<sub>2</sub>) or HgCdTe (CO, CH<sub>4</sub>, N<sub>2</sub>O) detectors.

The CO<sub>2</sub> QCL spectrometer is based on differential absorption by the nearly temperature-independent fundamental rovibrational transition at 2320 cm<sup>-1</sup> through 10-cm dual absorption cells (sample and reference) operated at 50 torr. The demonstrated precision for this instrument is ~50 ppbv·Hz<sup>-1/2</sup> for  $|\Delta[\text{CO}_2]| < 50$  ppmv.

The dual QCL spectrometer is based on absorption by fundamental transitions through a low weight, fast response (~1 s) 76-m astigmatic mirror multipass Herriot cell operated at 50 torr. The demonstrated 1-s precisions for CO, CH<sub>4</sub> and N<sub>2</sub>O are ~0.4 ppbv, ~0.6 ppbv, and ~0.06 ppbv, respectively, which correspond to absorbance precisions on the order of ~3·10<sup>-5</sup> Hz<sup>-1/2</sup>.

Both spectrometers are vibrationally isolated and housed in temperature-controlled enclosures (a pressure vessel in the case of CO<sub>2</sub>). The humidity of sample and calibration gases is conditioned to less than 100 ppmv prior to detection in order to limit density variations to less than 0.01%. In order to ensure accuracy, we do frequent zeroing (~4-6 h<sup>-1</sup>) and frequent calibration with low- and high-span gases (~2-4 h<sup>-1</sup>), and sparingly with long-term standards (~0.5 h<sup>-1</sup>), all calibrated against NOAA primary standards.

The functionality of the spectrometers is enhanced by packaging in modular units that can be re-distributed to accommodate to various aircraft platforms. The instrument consumes 700 W (continuous) and weights 110 kg.

We present further instrumental details and measurements, including preliminary results from the first airborne deployment of the instrument on board of NASA's WB-57 during the TC4 mission.

## In-flights performances of a tunable diode-laser spectrometer for airborne measurement of carbon monoxide during tropical campaigns

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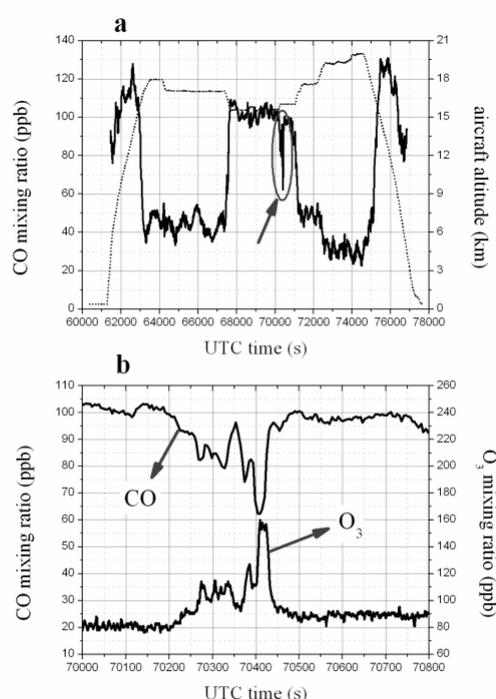
The design, the performances and examples of the field deployment results of the instrument COLD (Cryogenic Operated Laser Diode), a mid-infrared Tunable Diode Laser Spectrometer for trace gas detection in the upper troposphere-low stratosphere (UT\LS), are presented. The COLD instrument is designed, and fully qualified, for operation on a high altitude aircraft, specifically for the stratospheric aircraft Miyashichev M55 Geophysica, able to operate routinely at an altitude up to 21-22 km. Performances achieved so far in-flight operation are a sensitivity of few ppb with a time resolution of 4 s.

In the last three years COLD was optimized for in situ measurements of Carbon Monoxide (CO) in the UT\LS and in 2005-2006 it was successfully employed during three tropical campaigns: TROCCINOX-2 (Tropical Convection Cirrus and Nitrogen Oxides Experiment) in Brasil, SCOUT-O3 (Stratospheric Climate Links with Emphasis on the Upper Troposphere and Lower Stratosphere) in Australia and AMMA (African Monsoon Multidisciplinary Analysis) in Burkina Faso.

The results obtained during the campaigns are presented and discussed to demonstrate the in-flight performances of the instrument.

When in situ measurement of trace gases are performed from an aircraft having a cruise speed of hundreds m/second, a fast response is necessary. In particular, the COLD time resolution of few seconds makes possible the resolving of fine structures of few tens of km, as shown in Fig.1. An example of CO fast structure (included in the circle of Fig. 1a and zoomed in Fig.1b) was observed during TROCCINOX-2 campaign and was confirmed by ozone (O<sub>3</sub>) concentration measurements performed by the FOZAN (Fast OZone ANalyser) instrument. The fast CO decrease, for a constant altitude of about 16 km, is a clear indicator of direct injection of air from the LS into the UT. For a deeper analysis of these fine structures, transport models of very short time-scale are needed.

Finally, CO vertical profiles and correlation-plots between CO and O<sub>3</sub> are showed and analysed to make a comparison between different campaigns. Irreversible mixing of stratospheric and tropospheric air, connected with strong convection activity, is clearly identified by the analysis of the CO-O<sub>3</sub> correlation.



**Fig.1** - TROCCINOX-2 flight of the 5th of February 2005, from Araçatuba (Brazil). **a)** CO mixing ratio (solid line) and aircraft altitude (dash line) vs universal time. The zoom of the CO structure, included in the circle and pointed with the arrow, is shown in Fig. b. **b)** Fine structure: CO and O<sub>3</sub> mixing ratio vs universal time.

## Development of a small balloon-borne instrument for the study of water vapor in the upper troposphere and lower stratosphere

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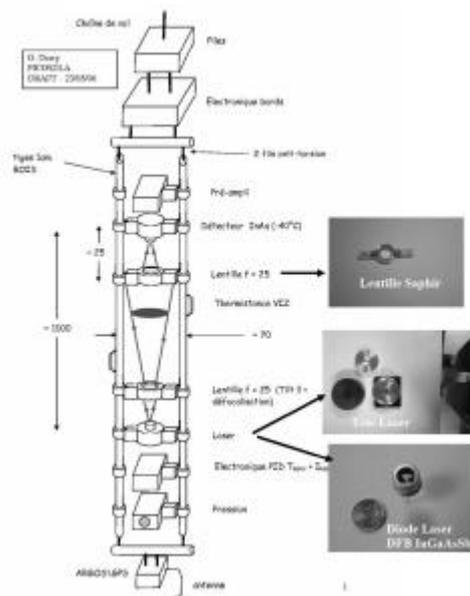
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Water vapor is one of the major component of the climatic system. Chemical or dynamic process which control water vapor in the upper troposphere (UT) and lower stratosphere (LS) are not well known in particular in tropical regions. This unawareness comes mainly from the difficulty to measure water vapor in the UT-LS in particular as temporally and spatially localized process are of interest. Meteorological balloon-borne measurements may be interesting for these observations as they will permit to increase the frequency of the launchings and also to make these launchings near the convective cells.

In the 2.7  $\mu\text{m}$  spectral range, new-generation multi-quantum wells room-temperature laser diodes are now available. High rovibronic transitions of  $\text{H}_2^{16}\text{O}$  are featured in this spectral region. These lasers have been tested in Reims and their spectral emission properties are very good. They permit to develop low weight sensors (< 2 kg) that can be used under meteorological balloons (RAVEN type 500  $\text{m}^3$ ). A new sensor called Pico-SDLA makes possible the in situ measurement of water vapor in the UT-LS with the same performance than SDLA and micro-SDLA (100 ms temporal resolution, absolute uncertainty less than 5%, measurement dynamics of 4 orders of magnitude). The sensor is equipped with an UHF emitter-receptor at 400 MHz with GPS and GSM. This system is totally independent. The expanded view of this instrument is presented in the figure.



This project covers many scientific objectives. The in situ study of tropical water vapor like for HIBISCUS and SCOUT campaigns is the first one. In particular Pico-SDLA may be the main instrument of a tropical campaign in Bauru in March 2009. Secondly the study of long-term tendencies of stratospheric water vapor is very interested. The autonomy of the system makes possible its use from meteorological stations for regular soundings of the atmosphere from small balloons. Moreover the Pico-SDLA instrument may equipped in permanence some other balloon instruments to give an in situ water vapor measurement. Finally as Pico-SDLA is a simple instrument, it may be used on planes, for example on French research planes for a high temporal resolution measurement of water vapor (100 Hz) in the low and high troposphere.

## **Argus: A compact, dual channel, mid-IR tunable diode laser spectrometer for use on multiple airborne platforms**

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The Argus instrument was originally developed for use on uninhabited aerial systems (UAS). Due to its small size (40cm x 30 cm x 30 cm) Argus has been integrated on many platforms for stratospheric and tropospheric research. For example, it has been deployed on balloons up to 30 km, on the NASA ER-2 aircraft to the North Pole, on the WB-57 to the equator and most recently on the Altair and Ikhana UAS during NASA fire missions.

Argus is a dual channel mid-IR tunable diode laser spectrometer operating at 3.3  $\mu\text{m}$  and 4.5  $\mu\text{m}$  and has been used to measure  $\text{N}_2\text{O}$ , CO and  $\text{CH}_4$ . The two lead salt laser diodes are mounted in a custom liquid nitrogen dewar along with the detectors. The two beams are focused into a Herriott multi-pass cell with 36 m path length and then collected on mercury cadmium detectors. The lasers are rapidly swept over the spectral lines of interest. To further increase signal to noise, the lasers are modulated and custom lock-in amplifiers are used for second harmonic detection.

Argus was involved in the first *in-situ* discovery of boreal forest fire smoke deep in the stratosphere during the NASA CRYSTAL-FACE mission in 2002. More recently Argus participated in flights in support of the validation of the Tropospheric Emission Spectrometer (TES) instrument and the Microwave Limb Sounder (MLS) instrument, both satellite instruments on the NASA Aura satellite.

This paper describes in detail the versatile instrument design that allowed easy integration on the different platforms and discusses the results obtained during recent missions.

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J. Lopez *et al.*: "TES carbon monoxide validation during two AVE campaigns using the Argus and ALIAS instruments on NASA's WB-57F", *Journal of Geophysical Research*, submitted (2007)

## **Airborne in-situ trace gas measurements during HOOVER with the three laser quantum cascade laser absorption spectrometer TRISTAR**

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The Quantum Cascade Laser Absorption Spectrometer TRISTAR is a three channel instrument with the capability of measuring four different species. Its employment and performance during the aircraft based measurements of the HOOVER campaigns are described. We present first results of the measurements during HOOVER and the principle of measuring two species with one laser. This work also focuses on signal processing algorithms of TRISTAR and data evaluation with the software IGOR Pro. IGOR Pro is a scientific graphing, data analysis, image processing and programming software. It allows post flight data evaluation including processing of the ambient, background and calibration spectra regarding background subtraction and filtering of high frequency noise with Fast Fourier Transformation (FFT).

## **Performance and design of TRISTAR: A compact three laser quantum cascade laser spectroscopy instrument for airborne measurements**

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TRISTAR (Tracer In-Situ Tdlas for Atmospheric Research) is a robust system designed for use in a limited space with little or no onboard operator input. TRISTAR has been recently deployed on a 35 A Lear Jet measuring CO, and HCHO during the GABRIEL campaign. The design and the performance of the instrument during this field campaign will be discussed. The performance of the instrument during this airborne campaign was examined for the two species and the precision for CO was determined to be 0.5% ( $2\sigma$ ). The detection limit ( $1\sigma$ ) for a 2 second average for HCHO was ~500 pptv, which was reduced to 150 pptv for a 2 minute time interval average. The improvements due to temperature and pressure stabilization will also be discussed.

## **Airborne Measurements of CO and NH<sub>3</sub> during ICARTT 2004 using TDLAS**

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ICARTT, International Consortium for Atmospheric Research on Transport and Transformation, occurred during the summer of 2004. The Canadian component focused on Transportation and Transformation in Clouds. The inaugural flight of a 2 channel airborne TDLAS from York University occurred during this study aboard a Convair 580 operated by the National Research Council of Canada. Using the two-channel instrument, CO and NH<sub>3</sub> were measured at 2095 and 964.4 cm<sup>-1</sup> respectively with a 15 second cycle time with further averaging of NH<sub>3</sub> over appropriate time periods spent within and outside of clouds. Measurements of CO using TDLAS are compared with those obtained by a vacuum ultraviolet fluorescence instrument. The precision of the TDLAS measurement of CO was determined to be between 0.5% to 1%. Features of the instrument design and performance will be described.

## CO<sub>2</sub> laser-based trace gas ethylene detector for airborne measurements over Texas

S. te Lintel Hekkert<sup>1\*</sup>, J. De Gouw<sup>2</sup>, C. Warneke<sup>2</sup>

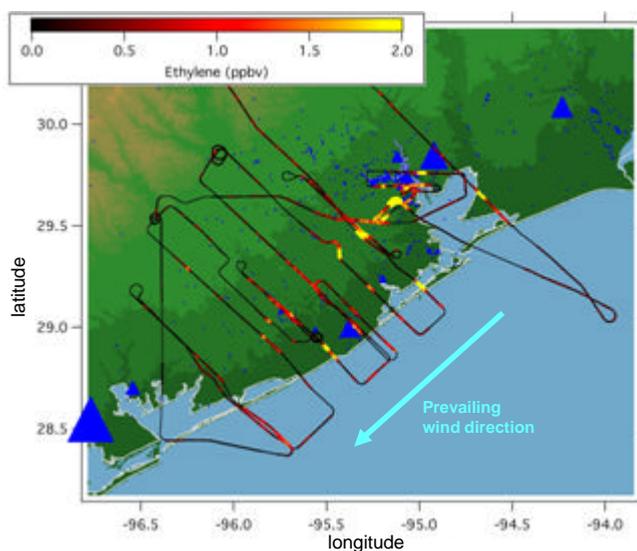
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During August-October 2006 the highly sensitive photo acoustic ethylene detector (ETD-300), developed by Sensor Sense B.V. has been involved in The Texas Air Quality Study, [TexAQS II](#). The aim of this study was to produce scientific information and data for better understanding of the causes of air pollution in Texas. State of the art trace gas detectors were used inside several aircraft and a research vessel for monitoring various volatile organic compounds (VOCs) responsible for photochemical pollution and regional haze during the summertime in Texas. Several years ago, researchers from the NOAA Earth System Research Laboratory found indications that ethylene plays an important role in the ozone chemistry in Houston. For monitoring the ethylene emissions in the atmosphere while cruising in an aircraft, special features are mandatory from an ethylene detector, namely high sensitivity, fast response time and capability to work in harsh conditions.

Sensor Sense successfully redesigned their standard ethylene detector to fulfil these requirements, and has developed an ethylene detector able to measure on-line about 300 pptv of ethylene within a 5 sec. time scale, extremely stable in critical conditions (i.e. excessive vibrations, temperature changes and pressure variations). Together with researchers from NOAA a gas sampling system was designed in order to be independent of pressure fluctuations when the plain was changing altitude. Characteristics of the ethylene detector and the sampling system will be presented. Data on ethylene emission measured from the aircraft during this campaign will be presented and compared with the emission of other VOCs in the atmosphere.



## TDLAS: an instrument based on near-infrared diode-laser technology for the in-situ monitoring of the Martian atmosphere

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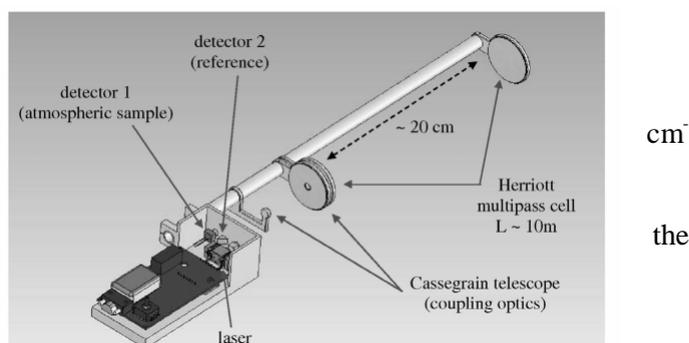
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A near infrared diode laser spectrometer, called TDLAS which stands for “Tunable Diode Laser Absorption Spectrometer”, is presently under development in our laboratory with the support of the CNES and the CNRS. The sensor aims at providing highly-resolved in situ measurements of H<sub>2</sub>O and CO<sub>2</sub> isotopologues in the Martian lower atmosphere. Two versions of the TDLAS sensor have been previously discussed: a lightweight (~ 150g) version measuring H<sub>2</sub><sup>16</sup>O and <sup>12</sup>C<sup>16</sup>O<sub>2</sub> at 1.88 μm [1] and a second version providing a further determination of two CO<sub>2</sub> isotopologues, <sup>13</sup>CO<sub>2</sub> and <sup>18</sup>O<sup>12</sup>C<sup>16</sup>O, at 2.04 μm [2], but with the cost of a higher weight for the sensor (500g). The principle of TDLAS is rather simple; the laser beam is propagated in the open atmosphere over a one-meter absorption path length, where it is partially absorbed by ambient molecule. The amount of absorbed laser energy can be related to the molecular densities using the Beer-Lambert law. Currently, we explore the possibility of measuring in situ the water vapor isotopes in the lower Martian atmosphere, which would strongly enlarge the potential scientific applications for the TDLAS sensor. The determination of isotopic ratios D/H, <sup>18</sup>O/<sup>17</sup>O/<sup>16</sup>O in the atmosphere is of interest for the search of biotic activity: life's catalyst preferentially use lighter isotopes during organic biosynthesis.

In the 2.64 μm spectral range, room-temperature multi-quantum wells laser diodes are now available and rovibronic transitions of H<sub>2</sub><sup>16</sup>O, H<sub>2</sub><sup>17</sup>O, H<sub>2</sub><sup>18</sup>O and HDO are simultaneously featured over a spectral window of less than 4<sup>1</sup>, which makes it possible to measure all the isotopes with one single laser. Nevertheless, the detection of the H<sub>2</sub>O isotopes requires to expand absorption path length from one to ten meters, which can be done using a compact optical multipass cell but makes the TDLAS sensor heavier (~1.5kg). (see photo).



As a first step to the development of the TDLAS version devoted to the H<sub>2</sub>O isotopes, we have carefully revisited in the laboratory the line strengths of the H<sub>2</sub>O isotopes transitions in the selected spectral windows near 2.64μm using a laser diode spectrometer. Furthermore, we have checked out the spectral emission properties of the selected multi-quantum well laser diode to ensure it is suitable for laser probing technique. We report here this spectroscopic work and will also present the version of the TDLAS instrument devoted to the H<sub>2</sub>O isotopologues measurements on Mars.

[1] T. Le Barbu; B. Parvitte; V. Zéninari; I. Vinogradov; O. Korablev and G. Durry, “Diode laser spectroscopy of H<sub>2</sub>O and CO<sub>2</sub> in the 1.877 μm region for the in situ monitoring of the Martian atmosphere”, *Applied Physics B* **82**, 133-140 (2006)

[2] T. Le Barbu; V. Zéninari; B. Parvitte; D.Courtois and G. Durry, “Line strengths and self-broadening coefficients of carbon dioxide isotopologues (<sup>13</sup>CO<sub>2</sub> and <sup>18</sup>O<sup>12</sup>C<sup>16</sup>O) near 2.04μm for the in situ laser sensing of the Martian atmosphere”, *Journal of Quantitative Spectroscopy and Radiative Transfer* **98**, 264-276 (2006)

## MILD: a laser altimeter transmitter for Mercury planetary orbiter

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We report on the design and preliminary tests on the breadboard (BB) of a laser source to be adopted in the transmitter unit of a laser altimeter, on board of future planetary missions. Reference scenario is the ESA BepiColombo mission to Mercury (presently scheduled to be launched in 2012) but possible applications to minor solar system bodies may be included.

The requirements for a source for spacecraft altitude measurement are different and very demanding: low beam divergence ( $M^2 < 1.5$ ), short (few-ns) high energy laser pulses, with good energy and length stability. Moreover, due to the thermally harsh environment of the Mercury orbit with expected large excursions in spacecraft temperature, the key aspect of the laser design is insensitivity of laser performance to temperature variations. To cope with the requested laser characteristics, we choose a master-oscillator-power-amplifier (MOPA) scheme. In this way we decouple the output pulse energy characteristics, which are driven basically by the Power Amplifier (PA) stage from the mode selection and pulse forming steps, which are provided by the Master Oscillator (MO). The MO is a fiber-end-pumped Nd:YAG rod, with a quasi-semi-confocal resonator. To achieve both the required pulse length and pulse length stability we adopt an RTP active Q-switch. To obtain the required amplification within a compact device, the chosen PA scheme is a diode side-pumped 10-pass Nd:YAG slab-crystal amplifier. The low-power input beam is totally-reflected within the side-pumped slab, producing a 5-pass first amplification step, then it is sent backwards into the slab, undergoing a second 5pass zig-zag path into the gain medium. The amplified beam leaves the active medium on the same side where the low-energy input beam enters, with a small angle with respect to it, and it is coupled out because of this angular difference. The output of the laser BB is characterised on a 20° C temperature range, with particular attention to the PA performance.

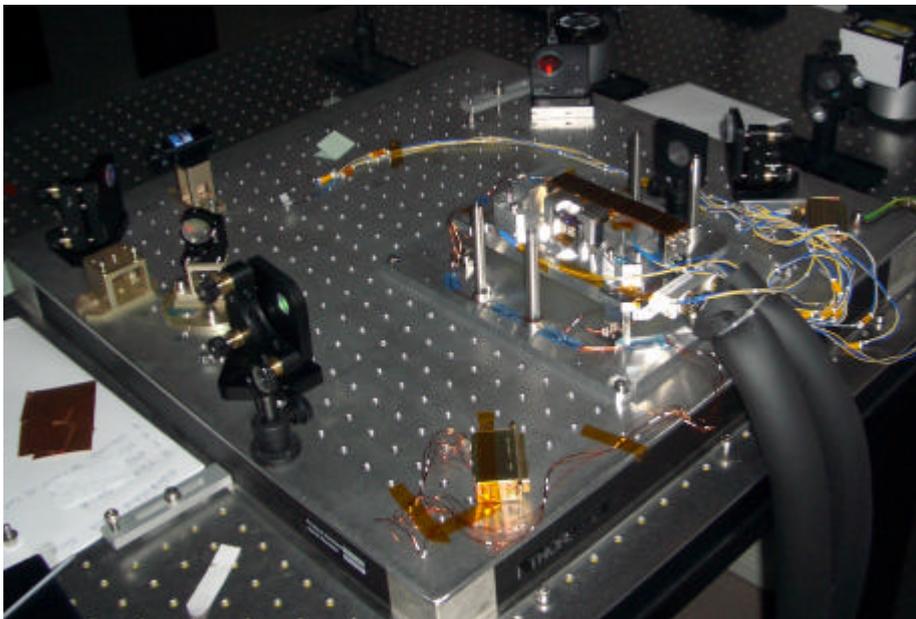


Fig. 1: Photo of the PA breadboard.

Acknowledgements: This work has been performed within the ESA contract no. 19368/05/NL/IA.

## Flight testing and laboratory calibrations of the HIAPER VCSEL hygrometer

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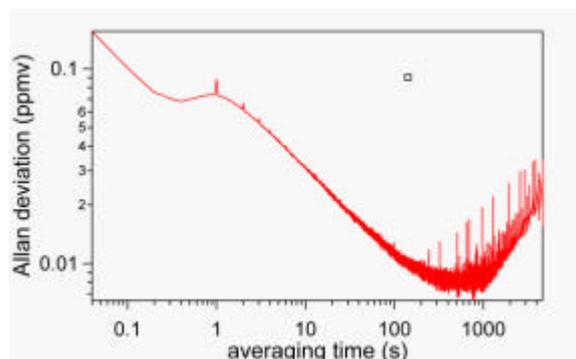
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A new water vapor instrument has been developed for the NSF/NCAR High-performance Instrumented Airborne Platform for Environmental Research (HIAPER) Gulfstream-V aircraft. Water vapor plays critical roles in the climate, chemistry, and dynamics of the troposphere and stratosphere. Unfortunately, measurements of atmospheric water vapor are surprisingly challenging due to its ubiquitous nature, large dynamic range (six orders of magnitude in absolute concentration), and efficient adsorption to instrument surfaces. These challenges are exacerbated when flying on a platform such as HIAPER with its high speed, large vertical and horizontal sampling capabilities, and fairly small payload.

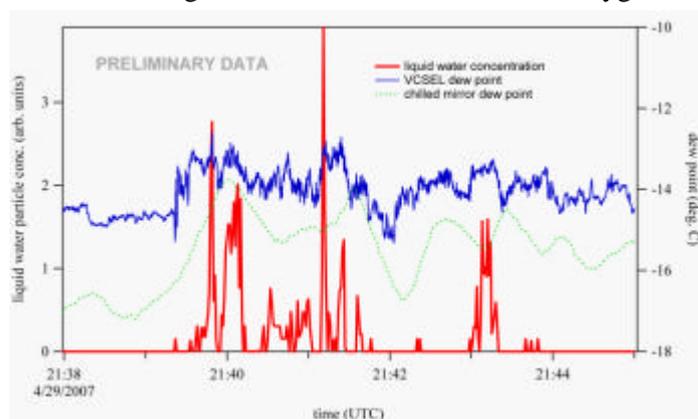
To help overcome the intrinsic challenges of water vapor measurements as well as those derived from sampling on HIAPER, a new hygrometer is being developed using a vertical cavity surface emitting laser (VCSEL) operating near a wavelength of 1854 nm. The large current tuning range of the VCSEL allows for both a weak (1853.37 nm) and strong (1854.03 nm) absorption line of water vapor to be probed with the same laser, allowing for a large dynamic. The laser is kept inside the aircraft while light is passed to the open-path cell through a fiber optic. Thus, no purging of water vapor in the optical train is necessary. The 25-pass external, optical cell is comprised of two 1.9 cm diameter mirrors separated by 15 cm.

The small size of the optical cell coupled with the fiber optic allows for some unique studies to be conducted in the laboratory. Experiments are being conducted to examine the accuracy, precision, and drift of the sensor over a range of pressures and temperatures. For example, Figure 1 shows an Allan deviation plot for ~ 1 ppmv H<sub>2</sub>O at ambient, laboratory conditions. Short-term precision at 1 Hz is ~ 8% of the signal. Longer-term drifts on timescales up to 1.5 hours do not complicate the measurement.



**Figure 1.** Allan deviation plot for ~ 1 ppmv H<sub>2</sub>O at laboratory conditions (T=295 K, P=780 hPa). Precision for 1 Hz measurements is ~ 8% of the signal, and long-term drift on the timescales up to 1.5 hours doesn't degrade the measurement.

The first flight tests of the HIAPER VCSEL hygrometer were conducted in April and May as part of the NSF Pacific Dust Experiment. Figure 2 shows the performance of the VCSEL hygrometer marine stratocumulus clouds. Fine scale structures are observed that are impossible to see with the chilled mirror hygrometer. The VCSEL data is also reasonably well-correlated with the 1 Hz cloud particle measurements. Such data will be inherently useful to assess cloud microstructure, dynamics, and nucleation processes. Future flight testing will occur onboard HIAPER in July 2007.



**Figure 2.** Preliminary data on HIAPER showing the VCSEL hygrometer dew point (thin solid line), chilled mirror hygrometer dew point (dotted line), and a proxy for cloud particles (thick, solid line). The 25 Hz VCSEL data resolves detailed cloud structure, unlike the chilled mirror.

Data from these flights as well as the laboratory will be discussed in the context of scientific needs for airborne water vapor measurements.

# **ISOTOPES**

## Advances and challenges in stable isotope infrared spectrometry

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In this paper we present an overview of the state-of-the-art of spectroscopic methods for measuring stable isotope ratios in small molecules of environmental and biological importance, as alternatives to the conventional method of isotope ratio mass spectrometry (IRMS), as well as recent developments following two previous reviews (Kerstel, 2004; Kerstel and Meijer, 2005).

Nowadays IRMS instrumentation is commercially available that reaches impressively high levels of precision, as well as throughput. Unfortunately, IRMS is incompatible with a condensable gas or a sticky molecule such as water. Apart from this, IRMS instrumentation is expensive, voluminous and heavy, confined to a laboratory setting, and usually requires a skilled operator. All or most of these issues may be addressed by optical measurement techniques.

The near and mid-infrared absorption spectra of most small molecules in the gas phase show a large number of highly characteristic rotational-vibrational transitions that are very sensitive to isotopic substitution. At sufficiently low vapor pressure and high instrumental resolution the individual ro-vibrational transitions are easily resolved, and can be uniquely assigned to a molecule of particular isotopic composition (isotopologue). Recording the spectrum containing abundant and rare isotopologue features, in both an unknown sample and an isotopically well-known reference material, enables one to relate the isotopic composition of the sample to that of the reference material in a manner as described in, e.g., Kerstel (2004).

In designing an infrared laser isotope ratio spectrometer, a number of issues have to be considered. Compromises are inevitable when it comes to selecting the wavelength region, gas cell design, and the specific detection technique.

Optical isotope ratio measurements have clearly matured to the point where the isotope analysis of a number of molecules has become competitive with IRMS in terms of accuracy. Sometimes, fractionation effects during sample handling constitute the dominant source of analytical errors (such as is the case with  $\delta^2\text{H}$  in water), and affect both methods. In other instances, the accuracy of the method is limited by analytical problems, such as temperature-induced apparent isotope shifts or etaloning effects (fringing) in the optical system. Although, it appears unlikely that an optical method will be able to reach the very high accuracy ( $\sim 0.03\%$ ) possible with IRMS for, e.g.,  $\delta^{18}\text{O}$  determinations on natural water or carbon dioxide samples, current optical instruments are coming close, and are certainly able to satisfy the needs of many users.

Of course, precision and accuracy are not the only factors to be considered when comparing laser spectrometry to IRMS. There are many applications for which other aspects, like robustness, portability, remote operation in a hostile environment, compactness, and the real-time measurement capability, are more important. Other advantages of optical methods that may be considered are the high selectivity, thus avoiding the need of chemical sample pretreatment, the non-destructive nature of the measurement, making it possible to recover the sample if needed, the absence of consumables (like an ionization source filament), and, low cost. Last but not least, methods based on direct absorption are conceptually simple, which helps reduce the required scale correction and normalization with respect to IRMS.

The arrival of a number of commercial suppliers of optical spectrometers signals the acceptance of end users of the technique. The near future will surely see even more precise and accurate, as well as more sensitive, devices. Also, more attention will be paid to sample handling and calibration strategies.

E. Kerstel (2004) Stable isotope ratio infrared spectrometry. Handbook of Stable Isotope Analytical Techniques. pp. 759-787. P.A. de Groot (Ed.) Elsevier.

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## The Harvard integrated cavity output spectroscopy (ICOS) isotope instrument

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Integrated Cavity Output Spectroscopy (ICOS) provides a powerful new technique for high-sensitivity measurements of trace gases in the atmosphere. We report on the development of the first ICOS-based in-situ field instrument. The Harvard ICOS Isotope Instrument measures the isotopic composition of water vapor in the upper troposphere and lower stratosphere, making individual measurements of H<sub>2</sub>O, HDO, and H<sub>2</sub><sup>18</sup>O in a single scan of a 2.7 micron quantum cascade laser. Instrument noise equivalent absorption is comparable to more traditional absorption spectrometers but signal in the new instrument is more than an order of magnitude improved: R ~ 99.98% mirrors provide an effective optical pathlength of over 4 km. High signal is needed for measurement of HDO in particular, whose concentration is less than 1 ppb in the dry stratosphere. The instrument has been mounted on NASA's WB-57 high-altitude research aircraft, flown on three science missions from 2005-2007, and yielded science-quality measurements of previously unobtainable sensitivity. We show raw and derived data from these missions and discuss the strengths and limitations of the ICOS technique.

## Continuous Measurement of CO<sub>2</sub> Isotopic Ratios by Infrared Spectroscopy using FTIR and QCL Instruments

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The <sup>13</sup>C/<sup>12</sup>C ratio measurement of atmospheric CO<sub>2</sub> (δ<sup>13</sup>C-CO<sub>2</sub>) provides a powerful tool to quantify CO<sub>2</sub> flux strengths of different ecosystem compartments. To date, the majority of CO<sub>2</sub> isotope studies are based on isotope ratio mass spectrometers (IRMS), thus requiring sample collection followed by laboratory analysis, which strongly limits the number and frequency of measurements. Alternative analytical concepts are based on the isotope specific absorption of the ro-vibrational transitions in the infrared spectral region. We will present the development of two transportable, optical instruments based on Fourier transform infrared spectroscopy (FTIR) and Quantum cascade laser absorption spectroscopy (QCLAS).

FTIR is a robust and well established method for gas analysis. However, numerous aspects must be considered to reach the precision and accuracy necessary for isotope ratio measurements. We have developed a novel calibration strategy, based on a robust partial least squares (PLS) algorithm in combination with a set of multi-component standard spectra [1]. Furthermore, gas handling was optimized to yield a very stable gas temperature and pressure. In the laboratory, an average accuracy for δ<sup>13</sup>C-CO<sub>2</sub> of 0.4 ‰ and a precision of 0.15 ‰ (σ<sub>Allan</sub> @ 600 s) was achieved. In a field campaign, the FTIR measurements were compared to standard laboratory-based IRMS measurements made on flask samples. The average difference for δ<sup>13</sup>C-CO<sub>2</sub> was 0.5 ‰ (n = 83). Very good agreement was found for the carbon isotope content of the respired CO<sub>2</sub> (δ<sup>13</sup>C<sub>R</sub>) determined by FTIR spectroscopy and IRMS. Additional trace gases such as CO, N<sub>2</sub>O and CH<sub>4</sub> were simultaneously analyzed.

A compact QCLAS was developed based on a pulsed QCL from AlpesLasers operating at 4.3 μm. Employing thermoelectrically cooled (TEC) components for both the IR laser light source and detector, the instrument can operate in a completely cryogenic free mode. A carefully selected, 0.6 cm<sup>-1</sup> spectral range in the ν<sub>3</sub> ro-vibrational band of CO<sub>2</sub> allows for simultaneous concentration measurements of <sup>16</sup>O<sup>12</sup>C<sup>16</sup>O, <sup>16</sup>O<sup>13</sup>C<sup>16</sup>O and <sup>18</sup>O<sup>12</sup>C<sup>16</sup>O in ambient air. Based on very encouraging results with a preliminary setup [2], a dual multipass-cell arrangement was designed to analyze the difference between the sample spectra and the simultaneously acquired reference spectra. This approach significantly improves the spectrometer performance due to the cancellation of correlated noise components specific to this method. Using the Allan variance technique, δ<sup>13</sup>C-CO<sub>2</sub> has a 1 s standard deviation of 0.6 ‰ and a variance minimum at 430 s corresponding to a σ<sub>Allan</sub> of 0.04 ‰. Further optimization steps and field measurements are planned during the summer 2007.

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- [2] B. Tuzson; M. J. Zeeman, M. S. Zahniser, L. Emmenegger, Quantum cascade laser based spectrometer for in-situ stable carbon dioxide isotope measurements, *Infrared Physics & Technology*, in print.

## Long-path absorption spectrometers for determining $\delta^{13}\text{C}$ in $\text{CO}_2$ at field sites

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We report on the laboratory testing of two diode laser spectrometers intended to measure the carbon isotopic composition of  $\text{CO}_2$  respired by soil microbes at forest sites. Both instruments work by detecting the long-path absorption of a DFB diode laser beam by paired  $^{13}\text{CO}_2$  and  $^{12}\text{CO}_2$  transitions near 2  $\mu\text{m}$  wavelength. The first employs Wavelength Modulation Spectroscopy (WMS) in a Herriot-type multiple reflection cell with an effective path length of about 20 m. The second employs Optical Feedback Cavity-Enhanced Absorption Spectroscopy (OF-CEAS) in a V-shaped, high-finesse cavity with an effective path length of over 1 km. Unfortunately, the accuracy of the WMS instrument in determining  $\delta^{13}\text{C}$  at ambient  $\text{CO}_2$  concentrations has been found to be limited to about  $\pm 2\%$  by persistent optical fringe-like effects, which will be discussed in some detail. The OF-CEAS instrument, on the other hand, has several advantages over the WMS instrument, including a wider dynamic range of detection and a scan rate that is two orders of magnitude faster. We will focus on the laboratory performance of the OF-CEAS spectrometer, and on its potential for application to field studies.

## **Tunable diode-laser spectrometer for atmospheric measurement of the isotopic ratio $^{13}\text{CO}_2/^{12}\text{CO}_2$**

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We have developed a Tunable Diode Laser Spectrometer, called SIMCO, to measure the  $^{13}\text{CO}_2$  and  $^{12}\text{CO}_2$  concentrations and thus the isotopic ratio  $^{13}\text{CO}_2 / ^{12}\text{CO}_2$  in the atmosphere. For that we used a direct absorption spectroscopy technique with a mid-IR lead salt laser diode. We measure the concentrations of the two isotopomers with a couple of line around  $2290.1\text{ cm}^{-1}$ , by fitting a line profile model taking into account the confinement narrowing effect to achieve a better accuracy. A standard deviation of less than 0.5 ‰ for an integration time of 4 s has been showed for the concentrations of atmospheric  $\text{CO}_2$ .

After a description of the instrument, we will show its current performances. Intercomparison results of our instrument with Isotopic Ratio Mass Spectrometer (IRMS) and Gaz Chromatographe (GC) will also be presented.

## Simultaneous measurements of multiple gas species and the $^{13}\text{C}/^{12}\text{C}$ isotope ratio in $\text{CO}_2$ from a wood-based combustion emission by laser absorption spectroscopy

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We report on the development and application of a compact and field-deployable spectrometer based on fiber-coupled continuous-wave (CW) Telecom external cavity diode laser (ECDL, Tunic Plus). The ECDL was widely tunable from 1500 to 1640 nm (C and L band) with an output power up to 3 mW and an effective laser linewidth of less than 1 MHz. A multipass cell (New Focus – model 5612) in Herriott configuration with an optical path of 100-m was used to enhance the detection sensitivity. The emerging signal from the cell was detected with an InGaAs photodiode detector (New Focus – model : Nirvana 2007). The gas pressure inside the cell was measured and controlled with a pressure transducer (MKS 640). A two-stage diaphragm pump (KNF Neuberger) was used to evacuate the cell and provide a flow up to 5 NI/min for continuous *in-situ* measurements.

The developed instrument has been used for measurements of the  $^{13}\text{C}/^{12}\text{C}$  isotope ratio in  $\text{CO}_2$  and concentrations of combustion emission gas from a wood-fired boiler located at Flimwell (East Sussex, UK). Gas sampling in the flue of the wood-fired boiler has been made for two different operating conditions at different temperatures : one was at  $T\sim 110\text{ }^\circ\text{C}$  (full burn regime) and the other at  $T\sim 70\text{ }^\circ\text{C}$  (slumber regime). Based on the absorption spectra of the combustion emission, four gas species have been identified and quantified. Simultaneous measurements of multiple species from gas emission has been performed by selection of optimum lines in terms of high signal-to-noise ratio and interference free between species. Concentrations of  $\text{C}_2\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  were determined by least-squares fitting of a Voigt lineshape to the experimental absorption spectra.

The isotopic ratio of  $^{13}\text{CO}_2/^{12}\text{CO}_2$  has been measured as well. The averaged value of the  $^{13}\text{CO}_2/^{12}\text{CO}_2$  ratio is found to be  $(1.101\pm 0.004)\%$ . The corresponding  $\delta$ -value relative to PDB standard is  $(-20.17\pm 3.53)\%$  that is in good agreement with the typical value of  $(-25\pm 2)\%$  for wood.

### **Acknowledgments**

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## **$^{12}\text{CO}_2/^{13}\text{CO}_2$ ratio measurement by off-axis cavity-enhanced absorption spectroscopy**

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A DFB diode laser sensor based upon off-axis cavity-enhanced absorption spectroscopy at 1605.5 nm has been developed for  $^{13}\text{C}^{16}\text{O}_2/^{12}\text{C}^{16}\text{O}_2$  isotope ratio measurements in synthetic air and human breath. A noise-equivalent absorption sensitivity of  $3.9 \times 10^{-10} \text{ cm}^{-1} \text{ Hz}^{-1/2}$  has been determined for a cavity base length of 28.2 cm and averaging 4000 scans within 8.688 s. For 5%  $\text{CO}_2$  concentration measurements,  $\delta^{13}\text{C}$  standard deviations of 1.8‰ and 3.7‰ have been estimated for five successive measurements based on peak height and integrated area estimations at 107.9 Torr, respectively. The contributions of amplified spontaneous emission of the laser and a radiation that is spatially uncoupled into the cavity mode have been described for cavity transmittance measurements. The limitations of the developed sensor and further steps towards precision and accuracy improvements are discussed.

## **A theoretical analysis of marijuana grow house detection by TDLAS using the $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ isotope ratio**

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The theoretical analysis of a method to indirectly detect marijuana grow houses is described which is based on the difference between the  $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$  ratio emitted by plants and the background ratio in the downwind plume. The ratio is estimated by a TDLAS gas flux analyzer, which measures the horizontal wind vectors and the gas concentrations, using two NIR lasers and the HITRAN  $\text{H}_2^{16}\text{O}$  line @  $7161.4\text{ cm}^{-1}$  and the HITRAN  $\text{H}_2^{18}\text{O}$  line @  $7222.3\text{ cm}^{-1}$ . The  $\text{H}_2\text{O}$  downwind plume concentrations are modeled for marijuana grow houses of various plant surface area using the meteorological variables wind speed and stability to define the instrument detection limits, optimal sensing heights and meteorological conditions. Error sources such as marijuana grow houses fuel combustion and external plants are included in the analysis. The instrument, which is mounted in a van type vehicle with a GPS locator, is driven on a grid pattern of streets to identify potential marijuana grow houses and their geographic positions. The detection strategy uses the  $\text{H}_2^{16}\text{O}$  mole fraction measurement ratio of house plume to background to identify candidate houses. A follow-up measurement on the candidate houses of the  $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$  ratio in the downwind plume is performed with the vehicle stationary to improve the  $\text{H}_2^{18}\text{O}$  signal to noise. Analysis results indicate that typically sized grow houses can be identified.

## Long-term continuous monitoring of atmospheric CO<sub>2</sub> stable isotopic ratios using a 4.3 μm pulsed QCL

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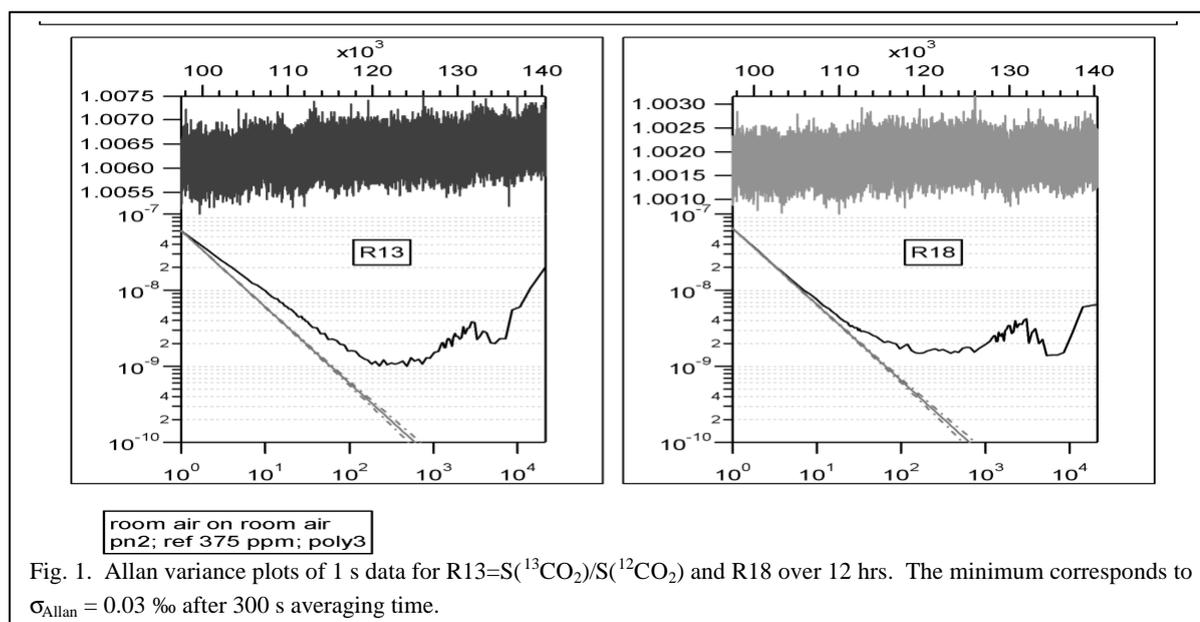
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Real time methods to monitor the stable isotopic ratios of carbon dioxide are needed to quantify the sources and sinks of this centrally important greenhouse gas. This is an extreme instrumental challenge since the ratios need to be measured with an accuracy of approximately one part in ten thousand or 0.1‰. We use tunable infrared laser differential absorption spectroscopy with pulsed QC lasers to address this challenge. QC lasers are attractive optical sources since they do not need cryogenic fluids, they have stable single mode spectral output and offer optical simplicity. We have used a QCL instrument to perform long term (>5 months) monitoring of ambient air from the roof top of our laboratory to observe seasonal changes in both <sup>13</sup>C/<sup>12</sup>C and <sup>18</sup>O/<sup>16</sup>O.

Our optical system employs a dual-cell arrangement with ambient air flowing through the sample cell and a reference gas flowing through the reference cell. Both <sup>13</sup>C/<sup>12</sup>C and <sup>18</sup>O/<sup>16</sup>O ratios can be obtained in a single spectral window near 2310 cm<sup>-1</sup>. Spectral analysis is applied to the ratio of the sample and reference spectra, canceling correlated noise components. Because the absorption lines of the isotopic species have different temperature dependences, temperature stability is critical. The optical system is temperature controlled and the two multipass cells are thermally coupled and individually monitored with a precision of 1 mK. The ratio technique compensates for temperature sensitivity, as well as for drifts in laser line width, frequency, tuning rate and power variation. Stability against drift is improved with periodic (hourly) additions of zero-air and standard gases. We have developed a calibration system that uses a minimal number of standard gases to achieve excellent precision over a wide range of sample gas CO<sub>2</sub> concentrations.

The stability of the thermally stabilized dual-cell QCL system has been evaluated using the Allan variance technique. The Allan plot (Fig 1) shows a 1-sec RMS of 0.2‰, and a minimum  $\sigma_{\text{Allan}}$  of 0.03‰ after 300 seconds integration using a LN<sub>2</sub> cooled detector which will be compared to data using thermoelectrically cooled detectors. In the near future we will compare performance of the instrument using a continuous wave (CW) QCL operating in the same spectral region.



## Cryogenic free QCLAS for simultaneous and continuous mixing ratio measurements of CO<sub>2</sub> isotopologues in ambient air

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Interaction between terrestrial ecosystems and the atmosphere occurs via a number of processes including carbon dioxide exchange during photosynthesis and respiration. Stable isotope analysis of atmospheric CO<sub>2</sub> is an excellent tool to investigate the mechanisms controlling these processes at different spatial and temporal scales. However, the required continuous and high precision isotopic analysis still represents a real instrumental challenge.

We demonstrate that a pulsed, quasi room temperature quantum cascade (QC) laser emitting in the carbon-dioxide fundamental bands at 4.3 μm is an excellent choice to build a field deployable isotope ratio analyzer. The relatively high power output of the QCL permits to employ thermoelectrically cooled (TEC) IR-detectors so that the instrument can operate in a complete cryogenic free mode that greatly facilitates *in-situ* applications. The instrument is based on differential absorption spectroscopy; a dual multipass-cell arrangement is used for simultaneous sample/calibration gas measurements and leads to an increased precision by ratioing the absorbance and analyzing the resultant spectra. With this approach, the effects of laser frequency fluctuations on both the peak position and the laser line width can be minimized. Furthermore, we have carefully selected a spectral window near 2310 cm<sup>-1</sup> such that within the tuning range of the QCL laser the concentration of all three main stable carbon dioxide isotopologues (<sup>16</sup>O<sup>12</sup>C<sup>16</sup>O, <sup>16</sup>O<sup>13</sup>C<sup>16</sup>O and <sup>18</sup>O<sup>12</sup>C<sup>16</sup>O) can be measured, allowing the simultaneous determination of both <sup>13</sup>C/<sup>12</sup>C and <sup>18</sup>O/<sup>16</sup>O ratios. To obtain the necessary precision and robustness, a number of key aspects were optimized or developed, including a water cooled dual TEC IR-detector assembly, temperature stabilization of the optics, thermal coupling of the dual absorption cells, pressure control and calibration procedure. A precision of the isotope ratios well below 0.1‰ is achieved for 200 s averaging time. The short-term precision (1σ) for measurements of individual CO<sub>2</sub> isotopologue mixing ratios is at the 0.1 ppmv level.

Laboratory performance tests regarding instrument stability and precision as well as cross validation with an isotope ratio mass spectrometer will be presented. Moreover, we aim to demonstrate field measurements of continuous and simultaneous measurements of <sup>13</sup>C/<sup>12</sup>C and <sup>18</sup>O/<sup>16</sup>O ratios at atmospheric mole fractions. A time resolution of up to 10 Hz can be achieved, because there is no need for pre-treatment (except drying) or pre-concentration of the air samples. This should allow the combination of isotope ratio analysis with Eddy-covariance dynamic flux measurements.

## Analytical Index

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### A

Agishev R. ....	28
Akikusa N. ....	5; 68
Al Naimee K. ....	44
Allen N.T. ....	102
Aluculesei A. ....	63
Amarouche N. ....	91
Anderson J.G. ....	102
Anlauf K. ....	95
Arecchi F.T. ....	44
Arnone D. ....	7
Asobe M. ....	29
Axner O. ....	24

---

### B

Baer D. ....	12
Bakirkin Y.A. ....	31
Baran S.G. ....	33
Bassi D. ....	55
Bauer C. ....	26
Beese H. ....	30
Bell C.L. ....	34
Bichlmeier S. ....	18
Blaser S. ....	6; 26
Bohman A. ....	30
Bonserio C. ....	79
Boschetti A. ....	55
Boucher D. ....	67; 106
Bouchier A. ....	43
Bozem H. ....	85; 93; 94
Burns I.S. ....	73

---

### C

Camy-Peyret C. ....	105
Cao Z. ....	32
Capanni A. ....	98
Carpentieri M. ....	65
Castagnoli F. ....	90
Castrillo A. ....	104
Catoire V. ....	62
Cattaneo H. ....	25
Chen H. ....	8
Chen W. ....	32; 61; 67; 106
Chen Y. ....	8
Chu P.M. ....	21
Ciaffoni L. ....	35
Cicchi R. ....	48
Ciofini M. ....	98
Corti A. ....	65
Cousin J. ....	67; 106
Crivello S. ....	7
Croizé L. ....	105
Crosson E. ....	10; 54; 64
Cummings B. ....	35
Curl R.F. ....	31

---

### D

D'Amato F. ....	65; 90
Daube B.C. ....	89
Davis K. ....	64
Day T. ....	7
De Blasiis D. ....	79
De Gouw J. ....	96
De Pas M. ....	90
DeGiorgi V. ....	48
Deng L. ....	32
Deninger A. ....	4
Di Francesco F. ....	53
Diskin G.S. ....	86
Duffin K. ....	45
Durry G. ....	62; 66; 91; 97
Dyoff C. ....	23

---

### E

Ebert V. ....	39; 40; 59; 71
Edamura T. ....	5; 68
Elder A.D. ....	51
Elliott S.E. ....	75
Emmenegger L. ....	103; 109; 110
Erbert G. ....	41

---

### F

Fallows E.A. ....	77
Favilla E. ....	98
Fernholz T. ....	39
Fertein E. ....	106
Fioravanti M. ....	16
Fischer H. ....	85; 93; 94
Fischer M. ....	3
Fittschen C. ....	63
Flesch T.K. ....	50
Foltynowicz A. ....	24
Fontana R. ....	42
Fourmentin M. ....	67; 106
Frank J.H. ....	51
Freude W. ....	23
Fried A. ....	23; 88
Fritsch T. ....	52
Fujita K. ....	5; 68
Furuta S. ....	5

---

### G

Gambino M.C. ....	42
Gao X. ....	32; 61
Garnache A. ....	43
Gatilova L. ....	81
Gianfrani L. ....	104
Giannini M. ....	74; 80
Gibert F. ....	66

Gierszewska M.....	60
Giuntini M.....	90
Gong Z.....	32
Gouin J.F.....	95
Grähler W.....	30
Gréus C.....	2
Gurk C.....	85; 93; 94

---

## **H**

Han L.....	32
Hancock G.....	33; 34; 75
Hanisco T.F.....	102
Harper L.A.....	50
Harren F.J.M.....	47
Harris G.W.....	95
Hering P.....	52
Hernberg R.....	25; 72
Herndon S.C.....	109
Hodges J.T.....	21
Holdsworth R.J.....	15; 38; 82; 107
Hoobler R.....	10
Hult J.....	73
Hunsmann S.....	59
Hvozدارa L.....	6; 26

---

## **I**

Iannotta S.....	55
-----------------	----

---

## **J**

Jänker B.....	23
Jeyasekharan A.D.....	51
Jiménez R.....	89
Johnstone W.....	45
Joly L.....	62; 66; 91; 97
Jost H.J.....	13; 92

---

## **K**

Kaminski C.F.....	51; 73
Kan H.....	5; 68
Kaspersen P.....	14; 30
Kassi S.....	67
Kasyutich V.L.....	15; 38; 82; 107
Keen K.A.....	76
Kerstel E.....	101
Keutsch F.N.....	102
Kidd G.E.....	108
Klehr A.....	41
Kluczynski P.....	36
Koeth J.....	3
Königstedt R.....	85; 93; 94
Kort E.A.....	89
Kosterev A.A.....	31

---

## **L**

Lang N.....	78
Lapson L.R.....	102

Lapucci A.....	98
Laurila T.....	25; 72
Legge M.....	3
Lelieveld J.....	85; 93; 94
Lewicki R.....	22; 31
Leyva I.....	44
Liang W.....	32
Lim T.T.....	54
Lison F.....	4
Loccioni C.....	16; 53
Loewenstein M.....	92
Lopez J.....	92
Lotti T.....	48
Lundqvist S.....	36

---

## **M**

Ma W.....	24
Manninen A.....	72
Marino I.P.....	44
Markus M.....	18
Martin N.A.....	82
Martin P.A.....	15; 38; 76; 82; 107
Massi D.....	48
Mazzinghi P.....	65; 90
McGettrick A.J.....	45
McManus J.B.....	9; 89; 109; 110
McNaghten E.D.....	76
Meucci R.....	44
Miles N.....	64
Miller J.H.....	77
Mohn J.....	103
Mondelain D.....	105
Montori A.....	90
Moyer L.....	102
Muller A.....	6; 26
Muolo M.....	74; 79; 80
Mürtz M.....	49; 52
Myara M.....	43

---

## **N**

Nelson D.D.....	9; 89; 109; 110
Nishida Y.....	29

---

## **O**

Ochiai T.....	5; 68
Oh D.....	11
Oikari R.....	72
Orghici R.....	60
Ortsiefer M.....	2

---

## **P**

Paige M.E.....	99
Pampaloni E.....	42
Pappalettere C.....	74; 79; 80
Parchatka U.....	85; 93; 94
Park S.....	89
Parkes A.M.....	76
Parvitte B.....	62; 66; 91; 97
Paul J.B.....	13; 102

Pavone F.S. ....	48
Perez J.P. ....	43
Peveall R. ....	35; 75
Pezzati L. ....	42
Podolske J.R. ....	86
Pritchett R. ....	7
Pushkarsky M. ....	7

---

## R

Rascher U. ....	59
Ravegnani F. ....	90
Reinicke M. ....	78
Rella C. ....	10
Richardson S. ....	64
Richter D. ....	23; 88
Ritchie G.A.D. ....	27; 33; 34; 35; 75
Rivière E. ....	91
Robert C. ....	62
Romanini D. ....	43; 67
Romano C. ....	26
Romano M. ....	65
Rönneberg E. ....	2
Röpcke J. ....	70; 78; 81
Roskopf J. ....	2
Rousseau A. ....	81
Russo A. ....	16

---

## S

Sachse G.W. ....	86
Sagnes I. ....	43
Salviati A. ....	55
Sani E. ....	98
Sayres D.S. ....	102
Schade W. ....	26; 60
Scherer J.J. ....	13
Schiller C.L. ....	85; 93; 94; 95
Schmid H.P. ....	58
Schmidt F. ....	24
Schoemaeker C. ....	63
Schossig T. ....	26
Schurr U. ....	59
Scotoni M. ....	55
Seufert J. ....	3
Sharma A.K. ....	26
Shau R. ....	2
Shorter J.H. ....	9
Signoret P. ....	43
Silver J.A. ....	99
Smith J.S. ....	102
So S. ....	31
St Clair J. ....	102
Staebler R. ....	95
Stancu G.D. ....	78
Steinbach A. ....	78
Stewart G. ....	45
Sugiyama A. ....	5; 68
Sumpf B. ....	41
Suschek C.V. ....	52
Suzuki H. ....	29
Svanberg S. ....	20
Swartling J. ....	51

---

## T

Tadanaga O. ....	29
Taig C.A. ....	82
te Lintel Hekkert S. ....	96
Thiebaud J. ....	63
Tittel F.K. ....	22; 31
Tommasi L. ....	98
Tränkle G. ....	41
Tulip J. ....	50
Tuzson B. ....	103; 109; 110

---

## U

Uehara K. ....	68
Ulanovsky A. ....	90
Umeki T. ....	29

---

## V

van Helden J.P. ....	75
van Leeuwen N.J. ....	33; 34; 37
Venkitaraman A.R. ....	51
Viciani S. ....	65; 90

---

## W

Wagner S. ....	40; 59
Wahl E. ....	10
Waldvogel S. ....	60
Walega J. ....	23; 88
Warneke C. ....	96
Weber M. ....	10
Webster C.R. ....	87
Wege S. ....	78
Wehr R. ....	104
Weibring P. ....	23; 88
Weida M. ....	7
Weinstock E.M. ....	102
Welzel S. ....	81
Werle P. ....	23; 90
Werner R. ....	3
Willer U. ....	26; 60
Wittmann A. ....	6
Wofsy S.C. ....	89
Woods P.T. ....	8
Wu T. ....	61
Wunderle K. ....	39; 40; 59
Wysocki G. ....	22; 31

---

## X

Xu C. ....	32
------------	----

---

## Y

Yan W.B. ....	8
Yanagawa T. ....	29
Young J. ....	15; 82

---

**Z**

Zahn A.....23; 84  
Zahniser M.S.....9; 57; 89; 103; 109; 110

Zeeman M.J.....103  
Zeninari V.....62; 66; 91; 97  
Zhang W.....32; 61  
Zhao W.....61  
Zondlo M.A.....99