ABSTRACTS OF PAPERS

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Tunable Diode Laser Spectroscopy

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TDLS 2007 CONFERENCE SCHEDULE

Monday 9	**Tuesday 10**	**Wednesday 11**	**Thursday 12**	**Friday 13**
8:45 - 9:00 Welcome addresses				
9:00 - 9:45 M. Havenith	**9:00 - 9:45 Yunjie Xu**	**9:00 - 9:45 D. Mondelain**	**9:00 - 9:45 M. Sigrist**	**9:00 - 9:45 R.F. Curl**
9:45 - 10:30 H. Kanamori	**9:45 - 10:30 Jay Jeffries**	**9:45 - 10:30 A.R.W. McKellar**	**9:45 - 10:05 L. Nguyen**	**9:45 - 10:30 C. Gmachl**
			10:10 - 10:30 D. Barat	
10:30 - 11:00 COFFEE BREAK	10:30 - 11:00 COFFEE BREAK	10:30 - 11:00 COFFEE BREAK	10:30 - 11:00 COFFEE BREAK	END OF MEETING
11:00 - 11:20 F. Schmidt	**11:00 - 11:20 L. Emmeneger**	**11:00 - 11:20 M.I. Belovolov**	**11:00 - 11:40 M. Zendel**	
11:20 - 11:40 D.B. Stavroskii	**11:20 - 11:40 I. Courtillot**	**11:20 - 11:40 D. Nelson**		
11:40 - 12:00 J. Koeth	**11:40 - 12:00 V.A. Kapitanov**	**11:40 - 12:00 A. Grossel**	**11:40 - 12:00 N. Peter**	
12:00 - 14:00 LUNCH TIME	12:00 - 14:00 LUNCH TIME	12:00 - 14:00 LUNCH TIME	12:00 - 14:00 LUNCH TIME	
14:00 - 15:45 POSTERS Session A	**14:00 - 15:45 POSTERS Session B**	**14:00 - 18:00 Hautvillers Epernay Champagne EXCURSION**	**14:00 - 15:45 POSTERS Session C**	
15:45 - 16:15 COFFEE BREAK	15:45 - 16:15 COFFEE BREAK		15:45 - 16:15 COFFEE BREAK	
16:15 - 18:00 POSTERS Session D	**16:15 - 18:00 POSTERS Session E**		**16:15 - 18:00 POSTERS Session F**	
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Part 1. Invited Lectures

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L-1

High resolution laser spectroscopy of cold and ultracold molecular aggregates

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High resolution spectroscopy has allowed us to study the fundamental question of double proton tunneling. We were able to measure the fully resolved infrared spectrum of formic acid dimer which allowed us to determine the tunnelling splitting. High resolution IR - spectra in the region of the antisymmetric C-O stretch vibration have been recorded for $(HCCOH)_2$ and its isotopomers [1, 2]. This allowed us to determine for the first time the proton transfer time in a double hydrogen bonded prototype system.

As a second problem which was addressed by our studies we have investigated the coupling to collective excitations in superfluid helium droplets. By investigation of the IR-spectra of NO and CO, we could establish general rules which describe the phonon-rotation coupling in these finite size quantum systems [3, 4, 5].

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L-2

Applications of Phase-Locked Diode Lasers with Optical Frequency Combs to Ultra High-Resolution Spectroscopy and Quantum Computing of Molecules

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The octave spread optical frequency comb consisting of millions of equally spaced modes made significant progress in the optical frequency standards and, thus, Haensch and Hall were awarded the Nobel Prize in 2005 for their contributions to the development. However, in spite of many noble qualities of the optical comb, the power of each mode is less than 10^{-7}W, so that it is not practical to use itself as a light source for high-resolution spectroscopy. By introducing another higher power laser to the optical comb system through the technique of optical phase-locking method, the noble qualities of the optical comb is transferred to the external laser. Then it would be possible to apply it not only in ultra high resolution spectroscopy such as parity violation in chiral molecules [1] and time variation of fundamental physical constants [2], but also in the research field of quantum computing.

In this work, we use Fabry-Perot type diode lasers in the near infrared region. In order to establish the optical phase locking, the jittering at the free running condition is reduced to 1 MHz by using Littrow external cavity, then heterodyne beat signal between the LD and optical comb detected by a photo mixer is feed back to the injection current of the LD. When the optical phase-lock is completed, the width of the beat spectrum is narrower than 0.1 Hz. Further, the second LD is simultaneously optical phase-locked to a different mode of the optical comb as well. The beat spectrum of these two LD's is shown in the figure, in which the width is also suppressed to less than 0.1 Hz. The phase of the beat signal is easily controlled by changing optical delay in the two LD paths.

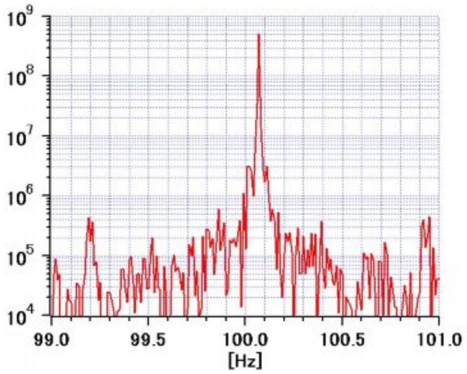

Fig. The down-converted beat spectrum between two LD's. Each LD is phase-locked to a different mode of the optical comb, respectively.

By using these two LD's as light sources, we tried Optical-Optical Double Resonance (OODR) experiments in some atomic and molecular systems, and found that it is possible to do not only ultra-precise spectroscopy limited by interaction time broadening, but also to control a quantum phase of matter. The latter is an indispensable operation for quantum computing.

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L-3

Application of Lead Salt Diode Lasers and Quantum Cascade Lasers for Infrared Spectroscopy of Jet-Cooled Molecules and Complexes

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The combination of infrared laser spectroscopy with a molecular expansion is a powerful technique to investigate medium sized organic molecules and their molecular clusters. Because of the high level densities of these molecular systems, it is essential to have a highly sensitive infrared spectrometer for their spectroscopic studies. In addition, it is high desirable to have simple and robust designs so that such a spectrometer can be used routinely with little maintenance.

In this report, we present the design and construction of several pulsed molecular beam mid-infrared spectrometers based on tunable lead salt diode and quantum cascade lasers. The first one is a mid-infrared continuous wave cavity ring-down spectrometer using lead salt diodes [1]. A pulsed molecular beam assembly with a home-made slit nozzle was constructed and incorporated into the spectrometer. A computer program was developed to automate and to synchronize the timing of the cavity ring-down experiments with the pulsed molecular beam. To initiate a cavity ring-down event, a frequency detuning scheme is exploited to effectively block the laser from entering the ring-down cavity by rapidly shifting the laser frequency. With a lead salt diode laser as laser source, the standard deviation of the experimental ring-down time, *i.e.* $\sigma(\tau)/\langle\tau\rangle$, was 0.63%, corresponding to a noise-equivalent absorption of 8.0×10^{-7} at a fixed laser frequency with an evacuated cavity with 10 averaging cycles. The second one is a rapid scan spectrometer where the sample cell is a pair of astigmatic mirrors aligned for 182 passes [2]. The third one is an off-axis cavity enhanced absorption (OA-CEAS) spectrometer based on a cw quantum cascade laser operating in the 5.7 micron region. The last two spectrometers are operated under rapid scan mode. The high resolution infrared spectra of methyl lactate, propylene oxide, and the cyclopropane-carbon dioxide complex will be presented. The advantages and disadvantages of the above techniques in their application to the high resolution infrared studies will be discussed.

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L-4

Tunable diode laser sensors for combustion and propulsion applications

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Tunable diode laser (TDL) absorption diagnostics provide unique capabilities for *in situ* sensing of reactive flows, and as a result such sensors are utilized increasingly in the development and control of advanced combustion systems. This presentation will provide an overview of recent progress in the evolution of TDL absorption, a line-of-sight technique with the capability of fast or even continuous measurements of multiple flowfield quantities including species, temperature and mass flux.

Practical combustion systems have high temperature and often high pressure leading to overlap and blending of transitions from small molecules that have well-resolved structure in more benign environments. Quantitative measurements in these environments require an accurate database for the linestrength as well as collision-broadening and collision-shifting parameters for not only the target transition but also the neighboring transitions that are blended by collision broadening. Absorption by two or more overtone or combination band transitions of water vapor has often provided the means of rapid measurement of temperature in combustion environments. Wavelength modulation techniques that have long been successful for the measurement of trace species in the atmosphere can be exploited for rapid analysis of absorption signals, and the TDL intensity modulation using injection-current tuning provides a normalization signal. Such rapid temperature sensors provide the potential to use local heat release as a control variable, and a successful demonstration of a TDL temperature sensor to suppress combustion instabilities and lean blow-off in a laboratory flame will be described. The rapid growth of practical combustion applications of near-infrared TDL methods will be highlighted with examples including IC engines, pulse detonation engines, scramjets, hypersonic tunnels, shock-heated flows, and coal-fired power plants.

We have also made recent progress in TDL-based absorption measurements in the mid-infrared. For example, diode lasers near 2.7 μm offer the ability to sense transitions in fundamental vibrational bands of water vapor and strong combination bands of CO_2, enabling measurements over much shorter path lengths, and our use of these lasers will be described. The non-linear production of tunable mid-infrared from the difference frequency of near-infrared TDLs has enabled the development of sensitive sensors for hydrocarbon fuels in the C-H stretching vibrational transitions near 3.4 μm. Rapid switching between two mid-infrared wavelengths provides sensitive differential absorption measurements in a variety of reactive environments, and experiments describing these mid-infrared results will be discussed.

L-5

Study of molecular line shape models and line parameters in the 15 to 298 K range

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Since several years, we develop different absorption cells to realize spectroscopic measurements on molecules in gaseous phase at low temperature (until several Kelvin)[1,2,3] to study line shape models and line parameters. For that we use either standard direct absorption spectroscopy or the collisional cooling technique depending on the temperature of the measurements and on the liquefaction temperature of the studied gas. In this presentation, we will first explain the motivations of this experimental work and describe the collisional cooling technique. After a brief review of our previous studies (mainly on CO), we will present our latest results obtained on methane and carbon dioxide using our new cold Herriott cell [4].

References:

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L-6

TDL spectroscopy of helium clusters

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The properties of cold (~0.2 K) helium clusters, ^4He_N-X, are studied as a function of size, N, by observing vibration-rotation spectra of an IR chromophore molecule, X. The experiments involve direct absorption of a Pb-salt TDL beam in a pulsed supersonic expansion from a cooled (120-270 K) jet nozzle. The laser is multipassed through the jet and operates in a rapid-scan mode with background subtraction and signal averaging. Cluster sizes from $N = 0$ and 1 (small molecule limit) up to ~100 are covered, often with atom-by-atom resolution. A number of approaches are used for cluster size assignment: dependence of the spectra on conditions such as jet backing pressure, comparison with microwave observations, and isotopic substitution. For X = OCS, we resolve and assign [1] spectra for virtually every N-value from 1 to 70, as shown in Fig. 1. Similar results are obtained for X = N_2O or CO_2, but some size ranges are incomplete due to spectral overlap. Large clusters are also detected for X = CO, but the spectra are rather different. Notable results are that spectral lines remain sharp (~0.001 cm^{-1}) even for larger clusters, and that B-values show broad oscillations as a function of cluster size, experimentally marking the evolution of superfluid helium solvation shells around the probe molecule.

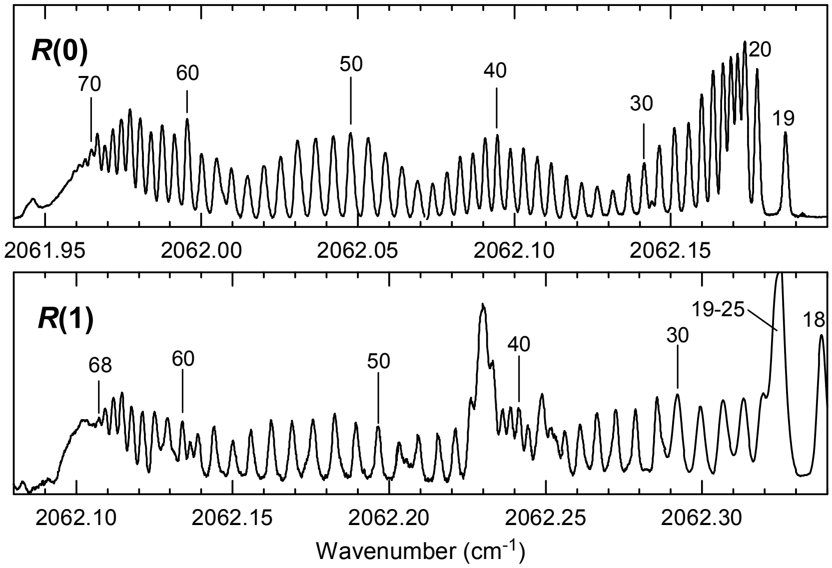

Fig.1. Observed spectra showing R(0) and R(1) transitions of He_N-OCS clusters for $N \sim 18$ to 70. Each panel is a composite of traces obtained with different jet conditions.

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L-7

Trace Gas Monitoring with IR Laser-Based Detection Schemes

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Trace gases play a key role in various areas such as air pollution, climate research, industrial process control, agriculture, food industry, volcanology, workplace safety and medical diagnostics. In recent years, laser-spectroscopic sensing devices have attracted a lot of interest as they enable high detection sensitivity (down to sub-ppb concentrations) and selectivity (including differentiation between isotopomers and isomers), multi-component capability and large dynamic range (several orders of magnitude in concentration) and generally neither sample-preparation nor -preconcentration are required. However, the laser source characteristics in terms of available wavelengths, tunability, linewidth, power, operation temperature, etc., as well as the combination with appropriate sensitive detection schemes are crucial for the success of laser-based sensing. As the fundamental molecular absorption ranges lie in the mid-infrared, emphasis is on lasers in the range between ca. 3 and 15 μm. Available sources include CO- and CO_2-lasers, lead salt diode lasers, quantum cascade lasers and nonlinear optical systems (optical parametric oscillators (OPOs) and difference frequency generation (DFG)). In some applications with reduced sensitivity requirements, near-IR lasers such as external cavity diode lasers, may be appropriate sources as well. Most common detection methods include direct absorption in multipass cells (eventually combined with wavelength modulation), photoacoustic and cavity ringdown spectroscopy. We shall illustrate the performance and potential of laser-based systems with own examples of applications in diverse areas.

Within the frame of a previous measurement campaign we demonstrated field sensing with an unattended mobile CO_2-laser-photoacoustic system employed for time-resolved street traffic emission [1] and in collaboration with an industrial partner, we performed a feasibility study for on-line sensing of acetylene (C_2H_2) contaminants in an ethylene (C_2H_4) carrier gas flow [2].

A current project focuses on the detection of methylamines in human breath as possible tracers for liver or renal diseases. First spectroscopic studies on air samples containing given concentrations of di- or tri-methylamine with a near-IR diode laser cavity ringdown and a mid-IR DFG absorption spectrometer will be discussed. A further project is aimed at laser spectroscopic analyses of doping agents used by athletes in sports [3]. As an example the diastereoisomers ephedrine (illegal in sports) and pseudoephedrine (legal use) are investigated with a broadly tunable DFG source and a home-made heatable multipass cell [4] with the goal to identify these compounds at trace levels in urine samples. Finally, mid-IR laser-spectroscopic isotope ratio measurements of CO, CO_2 and N_2O isotopomers are in progress and will be discussed in a separate presentation.

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L-8

Application of Quantum Cascade Lasers to trace gas analysis

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Quantum cascade (QC) lasers are virtually ideal IR sources for trace gas monitoring with their only significant limitation being a tuning range that is currently limited to about 100 cm^{-1}. They can be fabricated to operate at any of a very wide range of wavelengths from about 80 μm to about 3 μm. Seizing the opportunity presented by the mid-IR QC lasers, several groups are actively applying them to trace gas sensing [1](to list a few). In our laboratory we have explored the use of several methods for carrying out absorption spectroscopy with these sources: multipass absorption spectroscopy [2], cavity ring down spectroscopy [3], integrated cavity output spectroscopy (ICOS) [4], and quartz-enhanced photoacoustic spectroscopy (QEPAS) [5]. Practical applications from our laboratory include: monitoring of formaldehyde in the Houston atmosphere [6], monitoring of NO in the human breath [7], monitoring NH_3 in NASA bioreactor [8] and detection of traces of CO in propylene [9]. There is a website [10] with a complete listing of publications on trace gas sensing at Rice.

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[10] http://www.ece.rice.edu/lasersci/detectio.html

L-9

Recent results in Quantum Cascade Lasers and the lasers' role in trace gas spectroscopy

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Quantum Cascade (QC) lasers are a rapidly evolving mid-infrared, semiconductor laser technology based on intersubband transitions in multiple coupled quantum wells. The lasers' key strengths are their considerable wavelength tailorability across the entire mid- to far-infrared wavelength range, high power and high-speed operation, room temperature capabilities, and fascinating design potential. As such QC lasers are near-ideal light sources for mid- and far-infrared laser spectroscopy.

In this presentation, we will first give an overview of QC lasers followed by a discussion of several recent highlights, such as the quest for high performance operation and the implementation of unconventional laser schemes. For high-performance, we examine room temperature continuous wave operated QC lasers in the 8 – 10 μm wavelength range for both their temperature dependence of the loss and gain as well as their behavior above laser threshold. A model capable of describing the thermal as well as Stark effect roll-over is presented. For thermal roll-over, the maximum operating temperature can be well predicted. The broader availability of room temperature continuous wave QC lasers has gained significant credibility for the lasers for trace gas sensing.

In the area of novel QC laser designs, we present evidence for difference frequency generation in the mid-infrared. Light at the difference frequency (λ = 13.3 μm) is detected from a two-wavelength (λ = 5.3 μm and 8.8 μm) laser processed with a split-ridge configuration. We furthermore present evidence for the first observed "cascaded" laser emission in QC lasers, demonstrating a dual wavelength (~ 9.6 μm and ~ 8.2 μm) laser with electrons undergoing two consecutive, lasing, optical transitions in each active region. Such wavelength flexibility is a hallmark of QC lasers, and opens up innovative applications of the lasers for laser spectroscopy. One area of specific interest are gain broadened, external cavity-tuned QC lasers. We present an alternative method for anti-reflection surfaces for such lasers.

We will conclude with a brief review of the state of the art of QC laser applications, especially in trace gas sensing, and an outlook at the challenges and promises ahead for QC laser applied to spectroscopy.

This work is conducted in collaboration with Afusat Dirisu, Kale J. Franz, Anthony J. Hoffman, Scott S. Howard, Zhijun Liu, and Daniel Wasserman, and with the groups of Fow-Sen Choa, Deborah L. Sivco, Frank K. Tittel, Fred J. Towner, and Xiaojun Wang, and is supported in part by the NSF, MIRTHE (NSF-ERC), PCCM (NSF-MRSEC), and DARPA.

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P-1

Fiber Laser Based NICE-OHMS for ultra-sensitive trace species detection

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Noise-immune cavity-enhanced optical-heterodyne molecular spectroscopy (NICE-OHMS) is today's potentially most sensitive laser-based absorption technique [1]. The powerfulness of the technique comes from the fact that it efficiently combines absorption path length enhancement by optical cavities with intensity noise reduction by modulation techniques, and that it is "immune" to residual frequency noise with respect to the cavity mode. Despite its unique features, including the possibility to perform Doppler-broadened and Doppler-free measurements with the same spectrometer, NICE-OHMS has, so far, not been used for analytical applications, which can, for the most part, be attributed to difficulties with locking the laser frequency to the cavity mode.

This contribution reports on the development of a compact NICE-OHMS spectrometer, aimed at ultra-sensitive trace species detection [2]. The spectrometer is based on a DFB-laser pumped, erbium doped fiber laser, whose narrow linewidth (1 kHz over 120 ms) simplifies the locking of the laser frequency to the cavity mode considerably. Moreover, integrated-optics devices, such as a fiber-coupled electro-optic modulator, allow for a compact setup with a short free-space optical path and a minimum of bulk optical components.

In addition, a general theoretical description of NICE-OHMS signals is provided that combines the existing theories for frequency modulation (FM) and wavelength modulation (WM) spectroscopy. The description is presented in terms of the analyte concentration and valid for demodulation at an arbitrary FM detection phase. The possibility to extract the concentration from NICE-OHMS signals measured at an arbitrary FM phase simplifies the use of the technique. Explicit expressions for Doppler-broadened NICE-OHMS lineshapes are given, which are in excellent agreement with the measurements.

In a first demonstration, using a cavity with a finesse of 1400, acetylene has been detected on a Doppler-broadened transition around 1531 nm. A limit of detection of 130 ppt, corresponding to an absorption of $2.4\cdot10^{-9}$ cm^{-1}, was obtained with a setup that suffered from some technical limitations. A significantly higher detectability can therefore be expected from future measurements.

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P-2

Noncontact detection of explosives by means of TDLS

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Explosives are not stable substances. Those can decay even at room temperature. Half-life time varies from years to tenth of years. Rather simple decay products can be considered as perspective objects for detection via TDLS technique.

Experimental investigation of the explosives decay using Fourier-transform spectrometry and TDLS was carried out. Results of the investigation are presented. NO, N_2O, CO, NH_3 were observed in decay products. Analysis of temperature dependences of appearance rates of the decay products gave estimates of activation energies close to 1 eV.

A model of covered explosive with a hole in the cover is discussed. It is proved that flux of decay products is higher in several orders than flux of explosives vapor.

Two experimental models of diode laser spectrometer which can be used for noncontact detection of explosives are presented.

The first model was designed for local measurements. High sensitivity of the model is achieved due to using of multipass cell. The cell based on Chernin matrix system has 39 m optical length in a volume of about 2 liters. This model of diode laser spectrometer was used in experiments of noncontact detection of ammonium nitrate based explosives. Results of the experiments are presented and discussed.

The second model was designed for remote measurements. It includes telescope system to collect weak signal reflected (or scattered) from remote object. This model can include up to three diode lasers. Simultaneous remote detection of NH_3, CH_4, and CO_2 was demonstrated. Remote detection of NH_3 in moving car was demonstrated too.

P-3

Widely tunable Quantum Cascade Lasers for sensing applications

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During the last few years, considerable interest has emerged to use quantum cascade lasers (QCL) for sensing applications. The immense advantage of QCLs in this field is the fact, that absorption features of many technologically and ecologically relevant gases are much more dominant in the mid infrared spectral regime than in the near infra red, where conventional laser based sensors are working.

These lasers also exhibit a wider spectral tuning range than interband laser diodes in the near infra red. To fully exploit this wide tunability we have manufactured distributed feedback (DFB) QCLs with multiple current injection segments. Each segment is independently addressable and can support a distinct laser emission wavelength. This way a monolithically integrated laser device with multiple wavelengths in single mode operation becomes possible. Fig. 1 shows various spectra obtained from one DFB device using different segment currents and laser temperatures. This wide tuning range (in this case 105 nm) paves the way novel applications in sensing e.g. multi-component gas analysis at high spectral resolution.

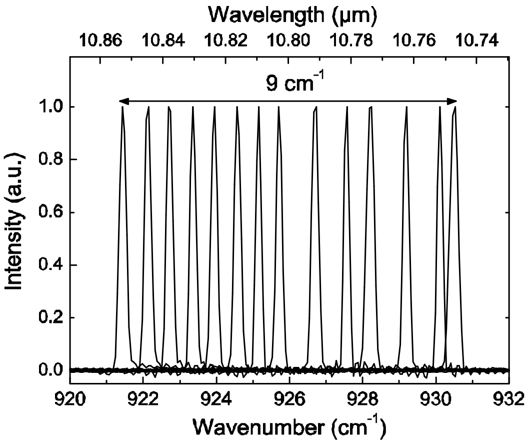

Fig.1. Single mode emission spectra of a multi segment DFB QCL obtained by temperature and segment drive current variation covering a range of over 9 cm^{-1} (105 nm).

P-4

Cryogen free quantum-cascade laser based spectrometer for high precision isotope ratio measurements of atmospheric CO_2

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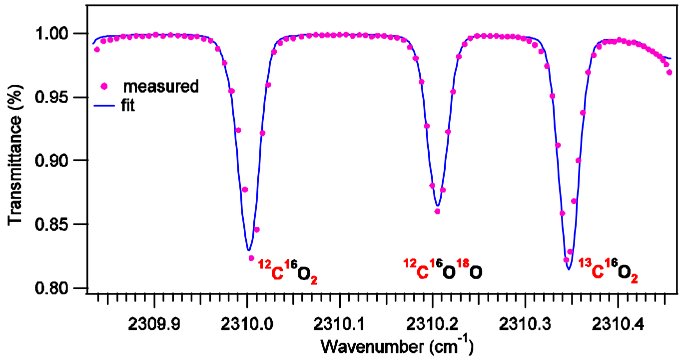
Interaction between terrestrial ecosystems and the atmosphere occurs via a number of processes including carbon dioxide exchange during photosynthesis and respiration. Global climate changes have the potential to alter ecosystem functioning through their effects on these gas exchange processes. Stable isotope analysis of atmospheric carbon dioxide is a powerful tool to study these influences. However, this requires continuous and very high precision isotopic analysis, which represents a real instrumental challenge.

We show 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, on-line and in-situ 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 field applications. The instrument is based on differential absorption spectroscopy; a dual multipass-cell arrangement is used to analyze the difference between the sample spectra and the simultaneously acquired reference spectra. Small, 0.3 l multipass cells are employed to optimize the instrumental response. The novel optical design assures a matched reference and sample path while keeping the overall system simple for easy adjustments and alignment maintenance. Furthermore, we have carefully selected a spectral window near 2310 cm^{-1} such that within the tuning range of the QCL laser the concentration of all three main stable carbon dioxide isotopologues ($^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$ and $^{18}O^{12}C^{16}O$) can be measured, allowing the simultaneous determination of both $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios. To obtain the necessary precision and robustness, a number of key aspects were optimized or developed, including a dual TEC IR-detector assembly, thermal coupling of the dual absorption cells, temperature stabilization of the optics, pressure control, calibration procedures and pulser electronics. Typically a precision of the isotope ratios significantly below 0.1‰ is achieved for 200 s averaging time. The short-term precision (1σ) for measurements of individual CO_2 isotopologue mixing ratios is at the 0.1 ppmv level.



The cryogenic-free instrument employing a state-of-the-art pulsed QC-laser can be operated unattended in the field and provide for the first time continuous and simultaneous measurements of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios at atmospheric mole fractions. Furthermore, 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 permits the combination of isotope ratio analysis with Eddy-covariance dynamic flux measurements.

P-5

NO_2 trace detection with a blue diode laser and a high finesse cavity injected by optical feedback

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In order to reach the sub-ppb NO_2 detection level required for environmental applications, we are developing a spectrometer that exploits laser sensitivity to Optical Feedback (OF) induced by a high finesse cavity. OF enables transient laser frequency locking to cavity resonances and laser bandwidth narrowing during a frequency scan, resulting in optimal laser coupling and broad transmission profiles for the cavity modes. This allows fast acquisition rates over four decades of dynamic range with excellent linearity. We initially developed OF-Cavity Ring Down Spectroscopy [1] and OF-Cavity-Enhanced Absorption Spectroscopy [2] both in the IR domain using distributed feedback diode lasers, with routine sensitivities of 10^{-9} cm^{-1} [3]. However, these lasers are only available in the range 1-2µm where no NO_2 strong transitions occur. On the other hand, this molecule has intense electronic transitions around 400nm, a spectral region where Extended Cavity Diode Lasers (ECDLs) are now available.

Very recently, we demonstrated that the sensitivity of these blue emitting ECDLs to optical feedback is fully compatible with OF-CRDS and OF-CEAS. A sub-ppb detection limit was obtained for NO_2 by preliminary OF-CEAS measurements with an ECDL source emitting around 411 nm [4]. We will describe the simple and compact optical set-up together with the gas handling system dedicated to NO_2 trace measurements, and we will report on the spectrometer performance.

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P-6

High resolution ethylene absorption spectrum between 6035cm^{-1} and 6210 cm^{-1}

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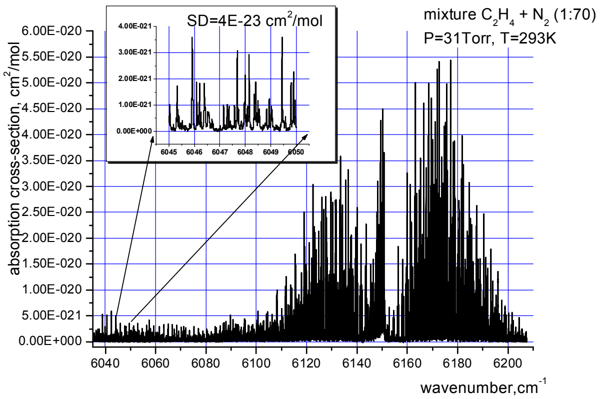
The ethylene (C_2H_4) molecule is present in planetary atmospheres like Jupiter, Uranus, Neptune, Saturn and its satellite Titan. It is also present in Earth's atmosphere. It is part of the exchange processes with the biosphere (vegetation, forest fires) and of the chemical processes such as combustion of fossil fuels, and processing of natural gas in petrochemical facilities. Ethylene is an atmospheric pollutant of VOC (Volatile Organic Compound). Its halogenated derivatives belong to the CFC pollutant family which contribute to destroy the ozone layer. We can add that ethylene is involved in the synthesis of plastics and in fruits maturation. For all these reasons, it is necessary to be able to measure very weak concentrations of this molecule in atmosphere.

One of the experimental techniques used to reach the objectives (astrophysical, atmospheric or industrial) is the high resolution infrared molecular spectroscopy, involving the fundamental study of the vibration-rotation of the molecule. Today the near infrared spectral region between 6035cm^{-1} and 6210 cm^{-}1 is widely used to design such a system.

The high resolution spectrum of the ethylene molecule is presented in modern database like HITRAN 2004 only in 1000 cm^{-1} and 3000 cm^{-1} region. Literature data on ethylene NIR absorption are scarce and spectral resolution is low.



Near-infrared diode laser spectrometer with two resonant photoacoustic detectors (PAD) was designed and firstly applied to study the absorption spectrum of CH_4 [1]. The use of two PADs provides the precise measurements of absorption line centre pressure shift and for calibrating of the wavelength scale with uncertainty 10^{-3} cm^{-1}. The spectral resolution is 2E-4 cm^{-1} and the threshold sensitivity is 4E-23 cm^2/mol.

We present the results the ethylene high resolution near infrared spectrum as well as the procedures of measurements and calibration. Figure 1 presents general view of ethylene absorption spectrum.

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P-7

Advances in fiber optics for Diode Laser Spectroscopy

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We review recent achievements in fiber optics and fiber-coupled diode lasers, which can be useful for diode laser spectroscopy.

1. Microstructured optical fibers for gas sensor applications

- Holey fiber is shown to be promising as a stable transmission medium insensitive to bending and microbending losses.

- Interaction between light and gas in the holes can be as high as 95% in hollow-core fibers [1]. Hollow-core photonic crystal fibers (PCF) are suitable for in-line gas sensor application. Methane spectrum measurements with a 1.8 m PCF have been demonstrated [2].

- Generation of broadband flat continua of visible and IR light in a highly nonlinear holey fiber is suitable for high-resolution spectroscopy. Acetylene absorption lines in the 1500-nm region has been demonstrated [3].

- A D-shape fiber-based in-line hydrogen sensor. The sensor uses the effect of hydrogen on a palladium foil attached to the D-shape fiber with a fiber Bragg grating written in the fiber core, has been demonstrated for hydrogen measurement in a concentration range from 0.1 to 4 Vol% hydrogen in nitrogen [4].

2. New single-frequency lasers

- High-power, ultra-stable, single-frequency doped-fiber external-cavity, grating-semiconductor lasers [5,6].

- Tunable single-frequency diode lasers with an FBG-based external cavity have been proposed for spectroscopy and gas analysis using selected absorption lines. This approach has been applied to detection of R7 line of the methane at $\lambda = 1.645$ μm [7] and ammonia at 1.52 μm [8].

- Broad-band continuously tunable all-fiber DFB lasers based on Er/Yr doped fiber cavity demonstrate a tuning range of up to 27 nm [9]. A fiber ring laser with a 40-nm tunability and a 750-Hz linewidth has been demonstrated. Wide tunability is achieved owing to stretching the grating [10]. These lasers can be advantageous for TDLS than DFB laser diodes.

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P-8

Long-term continuous isotopic ratio measurements of atmospheric CO_2 in Billerica, MA using a 4.3 μm pulsed QCL

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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 at least one part in ten thousand or 0.1 ‰. We use tunable infrared laser differential absorption spectroscopy with pulsed QC lasers (QC-TILDAS) to address this challenge. QC lasers are attractive optical sources due to: 1) absence of cryogenic fluids, 2) stable single mode spectral output, 3) optical simplicity.

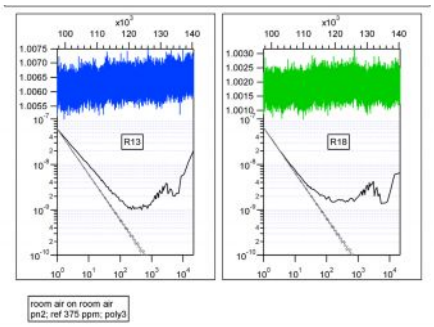

Fig. 1. Allan variance plots of 1 s data for $R13=S(^{13}CO_2)/S(^{12}CO_2)$ and R18 over 12 hrs. The minimum corresponds to σ_{Allan} = 0.03 ‰ after 300 s averaging time.

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 $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios can be obtained in a single spectral window near 2310 cm^{-1}. 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.

The long term 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 σ_{Allan} = 0.03 ‰ after 300 sec integration using a LN2 cooled detector.

We have used this instrument to perform long term (>3 months) monitoring of ambient air from the roof top of our laboratory. The data in Fig. 2 shows deviations in R13 and R18 relative to a calibration standard. The morning and evening signatures of local automobile traffic and residential heating by fossil fuels are evident in both elevated CO_2 and diminished R13 and R18.

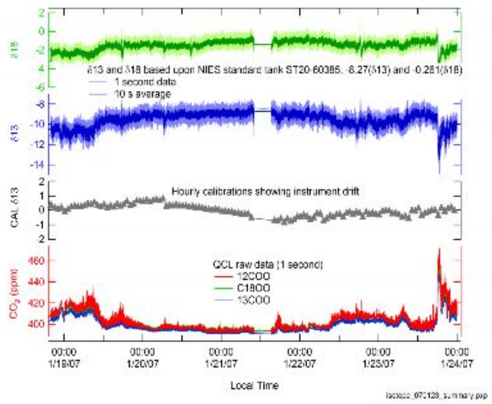

Fig. 2. Roof-top monitoring of ambient CO_2 isotopologues. Long term instrument drift is corrected by hourly additions of calibrated air.

P-9

Multigas detection at atmospheric pressure with a quantum cascade laser photoacoustic spectrometer around 7.9 µm

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Ten years ago the Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA, Reims, France) has developed a photoacoustic cell based on differential Helmholtz resonance for infrared gas detection [1]. This cell was used in conjunction with a near-infrared diode laser to detect methane. In recent years molecular gas lasers and diode lasers have been widely used for in-situ pollution monitoring. The photoacoustic sensor described here represents an effective spectroscopic technique for detection of ambient trace gases due to its intrinsically high sensitivity, large dynamic range and comparatively simple instrumentation. The detection limit of this technique is mainly determined by the characteristics of the laser used (output power, tunability, single mode emission…) and the photoacoustic cell sensitivity. The feasibility of methane detection has been demonstrated with near-infrared diode lasers and the system has been improved significantly so as to increase sufficiently the sensitivity for sub-ppm methane detection [2].

The use of quantum cascade laser gives the possibility to improve the detection limit thanks to its high power and its emission in fundamental bands. A first quantum cascade laser emitting in the 7.9µm region was used for the methane detection in ambient air. A detection limit of 3 ppb was achieved [3]. A second quantum cascade laser emitting in the 5.4µm region was used for the NO detection. A detection limit of 20 ppb was achieved [4]. Unfortunately these lasers work at cryogenic temperatures. The development of an in situ sensor is more difficult with this kind of technology. The results presented here will show the possibility of multi-gas detection (CH_4, N_2O, H_2O…) at atmospheric pressure with our photoacoustic spectrometer used in conjunction with a quantum cascade laser working at room temperature and emitting around 7.9µm. The achieved detection limits are slightly less than those obtained with the cryogenic lasers because the power is lower. However these results are amply sufficient to measure gas concentrations in air flux. The best practical modulation way is on-off modulation where the obtained signal is directly related to the molecular concentration. The detection limits obtained are in the same order of magnitude than that of the typical multipath (100 m length) absorption spectroscopy systems. The main advantages of photoacoustic spectrometers in comparison to these systems are the compactness of the system, the ease of use at atmospheric pressure, the insensitivity to optical misalignment and the very weak volume of the cell giving the possibility to install the sensor in a moving system and to make real-time in situ measurements at quite a high speed.

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P-10

Helium- and Argon-broadening coefficients of ethylene lines in the ν_7 band

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Growing interest to complex hydrocarbon as probing molecules for diagnostic purpose requires a detailed knowledge of isolated line spectral parameters, such as collisional line widths. Being one of complex hydrocarbons, ethylene C_2H_4 formed by the photodissociation of methane was found as a minor component of the Earth's and planetary atmospheres (Saturn, Jupiter and Titan) [1]. However, the collisional line widths of C_2H_4 are difficult to measure accurately because of the high density lines. They require a high-resolution spectrometer and rather low pressures of the perturber to minimize overlapping between neighboring lines. To our knowledge, except the measurements on N_2- as well as on H_2- and self- broadening coefficients in the ν_7 band of C_2H_4 [2-6], no any ones by rare gases have been yet reported.

In this work, we measure the He- and Ar- broadening coefficients of 35 lines in the ν_7 band of C_2H_4 at room temperature, using a high resolution diode–laser spectrometer (in order of 5×10^{-4} cm^{-1}). These lines with J values ranging from 3 to 23 are located between 919 and 1024 cm^{-1}. The collisional widths are obtained by modeling individually these spectral lines with the Voigt profile, which considers separately Doppler and collisional broadenings, as well as with the Rautian and Galatry ones, taking into account the collisional narrowing due to the molecular confinement (Dicke effect). Two latter models provide lager broadening coefficients than the Voigt profile.

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P-11

DFB laser diodes in the 2-2.7µm range for absorption spectroscopy

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The mid-infrared 2-2.5 µm region of the electromagnetic spectrum is attractive for trace gas sensing due to the presence of strong absorption bands of several species of industrial interest. Moreover, its location in the so-called transparency window, where absorption from the main infrared active atmospheric compounds (H_2O and CO_2) is weak [1], makes the analysis of other molecules easier. On the other way, the 2.5-2.7 µm region shows strong water vapour absorption lines making this range well adapted to water measurements and isotopic ratio studies.

For spectroscopic applications, single-frequency and continuously tunable emission is required. DFB (Distributed FeedBack) laser diodes are hence well suited for gas sensing applications. The IES (Institut d'Electronique du Sud) laboratory of Montpellier University has been working on antimonide laser diodes and their applications in gas analysis for about fifteen years. The devices are fabricated by molecular beam epitaxy (MBE) on GaSb substrate. The low gap materials used give access to the mid-infrared wavelength range ($\lambda > 2$ µm). The range between 2 to 2.7 µm has especially been studied. In this work, we will focuse on the fabrication and characterisation of DFB devices operating around 2.6-2.65 µm. The laser structure is realized, in one step, by solid-source MBE in a Varian Gen II machine on an n-type (100) GaSb substrate with a 1 µm-thick active region based on two $Ga_{0.57}In_{0.43}As_{0.11}Sb_{0.89}$ 16 nm-thick compressively strained quantum wells embedded between a barrier and a waveguide made of $Al_{0.30}Ga_{0.70}As_{0.03}Sb_{0.97}$ [2].

A DFB process has been developed based on a metal grating patterned on each side of the 5 µm ridge, giving a complex coupling effect [3]. This process can be adapted to each material and wavelength. The final devices operate in the continuous-wave regime at room temperature with a threshold current of about 100 mA at 20°C and a characteristic temperature of 57 K. A single frequency emission is obtained between 2.6 µm and 2.65 µm with a side mode suppression ratio reaching 25 dB and a continuous tuning of 2 nm.

This work has also been supported by the Centre National d'Etudes Spatiales (CNES) under contract n° R&T SU-0003-005.

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Part 3. TDLS for IAEA Safeguards

S-1 IAEA Safeguards: challenges in detecting and verifying nuclear materials and activities
M. Zendel

S-2 Tunable Diode Laser Spectroscopy as UF_6 Monitoring Technique
Natacha Peter, Marius Stein, Alexander Nadezhdinskii

S-1

IAEA Safeguards: challenges in detecting and verifying nuclear materials and activities

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The Safeguards System of the International Atomic Energy Agency (IAEA) is designed to ensure that States use nuclear technology solely for peaceful purposes by detecting and verifying nuclear materials and activities. At present the IAEA applies safeguards activities in more than 900 nuclear facilities around the world. The variety of physical and chemical properties of nuclear materials including their storage environment and the complexity of nuclear activities require a wide range of different verification and detection tools. Ongoing development is necessary to provide the IAEA's inspectorate with the best possible tools to perform the various safeguards activities.

New and improved technologies to enhance Safeguards verification are discussed and detection tools to meet the various safeguards challenges are presented.

The paper describes the efforts of the IAEA inspectorate to verify independently the inventories and flows of declared nuclear material and to confirm that existing nuclear activities are carried out as declared. Detection activities, capable to find possible undeclared nuclear materials and nuclear activities such as undeclared enrichment and reprocessing, are elaborated.

The IAEA is a strong promoter of nuclear technology for peaceful purposes, which is increasingly used throughout the world, but at the same time the IAEA needs to provide the assurance that nuclear material and nuclear technology is not misused to build nuclear weapons.

S-2

Tunable Diode Laser Spectroscopy as UF_6 Monitoring Technique

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Tunable Diode Laser Spectroscopy (TDLS) uses diode lasers tuned to access specific regions of the mid-infrared of the electromagnetic spectrum; spectral regions where gases of interest for detection such as Uranium Hexafluoride (UF_6) have strong spectral absorption. The Natural Sciences Centre of the General Physics Institute in Moscow, along with its joint venture partner Canberra Albuquerque, Inc., has developed a portable system that uses TDLS to detect the presence of UF_6 isotopes in-situ as well as, more importantly, the percentage of enrichment of the involved process.

This technology is appealing for application towards safeguards for two reasons. It provides a non-invasive method of isotopic measurement, and can be performed in-situ with real-time data processing. The in-situ use of TDLS is of interest to traditional safeguards (e.g., UF_6 samples are sent to International Atomic Energy Agency (IAEA) laboratory facilities for destructive analysis) as well as under the IAEA's expanded responsibilities under the Additional Protocol.

Optical monitoring methods such as diode laser spectroscopy allow non-contact isotopic measurement to be combined with real-time data processing. This potential means that new applications for safeguards use, such as a TDLS-based enrichment monitoring system, are possible. Although such development efforts are technically feasible in principle and are encouraged by the IAEA, their political impact on safeguards implementation and their economic feasibility compared to the current establishment monitoring system must first be addressed. If such concerns are properly managed, TDLS can become the future enrichment safeguards system for enrichment facilities.

Part 4. Poster presentations

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A-12 **Detection of trace water content in high-purity ammonia by means of diode-laser spectroscopy**
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A-15 Line parameters of NO_2 and H_2CO in the 3 microns region studied using a compact CW difference frequency generation laser

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A-16 A High Sensitivity, Non-Cryogenic, Compact Monitor for Ammonia Using a Pulsed Quantum Cascade Laser

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A-18 Advances in fiber optics for Diode Laser Spectroscopy

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A-1

Influence of optical feedback noise on tunable laser diode spectroscopy

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Distributed feedback (DFB) laser diodes having relatively high coherence are key devices in sensing equipment. The high coherence has supported the performance of the sensing equipment. The performance related to the coherence is, however, easily deteriorated by optical-back reflection from distant mirrors such as optical fiber-end [1]. This paper presents the influence of the optical feedback noise on laser diode spectroscopy.

The laser diode used was a strained quantum well DFB laser diode lasing at 2008 nm (KELD1G5B2TA, NEL Co.). The output power from the laser was coupled with a 1550-nm single-mode silica fiber, and the optical-back reflection was generated at the end of the fiber by changing the reflectivity. The optical output from the fiber was passed through a 4-cm-thick cell filled with CO_2. Here, the lasing wavelength was changed by controlling the laser temperature.

Typical CO_2 –absorption spectra under optical feedback are shown in Fig. 1. A clearand sharp spectrum was observed when no optical feedback was given (see Fig. 1 (a)). Longitudinal-mode fluctuation and mode hopping occurred under weak optical feedback. This instability tremendously degraded the absorption spectra, and the spectrum was quite noisy and lost the absorption peak (see Fig. (b)). Under strong optical feedback, the coherence collapse was generated, and the lasing spectral linewidth quickly broadened to about 0.2 nm. This broadening degraded the resolution of the absorption spectra, and clear absorption peaks were not monitored (see Fig. (c)).

The influences of optical feedback noise on gas sensing spectra has been clarified from these results.

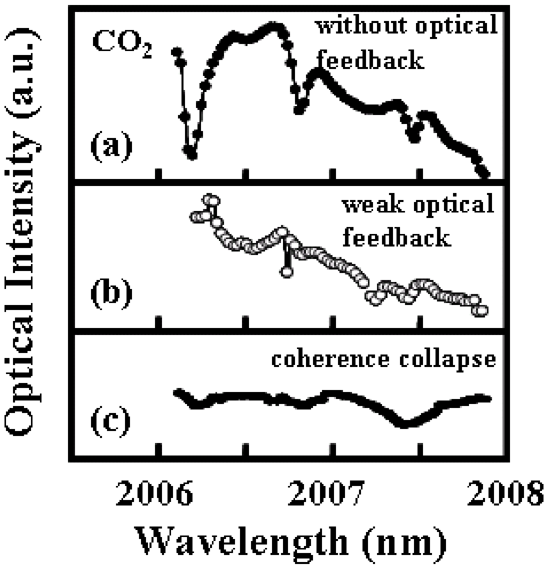

Fig.1 CO_2 –absorption spectra

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A-2

A calibration free approach to tunable diode laser spectroscopy with wavelength modulation

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Tunable diode laser spectroscopy (TDLS) with wavelength modulation is a popular choice for gas composition measurement in a growing number of industrial process control applications The basic technique uses direct current modulation of diode laser output, generating simultaneous modulation of the output power and wavelength / frequency. In the conventional approach, the target signal for measurement purposes is the amplitude modulation (AM) component generated at the receiver by the interaction of laser frequency modulation (FM) with a rotational / vibrational gas absorption line function. However, this leads to a number of calibration / scaling factor issues which, although addressable, lead to accumulated errors in the final determination of gas concentration. Such issues are particularly problematic in industrial applications where the pressure may be varying and unknown, as the pressure broadened line width strongly influences the signal amplitudes. In addition, direct modulation of the laser output power gives rise to amplitude modulation components at the receiver which distort the recovered target signals, again leading to errors. Here we report an alternative approach in which we exploit the phase difference between the laser AM and the FM. This new technique results in the direct recovery of the absolute gas line absorption or transmission function from which both the gas concentration and the pressure may be obtained from its depth and line width respectively. The method is absolute with no need for calibration, thus eliminating the difficulties with the conventional approach. In our presentation, we report the basic principles of the technique and its validation through a number of methane gas concentration and pressure measurements.

In order to realize accurate measurements of the line width of a gas absorption line, an accurate wavelength scale must be applied to the recovered time based signals. Due to issues of repeatability and non linearity of the current / wavelength curve of diode lasers, in situ wavelength referencing is required in any stand alone instrumentation. We also report a convenient, high resolution, on line approach to wavelength referencing using a fiber ring resonator. Again validation is demonstrated by the reported measurements.

A-3

Higher order nonlinear components of the refractive index in dark and bright coherent states

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We present measurements of the refractive index and the absorption coefficient of atomic cesium obtained in the two different closed degenerate two-level systems existing in the D_2 line. These lines show very different features: one is characterized by electromagnetically induced transparency and the other by electromagnetically induced absorption. Such absorptive characteristics are accompanied by extremely steep dispersive patterns in the vicinity of the dark or the white resonance. The intensity-dependent phase-shift of cesium was measured at low light intensity. From the measured phase-shift spectra it was possible to extract information on the probe refraction within the cesium beam. We found not only a huge linear refractive coefficient, as one can expect from the steep dispersive patterns, but also nonlinearities of higher orders which varied as a function of the applied coupling-laser intensity. Compared with usual nonlinear media such nonlinearities resulted orders of magnitudes larger in value.

The investigations were performed with a phase-locked three-laser-beam heterodyne interferometer [1,2]. We used a frequency-stabilized coupling laser, an off-resonant reference laser and a tunable probe laser. All lasers were single-mode diode lasers, passively stabilized by optical feedback from an external cavity [3]. The coupling laser drove the closed hyperfine transition of interest and was actively locked to it with an error signal generated by frequency modulation spectroscopy. The off-resonant reference laser, phase-locked to the coupling laser frequency, was required for the phase-shift measurements. The probe laser frequency was scanned around that of the hyperfine transition, while remaining phase-locked to the reference laser frequency. For sake of distinguishability the probe-laser and coupling-laser fields had orthogonal polarization and were superimposed at a power beam splitter. To minimize the Doppler effect, the laser beams crossed an orthogonally-propagating cesium atomic beam.

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A-4

Temperature dependence of Ar-broadening coefficients of C_2H_4

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Ethylene C_2H_4 is a minor component of our atmosphere but also of planetary atmospheres (Saturn, Jupiter and Titan). The knowledge of the temperature dependence of the broadening coefficients is necessary to develop atmospheric models. It is the reason why we have studied the mixture C_2H_4+Ar at various temperatures between 200 and 300K.

This work is in progress. At this time, the spectra were measured at two temperatures (273.2 and 248.2K). These measurements have been realized with the same tunable diode-laser spectrometer used for the room temperature study [1]. In the present work, the spectrometer was equipped with a home-made absorption cell which can be cooled by a liquid-N_2 flow [2]. The measurements have been realized on about ten lines in the ν_7 band for the same transitions than in [1] in order to study the temperature dependence of the pressure broadening coefficients.

The collisional widths are obtained by modeling individually these spectral lines with the usual profiles of Voigt, Rautian and Galatry. From these results, we determine the *n* parameter of the temperature dependence of each broadening coefficient.

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A-5

Measurements of spectroscopic parameters of N_2O near 1270 cm^{-1} for the in situ laser sensing of the atmosphere with SPIRALE instrument

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A quantum-cascade spectrometer was used in the laboratory to produce accurate measurements of spectroscopic parameters of N_2O near 7.9 µm. The studied spectral region which is suitable for the in situ laser sensing of N_2O in the middle atmosphere from balloon-borne platforms was investigated by use of a continuous-wave distributed feedback quantum-cascade laser. The SPIRALE instrument (SPectroscopie Infra-Rouge par Absorption de Lasers Embarqués) is a spectrometer using six tunable diode lasers and dedicated to the balloonborne in situ measurement of chemical compounds in the upper troposphere and the stratosphere [1]. The retrieved N_2O concentrations by the instrument are directly dependent from the good knowledge of the spectroscopic parameters of the used ro-vibrational transitions.

The GSMA laboratory is well equipped for the high resolution determination of spectroscopic parameters for atmospheric applications [2]. The spectral region ranging from 1275 to 1279 cm^{-1} concerns the P branch of the ν_1 fundamental vibration band of N_2O centered at 1285 cm^{-1}. Line positions and strengths seem to be well known but are measured in this work. Air-broadening coefficients and their variation with temperature must absolutely be measured since the latter is the same in the HITRAN database whatever the transition. The region is studied using a room-temperature quantum cascade laser from Alpes Lasers. The laser tunability permits to reach 5 lines of the ν_1 band of N_2O from P7 to P11. The line strengths of N_2O were studied with a spectrometer using a single pass cell of 1 cm long and pressures varying from 0.02 up to 0.1 torr. The air-broadening coefficients and their variation were studied using a multipass White type cell of 2 meters long and total pressures varying from 10 to 100 torr. All the parameters are thoroughly compared to relevant molecular databases and other experimental results. These spectroscopic data will be used to obtain atmospheric concentrations of N_2O from the SPIRALE data from older and future campaigns.

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A-6

Sensors for chemical analysis of trace gases based on widely tunable Quantum Cascade Lasers

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The recent development of trace gas sensor technology based on the use of widely tunable, single frequency, continuous-wave (cw), thermoelectrically cooled (TEC) quantum cascade lasers (QCLs) will be reported. This technology now permits the detection and quantification of molecular gas species with both resolved and unresolved absorption bands in the mid-infrared as well as the monitoring of multiple gas species for applications in such diverse fields as in environmental monitoring, industrial process control, medical diagnostics and homeland security [1].

Several specific QCL designs have addressed this issue [2-5]. An external cavity (EC) configuration is used to obtain single mode operation at any wavelength within the active medium gain profile. A widely tunable QCL source based on a novel EC-QCL architecture [6] was recently demonstrated with cw TEC QC gain chips operating at 5.2 and 8.6 μm. The EC QCL configuration employs a piezo-activated cavity mode tracking system for mode-hop free wavelength scanning. The mode-tracking system provides independent control of the EC length, diffraction grating angle and laser current. To-date using a 5.2 μm QCL gain medium a coarse laser frequency tuning range of ~ 155 cm^{-1} as well as continuous mode-hop free tuning range of up to 2 cm^{-1} with a maximum available optical power of ~ 11mW was demonstrated. Wide wavelength tunability and a narrow laser linewidth of < 30 MHz, which allowed resolving spectral features separated by less than 0.006cm^{-1} makes this EC-QCL based light source ideally suitable for high resolution spectroscopic applications and multi-species trace-gas detection. The recent availability of a MOCVD grown buried heterostrusture QC gain medium operating at 8.6 μm [7] resulted in single mode laser frequency tuning range of 135 cm^{-1} with a maximum cw output power of ~50 mW. An application of a broadly tunable EC-QCL for single and multi-species quartz enhanced photoacoustic spectroscopic (QEPAS) detection at the ppb-level will be reported for two molecules with unresolved rotational structure and overlapping broadband absorption features at 1208.62 cm^{-1}: Freon 125 (C_2HF_5), a convenient safe simulant for toxic chemical and biological agents, and acetone (CH_3COCH_3), a recognized biomarker for diabetes.

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A-7

Saturation spectroscopy of Xe^{I} and Xe^{II} in the near infra red for the diagnostic of Hall Effect Thrusters in the field of Spatial Propulsion

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The spatial propulsion uses Hall Effect Thrusters for namely the control of geostationary communication satellites [1]. Xenon ions produced by an annular plasma are responsible of the impulse (see Fig.1). Improvement and recent development of thrusters need very precise characterisation of xenon at the output and in the channel plasma. LIF and spectroscopy are currently used [2] but could be more efficient with a better knowledge of atomic and ionic structure.

We present our first results on measurements using Toptika tunable Diode Laser Spectroscopy in the near infrared around 834,7 nm.

Excited and ionized xenon are produced by a RF discharge in a quartz windows ended tube. For absorption spectroscopy, the laser beam is splitted in 3parts: two weak parallel and colinear beams (the probe and the reference beams) and the more intense pump beam counterpropagating with the probe beam.

However a better sensitivity is required for measuring the structure of the ionic line. We develop saturation spectroscopy coupled to intermodulation technique.

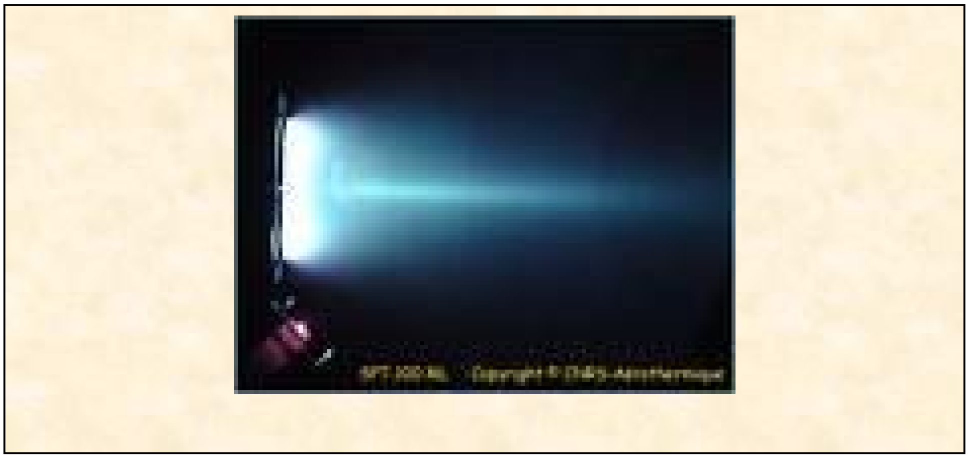

Fig.1 SPT 100 Hall Thruster in operation

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In the frame of the activities of the French research group GDR CNRS/CNES/SNECMA/Universités 2759 "Propulsion spatiale à plasma"

A-8

Development of tunable diode laser absorption spectrometer for measuring N_2O in the air

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IR Diode lasers are widely used as a tunable light source for high resolution spectroscopy commonly referred as tunable diode laser absorption spectroscopy (TDLAS) [1]. A lead salt diode laser which has 5㎛ launching wavelength (~2300 cm^{-1}) is used to measure ambient N_2O gas concentration in air [2-3]. Absorption data can be collected for the time profile of the gas in the long closed-pathlength setup. To do quantitative analysis, the spectral line position of N_2O was confirmed with HITRAN database. N_2O calibration curve and absorption coefficients were also obtained. The real time data can be collected for 5 meter pathlength up to 2.5 hours without any interruption. In the laboratory condition, various N_2O emission reactors were continuously monitored up to 0.5 ppm N_2O level [4]. The results obtained in this study are compared with those of simultaneously conducted analytical experiments.

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A-9

Cryogen free quantum-cascade laser based spectrometer for high precision isotope ratio measurements of atmospheric CO_2

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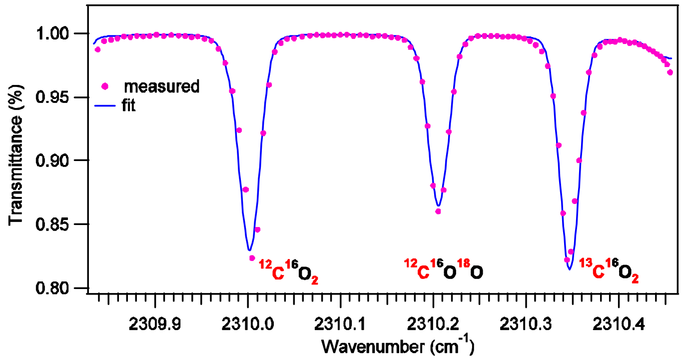
Interaction between terrestrial ecosystems and the atmosphere occurs via a number of processes including carbon dioxide exchange during photosynthesis and respiration. Global climate changes have the potential to alter ecosystem functioning through their effects on these gas exchange processes. Stable isotope analysis of atmospheric carbon dioxide is a powerful tool to study these influences. However, this requires continuous and very high precision isotopic analysis, which represents a real instrumental challenge.

We show 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, on-line and in-situ 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 field applications. The instrument is based on differential absorption spectroscopy; a dual multipass-cell arrangement is used to analyze the difference between the sample spectra and the simultaneously acquired reference spectra. Small, 0.3 l multipass cells are employed to optimize the instrumental response. The novel optical design assures a matched reference and sample path while keeping the overall system simple for easy adjustments and alignment maintenance. Furthermore, we have carefully selected a spectral window near 2310 cm^{-1} such that within the tuning range of the QCL laser the concentration of all three main stable carbon dioxide isotopologues ($^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$ and $^{18}O^{12}C^{16}O$) can be measured, allowing the simultaneous determination of both $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios. To obtain the necessary precision and robustness, a number of key aspects were optimized or developed, including a dual TEC IR-detector assembly, thermal coupling of the dual absorption cells, temperature stabilization of the optics, pressure control, calibration procedures and pulser electronics. Typically a precision of the isotope ratios significantly below 0.1‰ is achieved for 200 s averaging time. The short-term precision (1σ) for measurements of individual CO_2 isotopologue mixing ratios is at the 0.1 ppmv level.



The cryogenic-free instrument employing a state-of-the-art pulsed QC-laser can be operated unattended in the field and provide for the first time continuous and simultaneous measurements of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios at atmospheric mole fractions. Furthermore, 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 permits the combination of isotope ratio analysis with Eddy-covariance dynamic flux measurements.

A-10

DL frequency large amplitude modulation

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The goal of present paper is to analyzed influence of DL excitation current modulation on possible improvement in TDLS operation. Intensity and frequency modulation by excitation current is well developed area of DL physics [1]. Different modulation techniques were used in TDLS. However, these approaches were not optimal taking into account DL physical properties. Resent TDLS operation regime includes DL frequency large amplitude modulation. Fig.1 presents transformation of Doppler line as function of current modulation amplitude.

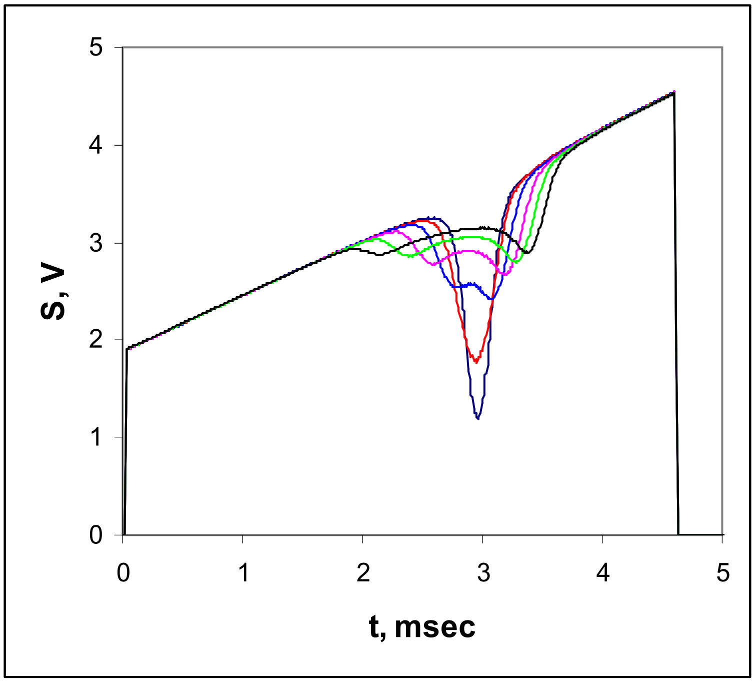

Fig.1 Transformation of water vapor Doppler line with current modulation amplitude (0, 4.7, 9.4, 14.1, 18.8, 23.5 mA)

Optimal modulation approach to achieve fundamental limit of minimum detectable absorption will be considered both based on theoretical and experimental investigations.

Achievement of minimum detectable absorption below 10^{-7} will be demonstrated.

References:

[1] See for example: G.Morthier, P.Vankwikelberge, Handbook of Distributed Feedback Laser Diodes, Artech House, Inc., Boston, 1997, and references

A-11

Noncontact explosives detection by means of TDLS

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A majority of the explosives detection techniques now in use, such as gas-chromatography or ion-drift spectroscopy, need sampling and sample preparation and can not be used for stand-off detection. The optical methods, such as TDLS, allow remote sensing.

Saturated vapor pressures of many explosives at room temperatures are too small and that gives almost no chances to detect them directly by optical methods. However, explosives are metastable compounds and their presence could be found by detection of gaseous products of their decay. In this report we present an attempt to detect ammonium-nitrate based explosives by detection of gaseous ammonia NH_3. For safety reasons most of experiments were conducted with explosives substitute: ammonium fertilizer (containing mostly ammonium nitrate NH_4NO_3), which in many cases is one of the components of ammonium-nitrate based explosives.

The experiments were conducted with diode laser NEL 537799 (1,51 μm) and “Chernin” multipass cell with base length 25 cm and optical path 39 m. In some experiments multipass cell was placed into closed glass box with sizes 39x15x16 cm^3 together with samples under investigation. An example of ammonia concentration record of one of the samples under investigation is shown on Fig. 1.

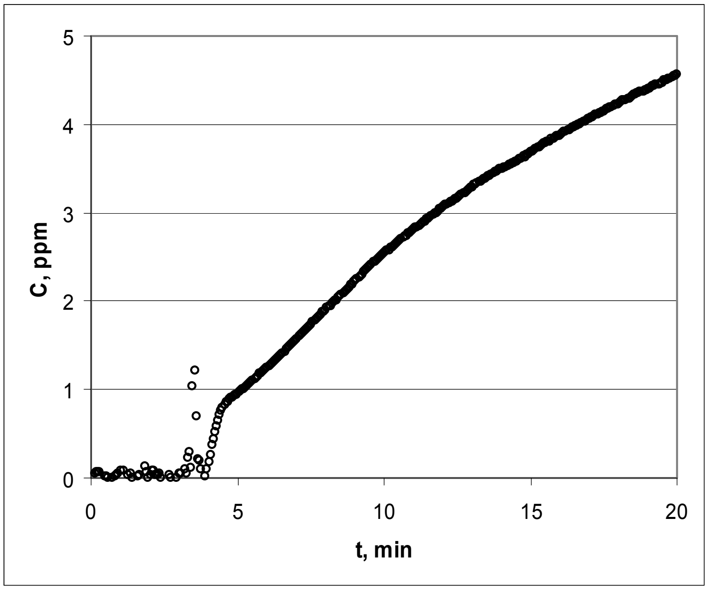

Fig. 11 Example of standoff explosive inside glass box detection via ammonia monitoring

The decay rate for this sample was found to be 2.4 10^{13} of NH_3 molecules/(sec g). The curve shape is determined by ammonia molecules diffusion in air above the sample. Ammonia molecules interaction with different materials was investigated. Influence of different wrappings and humidity on ammonia measurement will be presented.

In the other experiments air was pumped through the cell to measure ammonia concentration spatial distribution in facility where the sample under detection was installed.

A-12

Detection of trace water content in high-purity ammonia by means of diode-laser spectroscopy

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The aim of this work was the development of an as-simple-as-possible instrument for trace water concentration measurements in high-purity ammonia. A near IR diode–laser based instrument has been applied for measuring of humidity in on-line detection of water in ammonia during a process of industrial rectification. The results of water concentration measurements were compared with alternative techniques (first of all, dew-point meter) and rather good agreement was achieved. A sensitivity of such simple diode-laser based instrument for direct measurement was estimated as 1 ppm. A method of comparing of the whole amount of water containing in initial ammonia and integrated volume of water containing in heavy fraction extracted during rectification process gives even lower detection limit of less than 1 ppm depending on purity of initial ammonia.

Results of application of this method to some samples of ammonia with different water concentration are presented in the Table below:

Technical ammonia brand A	200 ppm
Cryogenic dried ammonia	53 ppm
Recrification column dried ammonia	0.1 ppm

As could be seen, method of calculating of integral amount of water during process of rectification gives residual amount of water on the level of 0.1 ppm for ammonia with small initial concentration (6.5 ppm).

A-13

Remote human detection

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Remote detection is important application of TDLS. Between many possible scenarios, remote human detection is very attractive. Humans are source of several molecules that can be detected by TDLS. One of these molecules is CO_2. CO_2 is one of atmosphere components (~ 300 ppm). CO_2 concentration in human breath is significantly higher (~ 3 %). Hence, presence of additional CO_2 concentration detected remotely can be signature of human presence in location under control.

To test the scenario under consideration DL based instrument developed for CO_2 remote measurement (see separate poster) was used. The instrument contained DL module (1.62 μ) was installed in room. Collimated laser beam was directed through room windows to windows of room under control located in other building. Distance between buildings was 40 m. Scattered light was detected by receiving optics and focused on PD. Fig.1 shows example of human presence detection in room under control.

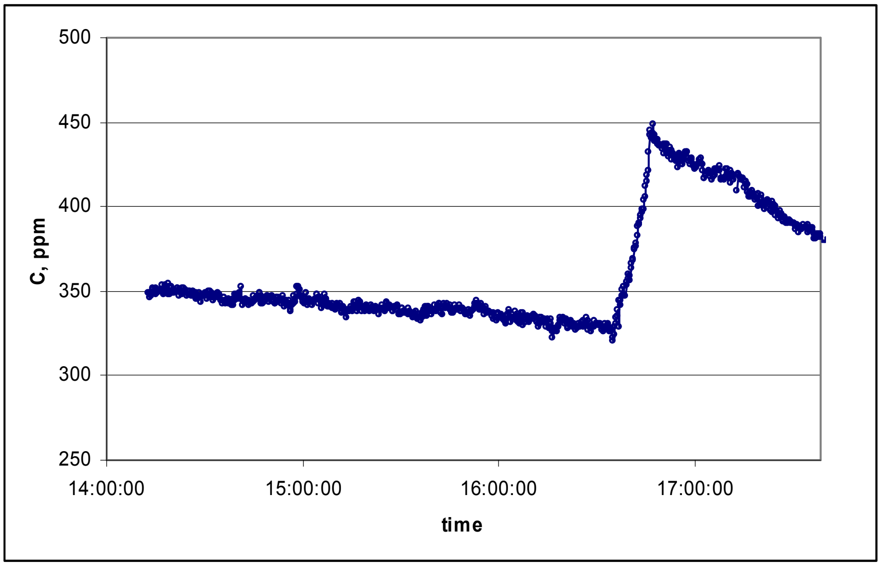

Fig.1 Remote detection of human presence by remote measuring of CO_2 concentration

Instrument monitored CO_2 concentration continuously. Around 16:40 group of 5 people came in room under control. Pronounce increase of CO_2 concentration can be observed. After 5-7 minutes the group left the room under control and CO_2 concentration decrease due to ventilation took place.

There other molecules being signatures of human presence. TDLS instrument for multy-molecules detection will be presented and analyzed.

A-14

Progress of portable natural gas pipeline leak detector based on NIR diode laser absorption spectroscopy

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China natural gas industry for long period slower growing has come into a fast increasing stage. To solve the unbalance distribution problem of china natural gas, it must take the large-scale transportation of natural gas. Therefore, building the main pipelines of natural gas transportation will be the developing stratagem of china energy source in long periods. For the long transport pipelines, the leakage of the natural gas is unavoidable. Detecting leakage sources is help to avoid the happen of fateful accident, and to reduce the economic loss.

There are many kind methods to monitor the pipeline leakage, but the detection efficiency of currently available natural gas detectors is very lower. With the development of narrow linewidth diode lasers, the detection based on NIR diode laser absorption spectroscopy with high sensitive and remote offers a new means for leak surveying.

We have designed and demonstrated a portable natural gas pipeline leak detector based on DSP processor (figure 1). To eliminate or reduce the inherent laser, electrical and optical noise of the detector, we use Kalman digital filter. Figure 2 shows the concentration fluctuation with time, and compare the true gas concentration variations after and before Kalman filter, we can see the fluctuation error is about ±15% before filtering, the fluctuation error after filtering is about ±3%. The experimental result show our detector can remote detect 25m distance with detection sensitivity of less than 100ppm·m, which weight is about 2kg.

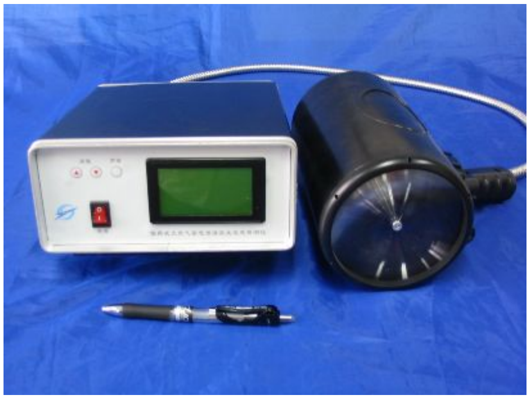

Figure 1 developed the prototype remote detector of nature gas pipe leakage

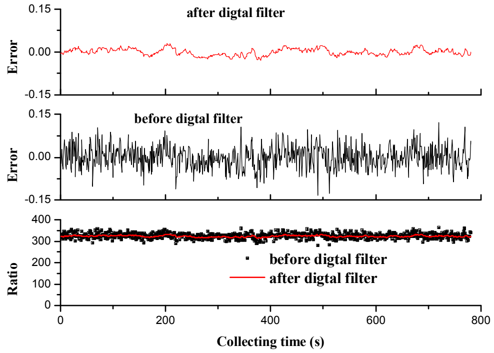

Figure 2 the ratio between second and first harmonic signals after and before filtering

A-15

Line parameters of NO_2 and H_2CO in the 3 microns region studied using a compact CW difference frequency generation laser

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Thanks to their wide tuning range, the low noise and very narrow line width, cw DFG lasers are interesting for various spectroscopic applications in the mid-infrared. In this paper, we report the development and application of a compact DFG source for laboratory studies, using the quasi-phase matching in periodically poled $LiNbO_3$ (PPLN). Monochromatic infrared radiation tuneable in the 3 to 5 µm range is obtained using a Nd:YAG laser at 1064 nm (maximum power 800 mW, linewidth 1 kHz) and an external cavity diode laser operating in the 815-885 nm range (linewidth 1 MHz), a spectrometer that was already used recently for a study of line-mixing in the 1-0 band of HI [1]. Here we report absorption spectra of NO_2 and H_2CO at very high spectral resolution (1 MHz) and high signal-to-noise ratio (up to several 1000), with typical integration times of a few minutes for mode-hop free scans covering 0.1-0.4 cm^{-1}. For NO_2, we have measured 27 line intensities in the $\nu_1+\nu_3$ band (which is widely used for atmospheric remote-sensing) and 8 line intensities in the weaker "hot" band $(\nu_1+\nu_2+\nu_3)-\nu_2$. Very good agreement with the line parameters of Mandin *et al.* [2] is observed. For H_2CO, we have observed some discrepancies between the line intensities of our measurements in the 2817-2826 cm^{-1} region and the results of Perrin *et al.* [3].

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A-16

A High Sensitivity, Non-Cryogenic, Compact Monitor for Ammonia Using a Pulsed Quantum Cascade Laser

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Emission of ammonia (NH_3) to the atmosphere is a major environmental concern and a potential health hazard, but the accurate measurement of ammonia sources requires improved instrumentation. There is a need for a high sensitivity, fast response, autonomous, continuous ammonia instrument to monitor present emissions, quantify the effectiveness of control measures, and evaluate the effects of ammonia emissions on local and regional soils, groundwater, and atmospheric environments. We have addressed this problem by developing an ammonia monitor based on high resolution infrared absorption spectroscopy using a thermoelectrically cooled quantum cascade (QC) laser at 967 cm^{-1}. An optically immersed thermoelectrically cooled infrared detector rather than a liquid nitrogen cooled detector allows us to operate the instrument autonomously for long time periods (several weeks). We have designed and constructed a novel, totally non-cryogenic, high sensitivity QC laser instrument for ammonia detection to achieve these goals and additional ones of compactness, and lower cost. Improved detector sensitivity at 10 microns, advances in the collection and transport of the laser beam through a 76 meter astigmatic multipass absorption cell, and improvements in the laser pulse electronics and temperature control have led to sensitive detection of ammonia with a noise level (rms) of 0.2 parts-per-billion-volume (ppbv) in a 1 second measurement time. An Allan variance plot of 10 hours of continuous measurements of room air is shown in Figure 1. With signal averaging we can achieve a reduced noise level of 0.04 ppbv in 60 sec. The compact ammonia monitor including optical and electronics modules fits inside a 17" x 24" x 10.5" rack mountable box (see Figure 2) and weighs just 25 kg.

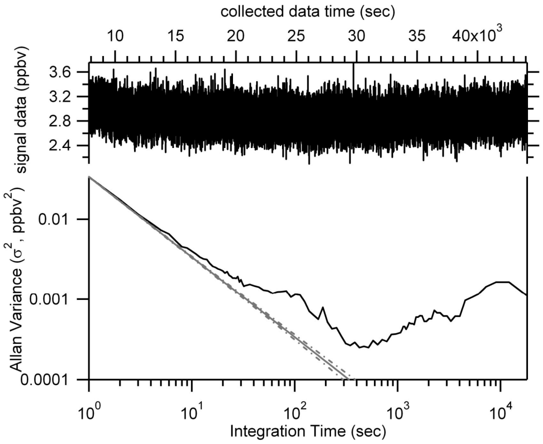

Figure 1. Allan variance graph of 10 hours of continuous NH_3 measurement showing minimum in variance corresponding to 0.02 ppbv in 400 seconds.

Figure 2. Photograph of the compact ammonia instrument (without covers). Optical module is on the left; electronics module is on the right.

A-17

Analysis of Human Breath using Laser Absorption Spectroscopy in the Near Infrared

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Human breath has been studied since centuries. Carbon dioxide (CO_2), water (H_2O) and oxygen (O_2) are major compounds in exhaled breath. Recently, several hundred chemical species (CO, NO, H_2CO, VOCs ...) have been identified in human breath, and some of them are biomarkers of various diseases (asthma, lung cancer, liver disease, ...). Breath analysis can be used for medical diagnostics as a fast, low cost, easy to perform non-invasive procedure [1].

Recent progress in optophotonics technology provides a new assay tool for breath analysis using laser absorption spectroscopy capable of performing sensitive, specific and fast detection of trace gas in human breath without sampling. In this paper, analysis of smoker exhaled breath using laser absorption spectroscopy will be reported. The analytical instrument is based on a fiber-coupled Telecom external cavity diode laser (ECDL, Tunics Plus) emitting single mode and single frequency radiation with an output power up to 5 mW [2]. This laser source is mode-hop free continuously tunable in the near infrared from 1500 to 1640 nm (C and L band) with a tuning resolution of 0.001 nm ($\sim 4\times10^{-3}$ cm^{-1}). The laser emission linewidth, determined by heterodyne measurements, is less than 1 MHz. A 100-m multipass cell in Herriott configuration is used for direct absorption spectroscopy application.

The 13C/12C isotope ratio in CO2 (13C16O2/12C16O2) was determined. The delta-value δ13C was found to be (–21.5±4.2)‰ for a smoker versus (–14.9±3.7)‰ for a non-smoker. Further improvement in measurement precision can be realized by use of cavity enhanced absorption spectroscopy, such as cavity ring-down spectroscopy (CRDS) or integrated cavity output spectroscopy (ICOS), in conjunction with dual-path balanced absorption technique in order to meet a precision <1 ‰.

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A-18

Advances in fiber optics for Diode Laser Spectroscopy

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We review recent achievements in fiber optics and fiber-coupled diode lasers, which can be useful for diode laser spectroscopy.

1. Microstructured optical fibers for gas sensor applications

- Holey fiber is shown to be promising as a stable transmission medium insensitive to bending and microbending losses.

- Interaction between light and gas in the holes can be as high as 95% in hollow-core fibers [1]. Hollow-core photonic crystal fibers (PCF) are suitable for in-line gas sensor application. Methane spectrum measurements with a 1.8 m PCF have been demonstrated [2].

- Generation of broadband flat continua of visible and IR light in a highly nonlinear holey fiber is suitable for high-resolution spectroscopy. Acetylene absorption lines in the 1500-nm region has been demonstrated [3].

- A D-shape fiber-based in-line hydrogen sensor. The sensor uses the effect of hydrogen on a palladium foil attached to the D-shape fiber with a fiber Bragg grating written in the fiber core, has been demonstrated for hydrogen measurement in a concentration range from 0.1 to 4 Vol% hydrogen in nitrogen [4].

2. New single-frequency lasers

- High-power, ultra-stable, single-frequency doped-fiber external-cavity, grating-semiconductor lasers [5,6].

- Tunable single-frequency diode lasers with an FBG-based external cavity have been proposed for spectroscopy and gas analysis using selected absorption lines. This approach has been applied to detection of R7 line of the methane at $\lambda = 1.645$ μm [7] and ammonia at 1.52 μm [8].

- Broad-band continuously tunable all-fiber DFB lasers based on Er/Yr doped fiber cavity demonstrate a tuning range of up to 27 nm [9]. A fiber ring laser with a 40-nm tunability and a 750-Hz linewidth has been demonstrated. Wide tunability is achieved owing to stretching the grating [10]. These lasers can be advantageous for TDLS than DFB laser diodes.

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Poster Session B

B-1 Long term continuous frequency stabilization of an external cavity diode laser using mode referencing

D. McInerney, C. Charlton, M. Lynch, J.F. Donegan, and V. Weldon

B-2 Absorption spectroscopy in a high-finesse optical cavity applied to the study of radicals produced in a low pressure plasma discharge

M. Triki, M. Chenevier, N. Sadeghi, D. Romanini

B-3 Oxygen detection using a differential Helmholtz-based photoacoustic sensor operating in the 760 nm range

M. Mattiello, M. Gyger, L. Thévenaz

B-4 Diode-laser spectroscopy: O_2- and air-broadering coefficients in the ν4 band of $^{12}CH_4$ at room temperature

Bénédicte Martin, Muriel Lepère

B-5 Laboratory tests of a quantum cascade laser in continuous and pulsed mode

B. Grouiez, L. Joly, B. Parvitte, D. Courtois, V. Zéninari

B-6 TDL measurements of formaldehyde release during the fabrication of noNwoven fabrics

B. Hanoune, L. Baelde

B-7 Detection of no at low ppb·m concentrations by UV diode laser direct absorption spectrometry at 226.6 nm

Jie Shao, Lemthong Lathdavong, Phaythoune Thavixay, and Ove Axner

B-8 Gas concentration and temperature measurements using widely tunable long -wavelength VCSEL

Alexandre Lytkine, Alan Lim, Wolfgang Jäger, and John Tulip

B-9 Use of diffuse reflections in TDLAS: implications of laser speckle for gas absorption measurements

D. Masiyano, J. Hodgkinson, and R.P. Tatam

B-10 Speckle noise in TDLS

Alexander Nadezhdinskii

B-11 Trace gas multi-component remote monitoring system

A.G. Berezin, S.L. Malyugin, A.I. Nadezhdinskii, D.Yu. Namestnikov, Ya.Ya. Ponurovskii, I.P. Popov, Yu.P. Shapovalov, D.B. Stavrovskii, I.E. Vyazov

B-12 Measurement of formaldehyde concentration in air by 1.78 μ VCSEL

S.M. Chernin, S.L. Malyugin, S.V. Malyugin, A.I. Nadezhdinskii, D.Yu. Namestnikov, Ya.Ya. Ponurovskii, I.P. Popov, Yu.P. Shapovalov, V.Ya. Zaslavskii

B-13 Analytical potentialities of the differential scattering method for remote monitoring of toxic aerosols with the use of near-IR range diode lasers
Sh.Sh. Nabiev, A.V. Volodin, D.V. Glukhov, A.N. Zhitov

B-14 O_3 and NH_3 line parameters in the 10 microns region STUDIED using TDLAS
N. Ibrahim, P. Chelin, J. Orphal, A. Gratien, B. Picquet-Varrault, J.-M. Flaud, M. Dhib, and H. Aroui

B-15 QCL Based FARADAY modulation spectroscopy for detection of uv-induced nitric oxide production from aqueous solutions
Thomas Fritsch, Christoph V. Suschek, Peter Hering, Manfred Mürtz

B-16 Applications for Quantum Cascade Lasers in High-Resolution Spectroscopy
Peter Kroetz, Dusan Stupar, Guido Sonnabend, Manuela Sornig, Jürgen Krieg, Fabrizio Giorgetta, Esther Baumann, Daniel Hofstetter, Nicolas Hoyler, Marcella Giovannini and Rudolf Schieder

B-17 A new portable spectrometer using a compact and very long path optical cell for in situ sensing of atmospheric trace gases
C. Robert and V. Catoire

B-1

Long term continuous frequency stabilization of an external cavity diode laser using mode referencing

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The emission from an external cavity diode laser (ECDL) is frequency stabilized to a water (H_2O) vapour absorption line at 935 nm using wavelength modulation spectroscopy (WMS) by means of a dual feedback locking loop. For such frequency locking to operate successfully on a long time scale the mode profile characteristic of the laser must remain constant. Unfortunately, in general, this is not the case for widely tuneable laser diodes [1, 2] including the ECDL referred to above since their emission characteristics are environment and age dependent.

A novel mode referencing technique is demonstrated which, in conjunction with the feedback locking procedure, ensures the emission frequency of the device remains locked in the presence of environmental and other effects that cause the operational characteristics of the laser to drift increasing the risk of mode hopping. The mode referencing technique utilises a characteristic of the power emitted from such a laser, to continuously compensate for any drift in laser's operational characteristics and hence enable the frequency locking feedback to operate long term in an uninterrupted fashion.

Keywords: Mode referencing, External cavity diode laser, Frequency stabilization.

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B-2

Absorption spectroscopy in a high-finesse optical cavity applied to the study of radicals produced in a low pressure plasma discharge

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The technique OF-CEAS (Optical-Feedback Cavity-Enhanced Absorption Spectroscopy) is a highly sensitivity absorption spectroscopy method that was developped and patented at LSP [1-3]. OF-CEAS was conceived to detect trace gases by using DFB (Distributed Feed-Back) diode lasers from the optical-fibre telecommunication market. OF-CEAS consists in measuring the transmitted intensity of successive resonances of a high finesse cavity whose injection exploits optical feedback (see Fig.1). The method has been subsequently extended to External-Cavity Diode Lasers (ECDL). The main advantage of these sources, compared to DFB diodes, is their tunability within a broader wavelength range.

In this work, we have developped and optimised an experimental setting with an ECDL diode operating in a 100 nm range around 1630 nm. This spectral region is particularly suitable to the study of small molecules possessing CH bonds (methane, ethylene, acethylene...), as well as CH_n radicals present in flame or plasma discharges. The system is composed by a V-shaped cavity (formed by three high-reflectivity mirrors) disposed around a cell of 80 cm length, equipped with electrodes and connected to a vacuum system. OF-CEAS spectra of good quality are obtained at low pressure In order to generate CH_n radicals, we inject argon containing methane at low concentration and produce plasma by a continuous electric discharge directly inside the high finesse cavity.

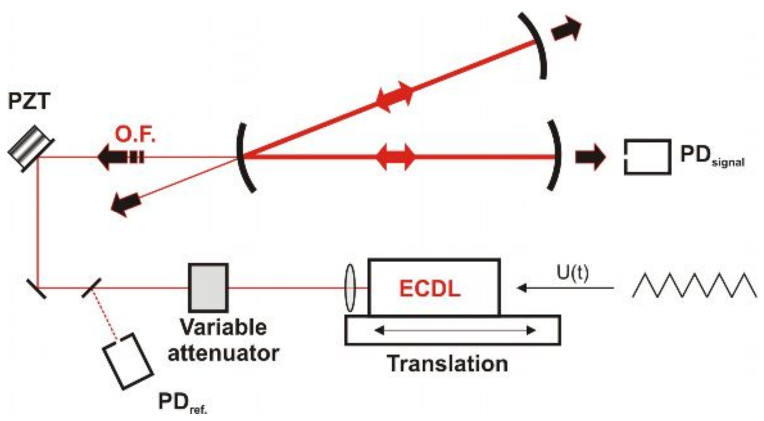

Fig.1 Cavity injection by Optical Feedback (OF)

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B-3

Oxygen detection using a differential Helmholtz-based photoacoustic sensor operating in the 760 nm range

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Breathe analysis is a major topic for the study of living systems, since it provides direct information on health and life quality of animals in laboratories, in particular for metabolic studies.

We report here the development of a differential photoacoustic (PA) sensor based on a Helmholtz-type resonator and on a VCSEL laser emitting in the 760 nm range. This type of resonator is made of two volumes connected by a thin duct. Among others, its most interesting property for differential measurements is that the acoustic wave in one volume is π-shifted with respect to the other volume at the resonant frequency. Such a Helmholtz resonator is therefore an intrinsically differential system if the 2 gas samples are separately inserted into each of the 2 volumes.

A membrane, tuned at the same resonant frequency than the cell, is placed mid-way of the connecting duct, playing the double role of separating the gas mixtures of the two volumes (e.g. inspired air in one, expired air in the other) and keeping the acoustic coupling between them, in order to still exploit the acoustic enhancement at resonance and to keep the phase-shifting equal to π.

First photoacoustic measurements for differential oxygen detection are reported here, showing a promising potential for the breathe analysis application.

B-4

Diode Laser Spectroscopy: O_2- and air-broadering coefficients in the ν_4 band of $^{12}CH_4$ at room temperature

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Methane is a molecule of a great interest. Indeed, this molecule is notably a minor component of our atmosphere [1] with an important effect on the climate, and of planetary atmospheres (Saturn, Jupiter …). The atmospherists need very accurate measurements [2] to improve their atmospheric models. In this work, we determine precisely line broadenings using a tunable diode laser.

We have measured O_2-broadening coefficients of $^{12}CH_4$ at room temperature. Those coefficients have obviously atmospheric applications especially for terrestrial atmosphere. In this study 51 collisional broadening coefficients have been measured. The wavenumber of studied transitions was comprised between 1236 cm^{-1} and 1373 cm^{-1} with the quantum rotational number J between 0 and 12. The pressures were measured with absolute MKS Baratron gauges and were comprised between 20 and 90 mbar.

The collisional broadening coefficients are obtained by fitting theoretical profiles on individual experimental lineshapes. We considered the Voigt profile and the Rautian model. The Voigt profile, used by most of spectroscopists, provides quite good results. However, we prefer the Rautian model because it takes into account the collisional narrowing named Dicke effect. To complete this work, we have also deduced 32 air-broadening coefficients from our results obtained previously for CH_4-N_2 mixture [3] and from this study.

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B-5

Laboratory tests of a quantum cascade laser in continuous and pulsed mode

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The Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA, Reims, France) has developed laser spectrometers based on quantum cascade lasers (QCL). Since the first realization of a QCL in 1994, many applications have been studied: communications, (for example, high-speed digital data transmission and optical free-space high-speed links), detection and quantification of trace gases, and high-resolution spectroscopy. Those lasers are unipolar lasers and the emitted wavelength is entirely determined by quantum confinement. The same material can be used from the mid-infrared to the THz region without having to rely on small band gap semiconductors.

Many works were realized in the GSMA using continuous wave (cw) QCL. We have reported spectral linewidth measurements [1], line strengths and broadening coefficients measurements [2], preliminary results of heterodyne detection in the 9 µm region [3], methane detection on the ppb level by photoacoustic spectroscopy [4] and water vapor isotope ratio measurements in air [5]. Thus our lab well masters the cw QCL use. We have now decided to extend our capabilities using pulsed mode QCL. The same QCL from THALES (France) was tested in the two emission modes. We will present here the first laboratory tests realized and the main comparisons between these two modes in terms of wavelength emission, total spectral coverage, continuous tunability, power… Moreover the laser in continuous mode has been used to record SO_2 spectra. These records will be compared with the main databases and a new calculation realized in this region [6].

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B-6

TDL measurements of formaldehyde release during the fabrication of noNwoven fabrics

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Following the recent reclassification of formaldehyde as a human carcinogenic compound, new recommendations have been issued for the exposure to formaldehyde, in particular in the workplace, and the lowering of the permissible long-term and short-term exposure limits is considered, down to 16 ppb for an 8-hour exposure and 100 ppb for a 15-minute exposure [1]. If the average long-term concentrations of formaldehyde can be easily measured using a carbonyl derivative HPLC method, the short term variations are not accessible by this method, and tunable diode laser spectroscopy is a convenient alternative technique.

In this context, we have applied our variable pressure tunable diode laser spectrometer [2] to the real time quantification of formaldehyde in a non-woven fabric manufacturing plant, where formaldehyde is either used or formed during the process. Formaldehyde was monitored at 2829.5 cm^{-1}, and concentrations in the production hall ranging from 40 to several hundreds ppb were measured, depending on the manufacturing process.

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B-7

Detection of no at low ppb·m concentrations by UV diode laser direct absorption spectrometry at 226.6 nm

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Nitric oxide (NO) is a reactive and strongly toxic pollutant that gives rise to health effects, contributes to ground-level ozone, and causes acid rain. Permissible emission levels of NO are facing increasingly strict regulations in our society. On-line detection techniques with sub-ppm·m detectabilities of NO are therefore needed. The detectability of ordinary TDLAS for NO is insufficient because of: (i) a combination of a lack of commercially available and reliable diode lasers at suitable transition bands; and (ii) weak transition strengths. The first and second overtones appear at 1.8 and 2.65 µm, respectively, which have weak line strengths, typically around $5 \cdot 10^{-23}$ and $4 \cdot 10^{-22}$ cm^{-1}/molecule cm^{-2}. Detection limits in the order of 140 and 1 ppm·m, respectively, have been demonstrated [1,2]. These wavelength regions are also strongly affected by interferences from H_2O. This has limited their use for practical detection of NO. One means to improve on this is to detect NO on its fundamental vibration band, at around 5.2 µm. It has been found that this band has line strengths that are ~50 times larger than that of the first overtone (~$2 \cdot 10^{-20}$ cm^{-1}/molecule cm^{-2}). NO has been detected on this band, using quantum cascade lasers, with a detection limit (S/N = 1) of 0.5 ppm·m [3]. This field attracts presently significant attention worldwide.

We have chosen to improve on the detectability of NO by using electronic transitions since they have line strengths that are yet another two orders of magnitude larger. In addition, such transitions are expected to be less affected by spectral interferences. This makes electronic transitions an interesting alternative for absorption spectrometry. We present a first demonstration of a *fully*-diode-laser-based system for detection of NO on its $X^2\Pi(v''=0)$ - $A^2\Sigma^+(v'=0)$ band at 226.6 nm utilizing mW powers of light [4]. The diode laser system consists of an external cavity diode laser producing 40 mW of cw light around 907 nm. The light passes a tapered amplifier, producing 700-800 mW of light. This light is fed into an external cavity, locked to the laser light by the Pound-Drever-Hall technique and containing a $KNbO_3$ crystal, that produces 300 mW of light at 453 nm. This light is fed into a second external cavity containing a BBO crystal producing a few (3 – 10) mW of light at around 226.6 nm. The UV power of the laser is regulated by a "noise eater" to reduce intensity fluctuations.

A significant improvement in the detectability of NO has been achieved by simple differential detection. A detection limit of 3 ppb·m (S/N = 3) under low pressure conditions was obtained for a peak absorption of $2.3 \cdot 10^{-4}$. The strength of the targeted lines was assessed to $3.1 \cdot 10^{-18}$ cm^{-1}/molecule cm^{-2}. A simulation model of NO absorption within this absorption band was developed. The measured line strengths agree well (within 3%) with model calculations. The instrumentation has also been used to assess the collision broadening and shift of NO in N_2 to 0.581 and -0.174 cm^{-1}/atm, respectively.

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B-8

Gas concentration and temperature measurements using widely tunable long -wavelength VCSEL

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We present a new technique for simultaneous gas concentration and temperature measurements using widely tunable laser diodes. The method involves interrogating two spectral intervals sequentially with a single laser diode. Each spectral interval contains one absorption line of a pair of lines chosen for optical thermometry. The laser frequency is switched between the intervals by modulating an injection current to acquire each absorption line one by one. The rate of the laser scan over each interval is adjusted to make the intervals relatively narrow, while the modulation frequency may depend on application. This measurement strategy allows to avoid many difficulties of traditional TDLS techniques of optical thermometry where single laser scans are used to cover broad spectral intervals. The difficulties include undesirable amplitude modulation of laser output, non-linear frequency tuning, and a relatively low resolution of absorption lines acquired within a broad single scan.

In our experiments we used a long-wavelength InP-based 1577-nm VCSEL with buried tunnel junction manufactured by VERTILAS GmbH (Germany). The laser beam collimated with an aspheric lens with focal length of 4.5 mm was directed into a 50-cm cryogenic absorption cell filled with CO_2 at pressures varying from 1 bar to few mbar at room temperature. A high-accuracy Baratron capacitive pressure transducer was used to measure the pressure inside the absorption cell with a resolution of 10^{-5} bar. The laser beam that passed through the absorption cell was monitored with a DC-10 MHz InGaAs photodetector (sensitive area ~ 1 mm) connected to a 12-bit analog-to-digital converter (NI model PCI-MIO-16E, 1.2 Ms/s) plugged into a personal computer. Cooling the absorption cell with liquid N_2 allowed us to set the gas temperature inside the cell to any point between 100 and 300 K. For temperature measurements we have chosen CO_2 rotational lines R10 and R22 of the $2\nu_1+2\nu_2^0+\nu_3$ branch. To switch the laser between the lines spaced by 6.42 cm^{-1} we modulated the injection current with a 1-kHz square waveform with an offset and a linear ramp superimposed on each pulse. The parameters of absorption lines were measured using LabVIEW 8.0 software to extract both gas concentration and temperature. The results of temperature measurements using optical thermometry were in a good agreement with readings of the pressure transducer and of two thermocouples placed inside the cell.

The gas sensor described in the present work was designed for the exploration of the Martian atmosphere. In the further developments of the method we have modulated VCSELs with sine waveforms with frequencies up to ~ 1 MHz to interrogate two gas absorption lines with different spacing. The amplitude of the modulation current was adjusted to scan the target lines at maxima and minima of the sine waveform. The technique of fast switching between two spectral intervals can be used with any widely tunable laser diode in many applications of ultra-fast optical thermometry including *in situ* monitoring of combustion processes.

B-9

Use of diffuse reflections in TDLAS: implications of laser speckle for gas absorption measurements

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Tunable diode laser absorption spectroscopy (TDLAS) has great potential in trace gas detection, with applications in health, safety and environmental monitoring. The attractiveness of TDLAS includes high sensitivity, specificity and high detection speed. However the sensitivity of many TDLAS practical systems is limited by the well known formation of unintentional Fabry-Perot interference fringes generated in the optical path between the source and detector. Although it might be possible to design out the problem, such measures are usually complicated and can be difficult to maintain in field instruments.

In recent years there has been interest in using diffuse reflections within the optical path, in the following diverse areas; use of remote “laser pointer” style gas detectors where the light is backscattered from a rough surface at ground level, use of integrating spheres as multi-path gas cells and insertion of diffuse reflecting or transmitting materials in the optical path.

We have taken this concept further by investigating the deliberate use of optical scattering in TDLAS by using diffusely reflecting materials as a means of eliminating interference fringes. This approach has several potential benefits: (a) reduced complexity and costs in instrument manufacture, and (b) making systems less susceptible to misalignment, thereby increasing field robustness. However the use of diffuse reflections introduces laser speckle that can contribute a random, rather than periodic, uncertainty to gas measurements. We have undertaken a systematic study of these effects.

We have established a method for quantifying the uncertainty due to speckle and investigated methods of reducing it. The analysis has been based on a wavelength modulation spectroscopy (WMS) model at 823nm to take advantage of cost effective CCD cameras that allow us to image and characterise the speckle for different optical configurations. We will present results from this model that confirm the viability of the technique and quantify the level of uncertainty that is introduced, for both interferometric and non-interferometric speckle. Predictions of the model will be tested by making actual gas measurements using WMS on the 1650 nm methane absorption line at a later date.

B-10

Speckle noise in TDLS

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In [1] it was shown that fundamental limit of sensitivity due to Diode Laser (DL) quantum noise can be achieved in TDLS when resonance molecular absorption is considered. This corresponds minimum detectable absorption below 10^{-7} for 1 sec averaging time.

At present time one of promising modification of DL based system are systems installed on vehicles, helicopters, airplanes, etc. detecting scattered laser light from topography reflector. When we’ve started investigation of sensitivity of such systems presence of additional noise was observed (Fig.1) reducing sensitivity more than 1000 times.

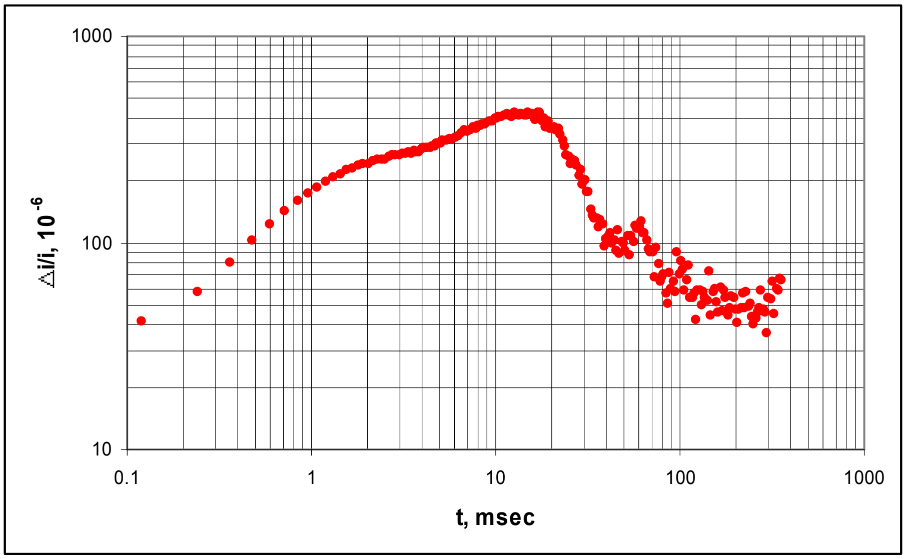

Fig.1 Allan plot of relative photocurrent noise Δi/i for DL based system with topography reflector.

Characteristic feature of such systems is presence of scattered light from topography reflector and relative system movement with respect to the reflector. Without movement no additional noise was observed. As the origin of this noise speckle pattern of scattered light was assumed. Up to author knowledge, for the first time this type of noise for TDLS system with topography reflector was considered in [2].

Speckle pattern of scattered light will be analyzed and modeled. Experimental investigations of additional noise will be presented and compared will predictions of analysis and modeling.

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B-11

Trace gas multi-component remote monitoring system

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Multi-component trace gas concentrations monitoring system was developed. The present configuration has a chance of simultaneous registration of up to six molecular objects.

The system incorporates: telescope MCT 180/1800 with 180 mm diameter and 1800 mm focal distance receiving mirror, set of tunable diode lasers on necessary wavelengths, power supply controller for diode lasers and photodetectors, and general-purpose PXI chasses NI PXI-1031DC which allows simultaneous three multi-channel input/output boards NI PXI-6289M operation, and each of them in its turn allows processing up to two independent laser channels. Each laser channels actually is an independent spectrum analyzer for one molecular object.

We used DFB heterolasers with fiber output produced by NTT Electronics (NEL) company for near IR-range. The opto-electronic characteristics of these lasers allow frequency tuning by temperature within the range 50 cm^{-1}, and with a help of current tuning within the range of 2 cm^{-1}.

The monitoring was performed by means of distance irradiation of topographic or any other target by tunable diode lasers and in receiving and processing of small part of radiation, scattered by target. An employment of one as well as all six laser channels simultaneously was possible.

In order to obtain several molecular objects detection multiplexing regime for signal processing was applied. It implied successive operation of different lasers with a use of general synchronization. So, a use of time multiplexing mode allowed conduction of simultaneous measurements of several molecules contents (in present configuration up to 6). At that, single measurement time was proportional to the number of molecular components. The time of single measurement for all six molecular objects concentration simultaneously was 1.7 msec.

DL were fed by trapezoid-waveform pulses with 500 μsec pulse duration. Delay time between pulses from different lasers was 100 μsec. All concentration measurements and alarm of excess of permissible concentration are displayed on the computer screen and occurred in real-time. System operated under the control of program which was specially written in graphical programming NI LabVIEW 7.1.

B-12

Measurement of formaldehyde concentration in air by 1.78 μ VCSEL

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Trace formaldehyde (H_2CO) concentration detection in air is interesting for several applications: atmosphere monitoring, H_2CO detection in buildings, in industry, etc. Formaldehyde is an important reactive intermediate product in troposphere hydrocarbon oxidation initiated by the OH radical. The H_2CO concentration in the atmosphere is in the 1 to 10 ppb range [1–3]. It is also a well-known pollutant that is emitted due to incomplete combustion processes [4]. Formaldehyde is a chemical widely used in many industrial manufacturing processes due to its high chemical reactivity and good thermal stability. Widely used building materials like foams and numerous consumer paint and polymer products contain formaldehyde.

Goal of present paper was to investigate possibility to develop instrument to measure trace formaldehyde concentration using near IR VCSEL (Vertical Cavity Surface Emitting Laser). Instrument developed contains as main components: VCSEL (1.78 μ), "Chernin" multi-pass cell (39 m), InGaAs photo-detector, electronics (see separate poster). Results of sensitivity analysis of the system will be presented as well as investigations of VCSEL generation characteristics and its fine far field diagram. Specific feature of the instrument under investigation was absence of H_2CO reference cell. Reference cell with water vapor was installed in reference channel to stabilize VCSEL frequency tuning [5].

There is only one source of H_2CO spectra in near IR [6] known for authors. Most pronounced formaldehyde absorption features are located are in 5500 – 5700 cm^{-1} spectral range. Using instrument developed formaldehyde absorption spectra were obtained in range 5578 – 5605 cm^{-1}. Optimal spectral range was determined [see 7] to have no interference with atmosphere water, methane, and CO_2.

Minimum detectable concentration of H_2CO was found to be 1.3 ppb for 1 sec averaging time. Averaging time increasing demonstrated white noise behavior up to 100 sec. However, long averaging times are not acceptable for real applications.

Several examples of instrument operation will be presented and analyzed.

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B-13

Analytical potentialities of the differential scattering method for remote monitoring of toxic aerosols with the use of near-IR range diode lasers

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Advances in the methods and instrumentation for remote indication of aerosols have been favored over the past five years first and foremost by a threat of terrorist organizations using toxic agents in various crowded places (underground and railway stations, airports, etc.). Toxic agents in battle forms (vapor, aerosol, drops) are capable of traveling at large distances downwind, penetrating into houses or various shelters and retaining their injuring action for a long time. Toxic agent effect in atmosphere and on locality depends on physicochemical performances of the agent, such as volatility, viscosity, surface tension, melting and boiling temperatures, and environmental stability indices. The group of the most dangerous toxic agents which are highly toxic fluorine-containing chemical substances incorporates sarin, soman, tabun, and V-gases. On ingress into a human body, these agents inhibit ferments responsible for regulation of nervous impulsing, mainly in respiratory, blood circulation and cardiac systems. This determines the urgency of works currently in progress aimed at the development of new methods of remote indication of aerosols and designing instrumentation on their basis that would ensure fast detection and identification of aerosols of a variety of toxic agents in trace concentrations, monitoring of failures at chemical plants, and chemical weapon manufacturing by terrorist organizations.

This report substantiates an approach to remote indication of aerosols of toxic agents based on the differential scattering (DS) method in the field of composite frequencies and overtones of valence C-H vibrations with the use of the most promising for today near-IR range diode lasers (DL).

The determination of analytical potentialities of the DS method for remote indication of aerosols of V-gases presupposes availability of information on optical constants and spectral dependences of back-scattering of V-gases aerosols and interfering admixtures in the range under study. No such data are available for the near-range of the spectrum, in particular, the range of overtones and composite CH-vibrations (λ =0.8-2.5 µm). Therefore, we have performed calculations of the true and imaginary parts of the complex refraction index for V-gases, their models and interfering admixtures, as well as spectral behavior of efficiency factors of back-scattering of aerosols of the substances in question.

Algorithms and codes have been developed and calculations made after the Mie theory of the spectral behavior of the back-scattering efficiency factor for polydisperse aerosols of V-gases and their models (triisobutyl phosphate, triethylamine, etc.), and interfering admixtures (water, turbine oil, glycerin, etc.) in approximation of spherical isotropic aerosol.

Possible ranges of remote detection of V-gas aerosols (for battle flux density of 100 mg/m^2) have been calculated by the differential scattering method in the near-IR range with a diode laser based lidar (E_{pulse}= 500 µJ, t_{pulse} = 30 ns) and various types of receivers: Ge (300 K, $D^*=1\cdot10^{12}$ cm·Hz$^{1/2}$·W^{-1}, a·b=0.01 cm^2; Δf=5 MHz for λ_{oper2}=1.691 µm); an avalanche photodiode ($D^*= 1\cdot10^{17}$ cm·Hz$^{1/2}$·W^{-1}, a·b=0.01 cm^2; Δf=5 MHz for λ_{oper1}=0.911 µm) and a receiving telescope with a 0.1 m^2 aperture to make 2.6-4.5 km and 5-10 km, accordingly, on meteorological viewing distance of 3-5 km for one laser pulse with detection probabilities P_{detect}=0.95.

B-14

O_3 and NH_3 line parameters in the 10 microns region STUDIED using TDLAS

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Atmospheric remote-sensing by infrared spectroscopy requires the selection of appropriate spectral regions covering features of trace species with sufficient absorption for accurate quantitative measurements. In particular, the spectral region around 10 µm is very important for the study of atmospheric O_3 and NH_3. For O_3, the most important species, there exist significant uncertainties concerning the agreement between absolute line intensities in the mid-infrared and absorption cross-sections in the ultraviolet [1]. For NH_3, there is still lack of experimental studies concerning pressure-shift which is interesting both for atmospheric studies and theoretical investigations.

The experimental work described here was carried out using a single-mode lead-salt diode laser (operated in the 80-100 K range) that is tuneable between 1030 and 1070 cm^{-1} in mode-hop free steps of about 0.1-0.4 cm^{-1}, a simple Pyrex absorption cell (100 cm) at room temperature (296 K), and a MCT detector at 77 K. The laser tuning (obtained by sweeping the injection current) was monitored using a Germanium etalon (spacing 0.03 cm^{-1}) and a small (20 cm) absorption cell with OCS at very low pressure, that were measured using a second MCT detector in order to achieve an accurate wavenumber calibration. For the study of O_3 line parameters, the ultraviolet absorption was measured simultaneously in the same absorption cell, using thin Germanium plates as dichroic filters and a PC-based diode-array spectrometer. In addition, the O_2-broadening coefficients of O_3 were determined. Note that over the entire pressure range, no significant Dicke-narrowing or line-mixing effects were observed. For NH_3, accurate pressure-broadening and -shift coefficients were determined using O_2, N_2, and air, and compared with theoretical calculations.

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B-15

QCL Based FARADAY modulation spectroscopy for detection of uv-induced nitric oxide production 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 NO_2^-, from which in the presence of UV radiation and water NO is produced. The reaction pathway is theoretically predicted, but not yet experimentally proven. Within the reaction pathway from NO_2^- to NO, it is predicted that free radicals (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 NO_2. We used nitrogen to transport the gaseous NO from the reaction chamber to our cw-QCL based Faraday Modulation Spectrometer (FAMOS), 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 [1].

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 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.

Due to its extreme selectivity on NO, the FAMOS technique is an excellent method for measuring NO production from aqueous solutions.

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B-16

Applications for Quantum Cascade Lasers in High-Resolution Spectroscopy

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We present new results and observations using quantum cascade lasers (QCL) as local oscillators and QC-detectors within our 'Tuneable Heterodyne Infrared Spectrometer' (THIS) [1]. Achieving an unprecedented spectral resolution in the mid-infrared of more than 10^7, THIS is capable of measuring for example winds on Mars [2] and Venus and will be used in the future to search for methane on Mars, molecules in protoplanetary discs and molecular hydrogen in the interstellar medium. It is proposed as a second generation instrument on board the Stratospheric Observatory for Infrared Astronomy (SOFIA).

New technical developments include the integration of a totally reflective external cavity system to achieve continuous broadband tuneability of the QCL local oscillator to the astrophysically needed wavelength. With the appropriate QCL [3], tuning ranges of up to 2 micrometer are achievable. While no scans are necessary, laser stability of less than 1 Mhz is mandatory for the ultra-high resolution purposes. Stability measurements in a cassegrain test setup will demonstrate the abilities and performance possibilities of this setup at real telescopes.

Novel detection techniques are being explored using recently developed quantum cascade detectors [4]. First tests of a 16.5 micron detector will be shown which might lead to a feasible system for the detection of the 17.035 micron transition of molecular hydrogen. Other possibilities with Mercury-Cadmium-Telluride and Quantum-Well-Infrared-Photodetectors are also discussed.

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B-17

A new portable spectrometer using a compact and very long path optical cell for in situ sensing of atmospheric trace gases

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Our laboratory developed sometime ago a balloon-borne infrared absorption spectrometer (SPIRALE) with six tunable diode lasers for sensing the upper troposphere and the stratosphere [1]. This instrument allows for simultaneous accurate *in situ* measurements of more than ten trace gases with very high (< 10 m) vertical resolution, in an air-open Herriott cell of 3.5 m long leading to a total optical path > 430 m. With the advents of external-cavity diode lasers and quantum-cascade lasers, and the invention by our laboratory of a new type of a simple, stable and compact multiple-reflection long path optical cell [2] (international patent demand PCT: WO2007/017570 A1), the miniaturization of SPIRALE instrument with the same performances becomes possible. A laboratory prototype has been built and is presented.

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Poster Session C

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C-16 Two channel photo-acoustic diode laser spectrometer and fine structure of methane absorption spectra in 6070-6180 cm^{-1} region
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C-1

Influence of ethylene neighbor spectral lines on the methane content measurement with the diode laser methanometer at 1.65 μm

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Spectroscopic measurements in the range of about 1.65 μm have revealed that spectral lines of ethylene are present in this range along with methane spectral lines [1], and HITRAN database has no parameters of these ethylene lines. Particularly, when measuring with the laser methanometer having the frequency radiation tuning range about 6000–6080 cm^{-1} it was found that several ethylene absorption lines are located near the methane analytical line (*R*3 triplet $2\nu_3$ centered at 6047 cm^{-1}) [2]. Ethylene can be present together with methane in the samples under study, distorting the recorded spectrum of the methane analytical line. This distortion can produce some error in the revealed methane concentration. The aim of this study is to estimate numerically the error in the determination of the methane concentration caused by the presence of ethylene of different concentrations in the samples under study when detecting the methane with diode laser methanometer at 1.65 μm.

Calculations were performed in two stages. First, model spectra were used. Since the gas pressure in the reference and analytical methanometer cells is close to the atmospheric one, then we used Lorentzian line contour in calculations. It was assumed that the methane absorption in the considered wavenumber range is conditioned by *R*3 triplet only. Since individual lines of the triplet are unresolved at the atmospheric pressure, the methane spectrum was modeled by a single line. The ethylene spectrum was modeled by two lines, whose parameters were chosen in such a way that the calculated and experimental spectra visually were close to each other. It was also assumed that the signal in the reference channel is caused only by methane absorption, and in the analytical one – by a mixture of methane and ethylene in air. Therefore, a random noise was added to the calculated signals. The methane concentration in the methanometer is calculated from the correlation coefficient, therefore in numerical simulation the correlation coefficient of signal third derivatives was also calculated. The dependences of the correlation coefficient on the ratio ethylene/methane absorption and noise level have been built. The same signal processing procedure was used in the second stage, but the experimentally measured spectra of methane and ethylene were used; the methane concentration in the cell was determined from the obtained correlation coefficient. The dependences of errors in determination of the methane concentration on the ethylene concentration and noise level are presented.

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C-2

Wavelength modulation spectroscopy using near infrared diode lasers: Applications to rubidium and trace NO_2 detection

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Employing tunable diode lasers operating in the visible region and wavelength modulation spectroscopy techniques, we studied the sensitivity for the detection of nitrogen dioxide. Various intense overtone excitations were investigated. Wavelength tuning was accomplished by modulating the injection current of the diode laser with a very low frequency ramp signal. For harmonic detection, this is further modulated by a sine wave of low amplitude at high frequencies. The first, second, third and fourth harmonic spectra were recorded. The lineshapes were investigated at different modulation frequencies and amplitudes. The sensitivity of detection is calculated using a reference cell and from the signal to noise ratio of the observed harmonic spectra.

The important features of modulation spectroscopy technique are studied by investigating the hyperfine structure of 780 nm atomic level of Rubidium using Doppler limited spectroscopy techniques. The hyperfine structure of the 780 nm excitation results in well separated four hyperfine levels that are excellent candidates to investigate the harmonic detection. As we go to the higher harmonic detection, the signal intensity goes down where as the noise level is reduced. Thus, there is a trade off in the signal intensity for noise reduction. The detailed study of the harmonic spectra of the hyperfine levels and Rubidium will be presented. These data provide optimal modulation parameters to obtain maximum signal to noise ratio for higher harmonic detection. The observed line shapes are compared with the modulated Lorentzian lineshapes. To the best of our knowledge, the wavelength modulation spectroscopy of Rubidium and NO_2 at 780 nm are reported for the first time using diode lasers.

We expect to receive an external cavity tunable quantum cascade laser soon. We hope to present some preliminary results on the detection of nitrogen dioxide using the quantum cascade lasers and wavelength modulation spectroscopy techniques.

C-3

Development of a compact instrument using fiber laser based difference-frequency generation source for chemical gas detection

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In the present paper we report on the development of a compact mid-infrared (MIR) laser source operating at room temperature for trace gas detection of chemical species. The laser source, emitting between 3.15 and 3.43 µm, is based on continuous-wave (CW) difference-frequency generation (DFG) in a periodically poled LiNbO3 (PPLN) crystal. Two CW fiber lasers were used as difference-frequency mixing sources : one is an ytterbium (Yb^{3+}) doped fiber laser (YDFL, IPG LASER GmbH) operating at ~1062 nm, and the other is an erbium (Er^{3+}) doped fiber laser (EDFL, IPG LASER GmbH). The EDFL is tunable from 1543 to 1601 nm with a mode-hop free frequency tuning of about 2-3 cm^{-1} [1]. Both lasers have a narrow linewidth (less than 1 MHz) and high single mode/single frequency output power (up to 1 W). Two laser beams were coupled together via a WDM (OZ Optics Ltd.), collimated and then focused into a temperature controlled multi-channel 50-mm long PPLN crystal (Deltronic, Inc.). With a pumping configuration mentioned above, infrared radiation from 3.15 to 3.43 µm (2915 to 3175 cm^{-1}) has been produced by quasi-phase-matched DFG in the PPLN by means of a period of Λ=29.9 µm in conjunction with temperature tuning from 50 to 180 °C. DFG-based laser powers of more than 200 µW with a linewidth of ~1 MHz were obtained by mixing the outputs from the EDFL (1570.2 nm, 634 mW) and the YDFL (1062.6 nm, 516 mW). The corresponding DFG power conversion efficiency was ~0.6 mW/W^2.

The MIR spectral region is usually highly attractive for ultra-sensitive trace gas spectroscopy, owing to the strong absorptions of fundamental transitions. The spectroscopic characteristics of the DFG source have been evaluated using high resolution absorption spectra of ethylene (C_2H_4) of the ν_9 band near 3.23 µm in terms of line parameters (such as line strength, self- and air-broadening coefficients). The experimental results were in agreement with those given in the HITRAN database. DFG absorption spectra of benzene (C_6H_6) vapor of the ν_{12} band near 3.28 µm have been recorded and studied in order to demonstrate the feasibility of benzene vapor detection by DFG laser absorption spectroscopy.

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C-4

Diode Laser Spectroscopy: Collisional shift coefficients of C_2H_2 perturbed by N_2

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The collisional shift coefficient of four absorption lines of C_2H_2 perturbed by N_2 has been measured with a tunable diode laser spectrometer adapted to shift measurements. For this purpose, two absorption cells are put in the laser beam, in a way of observing simultaneously an absorption line of C_2H_2 shifted by N_2 and the same line of C_2H_2 at very low pressure. That gives a perturbed line as well as the unperturbed same line of C_2H_2 used as reference.

Four absorption lines in the R-branch of the $\nu_4+\nu_5$ band have been studied at twelve different partial pressure of N_2. For each pressure, the collisional shift is obtained by fitting the reference line superposed to the perturbed line, with an addition of two Voigt profiles, or an addition of a Voigt and a Rautian profiles. A linear regression is done, to deduce the collisional shift coefficient.

C-5

Development of a compact CO_2 sensor based on near-infrared laser technology for œnological applications

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The Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA, Reims, France) has developed a lot of various laser spectrometers using direct-absorption, heterodyne, or photoacoustic spectroscopy for the study of the atmospheres. These spectrometers use different types of infrared lasers such as telecom-type near-infrared diode lasers, Pb-salt mid-infrared diode lasers, multi-quantum wells diode lasers and quantum cascade lasers. For example a compact CO_2 sensor open to the atmosphere and based on near-infrared laser technology has recently been developed [1]. The instrument is designed to measure in situ CO_2 concentrations open to the atmosphere at ground level. Absorption lines were carefully selected around 2.68 µm to minimize interferences from neighboring water vapor transitions.

Based on this technology we now develop the same type of instrument for œnological applications. This work is realized in collaboration with the Laboratoire d'Œnologie et Chimie Appliquée in our university [2]. The work consists in the conception and the optimization of a laser detection system for the measurements of CO_2 in sparkling wines such as champagne from production (cells, bottles) to tasting (flute or goblet). The progressive desorption of dissolved CO_2 in the champagne is responsible for bubble formation. Moreover CO_2 may also escape by diffusion at the air-champagne interface. This invisible process is more difficult to quantify. Details on kinetics of CO_2 desorption are not well known and interactions between CO_2 and aromatic molecules during tasting have not been studied. A first step in the understanding of the role of CO_2 will be to precisely measure its concentration on top of the flute or the goblet. This measurement may be done by infrared laser technology. We will present here the development of the instrument adapted to these measurements and the first results obtained.

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C-6

Fiber-optic evanescent-field sensor for detection of explosives or CO_2 dilluted in water

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Evanescent-field spectroscopy enables direct detection of substances even at places that are not accessible to conventional absorption spectroscopy. The decrease in transmitted power through a waveguide depending on the presence of an absorbing species at the interface where total internal reflection occurs can be used to detect substances selectively.

We present different applications of this sensing method. For monitoring of the sequestration of CO_2 in deep aquifers, sensors are needed that can operate within bore holes in depths of up to 800 m. They need to be chemically and mechanically stable and portable. First results of the sensing of CO_2 diluted in water using a DFB diode laser operating at λ=1570 nm are shown. A standard optical fiber without cladding serves as sensing element. Figure 1 shows the change in signal when CO_2 is ingested into the cell and when the cell is heated and therefore the amount of diluted CO_2 is reduced.

Due to the low vapor pressure of TNT optical sensing is very difficult because there are only trace amounts of the substance in the gas phase. Therefore, the sensing element is coated with a film containing receptor molecules (triphenylen ketals). The incorporation of TNT into the receptor is reversible and very fast. The colorless receptor molecules and the colorless explosive build an intense colored interstitial compound which possesses a charge-transfer band in the spectral region between 500 and 550 nm. This color change can be easily detected at 532 nm with evanescent field spectroscopy.

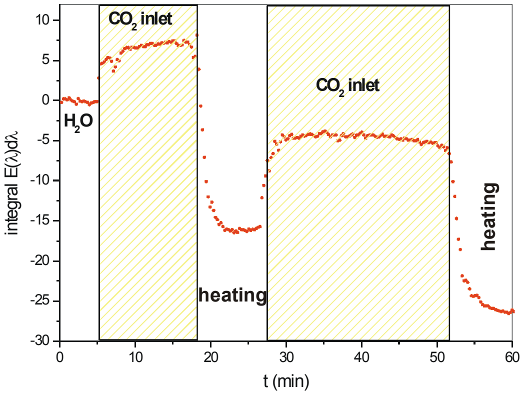

Fig.1 Measurements with an evanescent-field fiber sensor: a) uncoated sensor for CO_2 measurements, b) sensor coated with receptor molecules for TNT detection.

C-7

A scrutiny of NICE-OHMS for trace species 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 species detection, mostly due to its technical complexity.

The present work describes the first steps taken by our group towards practical realization of a compact and less complex, yet highly sensitive, NICE-OHMS spectrometer, which can be used both in the Doppler-broadened and the Doppler-free regime. The signal generation process is described in detail for both modes of operation. The dependence of signal strengths and shapes on analyte concentration and various parameters, e.g. FM detection phase, WM modulation amplitude, intracavity pressure and power, is scrutinized using a theoretical description that combines the standard FM nomenclature with the Fourier series formalism of WM.

The advantages and disadvantages of Doppler-broadened and Doppler-free NICE-OHMS for trace species detection, as well as the optimum conditions and dynamic range, are addressed. The discussion is supported by experimental results obtained for detection of acetylene in sub-ppb concentrations around 1531 nm with a NICE-OHMS spectrometer based on an erbium doped fiber laser and other fiber coupled components [2].

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C-8

Oxygen Spectroscopy for Characterization of Pharmaceutical Solids

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Characterization of solid pharmaceuticals, from monitoring of solid state reactions to understanding tablet dissolution, is of great interest for the pharmaceutical industry [1]. In early stages of pharmaceutical development a whole range of techniques for characterization of the solid state are available, addressing for example particle size and shape, density, porosity, calorimetry, thermo-mechanical properties and crystallinity [2]. However, most of these techniques are slow and not well suited for increasingly important fast laboratory-based or process applications. These new needs are captured by the term Process Analytical Technology (PAT), describing a holistic approach to pharmaceutical manufacturing based on in-depth understanding through advanced process sensors and modeling tools [3]. In this context, tools based on spectroscopic techniques offer obvious advantages owing to their speed, compactness, versatility and ability to perform non-invasive analysis.

By utilizing the contrast between sharp absorption features of free gases, and the broad features exhibited by many solid materials, it is possible to extract information on gases dispersed within solids [4]. In this work we show the potential of using wavelength modulation spectroscopy of molecular oxygen for characterization of pharmaceutical solids. We present results from a study of pharmaceutical tablets made from different sieve fractions (particle size distributions) and with different compression forces, see Fig. 1. Since multiple scattering causes photon pathlengths to greatly exceed sample dimensions we also perform complementary time-of-flight spectroscopy to determine actual photon pathlengths.

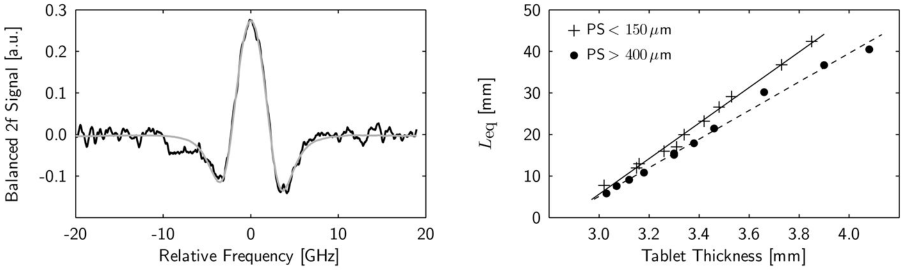

Fig.1 Raw data example (*left*) and absorption measured in equivalent atmospheric pathlength L_{eq} versus tablet thickness (same weight) and granulate particle size (PS) (*right*).

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C-9

Extended continuous tuning of a single frequency optically pumped VECSEL emitting at 2.3 µm

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We present the current status of our work on a GaSb-based semiconductor laser source of type Vertical External Cavity Surface Emitting Laser (Fig.1) optically pumped by a 100mW, 830 nm diode laser [1]. This VECSEL emits at room temperature a few mW around 2.3 µm, a wavelength interesting for the sensitive measurement of several atmospheric trace molecules (CH4, NH_3, CO, CO_2…). We demonstrate single longitudinal and transverse mode operation with broad frequency tuning (exceeding 15 cm^{-1}[2]).

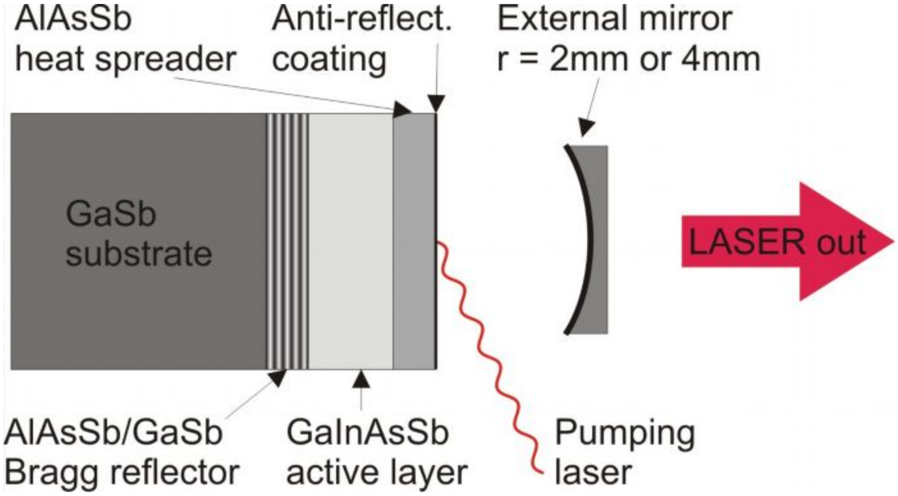

Fig.1 Diagram of VECSEL

We are currently working on: (1) the optimisation of the system as a compact robust tuneable source; (2) the coupling of the VECSEL with a high finesse optical cavity in order to increase the sensibility of trace measurements, where we will explore the use of optical feedback [3]; (3) the automatic broad band frequency tuning under computer control.

References:

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C-10

Trace HF Molecule Detection in Atmosphere Using Tunable Diode Lasers

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The necessity of detection of trace HF concentrations may arise in order to check the leaks of UF_6 from the containers or technological processes, as well as to reveal the illegal activity in the manufacturing of 235-isotope enriched uranium. HF is a volatile compound and can be detected with high sensitivity by diode laser based device.

This report for the first time suggests a compact device prototype for rapid analysis of trace HF quantities in atmosphere with the use of near-infrared diode lasers (DL) and multi-path cell (Fig1).

NEL DFB DL with fiber output is using operating at 1.285 μ. Our traditional operation regime was using [1]. The lasing frequency domain (7788-7790 cm^{-1}) has been chosen to ensure detection of HF absorption line. Electronics controlling the device along with single-mode-fiber-coupled diode laser and reference cell were mounted in separate box, connected to multipass cell via optical fiber and to computer via electric cable. The device was run by computer program written in "LabVIEW-7.1". The device was powered by rechargeable battery; the energy supply was enough for 8 hrs of continuous operation. The main destination of the sensor was the monitoring of HF content in the ambient air. The instrument prototype has been tested at the IAEA, Austria in 2006.

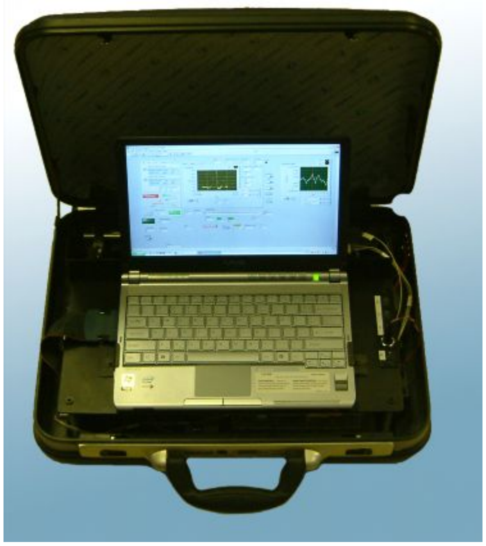

Fig 1. Photo of the compact prototype of the device intended for rapid analysis of trace quantities HF in atmosphere with the use of near-infrared diode lasers (DL) and multi-path cell.

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C-11

$^{138}UF_6$ and $^{135}UF_6$ spectra measurement in mid IR spectral range

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Measurement of UF_6 enrichment is important part of IAEA safeguards. In [1] it was demonstrated that TDLS is efficient technique for such application. However, in this paper it was shown that sensitivity was determined by noises of DL and PD in use, and accuracy was limited by absence of precise information about $^{138}UF_6$ and $^{135}UF_6$ spectra. Further improvement is necessary for the technique real application in IAEA safeguards.

In present paper next step of development of UF_6 enrichment monitor to be used in IAEA safeguards will be presented. There were two main goals.

The first one was to develop instrument with higher sensitivity. The instrument contains mid IR DL (Laser Components) having current frequency tuning range ~ 2.5 cm^{-1} and photo-diodes (Kolmar Technologies). Analysis of the instrument sensitivity will be presented. Photodiode with modified preamplifier is close to necessary requirements. In future modifications DL has to be replaced with one having current frequency tuning range > 5 cm^{-1} and instead of cryostat no liquid nitrogen cryo-cooler has to be used.

Laboratory prototype of the instrument was developed. The instrument contains two channels. In reference one either Ge etalon (0.125 cm^{-1}), or reference cell (CH_4 or C_2H_2) were installed to determine DL frequency tuning curve and absolute frequency calibration, respectively. Analytical channel contains cell with UF_6 under investigation. If absorption cross-sections of $^{138}UF_6$ - σ_8 and $^{135}UF_6$ - σ_5 are known, absorption spectrum of sample under investigation can be presented as follows:

$$K(\nu) = P\left[R\sigma_8(\nu) + (1-R)\sigma_5(\nu)\right]$$

Here P is UF_6 partial pressure and R is U isotope ratio for the given sample. Hence, to achieve necessary accuracy in isotope ratio determination – R, absorption cross-sections of UF_6 isotopomers have to be measured very accurately.

The instrument developed was used to measure absorption crossections of $^{138}UF_6$ and $^{135}UF_6$. Spectra obtained and their analyses will be presented.

References:

[1] A.Nadezhdinskii, Ya.Ponurovskii, D.Stavrovskii, D. Bolyasov, G.Grigoriev, N.Gorshunov, S.Malyugin, Sh.Nabiev , in TDLS 2005, Abstracts of papers, Florence, Italy, 2005, p.121

C-12

Explosive decay product detection inside moving vehicle using TDLS

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Explosives are energetic substances, which are unstable and can decay even at room temperature. Decay probability is low; the half-life period varies from years to tenth of years. Molecular products of this decay can be detected via TDLS technique (see separate poster). In this paper we will consider a scenario for detection of explosive decay products inside a vehicle passing through a check point.

The detector contains a DL module with fiber output, electronics, and optics. DL radiation is collimated in a parallel beam and is directed to a reflector located 5 – 50 m from the detector. DL light scattered by the reflector is received by a 5 cm telescope and is focused on the photo-diode. Instrument sensitivity will be analyzed. Sensitivity was limited by the thermal noise of photo-diode trans-impedance preamplifier resistor.

Indoor and outdoor tests were performed both in Moscow and Albuquerque.

For safety reasons most experiments were conducted with ammonium fertilizer (containing mostly ammonium nitrate NH_4NO_3), which in many cases is one of the components of ammonium-nitrate based explosives. For indoor tests a glass box with a sample of ammonium nitrate was used.

The sample under investigation was installed in a vehicle for outdoor tests.

Fig.1 shows an example of the results of these tests when the vehicle passed through the check point. From raw data both transmission (A) and concentration of ammonia (B) were determined

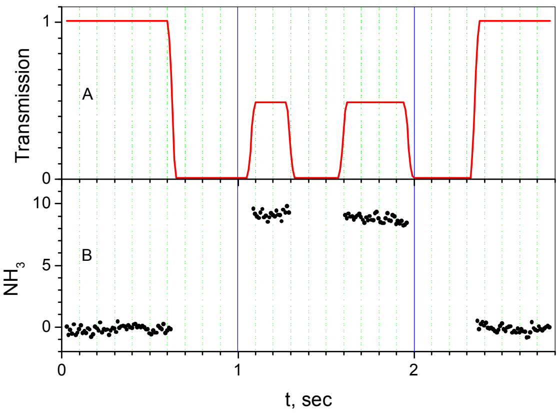

Fig.1 Explosive decay product detection inside moving vehicle (5 km/h).

The concentration of ammonia is presented in units of alarm threshold (3σ). A low speed was chosen for demonstration purposes. In the present configuration reliable operation was observed at speeds up to 50 km/h. Field tests are planned for this summer.

C-13

Tunable Diode Laser Spectroscopy as UF_6 Monitoring Technique

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Tunable Diode Laser Spectroscopy (TDLS) uses diode lasers tuned to access specific regions of the mid-infrared of the electromagnetic spectrum; spectral regions where gases of interest for detection such as Uranium Hexafluoride (UF_6) have strong spectral absorption. The Natural Sciences Centre of the General Physics Institute in Moscow, along with its joint venture partner Canberra Albuquerque, Inc., has developed a portable system that uses TDLS to detect the presence of UF_6 isotopes in-situ as well as, more importantly, the percentage of enrichment of the involved process.

This technology is appealing for application towards safeguards for two reasons. It provides a non-invasive method of isotopic measurement, and can be performed in-situ with real-time data processing. The in-situ use of TDLS is of interest to traditional safeguards (e.g., UF_6 samples are sent to International Atomic Energy Agency (IAEA) laboratory facilities for destructive analysis) as well as under the IAEA's expanded responsibilities under the Additional Protocol.

Optical monitoring methods such as diode laser spectroscopy allow non-contact isotopic measurement to be combined with real-time data processing. This potential means that new applications for safeguards use, such as a TDLS-based enrichment monitoring system, are possible. Although such development efforts are technically feasible in principle and are encouraged by the IAEA, their political impact on safeguards implementation and their economic feasibility compared to the current establishment monitoring system must first be addressed. If such concerns are properly managed, TDLS can become the future enrichment safeguards system for enrichment facilities.

C-14

NO_2 trace detection with a blue diode laser and a high finesse cavity injected by optical feedback

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In order to reach the sub-ppb NO_2 detection level required for environmental applications, we are developing a spectrometer that exploits laser sensitivity to Optical Feedback (OF) induced by a high finesse cavity. OF enables transient laser frequency locking to cavity resonances and laser bandwidth narrowing during a frequency scan, resulting in optimal laser coupling and broad transmission profiles for the cavity modes. This allows fast acquisition rates over four decades of dynamic range with excellent linearity. We initially developed OF-Cavity Ring Down Spectroscopy [1] and OF-Cavity-Enhanced Absorption Spectroscopy [2] both in the IR domain using distributed feedback diode lasers, with routine sensitivities of 10^{-9} cm^{-1} [3]. However, these lasers are only available in the range 1-2µm where no NO_2 strong transitions occur. On the other hand, this molecule has intense electronic transitions around 400nm, a spectral region where Extended Cavity Diode Lasers (ECDLs) are now available.

Very recently, we demonstrated that the sensitivity of these blue emitting ECDLs to optical feedback is fully compatible with OF-CRDS and OF-CEAS. A sub-ppb detection limit was obtained for NO_2 by preliminary OF-CEAS measurements with an ECDL source emitting around 411 nm [4]. We will describe the simple and compact optical set-up together with the gas handling system dedicated to NO_2 trace measurements, and we will report on the spectrometer performance.

References:

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C-15

New Method based on wavelength modulation spectroscopy for measurement and characterization of the current to wavelength tuning frequency response of VCSEL

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A method is introduced for the measurement of the amplitude response of the wavelength tuning behavior of VCSEL using WMS (wavelength modulation spectroscopy) [1]. To measure a wavelength a FM to AM conversion is usually needed. Instead using a Michelson interferometer to realize this [2], a gas absorption line is used for that purpose. The wavelength of the laser light is sinusoidal modulated at frequency f and the signal at $2f$ (2f signal) is measured after the light passed through a gas with an absorption line in the used wavelength range. The 2f signals are analyzed for determining the wavelength modulation amplitude for several modulation frequencies. The gas parameters are held constant during the measurement. If the amplitude of the modulation current is constant, we can determine the wavelength modulation amplitude by analysis of the distance between the two zero-crossings of the measured 2f signal, and so compute the amplitude response of the thermal behavior of the laser. To verify the result we also measured time-resolved optical spectra with a Vertex 70 spectrometer and determined the wavelength modulation amplitude directly. The results from both methods show good agreement in the frequency range of 1 kHz – 5 MHz. Adapting an amplitude response model, we see that the VCSEL clearly has no first order low pass behavior, but follows a square root law for frequencies above the 3 dB cut-off frequency (about 100 kHz). As a consequence the lasers step response is not an exponential function, and can not be used to determine the thermal time constant of the laser, as easily as in the case of a first order low pass.

With this new method two lasers were characterized:

1. 1854nm VCSEL (Vertilas GmbH) by use of a H_2O line.
2. 763nm VCSEL (ULM Photonics) by use of an O_2 line.

In contrast to the measurement with a spectrometer or an interferometer the new method neither requires nonstandard equipment nor difficult mechanical setup.

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[1] J. Reid and D. Labrie, Applied Physics B, 26, 203-210 (1981)
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C-16

Two channel photo-acoustic diode laser spectrometer and fine structure of methane absorption spectra in 6070-6180 cm^{-1} region.

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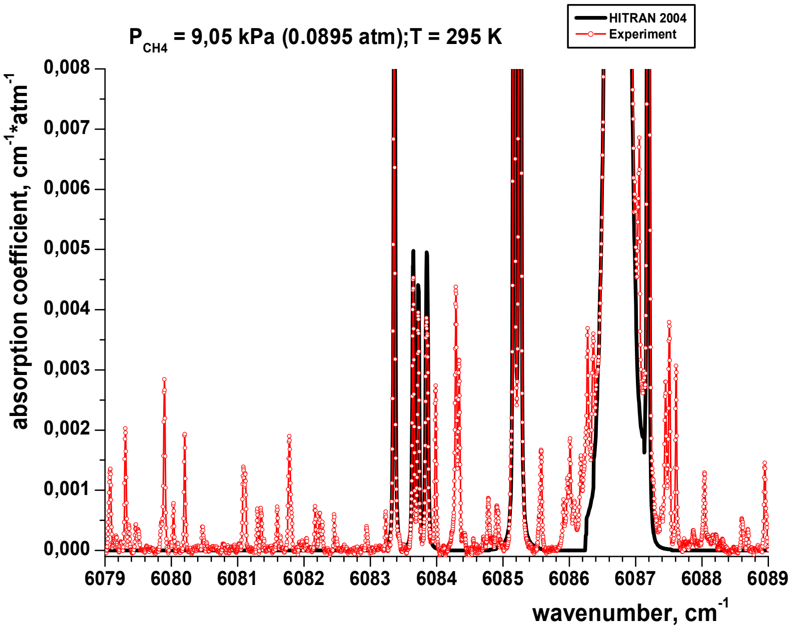
We describe the hardware and software of the high-sensitive two channel photo-acoustic spectrometer with a near infrared diode laser. A semiconductor TEC-100 laser with outer resonator generates a continuous single-frequency radiation in the range of 6040 – 6300 cm^{-1} with spectral resolution better that 10 MHz. The newly designed model of photo-acoustic cells in the form of a ring type resonator was used in the spectrometer, and the system allows the measurement of a weak absorption coefficient equal to 1.4 E-7 cm$^{-1}\cdot$Hz$^{-1/2}$ with a laser radiation power of 0.003 W.

The spectrometer described above allows one to measure:

1. line strengths and line positions in weak absorption spectra of gases with high resolution;
2. the accurate measurements of absorption line shape, half-width, and shift of spectral line induced by pressure or temperature.

The methane absorption spectra within a range of 6080 – 6180 cm^{-1} were measured with a spectral resolution of 10 MHz and the signal to noise ratio more than 10^3. 600 absorption lines were recorded, which is twice as many as in HITRAN-2004. The accurate measurements of the half width and shift of methane unresolved triplet R3 of 2ν$_3$ band permit us to determine values of the broadening and shift coefficients for CH_4 – Air, CH_4– N_2, and CH_4 – SF_6 mixtures.



The part of methane absorption spectrum in a range 6079 – 6089 cm^{-1}, as compared to HITRAN 2004 database is shown on figure.

C-17

CO_2 measurements in combustion environments using near-infrared diode-laser sensor

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A laser diode sensor system based on absorption spectroscopy techniques has been developed for nonintrusive measurements of CO_2 in high-temperature environments. A laser diode absorption method to measure CO_2 gas concentration was developed using a distributed feedback (DFB) laser diode emitting in the infrared region near 1.578 μm (Transition R(16) band $2\nu_1 + 2\nu_2 + \nu_3$). CO_2 concentration measurement was obtained considering Lambert-Beer law applied to a single absorption line.

The results demonstrate the utility of laser diode sensors for fast in-situ measurements of important combustion parameters as well as for emissions-monitoring and closed-loop control applications.

Poster Session D

D-1 Molecular alignment effects on rapid passage signals of nitrous oxide
G. Duxbury, N. Langford, S. Wright, and M. T. McCulloch

D-2 High resolution ethylene absorption spectrum between 6035cm^{-1} and 6210 cm^{-1}
V.A. Kapitanov, Yu.N. Ponomarev

D-3 External cavity diode laser based spectrometer for monitoring of gas emission and measurements of the $^{13}C/^{12}C$ isotope ratio in CO_2 from a wood-based combustion
Julien Cousin, Weidong Chen, Stéphane Plus

D-4 Molecular relaxation effects on hydrogen chloride photoacoustic detection
J-Ph. Besson, S. Schilt, L. Thévenaz

D-5 Diode laser spectroscopy of CO_2 in the 2.064 µm region for lidar applications
V. Zéninari, L. Joly, F. Gibert, A. Grossel, B. Grouiez, M. Mulier, B. Parvitte, G. Durry

D-6 Detection of explosives in the mid-infrared with Quantum Cascade Lasers and a fiber coupled sensor
C. Bauer, U. Willer, A.K. Sharma, C. Romano, T. Schossig, W. Schade, A. Netuschill, Stephane Blaser, Lunos Hvozdara, and A. Muller

D-7 DFB laser diodes in the 2-2.7µm range for absorption spectroscopy
D. Barat, A. Vicet, J. Angellier, Y. Rouillard, S. Guilet, L. Le Gratiet, A. Martinez, A. Ramdane

D-8 Off-Axis Integrated Cavity Output Spectroscopy based H_2S Trace Detection in the Near-Infrared
Weidong Chen, Anatoliy A.Kosterev, Frank K.Tittel

D-9 Ultra compact Herriott cell for optical gas sensor applications
Matthias Steffen, Johannes Herbst, Jürgen Wöllenstein, Armin Lambrecht

D-10 Improved Diode Laser Spectrometer for Ortho/Para ratio measurements in water vapor
A.I. Nadezhdinskii, D.Yu. Namestnikov, K.P. Pavlova, Ya.Ya. Ponurovskii, D.B. Stavrovskii

D-11 Experimental study of spontaneouse decay of some explosives
A.I. Nadezhdinskii, D.B. Stavrovskii

D-12 Intercalibration measurements of ethylene absorption spectrum with 3·10-4 см-1 resolution on two types of diode laser spectrometers
V.A. Kapitanov, Yu.N. Ponomarev, D.Yu. Namestnikov, Ya.Ya. Ponurovskii, S.L. Malyugin

D-13 Mid-infrared frequency synthesizers: novel precise rulers for molecular spectroscopy
P. Malara, P. Maddaloni, G. Gagliardi, and P. De Natale

D-14 Temperature dependence of pressure broadening and shifts of acetylene at 1550 nm
J. L. Hardwick

D-15 Straightforward modeling of the *n*th harmonic signals used in wavelength modulation spectroscopy and their mathematical properties
A. Hangauer, J. Chen, and M.-C. Amann

D-16 Spatial monitoring of gaseous reactor atmospheres by Laser Diode Spectroscopy
T. Kuntze, M. Dickert, W. Grählert, V. Hopfe

D-17 Detection of HCl in combustion chamber using 1.74µm DFB laser diode
Mariagrazia Muolo, Marco Giannini, and Carmine Pappalettere

D-1

Molecular alignment effects on rapid passage signals of nitrous oxide

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When studying low pressure gases <1 Torr, using intra-pulse quantum cascade laser spectroscopy and a long absorbing path length, non-linear optical processes can be readily observed on the temporal signal [1,2]. These non-linear signals appear on transitions with large number density and significant dipole moments and occur because the rate of collision induced de-phasing in a low pressure gas is less than the rate at which the frequency sweeps through the transition of interest.

We will describe the observation of dependence of the rapid passage signals of the P9 to P11 transitions of nitrous oxide on the molecular alignment. This alignment is responsible for the strong free induction decay signals, which we have previously observed from these lines [3]. The measurements were made by use of our intra-pulse spectrometer which comprises a pulsed, distributed feedback quantum cascade laser designed to operate around 1275 cm^{-1} and an astigmatic Herriott cell configured to give an optical path length of 110 m, together with a 0.5 ns time resolution infrared detection system. The laser was excited with pulses of up to 2.0 µs resulting in spectral windows of up to 4 cm^{-1}.

The experimental data will be related to numerical simulations of the Maxwell-Bloch equations, in which we have included the effects of the Doppler velocity distribution [1,2], and also the differential pumping of the M_J sub-levels which leads to the molecular alignment.

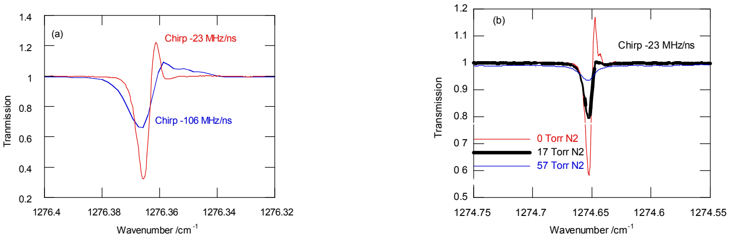

Fig. 1 (a) Observed response from spectrometer for P(10) line different chirp rates. Recorded with a gas pressure of 0.4 mTorr. (b) Observed response for P(12) line when N2 is added as a buffer gas.

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D-2

High resolution ethylene absorption spectrum between 6035cm^{-1} and 6210 cm^{-1}

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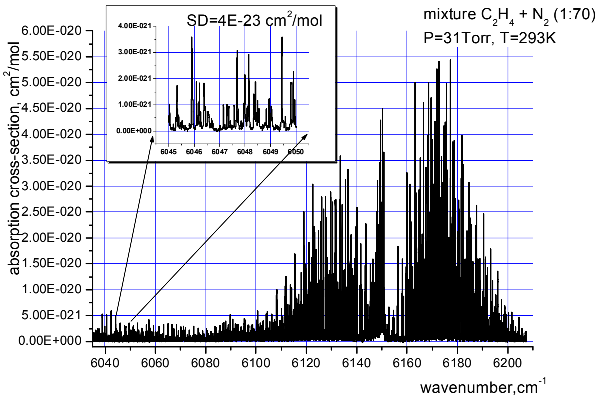
The ethylene (C_2H_4) molecule is present in planetary atmospheres like Jupiter, Uranus, Neptune, Saturn and its satellite Titan. It is also present in Earth's atmosphere. It is part of the exchange processes with the biosphere (vegetation, forest fires) and of the chemical processes such as combustion of fossil fuels, and processing of natural gas in petrochemical facilities. Ethylene is an atmospheric pollutant of VOC (Volatile Organic Compound). Its halogenated derivatives belong to the CFC pollutant family which contribute to destroy the ozone layer. We can add that ethylene is involved in the synthesis of plastics and in fruits maturation. For all these reasons, it is necessary to be able to measure very weak concentrations of this molecule in atmosphere.

One of the experimental techniques used to reach the objectives (astrophysical, atmospheric or industrial) is the high resolution infrared molecular spectroscopy, involving the fundamental study of the vibration-rotation of the molecule. Today the near infrared spectral region between 6035cm^{-1} and 6210 cm^{-}1 is widely used to design such a system.

The high resolution spectrum of the ethylene molecule is presented in modern database like HITRAN 2004 only in 1000 cm^{-1} and 3000 cm^{-1} region. Literature data on ethylene NIR absorption are scarce and spectral resolution is low.



Near-infrared diode laser spectrometer with two resonant photoacoustic detectors (PAD) was designed and firstly applied to study the absorption spectrum of CH_4 [1]. The use of two PADs provides the precise measurements of absorption line centre pressure shift and for calibrating of the wavelength scale with uncertainty 10^{-3} cm^{-1}. The spectral resolution is 2E-4 cm^{-1} and the threshold sensitivity is 4E-23 cm^2/mol.

We present the results the ethylene high resolution near infrared spectrum as well as the procedures of measurements and calibration. Figure 1 presents general view of ethylene absorption spectrum.

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D-3

External cavity diode laser based spectrometer for monitoring of gas emission and measurements of the $^{13}C/^{12}C$ isotope ratio in CO_2 from a wood-based combustion

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We report on the development and application of a compact and field-deployable spectrometer based on fiber-coupled continous-wave (CW) Telecom external cavity diode laser (ECDL, Tunics Plus), widely tunable from 1500 to 1640 nm (C and L band) with an output power up to 3 mW and an effective laser linewidth 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 focused onto 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 Nl/min for continuous *in situ* measurements.

The developed instrument has been used for measurements of the $^{13}C/^{12}C$ isotope ratio in CO_2 and concentration determination of combustion gas from a wood-fired boiler located at Flimwell (East Sussex, UK) [1]. 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~110 °C (full burn regime) and the other at T~70 °C (slumber regime). Based on the absorption spectra of the combustion emission, four gas species have been identified and quantified ; and the isotopic ratio of $^{13}CO_2/^{12}CO_2$ has been measured as well. The averaged value of the $^{13}CO_2/^{12}CO_2$ ratio is found to be $(1.101\pm0.004)\,\%$. The corresponding δ-value relative to PDB standard is (-20.17 ± 3.53) ‰ that is in good agreement with the typical value of (-25 ± 2) ‰ for wood. Simultaneous monitoring of multiple species from gas emission has been performed by selection of optimum lines in terms of high signal-to-noise ratio measurements and interference free between species. The concentration of C_2H_2, CO, CO_2, and H_2O were determined by least-squares fitting of a Voigt lineshape to the experimental absorption spectra.

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D-4

Molecular relaxation effects on hydrogen chloride photoacoustic detection

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Photoacoustic spectroscopy (PAS) is a widely recognized method for its high performances in trace gas measurements. This technique provides many advantages such as a high selectivity and sensitivity, on-line, real time and contactless measurements in a compact experimental arrangement. It is based on the periodic absorption of a modulated laser beam tuned to an absorption line of the gas to be detected, so that the absorbed energy induces a periodic heating in the sample and an acoustic wave is generated through normal thermal expansion. Molecular relaxation of the rovibrational energy into sample heating is a key step in the generation of the photoacoustic (PA) signal. This effect is assumed to be instantaneous in most of the cases, since it is much faster than the time scale of the laser modulation. However, in some particular gas mixtures, it turns out that this relaxation is much slower and thus strongly influences the generation of the PA signal.

In this work, we present relaxation effects occurring in hydrogen chloride (HCl) detection at sub-ppm level using a near-infrared laser diode emitting at 1738 nm. The influence of a gas mixture composed of helium (He) and nitrogen (N_2) on the PA signal was first investigated. A decrease of the sensor sensitivity of about 50% was observed when 10% of N_2 was added to the gas mixture, due to the vibration-to-vibration (V-V) energy transfer that occurs as a result of HCl-N_2 collisions and the long relaxation time of the excited N_2 (ν=1) state. A second gas mixture, composed of He and oxygen (O_2) was studied to compare the relaxation effects on the PA signal. V-V energy transfer due to HCl-O_2 collisions also occurs which lead to a partial transfer of energy to the O_2 (ν=1) excited state, which also presents a long relaxation time. However, the relaxation effects in this second gas mixture were more complex, since it was observed that He acted as a catalyst on the HCl-O_2 gas mixture, thus strongly modifying the sensor response. Molecular relaxation effects are explained by considering the deactivation pathway of the excited HCl molecules, based on the energy diagrams of the different molecules involved in the process and a qualitative model is presented. In addition, the role of water vapor (H_2O) acting as a catalyst in the HCl-N_2-He and HCl-O_2-He systems was also clarified. It was observed that about 0.5% of H_2O in the HCl-O_2-He gas mixture and 0.8% in the HCl-N_2-He system were sufficient to retrieve the maximum of the PA signal.

D-5

Diode laser spectroscopy of CO_2 in the 2.064 µm region for lidar applications

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A diode laser spectrometer was used in the Groupe de Spectrométrie Moléculaire et Atmosphérique of Reims (France) to study CO_2 line intensities, self-broadening coefficients and air-pressure-broadening coefficients near 2.063 µm. The studied spectral region is suitable for the sensing of CO_2 in the middle atmosphere from Lidar experiment. A 2µm heterodyne differential absorption lidar (HDIAL) has been operated at the Laboratoire de Météorologie Dynamique (Paris) to monitor the CO_2 mixing ratio in absolute value at high accuracy in the atmospheric boundary layer. Horizontal measurements at increasing range are made to retrieve the optical depth. The experimental setup takes advantage of a heterodyne lidar developed for wind velocity measurements [1]. However, discrepancies between the lidar data and in situ measurements were reported that led the authors to question the accuracy of the spectroscopic parameters listed in the HITRAN database that were used for the retrieval.

The GSMA laboratory is well equipped for the high resolution determination of spectroscopic parameters for atmospheric applications [2]. The spectral region ranging from 4843 to 4848 cm^{-1} which is suitable for the measurement of atmospheric carbon dioxide mixing ratios was studied using a new generation commercial diode laser from Nanoplus. Three lines of the $(20^01)_{III} \leftarrow (000)$ band of CO_2 have been studied. The results of intensity measurements and self-broadening coefficients are compared to previous determinations and available databases. Furthermore the air broadening coefficients for these transitions are also reported and analyzed. Finally, these new parameters are used for the calculation of atmospheric CO_2 mixing ratio with the heterodyne differential absorption Lidar from the LMD. These new parameters demonstrate a dramatic improvement of the retrieved atmospheric CO_2 concentrations.

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D-6

Detection of explosives in the mid-infrared with Quantum Cascade Lasers and a fiber coupled sensor

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Explosives can be generally divided into two different classes: those containing nitro-groups (e.g. TNT, RDX) and those based on peroxides (e.g. TATP). The detection of the first group is hindered by the relatively low vapor pressure leading to very low concentration in ambient air which results in the necessity of pre-concentration or means of generating higher concentrations of gaseous constituents. Stand-off detection of RDX is demonstrated via measurement of NO generated by pulsed laser fragmentation (PLF) of the explosive on a contaminated surface as shown in the schematic in fig. 1a. Energetic material can be distinguished from other substances by analyzing the ratio of NO and NO_2 after PLF [1]. TATP on the other hand, has a high vapor pressure and measurements are possible in ambient air above a sample. Figure 1b shows the setup of the fiber coupled sensor and fig. 1c a typical spectrum recorded without averaging when the sensor head with an optical path length of 15 cm is positioned in the vicinity of a TATP probe. Quantum cascade lasers are used for sensitive and selective absorption spectroscopy in the mid-infrared spectral region for both approaches.

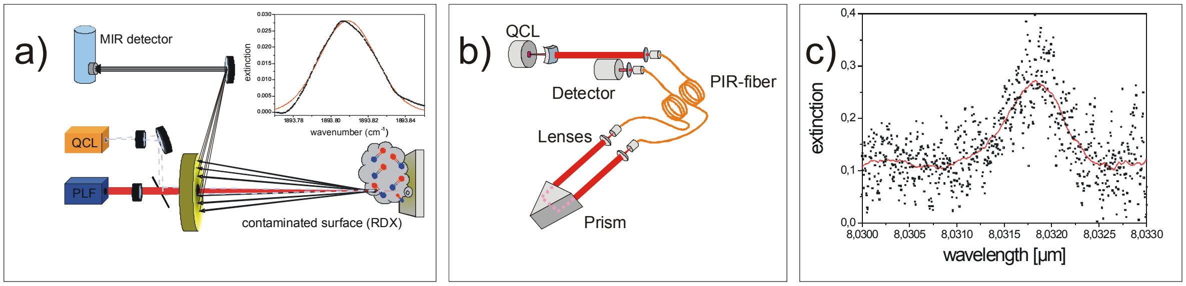

Fig.1 a) Stand-off detection of NO subsequent to PLF of RDX, b) setup of the fiber-coupled laser sensor system, c) spectrum of TATP measured with the fiber coupled sensor in ambient air near a TATP sample.

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D-7

DFB laser diodes in the 2-2.7µm range for absorption spectroscopy

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The mid-infrared 2-2.5 µm region of the electromagnetic spectrum is attractive for trace gas sensing due to the presence of strong absorption bands of several species of industrial interest. Moreover, its location in the so-called transparency window, where absorption from the main infrared active atmospheric compounds (H_2O and CO_2) is weak [1], makes the analysis of other molecules easier. On the other way, the 2.5-2.7 µm region shows strong water vapour absorption lines making this range well adapted to water measurements and isotopic ratio studies.

For spectroscopic applications, single-frequency and continuously tunable emission is required. DFB (Distributed FeedBack) laser diodes are hence well suited for gas sensing applications. The IES (Institut d'Electronique du Sud) laboratory of Montpellier University has been working on antimonide laser diodes and their applications in gas analysis for about fifteen years. The devices are fabricated by molecular beam epitaxy (MBE) on GaSb substrate. The low gap materials used give access to the mid-infrared wavelength range ($\lambda > 2$ µm). The range between 2 to 2.7 µm has especially been studied. In this work, we will focuse on the fabrication and characterisation of DFB devices operating around 2.6-2.65 µm. The laser structure is realized, in one step, by solid-source MBE in a Varian Gen II machine on an n-type (100) GaSb substrate with a 1 µm-thick active region based on two $Ga_{0.57}In_{0.43}As_{0.11}Sb_{0.89}$ 16 nm-thick compressively strained quantum wells embedded between a barrier and a waveguide made of $Al_{0.30}Ga_{0.70}As_{0.03}Sb_{0.97}$ [2].

A DFB process has been developed based on a metal grating patterned on each side of the 5 µm ridge, giving a complex coupling effect [3]. This process can be adapted to each material and wavelength. The final devices operate in the continuous-wave regime at room temperature with a threshold current of about 100 mA at 20°C and a characteristic temperature of 57 K. A single frequency emission is obtained between 2.6 µm and 2.65 µm with a side mode suppression ratio reaching 25 dB and a continuous tuning of 2 nm.

This work has also been supported by the Centre National d'Etudes Spatiales (CNES) under contract n° R&T SU-0003-005.

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D-8

Off-Axis Integrated Cavity Output Spectroscopy based H_2S Trace Detection in the Near-Infrared

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Demonstration of hydrogen sulfide (H_2S) trace gas detection by means of off-axis integrated cavity output spectroscopy (OA-ICOS) [1,2] using a DFB telecommunication laser will be reported. In this work, the OA-ICOS cavity consisted of two 1" diameter spherical mirrors (1 m radius of curvature) separated by a 0.5 m long quartz coated stainless steel tube. The mirrors reflectivity was ~99.995 % at 1560 nm as specified by the manufacturer (Los Gates Research). The experimentally determined effective optical path length was ~700 m. The diode laser source used was a continuous-wave GaInAsP DFB laser diode (JDS Uniphase) operating in the near infrared at ~1571.8 nm (6362 cm^{-1}). The single mode diode laser was fiber pigtailed with a maximum output power of 63 mW and linewidth of <350 kHz. Frequency turning of the diode laser can be carried out either by varying the temperature (over 10 cm^{-1} with a tuning rate of ~0.4 cm^{-1}/K) or scanning the injection current (over more than 1 cm^{-1}). An amplified, switchable-gain InGaAs detector (PDA10CS, Thorlabs) was used for the radiation detection after the optical cavity.

The R(20) CO_2 line of the $3\nu_1$ band at 6362.5038 cm^{-1} was used in this work for frequency reference and determination of the effective optical path length of the OA-ICOS cavity using a calibrated CO_2 concentration. A gas standard generator (KIN-TEK Model 491 M) provided a traceable calibration standard of H_2S. The H_2S concentrations ranged from 24 to 2.4 ppmv in the diluting gas (nitrogen). The ICOS cell pressure was maintained at 100 Torr by means of a pressure controller (MKS Instruments type 649). Absorption spectra of H_2S were acquired by scanning the DFB laser current at 10 Hz, corresponding to ~1 cm^{-1} frequency scans encompassing the 6362.85 cm^{-1} H_2S absorption line. Typically, 1000 spectral scans were averaged for each H_2S concentration measurement. Based on the experimentally estimated SNR of the OA-ICOS signal, the corresponding minimum detectable concentration (MDC) was found to be 700 ppbv (SNR=3). Further improvement in detection sensitivity can be realized by use of OA-ICOS in combination with wavelength modulation [3,4].

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D-9

Ultra compact Herriott cell for optical gas sensor applications

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Multi reflection cells like the White or the Herriott type are used in gas spectroscopy in order to increase an absorption signal by stretching the optical path. We present a Herriott cell with a minimized volume implemented in a setup for oxygen measurement. The absorption of the oxygen line at 763.84 nm is measured by tuneable diode laser spectroscopy (TDLS). A fiber coupled Vertical Cavity Surface Emitting Laser (VCSEL) scans the narrow wavelength range around the P9P9 line of the P-branch of the oxygen A-band transition.

The Herriott cell type is suitable for minimizing the cell volume because it is made of two spherical mirrors in comparison to the White cell with three mirrors. The optimized cell (fig. 1) provides high sensitivity by a long optical path and fast detection of gas concentration changes because of the small sample volume which enables a fast gas exchange. The optical path length is longer than 5 m within an enclosed volume of 40 ml. The design with separated in and out coupling holes in the mirrors enables small hole diameters which determine the maximum numbers of reflections. The distance of around 100 mm between the mirrors determines the real numbers of reflections (55).

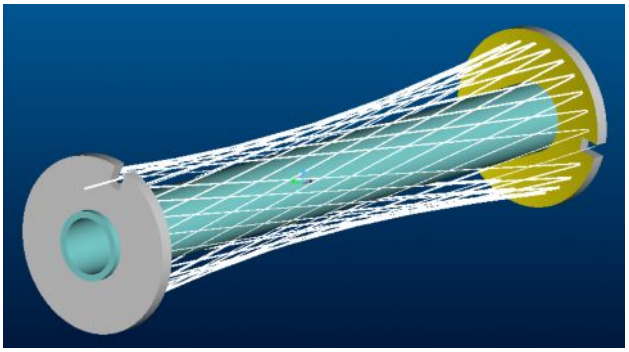

Fig. 1: Side view (left) of the optical pathway simulation of the Herriott cell. The path length is 5,5 m in 40 ml cylindric volume.

The fiber coupling of the gas cell enables gas concentration detection in highly inflammable environments because light source and control electronics are separated from the sample volume with its temperature and pressure terms and gas composite. This would be important if the oxygen concentration has to be controlled to avoid explosive gas composites by too high oxygen concentrations. The concentration measurement can be realized by TDLS at 763 nm cross sensitivity free.

The presented Herriott cell merges robustness, low cost, compactness and is used for high sensitivity applications.

D-10

Improved Diode Laser Spectrometer for Ortho/Para ratio measurements in water vapor

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The main isotopomer of water – $H_2{}^{16}O$ is a mixture of two nuclear spin isomers. The sum of nuclear spins of hydrogen atoms could be either equal to 1 in ortho molecule or equal to 0 in para molecule. Each spin isomer has its own system of rovibrational levels. Optical transitions between levels of different spin isomers are strongly forbidden. Number of ortho isomer molecules is three times greater than number of para isomer molecules in the thermal equilibrium state at room temperature.

Earlier it was shown that TDLS is a good technique for ortho/para ratio measurements in water vapor [1,2]. Interest to this kind of measurements is connected with probable medicine application of para-enriched water (NMR-tomography).

In our previous report a DL-spectrometer designed for ortho/para ratio measurement was demonstrated [2]. In this work improved spectrometer is presented. Optical part of the spectrometer consists of DFB laser with fiber output (1.392 µm), gas cell (20 cm long) and detector (germanium photodiode). Such kind of diode laser and so simple optical scheme give an opportunity to minimize the influence of interference of direct and scattered light beams. For the same purpose the windows of the gas cell are tilted with respect to axes of laser beam. The detector window is tilted too.

Spectral lines of ortho-water (7181.15578; 7182.20911; 7183.01579) and of para-water (7182.94962) were chosen for the measurements [3].

The spectrometer was tested in experiments with pure water vapor in the pressure range of 0.01 – 10 torr. The effect of selective sorption of ortho and para spin isomers of water was demonstrated.

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D-11

Experimental study of spontaneouse decay of some explosives

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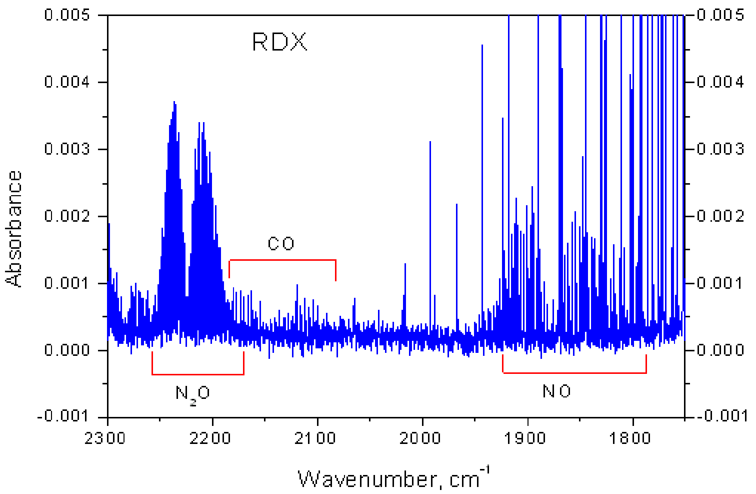
Explosives are so-called energetic substances, which are unstable and can decay even at room temperature. Decay probability is low enough, so half-life period varies from years to tenth of years. The interest to experimental study of the explosives decay is connected with the problem of noncontact detection of those substances. The aim of our study was to find rather simple decay particles - molecules, which can be detected via TDLS technique.

In this study samples of some explosives were placed in a stainless still vessel, which was evacuated and then filled with pure nitrogen. The vessel was exposed at room or higher temperature (in thermostatic apparatus). Intervals of the exposition were from some minutes up to some hours. After this exposition resulting gas mixture was introduced into a multiple-pass cell, which was a part of Fourier-spectrometer (Bruker IFS-66 v/S). Absorption spectra of the gas mixture were recorded in the range of 5000–800 cm^{-1} with resolution of 0.25 cm^{-1}. A fragment of the spectrum obtained for RDX-based plastic explosive is presented in the Fig.1.

For all the explosives containing NO_2 groups NO and N_2O (one or both) were detected. In some cases CO was observed. Rates of appearance of the gases were measured. Analysis of the temperature dependences of the rates gave estimates of activation energies. All of them were close to 1 eV. NH_3 was detected for the explosives containing ammonium nitrate.



D-12

Intercalibration measurements of ethylene absorption spectrum with $3\cdot10^{-4}$ см$^{-1}$ resolution on two types of diode laser spectrometers

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There were made independent measurements of high purity (99,99%) gaseous ethylene absorption spectrum at 6046-6067 см$^{-1}$ spectral range on two laser spectrometers. In first one were used two differential type resonant photoacoustic cells, which allow to register absorption spectrum at two different pressures (or two different gases) simultaneously [1]. In second spectrometer for measurement of transmission spectrum was used cell with multipass matrix system by S.M. Chernin with 39 m full optical path length. The source of radiation in optico-acoustical spectrometer was tunable diode laser ТЭС-100 (Sacher Laser Technik) with generation line width which is not exceed 10 МГц, and 3-7 мВт output power. In second spectrometer was used DFB DL with fiber output (λ=1,651 мкм, 20 мВт output power). Measurements were made at 20 Torr ethylene pressure and 293K temperature. Fig.1 represents a result of comparison of measured spectrums (one of full spectrums fragments) from which full good consent of received data is obvious.

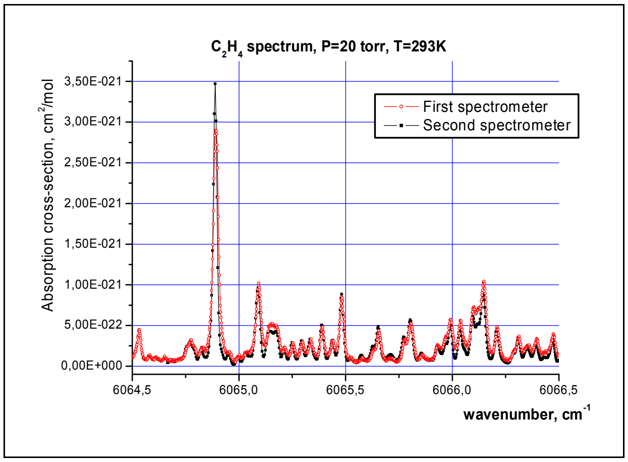

Fig. 1. Fragment of comparison ethylene measured spectrums by two spectrometers.

As a whole the difference in absorption cross-section measured values does not exceed 10%, and discrepancy in lines centers position ≤ 0.002 cm^{-1}. Results represent identity of obtained spectral information. Conducted intercalibration allows improving OA spectrometer sensitivity value.

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D-13

Mid-infrared frequency synthesizers: novel precise rulers for molecular spectroscopy

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The advent of optical frequency synthesizers (OFSs) based on mode-locked femtosecond (fs) lasers has represented a breakthrough in the field of high precision spectroscopy and accurate frequency metrology. In particular, in the visible/NIR spectrum, where the first OFSs worked, precisions approaching 1 part in 10^{15} where achieved in atomic transitions energy measurements. It is straight that the extension of OFSs to the mid-IR region is crucial for absolute frequency measurements on molecular ro-vibrational spectra.

In this work we present two different approaches, both involving a difference frequency generation (DFG) process, aiming to transfer the metrological performance of OFSs to the mid IR region.

The first scheme consists in phase-locking the DFG pumping sources, whose wavelengths lay in the telecom range, to the teeth of the near-IR frequency comb generated by an OFS. In this way the pump and signal frequencies are directly linked to the Cs primary standard via a global positioning system (GPS) time receiver. Hence the idler beam frequency is determined directly by their difference, disregarding of the comb's carrier-to-envelope offset-frequency, that is canceled out in the nonlinear process. The described scheme allows absolute frequency determination of any molecular transition in the DFG tuning range. In particular, spectroscopic measurements of CO_2 were carried out with this method around 4.2 μm [1].

The second approach presented in this work consists in shifting the frequency comb itself in the mid infrared region via difference frequency generation [2].

The mid-IR frequency comb was realized by DFG process between a continuous-wave (cw) laser source, representing the pump, and a near-IR, fiber-based OFS as signal beam. The idler radiation is a 180 nm-wide mid-IR comb whose central wavelenght can be tuned, by tuning the pump wavelength, to cover the whole region from 2.9 to 3.5 μm. By phase-locking the pump laser to the near-IR OFS, the mid-IR comb gets rid of the offset frequency and maintains its direct link with the Cs primary standard. The flexible character of this approach allows for a full and direct control of the comb features by simply acting on the parameters of the cw pump laser.

In order to demonstrate that the generated comb can be properly used as a direct frequency ruler, an external cw DFG source was phase-locked to the closest mid-IR comb tooth and used for high-precision molecular spectroscopy of CH_4.

It is straight that this approach offers the opportunity of easy comb-referencing for direct laser sources operating in the mid-IR, such as quantum cascade lasers, opening new perspectives for absolute frequency measurements on ro-vibrational molecular transitions, accurate determination of molecular constants and frequency grids with improved precision. Furthermore, the possibility of using the mid-IR frequency comb as a direct spectroscopic source is also taken in account. In this perspective, some recently proposed detection schemes for the near IR are at present being implemented in this spectral region [3,4].

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D-14

Temperature dependence of pressure broadening and shifts of acetylene at 1550 nm

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Pressure broadening and shift coefficients for acetylene perturbed by the rare gases, hydrogen, and nitrogen have been measured at -77 C. Measurements have been made for the *P*(30) through *R*(25) lines of the $\nu_1+\nu_3$ band of $^{12}C_2H_2$ using a commercial external cavity diode laser spectrometer (New Focus 6428). The spectra were calibrated with as low-pressure acetylene cell for absolute wavenumber calibration and an internally coupled Fabry-Perot interferometer with a free spectral range of 0.097 cm^{-1} for relative wavenumber calibration. This calibration procedure provides and absolute wavenumber accuracy of approximately 10 MHz, allowing the reliable measurement of pressure shifts of the order 10^{-3} cm^{-1}/atm.

D-15

Straightforward modeling of the n^{th} harmonic signals used in wavelength modulation spectroscopy and their mathematical properties

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Several formulas exist for expressing the WMS n^{th} harmonic signal in terms of the transmission function T(λ) [1], [2]. But these only hold for a specific transmission profile (e.g. lorentzian) or are an infinite series expansion that is not convenient/applicable for practical cases. Here we use the integral transform representation of the n^{th} harmonic signal, and give some of the properties that directly follow from this viewpoint. For ideal WMS the n^{th} harmonic signal is formed by convolution of the transmission function with a fixed kernel, which depends on the order n and the modulation amplitude A. Since an analog filter is mathematically realized by a convolution, the generation of the n^{th} harmonic can be seen as a filtering of the transmission function, when this is interpreted as a signal. This gives an intuitive description of the generation of the harmonic signals. The frequency response of this "n^{th} harmonic filter" is given by the Fourier transform of the convolution kernel: the n^{th} Bessel function J_n. So many of the known properties of the Bessel function can be applied. Some results are

1. The average of the n^{th} harmonic signal ($n>0$) for arbitrary transmissions is zero.
2. The weighted sum of the n^{th} harmonic signals is the transmission again.
3. Recursion formula: the n^{th} harmonic signal can be expressed in terms of $(n-1)^{\mathrm{th}}$ and $(n-2)^{\mathrm{th}}$ harmonic.
4. Easy understanding how the n^{th} harmonic signal of voigt profiles is related to the one of lorentzian profiles.
5. Understanding how the laser spectral line width affects the n^{th} harmonic.

It is important to note that the first three formulas hold for arbitrary transmission profiles, and so are applicable in practically occurring non-ideal cases.

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D-16

Spatial monitoring of gaseous reactor atmospheres by Laser Diode Spectroscopy

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Numerous CVD processes are characterized by simultaneous or consecutive use of various reactive (precursor) gases. The homogeneity of the gas atmosphere significantly defines the characteristics of corresponding coatings. Since quality and costs are directly linked to process gas composition and spatial gas concentration distribution, there is a strong need for monitoring. State-of-the-art spectroscopic methods like Fourier-Transform Infra-Red spectroscopy (FTIR) or Laser Diode Spectroscopy (LDS) increasingly enter facilities for quality management purposes. Distinguished by their path-integrative and stationary measurement, they don't give spatial information about gas concentration profiles within reactors.

Merging the LDS monitoring method with tomography imaging techniques gave a powerful measuring tool to spatially diagnose a gaseous atmosphere consisting of more than one component. Evident advantages are non-invasive in-situ - operation, highest selectivity and sensitivity and good spatial resolution. The development and testing of an appropriate monitoring system was divided into the tasks (a) reactor modification and semi-automatic sensor setup development (Fig.1), (b) fluid-dynamic simulation, data acquisition and processing and (c) spectroscopic analysis of generated gas concentration profiles exemplarily using ammonia in nitrogen NH_3/N_2 (Fig.2).

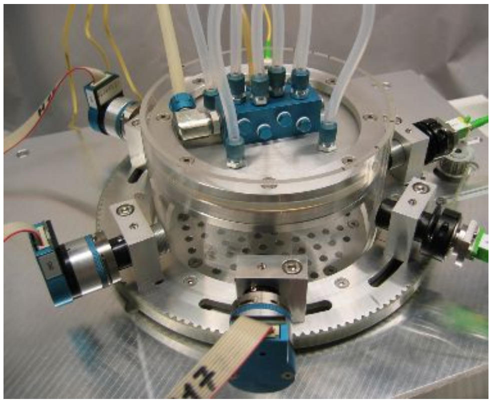

Fig.1: 3-Channel-LDS – Monitoring of NH_3/N_2 - Atmosphere

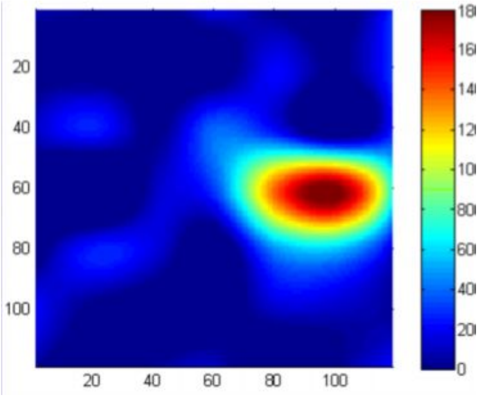

Fig.2: Tomographic reconstruction of NH_3 in N_2

Using tomographic methods, 2-dimensional NH_3 concentration profiles in a CVD reactor were monitored. Data acquisition in various reactor levels even gave information about spatial gas distribution.

D-17

Detection of HCl in combustion chamber using 1.74µm 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 µm, 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.

Poster Session E

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E-1

In flight QC laser spectrometer measurement of ambient methane, nitrous oxide and water using the NERC ARSF DORNIER aircraft

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Intra-pulse spectroscopy [1] is a powerful technique for the detection of trace level gases. In this scheme a pulse from a frequency swept quantum cascade (QC) laser is used to probe the gases of interest, and the correlation between the frequency sweep and the temporal evolution of the pulse allows real-time identification of the spectral features of the gases [2].

We will describe the new aircraft deployable version of the spectrometer. It contains a distributed feed-back QC laser operating around a wavelength of 7.84 µm (a wavenumber of 1275 cm^{-1}) and an astigmatic Herriott cell having a path length of 100 m. The frequency resolution of our system is determined by the changing rate of frequency down-chirp during the pulse. It ranges from 0.01 cm^{-1} at the start of the pulse to 0.005 cm^{-1} at the end. The intra-pulse scan range is from 2.5 to 4 cm^{-1}. Within this range we can detect ambient concentrations of methane nitrous oxide and water. Owing to the wide scan range we can observe three strong lines of nitrous oxide, three of methane and one of water. Examples will be shown of the variation of the concentrations of these gases during a low level flight path of the NERC ARSF Dornier aircraft from Oxford Airport to Haverfordwest, Pembrokeshire, and also in a circuit over Oxfordshire, in October 2006. The signal to noise ratio obtained, once the equipment stabilized, was close to they obtained in a laboratory environment, see Fig. 1.

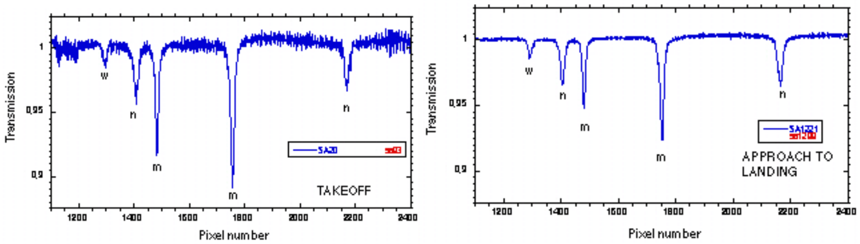

Fig.1 Transmission spectra on take off at Oxford Airport and final approach to Haverfordwest Airport, w water, m methane, n nitrous oxide

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E-2

Diode laser based photoacoustic detection of csrbon 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 has potential for compact, selective, and sensitive gas diagnostics [1-3]. In this work diode laser induced photoacoustic pressure waves were monitored with a novel micromechanical silicon cantilever pressure transducer. The sensing technique was applied to the detection of carbon dioxide and oxygen.

The novel pressure transducer is based on a micromechanical silicon cantilever whose deflections due to the incident pressure waves are monitored with a compact optical Michelson interferometer [4]. In this work a photoacoustic cell having 20 cm^3 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.

In the detection of carbon dioxide a 30 mW distributed feedback (DFB) 1572 nm diode laser 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 commercial 1 Watt optical fiber amplifier sub-ppm detection limits for carbon dioxide were demonstrated [5]. The cantilever based PAS was also used to detect oxygen. 5000 ppm detection limit for oxygen was obtained with a 0.5 mW 762 nm vertical cavity surface emitting laser (VCSEL). On the other hand a 30 mW DFB laser operating at 763 nm resulted in a noise equivalent detection limit of 20 ppm [6]. To date the best normalized noise equivalent sensitivity obtained with the cantilever based PAS is 1.7×10^{-10} $cm^{-1}WHz^{-1/2}$ [7].

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E-3

Laser-spectroscopic determination of isotop ratios at trace levels using difference-frequency generation

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Isotopic compositions of trace gases yield important information about their origin and can be used for process identification or as tracer. For example in ecosystem research isotopic ratios of CO_2, H_2O, N_2O NO and NO_2 are of interest as they enable to determine the source of, e.g., CO_2 (soil, plants, or combustion during energy conversion as a result of anthropogenic activity).

Our project focuses on high precision measurements of isotopic ratios of gases at trace concentrations, particularly of N_2O, CO and CO_2 isotopomers at ppm levels. The $^{15}N/^{14}N$ ratio of N_2O is of special interest because the isotopomers $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$ cannot be distinguished by isotope-ratio mass-spectrometry (IRMS) directly as it is possible with laser spectroscopy. Other important isotopic ratios in this project are $^{13}C/^{12}C$ and $^{18}O/^{16}O$ in CO_2 and CO.

These molecules have their strongest absorption lines in the mid-IR between 4 µm and 5 µm. At these wavelengths the choice of laser sources is rather limited. We built a system based on difference-frequency-generation (DFG) using a periodically poled $LiNbO_3$ crystal (MgO:PPLN), a Nd:YAG laser (1064 nm) as pump laser and an external cavity diode laser (853 – 870 nm) as signal laser. This cw source offers room-temperature operation, large tuning range (4.3 µm – 4.7 µm with only one PPLN grating) and narrow linewidth (1MHz) [1].

Two different detection schemes were tested, either all isotopomers were measured using only the long path (36 m) of the multipass cell or with a balanced path length setup, where the main isotope is measured with a beam along a short path (40 cm) in the multipass cell. To improve the precision of the measurement the isotopomers were measured simultaneously in the sample cell and in a single-pass reference cell also offering two different path lengths.

For N_2O a precision of 3‰ for a single measurement and a long-term reproducibility of 6‰ were achieved for the $^{14}N^{15}N^{16}O/^{14}N_2{}^{16}O$ ratio at 825 ppm, when using wavelength modulation and only long path detection [2]. For CO a short-term reproducibility of 5‰ for $^{13}C^{16}O/^{12}C^{16}O$ and 11‰ for $^{12}C^{18}O/^{12}C^{16}O$ were achieved at 300 ppm, when using wavelength modulation and balanced path length detection. The two main problems, which currently limit the precision and reproducibility, are the low signal-to-noise ratio on the detector and the degradation of the external cavity diode laser used in the DFG-system, resulting in an insufficient side-mode suppression.

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E-4

QEPAS based detection of H_2S and CO_2 using a near-IR DFB diode laser

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Near-infrared DFB diode lasers in the 1.3-1.6 μm region developed primarily for telecommunication applications are presently the most reliable and affordable sources for spectroscopic molecular gas analysis. Overtone and combination vibrational bands found in this spectral region are sufficiently strong to satisfy many practical applications when advanced spectroscopic techniques are employed. In this work we used a Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS) approach [1] to detect CO_2 and H_2S impurities in nitrogen or air. These molecules have overlapping NIR absorption bands, which allows the detection of both molecules using one DFB diode laser operating at λ=1.57 μm. The absorption lines selected to monitor H_2S and CO_2 concentrations were at 6357.62 and 6361.25 cm^{-1} respectively. The achieved sensitivity and the impact of the presence of H_2O vapor on the sensor performance will be reported.

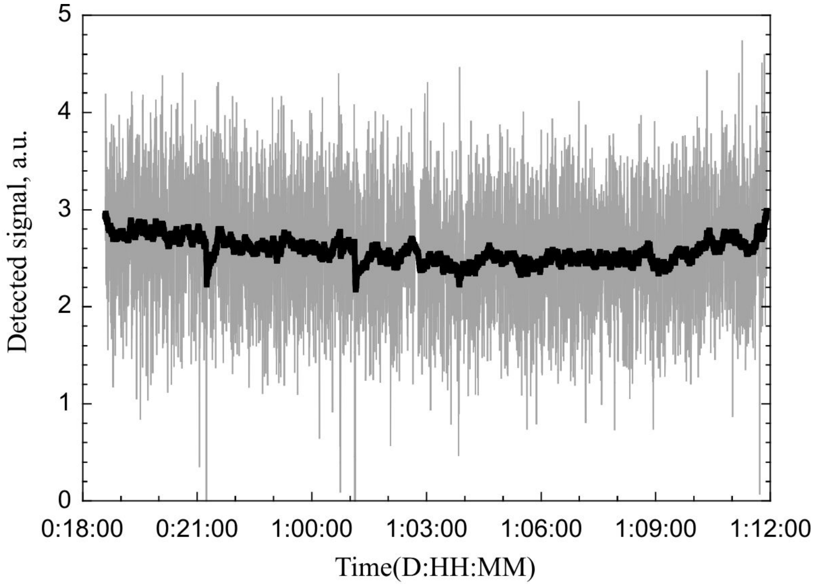

Fig.1. Overnight monitoring of the quartz enhanced photoacoustic signal corresponding to CO_2 concentration in the laboratory air. Gray curve: lock-in amplifier output, time constant 5s, 6 dB/octave, sampled every 12s. Black curve: running exponential average of the same data. A ~15% decrease of CO_2 concentration by 6 am is detected.

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E-5

Standoff Sensing of Respiration with TDLAS

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Rate of respiration is a physiological indicator of stress, such as in individuals who have suffered injury or who are intent on destructive acts or subterfuge. To measure respiration, it is sometimes desirable to monitor non-cooperative subjects from afar with a covert standoff sensor. Utilizing Tunable Diode Laser Absorption Spectroscopy (TDLAS) [1,2], we built and demonstrated a standoff CO_2 sensor that detects human respiration from a distance up to 35 meters,. The platform delivers collimated laser light onto a passive surface and collects back-scattered light; it measures CO_2 concentration integrated along the laser path. Respiration rate is monitored by measuring breath CO_2 concentration as an additive signal to the path integrated ambient CO_2 concentration.

Exhaled breath contains about 3% CO_2, while the ambient CO_2 concentration is less than 0.04%. Fig. 1 shows breath detection from 4 meter standoff using the subject's facial region around the chin and mouth as the scattering surface. We can detect breath from 35 m using a cardboard surface for backscattering.

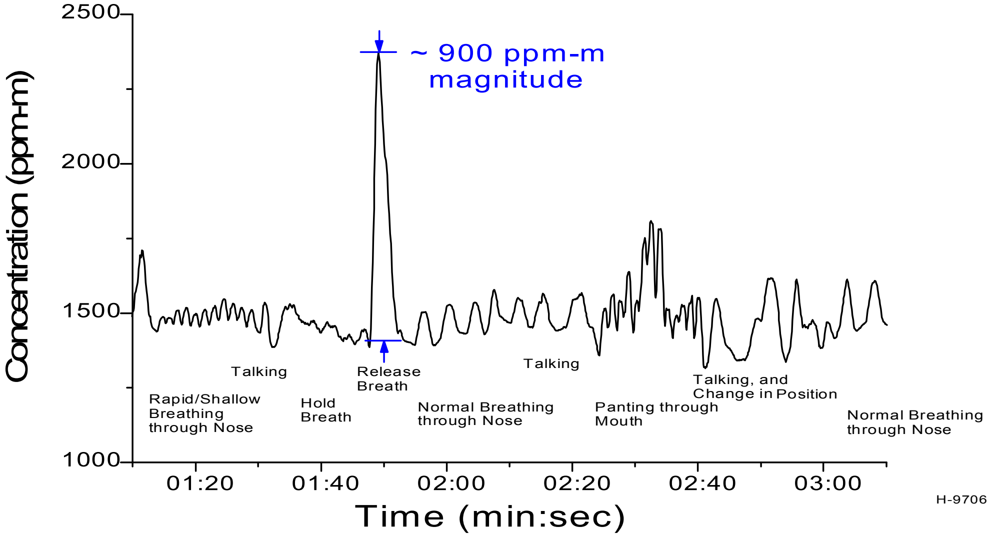

Fig.1: Respiration profiling from 4 meters, facial illumination

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E-6

Coupled use of DFB laser diode and photoacoustic cell for spectral control of a pulsed laser source and differential absorption lidar application

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The LMD/IPSL (France) has conducted the development of a 2-µm Heterodyne Differential Absorption Lidar (HDIAL) for atmospheric CO_2 mixing ratio measurements [1]. The main criterion for such a measurement is the accuracy which is to be better than 0.5 %. This raises the issue of 1) spectroscopic data [2] and 2) the spectral stability and purity of the laser source. We are currently involved in improving the HDIAL system by the coupled use of a new photoacoustic cell (PAC) (DDHR: Differential Doubly Helmholtz Resonator) and a DFB laser diode.

First, the DFB laser diode is used to test and characterize the response of the DDHR PAC system and then to precisely locate the CO_2 absorption lines of interest in the 2.05-2.07 µm domain. This is done by a modulation of the cw DFB beam by a mechanical chopper in a 50/50 duty cycle and using a synchronous detection. The control of the DFB laser diode by the PAC can provide a spectral reference for the control of the Tm,Ho:YLF pulsed laser source of the HDIAL system using a heterodyne beat between the DFB spectral reference and the pulsed source. The precision to reach is a maximum spectral fluctuation of 1.5 MHz over 10 seconds.

Secondly, DFB laser diodes are integrated as local oscillators in a 2-µm Heterodyne Differential Absorption Lidar. A spectral loop is achieved with respect to the PAC signal for spectral stabilization. This application is limited by the isolation issue of the laser diode from parasitic pulse coming from the ring cavity. However, the spectral loop enables to obtain precise and stabilized wavelengths for an accurate HDIAL CO_2 mixing ratio measurement in the middle atmosphere.

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[2] see Zeninari et al. paper in this conference

E-7

Widely tunable Quantum Cascade Lasers for sensing applications

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During the last few years, considerable interest has emerged to use quantum cascade lasers (QCL) for sensing applications. The immense advantage of QCLs in this field is the fact, that absorption features of many technologically and ecologically relevant gases are much more dominant in the mid infrared spectral regime than in the near infra red, where conventional laser based sensors are working.

These lasers also exhibit a wider spectral tuning range than interband laser diodes in the near infra red. To fully exploit this wide tunability we have manufactured distributed feedback (DFB) QCLs with multiple current injection segments. Each segment is independently addressable and can support a distinct laser emission wavelength. This way a monolithically integrated laser device with multiple wavelengths in single mode operation becomes possible. Fig. 1 shows various spectra obtained from one DFB device using different segment currents and laser temperatures. This wide tuning range (in this case 105 nm) paves the way novel applications in sensing e.g. multi-component gas analysis at high spectral resolution.

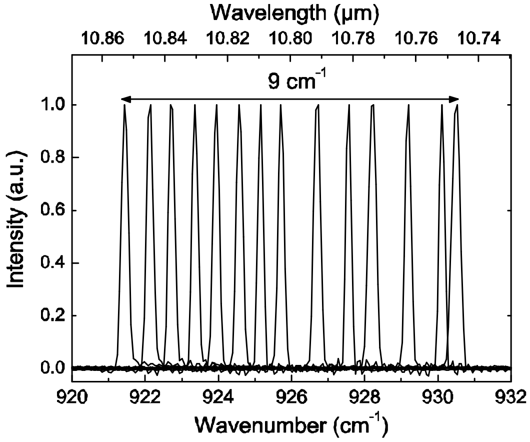

Fig.1. Single mode emission spectra of a multi segment DFB QCL obtained by temperature and segment drive current variation covering a range of over 9 cm^{-1} (105 nm).

E-8

High sensitivity photoacoustic detection of NO_2 with a blue diode laser

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Advances in GaN-based semiconductor lasers have recently led to the availability of diode lasers in the blue wavelength region with output powers in the few hundred mW range. We report on the achievement of a detection limit for the photoacoustic detection of NO_2 in N_2 of 200 parts per trillion using a photoacoustic cell with a resonator length of 10 cm, 1 s integration time, and an amplitude-modulated 300 mW blue diode laser (see Fig. 1). The normalized minimum detectable absorption coefficient was 1×10^{-9} cm^{-1} W/Hz$^{0.5}$. The NO_2 concentration was determined with a reference technology (chemoluminescence).

The effect of mixing O_2 and H_2O to the NO_2/N_2 mixture was investigated. Addition of O_2 resulted in a change of the resonance frequency of the cell, but in no direct photoacoustic response. A small indirect effect on the photoacoustic signal was observed for O_2 and H_2O; with O_2 addition leading to a decrease in signal amplitude and H_2O addition leading to an increase in signal amplitude (see Fig. 2). The NO_2 relaxation rate and the effect of H_2O on the NO_2 photoacoustic signal were measured in more detail. A simple model was made to explain the observed effects.

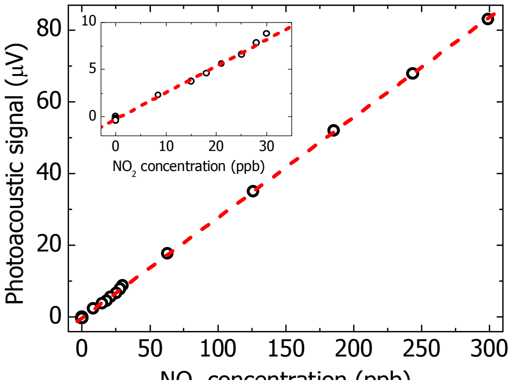

Fig. 1 Photoacoustic signal versus NO_2 concentration as determined by chemoluminescence. The inset shows the same measurement for low NO_2 concentrations.

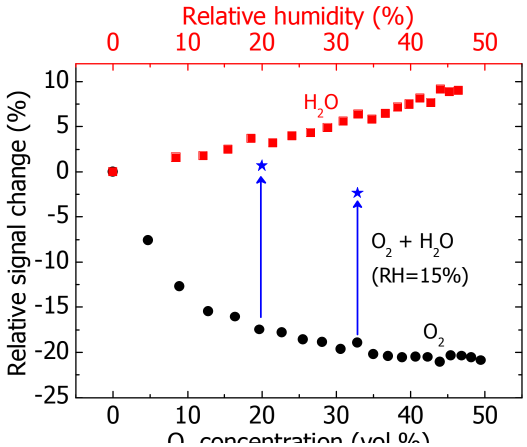

Fig.2 The effect of O_2 and H_2O on the NO_2 photoacoustic signal.

E-9

Measurement of oxygen concentration in methane by Tunebale Diode Laser Spectroscopy

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An important application of oxygen concentration measurement is the control of oxygen in natural gasoline to avoid an explosive gas mixture. The requirement is to measure the concentration below a limit of 5000 ppm with accuracy with 200 ppm.

The vertical cavity emitting laser (VCSEL) scans the wavelength range around the P9P9 absorption line of the oxygen A-band transition at 763 nm (Fig.1). The extractive gas measurement is done in a multi reflection cell. This compact White cell provides an optical path length of 3 m to increase the absorption signal. Because of the weak transmission changes by the absorption the optical setup is designed to show very low interferences ($<10^{-4}$). The photodiode signal is processed by lock-in technique which enables to filter out the noise and to increase thus the sensitivity. The received data is the second derivative of the absorption line (Fig.2). The amplitude of this signal is proportional to the concentration and can be calibrated by a gas concentration stage.

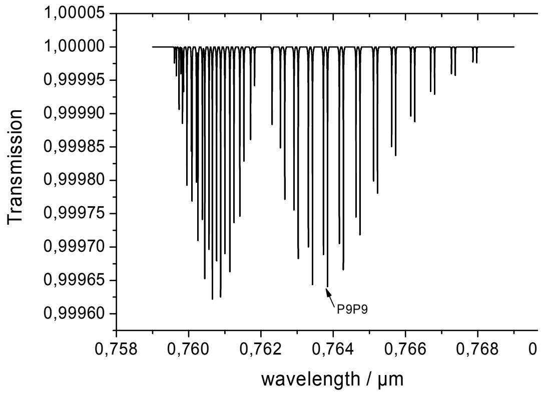

Fig. 1: Oxygen absorption line spectrum at 760nm by Hitran data base (0.1 % oxygen, 3m optical path length, 1 bar, 296 K).

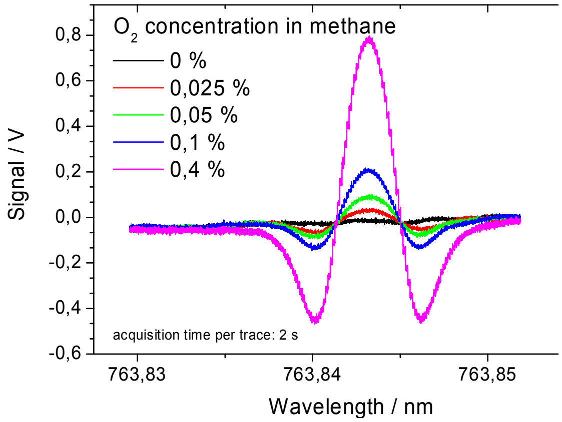

Fig. 2: Measured derivative spectra of the P9P9 absorption line at different oxygen concentrations.

The oxygen is mixed with composites of natural gasoline to check the cross sensitivity. There is no absorption of water or methane or other hydrocarbons at 763.84 nm.

The analyses of a gas concentration stage results a noise equivalent concentration of 14 ppm. The drift measurement of six hours shows a maximum deviation of 70 ppm.

The combination of the special optical setup and derivative spectroscopy enables high sensitivity for monitoring small gas concentrations.

E-10

Long-term unattended TDLS systems operation

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Main gaol of this paper is to demonstrate long-term unattended operation of TDLS system. Other motivation of the work was related to ecological situation worsening in big cities and industrial estates that needs continuous monitoring of main air constituents as CO_2, methane, etc. Finally, CO_2 and methane are known as greenhouse gases and their monitoring is required for global climate change problem. Taking into account above mentioned gaols, two systems were developed and installed for long-term unattended operation.

First instrument measuring CO_2 concentration contained DL module (1,602 μ) was installed in room. Collimated laser beam was directed through room windows to windows of room located in other building. Distance between buildings was 40 m. Receiving optics (10 cm in diameter) detected scattered light and focused it on PD. This instrument is in operation from September 2005 and measured CO_2 concentration in atmosphere between buildings. From raw data also Sun illumination and atmosphere transmission were determined (Fig.1).

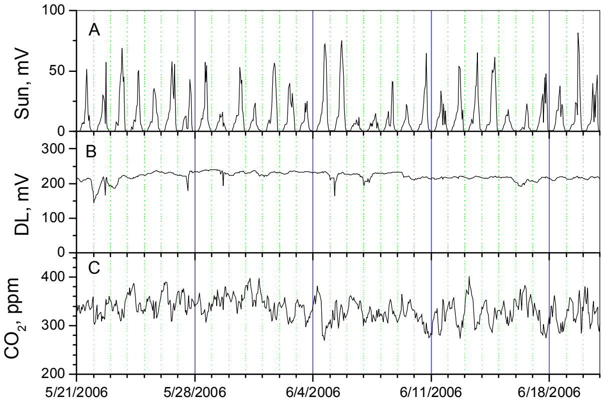

Fig.1 Fragment of Sun illumination (A), received DL radiation (B), and CO_2 concentration (C) monitoring.

Second instrument is measuring CH_4 concentration using DL (1,651 μ). Rest instrument scheme is similar to previous one. During summer 2006 it was installed in the same manner as first instrument and measured methane concentration between two buildings (100 m distance). Then it was installed in corridor of DLS department. Distance between the instrument and reflector is 35 m. As addition, the instrument temperature is measuring simultaneously.

Results of long-term monitoring campaign will be presented and analyzed.

E-11

Tests of trace gas concentration multi-component remote monitoring system

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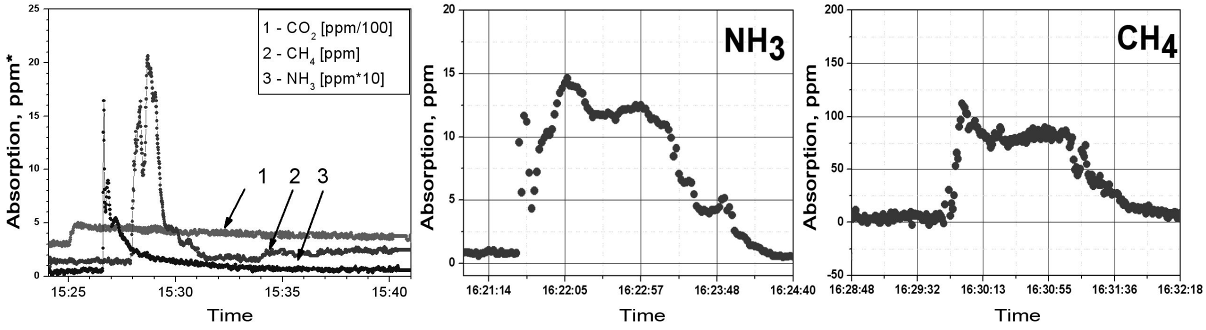
The laboratory and field tests of multi-component system for trace gas remote monitoring were conducted for three molecular objects: CO_2, CH_4 and NH_3.

We used DFB heterolasers with fiber output produced by NTT Electronics (NEL) company for near IR-range. For registration of CO_2, CH_4 and NH_3 molecular objects correspondingly lasers NEL 503076 (1,60 μ), NEL 503520 (1,65 μ) and NEL 537799 (1,51 μ) have been chosen. The opto-electronic characteristics of these lasers allowed frequency tuning by temperature within the range 50 cm^{-1}, and with a help of current tuning within the range of 2 cm^{-1}.

At laboratory tests registration of three gases was accomplished in turns with small intervals between measurements. In a process of measurements in 50 m optical path between laser and topographic reflector (in one direction) was used. The gases under investigation were injected into 100 l box with glass windows. Following volumes of gases were injected: CO_2 (99,96%) – 5 l, CH_4 (99,99%) – 0,5 l and NH_3 (99,99%) – 0,01 l. Figure 1 (a) shows results of these gases concentrations simultaneous measurements as a function of time. Here concentrations are presented taking into account box length. The main result of data presented on figure is an absence of interference of different samples measurement. This circumstance is important and characterizes selectivity of measurement method.



(a) (b) (c)

Fig.1 Tests of trace gas multi-component remote monitoring system

(a)-Simultaneous registration of 3 gases on 50 m optical path

(b),(c)-Registration of ammonia and methane correspondingly in closed car from 80 m distance

Figures 1(b) and 1(c) show NH_3 and CH_4 remote gases registration inside closed car from 80 m distance. One can see process of gas puffing in car enclosure, its mixing, achievement of equilibrium concentration and car ventilation.

The achieved sensitivities for the system of remote multi-component monitoring of gases on 100 m path were: for CO_2 – 30 ppm, for CH_4 – 0,3 ppm and for NH_3 – 1 ppm.

E-12

Fine structure of near and far field diode laser emission diagram

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Results of speckle noise investigation (see separate paper) shows that additional noise in Diode Laser (DL) based system with topography reflector is formed on the reflector surface in presence of relative movement. Hence, origin of additional noise is due to fine structure of DL emission far field diagram. Examples of emission far and near field diagrams for different DL modules will be presented. Fig.1 shows results of above mentioned investigation for one of DL modules under investigation (Laser Components).

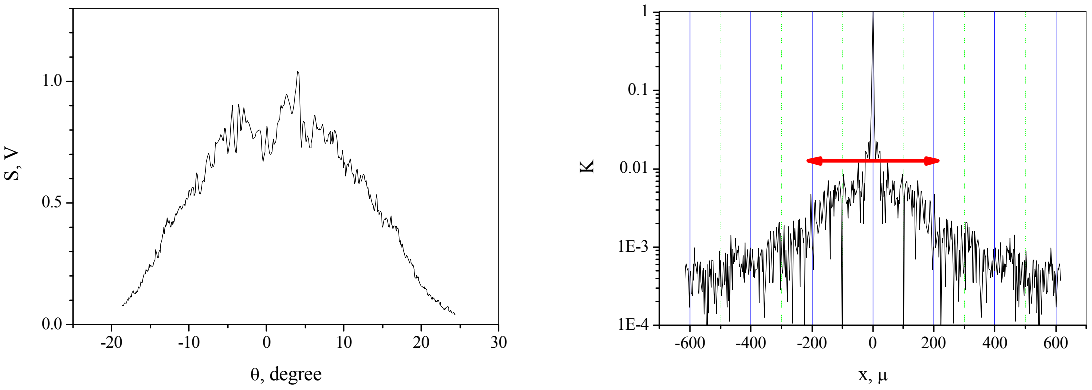

Fig.1 Example of DL emission far (left) and near (right) field diagrams

Arrow on right picture presents DL chip dimension. Presence of coherent DL emission on DL facet due to scattering in DL active area produces speckle pattern both in near and far field. These patterns result in far field fine structure and DL “baseline”. Several DL modules were investigated including DL with single mode fiber output.

Results obtained were analyzed with respect to DL module structure to determine origin of TDLS sensitivity limitations and ways of sensitivity improvement. As result fundamental limit of sensitivity due to DL quantum noise [1] was achieved both for traditional systems and DL based systems with topography reflector.

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E-13

Application of near-IR range diode lasers for remote detection of rocket fuel ingredients: possibilities and outlooks

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Extension of the spectroscopic applicability of tunable diode lasers (DL) is favored by a number of unique performances of these lasers, such as a possibility of providing laser generation of the required wavelength, high monochromaticity, fairly wide tuning range, narrow (10^{-4} cm^{-1}) lasing spectrum, high stability, low power consumption, compactness, etc.

In earlier days, the activities on remote control of rocket fuel ingredients, such as asymmetric dimethyl hydrazine (heptyl), nitrosodimethylamine, tetramethyl-tetrazen, etc. which are strong toxicants and cause severe damage to human health, were carried out with the use of tunable DL of medium-IR range where basic absorption frequencies of the majority of rocket fuel molecules are located. However, the necessity of deep cooling of these systems hindered their introduction to practice, including environmental monitoring. Passing over to uncooled lasers of the near-IR range has made it possible to overcome this shortcoming, but detection in this case occurs in the region of much less intensive combined vibrations and overtones thus resulting in a certain loss of sensitivity which is compensated by signal accumulation.

This report grounds good promises of the application of the above-said range of wave lengths, namely: a relatively low absorption coefficient in the bands of composite frequencies and overtones is compensated by accumulation of a signal and a high pulse repetition rate, as well as by the fact that selectivity of identification of multicomponent gas-aerosol mixtures increases essentially due to the differences of anharmonicity of C-H vibrations for the molecules of rocket fuel ingredients.

It is shown, that in the field of lasing of near-IR diode lasers, nitrosodimethylamine and dimethyl hydrazine molecules have bands with relatively high absorption coefficients. E.g., the absorption coefficient for the 1-st overtone of valence C-H vibrations of nitrosodimethylamine for the 5931.0 cm^{-1} band makes $2.32 \cdot 10^{-21}$ cm^2/molecule, and this magnitude for tetramethyl-tetrazen for the 5860.6 cm^{-1} band makes $2.38 \cdot 10^{-21}$ cm^2/molecule. As can be seen, there is practically no difference in absorption cross-sections of the 1-st overtone of CH_3-groups of tetramethyl-tetrazen and nitrosodimethylamine, despite of a twofold difference in the number of methyl groups in these molecules.

It is demonstrated, that the maximum track length for a lidar equipped with a corner reflector for the 3 mW power of a diode laser (λ=1.5–1.75 μm) makes 1-2 km, its sensitivity being at the level of rocket fuel ingredients MPC. In case of application of an air-based lidar (installed on board a helicopter) with radiation reflection from underlaying surfaces, rocket fuel ingredients of the MPC level are detectable at distances of 100-500 m with the photodetector sensitivity of 1.25·10-12 W/cm·Hz1/2, the receiving mirror diameter equal to 10 cm and the DL power of 10 mW. Our estimations have shown, that if the DL power increases up to 0.5 W, the probing range on reflection from an underlaying surface can reach 5-10 km.

E-14

3 Watt, 60 KHz linewidth CW OPO tunable from 1.4 to 3.9 microns

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We describe key operating characteristics of a high power single frequency CW OPO system which generates multi-Watt ultra-narrowband output ranging from 1400nm in the near-infrared to 3900nm in the mid-infrared. Spectral measurements at 3 microns wavelength have shown the linewidth to be <60kHz on a 500 microsecond timescale, and mode-hop free operation of as much as 16 hours has been demonstrated without active locking. Power levels in this range are between 1 and 5 Watts. Single frequency outputs in the visible are also generated though frequency mixing processes between pump and signal. Rapid mode-hop free tuning of 60GHz is achieved through piezoelectric tuning of the fiber laser pump source.

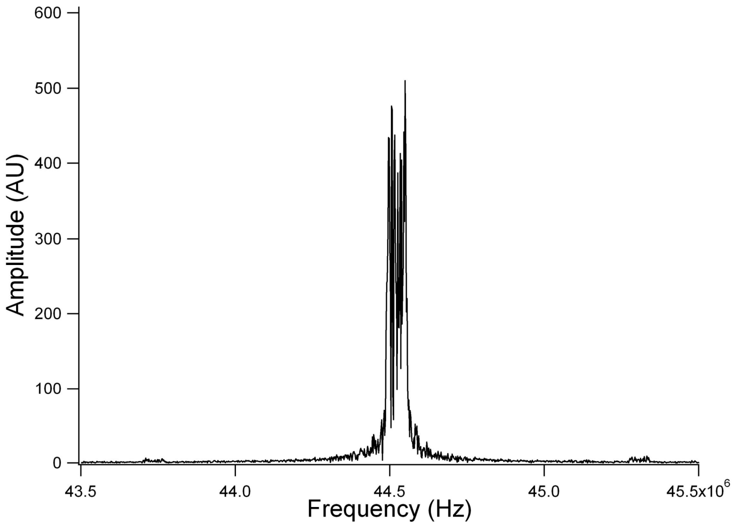

Fig.1 Linewidth measurement of CW OPO

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E-15

Open-path spectroscopy of ethylene and ammonia with Pulsed Quantum-Cascade Lasers

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We present the results of range-resolved gas concentration measurements in ambient air using pulsed quantum-cascade lasers (QCL) operating at room temperature near 10.3 μm (QCL-1) and near 10.9 μm (QCL-2). The lasers mounted on Peltier coolers in air-tight housings were excited with 200-ns current pulses. Both laser beams were collimated with ZnSe lenses with focal lengths of 38 mm. We utilized chirped laser pulses to scan laser frequency over target spectral features. To study the tuning properties of the lasers, we have applied the method of frequency markers [1] using an 1.2-m absorption cell. We utilized CO_2 absorption lines at 966.25 cm^{-1} and 967.71 cm^{-1} (QCL-1) and C_2H_4 absorption line at 915.6 cm^{-1} (QCL-2) as frequency markers. The chirp rate was measured for both lasers as a function of peak injection currents and time with a 5-ns resolution within 200-ns laser pulses. For QCL-1 the average chirp rate was found to increase from 7.7 to 1.0 cm^{-1}/μs when peak injection current was increased from 7.1 to 7.9 A. Both lasers were capable of covering spectral intervals up to ~1.8 cm^{-1} with 200-ns chirped pulses. An initial maximum frequency of the intervals was defined by laser substrate temperature. Using QCL-1 with substrate temperature set to 24.0 ^{0}C we have scanned an NH_3 absorption line at 967.35 cm^{-1} with absorption cross-section of ~ $2.1 \cdot 10^{-18}$ cm^2. We have reached a C_2H_4 line at 915.6 cm^{-1} with absorption cross-section of ~ $1.6 \cdot 10^{-19}$ using QCL-2 with substrate temperature set to 20.8 ^{0}C.

To perform open-path spectroscopy we used a 50-% ZnSe beam splitter to direct a laser beam to a corner cube retroreflector (CCRR) with clear aperture of 60 mm placed at a distance up to 50 m from the laser. A returned laser beam was focused with an off-axis parabolic mirror with diameter of 75 mm onto a LN_2 cooled HgCdTe detector with a 100-MHz bandwidth. A range-resolved gas sensing has been demonstrated using a second CCRR with clear aperture of 30 mm inserted into a laser beam at a half distance of the first CCRR. Return signals were obtained from both CCRRs that allowed for gas concentration measurements in each section. A distribution of gas concentration can be retrieved with a set of CCRRs arranged along the absorption path [2].

In our preliminary experiments using QCL-1 we have found that NH_3 concentrations can be measured with a spatial resolution of ~ 30 m and detection limit of ~ 20 ppb·v per a 30-m section. A spatial resolution and detection limit for C_2H_4 was estimated to be of ~ 50 m and ~0.17 ppm·v per section, respectively. Open-path QCL-based systems can be developed for multi-species range-resolved trace gas sensing in the atmosphere over the ranges up to ~ 1 km.

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E-16

Tunable diode laser spectrometer for atmospheric measurements of the isotopic ratio $^{13}CO_2/^{12}CO_2$

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We have developed a Tunable Diode Laser Spectrometer to measure the $^{13}CO_2$ and $^{12}CO_2$ concentrations and thus the isotopic ratio $^{13}CO_2/^{12}CO_2$ in the atmosphere. This instrument is based on direct absorption spectroscopy technique using a lead salt laser diode in the mid-infrared. The two concentrations are measured using a couple of line around 2290.1 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 measured for the two concentrations.

After a description of the instrument principle and of its operating mode, 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.

E-17

Quantitative phase-shift off-axis cavity-enhanced absorption spectroscopy for the detection of NO_2 and CO_2 with diode lasers

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We present recent measurements obtained using phase-shift off-axis cavity-enhanced absorption spectroscopy for high sensitivity trace gas detection. A current-modulated violet diode laser emitting around 404 nm was used to measure nitrogen dioxide (NO_2) in diluted standard mixtures and in laboratory air. The optical cavity was formed by two concave mirrors each with a reflectivity of 0.999 and a separation of 43 cm. A noise equivalent detection limit of 1 – 2 ppb (S/N = 1) was obtained with a lock-in amplifier time constant of 1s. Allan variance analysis indicates an achievable limit of 0.24 ppb in 80 s at atmospheric pressure [1].

A similar off-axis aligned cavity was then used to measure carbon dioxide and carbon isotope ratios in the near-infrared with a DFB diode laser at 1605 nm. For 5% CO_2 concentration measurements, $\delta^{13}C$ standard deviations of 1.8 ‰ were obtained for five successive measurements [2].

For quantitative measurements, the effect of laser amplified spontaneous emission (ASE) has also been analysed for absorption measurements derived from the phase shift of an intensity modulated beam. It was shown that the ASE contribution to the cavity output light intensity can lead to an over estimation of absorption linestrengths [3].

References:

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[3] V.L. Kasyutich, P.A. Martin, and R.J. Holdsworth, Chem.Phys.Lett. 430, 429-434 (2006)

Poster Session F

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Y. Arita and P. Ewart

F-2 Fs-COMB referenced narrow linewidth diode laser system for coherent molecular spectroscopy
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F-12 Absorption spectra of HDO and HTO in near IR spectral range
A.I. Nadezhdinskii, D.Yu. Namestnikov, Ya.Ya. Ponurovskii, G.Yu. Grigoriev, S.L. Malyugin, Sh.Sh. Nabiev, V.Ya. Zaslavskii

F-13 From the desert to the clinic - a portable ethane gas sensor
Claire S. Patterson, Lesley C. McMillan, Miles J. Padgett and Kenneth D. Skeldon

F-14 Long-term continuous isotopic ratio measurements of atmospheric CO_2 in Billerica, MA using a 4.3 µm pulsed QCL

David D. Nelson, J. Barry McManus, Scott C. Herndon, Mark S. Zahniser, Bela Tuzson, and Lukas Emmenegger

F-15 Oxygen isotope ratio measurements in atmospheric CO_2 by means of a CW Quantum Cascade Laser at 4.3 µm

A. Castrillo, G. Casa, D.A. Parretta, and L. Gianfrani

F-16 Fiber-optic distributed acoustic sensors for gas leakage detection system

M.I. Belovolov, K.A. Zykov-Myzin

F-1

Multi-mode absorption spectroscopy

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Tunable diode laser spectroscopy for probing of multiple transitions, or transitions in multiple species, usually requires multiple lasers with time- or wavelength-division multiplexing [1,2]. We report a novel technique for tunable diode laser spectroscopy capable of simultaneous high resolution and wide spectral coverage suitable for combustion and environmental diagnostics. Multi-Mode Absorption Spectroscopy, MUMAS, uses a multimode diode laser with a spectrum covering up to 10 or 20 nm (~1 THz) capable of spanning an entire electronic-rotation-vibration band of a diatomic molecule. Injection current or cavity length modulation tunes all the modes simultaneously. Reduction of individual mode intensity is detected when they correspond to individual electronic-vibration-rotation transitions in the absorbing molecules. The time variation of the transmitted intensity produces a “fingerprint” signature for a given laser and molecule which carries information on the molecular density, quantum state populations and temperature.

The novel feature of MUMAS is its ability to detect simultaneously many transitions over a wide spectral range. Additionally multiple species can be detected simultaneously with high spectral resolution. This feature will be potentially significant in the mid-infra-red spectral region where species such as CO, CO_2, CH_4 etc have neighbouring absorption features.

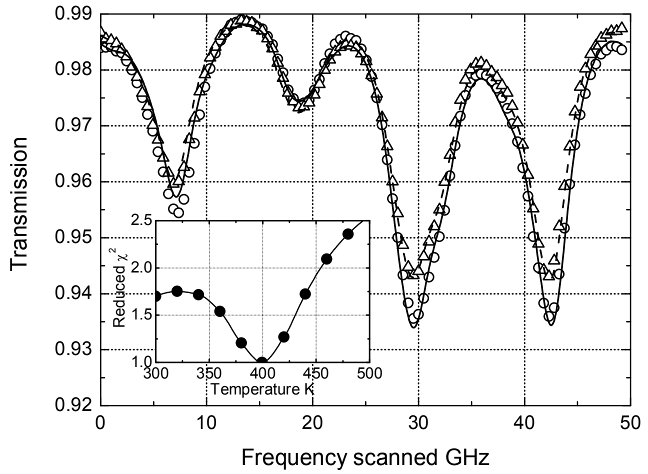

Figure 1. MUMAS spectra of O_2 showing data for temperatures of 291K (circles) and 400K (triangles). The insert shows χ^2 for temperature fit to data yielding a value of 400 ± 8 K.

MUMAS fingerprint spectra of molecular Oxygen on the weak A-band, $b^3\Sigma_g^- - X^1\Sigma_g^+$, around 760 nm is reported. Spectra are analysed to account for laser mode linewidth and spacing and lineshape effects. Fitting of data to model spectra as a function of temperature allows the temperature to be derived from the MUMAS spectra. Extension of the technique using diode laser pumped microcavity lasers in the infra-red based on Er/Yr doped glasses will be discussed for sensing of infra-red absorbing species.

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F-2

Fs-COMB referenced narrow linewidth diode laser system for coherent molecular spectroscopy

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We are currently preparing for experiments that aim at the generation of quantum coherence between individual rotational-vibrational states of cold molecules. The realization of molecular coherence between individual ro-vibronic states would provide the possibility to transfer concepts known from atom interferometry to molecular internal state interferometry. The latter could be applied to many high precision tests of fundamental physics. These types of molecular interferometers would require a multi-chromatic laser source that provides ultra-stable difference frequencies in the few THz or few 10 THz range. Up to now, this can only be realized by locking individual lasers, diode lasers in our case, to an optical fs-frequency comb. Phase-locking of diode lasers to a frequency comb is challenging because of the low signal-to-noise ratio of the corresponding RF beat notes and the large frequency or phase noise bandwidth of grating diode lasers.

Our approach to ease locking is to develop diode lasers which feature a reduced noise bandwidth. A reduction of the noise bandwidth corresponds to a reduction of the necessary RF-detector bandwidth which in turn results in an improved signal-to-noise ratio of the RF-beat note detection. Here we present a diode laser system operating at 1400 nm which is based on merging the concepts underlying the grating diode laser and the diode laser with resonant optical feedback (GEECDL, grating enhanced external cavity diode laser) [1]. Thus we combine the good over-all (few 10 nm) and continuous tuneability (up to 20 GHz) and the simple operation of grating lasers with the narrow line width (few 10 kHz) provided by diode lasers with resonant optical feedback. To demonstrate the laser systems potential for high resolution, highly accurate laser spectroscopy we frequency-lock the diode laser to a Ti:Sa-based fs-frequency comb and find a relative frequency drift of 314 Hz during 2.8 hours. The beat note linewidth corresponds to 300 kHz and is determined by the short term stability of the frequency comb. We present results on a beat note measurement between two similar laser systems which provides determination of the diode lasers short term frequency stability.

This work is supported by the Deutsche Forschungsgemeinschaft.

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F-3

MID-IR QCL-based sensor for field measurements of ambient CH_4

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We are developing mid-IR QCL-based sensors for field measurements of ambient CH_4 and CO_2. In this presentation, we report on characterization and field trials of the CH_4 field sensor. This sensor utilizes a Type II Quantum Cascade Laser (or Interband Cascade Laser, ICL) operating in cw mode at cryogenic temperature and near 3.4 µm to monitor CH_4. Allan variance analysis reveals that the precision is 15 ppbv for a 60 sec integration period. The precision of 15 ppbv represents a peak absorption of 5.3×10^{-5}.

We demonstrated the sensor at the Sallie's Fen Environmental Station in collaboration with the University of New Hampshire Climate Change Research Center. Emissions have been measured using a chamber technique either manually or, since 2001, automatically at 10 locations within the fen. The laser sensor measured the air sample and periodically switched to a 2 ppmv reference standard for span calibration. Figure 1 presents data measured by the laser sensor and by a colocated GC. The numbers in the boxes above each peak in the CH_4 concentration represent the particular chamber from which the sample originated. Breaks in the laser data trace represent the times during which the sensor was sampling the reference gas. Excellent agreement was obtained with the GC sensor.

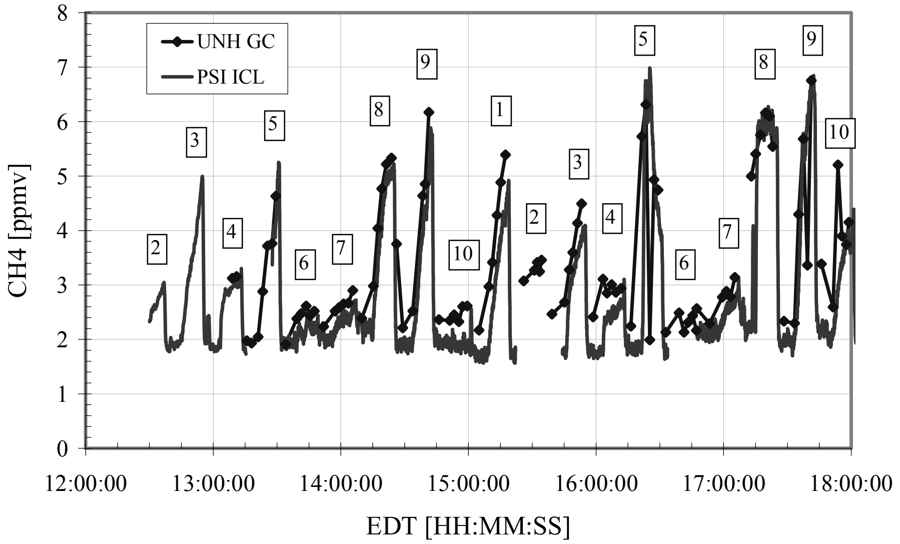

Fig. 1. Ambient methane measured at Sallies Fen site by the GC and the laser sensors. Data from 7/20/06 12:00 EDT.

F-4

Multigas detection at atmospheric pressure with a quantum cascade laser photoacoustic spectrometer around 7.9 µm

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Ten years ago the Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA, Reims, France) has developed a photoacoustic cell based on differential Helmholtz resonance for infrared gas detection [1]. This cell was used in conjunction with a near-infrared diode laser to detect methane. In recent years molecular gas lasers and diode lasers have been widely used for in-situ pollution monitoring. The photoacoustic sensor described here represents an effective spectroscopic technique for detection of ambient trace gases due to its intrinsically high sensitivity, large dynamic range and comparatively simple instrumentation. The detection limit of this technique is mainly determined by the characteristics of the laser used (output power, tunability, single mode emission…) and the photoacoustic cell sensitivity. The feasibility of methane detection has been demonstrated with near-infrared diode lasers and the system has been improved significantly so as to increase sufficiently the sensitivity for sub-ppm methane detection [2].

The use of quantum cascade laser gives the possibility to improve the detection limit thanks to its high power and its emission in fundamental bands. A first quantum cascade laser emitting in the 7.9µm region was used for the methane detection in ambient air. A detection limit of 3 ppb was achieved [3]. A second quantum cascade laser emitting in the 5.4µm region was used for the NO detection. A detection limit of 20 ppb was achieved [4]. Unfortunately these lasers work at cryogenic temperatures. The development of an in situ sensor is more difficult with this kind of technology. The results presented here will show the possibility of multi-gas detection (CH_4, N_2O, H_2O…) at atmospheric pressure with our photoacoustic spectrometer used in conjunction with a quantum cascade laser working at room temperature and emitting around 7.9µm. The achieved detection limits are slightly less than those obtained with the cryogenic lasers because the power is lower. However these results are amply sufficient to measure gas concentrations in air flux. The best practical modulation way is on-off modulation where the obtained signal is directly related to the molecular concentration. The detection limits obtained are in the same order of magnitude than that of the typical multipath (100 m length) absorption spectroscopy systems. The main advantages of photoacoustic spectrometers in comparison to these systems are the compactness of the system, the ease of use at atmospheric pressure, the insensitivity to optical misalignment and the very weak volume of the cell giving the possibility to install the sensor in a moving system and to make real-time in situ measurements at quite a high speed.

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F-5

Fuel tank O_2 sensing via wavelength modulation spectroscopy over broad environmental conditions

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We present results using Tunable Diode Laser Spectroscopy (TDLS) with the signal enhancing approach of Wavelength Modulation Spectroscopy (WMS) [1] to measure O_2 content in the head space of an aircraft fuel tank. This sensor is one of a number of recent PSI efforts to miniaturize commercial TDLS-based sensors [2,3]. The sensor employs a low-cost VCSEL laser at 760nm that is located remotely from the laser control and signal processing electronics in a separate module (Fig. 1), of which only the probe tube penetrates the fuel tank. The spectroscopic waveforms are, of course, sensitive to pressure and temperature. Our sensor measures those parameters independently and uses a calibrated correction algorithm to accurately report O_2 concentration regardless of environmental conditions over the aircraft flight and ground operating envelope (Fig. 2).

Fig.1 PSI TDLS sensor for fuel tank head space O_2 concentration, the GasScanO_2.

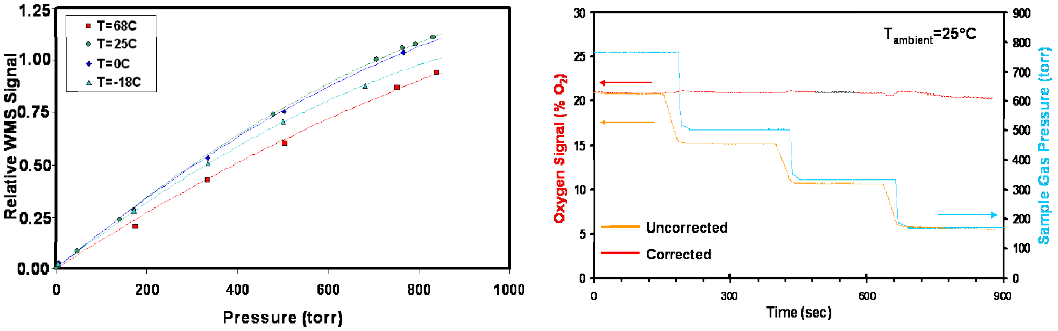

Fig.2 (Left) Relative average WMS signals (calibrated at 25°C, 1 atm) for room air at various stable environmental conditions. Solid lines are polynomial curve fits. (Right) Time-resolved pressure data (blue) and O_2 signals (10Hz data rate, 30sec running avg) deduced from WMS signals, with (red) and without (orange) correction via supplemental P and T measurement. In this record total pressure at the sampling probe is dropped in 3 steps over 15min.

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F-6

New Approaches for Improved TDL Manufacturing

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There actually is no day without news concerning global warming and global climate changes, and also safety regulations in production areas and public places. In order to meet the requirements of nature conservation and simple life protection many molecules have to be measured. So all around the world an increasing demand for measurements of molecular species in air and vacuum vessels has become obvious. Today the identification of gaseous species and especially the measurement of their absolute concentration is one the main challenge. Tunable diode laser absorption spectroscopy is here one of the best suited diagnostic methods meeting the need of high selectivity, high sensitivity, high measurement speed including reduced sample preparation combined with reliable, robust and versatile techniques. Over three decades tunable diode lasers are produced using the IV-VI material system, and still today a wide range of spectral positions is accessible. Lasers with IR emission from 500 cm^{-1} to 3300 cm^{-1} are used for basic research and industrial-like development subjects.

Just recently the extension of the emission wavenumber into the area beyond 3300 cm^{-1} up to 3400 cm^{-1} has been developed successfully. This opens the door for detection of new molecules, as e.g. OH-radicals, which is very important for plasma and environmental studies. The shortest emitted wavelength detected was 2.93 µm corresponding to 3412 cm^{-1} at an operation temperature of 84 K using cw current. The maximum working temperature was observed to be 110 K and the lowest measured threshold current found was 400 mA at 77 K using cw current, as well. These results were achieved by variation of the (Pb,Sr)Se active layer with finally high Sr-contents of up to 3.4 %, combined with an improvement of the epitaxial parameters.

Reduction of power consumption will help to extend life time and reduce size of cryogenic systems. With the use of ridge waveguides a reduction of power consumption has been achieved successfully. Epitaxial improvements as e.g. graded index layers were applied during wafer growth for lasers emitting at 3000 cm^{-1}. The corresponding MBE-processed wafer was used for ridge waveguide design developments. Here a wet and a dry etching technology has been applied to investigate stripe geometry on top of a double hetero structure laser design.

A good single mode behaviour with a tuning range of about 5 cm^{-1} has been observed. For example laser emission from 2948 cm^{-1} to 2953 cm^{-1} has been observed with an detected outpower of 350 µW. Smallest threshold current was measured to 70 mA at 80 K. The maximum operating temperature was 105 K.

F-7

Vibrational-rotational spectrum of GaF and the analysis with a non-Born-Oppenheimer effective Hamiltonian

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For analyses of high-resolution vibrational-rotational and rotational spectra of diatomic molecules, one must employ the non-Born-Oppenheimer Hamiltonian that includes the adiabatic and non-adiabatic corrections of the breakdown of the Born-Oppenheimer approximations. It has been shown that on applying such Hamiltonian to the determination of molecular parameters only clusters of the expansion coefficients for the adiabatic and non-adiabatic correction functions are determinable [1-3].

An effective non-Born-Oppenheimer rovibrational Hamiltonian [2] have been given as

$$\begin{aligned} H = {} & -B_e(1+\delta\Delta_B)\frac{\mathrm{d}^2}{\mathrm{d}\xi'^2} + \frac{B_e(1+\delta\Delta_B)}{(1+\xi')^2}\left(1+\sum_{i=1}\delta r_{iq}\xi'^i\right)J(J+1) \\ & + \frac{[\omega_e(1+\delta\Delta_\omega)]^2}{4B_e(1+\delta\Delta_B)}\xi'^2\left(1+\sum_{i=1}a_i(1+\delta\Delta_{aiq})\xi'^i\right). \end{aligned} \tag{1}$$

Since the non-Born-Oppenheimer parameters, $\delta\Delta_B$, $\delta\Delta_\omega$, $\delta\Delta_{aiq}$, and δr_{iq} (i=1, 2, …) in Eq. (1) that are the clusters of the expansion coefficients have different v, J dependences, these parameters are experimentally determinable [2, 4].

Only one study of vibrational-rotational spectroscopy of GaF [5], with medium resolution, has been reported so far. In this study, we measured vibrational-rotational spectrum of GaF with high resolution to determine physically significant parameters with the present analytic approach of the universal scheme [4] for the simultaneous analysis of many vibrational bands. A diode-laser spectrometer, Spectra Physics (Laser Analytics) SP5000 and an FTIR spectrometer Bruker IFS125HR have been used to observe Δv=2 and 1 transitions, respectively. The observed transitions, combined with the rotational lines reported in the literature were analyzed with the fitting parameters including correct non-Born-Oppenheimer parameters.

A result of analysis of reported rotational and vibrational-rotational transitions of HF that demonstrates the ability of the present universal scheme for determination of the physically significant parameters will also be presented.

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F-8

Gas correlation spectroscopy by multimode diode lasers

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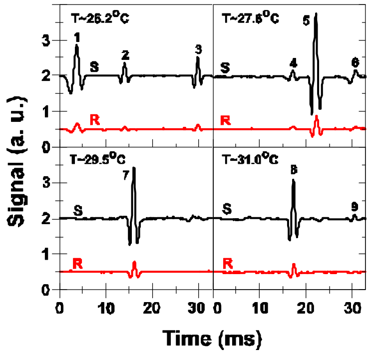
Tunable diode laser absorption spectroscopy (TDLAS) has been successfully demonstrated in fields raging from environmental monitoring, industrial process control and biomedicine, however, further widespread deployment of such systems for commercial gas sensing is often hampered by the rigorous requirement of single mode operation and wavelength stability.

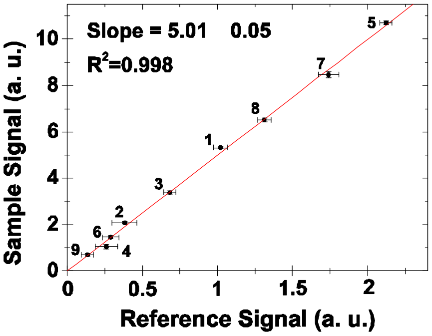
Multimode diode lasers – without qualifying as optimal spectroscopic sources – may allow for a much simpler, more robust and less costly design. This has been shown for oxygen detection by using a diode laser operated near its lasing threshold [1].

An important extension of the TDLAS technique is presented, based on employment of a fast wavelength-tunable multimode diode laser in a dual-beam configuration [2]. A theoretical relationship is derived between the intensity variation of partially-absorbed multiple modes and the target gas concentration. The concentration is retrieved by correlating simultaneously recorded WMS signals of the sample and the reference gas in a linear-regression procedure. Intensity fluctuations and wavelength shifts due to mode hops and temperature drift are automatically compensated for. High absorption probability is obtained within a limited tuning range by overlapping the laser multimode chart with the gas spectrum, thereby increasing the measurement precision and reliability.

This simple and robust scheme was demonstrated on acetylene analysis, but the method can be applied on any gas with dense and sufficiently sharp absorption lines.



Simultaneously recorded WMS signals of the sample (S) and the reference (R) cells



Linear regression between the sample and reference signal pairs

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F-9

Line intensities and pressure broadening of H_2O in the 0.8 microns region studied using ECDL spectroscopy

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H_2O is responsible for about 70 % of atmospheric absorption and plays a crucial role in radiative transfer especially for the evolution of the Earth's atmosphere and climate. For this reason accurate spectroscopic data – in particular in the near-infrared region – is essential for reliable quantitative studies of global warming and the various feedbacks related to this effect. The absorption spectrum of H_2O has been extensively studied over the past decades in the near-infrared and visible regions, but there remain significant discrepancies in the 10000-12500 cm^{-1} range even for the most intense lines. In particular, the line intensities obtained in 1997 by Ponsardin and Browell [1] are about 10-15 % higher than those in HITRAN2004. Also, there are differences of up to 20 % between the data of Schermaul *et al.* [2] and HITRAN2004. For the air-broadening coefficients, there is a difference of about 20 % between the values of Lucchesini *et al.* [3] and Ray *et al.* [4]. In the study reported here, we have studied 24 lines of H_2O in order to measure absolute line intensities as well as air- and self-broadening coefficients, using an external cavity diode laser emitting in the 815-885 nm range. The ECDL has a negligible apparatus function (line width 1 MHz) and a very high signal to noise ratio (better than 1000) and gave us thus the opportunity to study important effects such as Dicke narrowing (that has probably a non-negligible impact on the accuracy of radiative transfer calculations in this spectral region). Concerning the H_2O line parameters, our self-broadening coefficients are 6 % lower than those of HITRAN2004 and for absolute line intensities our results are 11 % higher than HITRAN2004 data, but in very good agreement with the values of Ponsardin and Browell [1]. These results were also confirmed by measurements of water vapor absorption lines in the mid-infrared region that were recorded simultaneously in the same cell using a difference frequency generation laser.

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F-10

TDLS operation regimes and data processing

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TDLS operation regimes classification will be given following [1] and recently obtained results both in techniques and methods improvement. Steps of operation regime related to physical properties of TDLS system components will be considered including:

1. Temperature stabilization
2. DL frequency tuning cycles stabilization
3. Special excitation current waveforms
4. Operation mode optimization
5. Time multiplexing regime
6. Etc.

Preliminary data processing used in recent generation of TDLS operation regime will be introduced and testing results will be presented including:

1. Subtraction of external illumination and PD Flicker noise influences (Optical zero module)
2. Subtraction of intensity variations (Even-Odd module)
3. Data optimal filtering (Correlation module)
4. Etc.

Data processing to obtain molecule under detection concentration will be presented including:

1. Vector presentation of raw data
2. Procedure of concentration determination from raw data based on vector algebra
3. The procedure optimization
4. Usage of orthogonalization procedures
5. Etc.

Using TDLS operation regime and data processing described achievement of fundamentally limited parameters will be demonstrated:

1. Temperature stabilization at 10^{-5} K level
2. DL frequency stabilization at 1 kHz level
3. Minimum detectable absorption below 10^{-7} level
4. Etc.

Possible future improvements of TDLS operation regimes and data processing will be considered.

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F-11

TDLS Electronics with Computer Control

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A new generation of electronics was developed for use in TDLS systems. These electronics are operational under full computer control. Optional capability exists to use both PCI and USB National Instruments boards.

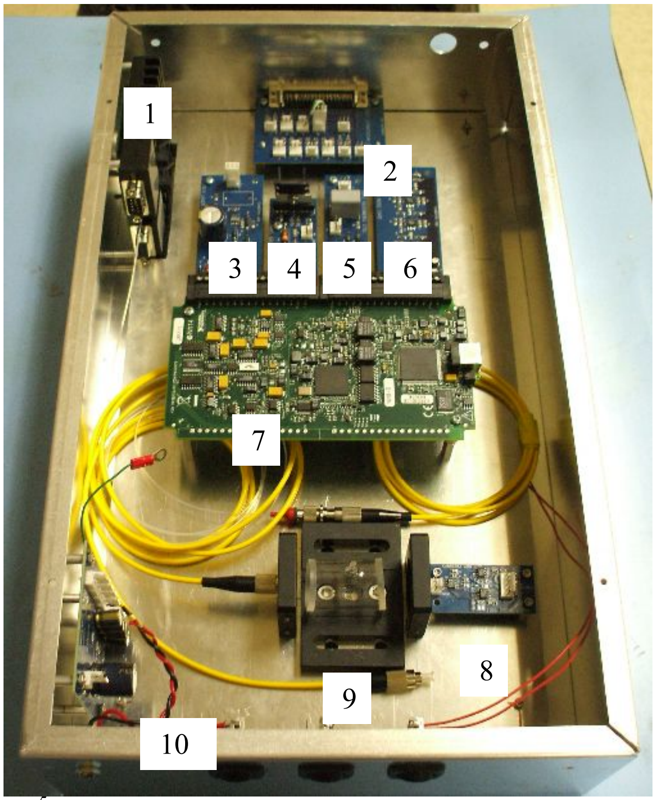

Fig.1 View of electronic prototype

Primary Components:

1. Diode laser module
2. Interconnect board for PCI NI DAQ
3. DL excitation current board
4. Thermo Electric controller board
5. Thermo sensor board
6. Power distribution board
7. USB NI DAQ
8. Photo diode with pre amplifier
9. Reference gas cell
10. Power supply board with 12 V DC or AC power

All fiber optical connection.

Results of tests of electronics system will be presented and discussed. The electronics provided DL temperature stabilization at 3 x 10^{-5} K level. Minimum detectable absorption achieved with this electronics is 10^{-7}.

Fig.1 shows the view of electronics prototype tested both in Moscow and Albuquerque. Initial manufacturing run of 25 electronics units has been completed.

F-12

Absorption spectra of HDO and HTO in near IR spectral range

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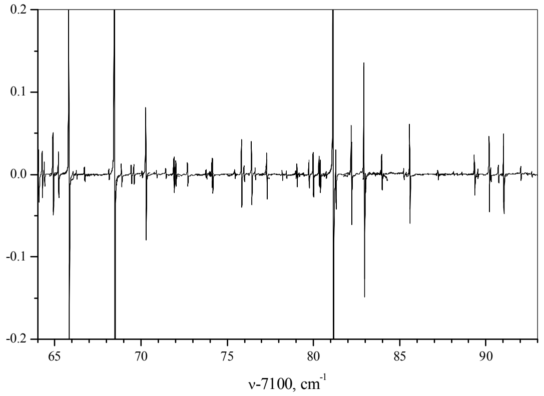
Different processes of nuclear fuel cycle are followed by release of deuterium – D and tritium – T (heavy and super-heavy hydrogen isotopes). Their isotope exchange with hydrogen in atmosphere water vapour leads to presence in air HDO and HTO molecules. Hence, presence of these water isotopomers near facility under inspection above their concentration in normal atmosphere is signature of nuclear activity. D is stable isotope, its natural abundance is 3.11 10^{-4} (for example see [1]). T is unstable isotope with decay time - 12.33 years. Its concentration in atmosphere is very low because main source of T generation in atmosphere is due to space neutrons (each minute ~ 10 atoms/cm^2).

All water isotopomers under consideration (H_2O, HDO, HTO) have absorption in near IR (overtone of H-O bond) and can be detected by TDLS with high sensitivity. H_2O spectra were investigated recently with very high sensitivity, while HDO spectra were obtained for natural abundance [2]. Up to authors knowledge there is no information about HTO in this spectral range. In present paper results of HDO and HTO spectra investigation using TDLS technique will be presented. Two channels DL spectrometer was developed for this purpose. One channel with interferometer Fabry-Perrot (0.0497 cm^{-1}) was used to determine DL frequency tuning curve. Absolute DL frequency calibration was performed using these channel containing cell with normal water vapour (Lcell =200 cm). In analytical channel sample cell (L=100 cm) were installed. DFB DL operated near 1.39 μ where water isotopomers absorption bands are located. Spectra were recorded in spectral range 7164-7193 cm^{-1}. Two samples were investigated: normal water and heavy water containing T (H:D = 0.57, T:D = 0.01). Fig. shows spectrum of heavy water spectrum. Lines observed in H_2O spectrum were in agreement with [1]. For heavy isotopomers we observed several disagreements demonstrating wrong lines identification for HDO and presence of additional lines with respect to [1]. Future spectra analysis is in progress.



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F-13

From the desert to the clinic - a portable ethane gas sensor

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Real-time trace ethane detection ethane offers unique potential in many diverse applications. In oil-prospecting, it offers remote evaluation of a survey area [1] and in medicine, it enables non-invasive breath monitoring of oxidative stress [2]. Traditional off-line methods for ethane analysis often rely on gas chromatography combined with mass spectroscopy and variants there of. It is only with the use of optical techniques that ultra-sensitive, real-time measurement has become possible.

We have developed a portable spectroscopy system with a sensitivity of 70 parts per trillion and a 1-second sampling rate [3]. Using a cryogenically cooled lead-salt laser, we perform second derivative wavelength modulation spectroscopy at 3.4μm. The instrument has a thermally-managed closed-loop refrigeration system eliminating the need for liquid coolants. Custom-written LabVIEW software allows automatic control by a laptop PC. The performance has been tested in a range of environments, both indoor and outdoor, industrial and clinical.

We are conducting pilot studies in collaboration with a number of hospitals and research groups across Scotland. On the industrial side, we are collaborating with Shell Global Solutions and other groups to miniaturise and improve the robustness of our technology, incorporating new laser sources such as quantum cascade lasers. In healthcare, we apply our technology to a variety of areas including intensive care, dialysis, radiotherapy and basic life-science research. We will outline the novel applications underway with the instrument and present results from a number of our interdisciplinary studies. We will comment on the use of tunable diode lasers in our systems and discuss the development of the next generation of our portable gas sensors.

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F-14

Long-term continuous isotopic ratio measurements of atmospheric CO_2 in Billerica, MA using a 4.3 µm pulsed QCL

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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 at least one part in ten thousand or 0.1 ‰. We use tunable infrared laser differential absorption spectroscopy with pulsed QC lasers (QC-TILDAS) to address this challenge. QC lasers are attractive optical sources due to: 1) absence of cryogenic fluids, 2) stable single mode spectral output, 3) optical simplicity.

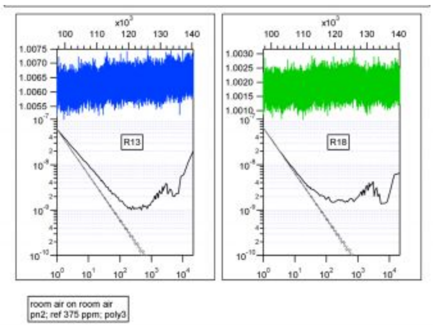

Fig. 1. Allan variance plots of 1 s data for R13=S($^{13}CO_2$)/S($^{12}CO_2$) and R18 over 12 hrs. The minimum corresponds to σ_{Allan} = 0.03 ‰ after 300 s averaging time.

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 $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios can be obtained in a single spectral window near 2310 cm^{-1}. 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.

The long term 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 σ_{Allan} = 0.03 ‰ after 300 sec integration using a LN2 cooled detector.

We have used this instrument to perform long term (>3 months) monitoring of ambient air from the roof top of our laboratory. The data in Fig. 2 shows deviations in R13 and R18 relative to a calibration standard. The morning and evening signatures of local automobile traffic and residential heating by fossil fuels are evident in both elevated CO_2 and diminished R13 and R18.

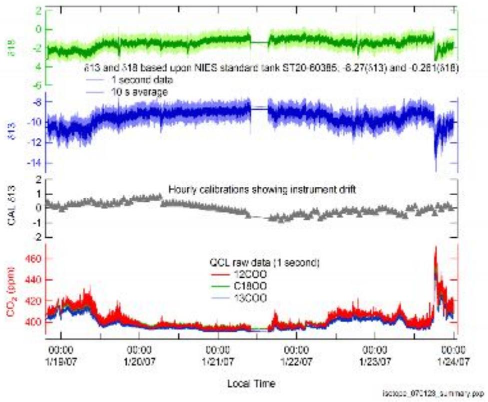

Fig. 2. Roof-top monitoring of ambient CO_2 isotopologues. Long term instrument drift is corrected by hourly additions of calibrated air.

F-15

Oxygen isotope ratio measurements in atmospheric CO_2 by means of a CW Quantum Cascade Laser at 4.3 μm

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Isotopic fractionation processes are based on differences in chemical and physical properties that depend on the mass of the elements involved. In the case of oxygen, fractionation processes for ^{17}O and ^{18}O usually occur in such a way that the isotope ratios, expressed in δ-units, follows the equation: $\delta^{17}O = 0.52 \times \delta^{18}O$ [1]. This gives rise, in a three-isotope plot, to what is usually referred to as the mass-dependent fractionation line. Although the great majority of processes follow this relation, a few important deviations have been observed in relevant stratospheric gases, including O_3, CO_2 and N_2O. Commonly named isotopic anomalies, they are determined by mass-independent fractionation mechanisms, which are not completely understood, yet. Even though Isotope Ratio Mass Spectrometry (IRMS) represents the standard method to measure stable isotope ratios, it is not ideally suited for studying the isotope anomaly in oxygen because of the mass overlap between $^{17}O^{12}C^{16}O$ and $^{16}O^{13}C^{16}O$. In fact, a complex and time-consuming sample treatment procedure is required, prior to analysis, to convert CO_2 to O_2 [2]. In the last few years, infrared laser spectrometry has clearly emerged as a valid alternative to IRMS, capable of ensuring accuracy and precision levels that are sufficient for many practical applications [3]. Moreover, optical instrumentation offers many advantages compared to IRMS, including being conceptually simple, having a compact design with low power consumption, enabling in-situ applications on different platforms.

We here report on our recent efforts to develop a new laser-spectroscopic methodology for simultaneous $^{17}O/^{16}O$ and $^{18}O/^{16}O$ isotopic ratio measurements, in atmospheric CO_2. It is based on a continuous-wave, liquid-nitrogen cooled, distributed feedback quantum cascade laser working at a wavelength of 4.3 μm. We present our first results on $\delta^{17}O$ and $\delta^{18}O$ measurements, which have been carried out by means of wavelength modulation spectroscopy, with 2nd harmonic detection, using a pair of single-pass absorption cells and a single MCT detector. The 1-σ precision in repeated determinations of $\delta^{17}O$and $\delta^{18}O$ is about 3 and 2 per mill, respectively. The possible application to the study of the isotopic anomaly transfer from O_3 to CO_2 is also discussed.

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F-16

Fiber-optic distributed acoustic sensors for gas leakage detection system

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Tunable diode laser absorption spectroscopy is very successful in gas species detection. Optical fibers give an additional advantage for remote sensing. A number of gas sensor techniques based on optical fibers have been tested over recent years (see, for example, [1,2]), including hydrogen optical fiber sensor [3].

Gas is present in the environment owing to leakage from high-pressure distribution pipelines, which are used to transport fluids or gases. Such leakages can occur as result of aging, corrosion, stress and strain, or fatigue. It is necessary to determine the precise location of the leaks along the length of the pipe. We have found experimentally that acoustic emission from a small leak (hole diameter of ~ 1 mm) can be detected by single mode optical fiber stretched along the pipe. The location of leaks can be determined to an accuracy of several meters. For this location sensing application, a novel configuration of a single-loop Sagnac interferometric acoustic sensor has been developed and tested [4]. This configuration is based on asymmetric desensitization of more than a half of the loop to phase modulation. We present a theoretical consideration of the performance of the sensor and an experimental verification test which demonstrates a high sensitivity of the Sagnac interferometer developed. It is closed to that of Michelson- or Mach-Zehnder-type interferometric fiber sensor. We obtained an accuracy of about 2 m in determining the coordinate of the sound action along the fiber, 1 km in the length. We have determined the sensitivity and the frequency response of a fiber coil acting as a local acoustic sensor in a fiber distributed sensor configuration.

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