



ABSTRACTS OF PAPERS

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*Tunable Diode Laser
Spectroscopy*

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TDLS 2009 Conference Schedule

Monday July 13	Tuesday July 14	Wednesday July 15	Thursday July 16	Friday July 17
8:45-9:00 Welcome Address				
9:00-9:45 A. ORR-EWING	9:00-9:45 G. WYSOCKI	9:00-9:45 U. WILLER	9:00-9:45 N. MOAZZEN-AHMADI	9:00-9:45 V. EBERT
9:50-10:10 S. Schilt	9:50-10:10 M.A. Bolshov	9:50-10:10 P. Martin	9:50-10:10 V. Artyushenko	9:50-10:10 J. Hodgkinson
10:15-10:35 D. Hofstetter	10:15-10:35 N. Nakayama	10:15-10:35 A. Lebrun	10:15-10:35 T. Svensson	
10:35-11:00 Coffee Break				
11:00-12:45 POSTERS Session A	11:00-12:45 POSTERS Session B	11:00-12:45 POSTERS Session D	11:00-12:45 POSTERS Session E	
12:45-3:00 Lunchtime		12:45-3:00 Lunchtime IAEA Working Group Lunch Meeting	12:45-3:00 Lunchtime International Advisory Committee Meeting	
4:00-4:20 A. Mullin	4:00-5:45 POSTERS Session C		4:00-5:45 POSTERS Session F	
4:25-4:45 J. Koeth				
4:50-5:10 A. Lytkine				
5:15-5:35 D. Mondelain				
6:30-8:30 Reception				
		7:30 Banquet		

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Part 1 Invited lectures

APPLICATIONS OF CW CAVITY RING-DOWN SPECTROSCOPY TO THE STUDY OF TRACE ATMOSPHERIC CONSTITUENTS

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Cavity ring-down spectroscopy (CRDS) with near-IR and visible diode lasers [1] has been used to develop optical sensors for measurement of trace constituents of the Earth's troposphere, and to study the optical properties of aerosol particles. Results will be presented of atmospheric measurements of NO₂ [2] and small volatile organic compounds (VOCs) [3]. The combination of pre-concentration techniques with cw CRDS allows detection limits for C₂H₂ to approach 10 pptv in ambient air. Gas-chromatographic separation of the analyte of interest from other atmospheric VOCs is not necessary because of the selectivity that is achieved through the choice of adsorbent materials in the pre-concentration trap and the measurement via characteristic ro-vibrational lines in the near IR spectrum. Difference frequency generation (DFG) using diode laser beams combined in a periodically poled lithium niobate (PPLN) waveguide enables generation of sufficient powers in the mid-IR region (at wavelengths around 3 μ m) for use in multipass and cavity enhanced absorption spectroscopy measurements, and recent results from these techniques will be compared [4].

The atmosphere contains a rich variety of aerosol particles produced from many different sources, and these particles contribute significantly to the radiative forcing of the troposphere. An optical feedback CRDS instrument has been developed for rapid measurement of the extinction of light by aerosol particles [5], and tested using polystyrene spheres of known diameter and refractive index. For single particles of diameter ~ 1 μ m, extinction cross sections can be measured from time-dependent cavity losses as particles traverse the laser beam. For smaller particles, statistical analysis of the variance in measured ring-down decay rates is used to extract extinction cross sections [6]. The outcomes, and potential pitfalls, of these measurements will be discussed.

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BROADLY TUNABLE EXTERNAL CAVITY QUANTUM CASCADE LASERS AND APPLICATIONS

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The mid-infrared (mid-IR) spectral region ($\sim 3\text{--}20\ \mu\text{m}$) is of particular importance for high sensitivity concentration measurements of chemical species in vapor phase, because many gases have their strongest ro-vibrational transitions in this spectral range. Application of tunable lasers, which enable measurements on and off resonance with a spectral absorption feature, allows for selective and sensitive spectroscopic measurements and for precise real time quantification of trace gas concentrations often without any sample preparation.

Quantum cascade lasers (QCLs) have proved to be robust tunable semiconductor laser sources for mid-IR spectroscopic applications [1]. Continuous wave, room-temperature QCL devices are now available for applications that require compact, high power ($>100\ \text{mW}$), liquid-nitrogen free, mid-infrared spectroscopic sources [2, 3]. Spectroscopic applications of conventional, narrowly tunable QCLs are primarily limited to target absorption lines of molecules with well resolved rotational-vibrational structure. In this work we focus on development of widely tunable mid-IR QCL sources based on external cavity configuration, which allow for high resolution spectroscopic measurements of multiple molecular species including complex molecules with wide absorption spectra. Several examples of broadly tunable EC-QCL sources exhibiting tunability of up to 15% of the center wavelength, $>100\text{mW}$ cw optical output powers, and capability of mode-hop-free tuning with spectral resolution of $<30\text{MHz}$ will be presented.[4]

A number of spectroscopic sensing applications that were enabled by the EC-QCL technology will be reported. Examples will include high resolution spectral measurements of small molecules (e.g. nitric oxide, ammonia) at atmospheric and reduced pressures, as well as detection of broadband absorbers with unresolved rotational structure (such as acetone, Freon, and ethanol) [5, 6]. These examples will also demonstrate capabilities of the EC-QCL technology used in combination with different spectroscopic measurement methods such as direct laser absorption spectroscopy, quartz enhanced photoacoustic spectroscopy (QEPAS), laser heterodyne radiometry, and Faraday rotation spectroscopy.

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THE USE OF QUANTUM CASCADE LASERS FOR THE DETECTION OF EXPLOSIVES: PROGRESS AND CHALLENGES

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Detection of explosives is an emerging task for maintaining civil security. Optical methods and especially TDLs are discussed as means for providing fast and reliable data. Selective and sensitive detection is possible in the mid-infrared spectral region, however, until recently, small and easily to operate laser sources were not readily available for applications outside the lab. The situation changes with the maturation of Quantum Cascade Lasers (QCL). We present detection methods based on photo-fragmentation and subsequent mid-infrared detection of the fragments for the detection of nitrogen based explosives. For this type of explosives the very low vapor pressure makes the use of direct spectroscopic techniques extremely difficult since the equilibrium concentrations are in the ppb to ppt range [1]. Peroxide based explosives like triacetone triperoxide (TATP) possess a much higher vapor pressure, making direct absorption spectroscopy possible [2,3]. In figure 1 a comparison of a FTIR measurement and the detection with a widely tunable external cavity QCL are shown. While the FTIR spectrum is based on averaging of the data over hours, the QCL measurement takes several seconds only.

The progress and challenges of the application of QCLs, also with respect to interferences with other molecules present, will be discussed.

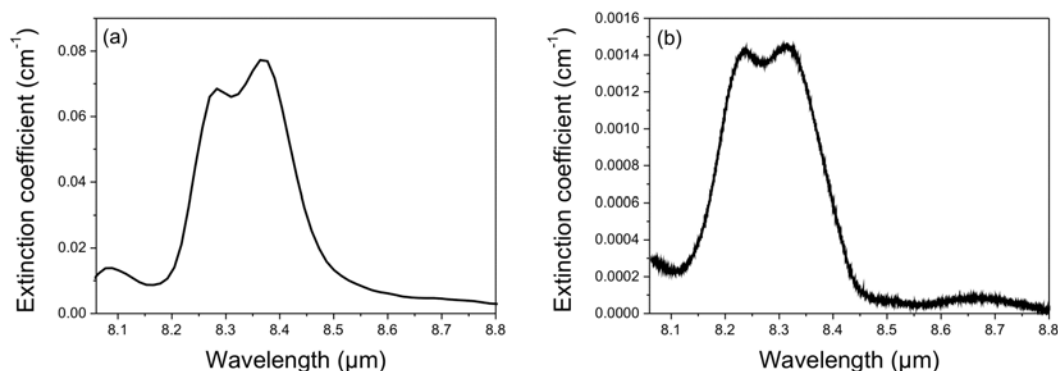


Fig.1 TATP spectra at ambient pressure, (a) FTIR measurement, (b) measurement with EC-QCL. Due to different samples the concentration was different for both measurements.

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L4

Laser spectroscopy of clusters of linear triatomic molecules using a rapid-scan pulsed supersonic jet expansion source

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During the past two years, our group has been systematically investigating the infrared spectra of weakly bound dimers and larger clusters formed from the closely related molecules CO_2 , N_2O , OCS , and CS_2 . The aim of the research is to probe the intermolecular forces in these systems by providing clear spectroscopic data against which theory can be benchmarked. As well, results on trimers, tetramers, and larger clusters may give insight into nucleation and condensation dynamics and into orientational disorder effects in molecular crystals. Each size of a cluster may have multiple isomers and may also have multiple vibrational bands corresponding to a given monomer vibration.

Our spectrometer is a pulsed supersonic jet apparatus with a tunable diode laser probe. The laser is used in a rapid-scan mode with continuous background subtraction. Multi-passing of the laser beam is accomplished using a toroidal mirror system (nominally 182 passes). The spectra are averaged typically for 500 to 1000 jet pulses. Our experimental technique does not give precise cluster size resolution. So the assignment and analysis of successive dimer, trimer, etc., bands is a synergistic process in that each newly assigned band helps “peel away” the total observed spectrum and to reveal further bands which may be partly hidden underneath. In this talk, I will describe the spectrometer and show some examples of spectra belonging to dimers, trimers, tetramers, and higher clusters of the triatomic molecules mentioned above.

ABSOLUTE OPTICAL IN SITU HYGROMETERS USING NEAR INFRARED DIODE LASERS : APPLICATION TO COMBUSTION AND ENVIRONMENTAL APPLICATIONS

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A highly accurate detection of gas phase water is of very high importance for a vast range of industrial applications ranging from full scale combustion processes, over engines and fire suppression and even to spray drying for the food industry. But also, environmental applications (with water being the most important greenhouse gas) have a severe need for precise, accurate and fast hygrometers to investigate the atmospheric water vapor budget in the troposphere and especially in the dry tropopause/stratosphere region. Particular interest exists to monitor the associated water fluxes between the most important compartments like pedosphere (soil) or the phytosphere (plants) both being very important for improved future climate models to estimate global warming development.

Sampling- and calibration-free laser-based techniques are here of highest interest to enable purely optical, non-contact, in situ hygrometers which avoid the significant problems associated with extractive humidity sensors and their calibration.

Especially Diode lasers, particular in the near infrared range, have a great potential for compact, light weight, non-contact hygrometers that are suitable for demanding applications in industry and environmental field measurements.

The paper will review our efforts to develop various application specific laser hygrometers ranging from applications in full-scale power plants [1,2] to balloon borne CH₄/H₂O sensors for the stratosphere [3] and then move over to recent results like the development of a VCSEL based in situ hygrometer at 1742 nm, its application to monitor gasification and biomass combustion processes, as well as the “water based” optical temperature measurement in diffusion flames. The wide tunability of the VCSEL Spectrometer also proved useful in investigating pressure broadening effects at pressure of up to 15 bar. In addition the paper will present recent results in environmental laser hygrometer applications like the absolute detection of interstitial water vapor in clouds, the spatially resolved detection of water vapor gradients around individual plant leafs using a multi-channel distributed fiber sensor network of independent calibration-free sensors or the validation of the calibration-free TDL approach by a comparison with gas chromatograph.

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Part 2 Oral presentations

P1

IMPACT OF WATER VAPOR ON 1.51 μm AMMONIA ABSORPTION FEATURES USED IN TRACE GAS SENSING APPLICATIONS

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Laser spectroscopy has demonstrated its relevance for various applications requiring sensitive and continuous ammonia monitoring at trace level. Different spectroscopic methods have been demonstrated so far (*e.g.* WMS, FMS, CRDS, PAS), which all benefit from recognized properties such as a sensitive and selective measurement. Interferences, *i.e.* a spurious signal at the sensor operating wavelength induced by nearby absorption lines of other species, can be minimized or even suppressed by a proper choice of the operation wavelength, sometimes also combined with reduced pressure operation. However, even in absence of interference, a spectroscopic gas sensor may be affected by the presence of other species as a result of modified line broadening giving rise to *cross-sensitivity* effects. For instance, N_2 -broadening of several NH_3 lines in the 1.5 μm spectral range has been shown to be $\sim 10\%$ higher in average than air-broadening [1, 2], illustrating the importance of a sensor calibration made in proper conditions when using a spectroscopic method that is sensitive to the width of the analyzed absorption line, as for wavelength modulation techniques. The influence of water vapor on NH_3 sensing can also be important in applications where humidity is subject to significant variations, especially for high temperature applications where high H_2O concentrations up to 25-30% may be encountered.

Only few data are available about broadening parameters of NH_3 lines in the near-infrared and no information about H_2O -induced broadening of NH_3 lines is known from the literature, making impossible an accurate quantification of the expected influence of H_2O on a NH_3 sensor. The reported work aims at quantifying the influence of water vapor on several NH_3 absorption features in the 1512-1516 nm range that are exploitable for gas sensing. For this purpose, absorption spectra of different NH_3 - N_2 - H_2O mixtures were measured using a 4 m multipass cell in conjunction with a fiber-coupled DFB laser. Multi-peak data processing was performed to extract the lines parameters from the recorded spectra. Measurements were performed in an oven at elevated temperature (70°C) in order to enable high H_2O partial pressures to be achieved. Results will be presented for three different NH_3 absorption features centered at 1512.2 nm, 1515.1 nm and 1516 nm. In the three considered wavelength ranges, an influence of water vapour was observed on the NH_3 absorption feature, but it was surprisingly not of great importance. For instance, a very small difference in the foreign-broadening factors due to H_2O and N_2 was observed for the 1512.2 nm NH_3 absorption feature ($g_{\text{H}_2\text{O}} = 0.15 \text{ cm}^{-1}/\text{atm}$ compared to $g_{\text{N}_2} = 0.12 \text{ cm}^{-1}/\text{atm}$). Therefore, the NH_3 absorption feature does not broaden significantly in presence of water vapour and the H_2O - NH_3 cross-sensitivity is shown to be of minor importance, which is beneficial for NH_3 sensing in largely varying H_2O conditions.

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QUANTUM CASCADE DETECTORS FOR APPLICATIONS IN THE MID-INFRARED WAVELENGTH RANGE

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We present design, fabrication, and characterization of a novel semiconductor-based mid-infrared sensor, the quantum cascade detector. Such a device typically consists of 10-20 active region periods. As Fig. 1 (left) shows, each period is made of a doped quantum well A and an undoped electron extraction region (B → H). Under absorption of infrared radiation with an energy corresponding to the separation between the ground state and the first excited state ($A_1 \rightarrow A_2$), electrons are being excited into the upper quantized state from where they tunnel into the extraction region. The latter transports them to the ground state of the following period (A_1'). In a real structure, this transport takes place in the vertical direction and does not require any external voltage bias. With these spectrally narrow photovoltaic detectors, we have achieved responsivities of 10 mA/W and detectivities of 10^{11} jones at 110K (see Fig. 1 (right)). These values are comparable to commercial mid-infrared state-of-the-art sensors such as QWIPs or mercury-cadmium-telluride detectors [1], [2].

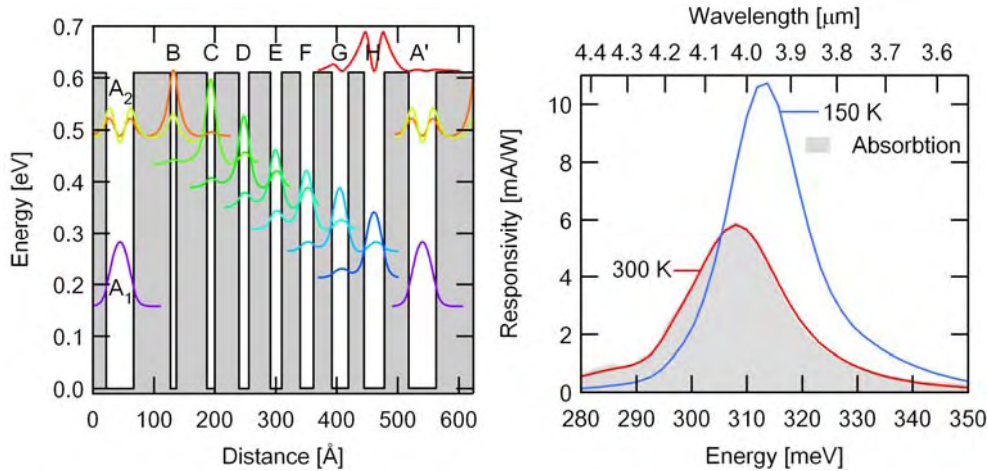


Fig.1 (left) Schematic band structure of a 3.96 μm quantum cascade detector. (right) Typical responsivity/absorption curves at temperatures of 150 K and 300 K.

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Transient TDL Studies of the Chemical Dynamics of Energized Molecules

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Time-resolved tunable diode laser spectroscopy (TDLS) is used to investigate new problems in the chemical dynamics of energized molecules. Molecules with large amounts of energy play key roles in combustion, plasmas and other high temperature environments. In these studies, molecules are prepared with large well-defined amounts of internal energy using pulsed laser excitation. The outcome of reactive, inelastic and elastic collisions is probed with transient TDLS at short times relative to the collision time. We report recent advances in determining full state-resolved distributions for collisional energy transfer and in characterizing the energy gain profiles of scattered molecules. We have developed a novel method for simultaneously measuring nascent appearance and depletion populations, such as shown in Figure 1, from which low-J state populations are determined. These studies account for all scattered molecules, and thereby yield a measure of the collision rate and the branching ratio for elastic and inelastic collisions.[1] In other experiments, hydrogen abstraction reactions of vibrationally excited molecules ($E=38000\text{ cm}^{-1}$) have been studied with TDLS. We find that vibrational energy enhances reactivity and that single vibrational quanta are used in reactions even though reactants contain a large excess of vibrational energy. On the other hand, vibrational energy inhibits abstraction reactions from methyl groups as the hindered rotors become free rotors upon excitation. A third area of research involves an optical centrifuge, a new technology that uses intense laser fields to generate molecules in ultra-high rotational states. We have used TDLS to measure the excitation and collisional dynamics of molecules prepared in an optical centrifuge.

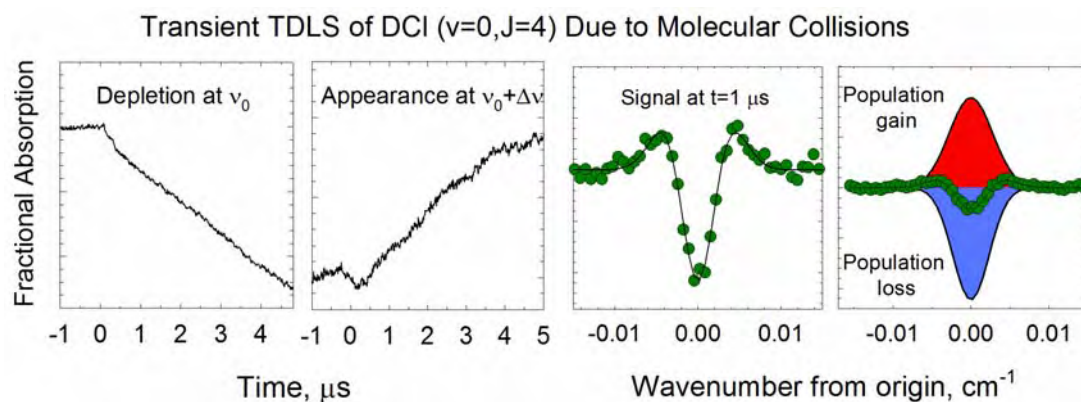


Fig.1 Transient TDLS signals for DCI ($v=0, J=4$) molecules due to collisions with highly vibrationally excited 2-picoline ($\text{C}_5\text{H}_5\text{NCH}_3$, $E=38,300\text{ cm}^{-1}$)

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MID INFRARED INTERBAND CASCADE LASERS FOR SENSING APPLICATIONS

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A growing demand for mid infrared (IR) light sources (wavelength $\approx 2.5\mu\text{m} - 20\mu\text{m}$) is developing in several fields of application. Compact and reliable laser sources in this wavelength regime exhibit excellent possibilities of use for example in the military (e.g. detection of explosives [1]) and commercial (e.g. industrial process control [2]) sector, partially owing to naturally occurring atmospheric transparency windows.

The wavelength range from $3\mu\text{m} - 4\mu\text{m}$ is particularly interesting for several sensing applications, such as the detection of hydrocarbons. Existing types of semiconductor laser sources have closed in on this wavelength area ([3], [4]). However, decreasing hole confinement and increasing Auger recombination in GaSb-based type I interband diodes limit their usability towards higher wavelengths of $\approx 4\mu\text{m}$. Intersubband quantum cascade lasers (QCL) approach the mentioned wavelength range from above but suffer from fast phonon scattering losses. From both issues of the above described laser types emerges the need of a more efficient laser source in the $3\mu\text{m} - 4\mu\text{m}$ regime.

The discussed issues can be circumvented by using interband cascade lasers (ICL) [5][6]. These technologically demanding laser sources utilize optical transitions between an electron state in the conduction band and a hole state in the valence band in a cascade of Sb-based type-II QW structures. A broken-gap band edge alignment enables the tailoring of the emission wavelength by altering the cascade structures.

The ICLs presented here are a collaborative work between the university of Würzburg and nanoplus company. The lasers were grown by solid source molecular beam epitaxy on GaSb substrates and comprise 6 or more active cascades. Processing was conducted using a reactive ion etching system. Laser ridges with widths varying from $8\mu\text{m}$ to $100\mu\text{m}$ were etched deeply until below the active cascades. The structures were passivated by a several hundred nanometers thick passivation layer before evaporating the top and bottom contact. Different active zones were designed, yielding emission wavelengths covering the $3\mu\text{m} - 4\mu\text{m}$ range.

For sensitive scanning of single gas absorption lines monomode lasers are required. The feasible concept of ICL distributed feedback (DFB) lasers [7] is thus the goal aimed at to use the lasers in highly sensitive photonic sensor systems.

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Applied Physics Letters **92**, 071110 (2008)

A LOW-TEMPERATURE APPROACH TO EXTEND THE TUNING RANGE OF LONG-WAVELENGTH VCSELS

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We propose a simple technique to improve tuning capabilities of long-wavelength vertical-cavity surface-emitting lasers (VCSELs). It involves reducing the laser substrate temperature and increasing the amplitude of the laser modulation current. In addition to the shift of laser diode frequency with substrate temperature, we utilize the single-mode advantage of VCSELs and their ability to tolerate significantly higher currents at lower temperatures. In our previous work [1] we have studied 1512-nm and 1577-nm VCSELs in the 150-K temperature range using liquid nitrogen as a coolant.

In the present work we achieved a 25.7-cm^{-1} ($\sim 7.3\text{ nm}$) current-induced tuning range of a VCSEL at a substrate temperature of -55°C controlled with a Peltier element. Fig. 1 illustrates the improved tuning characteristics of the laser. Ethylene oxide and benzene spectra acquired with the laser in the 1693-nm and 1684-nm regions will be presented.

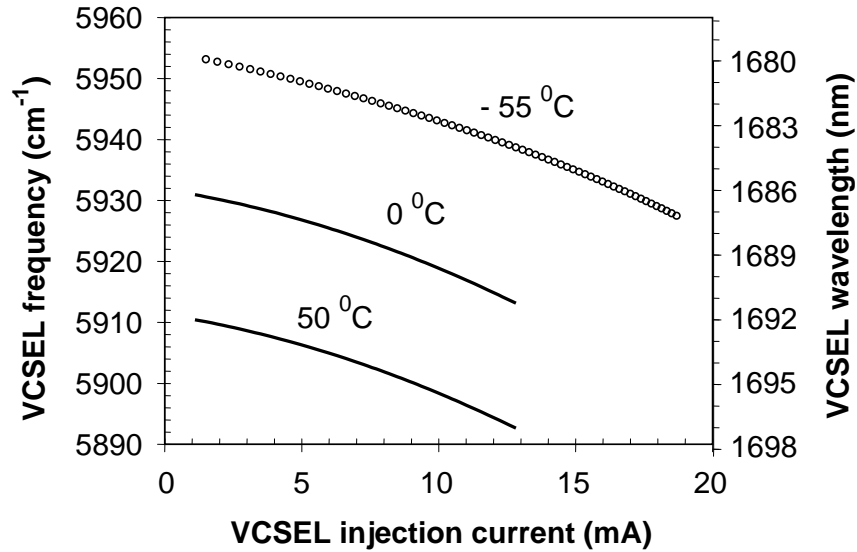


Fig. 1. Current-induced continuous tuning ranges of a 1693-nm VCSEL at various laser substrate temperatures. The combined temperature- and current-induced single-mode tuning range exceeds 60 cm^{-1} ($\sim 17\text{ nm}$). A 25.7-cm^{-1} ($\sim 7.3\text{ nm}$) spectral interval can be scanned at -55°C at a 1-kHz rate using a 18 mA (peak-to-peak) ramp modulation.

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IMPROVEMENT OF ISOTOPIC COMPOSITION MEASUREMENTS OF ATMOSPHERIC CO₂ USING CORRELATIONS BETWEEN THE REFERENCE AND THE MEASUREMENT CELL

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We have recently developed a tunable diode laser spectrometer, named SIMCO [1] (Spectrometer for Isotopic Measurements of CO₂) to measure the ¹³CO₂ and ¹²CO₂ concentrations in atmospheric air. This instrument is based on direct absorption spectroscopy and uses one absorption line for each isotope near 2291.6 cm⁻¹ to determine the concentrations by fitting the line profiles. To be really useful for atmospheric purposes, the isotopic composition $\delta^{13}\text{CO}_2$ has to be measured with a high level accuracy (better than 0.2‰) at a frequency faster than one measurement per minute. To achieve such a goal we need to alternate quickly (20 s - 20 s) the measured gas (here from a tank) with a calibration gas. The existing correlations between measurements of this calibration gas (passing through the sample cell; here a multipass Herriott cell) and the reference cell (static in the present case) are used to correct retrieved concentrations from short and long term fluctuations of the instrument. A correction method using the correlation between sample and reference seems to provide very precise results as compared to the simpler correction initially implemented. Thanks to this new method, we have achieved $\delta^{13}\text{CO}_2$ measurements with an accuracy of 0.3‰ (see Fig 1) for an integration period of 40 s, a value quite comparable to the atmospheric requirements.

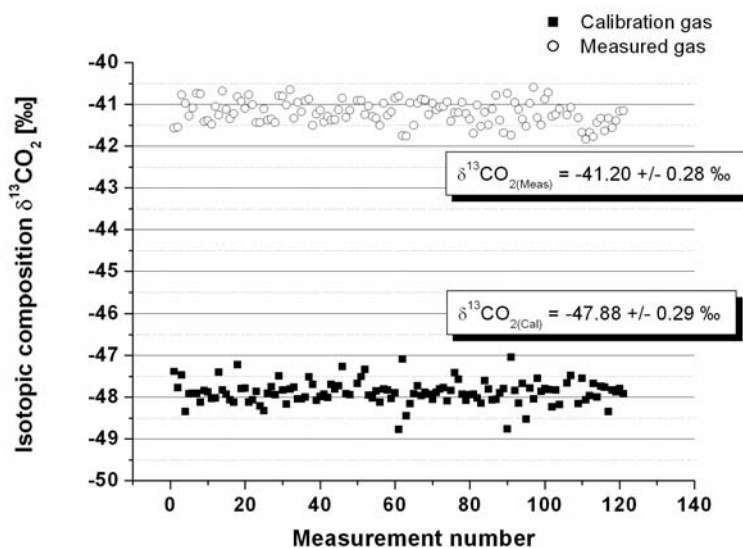


Fig 1. Measured isotopic composition from a tank (air + 422.91 ppmv of CO₂; $\delta^{13}\text{CO}_2 = -40.90\text{‰}$) using a calibration gas (air + 366.61 ppmv of CO₂; $\delta^{13}\text{CO}_2 = -47.92\text{‰}$) and the correlation method
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TDL MEASUREMENTS OF TEMPERATURE AND WATER VAPOR CONCENTRATION IN A HOT ZONE

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TDL absorption technique and appropriate instrumentation for measurements of temperature and water vapor concentration in a hot zone, characterized by rather strong fluctuations, vibrations and different optical and electrical noises, are developed (see C12). The experimental spectra were registered using a single DFB laser which covered about 1 cm^{-1} in one scan. The following absorption lines of H_2O were used: 7189.344 cm^{-1} ($E'' = 142 \text{ cm}^{-1}$), 7189.541 cm^{-1} ($E'' = 1255 \text{ cm}^{-1}$), 7189.715 cm^{-1} ($E'' = 2005 \text{ cm}^{-1}$). Relatively high intensities of the selected lines enabled detection of the direct absorption.

The technique was applied for detection of temperature and H_2O concentration in the post-combustion zone of the supersonic air-fuel flows (see D12). Mach number of the flow in duct was $M = 2$, static pressure in flow $P_{\text{st}} = 150\text{--}300 \text{ Torr}$, static temperature T_{st} up to 1500 K . The optical path of the testing DL beam inside the camera was 7 cm . The combustion process in the supersonic flow was ignited and sustained by the pulsed electric discharge. Air was used as the oxidant, hydrogen or ethylene were used as the fuel. The duration of a single run including gas flow injection, plasma ignition, combustion and cooling was about 0.5 s . The duration of plasma-assisted combustion was about 80 ms . The duration of each TDL scan was about $830 \text{ }\mu\text{s}$, thus 600 laser frequency scans were registered during the whole process of 0.5 ms .

At the first step of data processing 2D image of the transient absorption spectra was constructed (see E10). The hot zone parameters were obtained as the result of fitting of the experimental spectra by the simulated one constructed using the HITRAN and SPECTRA databases. Parameters of the post-combustion zone were measured for different conditions of air and hydrogen or ethylene fuel mixing and different geometry of electric discharge. The high signal-to-noise ratio enabled to obtain the temporal behavior of temperature with the resolution of $\sim 1 \text{ ms}$. Precision of the temperature evaluation was estimated to $\sim 40 \text{ K}$.

NOVEL OPTICAL FIBER PROBE FOR CAVITY RING DOWN SPECTROSCOPY

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This paper presents a novel optical fiber probe for cavity ring down spectroscopy (CRDS). Cavity ring down spectroscopy is ordinarily used to detect trace components in gas or liquid with high sensitivity [1]. This CRDS is also applied to some sensing systems employing a fiber loop with a micro gap or hole [2, 3]. The gap or hole is filled with gas or liquid to be examined, and then an optical pulse repeatedly passed it in the loop. The amount of trace component is estimated by the decay time constant of the optical pulse train which is monitored at the outside of the loop. An optical cavity composed of twin fiber Bragg gratings is sometimes used to confine optical pulses between the gratings instead of the fiber loop. The newly developed optical fiber probe in this study has a very compact sensing head when compared with those systems.

An optical cavity composed of twin Fiber Bragg Gratings (FBGs) was formed in an optical fiber, and a micro-hole, which is a 15- μ m-diameter through-hole, was set within the optical cavity to store a liquid sample. The reflectivity of the FBG was designed to be 99.99% to confine an optical pulse within the optical cavity. The center wavelength of the grating was set at 1552 nm, which corresponds to the absorption wavelength range of sugar solution. An optical circulator was used at the opposite end of the sensing head to separate an optical output pulse from input pulse. This structure enables an optical fiber probe to insert into samples and miniaturizes the CRDS system.

By using the developed fiber probe, damping pulse trains corresponding to the cavity mode were monitored when the probe was inserted into water and sugar solution. Here, a DFB laser diode lasing at 1552 nm was used as an optical source. The lasing wavelength of the laser diode was changed and stabilized by using a thermoelectric cooler. The basic operation of the novel probe has been confirmed from these results.

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APPLICATION OF MID-INFRARED AND NEAR-INFRARED DIODE LASER SPECTROSCOPY TO THERMAL AND PLASMA-ENHANCED CVD

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Atmospheric pressure chemical vapour deposition (CVD), both thermal and plasma-enhanced (PE-CVD), are used for growing thin films such as tin oxide which is a transparent conducting oxide used in low-emissivity glazing and solar cells. Non-thermal plasmas combined with CVD enable coating onto heat sensitive substrates. This work describes the application of near-infrared and mid-infrared diode laser absorption spectroscopy to the study of such industrially important processes.

In one example, a near-infrared diode laser operating at around 1742 nm is used to spatially monitor HCl produced in the thermal CVD reaction of dimethyl tin dichloride and oxygen. 3D mapping of the active region is feasible and this has already proven useful for both new coating head designs and for correlating with film properties [1].

In a second study, silica films used as a barrier layer have been produced by atmospheric pressure PE-CVD from TEOS and DDS. A mid-infrared lead-salt diode laser [2] has been used in an in situ arrangement to monitor the CO produced in the precursor oxidation. Additionally, a parametric study involving in line FTIR and in situ near-infrared diode laser measurements, as well as optical emission spectroscopy has been used to produce a response surface model that relates gas concentrations and electrical parameters with film growth and film hardness [3]. Recent work has involved a cw room temperature quantum cascade laser for the CO measurements [4].

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Status of the Tunable Diode Laser Spectroscopy Contribution to International Safeguards Verifications

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The IAEA has the responsibility to carry out the verification of the correctness of the declarations of the state nuclear material involved in peaceful applications, and to substantiate the completeness of the declaration thus ensuring the absence of undeclared nuclear material and activities. Therefore the IAEA has a need for accurately assaying both the nature and quantity of the declared nuclear material in bulk quantities but also to detect minutes traces of nuclear material or related indicators in case of undeclared activities. A working group of international experts advises the IAEA on TDLS for safeguards applications and formulate recommendations on further developments. Within this framework, the IAEA in partnership with the General Physics Institute in Russia and Canberra Albuquerque, Inc. in the USA developed a portable instrument able to detect hydrofluoric acid (HF) in air at ppb levels which is indicative of operations using UF₆, e.g. enrichment activities. This instrument is now in the final phase of validation before use as a detection tool for routine inspections. The second TDLS application envisaged for safeguards is the accurate determination of uranium enrichment as an alternative to destructive analysis (DA). In 2007, an experimental TDLS measurement system dedicated to the determination of uranium enrichment in UF₆ gas was proven to be capable of achieving levels of accuracy comparable to DA. General Physics and Kurchatov Institutes in Moscow have identified avenues for improvement of the existing experimental system. Laser Component GmbH supported by the German Support Program to the IAEA safeguards is developing improved, high precision lead salt lasers with extended tuning ranges and a new dewar vessel to achieve better temperature control. Kurchatov institute worked in 2008 to improve the UF₆ gas handling technology and in particular to minimize the spurious memory effects detected during the 2007 measurement campaigns. As soon as available, General Physics Institute will integrate the improved components into a compact optical path immune to perturbations such as presence of humidity or temperature fluctuations. Once the technology has matured sufficiently, the manufacturing will be undertaken to industrial standards with the aim of installing these systems at enrichment plants under IAEA safeguards as soon as possible. The IAEA has also started to investigate Quantum Cascade Lasers (QCL) as an alternative to the lead salt lasers. GPI will test a QCL from Laser Components in 2009.

The paper describes the progress of TDLS applications for safeguards applications as recommended by the IAEA TDLS working group and explores future development needs such as the use of TDLS for detection of tritium traces and use of high UF₆ absorption cross section at 16 µm. These applications are still investigated but completion of the ongoing development project remains the IAEA priority.

FIBER OPTICS FOR FLEXIBLE LASER SPECTROSCOPY

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The latest development in IR-fiber optics expands spectral range of process-spectroscopy from 0.2-2.4 μm to Mid IR-range up to 18 μm (20.000 to 550 cm^{-1}). Up to now fibre systems used for process-control applications by absorption/transmission, reflection, fluorescence and Raman-spectroscopy were limited to silica fiber transmission 0.2-2.4 μm . Nowadays IR-glass fibres, Polycrystalline PIR-fibres and Hollow Waveguides can also cover Mid IR-range up to 18 μm , including “finger-print” Mid IR-range where specific absorption bands of molecular vibrations are concentrated. These fundamental vibration bands in Mid IR are 100-1000 times more intensive and more narrow compared to their 2nd & 3rd overtones at shorter wavelengths <2 μm . But in addition to this factor complete fibre spectroscopy system should be optimized taking into account other parameters of its components: intensity of light source, sensitivity of detector and efficiency of their coupling with fibres and optical cell.

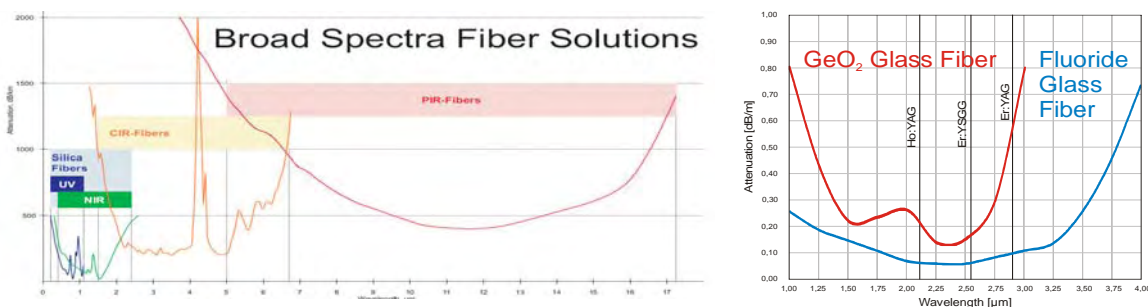


Fig.1 Attenuation spectra for: a) Silica, CIR- & PIR-fibres; b) GeO & ZBLA-fibers

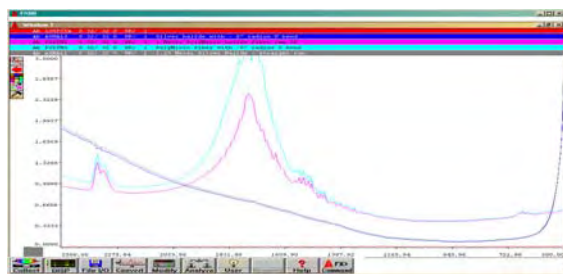


Fig.3 Attenuation for PIR-fiber (blue) & Hollow Waveguide range;

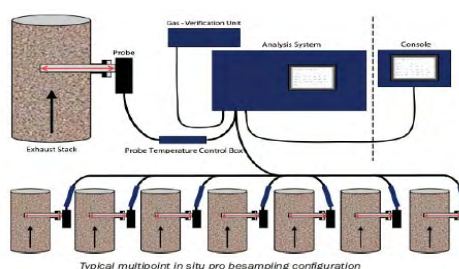


Fig.4 QCL-system with PIR-fiber probes for remote exhaust control in 4.48-7.43 μm

SPETROSCOPY OF GASES CONFINED IN NANOSTRUCTURES

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Studies of confined matter is of great importance in many areas of science and technology. A prominent example is the vast and rapidly advancing field of porous materials, where confinement and large surface areas gives rise to a multitude of interesting and useful phenomena. Important topics include for example ion exchange, catalysis, molecular sieving and separation, gas storage, chemical sensing, melting and freezing under confinement, and luminescence of porous silicon [1-3]. The interaction of gases of porous materials is of major importance in many of these areas.

Our department has previously shown that TDLAS can be used to study gases inside various light scattering solid materials [4]. Recent advances in our efforts include significant improvements in sensitivity [5] and characterization of porous pharmaceutical materials [6]. While our previous work has dealt with gases confined in larger cavities, we now show that high-resolution diode laser absorption spectroscopy also can be used to study gases confined in nano-sized cavities in porous materials. We use the near-infrared A band of molecular oxygen to interact with gas molecules located in subwavelength pores of sintered alumina (Al_2O_3). We discuss light propagation issues, and address the severe problem of interference fringes originating from multiple scattering. We report on strong lineshape broadening due to tight three-dimensional gas confinement, and thus enter a new domain of laser spectroscopy. Our approach provides new opportunities for studies of confined gases and vapours, as well as molecule-surface interactions in porous materials (*e.g.* surface chemistry). In addition, our findings open new ways for characterization of porous materials. Finally, this domain of laser spectroscopy constitutes a new challenge for the theory of lineshapes. The origin of the observed lineshape broadening is under investigation, and may be related to for example van der Waal interactions [7] and wall collisions [8].

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GAS ABSORPTION CELLS FOR TDLS EMPLOYING OPTICAL DIFFUSERS

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Many TDLS systems are limited by interference fringes formed by unintentional Fabry-Perot etalons between the source and detector [1], often involving reflections from gas cell windows [2]. The fringe spacing can be in the same wavelength range as gas absorption linewidths, which can distort or obscure the absorption line. Design techniques to reduce etalon formation include; the use of optical isolators, use of reflective rather than refractive optics, angling and antireflection (AR) coating of surfaces [3]. Techniques for reducing the amplitude of the fringe signal include mechanical oscillation of components [1], use of an additional laser diode modulation [4], use of alternative waveforms [5] and postdetection filtering [6].

The alignment of the optical components such as angled windows is often critical. Tight tolerances on component alignment can cause manufacturing difficulties and can be difficult to maintain in field instruments. In this study we have explored the use of optical diffusers in gas cells as a means of (a) reducing optical interference fringes, and (b) making gas cells that are insensitive to misalignment, giving simpler manufacturing processes and greater field stability.

We have compared different cell geometries side by side, calculating the resulting levels of objective and subjective speckle noise. The best design has been built experimentally and compared to a conventional transmission cell that uses angled, wedged and AR coated windows, both cells having an optical pathlength of 10cm. Testing was performed with methane in air, using 2f wavelength modulation spectroscopy at 1651nm, with a 1s response time. The results show that although the short-term limit of detection (1σ) achieved using the new cell (11 ppm) was slightly inferior to the conventional design (3 ppm), its longer term stability was superior. We also present two techniques with potential to improve detection limits still further, by rotating or vibrating the diffuser in the gas cell, which has the effect of averaging over multiple speckles, reducing speckle – related uncertainty.

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A1

Remote (more than 100 m) explosives detection using TDLS

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Remote explosives detection is extremely important goal. A lot of researchers are working in this area. However, the problem is not solved [1, 2].

We've started investigations in this direction more than 20 years ago (history of this work will be presented in present poster). At the beginning we've tried to detect explosive vapor. 10 years ago it was realized that explosives molecules from explosive in wrapping can not be detected because of very low molecules flow $\sim 10^5$ mol/sec. At the same time alternative method of explosives detection was discovered. Explosives are unstable materials with lifetime of the order of 10 years (decay rate $\sim 10^{14}$ mol/g/sec). Quantum chemical calculations were performed (for TNT NO₂ or NO dissociation with activation energy 1 eV). Decay products of several explosive samples were investigated and decay rate was measured being significantly smaller due to secondary chemistry reactions of decay products with explosive material.

5 years ago it was found that for AN based explosives ammonia is decay product and non-contact explosives detection was demonstrated [3]. 2 years ago several explosives samples were investigated using GC-MS demonstrating the same GC peak. It was identified as HNCO – isocyanic acid. HNCO interaction with atmosphere water leads to ammonia. Hence, NH₃ is signature of nitrogen containing explosives.

TDLS based system for ammonia detection was developed (1 ppb for 1 sec averaging time). Backpack prototypes were manufactured both in US (Aquila, Albuquerque) and Russia (see B3). Field tests were performed both in US and Russia.

Several test scenarios were investigated. Samples of all explosives available were detected. 10 kg explosive sample was detected inside moving vehicle. 2 kg explosive sample was found inside building using gradient of measured explosives signature concentration. 300 kg explosive sample in wrapping was detected at 120 m distance down wind.

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A2

Diode laser spectroscopy of water isotopomers in near IR

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Water vapour spectra in 2 m cell were recorded in near IR spectral range (6900- 7400 cm^{-1}) using three diode lasers. Frequency tuning of each DL was around 30 cm^{-1} . Three water samples were investigated: H₂O - normal water, HDO - heavy water/normal water = 1/1, HTO - heavy water from reactor/normal water = 1/1. Fragment of spectra recorded is presented on Fig.1.

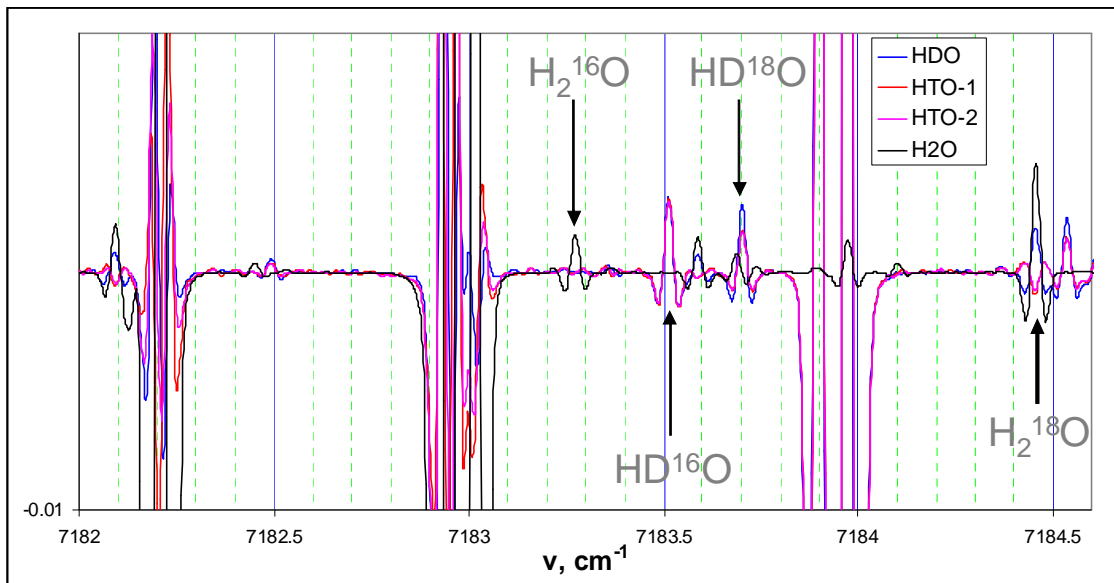


Fig.1 Spectra fragment of water samples under investigation

Spectra recorded by one DL (7166- 7192 cm^{-1}) were analyzed. Refer to HITRAN there are 192 lines of H₂¹⁶O, H₂¹⁸O, H₂¹⁷O, and HD¹⁶O. 103 of them having highest intensity were measured and are in agreement with HITRAN within its accuracy. In addition 68 new lines were measured. Samples under investigation had different isotope ratios. Sample HDO was enriched by ¹⁸O, while HTO was depleted. The fact simplified new lines identification as belonging to HD¹⁶O, HD¹⁷O, and HD¹⁸O.

A3

TDLs based complexes development for impurities detection in high-purity hydrides

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Pure hydrides (AsH_3 , PH_3 , NH_3 , GeH_4 , SiH_4) are used for semiconductors production. Quality of semiconductors manufactured depends on impurities presence. There are many possible impurities in hydrides. H_2O , NH_3 , H_2S and CO_2 are considered as most important. Family of TDLs complexes was developed to measure impurities concentration in real time. TDLs complexes developed had similar module structure. They contain DL with reference channel, electronic module, and PD modules. DL choice was determined by impurity to be detected. Selection of analytical line was determined by both impurity and main molecule spectra. These spectra were recorded by selected DL in spectral range of its tuning ($\sim 30 \text{ cm}^{-1}$). For AsH_3 and PH_3 in spectral range under consideration these spectra were recorded for the first time. Several TDLs complexes modifications were developed to follow requirements of purification process control (Fig.1). Fig 2 presents view of one of TDLs complexes developed.

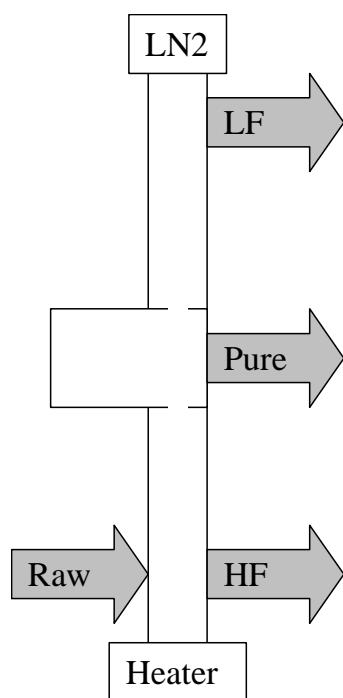


Fig.1 Block scheme of rectification column.

There are 4 gas flows of interest: raw material in, pure material out, and gas lines for light (LF) and heavy (HF) fractions



Fig.2 View of TDLs complex to measure NH_3 concentration in “raw”, “pure”, and “LF” channels.

TDLs complexes developed were installed at “Salut” (NN).

They are measuring automatically concentration of different impurities for different purification processes in real time (see C3).

Injection Seeded Single Mode Intra-Cavity Spectroscopy of the Oxygen A-Band

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The emission of single mode lasers is very sensitive to additional losses inside the cavity. This behaviour allows the quantitative measurement of absorption with high sensitivities by placing the absorber inside the cavity of the laser. Compared to multimode intra-cavity spectroscopy (ICAS), which so far provides a higher sensitivity, single mode ICAS provides a high spectral resolution with comparatively low technical effort. This technical advantage advises single mode ICAS systems for compact, mobile measurement systems.

The sensitivity of such a system strongly depends on the absorption strength, the loss rate of the laser, the total rate of spontaneous emission in all modes and the pump rate. The maximum reachable effective absorption path length is located at pump rates very close to threshold. At higher pump rates the additional absorption loss can be compensated by additional gain and the reduction of the output power is insignificant. To avoid mode hops caused by the additional loss a strong side mode suppression and a stable laser oscillation is necessary even at pump rates very close to threshold. Because any frequency selective element increases the losses of the cavity, it therefore also lowers the sensitivity.

Here a new technique is presented which extends the high resolution single mode ICAS with good tuning properties, which is achieved by injection-locking the test cavity to an external single mode laser. As a first demonstration we present single mode intra-cavity measurements of the oxygen a-band with this new technique, which ensures a stable single mode oscillation on the frequency of the injected signal without the need of any frequency selective element. In addition the spontaneous emission rate is strongly reduced and it is possible to control the gain of the laser over the injected optical power and the frequency detuning of the injected signal.

Detailed characterizations and model calculations on this technique are presented as well as a proposal for a two mode approach, which is based on the results and model calculations of the single mode technique.

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Spatially resolved, absolute H₂O vapor detection around acoustically levitated H₂O droplets

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In recent years, measurements of gas concentrations via TDLAS became a very attractive method of choice due to its affordable, reliable, precise and calibration-free character. The small size and fibre coupling option of DFB diode lasers in the 1.4μm region, as well as the optimized detector size and noise characteristics make TDLAS a valuable tool for the spatially resolved determination of heterogeneous gas fields on small scales.

One of this small scale processes is the evaporation dynamics of H₂O droplets. Due to its importance in atmospheric research as well as for the understanding of industrial drying processes, there is a high demand for investigations of spatial H₂O vapour structures around the droplet.

To determine the droplet's spatial evaporation structures, we developed a spatially scanning TDLAS spectrometer and applied it on acoustically levitated droplets to enable a completely

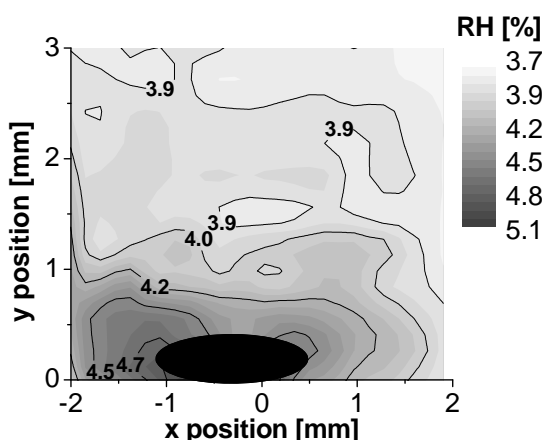


Figure 1: 2D H₂O concentration field around droplet

contact free measurement of the vapor field in the droplet's vicinity.

The laser spectrometer had an emission wavelength 1369.97nm and a beam diameter of 0.5mm. It was mounted on a horizontally and vertically moveable traversing stage system consisting of two DC motors.

By detecting the broadband losses caused by liquid water, we resolved the shape and the volume of the levitated droplet. By analyzing the molecular narrowband losses, we determined the 2D H₂O concentration field (figure 1) within an area of 3x4cm and a mechanical step size of 0.2mm.

With a short single absorption path length of only 4cm we achieved a concentration

resolution of 67ppm at a temporal resolution of 0.5Hz. This enabled us to extract vertical H₂O concentration profiles which could be verified by a theoretical, diffusion based evaporation model [1].

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MINIATURIZED RESONANT PHOTOACOUSTIC CELLS FOR TRACE-GAS DETECTION

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The miniaturized spectroscopic hardware is a promising field of application for the photoacoustic (PA) trace-gas detection technique powered by tunable diode lasers. In the report we discuss an approach to miniaturizing the resonant PA cell equipped with a commercial condenser microphone. The approach implies an optimization of design for the internal cell cavity in order to reduce the negative effect of parasite signals (they are, first of all, the background due to absorption of the laser beam in the cell windows and the noise initiated by external acoustic disturbances), which can play a great role for the small-sized PA cells. The optimization is performed with the help of numerical simulation of the acoustic signals generated inside the cell. Actually, such an approach can be applied to the cells with the internal volume down to a few cubic millimeters.

In the report we analyze also our practical experience in the field and present optimized PA cells with the internal volume under 1 cm³ (see Fig. 1). The cells can be used easily in a laser-intracavity scheme of trace-gas detection. To the moment, our tests (including experiments with a DFB laser diode and a quantum cascade laser) testify that the threshold detectable absorption for the cells is $\sim 10^{-8} \text{ cm}^{-1} \text{ W Hz}^{-1/2}$.

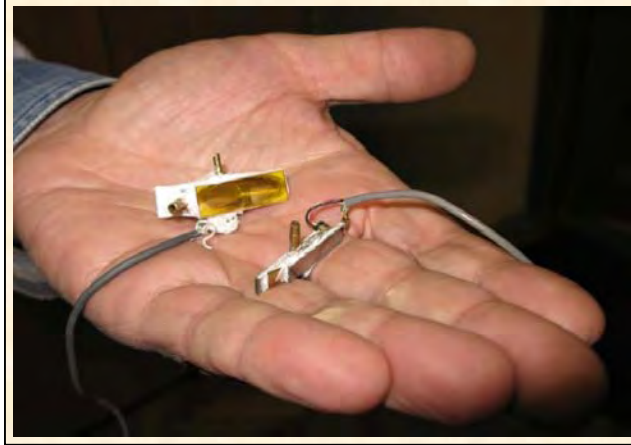


Fig.1. Our recent PA cells with Brewster windows. The left cell (*ZnSe* windows) has the internal volume $V \sim 500 \text{ mm}^3$ and clear aperture $d = 8 \text{ mm}$. The right one (*Ge* windows) is a cell with $V \sim 80 \text{ mm}^3$ and $d = 4 \text{ mm}$.

A7
**MULTI-WAVELENGTH LASER ABSORPTION TOMOGRAPHY
SYSTEM FOR MONITORING AND OPTIMISATION OF CHEMICAL
VAPOUR DEPOSITION REACTORS**

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Chemical vapour deposition (CVD) is an important technology used for the production of thin films and coating. Performance of CVD processes are characterised by complex interaction of fluid dynamics and chemical kinetics which are determined by pressure, temperature, species concentrations, flow rates and by the reactor geometry. We describe the development of a new optical multi-wavelength tomographic system for monitoring CVD reactors. The system enables reconstruction of the 2D distribution of gas concentration at the exit of the CVD coating head. The system incorporates two tunable lasers and a scanning mirror mounted on one moveable platform, whilst two photo detectors and second scanning mirror are mounted on another moveable platform. Both the positions of the platforms and the scanning mirrors are controlled by a LabView program, whilst the platforms are always on a circular orbit around the reactor. Transmittances of the space between the platforms can be recorded and then absorption spectra can be extracted at specific positions of the laser and photodetection heads and at various arrangements of laser beam trajectories. UV, visible, near-IR, mid-IR [1] laser based sources can be used to probe gas flow on the reactor output. Different algorithms [2 - 4] optimised for accurate 2D tomographic reconstruction of gas temperature and concentration of O₂, HCl, HF, H₂O, CO, CH₄ and other species (for instance, Ar, N₂⁺, Ti) can be implemented and analysed using the system. We will present results of our experiments in 2D image reconstruction with the system for monitoring and optimisation the CVD process.

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QUANTUM CASCADE DETECTORS FOR APPLICATIONS IN THE MID-INFRARED WAVELENGTH RANGE

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We present design, fabrication, and characterization of a novel semiconductor-based mid-infrared sensor, the quantum cascade detector. Such a device typically consists of 10-20 active region periods. As Fig. 1 (left) shows, each period is made of a doped quantum well A and an undoped electron extraction region (B → H). Under absorption of infrared radiation with an energy corresponding to the separation between the ground state and the first excited state ($A_1 \rightarrow A_2$), electrons are being excited into the upper quantized state from where they tunnel into the extraction region. The latter transports them to the ground state of the following period (A_1'). In a real structure, this transport takes place in the vertical direction and does not require any external voltage bias. With these spectrally narrow photovoltaic detectors, we have achieved responsivities of 10 mA/W and detectivities of 10^{11} jones at 110K (see Fig. 1 (right)). These values are comparable to commercial mid-infrared state-of-the-art sensors such as QWIPs or mercury-cadmium-telluride detectors [1], [2].

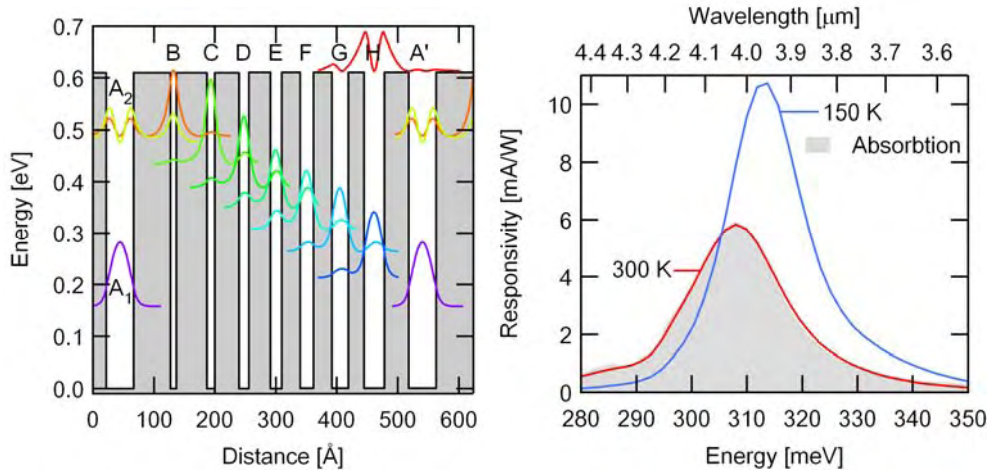


Fig.1 (left) Schematic band structure of a 3.96 μm quantum cascade detector. (right) Typical responsivity/absorption curves at temperatures of 150 K and 300 K.

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A9

Remote Methane Sensor Using Raman Amplified Open Path TDLS

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Reported here is a long-range optical methane sensor designed with the purpose of enabling more efficient leak monitoring of natural gas pipelines, oil rigs and gas containers including ships. Combining sensitive Wavelength Modulation Spectroscopy (WMS) and a high power Raman amplifier system, the sensor launches a high power 1650.95nm signal at an inspection site at a distance of around 100m and analyses the backscatter via a large Fresnel lens to detect methane concentrations of 100ppm in a 1m gas cloud up to 100%.

The work comprises the design and testing of a low-noise high-power fibre Raman amplifier system as a remote methane sensing source. Seeded by a single-mode 1650.95nm laser (DFB), upon which the WMS modulation is applied, the Raman amplifier produces a high-power, narrow-band methane sensing signal. Key to the system's competitive advantage is its low cost, small size, low weight, high reliability and superior performance when compared to bulk long-range airborne systems. This results from designing a fibre based system that is constructed entirely from standard communications fibre and components.

Lab trials at 11m have been conducted and show by extrapolation that a 1m cloud of methane at a concentration of 100ppm can be detected with a signal to noise ratio of 3:1 at a range of >100m.

DIODE-LASER MEASUREMENT OF THE SELF- AND N₂- BROADENING AND SHIFT COEFFICIENTS IN THE $\nu_4+\nu_5$ BAND OF ACETYLENE FROM LOW TO ROOM TEMPERATURE

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Acetylene is a minor component of our atmosphere [1], as well as of Jupiter [2], Saturn and its satellite Titan [3], Uranus [4] and Neptune [5] atmospheres. The analysis temperatures for Voyager I et II, in the Titan and Jupiter atmosphere were about 130 K, around 90K in Saturn and around 59K Neptune in atmospheres. To retrieve the C₂H₂ abundance in some of these atmospheres, self- and N₂-broadening and shift coefficients and their temperature dependencies are needed.

Using a tunable diode-laser spectrometer [6] adapted with a home made low temperature absorption cell [7], we have measured the self- and the N₂-broadening coefficients of absorption lines in the $\nu_4+\nu_5$ band of acetylene located around 1330 cm⁻¹. For each line under study, we have recorded spectra at 6 temperatures, from 173 to 298 K.

The experimental determination of self- and N₂- broadening coefficient were performed by fitting to the experimental profile of each line recorded at each temperature, a theoretical one from the Voigt, the Rautian and the Galatry models. The latter take into account the Dicke effect, a narrowing due to the molecular confinement.

The experimental shift was measured by a new experimental method which considers an unperturbed reference gas line as a wavenumber reference. The collisional shift coefficient was determined by fitting to the experimental profile of each acetylene line at each temperature, a theoretical one from the Rautian model. The reference gas (CH₄ or N₂O) which was at constant and low pressure and low absorption was fitted by a Gaussian profile.

From these values of broadening and shift, we have determined temperature dependencies of these coefficients.

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DEVELOPPEMENT OF A MULTI-SPECIES PROBE AROUND 2.6 μM WITH A BI-DIRECTIONAL ANTIMONIDE-BASED LASER DIODE

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We present the study and development of an instrument based on tunable diode laser absorption spectroscopy, using an antimonide based laser diode emitting around 2.6 μm [1-2] for the detection of water vapor, CH_4 and CO_2 . The laser was fabricated by molecular beam epitaxy in the IES laboratory. The active region of the device is based on InGaAsSb/AlGaAsSb quantum wells grown on GaSb(N) substrate. This device is working at room temperature in continuous wave regime and exhibits a few mW of emitted power.

The main targeted application of this probe is the study of water vapor flux in the arid grounds of Africa, to understand, control and regulate irrigation mechanisms. Another application is the measurement of CO_2 and CH_4 exchanges between the plant roots and the soil in rhizosphere [3].

We have developed a bi-directional laser mount dedicated to this application, which allows the use of the emitted beams from both facets of the crystal (without any facet treatment). The first beam is directed through a reference cell containing a calibrated mixture while the second beam is directed through the analyze cell (figure 1).

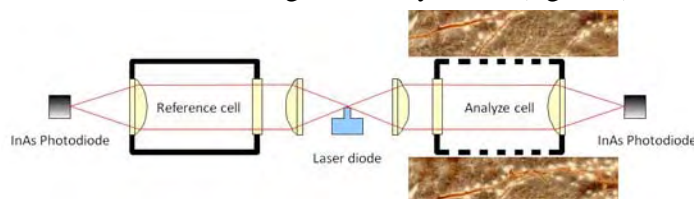


Fig. 1. Simplified optical setup

We will first show the characterization of the devices, and then we will discuss the first measurements made with the probe.

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Time-resolved lasing-characteristics of external-cavity quantum cascade lasers emitting in the mid-infrared

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There is a strong need for compact and robust spectroscopic MIR light sources offering high luminosity and versatility. Quantum cascade (QC) lasers fulfill these requirements almost ideally. For the spectroscopic detection of in particular complex compounds against a realistic chemical background a large spectral coverage is required. We present experimental results on a QC laser embedded in an external cavity (EC). Emmiting around 7.4 μm the system offers a broad band tuning exceeding 80 cm^{-1} located in the spectral fingerprint region of explosives such as TNT. The systems serves for spectrally resolved stand-off detection of explosives. By combining the EC QC laser source with a high performance IR imager a set-up based on multi-spectral MIR backscattering has been realized.

In this contribution we investigated the temporal evolution of the lasing spectrum of the EC-QC-Laser on a ns time-scale. After turn-on of the current pulse multiple-mode lasing starts at the gain maximum of the QC laser controlled by the cavity formed by the chip facets (Fig. 1). After a time delay of about 10 ns the QC laser begins to couple to the external cavity as seen from a change in lasing wavelength to that defined by the external grating as wavelength selective element, reaching steady-state operation after 24 ns. The characteristic time constant for the change from internal cavity modes to external cavity operation is derived to 15 ns, comparable to the photon lifetime in the external cavity of 4.5 ns.

The results are discussed on the basis of a rate equation model, providing insight into the energy transfer between internal and external laser cavity.

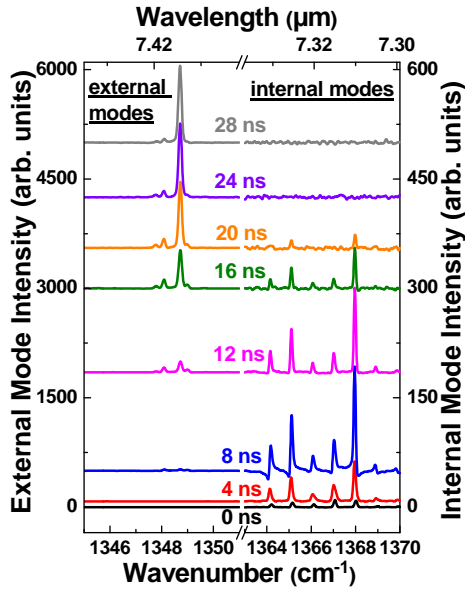


Fig.1 Time-resolved evolution of the emission of a EC-QCL

**SPR-ASSISTED MICROSCOPY FOR DETECTION OF
NANOPARTICLES AND VIRUSES.**

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We suggest a novel method for detection of particles by means of surface plasmon resonance assisted optical microscopy (SPR-assisted optical microscopy). The observation of the particles is based on local increasing of reflection from a thin metal film caused by a particle bound to the film in which surface plasmons are excited. The increasing of the light reflected in the vicinity of the particle is caused by interaction of surface plasmon waves with the particle. The intensity of this additional radiation corresponds to the effective scattering cross section which is about three orders of magnitude higher than by Mie scattering on the particle of the same size. As a result dielectric particles of 40 nm diameter can be detected with Signal-to-Noise Ratio of 5. The detection limit for polystyrene particles suspended in water is approximately 10-20 nm. This technique allows detection of viruses as well. Binding of HIV-like particles (modified uninformative HIV-viruses) in PBS biological buffer (Phosphate Buffered Saline) is demonstrated.

The size of the studied objects may be at least one order of magnitude less than the wavelength of the light used for the imaging. This allows studying of nanoparticles and viruses by means of visible-light laser sources. However high spatial homogeneity is needed to simplify the image processing procedure and to improve detection limits. Since speckles are present in the laser beam, alternative light sources should be found.

FREQUENCY CONVERSION OF HIGH-POWER SINGLE-FREQUENCY CW OPOs

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Continuous wave optical parametric oscillators (CW OPOs) are now established as commercial products providing spectroscopic output from 1400 to 4500 nm wavelengths. With the availability of single-frequency fiber-laser pump sources, the power available from CW OPOs is now at the multi-Watt level. As a result it is possible to efficiently frequency-convert the OPO output into the visible to near-infrared [1, 2]. We have performed single pass frequency conversion in MgO-doped PPLN to demonstrate second harmonic generation of the output of a 1064nm-pumped CW OPO. This provides a simple method to provide spectroscopic output from 700nm to 1400nm using a single nonlinear crystal. Preliminary experiments demonstrated an output of ~5mW of single frequency output between 991 nm and 1002nm (Figure 1), for ~1 Watt input at ~2 μ m. We will describe results of optimization of conversion efficiency and extension of the wavelength coverage demonstrated. In addition we will discuss intracavity and external cavity conversion as alternative methods, and the possibility of long-wavelength mid-infrared generation in materials such as orientation-patterned Gallium Arsenide (OP-GaAs).

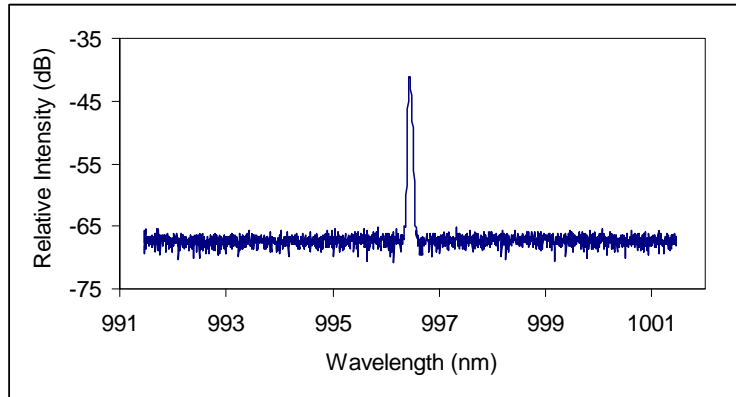


Fig.1 : Spectrum of frequency-doubled single-frequency signal wavelength output from a fiber-laser-pumped CW OPO.

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APPLICATION OF LARGELY TUNABLE MEMS-VCSEL TO GAS PHASE DERIVATIVE SPECTROSCOPY

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Near-infrared ($\lambda < 2 \mu\text{m}$) semiconductor diode lasers are attractive sources for gas monitoring thanks to their properties of room-temperature operation, unique spectral features and compatibility with telecommunication-grade optical components. Various molecular species of atmospheric and industrial interest have combination or overtone absorption transitions in this wavelength range and can be detected from percent down to ppm level using sensitive derivative spectroscopy techniques such as wavelength-modulation spectroscopy (WMS) in conjunction with a simple and cost-effective optical configuration.

Two kinds of laser sources are commonly used in NIR laser-based gas sensors, *i.e.* distributed feedback (DFB) lasers and vertical-cavity surface emitting lasers (VCSEL). These two types of lasers have shown for a long time the required properties for high sensitivity and high selectivity gas sensing, such as a spectral purity and stability to probe a single narrow ro-vibrational transition and modulation capabilities for the implementation of well-known techniques to improve the detection sensitivity, such as WMS. The tuning range of these lasers is limited to a few nanometers, so that sensors developed using these sources are most often restricted to the detection of a single species. In some applications, it would be attractive to detect more species simultaneously, which requires a larger laser tuning range. Micromechanically tunable VCSELs combining InP-based half-VCSEL technology with a GaAs micromachined mirror membrane (MEMS) developed in close cooperation between the Technical Universities of Darmstadt and Munich have shown very broad continuous tuning range up to 60 nm in the NIR. In these devices, coarse wavelength tuning and low frequency scanning is achieved by thermal heating of the mirror membrane, whereas finer wavelength adjustment and faster modulation is realized through laser injection current. Such a large tuning range enables for instance to detect CO, CO₂, NH₃, C₂H₂ and HI in the 1.52-1.58 μm range or CO₂, H₂O, NH₃ and HBr in the 1.95-2.01 μm range.

We report basic properties of a 1552-1572 nm MEMS-VCSEL for wavelength modulation spectroscopy applications. In particular, MEMS tuning and modulation bandwidth of the device have been measured. Characteristics of laser current modulation that are relevant for WMS implementation have been determined from laser modulation spectra measured with a high-resolution optical spectrum analyzer. Finally, preliminary results of CO₂ wavelength modulation spectroscopy obtained with this device are presented.

AN ALTERNATIVE METHOD TO INTERPULSE AND INTRAPULSE TECHNIQUES FOR PULSED QUANTUM CASCADE LASER SPECTROMETRY: THE INTERMEDIATE-SIZE PULSE TECHNIQUE

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The Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA, Reims, France) has developed laser spectrometers based on quantum cascade lasers. 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) quantum cascade lasers [1-10]. However, the reachable wavelengths are limited in this emitted way. Thus we have now decided to extend our capabilities using pulsed mode quantum cascade lasers.

Pulsed quantum-cascade-laser spectrometers are usually used to detect atmospheric gases with either the interpulse technique (short pulses, typically 5–20 ns) or the intrapulse technique (long pulses, typically 500–800 ns). Each of these techniques has many drawbacks, which we present. Particularly the gas absorption spectra are generally distorted. We demonstrate the possibility to use intermediate-size pulses (typically 50–100 ns) for gas detection using pulsed QCL spectrometers [11]. IR spectra of ammonia recorded in the 10 μm region are presented in various conditions of pulse emission. These experiences demonstrate the large influence of the pulse shape on the recorded spectrum and the importance to use our alternative method for gas detection with pulsed QCL spectrometers.

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Poster session B

B1

Fundamental Noises in TDLs

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Goal of this paper is to give overview of fundamental noises in TDLs.

There are 5 main subsystems in TDLs: electrons in PD; electrons, photons, and phonons in DL; and molecules under investigation. Each subsystem is origin of fundamental noises in TDLs. Interaction of several subsystems leads to special fundamental noise types to be considered in present paper.

Electron is particle in PD. It results in shot noise of PD photocurrent. Presence of spontaneous emission (quantum nature of light) leads to DL quantum noise. Electron is particle in DL – DL flicker noise (see C1). Electrons, phonons, and photons interaction in DL is origin of baseline (see D1). If noise origin is identified, this noise can be efficiently suppressed Fig.1.

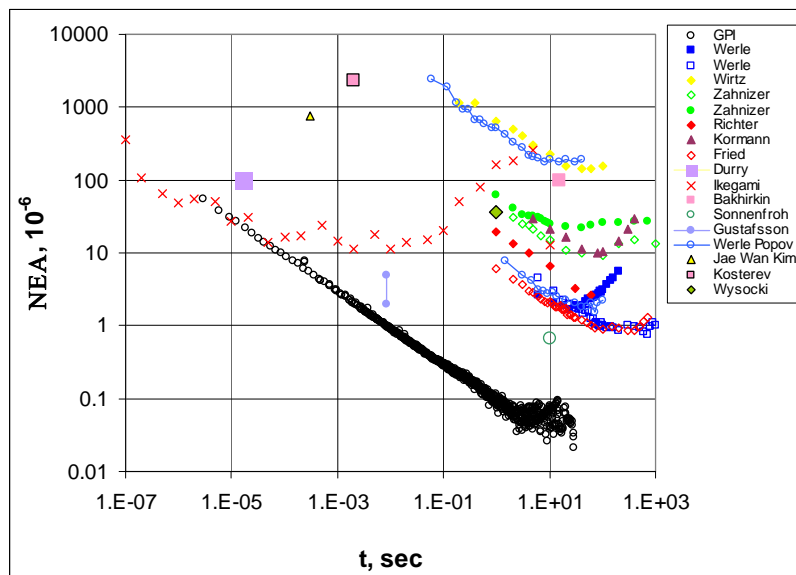


Fig. 1 Allan plot of NEA (Noise Equivalent Absorbance) as function of averaging time. Best results known for author are presented.

Fundamental limit of trace molecule detection due to diode laser quantum noise was achieved - NEA below 10^{-7} for averaging time above 1 sec (best result is equal $6 \cdot 10^{-8}$ for 5 sec averaging time). NEAC (Noise Equivalent Absorption Coefficient) is equal to $2 \cdot 10^{-12} \text{ cm}^{-1}$ for our system Chernin multi-pass cell (300 m) comparable with the best known results obtained in Stark spectroscopy. NEC (Noise Equivalent Concentration) for HF detection in near IR - 0.8 ppt. Next limitation mechanism was identified recently and we are waiting significant NEA improvement. As result improvement in all other parameters can be expected. Some comments will be given for inter-comparison results.

B2

TDLS complex development for airplane-laboratory “Atmosphere”

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Last year Russian State program started to build Airplane- Laboratories “Atmosphere” on Il-114 board (left).



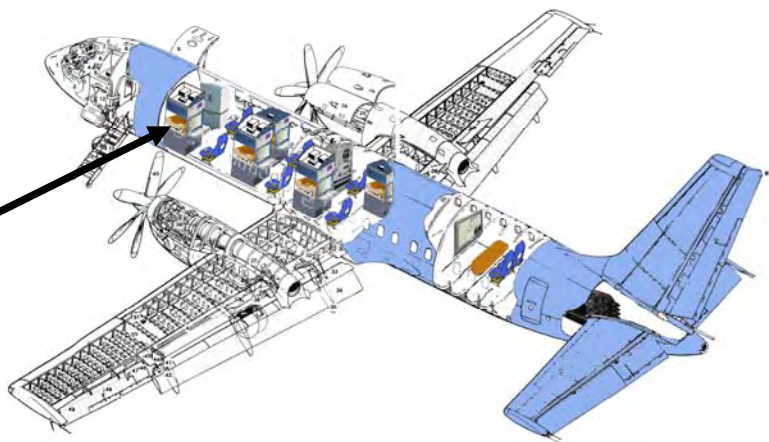
1. Navigation
2. Thermodynamics
3. Aerosol
4. Molecules concentration
5. Clouds
6. Atmosphere electricity
7. Atmosphere radioactivity

Development of above mentioned complexes is subject of broad collaboration. Central Airological observatory is responsible for coordination of this development.

In this paper we present development of Tunable Diode Laser Spectroscopy (TDLS) based complex to measure in real time concentration of main atmosphere molecular components.

TDLS complex

The complex consists of modules to measure concentration of H₂O, CO₂, CH₄, CO and their isotopomers.



B3

TDLS BASED EXPLOSIVES DETECTOR: DEVELOPMENT AND TESTING

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Ammonia is universal marker of nitrogen-contained explosives (see A1).

Sensitive ammonia detector based on TDLS technique was developed. Fig. 1 shows instrument developed layout drawing. Module A contains NEL DL ($\lambda=1512$ nm), fiber splitter, reference channel with reference cell (3 cm, 80 mBar of pure ammonia), and electronics; module B – batteries; C – “Chernin” multi-pass cell ($L = 39$ m). Aim of D module is to organize laminar air flow (arrows) through the “Chernin” cell. All these components were packed in a backpack. Total backpack weight with batteries is 8 kg.

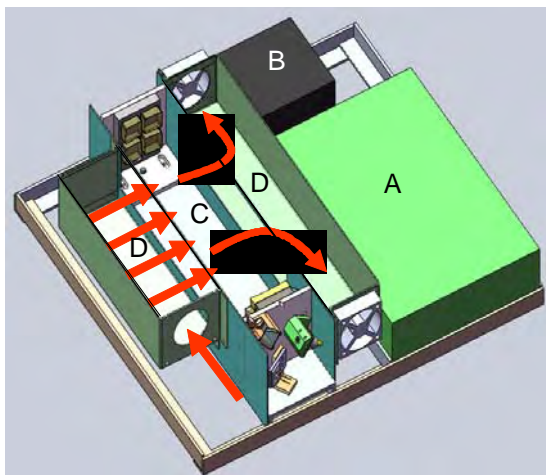


Fig. 1 Instrument developed layout drawing

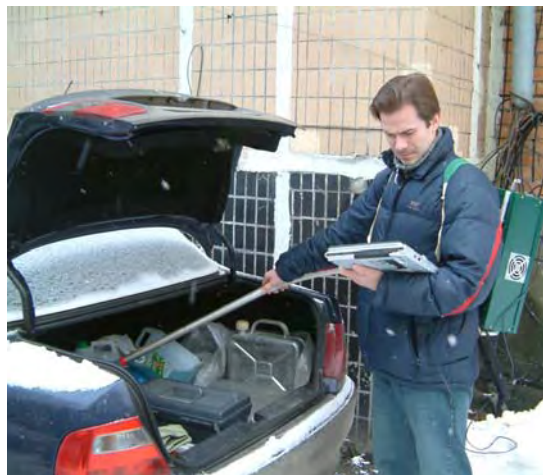


Fig. 2 Explosive sample detection in luggage space

Laboratory test of the instrument: NEC (Noise Equivalent Concentration) - 0.5 ppb for 1 sec averaging time. Indoor and outdoor tests were performed both at General Physics Institute and at test polygon near Moscow. Possibility of detection was demonstrated for different types and amounts of explosives.

Several scenarios of explosive sample detection using instrument developed were analyzed and tested. Fig. 2 presents example of 400 g TNT sample detection in vehicle luggage space. 2 kg AN explosive sample was found inside building by following concentration gradient. 300 kg explosive sample in wrapping was detected at 120 m distance.

Present work was supported in part by DOE-GIPP-347 (ISTC-3740P).

Transient TDL Studies of the Chemical Dynamics of Energized Molecules

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Time-resolved tunable diode laser spectroscopy (TDLS) is used to investigate new problems in the chemical dynamics of energized molecules. Molecules with large amounts of energy play key roles in combustion, plasmas and other high temperature environments. In these studies, molecules are prepared with large well-defined amounts of internal energy using pulsed laser excitation. The outcome of reactive, inelastic and elastic collisions is probed with transient TDLS at short times relative to the collision time. We report recent advances in determining full state-resolved distributions for collisional energy transfer and in characterizing the energy gain profiles of scattered molecules. We have developed a novel method for simultaneously measuring nascent appearance and depletion populations, such as shown in Figure 1, from which low- J state populations are determined. These studies account for all scattered molecules, and thereby yield a measure of the collision rate and the branching ratio for elastic and inelastic collisions.[1] In other experiments, hydrogen abstraction reactions of vibrationally excited molecules ($E=38000\text{ cm}^{-1}$) have been studied with TDLS. We find that vibrational energy enhances reactivity and that single vibrational quanta are used in reactions even though reactants contain a large excess of vibrational energy. On the other hand, vibrational energy inhibits abstraction reactions from methyl groups as the hindered rotors become free rotors upon excitation. A third area of research involves an optical centrifuge, a new technology that uses intense laser fields to generate molecules in ultra-high rotational states. We have used TDLS to measure the excitation and collisional dynamics of molecules prepared in an optical centrifuge.

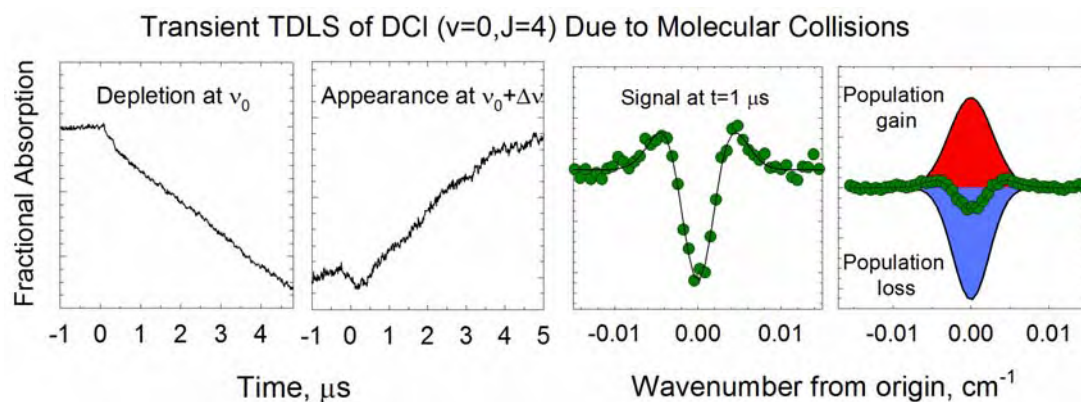


Fig.1 Transient TDLS signals for DCI ($v=0, J=4$) molecules due to collisions with highly vibrationally excited 2-picoline ($\text{C}_5\text{H}_5\text{NCH}_3$, $E=38,300\text{ cm}^{-1}$)

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B5

BROADLY TUNABLE, EXTERNAL CAVITY CW QUANTUM CASCADE LASER AND ITS APPLICATIONS TO MOLECULAR SPECTROSCOPY AND NO₂ TRACE GAS DETECTION

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The operational characteristics of a broadly tunable CW quantum cascade laser purchased from Daylight Solutions (Model TLS-CW-MHF) and its applications for molecular spectroscopy and the detection of trace atmospheric constituents such as NO₂[1] and complex molecules will be presented. The laser is operating mod-hop free over a range of 70 cm⁻¹ from 1600 to 1670 cm⁻¹ with a narrow linewidth (~ 0.001 cm⁻¹). We were able to record continuous spectra of NO₂ and water vapor mod-hop free over the entire range 1600 - 1670 cm⁻¹ and the observed intensities, linewidths, and line peak positions match well with the absorption spectra expected from HITRAN data corrected for the pressure broadening effects. We also performed wavelength modulation spectroscopy of the absorption spectra which enabled us to separate and detect the weak signals which are not visible in the simple absorption spectra thus enhancing the specificity and selectivity for trace gas detection. We report 100 ppb level for NO₂ detection limit with a short absorption cell (12.5 cm) and seven multipasses. The external cavity QCL is quite stable and repetitive scans of the spectra did not result in any detectable broadening of the absorption lines. The broad tunability allows the simultaneous detection of several species. The sensitivity of detection is considerably enhanced by each of the following: (1) integration of multiple lines over the tuning range, (2) repetitive scans and adding the spectra and (3) performing wavelength modulation spectroscopy over a wide range of the spectrum. Our results on Cavity Ring Spectroscopy for trace gas detection employing tunable QCL will also presented.

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TDLS SYSTEM FOR $^{12}\text{CO}_2/^{13}\text{CO}_2$ RATIO MEASUREMENTS BASED ON VCSEL AND HERRIOT SYSTEM

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Nowadays, $^{12}\text{CO}_2/^{13}\text{CO}_2$ ratio measurement is extensively used in geology (examination of the Earth structure geological aspects), ecology (for assessment of the balance of carbon-containing compounds in atmosphere and the problems of the global climate change), biology and medicine (isotopic breath-test), etc. One of the major challenges on taking such measurements is gaining high accuracy of the $^{12}\text{CO}_2/^{13}\text{CO}_2$ ratio definition which should be 0.1-0.2 ‰ for variety problems solution.

The paper discusses the results of designing and manufacturing of a TDLS system for the $^{12}\text{CO}_2/^{13}\text{CO}_2$ ratio precision measurement with the use of VCSEL and a multi-pass Herriot cell. A diode laser (DL) with a vertical pumping cavity was used as a radiation source in the TDLS system. The wavelength of the DL oscillation was $\lambda = 2004$ nm, and the lasing power was ≈ 300 μW . An optimal spectral range $4979.2 - 4980.0$ cm^{-1} has been established for simultaneous measurements of $^{12}\text{CO}_2$ (R19e of 21112 << 01101 band) and $^{13}\text{CO}_2$ (P14e of 20011 << 00001 band). The DL module control and the detected signal processing were performed with a NI DAQ I/O board. The DL operated in the pulse-periodic mode with pulse duration of 1-3 ms and pulse repetition rate of 200 Hz. The analytical channel of the TDLS system was equipped with an evacuated multi-pass Herriot cell with the 0.39-m basis and the full optical path of 15 m. The working pressure of the mixture under study varied over the range from 20 to 300 Torr. The reference channel where a cell ($l=20$ cm) with pure carbon dioxide with natural isotope abundance and $P=300$ Torr was used for DL frequency tuning cycles stabilization. DL frequency tuning was determined using calibrated Fabry-Perot etalon with free spectral range 0.0798 cm^{-1} . "Hamamatsu" InGaAs G8373 photodiodes with the $\text{NEP} = 2 \cdot 10^{-12}$ $\text{W/Hz}^{1/2}$ (Noise Equivalent Power) were used to detect signals both in the analytical and reference channels.

Preliminary tests of the TDLS system for the $^{12}\text{CO}_2/^{13}\text{CO}_2$ ratio measurements have revealed that under static conditions of a sample at $P=20-40$ Torr, the $^{12}\text{CO}_2/^{13}\text{CO}_2$ ratio measurement accuracy is 0.2 ‰; while on the continuous laminar pumping of the gas sample under study through the Herriot analytical cell it makes 0.5 ‰. Potentialities of further improvement of the $^{12}\text{CO}_2/^{13}\text{CO}_2$ ratio measurement sensitivity and accuracy of the suggested TDLS systems will be discussed.

COMPARISON OF NOISE EFFECTS IN DERIVATIVE AND DIRECT ABSORPTION TDLAS – A SIMULATION BASED APPROACH

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Derivative and direct absorption spectroscopy are two widely used variations of Tunable Diode Laser Spectroscopy (TDLAS) and both are used in a large field of applications [1]. Derivative spectroscopy relies on lock-in detection to reduce background signals and noise, while the direct absorption approach uses a combination of baseline fitting and extensive signal averaging. Compared to the derivative technique, direct absorption spectroscopy offers the potential for calibration-free measurements [2].

We present a comparative study of the two strategies based on a simulation that applies the concepts of derivative and direct absorption measurements to the same measurement task on a single ammonia absorption line in the NIR spectral range with the measurement time limited to 1s and a given maximum data acquisition rate of 1MSample/s. The effects of thermal amplifier noise, detector shot noise and relative intensity noise (RIN) of the diode laser with a 1/f spectral noise power distribution are considered. Special attention is paid to the influence of quantization noise, originating from the analog-to-digital conversion (ADC) of the photo detector signal. The noise parameters and the diode laser specifications are estimated based on measurements performed on real-world components.

As expected, results show that in the considered configuration, the SNR is essentially limited by RIN for both detection techniques. Quantization noise can be neglected for ADC-resolutions of 12bit or higher in this case. If RIN can be suppressed by use of a balanced detection scheme [3], the SNR improvement is more pronounced for the direct absorption measurement technique and an SNR performance comparable to or better than that of the 2f-system can be accomplished. Simulation results indicate that for RIN compensation ratios of 20dB and more, the effect of quantization noise becomes relevant in the direct absorption scheme even for resolutions as high as 16bit. In the derivative scheme, quantization noise remains negligible for resolutions higher than 12bit. This result can be qualitatively understood, given the fact, that in derivative detection the ADC quantization can be applied to a high-pass filtered, zero-mean signal containing the 1f- and 2f-frequencies, whereas in the direct absorption approach the full detector signal, including background, must be quantized.

In summary, the simulation results suggest that in direct absorption measurements with balanced detection and high RIN compensation ratio, a high-resolution ADC with 16bit to 18bit resolution should be used to achieve the maximum benefit from RIN compensation.

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PERFORMANCE COMPARISON OF TUNEABLE DIODE LASER PHOTOACOUSTIC SPECTROSCOPY SYSTEMS BASED ON CAPACITIVE AND CANTILEVER MICROPHONE DETECTION TECHNOLOGIES

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The performance of three photoacoustic cells for trace gas detection has been evaluated using near-infrared distributed feedback (DFB) tuneable diode lasers. The cells used in this investigation comprised a longitudinal resonator containing a single capacitive microphone, a differential cell containing two capacitive microphones and a cell containing a micro-machined silicon cantilever microphone. The performance of each cell was assessed using nitrogen-based gas mixtures containing trace quantities of carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄) and acetylene (C₂H₂). The analytes were detected either sequentially or simultaneously in each of the cells and the analytical performance was enhanced using erbium-doped fibre amplification to boost the optical power available for detection of CO, CO₂ and C₂H₂. In each case wavelength modulation spectroscopy (WMS), combined with phase-sensitive detection (PSD), was used to acquire data. The merits and limitations of each cell for application in single and multispecies detection by tuneable diode laser photoacoustic spectroscopy (TDL-PAS) were assessed.

We report what we believe to be the first demonstration of multispecies detection by TDL-PAS using a cell based on cantilever microphone technology. Simultaneous detection of CO, CO₂, C₂H₂ and CH₄ was achieved by modulation frequency divisional multiplexing the DFB outputs, each of which was tuned to an absorption line of a single analyte. Sensitivities ranging between 10⁻⁹ and 10⁻¹⁰ cm⁻¹ W Hz^{-1/2} were obtained for multispecies detection and were comparable to the best results quoted in the literature for detection of CO₂ at 1572 nm by TDL-PAS using a similar cantilever cell (4.6 x 10⁻⁹ cm⁻¹ W Hz^{-1/2}) [1].

We have also, for the first time, demonstrated multispecies trace gas detection using fibre-amplified DFBs with photoacoustic detection. In the case of the capacitive-type cells measurements were performed sequentially by time divisional multiplexing the DFB outputs. Whilst fibre amplification was shown to improve the performance of the TDL-PAS technique for the capacitive microphone-based cells, it proved to be of little benefit with the cantilever cell as detection limits in the low parts-per-million could readily be achieved with the few milliwatts of optical power available from the DFB lasers.

Although the performance of the cantilever cell proved to be superior to the capacitive cells, consideration of other factors such as cost, instrument robustness and thermal stability need to be considered when selecting a cell for incorporation in a TDL-PAS instrument. Cantilever microphone-based cells are considerably more expensive than cells containing capacitive microphones and are delicate devices, and the performance / cost balance must be carefully weighed.

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B9

Development of a copper 28 meter Herriott cell for absorption line parameter determination at temperatures between 300 K and 30 K.

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This poster describes the design and performance characteristics of an absorption cell that is fabricated entirely of copper. The base length of the cell is 37.1 cm. and it is of the Herriott design. The mirrors are copper with gold coating and the entrance and exit aperture diameter is 4 mm. The cell is designed for approximately 28.9 meters absorption path. The cell is designed to achieve temperature uniformity better than 0.01 K at all temperatures, and long term temperature stability better than 0.01 K, with improved performance at lower temperatures, below 70 K.

The system remains aligned at all temperatures between 300 K and 20K. This cell is designed for infrared studies of molecular dimers and van der Waals molecular complexes as well as the characterization of absorption line parameters at temperatures between 300K and 50K.

Cell performance specifications will be presented as well as first low temperature test spectra.

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The Keck Undergraduate Science program and the Sherman Fairchild Foundation at Connecticut College

IMPACT OF WATER VAPOR ON 1.51 μm AMMONIA ABSORPTION FEATURES USED IN TRACE GAS SENSING APPLICATIONS

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Laser spectroscopy has demonstrated its relevance for various applications requiring sensitive and continuous ammonia monitoring at trace level. Different spectroscopic methods have been demonstrated so far (*e.g.* WMS, FMS, CRDS, PAS), which all benefit from recognized properties such as a sensitive and selective measurement. Interferences, *i.e.* a spurious signal at the sensor operating wavelength induced by nearby absorption lines of other species, can be minimized or even suppressed by a proper choice of the operation wavelength, sometimes also combined with reduced pressure operation. However, even in absence of interference, a spectroscopic gas sensor may be affected by the presence of other species as a result of modified line broadening giving rise to *cross-sensitivity* effects. For instance, N_2 -broadening of several NH_3 lines in the 1.5 μm spectral range has been shown to be $\sim 10\%$ higher in average than air-broadening [1, 2], illustrating the importance of a sensor calibration made in proper conditions when using a spectroscopic method that is sensitive to the width of the analyzed absorption line, as for wavelength modulation techniques. The influence of water vapor on NH_3 sensing can also be important in applications where humidity is subject to significant variations, especially for high temperature applications where high H_2O concentrations up to 25-30% may be encountered.

Only few data are available about broadening parameters of NH_3 lines in the near-infrared and no information about H_2O -induced broadening of NH_3 lines is known from the literature, making impossible an accurate quantification of the expected influence of H_2O on a NH_3 sensor. The reported work aims at quantifying the influence of water vapor on several NH_3 absorption features in the 1512-1516 nm range that are exploitable for gas sensing. For this purpose, absorption spectra of different NH_3 - N_2 - H_2O mixtures were measured using a 4 m multipass cell in conjunction with a fiber-coupled DFB laser. Multi-peak data processing was performed to extract the lines parameters from the recorded spectra. Measurements were performed in an oven at elevated temperature (70°C) in order to enable high H_2O partial pressures to be achieved. Results will be presented for three different NH_3 absorption features centered at 1512.2 nm, 1515.1 nm and 1516 nm. In the three considered wavelength ranges, an influence of water vapour was observed on the NH_3 absorption feature, but it was surprisingly not of great importance. For instance, a very small difference in the foreign-broadening factors due to H_2O and N_2 was observed for the 1512.2 nm NH_3 absorption feature ($g_{\text{H}_2\text{O}} = 0.15 \text{ cm}^{-1}/\text{atm}$ compared to $g_{\text{N}_2} = 0.12 \text{ cm}^{-1}/\text{atm}$). Therefore, the NH_3 absorption feature does not broaden significantly in presence of water vapour and the H_2O - NH_3 cross-sensitivity is shown to be of minor importance, which is beneficial for NH_3 sensing in largely varying H_2O conditions.

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**PRELIMINARY GAS COMPOSITION INVESTIGATIONS AT
ELEVATED TEMPERATURES AND PRESSURES USING
CALIBRATION-FREE TDLS WITH THE RESIDUAL AMPLITUDE
MODULATION TECHNIQUE**

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Tunable Diode Laser Spectroscopy (TDLS) has been used to measure gas concentration and pressure in industrial systems, however, these measurements are dependent on the gas temperature and the partial pressures of other gases in the system [1]. In order to ensure the accuracy of TDLS, for the investigation of multi-component gases in harsh environments such as Solid Oxide Fuel Cells, or combustion processes, it is necessary to have detailed spectroscopic information at the operating temperatures and pressures, as well as have an understanding of the cross-broadening dependence of the various gases.

Further to these complications, conventional TDLS techniques are subject to calibration factors, leading to significant errors and measurement drift. A new calibration-free approach to TDLS, known as the residual amplitude modulation technique (RAM) [2], is used in the current investigations, allowing the extraction of absolute absorption profiles from the recovered signals.

A novel gas sensing test bed, operating at temperatures up to 900°C and pressures in the range of 1-8bar, is presented in detail. This system allows spectroscopic parameters of different gas species to be investigated, including line-strength, self-broadening, cross-broadening and temperature-dependent broadening, in order to improve gas sensing accuracy. Preliminary results will be shown for both steam and methane, and parameters, such as cross broadening coefficients for various gases, including nitrogen and carbon-dioxide will be discussed.

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B12

Measurement of formaldehyde concentration above aqueous solutions by TDLAS.

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Formaldehyde plays an important role in chemical industry, where it is a key reactant in many technological processes. It is also of great interest in atmospheric chemistry, where it is involved for instance in the production of HOx radicals that governs the tropospheric ozone cycle, or in the snowpack chemistry, which produces formaldehyde into the atmosphere at elevated concentration in coastal and ice-cap sites of Polar regions.

Even though the description of the vapor liquid equilibrium (VLE) of the system formaldehyde-water and the determination of thermodynamic properties of formaldehyde solutions have been the focus of several research groups over the last 80 years, large discrepancies exist for the gas phase data above concentrated aqueous solutions, even at ambient temperature. These discrepancies may illustrate possible experimental pitfalls when the gas phase concentration is measured indirectly, i.e. after recondensation into a liquid.

We investigate here the VLE of formaldehyde aqueous solutions of different concentrations at room temperature by directly probing the gas phase above the solutions. Formaldehyde is quantified at 2829.5 cm^{-1} using a liquid nitrogen cooled lead salt diode laser and a 32 meter multipass cell, installed on the variable pressure instrument developed in the laboratory [1]. Vapor pressures at atmospherically relevant formaldehyde concentrations are investigated at 295 K [2] and lower temperatures to derive Henry's coefficients.

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LASER-SPECTROSCOPIC STUDIES ON SURGICAL SMOKE

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Surgical smoke [1] is produced in surgery with lasers, ultrasonic scalpels and electroknives. Its chemical composition is of great interest since several toxic and carcinogenic substances have been detected in previous studies (e.g. [2]). However, quantitative information – essential for risk assessment – is generally missing. The goals of our project are to study *in vitro* and *in vivo* surgical smoke samples spectroscopically to obtain quantitative data about selected components of the samples, and to determine relationships between smoke composition and insufflant gas, surgical tool, tissue type and kind of (surgical) operation. We focus on smoke samples produced in laparoscopy (minimally invasive surgery) in a CO₂ atmosphere.

We present analyses of *in vitro* smoke samples (sampled at 100-120°C to increase sensitivity to low vapor pressure species) via mid-IR spectroscopy with a pulsed difference-frequency based laser spectrometer tunable between 3.18 and 3.55 μm [3]. First measurements have shown the presence of 13 ppm methane and ethylene, 3 ppm ethane and 1.1% water vapor (Fig. 1). Furthermore, by producing samples in a ¹³CO₂ atmosphere and measuring the ¹²CH₄ and ¹³CH₄ concentrations, we explore the issue of the origin of the carbon atoms in the produced smoke.

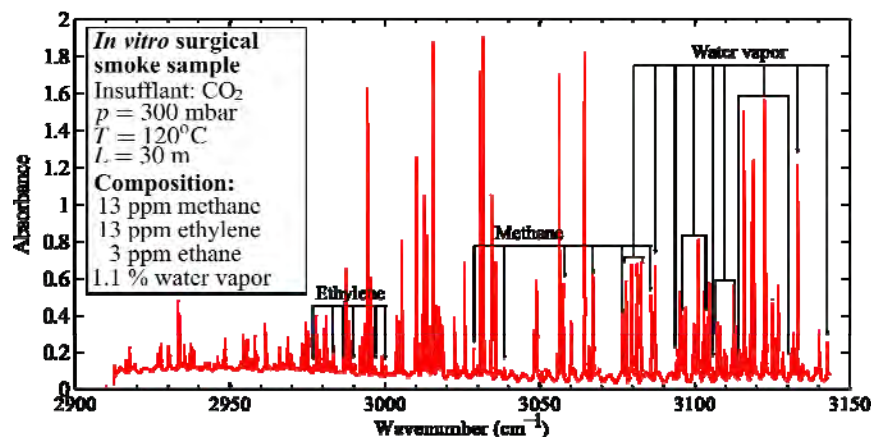


Fig.1 Typical spectrum of an *in vitro* surgical smoke sample, recorded in a heated multipass cell with a total length of $L = 30$ m. Some absorption lines of water vapor, methane and ethylene are indicated.

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AUTOMATED FREQUENCY CALIBRATION OF BROAD LASER SCANS FOR APPLICATIONS IN ABSORPTION SPECTROSCOPY

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We present a method for automated frequency calibration of broad laser scans using an absolute frequency mark and equal frequency intervals provided by a Fabry-Perot etalon. We implemented the method into an absorption spectrometer, as schematically shown in Fig. 1. The spectrometer was used to acquire spectra of ethylene oxide in the 1693-nm range.

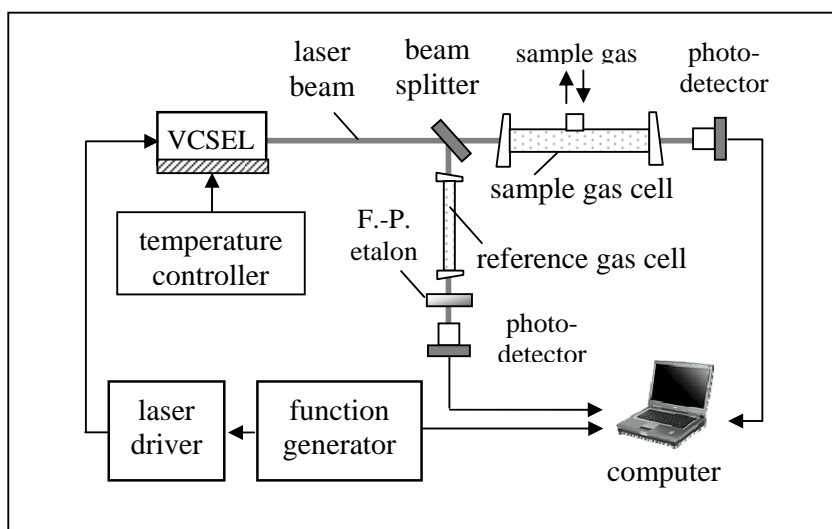


Fig. 1. The schematics of a VCSEL-based spectrometer with calibrated frequency scales.

The beam of a vertical-cavity surface-emitting laser (VCSEL) is collimated and then divided with a beam splitter between reference and probe arms of the spectrometer. The reference beam is directed through a 50-cm reference gas cell containing $3 \cdot 10^3$ ppm-v of CH_4 buffered with N_2 to a total pressure of 0.1 bar. A narrow CH_4 absorption line centered at 5903.28 cm^{-1} is utilized as a frequency mark. The reference beam also passes through a Fabry-Perot etalon with a free spectral range of 0.4 cm^{-1} . The probe beam is directed through a single-pass 63.5-cm sample cell filled with a gas mixture of ethylene oxide and air.

We developed a computer code that allows us to calculate an absolute frequency scale for each laser scan using the spectral information of the reference laser beam. High-resolution absorption spectra of ethylene oxide were obtained within a 10-cm^{-1} wide calibrated spectral interval. Further details of the proposed technique will be presented.

Gas Detection Device with a Multiple-Reflection Element

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The development of optical sensors is of special interest for monitoring gaseous pollutants and their concentration by the use of the interaction of an evanescent wave with surrounding molecules.

A novel evanescent field sensor has been developed which is applied for the detection of carbon dioxide during the sequestration process and for other different gases like CO, H₂S and N₂O, as well. This sensor element consist of a glass plate with a length of L=6 cm. A tunable DFB laser diode with an emission wavelength around 1,571 μm is used as light source. The laser light enters the multiple-reflection element via an aperture at one end, is propagated via multiple total internal reflections and returns from the plate through an aperture adjacent to the entrance aperture. Measurements in the gas phase have been performed with the multiple-reflection element and an absorption cell for reference and are shown in fig. 1.

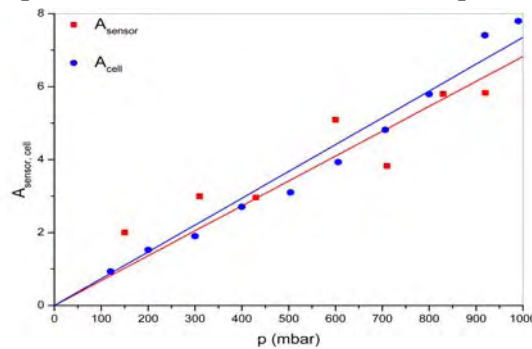


Fig.1 Integrated absorption coefficient depending on the pressure of CO₂ for direct absorption spectroscopy using an absorption cell (L=50cm) and using the multiple-reflection element (L=6 cm).

The sensitivity of an evanescent field sensor can be increased by coating the surface of the sensing element with ZnO nanowires [1]. A fused silica multimode step-index fiber with a core diameter of 200 μm and a length of L=2 cm has been coated with ZnO nanowires using the aqueous solution method. Measurements with this Nanosensor have been performed at different concentrations of CO₂ and H₂S. The limit of detection that can be achieved with the miniaturized sensor is comparable with that of a fiber optical sensor with a length of L=2m. This drastic increase of sensitivity will be investigated further and discussed during the conference.

References:

[1] S. Börner, R. Orghici, S.R. Waldvogel, U. Willer, and W. Schade, Appl. Opt. 48, 183-189 (2009).

INTERMEDIATE-SIZE PULSED QUANTUM CASCADE LASER SPECTROSCOPY FOR NH₃ DETECTION IN THE 10 μ m REGION

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Pulsed quantum-cascade-laser spectrometers are usually used to detect atmospheric gases with either the interpulse technique (short pulses, typically 5–20 ns) or the intrapulse technique (long pulses, typically 500–800 ns). Each of these techniques has many drawbacks. Particularly the gas absorption spectra are generally distorted. We have demonstrated the possibility to use intermediate-size pulses (typically 50–100 ns) for gas detection using pulsed QCL spectrometers [1]. IR spectra of ammonia recorded in the 10 μ m region are presented in various conditions of pulse emission.

For the NH₃ spectra recorded at low pressure (i.e. in the mbar range), the spectra show typical oscillations after the absorption. The Beer-Lambert law cannot explain these oscillations termed rapid-passage effect. The lifetimes of the levels (related to the Einstein coefficients) that are the basics of this law cannot take into account the individual comportment of the atoms. Thus a semi-classical theory based on the Maxwell-Bloch equations must be used to describe the comportment of the NH₃ absorptions in the 10 μ m region. Results with various tunability rates and various pressures will be presented.

For the NH₃ spectra recorded at higher pressure (i.e. in the 50 mbar range), the oscillations disappear. In this case the Beer-Lambert law could be reused. This paper will demonstrate that the intermediate-size technique give reliable measurements for NH₃ detection. Moreover the typical apparatus function (0.003 cm⁻¹ HWHM) is far lower from the typical apparatus function of the interpulse QCL spectrometers (0.015 cm⁻¹ HWHM).

[1] Grouiez B. et al, Optics Letters 2009, 34, 181-183

Poster session C

C1

DL Flicker Noise in TDLS and its Suppression

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It is known that flicker noise is one of the main limitations for trace molecular detection in TDLS. In present paper we are reporting identification of its origin. It is quantum nature of excitation current (electron is particle) together with DL nonlinear behaviour. It is known that last two effects lead to excitation current density flicker noise. The flicker noise under consideration influence on DL emission was analyzed. It was found that above mentioned mechanism can affect only DL near field pattern. Further analysis showed that in DL diagram there is direction where flicker noise is equal 0. Based on this fact new strategy of flicker noise suppression was developed (Fig. 2).

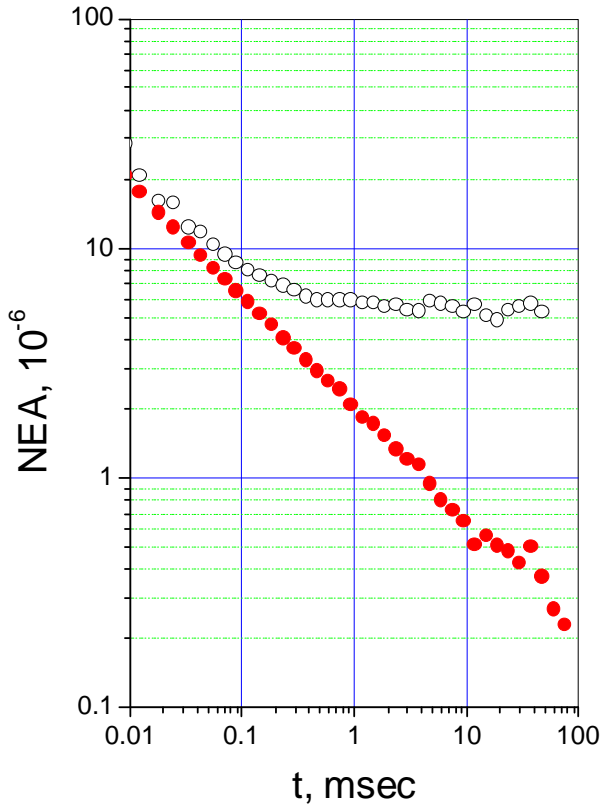


Fig. 2 Allan plot of NEA (Noise Equivalent Absorbance) as function of averaging time

Open and solid circles correspond to the same setup for two approaches. Open circles – traditional approach when part of DL radiation is focussed on PD and flicker noise can be observed. Typical NEA level in this case for different DL types and different techniques is $\sim 2 \cdot 10^{-5}$.

New strategy: no focussing elements. PD is installed in DL diagram direction where flicker noise is equal 0. Flicker noise is significantly suppressed. For new strategy NEA level below 10^{-7} was achieved for averaging time above 1 sec.

C2

“LINE-by-LINE” SOFTWARE FOR SPECTRA SIMULATION

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TDLs analytical applications frequently need operative optimization of DL and analytical spectral line choice. Analysis has to be done taking into account absorption of other molecules in gas mixture under investigation. For atmosphere: H₂O, CO₂, CH₄, O₂, etc. To solve this problem, software “Line-by-line” was developed based on “LabView 8.6” and spectral database “HITRAN-2004” [1]. Voigt profile line is using for absorbance calculation. Program interface is shown in Fig.1.

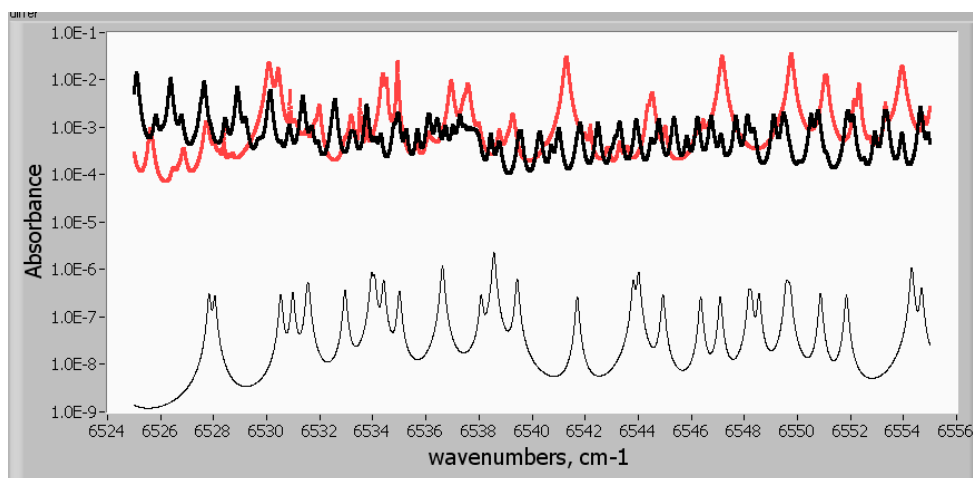


Fig.1 Interface of “Line-by-line” software

Presented simulation was performed for one of our DLs to detect NH₃ in human breath: CO₂ (thick black), H₂O (thick grey), and CH₄ (thin black). Following parameters were used: T = 297 K, L = 39 m, P₀ = 1 Barr, C = 3%, 2.1 %, and 10 ppm for CO₂, H₂O, and CH₄, respectively. Simulation using “Line-by-line” program takes less than 1 min. Similar to Fig.1 results were obtained for different applications for more than 50 DLs from NEL, Anritsu, LASER COMPONENTS, Nanoplus, and VERTILAS available at GPI. Some examples will be presented in poster.

Present work was supported in part by DOE-GIPP-347 (ISTC-3740P).

[3] <http://cfa-www.harvard.edu/HITRAN>

C3

REAL TIME CONTROL OF ARSINE AND PHOSPHINE PURIFICATION PROCESS USING TDLS

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TDLS based complexes were developed to measure impurities (H_2O , NH_3 , H_2S , CO_2) concentration in hydrides (see A3). The complexes were installed at “Salut” to control process of hydrides purification. Complex consists of 3 devices to measure particular impurity. Each device contains one reference and three analytic channels, measuring impurity concentration in upper - LF (light fraction), lower - HF (heavy fraction) and middle part (pure material) of low-temperature rectification column (see A3). Two rectification columns to produce high-purity arsine (AsH_3) and phosphine (PH_3) were equipped with complexes under consideration to control purification process in real time. Results of their operation will be presented and discussed.

Fig.1 presents example of real time ammonia measurement in phosphine. Upper curve - cell in one TDLS complex channel was automatically filled by gas from LF and then pump out subject for oscillations. Each period of this process removes impurity part from LF leading to impurity concentration reduction after 2 hours. At that time similar control process started for gas from HF using other TDLS complex channel. After 6 hours purification process is finished.

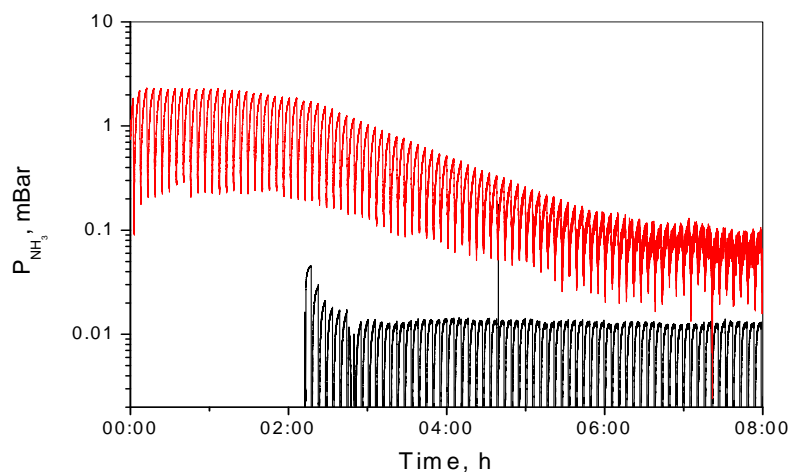


Fig.1 Ammonia monitoring in LF (upper) and in HF (lower) in phosphine

From Fig.1 NH_3 presence in LF and its absence in HF were found. It is opposite to traditional purification process consideration in chemistry: LF – impurities having higher evaporation temperature with respect to gas to be purified; HF – opposite situation.

Present work was supported in part by DOE-GIPP-347 (ISTC-3740P).

Miniaturized Sensor without Separate Reference Cell for Carbon-Monoxide Detection at 2.3 μm

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The detection resolution of a Carbon-Monoxide sensor is usually required to be in the lower ppm range, since the threshold limit value (TLV) of CO is 30 ppm. However, this resolution is inaccessible at wavelength $< 2.3 \mu\text{m}$ with only a few 10 cm optical path length, i.e. without using a multi-pass cell. Furthermore, to realize a compact CO sensor the number of optical components has to be minimized. In the presented sensor concept, the commonly used reference cell containing the target gas in high concentration for line-locking is omitted, but without deteriorating the sensor reliability. Wavelength stabilization is implemented instead by filling CH_4 in the photo-detector housing and using adjacent methane absorption lines in a wide spectral scan around the CO absorption line as wavelength markers. The wavelength calibration is performed using spectral scans covering 3 nm (duration 640 ms) every few seconds. In between the CO concentration is determined using narrow spectral scans (duration 80 ms) covering only the CO absorption line. Then a linear fit with CO and CH_4 spectral components and a linear baseline is carried out. The wide and fast spectral scan is made possible by using a 2.3 μm VCSEL [1], which in contrast to DFB lasers has a very wide current tunability of $> 4 \text{ nm}$. Fig. 1 shows the compact optical setup of the sensor with folded path geometry and the integrated reference cell. Fig. 2 demonstrates the sensor performance with a 22 h gas concentration measurement with corresponding Allan plot.

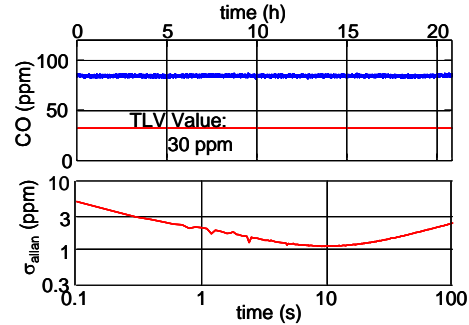
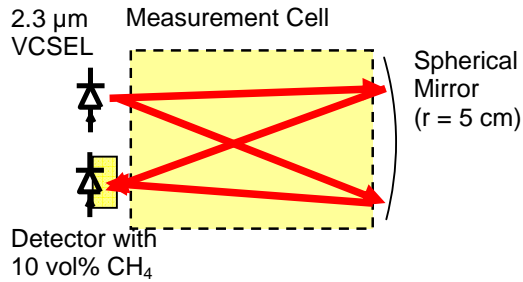


Fig. 1: Schematic of the CO sensor optics with overall feasible size of $\sim 7 \text{ cm}$. The photo-detector housing serves as reference cell containing 10 vol% CH_4 .

Fig. 2: CO measurement of 80 ppm with an averaging time of 20 sec (above). The CO standard deviation is 0.6 ppm (20 sec) and 2 ppm at 1 sec. The Allan plot is shown below.

The authors gratefully acknowledge the financial support by the Federal Ministry of Education and Research of Germany (Project 'NOSE', No. 13N877) and by the European Union (Project 'NEMIS', No. 031845).

[1] M. Ortsiefer, G. Böhm, M. Grau, K. Windhorn, E. Rönneberg, J. Roskopf, R. Shau, O. Dier and M.-C. Amann, Electronics Letters **42**, 640 (2006)

C5

GAS MEASUREMENTS USING A VERSATILE SPECTROMETER AND THE COMPARISON WITH HITRAN AND PNNL DATABASE

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Gas detectors based on laser spectroscopy have become standard equipment in industry and research environments due to their sensitivity, selectivity, and speed of measurement. Fields that are served include environmental monitoring, purity analysis of gases in the semiconductor industry, and leak detection in the oil and gas industry. Detectors are in general limited to measurement of a single component as they are equipped with standard diode lasers that lack wide tunability. We have developed a spectrometer which can detect tens of different gases down to (sub) part per billion levels. The system is based on cavity ringdown spectroscopy (CRDS) in combination with an optical parametric oscillator tunable from 2693 to 3505 nm (see Fig. 1). Using a *single* set of CRDS mirrors spectra were recorded of methane, ethane, water, methanol, ethanol and formaldehyde. Gas mixtures were gravimetrically prepared in cylinders or via dynamic generation using permeation tubes (formaldehyde).

Agreement between our data and Hitran database is good for water, reasonable for methane and poor for ethane and formaldehyde. Absorbance values of formaldehyde are on average 30% too low in Hitran which is in line with recent observations of Perrin *et al.* [1]. In contrast, good agreement is obtained with PNNL database for all gases studied so far (see Fig. 2 for ethane).

This work was financially supported by the Dutch Ministry of Economic Affairs and European Community's 7th Framework Programme, ERA-NET⁺, under the iMERA⁺ project - grant agreement No. 217257.



Fig. 1 Optical parametric oscillator with an output power up to 1.2 Watt.

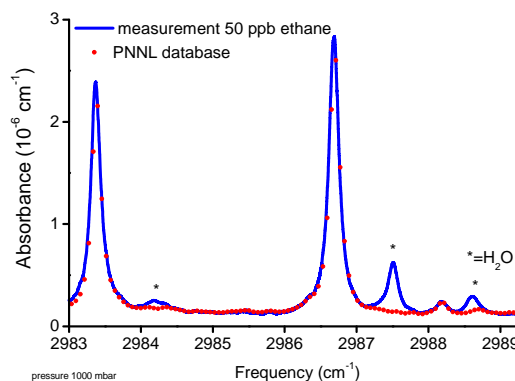


Fig. 2 Measurement of 50 parts per billion (ppb) ethane. Good agreement is observed with PNNL database.

- [1] A. Perrin, D. Jacquemart, F. Kwabia Tchana, N. Lacome. Journal of Quantitative Spectroscopy and Radiative Transfer (in press)

ASSESSMENT OF THE CARBON BALANCE OF FOREST ECOSYSTEMS WITH THE LASER CONTROL OF $^{13}\text{CO}_2$ ISOTOPIC TRACERS

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Recently, the ecology- and environmental protection-related researches make an ever-growing use of isotopic methods. While changes of the isotope composition of atmospheric gases have been studied (including TDLS methods) for a fairly long time, presently, the isotope composition of living organisms, plants, soil, water of rivers, seas and oceans is already under study. Biological fractionation of isotopes, carbon in particular, can be indicative of the dynamics of the ecological tension rise in the regions [1]. The extent of the isotope composition variation of a number of elements can provide a quantitative characteristic of the environmental pollution level. The recent years saw the use of isotopic tracers, in addition to measurements of isotopic composition drifts, for the researches of the dynamics of the environmental processes. The basic exchange processes occurring in forest ecosystems, such as photosynthesis, photorespiration, or breathing, produce an appreciable effect on the carbon isotope composition of atmospheric carbon dioxide. The carbon isotope composition of the biomass has the isotope composition of -25 35 ‰ owing to the predominant ^{12}C absorption in the course of photosynthesis. The photorespiration isotope effect returns CO_2 with the heavier isotope composition into the environment than that of carbon of the biomass, i.e., 20-30 ‰. The processes proceeding in soil also cause the supply of CO_2 into the environment with the isotope composition close to the isotope composition of carbon of the biomass. Consequently, taking measurements of the carbon dioxide isotope ratio and its concentration at 3-4 altitudes at different hours of the day provides the means of ascertaining the CO_2 sources or drains immediately in a forest and of assessing their average contribution into the total carbon balance.

The paper offers the experimental results of isotopic tracer injection during plant nutrition with enriched $^{13}\text{CO}_2$, the data on isotopic tracer distribution over various parts of plants, and the time history of the isotope composition dynamics. Besides, preliminary data is cited on a comparative study of the isotope composition of biomass carbon with a diode laser spectrometer based on VCSEL ($\lambda=2004$ nm), a Herriot multipass cell ($L_{\Sigma}=15$ m) and a HeliView mass-spectrometer. A conclusion has been drawn from the measurement results that sensitivity of a laser spectrometer practically matches that of a mass-spectrometer (0.1 ‰) and makes 0.2 ± 0.05 ‰. Feasibilities of using a laser spectrometer both in laboratory studies and for field measurements are discussed.

WAVELENGTH MODULATION SPECTROSCOPY: QUANTITATIVE ANALYSIS OF EXPERIMENTAL SPECTRA

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For almost 30 years, various laser-based methods have been developed for highly sensitive detection of trace gases. These techniques include direct absorption spectroscopy using long-path multipass cells, wavelength- and frequency-modulation and cavity-enhanced spectroscopies. In our work we focus on wavelength modulation spectroscopy (WMS) and, in particular, on data processing for quantitative analysis of gas absorption spectra.

Here we propose an innovative approach based on processing of a dc signal and the first harmonic (first Fourier coefficient) of the corresponding ac signal obtained with WMS. The *ansatz* is based on a concurrent modeling of the background dc and ac signals that leads to an analytical expression for the background dc signal and for the ratio $\delta\nu/A$ (where $\delta\nu$ - modulation amplitude, A - constant). By fitting the first harmonic of the ac signal unique values for line parameters (line strength and line width) and the constant A are readily obtained. Notably, the constant A appears twofold: first, any Fourier coefficient of ac signal should be divided by this constant; and second, A is found in the exponent of the Lambert-Beer's law, multiplicative to the absorbance. A does not depend on the modulation amplitude and is only a function of the modulation frequency ω . The constant reaches unity at very small modulation frequencies (\sim several Hz) and steadily decreases with increasing ω .

It is demonstrated that the data processing is capable for quantitative analysis. The advantage of this new approach is that absolute values for line parameters and gas concentration are obtained (with experimental uncertainties less than 0.1%), without need of reference measurements. Measurement of two absorption lines, corresponding to different isotopologues, will enable isotopic ratio determination with an error of less than 1‰.

Control of the laser emission frequency is very crucial. In order to get precise measurements the DFB laser temperature should be highly stabilized. It is noted that the study was performed with DFB lasers working around 1.6 μm , but the proposed approach can be easily applied to spectroscopy with other near and mid infrared lasers.

IMPROVEMENT OF ISOTOPIC COMPOSITION MEASUREMENTS OF ATMOSPHERIC CO₂ USING CORRELATIONS BETWEEN THE REFERENCE AND THE MEASUREMENT CELL

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We have recently developed a tunable diode laser spectrometer, named SIMCO [1] (Spectrometer for Isotopic Measurements of CO₂) to measure the ¹³CO₂ and ¹²CO₂ concentrations in atmospheric air. This instrument is based on direct absorption spectroscopy and uses one absorption line for each isotope near 2291.6 cm⁻¹ to determine the concentrations by fitting the line profiles. To be really useful for atmospheric purposes, the isotopic composition $\delta^{13}\text{CO}_2$ has to be measured with a high level accuracy (better than 0.2‰) at a frequency faster than one measurement per minute. To achieve such a goal we need to alternate quickly (20 s - 20 s) the measured gas (here from a tank) with a calibration gas. The existing correlations between measurements of this calibration gas (passing through the sample cell; here a multipass Herriott cell) and the reference cell (static in the present case) are used to correct retrieved concentrations from short and long term fluctuations of the instrument. A correction method using the correlation between sample and reference seems to provide very precise results as compared to the simpler correction initially implemented. Thanks to this new method, we have achieved $\delta^{13}\text{CO}_2$ measurements with an accuracy of 0.3‰ (see Fig 1) for an integration period of 40 s, a value quite comparable to the atmospheric requirements.

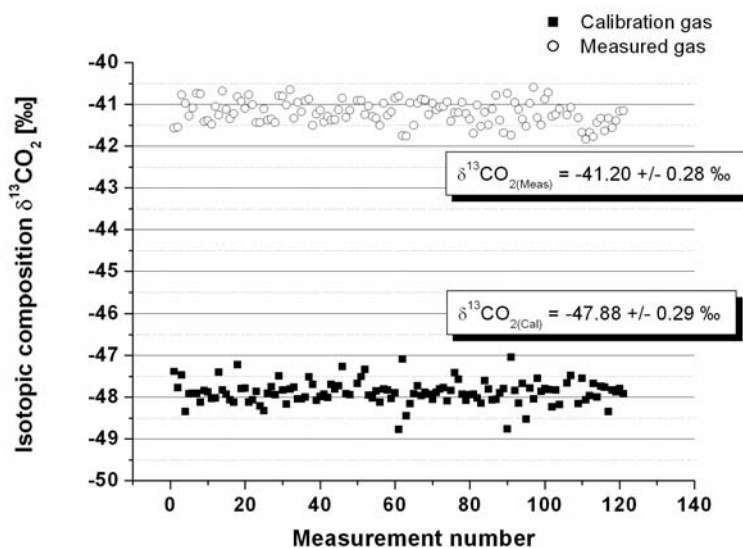


Fig 1. Measured isotopic composition from a tank (air + 422.91 ppmv of CO₂; $\delta^{13}\text{CO}_2 = -40.90\text{‰}$) using a calibration gas (air + 366.61 ppmv of CO₂; $\delta^{13}\text{CO}_2 = -47.92\text{‰}$) and the correlation method
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Multi-mode Absorption Spectroscopy of Oxygen using wavelength modulation and cavity enhanced techniques

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Multi-mode Absorption Spectroscopy, MUMAS, is a new technique offering simultaneously high spectral resolution and wide spectral coverage.[1] The method uses measurement of transmission through gas samples of radiation from a multi-mode diode laser or micro-cavity laser [2] that varies in time as the modes of the laser are scanned over only one mode-spacing. Measurement of multiple spectral lines over the relatively wide range is thus possible using a single laser and a single detector. Molecular concentration, temperature and pressure can be derived from fits to the MUMAS signature.[3]

We present results demonstrating improved signal to noise capability of MUMAS using wavelength modulation spectroscopy, WMS, and Cavity Enhanced Absorption Spectroscopy, CEAS. WMS at 1.83 kHz was applied whilst scanning the laser modes at 1 Hz for O₂ and air in a White Cell from 0 to 1 bar pressure giving an effective path of 21 m. CEAS was applied using an open cavity in air with cavity mirrors that were not optimized for the diode wavelength used. Nonetheless, S/N of > 220 for WMS and > 280 for CEAS/WMS were obtained for 2*f* detection indicating that significant further improvements to MUMAS sensitivity is possible using these techniques.

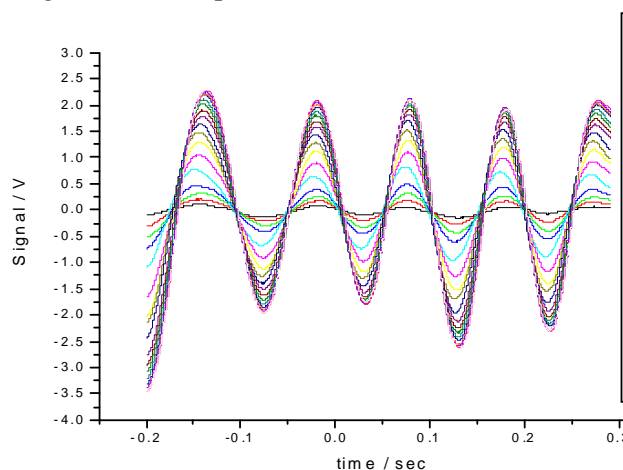


Fig. 1 WMS 2*f* spectra of MUMAS signature from O₂ near 760 nm recorded for O₂ pressures between 6 and 760 mbar.

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[2] Y. Arita and P. Ewart, Optics Express, Vol. 16, Issue 7, 4437-4442 (2008)

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OPTIMISING THE USE OF INTEGRATING SPHERES AS GAS CELLS FOR TDLS

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Integrating spheres are of great interest for use as optical absorption cells in tunable diode laser spectroscopy [1, 2]. Light entering the sphere is scattered by the internal walls with high diffuse reflectivity. After a few passes across the cell to remove the local effects of launch geometry, the irradiance over the surface is uniform. Compared with standard multipass optical cells such as White, Herriott or Chernin cells, integrating spheres offer long pathlengths without the need for precise alignment of the laser beam. Figure 2 shows a simplified model.

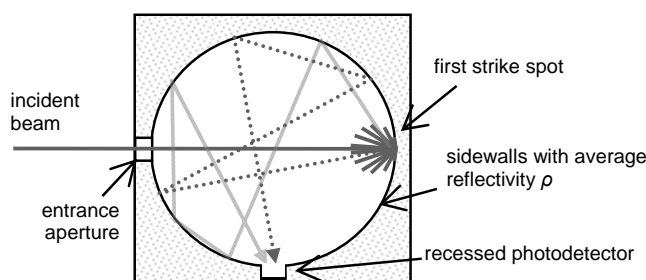


Figure 2. Simplified model of an integrating sphere, showing the incident beam making a first pass across the cell to the first strike spot and subsequent random multiple passes across the cell.

Although etalon – based interference fringes do not arise in integrating spheres, other potential issues exist, as follows;

- (i) At high concentration, randomised multiple pathlengths create a nonlinear response with an apparent deviation from Beer's Law. We have modelled this and show good agreement between our predictions and experimental data.
- (ii) If a laser diode is placed close to the entrance aperture, self mixing interference fringes will result from feedback from the first strike spot. If not removed, these fringes are the limiting source of measurement uncertainty.
- (iii) Random noise on the detector can result from the appearance of laser speckle [3]. Compared to conventional geometries, the situation is potentially complicated by multiple pathlengths and multiple virtual sources of illumination. We have imaged speckle fields inside integrating spheres and quantified the resulting noise levels for TDLS.

Testing with methane shows that, so long as these effects are understood and minimised, a performance improvement can be realised resulting from the increased optical pathlength.

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FIRST EVALUATION OF QUARTZ ENHANCED PHOTOACOUSTIC SPECTROSCOPY WITH A GASB BASED LASER DIODE EMITTING AT 2.3 μ .

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Quartz enhanced photoacoustic spectroscopy has first been proposed in 2002 by A. Kosterev [1]. This technique was a new method for gas detection inspired by photoacoustic spectroscopy but utilizing a very cheap detector which is the quartz tuning fork (QTF).

Ever since this date, it has shown both simplicity and performance, due to the use of many different semiconductor devices, from telecom to quantum cascade lasers [2].

Antimonide based laser diodes emitting around 2.3 μm [3] have been many used in spectroscopy. This wavelength region is particularly interesting because many species of industrial interest show strong absorption lines in an atmosphere transmission window.

We present here the preliminary experimental results on CH_4 detection (a few percents) at atmospheric pressure obtained with a GaSb based laser. The setup (fig. 1) is constituted by a laser emitting around 2.3 μm modulated at half the QTF resonant frequency (2f detection), a CaF_2 lens to focalize the laser beam between the two prongs of the QTF, a gas cell that contains the QTF, and a transimpedance amplifier used to convert into a voltage the QTF generated piezoelectric current.

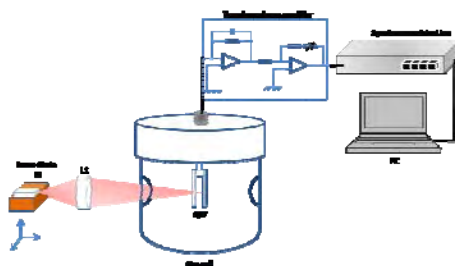


Fig. 1. Optical bench.

After a work on the optimization of experimental parameters, we plan to adapt this setup to the use of devices at longer wavelengths developed in the IES emitting above 3 μm . This work is supported by the Languedoc-Roussillon region and the ADEME (French Environment and Energy Management Agency).

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DEVELOPMENT OF EXPERIMENTAL TECHNIQUE FOR MEASUREMENTS OF TEMPERATURE AND WATER VAPOR CONCENTRATION IN A HOT ZONE

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TDL absorption techniques for simultaneous measurements of gas concentration and temperature in hot zones have been presented by several groups (for example, [1, 2] and references therein). We developed a single-DL approach and appropriate instrumentation for the optical thermometry of plasma-assisted combustion in air-fuel supersonic flow, ignited and sustained in experimental aerodynamic tube, characterized by rather strong fluctuations, vibrations and different optical and electrical noises.

The computer program was written for selection of the optimal pairs of absorption lines in the 1.3-1.4 μm region, which could provide the best signal-to-noise ratio for measurements in the temperature range 300 – 2000 K.

The fiber coupled DFB diode laser NLK1E5GAA from NEL generating in the 1.39 μm range was used. The following absorption lines of H_2O were selected: 7189.344 cm^{-1} ($E'' = 142 \text{ cm}^{-1}$), 7189.541 cm^{-1} ($E'' = 1255 \text{ cm}^{-1}$), 7189.715 cm^{-1} ($E'' = 2005 \text{ cm}^{-1}$). Relatively high intensities of the selected lines enabled detection of the direct absorption. To compensate for the intensity variations of the probing laser beam not connected with the absorption (intensity ramp, low frequency random amplitude modulation, technical noise, etc.) differential detection scheme was developed. The DL beam was divided to two approximately equal parts by optical multiplexer connected with the single mode fibers. One fiber routed the half of the beam to the test object; the second fiber routed the second half directly to the photodetector in the reference channel. Each fiber was coupled with the commercial gradient collimator. The developed scheme equalizes the signals in both channels and makes the baseline in the differential channel as flat as possible, thus enables to use simple 8-bit ADCs.

Signals were recorded by the two-channel digital oscilloscope Agilent 54621A. In one channel the signal of the differential scheme was detected, in the second channel - the DL intensity. In each channel 2×10^6 points were recorded and stored during a single supersonic flow pulse of about 500 ms. At first step of data processing the detected transient absorption spectra were transformed into 2D image. This procedure greatly simplified the general overview of data and selection of the most important periods of process evolution. Digital processing of 2D images was based on ImageJ [3], the free, open source program.

Different methods of retrieving hot zone parameters (temperature, total pressure and water vapor concentration) will be discussed and compared.

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An investigation of TDLS modulation schemes as applied to the Mid-IR spectral region by difference frequency generation in PPLN

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Tunable diode laser spectroscopy (TDLS) detection schemes have been widely investigated [1,2] in the near-IR due to the presence of overtone absorption lines in the species of interest and the availability of lasers which operate in the region. However, overtone lines are much weaker than their fundamental absorption line counterparts which, for many species, lie in the Mid-IR. Traditionally the 3-5 μ m wavelength region has been addressed by lead-salt lasers, but this technology does not lend itself easily to the implementation of TDLS modulation schemes. This paper presents an investigation of TDLS measurements using a system based on difference frequency generation (DFG), in periodically poled lithium niobate (PPLN), which has been used to address fundamental absorption lines of methane (CH₄) in the 3.4 μ m region.

The DFG system combines the outputs of two easily obtainable near-IR lasers in a fibre system for delivery to the PPLN crystal. This allows the TDLS modulations to be applied to the Signal wavelength source (1547nm DFB laser) while the Pump source (1064nm Bragg stabilised laser diode) is held static in power and wavelength. The TDLS modulation is therefore transferred to the Idler (3404nm) for interaction with the absorption line(s) of interest.

The configuration of the DFG system will be shown, detailing the main design features and sub-systems used to implement TDLS spectroscopy in the Mid-IR. Investigations of wavelength referenced direct detection and traditional 1f and 2f detection schemes will be presented; showing that the modulation indices found to maximize the measurable waveform parameters in Near-IR systems translate to this DFG-based Mid-IR system. In addition, an investigation of calibration free techniques such as the RAM method [3] and PDM [4] using the DFG system will be presented to provide a preliminary comparison with the detection sensitivities of the same techniques as applied in the Near-IR.

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C14

Measurement of water vapor D/H and $^{18}\text{O}/^{16}\text{O}$, $^{17}\text{O}/^{16}\text{O}$ isotope ratios by laser absorption spectroscopy at 2.73 μm and application to human breath analysis

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Abstract

We report on the measurements of water vapor D/H and $^{18}\text{O}/^{16}\text{O}$, $^{17}\text{O}/^{16}\text{O}$ isotope ratios by laser-based direct absorption spectroscopy near 2.73 μm . The spectrometer was then employed to measure the absorption spectra of exhaled water vapor for simultaneous determination of oxygen isotope ratios in human breath.

ABSOLUTE DIODE LASER-BASED *IN SITU* DETECTION OF HCl AND H₂O IN GASIFICATION PROCESSES

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The volumetric content of HCl and H₂O are important parameters for industrial combustion and gasification processes. HCl is of particular importance due to the problem of chlorine corrosion in technical combustion plants. A fast and accurate detection of HCl and H₂O by extractive methods is rather difficult due to soot contamination and condensation in the gasification processes. Here, *in situ* tunable diode laser absorption spectroscopy (TDLAS) offers an absolute and sampling-free measurement with high temporal resolution, excellent selectivity and sensitivity even under complex high temperature conditions [1,2].

To develop an absolute *in situ* HCl and H₂O spectrometer a special line selection software was used to determine optimal spectral areas for each of the two species [3]. For HCl the R3-line in the first HCl overtone at 1.742μm was chosen due to a good line strength also at high temperatures and the minimized cross-sensitivity to CO₂ and H₂O. For the detection of H₂O the (16 5 11 - 15 5 10) transition at 1.740μm was used due to the advantageous temperature dependence of the line strength. With a significant absorbance only at high temperatures this line allows measurements without the need for purging the areas adjacent to the measuring path itself. A specially selected vertical cavity surface emitting laser (VCSEL) permitted the setup of a highly sensitive diode laser absorption spectrometer that allowed measuring both species sequentially with one single spectrometer. The static and dynamic characteristics of the laser were determined accurately to enable an absolute and calibration-free measurement.

The spectrometer was successfully applied to the *in situ* HCl/H₂O detection in the reaction chamber of the Research Entrained Flow Gasifier, REGA, at the Forschungszentrum Karlsruhe. HCl could be detected with an optical resolution of $2.3 \cdot 10^{-4}$ OD (1σ) at a 1 sec. time resolution. With a reactor diameter of 0.28 m and temperatures up to 1100°C this permitted a HCl-detection limit of 125 ppm (35 ppm·m·Hz^{-0.5}). For H₂O the optical resolution was $1.9 \cdot 10^{-4}$ OD (1σ) at a 1 sec. time resolution i.e. a detection limit of 460 ppm (130 ppm·m·Hz^{-0.5}).

The presentation will discuss the setup and the characterization of the spectrometer as well as the results of the first *in situ* application.

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SPECTROSCOPIC LINE PARAMETERS OF CO₂ BY DIODE LASER SPECTROSCOPY NEAR 2 μ m FOR FUTURE SPACE-BASED DIAL APPLICATIONS

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Carbon dioxide has been identified as a key greenhouse gas due to its significant contribution to global warming and climate change. The relevant measurements to understand the processes that direct the carbon cycle are a crucial stake for the scientific community. Limitations in our current understanding of carbon cycle limit our capacity to predict future evolution of atmospheric CO₂ and global temperature on the Earth. These limitations are mostly due to our incapacity to localize and quantify in a proper way CO₂ surface sources and sinks. The possibility of a pulsed Differential Absorption Lidar (DIAL) active technique using echo from the ground appears as a promising technology for global monitoring of CO₂ from space. In order to infer accurate surface fluxes, atmospheric CO₂ concentration should be determined with a 1 ppm precision in integrated content over a total column. Such a measurement is very demanding for a DIAL instrument (especially on spectral properties of the laser source), but also needs for very accurate knowledge of spectroscopic parameters of the CO₂ absorption line chosen.

Firstly, simulations leading to the selection of the more appropriate line and the influence of spectroscopic parameters on CO₂ concentrations restitution are presented. In a second part, the determination of this spectroscopic parameters: intensity, air-broadening coefficient and its temperature dependence coefficient η of particular lines are presented with a precision never reached before. This experiment is conducted using a Diode Laser Spectrometer (DLS) using a DFB Nanoplus GmbH laser diode whose emitting frequency is around 2051 nm. These results exhibit significant improvement compared to the main spectroscopic database and are of significant importance as the global active sensing of CO₂ seems of major interest.

Poster session D

D1

Baseline in TDLS investigation and suppression

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Baseline plays key role for trace molecules detection using Tunable Diode Laser Spectroscopy (TDLS). For the first time for author knowledge it was mentioned in [1]. Baseline fundamental physical origin was proposed in [2]. Baseline in DL frequency tuning was investigated in [3]. In present paper investigation of several baseline formation mechanisms will be presented. When origin is known strategy of baseline suppression can be developed.

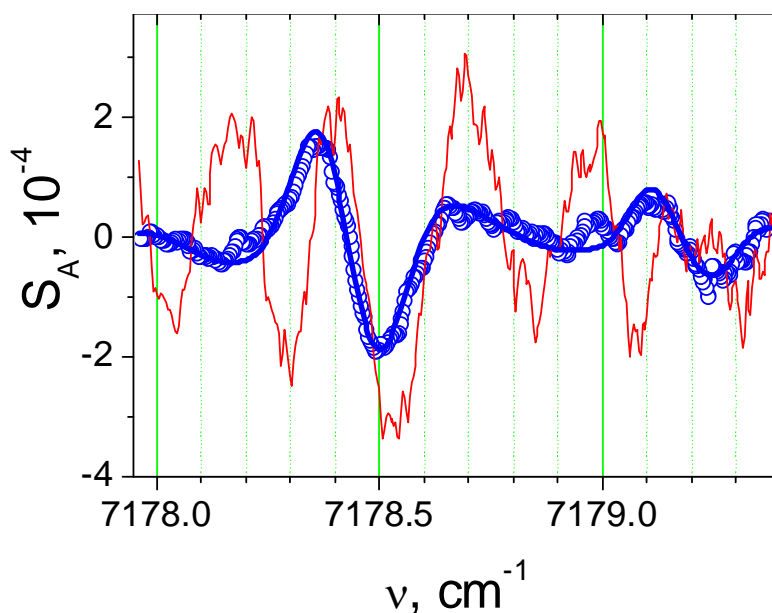


Fig.1 Trace water line detection in atmosphere.

Traditional approach (thin line) is limited by baseline. After baseline suppression weak water lines in atmosphere (circles) can be observed with good S/N ratio.

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D2

Accuracy in TDLS. TDLS as gas mixtures primary standard

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Accuracy is one of recent challenges for Tunable Diode Laser Spectroscopy (TDLS). Several TDLS applications require measurement accuracy at level 0.1 – 0.01 %. This accuracy is necessary for: UF₆ enrichment, isotope ratio (¹³C/¹²C, ¹⁸O/¹⁶O, D/H, ...), green house gases concentration (global climate changing), gas mixture standards development, screening medical diagnostics, etc.

Several error mechanisms of accurate measurements in TDLS were considered:

- Bouguer law correction due to rest gas influence on DL radiation interaction with molecule under investigation.
- Weak lines of hot bands, isotopomers, and atmosphere molecules presence.
- Line shape model using in fitting.
- Spectral lines mixing effect.
- Presence of spontaneous emission.
- DL emission spectrum.
- Baseline.
- Molecular gas non-ideal behavior.

When all error mechanisms mentioned above were identified, investigated, and suppressed, required accuracy can be achieved.

Possibility to achieve 10⁻³ accuracy for spectral line measurements in TDLS was demonstrated. Based on achieved accuracy and analysis performed, TDLS can be considered as high accurate primary standard for gas mixtures.

D3

TDLs instrument development for medical screening diagnostics

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Idea to use concentration of different molecules for medical diagnostics has long term history. We've started this work more than 15 years ago [1]. Many groups are working in this direction and obtained very interesting results. However, this approach continues to be in Labs, not in clinics. It considers one instrument (molecule) for one disease, for one specialist. It is cost non-effective.

Here we'd like to consider alternative approach. Human body is complicated optimized system. Any disease will remove it from equilibrium and can be detected. Example: temperature. All human has equilibrium temperature 36.6°C. Temperature change by 1°C (0.3 %) is disease signature. Similar is true for trace molecules concentration in blood. In equilibrium they have some value. Disease presence will shift equilibrium leading to significant change of trace molecules concentration in blood. The goal is to determine markers than can be used for screening medical diagnostics.

Human body is energetic system. Similar to explosives (see A1) ammonia can be considered as marker for very complicated processes from nitrogen in food to ammonia in blood. Any diseases in body subsystems involved in this complicated process will lead to ammonia concentration variation in blood.

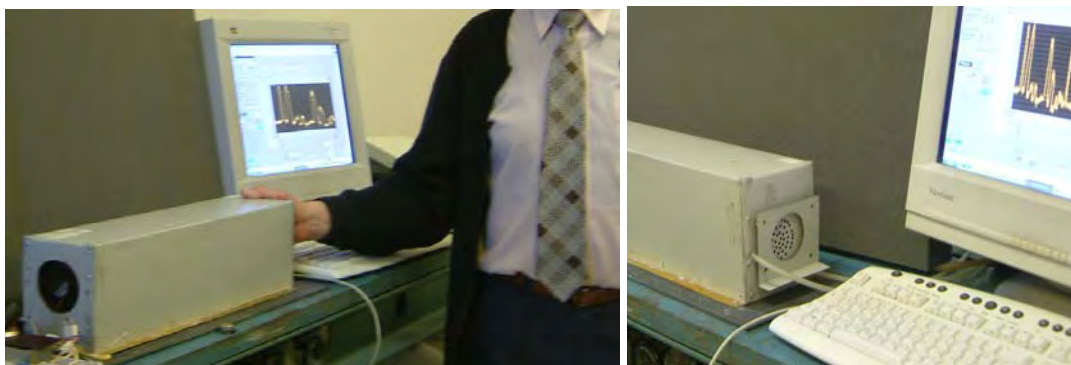


Fig.1 View of laboratory prototype developed and patient medical screening

In present poster we'll present laboratory prototype development (Fig.1) for medical screening diagnostics from palm using ammonia as signature. The prototype structure, its optimization and calibration will be considered.

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Tunable Diode Laser Spectroscopy with Optimum Nonlinear Wavelength Scanning

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Usually in direct spectroscopy or Wavelength Modulation Spectroscopy (WMS) the wavelength is linearly ramped to scan the gas absorption. In WMS the modulation index $m = \Delta\lambda/a_L$ is typically set to 2.2 aiming at the highest signal peak [1]. However, the signal to noise ratio (SNR) on the estimated gas concentration is not always optimized because the scanned signal form is not optimized. The signal form can be varied by nonlinear wavelength scanning and by varying m if the harmonic spectrum is detected. We present a universal criterion to determine the optimized signal form and - if WMS is applied - the optimized m .

If a linear least square curve fit is performed, the variance of the estimated parameter is proportional to the white noise variance on measurement data σ^2 : $\text{var}(\hat{p}_1) = ((\Phi^T \Phi)^{-1})_{11} \sigma^2$ with the model matrix $\Phi = (\phi_1; \phi_2; \dots)$ consisting of the linear components of the measurement spectrum e.g. gas absorptions, spectral baseline (offset/slope) and optional derivatives of the

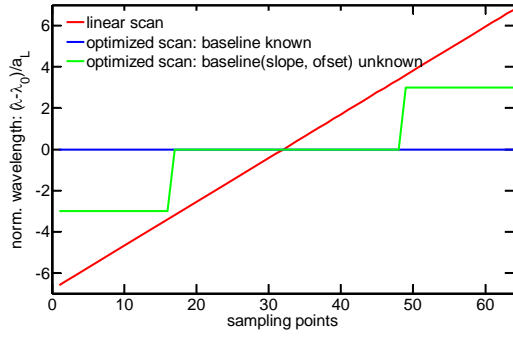


Fig. 3: Conventional linear wavelength scan (red) and optimum wavelength scanning function, if the spectral baseline is known: maximum sampling with $m_{\text{opt}} = 2.2$, (blue). Minimum and Maximum scanning ($N/4$: “left min.”, $N/2$: “max”, $N/4$: “min right” with $m_{\text{opt}} = 3.09$) is optimum if the slope and offset of the baseline is unknown (green). If other linear components e.g. interfering gas absorptions are included in the model, the optimum wavelength scanning function is obtained by numerical optimization.

spectral model with respect to non-linear parameters (i.e. a linearized general model). The scanning wavelength function and m have influence on $((\Phi^T \Phi)^{-1})_{11}$ and are therefore varied to maximize the SNR on the estimated gas concentration. The amplitude of the measured spectrum (second harmonic or transmission) is not a measure how good the concentration estimation is, since the curve fit gives - due to the different shapes of the spectra - different SNR improvements. This general theory enables a direct comparison between direct spectroscopy and WMS. If the spectral baseline (slope/offset) is unknown, the SNR of the concentration is increased by 30% and 70% by using the optimum scanning strategy (Fig. 3) for WMS and direct spectroscopy, respectively. If other interfering gas absorptions or a baseline with fringes is taken into consideration in the model, optimum wavelength scanning functions are obtained by numerical optimization.

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D5

APPLICATION OF MID-INFRARED AND NEAR-INFRARED DIODE LASER SPECTROSCOPY TO THERMAL AND PLASMA-ENHANCED CVD

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Atmospheric pressure chemical vapour deposition (CVD), both thermal and plasma-enhanced (PE-CVD), are used for growing thin films such as tin oxide which is a transparent conducting oxide used in low-emissivity glazing and solar cells. Non-thermal plasmas combined with CVD enable coating onto heat sensitive substrates. This work describes the application of near-infrared and mid-infrared diode laser absorption spectroscopy to the study of such industrially important processes.

In one example, a near-infrared diode laser operating at around 1742 nm is used to spatially monitor HCl produced in the thermal CVD reaction of dimethyl tin dichloride and oxygen. 3D mapping of the active region is feasible and this has already proven useful for both new coating head designs and for correlating with film properties [1].

In a second study, silica films used as a barrier layer have been produced by atmospheric pressure PE-CVD from TEOS and DDS. A mid-infrared lead-salt diode laser [2] has been used in an in situ arrangement to monitor the CO produced in the precursor oxidation. Additionally, a parametric study involving in line FTIR and in situ near-infrared diode laser measurements, as well as optical emission spectroscopy has been used to produce a response surface model that relates gas concentrations and electrical parameters with film growth and film hardness [3]. Recent work has involved a cw room temperature quantum cascade laser for the CO measurements [4].

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TDLS APPROACH TO A STUDY OF ABSORPTION LINE PROFILES OF HF MOLECULES IN THE ENVIRONMENT OF STRONG INTERMOLECULAR INTERACTIONS

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The paper discusses the results of a study of pure HF line profiles and those of its mixture with different gases (Ar, UF₆, F₂, etc.). To this aim, use was made of a specially designed TDLS system which incorporated a DL module consisting of a tunable DL with distributed feedback (DFB-DL) and fiber radiation outlet oscillating in the vicinity of the wavelengths of $\lambda=1.283\ \mu\text{m}$ (2-0 line of R0 HF). InGaAs photodiodes of the “Hamamatsu” G8373 series with the NEP (noise equivalent power) value better than $10^{-12}\ \text{W/Hz}^{1/2}$ were used as photodetectors. A self-broadening coefficient for pure HF and collisional broadening coefficients in its mixtures with the mentioned gases have been derived from the experimental HF spectra.

Analysis is made of spectroscopic modeling possibilities for problems of HF quantitative analysis with the use of Voigt, Galatry and Rautian-Sobelman profiles with regard for the Dicke effect, etc [1]. Outlooks of further improvement of the assessment procedure of HF concentration in open atmosphere are discussed.

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DIODE LASER SPECTROSCOPY USING A CALIBRATION FREE PHASOR DECOMPOSITION APPROACH WITH RAM NULLING

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A limiting factor of tunable diode laser spectroscopy (TDLS) analysis is the large unwanted residual amplitude modulation (RAM) background present on the recovered 1st harmonic signal. A novel approach to remove the background RAM will be presented. This new technique will be used alongside the phasor decomposition method (PDM) [1], a calibration free technique for recovery of the absolute gas absorption line-shape. The RAM nulling method developed, successfully removes the background by optical cancellation. This is achieved by placing a fibre delay line, which introduces a π phase change in the modulation signal, in parallel with the gas cell line. When these lines are coupled together the background signals are at anti-phase and hence cancel each other. The main benefit being that measurement sensitivity can be increased. Results illustrating RAM nulling whilst using the PDM technique for absorption line-shape recovery will be presented. Figure 1 shows a recorded PDM measurement illustrating the difference with and without RAM Nulling.

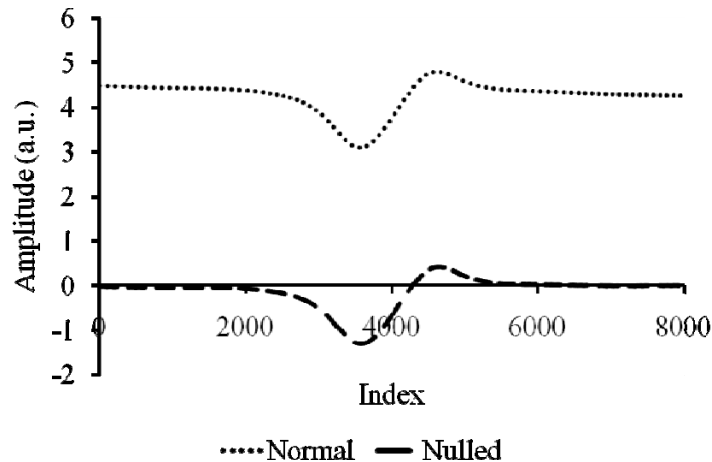


Fig.1 Mixed AM/FM signal with and without RAM nulling – 10.13%CH₄:N₂ @ 1.003Bar

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TEMPERATURE AND CURRENT COEFFICIENT OF LASING WAVELENGTH ON TUNABLE DIODE LASER SPECTROSCOPY

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The lasing wavelength of laser diodes is controlled by ambient temperature and injected current in TDLS. This paper discusses the physical mechanisms of temperature and current control of the lasing wavelength for TDLS.

Several kinds of Fabry-Perot and DFB laser diodes that lased at 1300, 1550, and 2006 nm were used in this study. For CO₂ gas sensing, the 2006-nm-band lasing light was collimated with a lens and passed through a gas cell filled with CO₂ gas (at atmospheric pressure). The optical signal was directly detected with a photodiode without any amplifier. The ambient temperature or current injected to the laser diode was changed by a 0.2°C- or 2-mA-step during gas monitoring.

The temperature and current coefficient of wavelength and absorption peak wavelength varied with the time interval of monitoring after changing the temperature or current. Their coefficients were, however, kept at fixed values if the time interval of monitoring were fixed at the same values. Lasing wavelength varies with temperature change due to the change in ambient temperature or Joule heating resulting from current injection. The rate of temperature change in the active layer depends on a transient phenomenon. Figure 1 shows the active layer temperature increase as a function of the current pulse width. The Joule heating gradually diffuses towards the outside of the active layer [1]. This behavior is closely connected to the rate and range of wavelength change under current modulation (see Figure 2). The heat is inversely transmitted from the ambient to the active layer of the laser diode when the ambient temperature changes. It is important to fix the time interval of monitoring after changing the ambient temperature or injected current.

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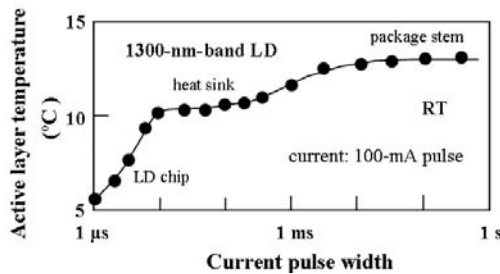


Fig.1 Active layer temperature change as a function of current pulse width.

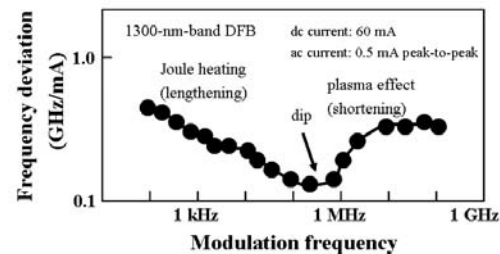


Fig.2 Wavelength (frequency) change as a function of modulation frequency.

D9

Improvements in Precision and Absorption Path Length for Low Temperature Absorption Spectroscopy and Collisional Cooling Experiments

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The first tunable diode Infrared collisional cooling results on a CH₃F Q branch, based upon the technology developed by De Lucia and co workers for the microwave, were reported in 1995, using first derivative spectra to show the results. Peak absorption for these spectral features was less than 0.75% transmission with an absorption path length of 4 centimeters. It became obvious that only strong absorbers could be studied with such short absorption paths, so, subsequently, a number of results were published with CO low J transitions using absorption paths of 4 to 20 centimeters.

Recently we reported results on CH₄ using an all copper Herriot design where, in addition to the cell body, the mirrors were also fabricated from copper and gold coated. The base length (separation of the mirrors) of this cell is 14.039 centimeters and the total path inside the cavity is 5.3348 meters.

These studies led to the determination of the first infrared measurements of temperature dependent Dicke narrowing, measurements of temperature dependent pressure shifts, temperature dependent line mixing and non linear temperature dependence of pressure broadening.

We recently optimized the 5.3 meter Herriott cell to achieve 12.8 meter absorption paths with a mirror separation of 16.866 centimeters. Using 10.4 centimeter diameter mirrors we recently achieved absorption path lengths in excess of 28 meters. We have achieved an increase of absorption path length by a factor in excess of 11000. This poster reviews recent developments as well as highlighting the developments in this area over the past 15 years (coinciding with the history of this conference).

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GAS ABSORPTION CELLS FOR TDLS EMPLOYING OPTICAL DIFFUSERS

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Many TDLS systems are limited by interference fringes formed by unintentional Fabry-Perot etalons between the source and detector [1], often involving reflections from gas cell windows [2]. The fringe spacing can be in the same wavelength range as gas absorption linewidths, which can distort or obscure the absorption line. Design techniques to reduce etalon formation include; the use of optical isolators, use of reflective rather than refractive optics, angling and antireflection (AR) coating of surfaces [3]. Techniques for reducing the amplitude of the fringe signal include mechanical oscillation of components [1], use of an additional laser diode modulation [4], use of alternative waveforms [5] and postdetection filtering [6].

The alignment of the optical components such as angled windows is often critical. Tight tolerances on component alignment can cause manufacturing difficulties and can be difficult to maintain in field instruments. In this study we have explored the use of optical diffusers in gas cells as a means of (a) reducing optical interference fringes, and (b) making gas cells that are insensitive to misalignment, giving simpler manufacturing processes and greater field stability.

We have compared different cell geometries side by side, calculating the resulting levels of objective and subjective speckle noise. The best design has been built experimentally and compared to a conventional transmission cell that uses angled, wedged and AR coated windows, both cells having an optical pathlength of 10cm. Testing was performed with methane in air, using 2f wavelength modulation spectroscopy at 1651nm, with a 1s response time. The results show that although the short-term limit of detection (1σ) achieved using the new cell (11 ppm) was slightly inferior to the conventional design (3 ppm), its longer term stability was superior. We also present two techniques with potential to improve detection limits still further, by rotating or vibrating the diffuser in the gas cell, which has the effect of averaging over multiple speckles, reducing speckle – related uncertainty.

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MEASUREMENTS OF THE O₂-BROADENING COEFFICIENTS OF LINES IN THE ν_9 BAND OF C₂H₆ BY DIODE-LASER SPECTROSCOPY

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Ethane is an important molecule in the atmosphere of the Earth [1], Titan [2], the giants planets [3-4], and comets [5]. To retrieve C₂H₆ abundances in these environments using remote sensing techniques, accurate reference spectroscopic line parameters are needed. The present work is concerned with the measurement of collisional broadening coefficients at very high resolution.

Only few measurements of the collisional broadening coefficients of ethane have been performed. Particularly, Blass et al. [6] measured the self- and N₂-broadenings in the ν_9 band, and Pine et al. [7] determined the air-broadening coefficients in the ν_7 band. More recently, our team measured self- and N₂-broadening coefficients in the ν_9 band [8-9]. However, it is the first time that these coefficients are measured for the ethane-oxygen mixture.

In the present work, we measured the O₂-broadening coefficients of absorption lines in the ν_9 band of ethane at room temperature, using a tunable diode-laser spectrometer [10]. For each line under study, we recorded spectra at 5 or 10 pressures of oxygen comprised between 3 and 21 mbar. The line profiles were individually fitted, at each pressure, with two line shape models: the Voigt profile and the Rautian and Sobel'man model which includes the Dicke narrowing. From these fits, we obtained the collisional half-widths at each pressure and then determined accurately the O₂-broadening coefficients.

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TDL MEASUREMENTS OF TEMPERATURE AND WATER VAPOR CONCENTRATION IN A COMBUSTION ZONE OF SUPERSONIC AIR-FUEL FLOWS

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The developed technique was applied for detection of temperature, static pressure and water vapor concentration in the post-combustion zone of the closed-type section of the supersonic aerodynamic tube. Mach number of the flow in duct was $M = 2$, static pressure in flow $P_{st}=150\text{-}300$ Torr, static temperature T_{st} up to 1500 K. The optical path of the testing DL beam inside the camera was 7 cm.

The combustion process in the supersonic flow was ignited and sustained by the pulsed electric discharge. Air was used as the oxidant, hydrogen or ethylene were used as the fuel. The duration of a single shot including gas flow injection, plasma ignition, combustion and cooling was about 0.5 s. The duration of the discharge pulse was 80-100 ms. The fuel injection starts 20-30 ms after plasma ignition and ends about 20-30 ms after the electric pulse is off. The duration of plasma-assisted combustion was about 80 ms.

The experimental data were registered using a single DFB laser which covered about 1 cm^{-1} in one scan. The duration of each scan was about 830 μs , thus 600 laser frequency scans were registered during the whole process of 0.5 ms.

At the first step of data processing 2D image of the transient absorption spectra was constructed. The hot zone parameters were obtained as the result of fitting of the experimental spectra by the simulated one constructed using the HITRAN and SPECTRA databases. Wavelength scale, baseline, static pressure, temperature and the concentration of water molecules in flow were the parameters of the fitting. Parameters of the post-combustion zone were measured for different conditions of air and hydrogen or ethylene fuel mixing and different geometry of electric discharge. The high signal-to-noise ratio enabled to obtain the temporal behavior of temperature with the resolution of ~ 1 ms. Precision of the temperature evaluation was estimated to ~ 40 K.

MID INFRARED INTERBAND CASCADE LASERS FOR SENSING APPLICATIONS

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A growing demand for mid infrared (IR) light sources (wavelength $\approx 2.5\mu\text{m} - 20\mu\text{m}$) is developing in several fields of application. Compact and reliable laser sources in this wavelength regime exhibit excellent possibilities of use for example in the military (e.g. detection of explosives [1]) and commercial (e.g. industrial process control [2]) sector, partially owing to naturally occurring atmospheric transparency windows.

The wavelength range from $3\mu\text{m} - 4\mu\text{m}$ is particularly interesting for several sensing applications, such as the detection of hydrocarbons. Existing types of semiconductor laser sources have closed in on this wavelength area ([3], [4]). However, decreasing hole confinement and increasing Auger recombination in GaSb-based type I interband diodes limit their usability towards higher wavelengths of $\approx 4\mu\text{m}$. Intersubband quantum cascade lasers (QCL) approach the mentioned wavelength range from above but suffer from fast phonon scattering losses. From both issues of the above described laser types emerges the need of a more efficient laser source in the $3\mu\text{m} - 4\mu\text{m}$ regime.

The discussed issues can be circumvented by using interband cascade lasers (ICL) [5][6]. These technologically demanding laser sources utilize optical transitions between an electron state in the conduction band and a hole state in the valence band in a cascade of Sb-based type-II QW structures. A broken-gap band edge alignment enables the tailoring of the emission wavelength by altering the cascade structures.

The ICLs presented here are a collaborative work between the university of Würzburg and nanoplus company. The lasers were grown by solid source molecular beam epitaxy on GaSb substrates and comprise 6 or more active cascades. Processing was conducted using a reactive ion etching system. Laser ridges with widths varying from $8\mu\text{m}$ to $100\mu\text{m}$ were etched deeply until below the active cascades. The structures were passivated by a several hundred nanometers thick passivation layer before evaporating the top and bottom contact. Different active zones were designed, yielding emission wavelengths covering the $3\mu\text{m} - 4\mu\text{m}$ range.

For sensitive scanning of single gas absorption lines monomode lasers are required. The feasible concept of ICL distributed feedback (DFB) lasers [7] is thus the goal aimed at to use the lasers in highly sensitive photonic sensor systems.

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MULTI-GAS SENSOR FOR FLEXIBLE OIL RISERS BASED ON QEPAS TECHNOLOGY

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Flexible oil/gas risers are multilayer pipe structures, with a plastic inner (fluid isolation) layer and metal outer layers providing the required strength capacity. The plastic layer is partially permeable for gas constituents, and these gases affect the corrosion rate of the metal layers. Continuous monitoring of the inter-layer gas composition will allow accurate predictions of the riser lifetime, extending the period between costly replacements.

Quartz enhanced photoacoustic spectroscopy [1] with near-infrared fiber coupled diode lasers was used as the basic technology for a multi-gas sensor. The advantages of this approach are: small size of the fiber coupled sensing module (spectraphone, Fig. 2), ready availability of the spectroscopic laser sources (DFB diode lasers), and high immunity to acoustic noise allowing long averaging times for enhanced sensitivity. The current sensor configuration incorporates two lasers, one MEMS based optical switch, and one spectraphone for detection of H₂S, CH₄, and CO₂, as well as miniature temperature, pressure, and humidity sensors. The achieved sensitivities, potential technological issues, and cross-influence of the species at high concentrations due to V-T relaxation effects and the speed of sound variation will be reported.



Fig. 1. Example structure of a flexible oil riser.

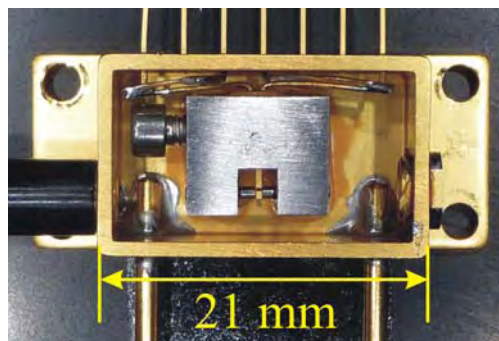


Fig. 2. Alignment-free fiber coupled QEPAS spectraphone.

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PRESSURE BROADENING OF THE H^{35}Cl R(3) ABSORPTION LINE IN THE FIRST OVERTONE AT UP TO 7 BAR

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The detection of HCl plays an important role in many issues of atmospheric chemistry as well as in combustion and gasification processes. The H^{35}Cl R(3) line in the first overtone region provides good spectroscopic characteristics for the detection of HCl at atmospheric conditions as well as in high temperature processes [1]. A sensitive measurement of the volumetric content of HCl especially in gasification processes with high process temperatures and pressures requires a precise knowledge of the spectroscopic line parameters. In particular the determination of the self and foreign broadening coefficients is of great interest because in the reference database HITRAN 2004 only the corresponding broadening coefficients of HCl with itself and with air are given [2]. Due to the discrepancy of the values for the pressure broadening coefficients and line strength between HITRAN 2004 and other authors [3] a precise measurement of these parameters was performed.

Using a new vertical cavity surface emitting laser (VCSEL) at $1.74\mu\text{m}$ with a wide current tuning range of 10 cm^{-1} a highly sensitive TDLAS spectrometer was developed to realize an analysis of the H^{35}Cl R(3) absorption line even under high pressures.

The determination of the self broadening coefficient was performed by using absorption line profiles of pure HCl in the range of 0 to 1 bar in a 10 cm gas cell. In order to evaluate the foreign broadening coefficients of HCl with other species the line strength was extracted first to correct for self broadening effects. Using these results the foreign broadening coefficients for HCl/ N_2 mixtures and HCl/ O_2 mixtures were determined for pressures from 1 to 7 bar in a special 25 cm long high pressure gas cell. All measured line profiles were fitted with the Voigt model using a non-linear Levenberg-Marquart algorithm resulting in excellent agreement between measured and fitted data. For a pressure of the HCl/ N_2 mixture of 7 bar an optical resolution of $8.5 \cdot 10^{-4}$ OD (1σ) at a 1 sec. time could be reached. With a cell diameter of 25 cm this enables a detection limit of 26 ppm ($78\text{ ppm}\cdot\text{m}\cdot\text{Hz}^{-0.5}$) and a signal-to-noise ratio of 400. For the self broadening coefficient a value of $0.21787\text{ cm}^{-1}/\text{atm}$ and for the line strength a value of $12.53 \cdot 10^{-21}\text{ cm}^{-1}/(\text{molec}\cdot\text{cm}^{-2})$ were found. With these values the foreign broadening coefficients were found to be $0.07307\text{ cm}^{-1}/\text{atm}$ for N_2 and $0.04001\text{ cm}^{-1}/\text{atm}$ for O_2 respectively. Additionally the foreign broadening coefficients of HCl with Ar, He and CO_2 were determined up to 1 bar and the measurements for these species up to 7 bar is actually in progress.

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D16

A COMPACT CO₂ SENSOR BASED ON DIODE LASER SPECTROSCOPY AT 2.7 μm FOR APPLICATIONS TO THE STUDY OF SPARKLING LIQUIDS

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From a strictly chemical point of view, champagne and sparkling wines are multicomponent hydro-alcoholic systems supersaturated with CO₂-dissolved gas molecules formed together with ethanol during the fermentation process. From the consumer point of view, the role of bubbling is indeed essential in champagne, in sparkling wines, and even in any other carbonated beverages. Without bubbles, champagne would be unrecognizable, beers and sodas would be definitely flat. However, the role of effervescence is suspected to go far beyond the solely aesthetical point of view. Actually, in enology, effervescence is believed to play a major role concerning flavor release and CO₂ discharge in glasses poured with champagne and sparkling wines. The myriad of bubbles nucleating on the flute's wall and travelling through the wine's bulk considerably enhances the perception of volatile organic compounds by considerably enhancing exchange surfaces between the wine and the atmosphere.

In order to study some of these phenomena, we report the development of an infrared laser spectrometer using commercial diode laser emitting at 2.68 μm [1]. The instrument is designed to measure CO₂ concentrations above a glass poured with a sparkling liquid. Details on the instrument design and data processing are provided. The new-generation diode lasers from Nanoplus Inc. with an emission wavelength around 3700 cm⁻¹ (2.7 μm) are suitable for monitoring carbon dioxide. The magnitude of the line strengths makes it possible to measure CO₂ with a small absorption path length. However, absorption lines were carefully selected to minimize interferences from neighboring water vapor transitions. The instrument performance allows to measure ambient CO₂ concentrations so that one can be very confident in the CO₂ concentrations measurements above the glass.

Results on the comparison of sparkling liquids such as 'Perrier' sparkling water, beer or champagne will be presented and compared to a model describing the flux of CO₂ discharging from glasses due to the contribution of bubbles [2]. Moreover we will present a study on champagne depending on the temperature of the liquid.

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Poster session E

E1

DL Frequency Tuning and Modulation by Current

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Current dependence of DL frequency was investigated both in time and frequency domains. DL frequency tuning by stepwise current pulse was measured to determine parameters of temperature diffusion equation for DL under investigation. In frequency domain harmonic modulation (100 kHz – 100 MHz) was added to excitation current. DL frequency modulation was measured using water line (left picture in Fig.1). In [1] measurements were performed only for 25 MHz modulation frequency.

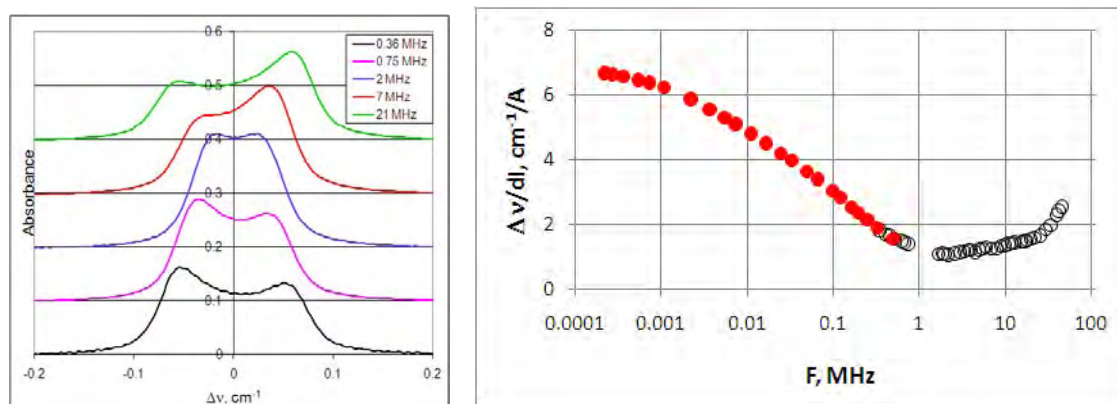


Fig.1 DL frequency modulation by excitation current

Results obtained are presented in right picture (Fig.1). Solid (time domain) and open (frequency domains) circles show good coincidence. DL frequency current modulation coefficient shows complicated non-monotone behaviour as function of modulation frequency. Model was developed based on properties of phonons (temperature) and electrons subsystems of DL. Model parameters were determined from independent experiments. Good agreement between model and experiment was obtained.

Line shape asymmetry in left picture (Fig.1) was explained. It is due to correlation between intensity modulation and frequency one. Asymmetry value is determined by relative intensity modulation and phase shift between frequency and intensity. Using the same model parameters good agreement between model and experiment was observed.

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E2

STABILITY OF MULTIPASS CELLS WITH DIFFERENT OPTICAL SCHEMES

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We present the results of comparison of four optical schemes which are often used for TDLS multipass cells: the Herriott type [1], astigmatic Herriott type [2], matrix four-objective Chernin cells [3, 4], and modified Herriott type with cut mirror, one half of which is slightly turned with respect to other [5]. A consideration was based on geometric optics approximation. The mathematical model allowed determination of the coordinates and angles at which the propagating beam hits the mirrors' surfaces. The coordinates of the n -th strike x_n, y_n were considered as the functions $F_{n,x}, F_{n,y}$ of the following parameters: input parameters (two coordinates and two angles), the positions of mirrors (three coordinates and three angles for each mirror) and the radii of curvature for each mirror (two radii in the case of astigmatic mirrors).

The first partial derivatives of $F_{n,x}, F_{n,y}$ on the parameters mentioned above were calculated and analyzed. Those derivatives can be considered as instability factors, describing shifts of output and intermediate beam positions with respect to initial parameters changes. The angle parameters were substituted by coordinate ones by multiplying angle tangents on corresponding mirror or input element sizes. The higher the instability factor is, the lesser an optical scheme is stable to a change of a given parameter.

The analysis showed the weak and strong sides of considered optical systems. The Chernin systems and cut mirror ([5]) system are highly unstable with respect to mutual position of objectives or mirror halves. For achieving stability in these cases rigid mounting of above mirrors is required. The Herriott system and its modifications could be made stable with respect to any of considered parameters, but not simultaneously to all of them. All systems are unstable with respect to change of base length (distance between opposite blocks of mirrors). The Chernin system is highly stable with respect to input beam direction.

The mechanism of etalon fringes appearance based on diffuse scattering of passing beam is discussed. The Chernin system is subject to this effect due to overlapping of images on objectives. The modified Herriott systems are subject to this effect due to partial overlapping of images at large number of passes.

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STUDY OF MOLECULAR LINE NARROWING PROCESSES BY CLASSICAL TRAJECTORY METHOD

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1. Traditional spectral line profiles (Rautian, Galatry, speed-dependent Voigt, etc.) widely used in experimental fitting practice contain parameters that serve as only "ad hoc" values corresponding to the considered borderline profiles, without referring to the narrowing process actually involved. In reality, not all collisions between molecules may be regarded as "soft" (Galatry profile) or "hard" (Rautian profile). As for speed-dependent Voigt contour, its narrowing originates from absolutely different nature than Dike (confinement) narrowing. 2. To obtain more accurate and physically substantiated fitting of experimental data it is necessary to apply self-consistent theory of line profile in conditions of collisional narrowing. It is evident that adequate profile theory should include both effects of narrowing (confinement phenomenon and speed dependence of relaxation parameters), naturally being valid for an arbitrary m_a/m_b ratio. Also this theory must reflect the correlation which obviously exists between velocity changing and dephasing collisions. These demands are fulfilled (at least in part) in recent unified theories of Lance and Robert [1] and of Ciurylo et al. [2]. However, these theories involve several parameters and functions of velocity which should be determined only from special molecular scattering calculations (namely, parameters of "hardness" of collisions, of correlation of velocity-changing and dephasing collisions, diffusion constant, speed dependence of line broadening and shift coefficients). 3. Scattering calculations of above mentioned parameters and functions should be performed with using realistic (anisotropic) intermolecular potential energy surface and employ correct description of molecular motion to avoid importing systematic errors. Classical trajectory approach is very promising to this effect being quite accurate, rapid and allowing for visual and self-consistent description of internal and translational motion of interacting particles.

The present study constitutes a very first attempt to extract detailed information needed in unified line narrowing theory [2] from simulation of classical trajectories. HF in a bath of argon was chosen as prototype system because of HF importance in UF₆ detection by means of TDLS. We have examined the following HF parameters: velocity dependence of line broadening and shift coefficients, degree of correlation between velocity-changing and dephasing collisions. The possible origins of HF line shape asymmetries have been analyzed as well.

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E4

Comparison of GaSb- and InP-based VCSELs at 2.3 μm

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In comparison to edge emitting lasers, vertical-cavity surface-emitting lasers (VCSELs) have several significant advantages for TDLS like longitudinal single mode operation, low power consumption and efficient electro-thermal wavelength tuning behavior. Electrically pumped devices, which can be operated continuous wave at room temperature, are particularly suitable for compact and low-cost applications. Recently, VCSELs based on both the GaSb and InP material system emitting at around 2.3 μm have been reported [1, 2].

In this paper the properties of both single-mode VCSELs are compared and their suitability for gas spectroscopy is analyzed. While the emission wavelength of 2.3 μm seems to be a limit for the InP material system, the GaSb material system allows for lasers significantly exceeding this wavelength, which is already demonstrated by the (commercially available) GaSb-based DFB lasers between 2.0 μm and 2.8 μm [3].

The 2.3 μm VCSELs are compared with respect of their static and dynamic tuning behavior (FM response), output power and beam-divergence. Some characteristic parameters are summarized in Table 1. It can be seen that the GaSb based laser has significantly higher dynamic tuning performance and a higher temperature tuning coefficient. The current tuning coefficient is slightly lower, which indicates a better thermal management inside the laser. The output power of the GaSb-based laser is still low, and likely to improve in the future when optimized laser designs are realized.

	Wavelength (μm)	Tuning coeff. (I)	Tuning coeff. (T)	FM cutoff- freq. (3 dB)	Beam divergence	Output Power
InP	2.365	1.1 nm/mA	0.17 nm/K	5.5 kHz	26 °	~300 μW
GaSb	2.326	0.9 nm/mA	0.23 nm/K	37 kHz	~ 40 ° (*)	~10 μW (*)

Table 1: Summary of laser parameters relevant in spectroscopy applications. The parameters (*) of the GaSb laser are likely to change in the future, since the laser – although it is spectrally single-mode – did not operate in the fundamental transverse mode.

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FIBER-COUPLED MULTI-POINT TDLAS HYGROMETER FOR CALIBRATION- AND SAMPLING-FREE MEASUREMENTS OF SINGLE LEAF TRANSPIRATION DYNAMICS

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The phytosphere as a main part of the biosphere plays a significant role for the atmospheric composition and thus for climatic processes. Plant transpiration is one of the most important steps in the global water cycle, as 64% of the global rainfall returns into the atmosphere through evaporation and transpiration [1]. But it is not fully understood although the response of stomata conductance and assimilation to light has been widely studied on different spatial and temporal scales for several plant species [2, 3]. To gain a more accurate understanding of plant transpiration and its ability to deal with fluctuating light environment a sampling- and calibration-free, four-channel TDALS hygrometer using near infrared (NIR) tunable diode laser absorption spectroscopy (TDLAS) at 1.37 μm was developed [4]. The main part consists of four neighboring, completely separated, fiber-coupled leaf chambers equal in size ($1 \times 8 \times 4 \text{ cm}^3$), designed to be placed on the abaxial surface of the leaf. The water concentration inside the boundary layer of the leaf is measured simultaneously in each mini chamber with a temporal resolution of about 0.5 Hz and an optical resolution of $1 \cdot 10^{-5}$ OD. For non-time critical applications the resolution of our system was determined via the Allan deviation to $3.1 \cdot 10^{-6}$ OD with a measuring time of 29.2 s. Taking into account the measurement rate of 23.3 Hz this would lead to a normalized resolution of $32 \text{ ppb} \cdot \text{m} \cdot \text{Hz}^{-1/2}$. We discuss the setup and performance of the 4-channel laser hygrometer and present first recordings of spatial and temporal dynamics of stomata conductance of single plant leaves induced by fast changing illumination conditions. Further improvements can be achieved by using a 2.7 μm hygrometer adapted to a single leaf [5].

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FIBER LOOP CAVITY RING-DOWN SPECTROSCOPY FOR MICROFLUIDS AND GAS SENSING

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High-sensitivity detection of compounds in small amounts of liquids is a necessity in modern analytical processes as e.g. in high performance liquid chromatography (HPLC). Fibre-loop ring-down spectroscopy (FLRDS) permits absorption detection of dilute liquid samples in volumes as small as a few picolitres. The technique is an analogue to gas phase cavity ring-down spectroscopy and is based on the measurement of the time it takes for a laser pulse to ring down in an optical fibre loop. This ring-down time is sensitive only to loss processes occurring in the fibre loop, e.g. scattering or absorption of sample inserted into a small gap between the two ends of the fibre loop. The optical decay constants are obtained by comparing the phase of intensity modulated cw-laser light entering and exiting the loop. Three different approaches were tested and interfaces were designed to intersect the fiber loop with microfluidic samples or gases.

The first setup uses UV-wavelength as many compounds have strong absorption features in this spectral region and it is of special interest for future combination with HPLC systems. Our UV-system consists of a diode laser (wavelength 405 nm) and a low loss fibre loop with an interface to insert samples. It has a detection limit of 0.33 cm^{-1} and a sample volume of 4.7 nL. Experiments with tartrazine solutions in phosphate buffer were performed and a detection limit of $4.7 \text{ }\mu\text{M}$ was determined. Furthermore, very first measurements of microparticles (diameter $5.89 \text{ }\mu\text{m}$) were performed at this wavelength and exhibited a detection limit of 5 particles inside the sample volume. The size of the particles used in this work is similar to those of human body cells, thus applications of the system in the field of biotechnology and biochemistry can be considered.

In the second case a liquid core waveguide is used where the analyte solution itself guides the light. A liquid core waveguide may be a tubing, capillary, or channel that is filled with the sample solution. This allows measurements of very low concentrations because of the long absorption path length but it also opens the possibility of a lab-on-a-chip approach. A liquid core waveguide system was built in house from a commercial fused silica glass capillary that was wound into a loop. Also a glass chip with waveguide channels was made and first absorption measurements were performed. There are two different ways of using these waveguides as detection schemes: The liquid core waveguide is the sample loop, which is similar to the capillary setup mentioned before or the liquid core waveguide only acts as a light guide within the chip, but is intersected by a microfluidic channel with a chromatographic column where the sample solution flows through.

Even lower detection limits may be reached with amplified ring-down spectroscopy (wavelength $1.5 \text{ }\mu\text{m}$), where a fiber amplifier compensates all other losses. Now the ring-down time is very long ($100 \text{ }\mu\text{s}$ compared to 140 ns) and small sample concentration changes have a huge influence on the ring-down time. This increases the number of paths through the sampling region to about 500. By using GRIN-lenses at the fiber end in the sample gap the sample gap width can be extended, which increases the sensitivity further. With this system a detection limit of $3.3 \cdot 10^{-4} \text{ cm}^{-1}$ is expected and even gas detection through overtone absorption should be feasible.

INTERFERENCE EFFECTS ASSOCIATED WITH THE USE OF OPTICAL DIFFUSERS IN TDLS

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The formation of interference fringes in TDLS, resulting from partial specular reflections for example from gas cell windows, is well-known [1]. Despite the use of angled, wedged and antireflection coated windows, small fringes can persist and often are the limiting factor affecting performance.

By using optical diffusers, which scatter incident light randomly, etalon – based interference fringes can be reduced or eliminated. However, other interference effects appear that can also cause troublesome performance limitations. We have studied and quantified a number of distinct effects that can appear in different configurations, and show how they can be minimized with careful design. We have studied reflective and transmissive diffusers, and different materials that act as surface reflectors, bulk reflectors or retroreflectors.

Random laser speckle

This contributes a random noise effect at the detector, which can be minimized by choice of aperture geometry [2]. The effects are reduced for small amplitude wavelength modulation.

Interferometric speckle

If a speckle field interferes with a second beam from eg a specular surface, interference fringes can result that are a direct analogy of familiar etalon – based fringes [2].

Self-mixing interference

This occurs when reflected light is coupled back into the laser diode, and for small levels of returned light results in a fringe-like sinusoidal modulation of the laser output. Interference can be caused by specular or diffuse reflections, and its effects can be reduced by simple intensity referencing.

Experimental data will be presented that identifies and quantifies each type of interference. By understanding and minimizing these effects, we can optimize the use of optical diffusers in gas cells as well as the use of TDLS based systems that rely on backscattered light from external, often remote, surfaces.

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NOVEL OPTICAL FIBER PROBE FOR CAVITY RING DOWN SPECTROSCOPY

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This paper presents a novel optical fiber probe for cavity ring down spectroscopy (CRDS). Cavity ring down spectroscopy is ordinarily used to detect trace components in gas or liquid with high sensitivity [1]. This CRDS is also applied to some sensing systems employing a fiber loop with a micro gap or hole [2, 3]. The gap or hole is filled with gas or liquid to be examined, and then an optical pulse repeatedly passed it in the loop. The amount of trace component is estimated by the decay time constant of the optical pulse train which is monitored at the outside of the loop. An optical cavity composed of twin fiber Bragg gratings is sometimes used to confine optical pulses between the gratings instead of the fiber loop. The newly developed optical fiber probe in this study has a very compact sensing head when compared with those systems.

An optical cavity composed of twin Fiber Bragg Gratings (FBGs) was formed in an optical fiber, and a micro-hole, which is a 15- μ m-diameter through-hole, was set within the optical cavity to store a liquid sample. The reflectivity of the FBG was designed to be 99.99% to confine an optical pulse within the optical cavity. The center wavelength of the grating was set at 1552 nm, which corresponds to the absorption wavelength range of sugar solution. An optical circulator was used at the opposite end of the sensing head to separate an optical output pulse from input pulse. This structure enables an optical fiber probe to insert into samples and miniaturizes the CRDS system.

By using the developed fiber probe, damping pulse trains corresponding to the cavity mode were monitored when the probe was inserted into water and sugar solution. Here, a DFB laser diode lasing at 1552 nm was used as an optical source. The lasing wavelength of the laser diode was changed and stabilized by using a thermoelectric cooler. The basic operation of the novel probe has been confirmed from these results.

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Applications of QCL based spectrometers for isotope ratio measurements in environmental research

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Isotope ratios of infrared active gases such as CO₂ and N₂O are excellent measure to investigate their sources, sinks and fate at local and global scales. This is possible, because of the characteristic isotopic fractionation induced by the physical and biochemical processes in which they are involved. However, such studies generally require extensive and long term measurements under field conditions, which is not feasible with standard isotope ratio mass spectrometers (IRMS). An alternative analytical technique based on direct absorption spectroscopy will be presented and the successful application of two compact, quantum cascade laser (QCL) based instruments will be shown.

One instrument was developed for continuous and high precision CO₂ isotope ratio (both ¹³C/¹²C and ¹⁸O/¹⁶O) measurements at ambient air concentration under field conditions [1, 2]. The combination of several new features makes it now possible to obtain a precision of 0.03‰ and 0.05‰ for δ¹³C and δ¹⁸O, respectively. The performance of the instrument was demonstrated in various field studies [2, 3], including grassland ecosystem – atmosphere exchange (gradient and eddy-flux method) and forest soil C-dynamics studies. The derived isotopic ratios were in excellent agreement with laboratory based IRMS measurements made on field-collected flask samples. The instrument is currently running at Jungfraujoch (3580 m a.s.l.) practically maintenance free and delivers for the first time continuous measurements of CO₂ isotopologues in the free troposphere. These time series will be combined with Lagrangian backward trajectory models for the seasonal and spatial characterization of CO₂ source regions.

The other spectrometer is intended for N₂O isotopomer analysis at trace level [4]. The intra-molecular distribution of ¹⁵N in N₂O can be used to obtain important information on the geochemical cycle of N₂O. Being a linear, non-symmetric molecule (N–N–O), the substitution of a nitrogen atom with its heavier isotope can take place at the centre (α site) or at the end (β site) position, resulting in two structural isomers. Since they have the same mass, their analysis by IRMS is only feasible through a complex analysis of NO⁺ and N₂O⁺. We take the inherent advantage of site selectivity of laser spectroscopy to perform direct measurements of δ¹⁵N^α and δ¹⁵N^β, respectively. Recent instrumental improvements resulted in a performance gain of a factor 5 compared to the previous setup [4]. The Allan variance minimum at 90 ppm N₂O is 0.1‰ for both ratios after 100 s averaging. The spectrometer is currently being coupled to an automated cryogenic pre-concentration unit for high precision measurements at ambient concentration.

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IMAGING AS A TOOL FOR DATA PROCESSING IN TDLS

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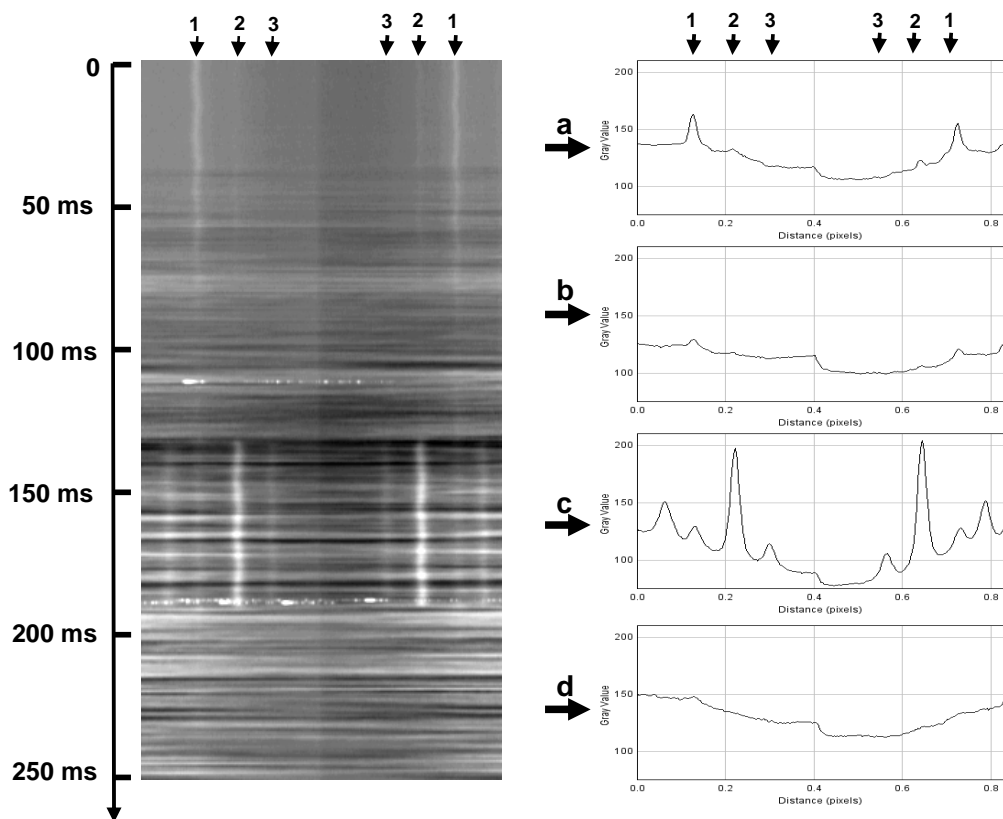
Recording of high-resolution spectra by repetitive sweeping of TDL current become now a standard procedure. We'll show that in many cases processing of such spectra can be simplified by presentation data as a 2D image in which rows correspond to single scans of TDL current and the following scans are arranged below the previous. This strategy greatly simplifies the general overview of data and enables to visualize peculiarities in different stages of the spectra evolution.

For the image processing we used ImageJ [1], the free, open-source software. Use of ImageJ plugins and procedures, such as dynamic profiler, background subtraction, filtering, etc. will be demonstrated as very useful in treatment TDL spectra. Interface and special macros for TDL spectra import and data processing have been written.

An example of 2D image constructed from TDL spectra of H_2O molecule in $1.39\ \mu\text{m}$ region obtained in one shot of the supersonic air-hydrogen flow is shown in Figure. Plots in the right are image horizontal profiles corresponding to averaging spectra for 50 ms.

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E11

Characterization of NIR-Lasers for Diode Laser Spectroscopy

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Despite of the importance to the results of Diode Laser Spectroscopy no sufficient information about the properties of the Diode Lasers can be found in the data sheets of the manufacturers. Only optical power and voltage vs. injection current and peak wavelengths at distinct currents and temperatures as well as side mode suppression can often be found. Additionally needed is much more, e.g.: frequency dependency of intensity and wavelength modulation, divergence angle, beam profile, line width, polarization grade and back reflection stability.

We present setups and compare results of measurements using Optical Spectrum Analyzer, FTIR Spectrometer, homodyne and heterodyne line width measurement methods. An approach to model temperature and frequency response is shown.

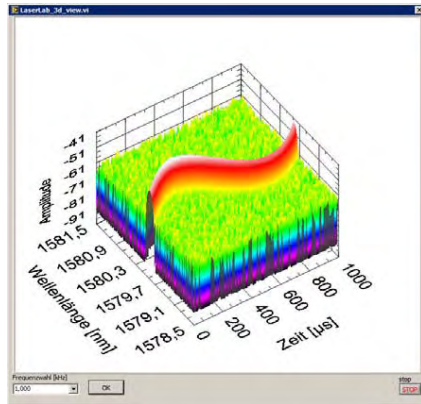


Fig1: Time resolved spectrometry of a Diode Laser @1kHz modulation

SPETROSCOPY OF GASES CONFINED IN NANOSTRUCTURES

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Studies of confined matter is of great importance in many areas of science and technology. A prominent example is the vast and rapidly advancing field of porous materials, where confinement and large surface areas gives rise to a multitude of interesting and useful phenomena. Important topics include for example ion exchange, catalysis, molecular sieving and separation, gas storage, chemical sensing, melting and freezing under confinement, and luminescence of porous silicon [1-3]. The interaction of gases of porous materials is of major importance in many of these areas.

Our department has previously shown that TDLAS can be used to study gases inside various light scattering solid materials [4]. Recent advances in our efforts include significant improvements in sensitivity [5] and characterization of porous pharmaceutical materials [6]. While our previous work has dealt with gases confined in larger cavities, we now show that high-resolution diode laser absorption spectroscopy also can be used to study gases confined in nano-sized cavities in porous materials. We use the near-infrared A band of molecular oxygen to interact with gas molecules located in subwavelength pores of sintered alumina (Al_2O_3). We discuss light propagation issues, and address the severe problem of interference fringes originating from multiple scattering. We report on strong lineshape broadening due to tight three-dimensional gas confinement, and thus enter a new domain of laser spectroscopy. Our approach provides new opportunities for studies of confined gases and vapours, as well as molecule-surface interactions in porous materials (*e.g.* surface chemistry). In addition, our findings open new ways for characterization of porous materials. Finally, this domain of laser spectroscopy constitutes a new challenge for the theory of lineshapes. The origin of the observed lineshape broadening is under investigation, and may be related to for example van der Waal interactions [7] and wall collisions [8].

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AN EXTERNAL CAVITY LASER FOR GAS SENSING APPLICATIONS IN THE 2.4- μm RANGE

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We present the results of our experiments with external cavity (EC) GaSb-based laser diodes supplied with a low-divergence waveguide and operating near 2.4 μm at room temperature. The laser structures were grown on Te-doped GaSb (100) epi-ready substrates by molecular beam epitaxy in a custom V90 system using conventional group-III effusion cells and valved cracker cells for As₂ and Sb₂ [1]. To decrease the fast-axis divergence of the laser beam, the refractive index contrast between the waveguide and cladding layer was relaxed by the reduction of Al content in the cladding layer [2]. Anti-reflection (AR) coatings were deposited on one of the facets of the Fabry-Perot devices using ion-beam sputtering. A step-down refractive index profile was designed to provide a facet reflectivity of $\sim 10^{-4}$. The lasers were mounted epi-side up onto Au-electroplated Cu/W (15%/85%) carriers using Ag epoxy. To stabilize the laser heat sink temperature we fastened the laser carrier to a copper mount with a large thermal capacity.

To achieve continuous tuning of the laser frequency, we employed a Littrow type EC configuration. The laser beam was collimated with AR coated aspheric sapphire lenses. The focal length of the lenses was varied in the range between 5 and 30 mm to study the effect of the laser beam diameter on the EC laser performance. A diffraction grating (300 grooves/mm, blazed for a wavelength of 2.5 μm) was mounted on an optical stage to allow its rotation and simultaneous translation along the optical axis of the laser resonator. The laser beam exited through the uncoated facet of the laser chip and was collimated with an AR coated lens for characterization of the laser beam parameters. Near-field distributions of the laser beam were studied using an infrared camera (Electrophysics Corp., model PV320). We employed the 721 Series laser spectrum analyzer from Bristol Instruments to measure laser emission spectra.

We measured laser output parameters using both the EC configuration and a short non-selective laser resonator formed with the uncoated facet and an external mirror. The results of the measurements will be presented, and applications of the laser for absorption spectroscopy will be discussed.

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High Power Tunable Green Light Generation using a PPMgLN

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All-solid-state-tunable-light source in ultraviolet region is a useful tool in the atomic spectroscopy. The tunable ultraviolet light around 270 nm can be achieved by the double stages of the frequency doubling of a DOFA (diode oscillator and fiber amplifier) system. The frequency doubling using a periodically poled crystal is a candidate technique at the first stage due to its simplicity and high conversion efficiency [1-2]. In the second stage, the frequency doubling using an external ring cavity is more efficient so far to produce high power ultraviolet light because of absorption and low conversion efficiency of a periodically poled crystal. The frequency doubled beam at the first stage should be a good beam quality for the mode matching in the ring-cavity of the second stage. Therefore, the spatial beam profile of the frequency doubled beam needs to be investigated.

In this study, we have used a commercial Yb-doped fiber amplifier system for increasing the power of the diode laser. The power of the diode laser has been amplified up to more than 10 W. The fundamental beam was inserted to a PPMgLN crystal with a length of 50 mm [Fig. 1]. The frequency-doubled power reached to more than 3 W at the pumping power of 12 W [Fig. 2]. The spatial profile of output beam was analyzed with the change of the input pumping power.

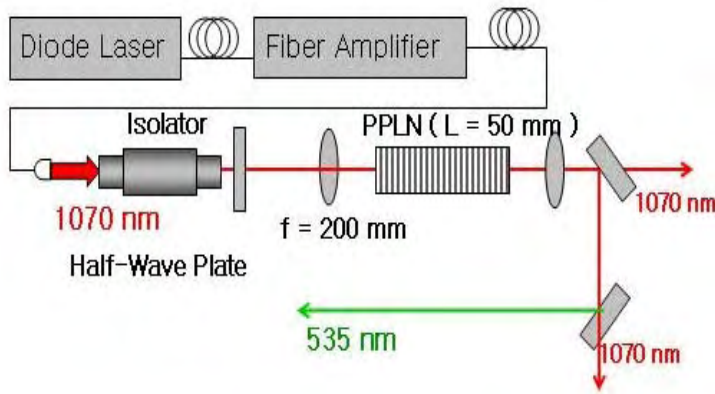


Fig.1 Experimental setup

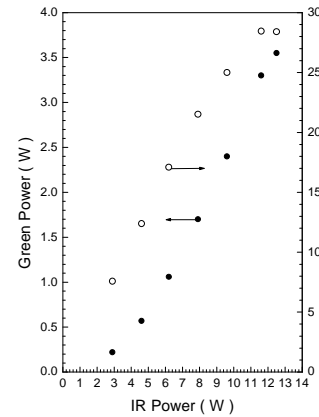


Fig.2 Frequency doubling efficiency by using a PPMgLN

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QUANTUM CASCADE LASER BASED-MONITORING OF THE SILANE DISSOCIATION FOR PHOTOVOLTAIC APPLICATIONS

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One of the biggest challenges of the thin-film silicon photovoltaic industry nowadays is the deposition of hydrogenated microcrystalline silicon in large-area industrial plasma-enhanced chemical vapor deposition (PECVD) systems [1]. A crucial parameter for the deposition of these thin-film photovoltaic cells is the silane dissociation efficiency, which is defined as the fraction of silane precursor molecules (SiH_4) that is dissociated during the film growth. By means of the silane dissociation efficiency, the film growth rate and the crystallinity of the film can be monitored in-situ.

Silane dissociation measurements present a considerable spectroscopic challenge because a wide range of process conditions need to be monitored in a low-pressure environment. Prior attempts were based upon intrusive and bulky instruments such as mass spectrometers or a Fourier transform infrared (FTIR) spectrometer [2]. We present for the first time laser-based silane dissociation measurements. These measurements were taken by comparing the silane absorbance before and after ignition of the glow discharge in a PECVD reactor. The underlying spectrometer is based on a Peltier-cooled continuous-wave single-mode quantum cascade laser (QCL) that is tuned around $4.5\text{ }\mu\text{m}$. The spectrometer is designed to measure intense roto-vibrational absorption lines of the ν_3 band of silane in a spectral range that is free from interferences with other absorbing species. It was calibrated with nearby R-branch ν_3 -band N_2O absorption lines. Room-temperature and continuous-wave operation are important because silane absorption lines are Doppler-broadened and have to be monitored in an industrial environment. To ensure the unobstructed guidance of the mid-infrared beam through large-area PECVD systems, a costumed-made telescope collimates the highly divergent QCL beam. The whole optical setup is compact and portable. It was successfully mounted on an industrial PECVD system commercialized by OC Oerlikon, Switzerland. The silane absorption lines found within the tuning range of the QCL feature a wide range of absorption strengths, thereby enabling dissociation efficiency measurements over any range of process conditions, even in a single-pass configuration of the laser beam through the deposition system. We will review the setup in detail and present doppler-resolved silane absorption lines, which are reported here for the first time, to the best of our knowledge. Finally, we will explain correlations between the spectroscopic measurements of the silane dissociation and the properties of the deposited films.

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Oxygen Sensor with Diffuse Reflector Employed in Harsh Conditions for Concentration and Pressure Measurements

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Optimization of the burning process in gas/oil furnaces is very important for pollution control and energy savings. An effective adjustment of the combustion can be performed by controlling the oxygen (O_2) content of the exhaust gas with requirements such as fast time response (< 1 sec), high sensitivity (0.1 vol% resolution), selectivity, in-situ measurement capability and long term stable operation. VCSEL-based oxygen sensors applied in aircraft fuel tanks have been already reported [1, 2, 3]. In comparison to these sensors, we report on a diffuse reflector based reflective geometry (Fig. 1) and microcontroller suited evaluation algorithm determining concentration and pressure simultaneously. The measured concentration values (200 ms intervals) have a standard deviation of 150 ppm (1σ), when Kalman filtering is applied and 750 ppm without filtering. The hot and humid combustion gas causes condensation on cold surfaces like the laser window, lens and the reflector. We found that the condensation introduces no additional noise source, but just acts as a plain intensity attenuation. With deployment of the diffuse reflector also fringes are minimized without requiring careful optical alignment. The real time least square curve fit algorithm is based on the Arndt model [4] and an advanced pre-calculation [5] using characteristic values of the second harmonic spectrum and determines both, the gas concentration and gas pressure each 200 ms (see Fig. 2 and Fig. 3).



Fig. 4: Oxygen sensor with a diffuse reflector (optical path length: 2×10 cm) and microcontroller based electronics

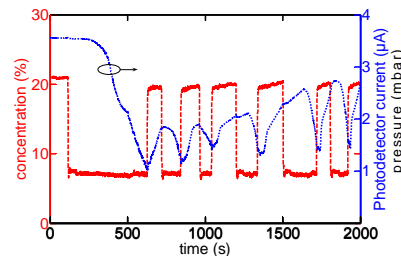


Fig. 5: Oxygen concentration (red) and photodetector current (blue) during the furnace on/off switching.

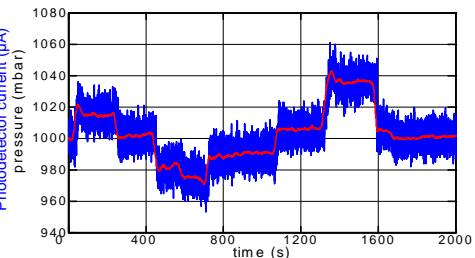


Fig. 6: Pressure measurement in every 200 ms (blue) and the 20s average (red). The pressure values were set manually to 1000, 1030, 1000, 970, 962, 973, 1000, 1049 and 1000 mbar.

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Poster session F

F1

HF instrument calibration

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Presence of HF molecule in atmosphere of nuclear facility is signature of UF₆ enrichment activity. Backpack instrument was developed to measure concentration of HF during IAEA inspections. In present paper we'll consider the instrument developed calibration.

Traditionally measurements of molecular concentration in TDLS are calibrated using calibrated gas mixtures. For dipole molecules such as HF, NH₃, H₂O, etc. this procedure is more complicated. Such molecules have long-range dipole-dipole interaction. It results in complex formation and molecular absorption on surfaces. Goal of present poster is to consider procedure of concentration measurements in TDLS and to demonstrate that TDLS is primary standard to measure impurity concentration. Fig.1 presents automatic procedure of continuous reference channel calibration of HF instrument developed.

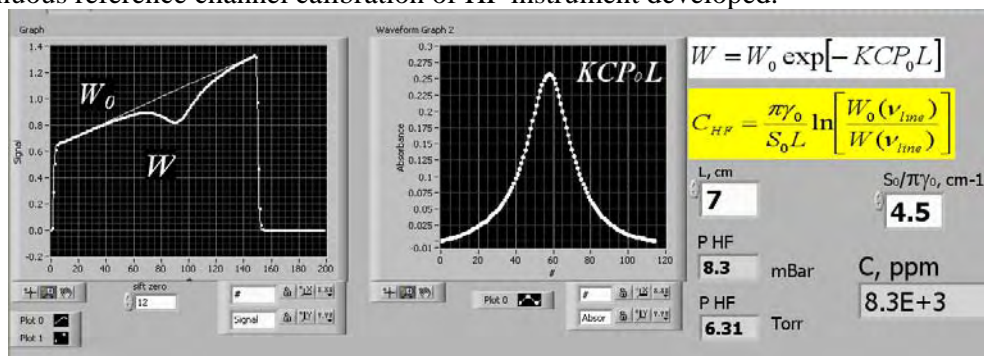


Fig.1 Automatic reference channel calibration

All steps of data recording and processing in TDLS instrument to measure HF concentration in atmosphere were analyzed. Pressure, temperature, and humidity dependence of measured values were considered. Based on physical laws, known cosmological constants, analysis, and calibrations performed, it was shown that TDLS is primary standard of HF concentration in atmosphere measurement with accuracy 20%. Noise equivalent HF concentration was 0.04 ppb for 10 sec averaging time using TDLS instrument developed.

Tests at facilities demonstrated possibility to detect undeclared activity using instrument developed.

Present work was supported in part by DOE-GIPP-347 (ISTC-3740P).

F2

HTO detection using TDLS

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Possible spectral ranges for HTO detection using TDLS were analyzed (Fig.1). Advantage and disadvantage of $2\nu_3$ was considered. Water vapour spectra in 2 m cell were recorded in near IR spectral range (7166- 7192 cm^{-1}) using diode laser. Three water samples were investigated: H₂O - normal water, HDO - heavy water/normal water = 1/1, HTO - heavy water from reactor/normal water = 1/1.

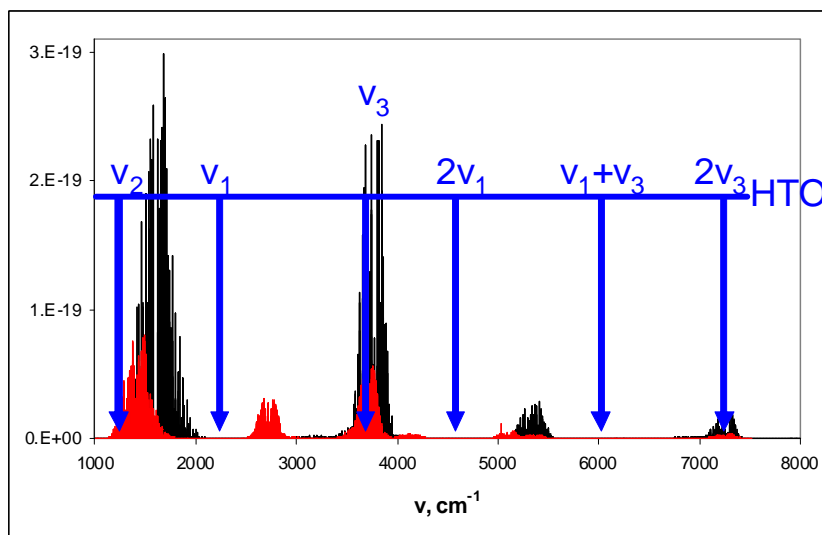


Fig.1 Water vapor absorption bands (HITRAN), arrows - HTO bands.

10 lines were assigned to HTO. For present HTO sample, T:D concentration was estimated to be $\sim 0.01\%$ and HTO absorbance was close to detection limit. For better HTO measurements higher enriched HTO sample is necessary. Noise equivalent HTO detection is $3.5 \mu\text{Ci}/\text{m}^3$. It is 10 times better than in mid IR [1] and is close to technical requirements.

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Present work was supported in part by DOE-GIPP-347 (ISTC-3740P).

REMOTE DETECTION OF HF MOLECULES IN OPEN ATMOSPHERE WITH THE USE OF TUNABLE DIODE LASERS

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Hydrogen fluoride is known to be a permanent companion of UF₆ which is formed practically at all the stages of interaction between UF₆ and its hydrolysis products with water vapors, gaseous components of an emergency release (leakage) and atmospheric gases [1]. A release (leakage) of uranium hexafluoride is attended by a sharp rise of HF concentration in atmosphere with the UO₂F₂ aerosol formation. The fact of the HF concentration rise in atmosphere can be useful in the practical activities of IAEA inspectors for detection of hidden works on uranium enrichment or other nuclear technologies [2].

This paper reports on the results of an investigation of manufacturability of a prototype device for prompt (in the on-line mode) remote measurements of HF trace amounts in atmosphere (with the path length up to 100 m, and a cat's eye as a reflector) with the use of near-infrared diode lasers (DL).

Measurements of HF trace amounts were taken with a DL module incorporating a tunable DL with distributed feedback (DFB-DL) and fiber radiation outlet oscillating in the vicinity of the wavelengths of $\lambda=1.283\ \mu\text{m}$ (2-0 line of R0 HF). A receiver-transmitter optical unit consisted of a collimator creating a parallel beam from the end face of the DFB-DL fiber radiation outlet, and a parabolic mirror with 150 mm in diameter and $f=130\ \text{mm}$.

The results of preliminary studies have shown that the minimal HF absorption value detectable within 30 ms in the remote mode corresponded to the HF concentration below 10.0 ppb which makes 0.02 of the MPC (500 ppb).

Discussed are different approaches to remote detection of HF molecules in open atmosphere, the major factors specifying the HF remote analysis sensitivity, feasibilities of using other types of DLs, quantum-cascade DLs among them, and potentialities of application of a hardware and software system of this type on mobile ground-based and air-based facilities.

Present work was supported in part by DOE-GIPP-347 (ISTC-3740P).

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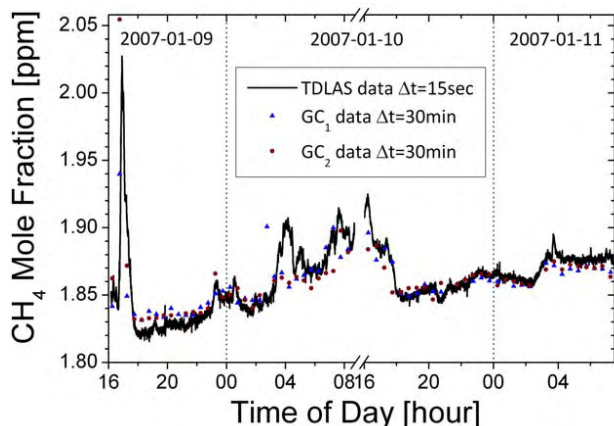
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CALIBRATION-FREE, OPEN-PATH MEASUREMENTS OF ATMOSPHERIC CH₄ BACKGROUND CONCENTRATIONS AND THEIR VALIDATION BY GASCHROMATOGRAPHY

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The high importance of methane as a major green house gas in combination with the rapid anthropogenic CH₄ increase requires a high precision observation of the absolute atmospheric CH₄ concentration. However, especially field measurements suffer from the need for frequent and tedious sensor calibrations with reference gases. Thus we developed a highly precise, sampling- and calibration-free open-path tunable diode laser absorption spectrometer and validated its absolute performance by a comparison with a precision calibrated gas chromatograph. The TDLAS instrument is based on a fiber-coupled high-power 1.653 μm DFB diode laser with 20 mW and an open Herriott-type multi path cell with 70 m absorption path length. Rapid wavelength scanning, scan averaging in combination with efficient disturbance correction software to compensate transmission fluctuations as well as background light enabled high sensitivity and temporal resolution as well as robustness to changing environmental conditions. To eliminate drifts in optical zero baseline of the spectrometer we developed an efficient background subtraction algorithm. A high precision measurement of the dynamic wavelength tuning properties of the diode laser in combination with an accurate



linearization of the severely distorted wavelength axis ensured excellent absolute accuracy. With a multi-line Rautian model fit of the 2 ν_3 R3 CH₄ line triplet [1, 2] and signal averaging over 15 seconds we achieved an optical resolution of 2.7×10^{-5} OD (1σ) which results in an excellent concentration resolution of 2.7 ppb CH₄. Absolute accuracy could be validated successfully by an independent comparison with a precision gaschromatograph calibrated to a NOAA reference gas standard. Over the

cause of nearly two days (figure) we find a mean difference between the GC and the uncalibrated TDLAS of only -0.1 %, corresponding to -3 ppb CH₄ which clearly demonstrates the extreme absolute accuracy of our CH₄ spectrometer

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Ammonia Detection in Exhaled Human Breath with a Quantum Cascade Laser Based QEPAS Sensor

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A quantum cascade laser (QCL) based breath sensor platform for medical applications employing a quartz-enhanced photoacoustic spectroscopy technique is reported. The detection sensitivity for exhaled ammonia is at a <10 ppbv concentration level with 0.5 s time resolution. This work demonstrates the implementation of a sensitive QCL based sensor platform for quantitative measurements of ammonia concentrations in exhaled breath. Exhaled human breath contains ~ 400 different trace gas species, mostly at ultra low concentration levels. Many of these gases can serve as biomarkers for the identification and monitoring of various types of human diseases or wellness states. Typical concentrations of ammonia in healthy human breath may vary from tens to few hundreds ppbv, whereas elevated levels (e.g. ≥ 1 ppmv) may indicate significant pathology. Monitoring of ammonia concentration in exhaled breath using laser spectroscopy techniques provides a fast, non-invasive diagnostic method for patients with a variety of medical conditions, including liver and kidney disorders, and helicobacter pylori infections. Therefore laser spectroscopy in combination with a mid-infrared, cw, high performance QCL is a promising analytical approach for real time breath analysis and the quantification of breath metabolites [1].

Our study of ammonia in human breath was performed with either a CW DFB QCL or a tunable EC-QCL based QEPAS sensor and using a wavelength modulation technique [2,3]. The DFB QCL operated at 5°C and provided a maximum power of ~30 mW. A tuning range of $\sim 4.5 \text{ cm}^{-1}$ by varying the injection current enabled the monitoring of an ammonia line at 1046.4 cm^{-1} . The EC-QCL was tuned to the $930.8 \text{ cm}^{-1} \text{NH}_3$ line, which is free from potential spectrally interfering species such as CO_2 , H_2O , and CH_3OH . Breath ammonia measurements were performed on a healthy volunteer over a three week period with DFB QCL. Performance characteristics for both the DFB-QCL and the EC-QCL sensor platforms operating with 2f and 1f wavelength modulation respectively will be reported.

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F6

A LOW-TEMPERATURE APPROACH TO EXTEND THE TUNING RANGE OF LONG-WAVELENGTH VCSELS

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We propose a simple technique to improve tuning capabilities of long-wavelength vertical-cavity surface-emitting lasers (VCSELs). It involves reducing the laser substrate temperature and increasing the amplitude of the laser modulation current. In addition to the shift of laser diode frequency with substrate temperature, we utilize the single-mode advantage of VCSELs and their ability to tolerate significantly higher currents at lower temperatures. In our previous work [1] we have studied 1512-nm and 1577-nm VCSELs in the 150-K temperature range using liquid nitrogen as a coolant.

In the present work we achieved a 25.7-cm^{-1} ($\sim 7.3\text{ nm}$) current-induced tuning range of a VCSEL at a substrate temperature of $-55\text{ }^{\circ}\text{C}$ controlled with a Peltier element. Fig. 1 illustrates the improved tuning characteristics of the laser. Ethylene oxide and benzene spectra acquired with the laser in the 1693-nm and 1684-nm regions will be presented.

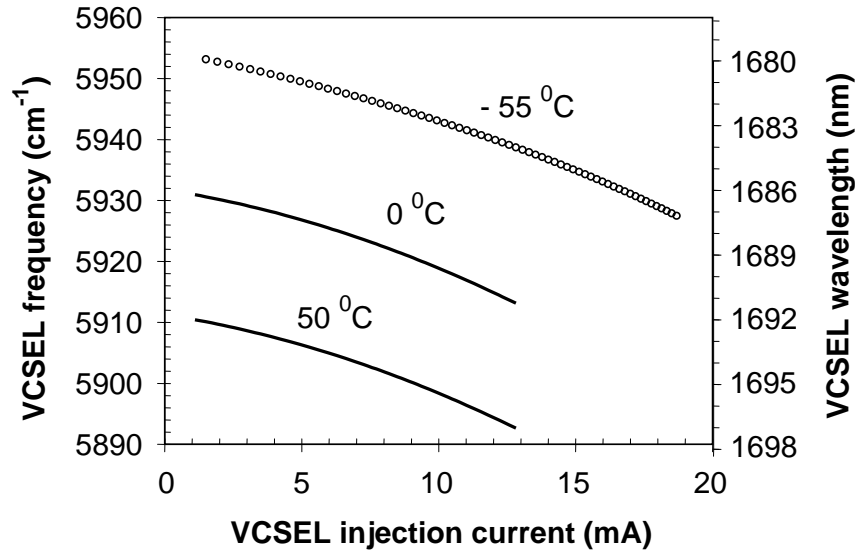


Fig. 1. Current-induced continuous tuning ranges of a 1693-nm VCSEL at various laser substrate temperatures. The combined temperature- and current-induced single-mode tuning range exceeds 60 cm^{-1} ($\sim 17\text{ nm}$). A 25.7-cm^{-1} ($\sim 7.3\text{ nm}$) spectral interval can be scanned at $-55\text{ }^{\circ}\text{C}$ at a 1-kHz rate using a 18 mA (peak-to-peak) ramp modulation.

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F7

Simultaneous measurement of $^{18}\text{O}/^{16}\text{O}$, $^{17}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ isotope ratios in exhaled CO_2 in human breath using a DFB laser operating at 2730 nm

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Abstract

A tunable continuous-wave mid-infrared laser spectrometer was developed for simultaneous measurement of oxygen and carbon isotope ratios in exhaled carbon dioxide in human breath. $^{16}\text{O}^{12}\text{C}^{18}\text{O}$, $^{16}\text{O}^{12}\text{C}^{17}\text{O}$, $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ absorption lines were simultaneously probed by direct absorption spectroscopy using a distributed feedback diode laser operating at room temperature near 2730 nm.

Temperature-corrected oxygen sensor based on multi-mode diode laser correlation spectroscopy

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The quantitative detection of oxygen is important for coal-combustion emission monitoring. Oxygen sensors based on laser absorption spectroscopy is greatly attractive because of the advantage of non-contact which makes the sensor inherently immune to the poisoning or corrosion problems.

Recently, we have reported on a novel oxygen sensor [1] based on the multi-mode diode laser based correlation spectroscopy (MDL-COSPEC) technique which was previously successfully demonstrated on CO₂ [2] and C₂H₂ [3]. This type of oxygen sensor has the merits of low-cost and stability. The laboratory demonstration measurements were performed at room temperature. In coal-combustion emission monitoring application, however, the exhaust gases are commonly analyzed at the tail of the flue with the typical temperature around 400 K.

In this work, oxygen sensing measurements were performed at various temperatures from 300 to 473 K to investigate the temperature effects on the concentration evaluation. Temperature correction methods at three different detection schemes simulating the condition of the flue tail are presented. With the effective temperature corrections, the accurate and precise oxygen measurements were realized by using the MDL-COSPEC based oxygen sensor (see Fig. 1).

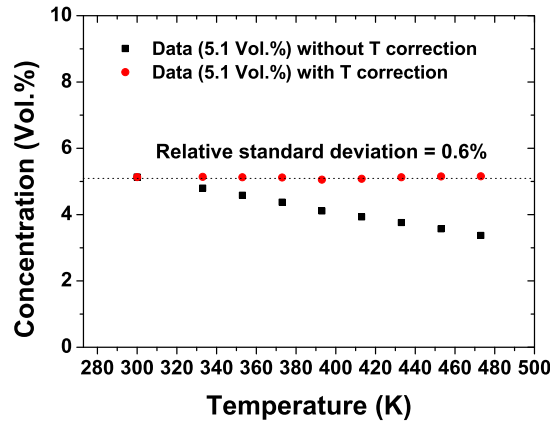


Fig. 1 Measurement results with and without temperature correction.

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F9

Ring-Down Spectroscopy in Optical Waveguides

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Cavity ring-down absorption spectroscopy is the method of choice for many applications in gas-phase sensing and - more recently - in the detection of dilute analytes in liquid solutions. The dramatic enhancement of the effective absorption path, which is characteristic for CRD measurements, is typically achieved by placing the sample in an optical cavity that is defined by two or more highly reflective mirrors. Here, we present CRD measurements that are conducted on cavities which instead consist of waveguide materials. In particular optical cavities were made of

- loops of optical fibers [1,2]
- circular channels containing a high refractive index liquid
- strands of single-mode fiber using Fiber Bragg Gratings as “mirrors”[3]
- microresonator spheres made from silica and polydimethylsiloxane [4] and
- silicon-on-insulator “race track” microresonators.

These cavities were interfaced to (micro-)analytical separation systems such as microfluidic “labs-on-a-chip”, capillary electrophoresis and even high-performance liquid chromatography (HPLC)[5]. As the sample interacts with the cavity, the ring-down time is decreased and absorption detection of small liquid samples is possible.

CRD measurements in waveguide cavities may also be extended to very sensitive refractive index measurements. By exploiting the response of long-period gratings (LPGs) and microresonators to refractive index changes, ppb-level chemical detection was carried out in water and air.

To increase the duty cycle of the measurement - and thereby the time response - we use phase shift measurements instead of the more commonly used time resolved decay measurements[6]. With these modifications waveguide CRD measurements fully exploit the recent advances in laser light source development.

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FIELD AND LABORATORY HYDROGEN FLUORIDE TRACE GAS DETECTION BY OF-CEAS

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We report on the development of an optically based instrument designed to detect trace gas of chemical agents with sensitivity in the ppb range. Efforts are made to develop rugged and compact experimental designs that can be used for field measurements. The spectroscopic technique employed is based on the Cavity Enhanced Absorption Spectroscopy (CEAS) which is a powerful technique to measure traces gas down to the ppb level.

In collaboration with the Université Joseph Fourier of Grenoble, an OF-CEAS (Optical Feedback – Cavity Enhanced Absorption Spectroscopy) [1-4] system is developed for in-situ real time detection of the industrial toxic hydrogen fluoride HF. Quantitative measurements are performed in the 1300-nm spectral range. Spectral overlap with the water vapour absorption lines is taking into account and long term stability is studied. Adsorption effects of highly reactive molecules like HF could drastically limit response time and accuracy of the instrument, so strong precautions must be taken in the design and material selection.

A first successful test was carried on at the Université de Franche-Comté : optical measurements results in good agreement with concentration obtained by a permeation oven, disagreement was less than 1-%. Furthermore the detection linearity of the OF-CEAS instrument was confirmed and the detection limit was about 0.3-ppb.

Further field measurements have shown that the detection sensitivity is limited by dust and aerosols, present in large quantities on industrial sites. A few filtration systems adapted to HF reactivity were tested and showed a good efficiency.

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INTEREST OF ABSORPTION AND TDLA SPECTROSCOPY FOR THE CONTROL OF INDUSTRIAL PROCESSES. APPLICATION TO H₂ MASSIVE PRODUCTION.

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Absorption spectroscopy in general, and TDLAS techniques in particular, are being used by a growing number of researchers and found their applications in a lot of fields of competence like atmospheric trace gas detection, isotopic composition measurement, industrial processes monitoring, combustion study, medical diagnostics or study of an ecosystem for example. In this communication, an example, where these methods bring significant advances in chemical research project: H₂ massive production is presented. Using nuclear heat together with a thermochemical cycle is a promising way to massively produce hydrogen, a potential energy vector. The sulphur-iodine cycle and the hybrid copper chloride thermochemical cycle are some good candidates for water splitting.

In the case of the sulphur-iodine thermochemical cycle, the overall efficiency of the process essentially depends on the efficiency of HI section. Using tools, such as a FTIR spectrometer for H₂O and HI concentrations determination, and a TDL spectrometer for I₂ measurements, have provided very significant results that will be useful to build a new thermodynamic model of the HI separation. This non-intrusive method has avoided any vapour change and prevented tedious experiments in harsh environments [1].

The same methodology is now applied for the study of the hydrolysis reaction of the thermochemical hybrid copper chloride cycle. The study of this reaction is very important to assess the viability of this cycle because this reaction is not thermodynamically favoured and it only occurs if a large excess of water is used. To better understand the influence of various parameters such as water stoichiometry, temperature, reaction duration, an experimental set up has been designed and realized. The experimental setup uses two spectrometers to study the speciation of the gaseous phase and optimize the kinetics of the hydrolysis reaction. Concentrations of HCl and H₂O are obtained by fitting experimental FTIR spectra with calculated spectra. Parasitic reactions can appear, leading to formation of Cl₂, measured by UV-Visible spectrophotometry.

At last, the high temperature reaction around 530°C is the only reaction of this copper chloride cycle which is thermodynamically favoured. A better understanding of its kinetics and the influence of the experimental parameters on this kinetics is needed. At last, an absorption spectrometer able to measure oxygen is under study. This instrument is based on a high finesse cavity and a DFB diode in order to access to the oxygen A band absorption spectra, near 763.5 nm. First preliminary results of this work will be presented.

[1] J. M. Hartmann *et al.*, International journal of hydrogen energy 34 (2009) 162 – 168

FIBER OPTICS FOR FLEXIBLE LASER SPECTROSCOPY

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The latest development in IR-fiber optics expands spectral range of process-spectroscopy from 0.2-2.4 μm to Mid IR-range up to 18 μm (20.000 to 550 cm^{-1}). Up to now fibre systems used for process-control applications by absorption/transmission, reflection, fluorescence and Raman-spectroscopy were limited to silica fiber transmission 0.2-2.4 μm . Nowadays IR-glass fibres, Polycrystalline PIR-fibres and Hollow Waveguides can also cover Mid IR-range up to 18 μm , including “finger-print” Mid IR-range where specific absorption bands of molecular vibrations are concentrated. These fundamental vibration bands in Mid IR are 100-1000 times more intensive and more narrow compared to their 2nd & 3rd overtones at shorter wavelengths <2 μm . But in addition to this factor complete fibre spectroscopy system should be optimized taking into account other parameters of its components: intensity of light source, sensitivity of detector and efficiency of their coupling with fibres and optical cell.

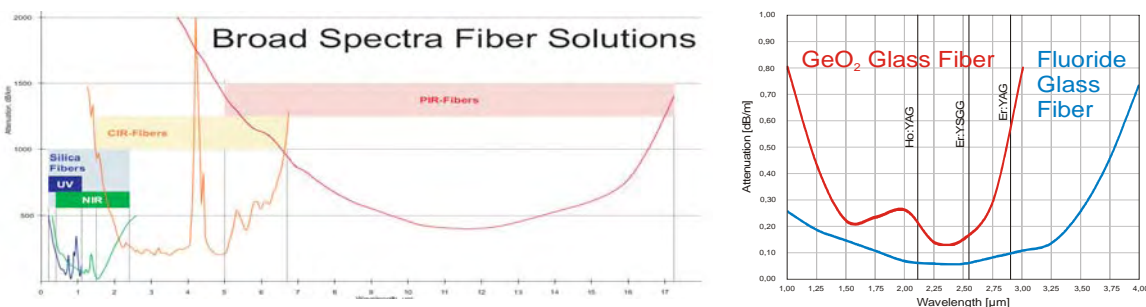


Fig.1 Attenuation spectra for: a) Silica, CIR- & PIR-fibres; b) GeO & ZBLA-fibers

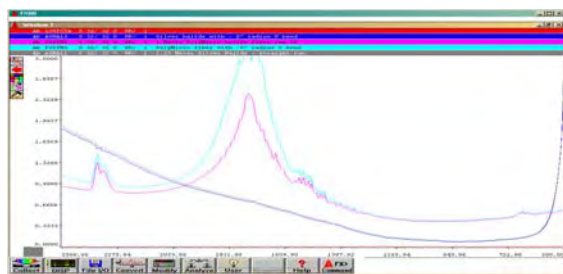


Fig.3 Attenuation for PIR-fiber (blue) & Hollow Waveguide range;

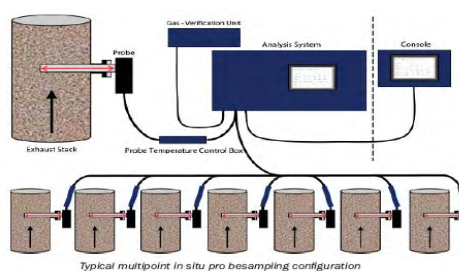


Fig.4 QCL-system with PIR-fiber probes for remote exhaust control in 4.48-7.43 μm

***In situ* sensing of molecular oxygen and water vapour for diagnostics of the human paranasal sinuses**

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We present results from a clinical trial of patients with sinus problems. The air-filled paranasal sinuses, located in the human skull are subject to complications such as blockage of the nasal ventilation and mucus obstruction [1]. Diagnostic tool used today are case history and computer tomography, which are unreliable and costly. Measurement of gas absorption in the sinuses, surrounded by tissue and bone, is possible due to the spectrally sharp gas imprint in contrast to the broadband absorbing ambience. Detection of gas in porous media was presented in 2001 [2] and has been demonstrated on e.g. food, pharmaceutical tablets, wood, and the human paranasal sinuses [2-5]. Monitoring molecular oxygen (760 nm) and water vapour (935 nm) in the sinuses could possible give diagnostic information about the activity and state of the cavity. The technique, data analysis, and some results from the clinical trial will be presented. The instrument used is based on two pigtailed DFB lasers and uses digital wavelength modulation spectroscopy [3]. As an example WMS signals of the maxillary sinus, obtained in the clinical trial are presented in Fig. 1. Here the light is inserted on the right side of the palate and detected on the cheekbone. The measured absorption corresponds to 30 mm of 21% O₂ and 25 mm of H₂O with a relative humidity of 100 % at 37°C.

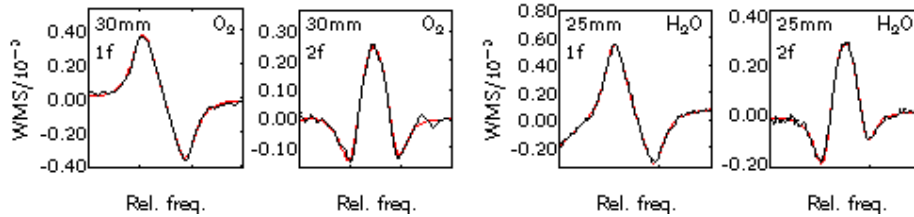


Fig.1 The 1f and 2f WMS signals of the right maxillary sinus.

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Laser Leak Sensor for a Coolant Leak Detection in a Nuclear Reactor

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A laser sensor for monitoring of a heavy water (D_2O) coolant leak in a pressurized heavy water reactor (PHWR) has been proposed and experimentally investigated.

A coolant leak could be detected instantly with high sensitivity using a tunable diode laser absorption spectroscopy (TDLS) when a coolant leaks from a reactor pressure boundary, such as a pressure tubes, delayed neutron (DN) tubes, or primary-to-secondary leakages in a steam generator. A laser leak sensor consists of a tunable diode laser, an absorption cell, a photo detector, a suction pump, and a control module.

When a heavy water coolant leaks to the atmosphere or to the secondary system, semi-heavy water (HDO) is produced by an isotope exchange reaction between heavy water (D_2O) and light water (H_2O), which is detected by the laser leak sensor with high sensitivity.

A laser sensor could provide more sensitive as well as real-time leak monitoring, compared to the conventional techniques, such as FT-IR or radiation monitoring technique, currently employed in PHWR [1-4].

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APPLICATION OF DIODE-LASER BASED FIBER AMPLIFIED LASER IN ATOMIC SPECTROSCOPY

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Figure. Experimental Setup for spectroscopic studies for Yb atom by using DOFA

5 μm VERTICAL EXTERNAL CAVITY SURFACE EMITTING LASERS (VECSEL) FOR SPECTROSCOPIC APPLICATIONS

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Mid-IR tunable VECSELs (Vertical External Cavity Surface Emitting Lasers) emitting at 4 - 7 μm wavelengths suitable for spectroscopic sensing applications are described. They are realized with lead-chalcogenide (IV-VI) narrow band gap materials.

The active part, a single 1 - 2 μm thick PbTe or PbSe gain layer, is grown onto an epitaxial Bragg mirror with two or three $\text{Pb}_{1-y}\text{Eu}_y\text{Te}/\text{BaF}_2$ layer pairs. All layers are deposited by MBE in a single run employing a BaF_2 or Si substrate, no further processing is needed. The cavity is completed with an external curved top mirror which is again realised with an epitaxial Bragg structure. Pumping is performed optically with a 1.5 μm laser (Fig. 1).

Maximum output power is currently up to 300 mW pulsed or 3 mW CW and operating temperatures up to 175K using an antiresonant design [1,2]. Here, we describe an adapted resonant design where lasing is observed up to above RT with >10 mW output power at 10 $^\circ\text{C}$. Still higher operating temperatures and/or powers are expected with better heat-removal structures and designs employing QW (Quantum-Wells).

At constant operating temperature, tuning up to several % of the central wavelength may be performed by changing the cavity length. By temperature tuning, wavelengths from 4 - 7 μm are accessible (Fig. 2). Shorter wavelengths are obtained with PbSe QW or $\text{Pb}_{1-y}\text{Eu}_y\text{Se}$, while longer wavelengths result with $\text{Pb}_{1-y}\text{Sn}_y\text{Se}$ active layers.

The advantages of mid-IR VECSELs compared to edge emitting lasers are their very good beam quality (circular beam with $<1^\circ$ cone diameter), simple structure, and their easy tunability without mode-hopping.

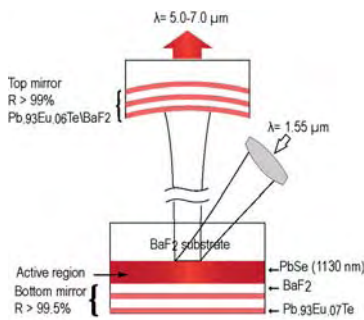


Fig.1. Schematic cross section of a mid-IR PbSe based optically pumped VECSEL

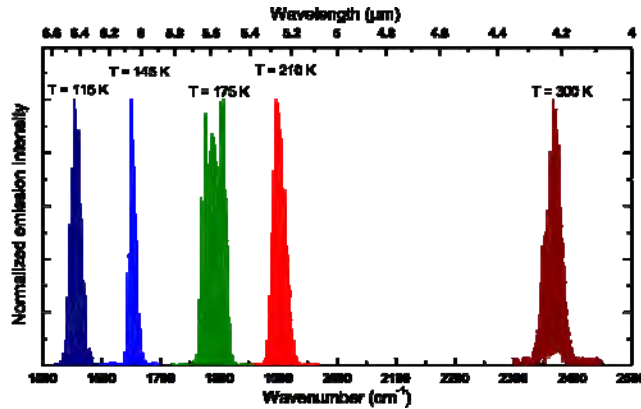


Fig. 2. Emission spectra at different temperatures with a PbSe active layer

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