ABSTRACTS OF PAPERS

8th International Conference on

Tunable Diode Laser Spectroscopy

July 11-15, 2011
Zermatt, Switzerland

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TDLS 2011 Conference Schedule

Monday July 11	**Tuesday July 12**	**Wednesday July 13**	**Thursday July 14**	**Friday July 15**
Session Chair M. Sigrist	**Session Chair M. Marangoni**	**Session Chair T. Sears**	**Session Chair G. Wysocki**	**Session Chair F. Tittel**
8:45-9:00 Welcome Address				
9:00-9:45 T.Sears	9:00-9:45 S.Kassi	9:00-9:45 M.Marangoni	9:00-9:45 G.Ritchie	9:00-9:45 F.Harren
9:50-10:10 W. Chen	9:50-10:10 Y.N. Ponomarev	9:50-10:10 F.K. Tittel	9:50-10:10 L. Emmenegger	9:50-10:10 M. Spiridonov
10:15-10:35 S. Schilt	10:15-10:35 F. Felder	10:15-10:35 M. Gianella	10:15-10:35 M. Liang	
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	12:45-3:00 Lunchtime International Advisory Committee Meeting	
Session Chair M. Lepere	4:00-5:45 POSTERS Session C		4:00-5:45 POSTERS Session F	
4:00-4:20 D. Hamilton				
4:25-4:45 T. Tsai				
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Part 1 Invited lectures

L1

FREQUENCY COMB-REFERENCED MEASUREMENTS OF PRESSURE BROADENING IN ACETYLENE

C. P. McRaven,[a] M. J. Cich,[b] G. V. Lopez,[b] Trevor J. Sears,[a,b] Daniel Hurtmans[c]
and A. W. Mantz[d]

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An extended cavity diode laser whose output is locked to a frequency comb has been used to measure pressure and line shape variation in rotational lines of the $\nu_1 + \nu_3$ combination band of acetylene as a function of collision partner and temperature. To check the accuracy of the spectrometer P(11) of this band was measured to be at 195 739.649 5135(80) GHz in agreement with published data. Broadening, shift and narrowing parameters for the $\nu_1 + \nu_3$ band were determined at a series of temperatures between 125 and 296 K with pressures varying between less than one Torr up to more than 800 Torr. At 296 K, and assuming a hard-collision model, we find, we find 0.146317(27), 0.047271(104), and –0.0070819(22) for the acetylene self-broadening, narrowing and shift, in units of cm^{-1}/atm, and 0.081129(35), 0.022940(74), and –0.0088913(25) respectively, for the nitrogen broadening parameters. The uncertainties are expressed as one standard deviation (in parenthesis) in units of the last digit reported. These parameters are 2-3 orders of magnitude more precise than those reported in any previous measurements. Similar analyses of the experimental data using soft collision and simple Voigt lineshape models were made for comparison. Experiments are continuing with He as a collision partner and others with H_2 are planned.

L2

HIGH SENSITIVITY DIFFERENTIAL ABSORPTION SPECTROSCOPY OF METANE IN THE 1.26 - 1.70 µm SPECTRAL RANGE FOR PLANETOLOGY APPLICATIONS

D. Mondelain, A. Campargue, S. Kassi, L. Wang

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In absence of a satisfactory theoretical modeling of the CH_4 spectrum, accurate and exhaustive experimental data in low temperature conditions are essential to study the atmosphere of Titan and of the giant outer planets. For instance, the transparency windows, corresponding to the weak absorption regions between the strong absorption bands, allow to access to the lower atmosphere composition and to the albedo of these planets.

We present a high sensitivity near infrared spectrometer for the study of methane by differential direct absorption spectroscopy (DAS) at liquid nitrogen temperature (LNT) [1]. It is based on a cooled absorption cell (142 cm long) coupled with a set of about 80 fibered DFB diodes permitting to continuously cover the 1.26 – 1.70 µm spectral region. A noise equivalent absorption (NEA) on the order of $\alpha_{min} \approx 5\times10^{-8}$ cm^{-1} could be achieved in a double pass configuration.

With this instrument we have exhaustively studied the strong absorption bands of natural methane (Figure 1), $^{13}CH_4$ and CH_3D. The study of the minor isotopologues – CH_3D particular – is very important as they may have a dominant contribution in the $^{12}CH_4$ transparency windows that we studied separately by CRDS at LNT. This will be illustrated in the case of CH_3D in the 1.28 and 1.58 µm methane windows at room temperature and 80 K. The DAS spectra of CH_3D allowed to identify all the transitions of CH_3D present in the CRDS spectra of methane in natural isotopic abundance.

Fig 1

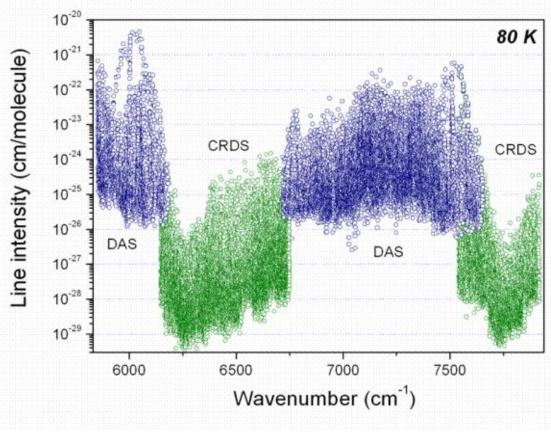

Fig.1 Overview of our line lists of "natural" methane. The tetradecad and the icosad regions were recorded by DAS while the 1.58 µm and 1.28 µm windows were

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[1] S. Kassi, B. Gao, D. Romanini, A. Campargue, Phys. Chem. Chem. Phys., 10, 4410-4419 (2008)

L3

Absolute frequency spectroscopy in the mid-infrared region through a comb-referenced quantum-cascade-laser

A. Gambetta[1]*, D. Gatti*[1]*, A. Castrillo*[3]*, G Galzerano*[2]*, P. Laporta*[1]*, L. Gianfrani*[3]*,*
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Direct referencing of a quantum-cascade-laser (QCL) at 4.3 μm to a near-IR comb [1] emitted by a two-branch Er:fiber oscillator is obtained by exploiting a very simple scheme based on a sum-frequency generation process between the QCL and the main output of the fiber oscillator [2]. Precise tuning of the comb repetition-rate allows the QCL to be scanned across the absorption line of a CO_2 gas sample, and line profiles to be acquired with extreme accuracy and reproducibility. The line central frequencies are retrieved with a standard deviation of 200 kHz in a regime of pressure- and Doppler-broadening with FWHM line-widths of ~150 MHz. Extension of this procedure to other lines and molecules by adoption of widely tunable extended-cavity QCLs offers the potential to redefine most spectroscopic data of the universally used HITRAN database in the crucially important fingerprint region. As representative examples of the experimental data, Fig. 1 (a) shows the beat signal used for QCL stabilization and Fig. 1 (b) reports the P(25) absorption line of the $C_{18}O_{16}O$ ν_3 band at a pressure of about 2 torr as a function of the comb repetition-rate.

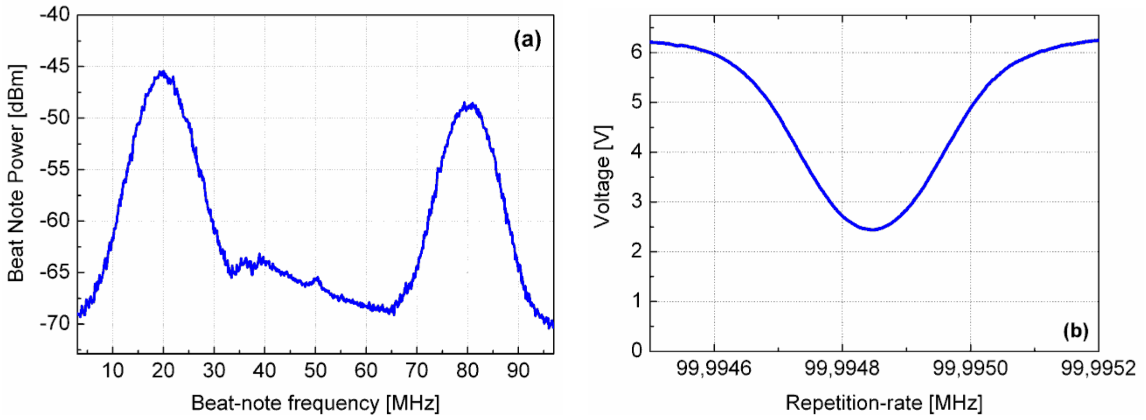

Fig. 1. (a) QCL-linewidth as registered with a 300 kHz resolution bandwidth. (b) Absorption profile of the P(25) CO_2 line at 2 torr.

References
[1] Th. Udem, R. Holzwarth, and T. W. Hänsch, Nature 416, 233-237 (2002)
[2] A. Amy-Klein, A. Goncharov, M. Guinet, C. Daussy, O. Lopez, A. Shelkovnikov, and C. Chardonnet, Opt. Lett. 30, 3320-3322 (2005)

L4

APPLICATIONS OF TDLS IN PHYSICAL CHEMISTRY AND PHYSIOLOGY

Grant A.D. Ritchie

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Tunable diode lasers have contributed to a huge variety of areas from fundamental spectroscopy to clinical diagnostics (cf, the scientific programmes associated with the TDLS conference series). In this presentation, I will focus on how both diode lasers and quantum cascade lasers (qcls) may be used in two such diverse areas, namely coherent spectroscopy and physiology. In the former area, I will focus primarily on non-linear spectroscopy, employing both pulsed and continuous wave qcls, with an emphasis on using such sources for ro-vibrational state preparation in small gas phase molecules. In the latter area, I will report on our most recent efforts to construct a real time O_2/CO_2/H_2O breath analyser, which is incorporated into a ventilation tube, for use in physiology and anesthetic research.

L5

OPO-based real-time breath monitoring by Off-Axis Integrated Cavity Output Spectroscopy

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Trace gases are distinctive indicators of biological processes occurring in plants, animals and humans. An excellent method for highly sensitive and selective detection of these volatile organic compounds is mid-infrared laser spectroscopy, where many molecules have strong distinctive absorption patterns. To capture the dynamics of the gas concentrations and detect multi-component gas samples we use a fast scanning near infrared diode laser with a mode-hop-free wavelength coverage tuning range (up to 5 cm^{-1}) at a speed of up to 100 THz/s. This tunable diode laser light is amplified in a fiber amplifier and converted to the mid-infrared wavelength region with a single resonant Optical Parametric Oscillator (OPO). The OPO is used as a passive converter and has several advantages in comparison other sources of coherent radiation in the mid-IR region: continuous tuning coverage between 2.5 - 4 μm, narrow linewidth (100 MHz) and continuous wave output radiation power of 1.2 W. In combination with Off Axis Integrated Cavity Output Spectroscopy, these advantages are used to build a rapid, sensitive, multicomponent trace gas detector for gases such as ethane, methane, acetone at sub-second time scale. The fast subsecond response time of the system is able to show quantitatively methane, ethane (C_2H_6), water, CO_2 and acetone (C_3H_6O) in single exhalations of human breath at the low part per billion levels.

Part 2 Oral presentations

P1

Recent progress in photonic monitoring of key atmospheric short-lived species

Weixiong Zhao[1, 2], Christophe Lengignon[1], Xiaojuan Cui[1,2], Tao, Wu[1], Eric Fertein[1], Cécile Coeur[1], Laurence Guinet[1], Gerard Wysocki[3], Weidong Chen[1,*]

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Ongoing changes in atmospheric composition due to both natural and anthropogenic influences affect not only climate and atmospheric processes but also have a negative impact on the air quality (hence human health), the OH radical cycle and ecosystems, and consequently on economic developments. Reliable long-term estimates of sources and sinks of key atmospheric species are essential for understanding tropospheric chemical processes and global environmental change. Contrary to the situation for monitoring of long-lived species such as greenhouse gases, accurate and precise direct concentration measurements of reactive short-lived species represent a real challenge because of their very short lifetime (1 to 100 s) and very low concentration in the atmosphere (down to 10^6 molecules/cm^3, corresponding to 0.1 pptv at ***standard temperature and pressure***). This requires the use of advanced analytical technology capable of performing interference-free high sensitivity *in situ* and real time monitoring.

In recent years, significant breakthroughs in photonics and spectroscopic measurement techniques have been made. In this presentation, we report on the recent progress in instrumental development for monitoring of photochemically active species (OH, HONO, NO_3, NO_2) playing a critical role in atmospheric chemistry using modern photonic sources (Quantum Cascade Laser, DFB diode laser, light emitting diode) in conjunction with high-sensitivity spectroscopic techniques such as Faraday rotation spectroscopy (FRS), Cavity Enhanced Absorption Spectroscopy (including off-axis integrated cavity output spectroscopy, OA-ICOS and incoherent broadband cavity enhanced absorption spectroscopy, IBBCEAS), and multipass cell based direct absorption spectroscopy (DAS).

Acknowledgments. This work is supported by the IRENI program of the Région Nord-Pas de Calais. W. Zhao thanks the IRENI program for the postdoctoral support. T. Wu acknowledges the "Bourses d'excellence Eiffel" for his Co-Ph.D. study in France. The support of the Groupement de Recherche International SAMIA between CNRS (France), RFBR (Russia) and CAS (China) is acknowledged.

P2

NOISE PROPERTIES OF AN OPTICAL FREQUENCY COMB STABILIZED TO THE 10^{-13} LEVEL

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Optical frequency combs (OFC) have revolutionized the domain of optical frequency metrology in the last decade by enabling to directly link optical and microwave frequencies. An OFC can be viewed as a huge number of equally-spaced singlemode lasers that are phase-coherently linked together and constitute a frequency ruler over a spectrum which can span as much as one octave. The optical frequency of each comb mode is determined by only two radio-frequencies, the comb repetition rate f_{rep} and the carrier-envelope offset f_{ceo} (global offset of the comb modes from exact harmonics of f_{rep}). Apart from frequency metrology, OFCs have found new applications in high resolution spectroscopy and trace gas sensing during the last years [1-2], as they constitute a versatile spectroscopic tool, combining an excellent accuracy, a high spectral purity and at the same time a broad spectral coverage.

In this work, we will discuss the frequency control and noise properties of highly stabilized OFCs. We will compare a state-of-the-art diode-pumped solid-state Er:Yb:glass oscillator (ERGO) developed and fully stabilized in our laboratories [3-4] with a commercial Er-fiber comb. We will show how the CEO frequency noise of our comb is improved compared to the fiber comb of similar servo-loop bandwidth, leading to a 20-fold reduction of the CEO contribution to the fractional frequency instability of a 1.5-µm comb line (contribution of 10^{-15} at 1 s integration time in our comb versus 2×10^{-14} in the fiber comb).

Traditionally, an OFC is used as an optical frequency synthesizer in high-resolution spectroscopy: the two comb frequencies (f_{rep} and f_{ceo}) are referenced to a microwave frequency standard (atomic clock) to generate absolute optical frequencies. In such a case, the fractional frequency instability of a comb line corresponds in the best case to that of the reference frequency, which is in the order of 10^{-13} at 1 s integration time for the best ones (active H-masers). We will show a fractional frequency instability of our comb at the level of 2×10^{-12} (@1 s) when referenced to a H-maser, experimentally measured from the Allan deviation of the beat signal between a comb line and a 1.56-µm ultrastable laser. An improved stability can be achieved by using the comb in the reverse direction, *i.e.* from optical to microwave. Today, ultra-narrow linewidth (<1 Hz) lasers locked to ultrastable high-finesse Fabry-Perot cavities can achieve a fractional frequency stability in the 10^{-15} range (@1 s) [5] and an OFC locked to such an optical frequency standard can transfer the high relative stability of the laser to a microwave signal, leading to an all-optical ultrastable microwave oscillator. We will present our OFC locked to a cavity-stabilized ultrastable laser, with preliminary ultrastable microwave generation showing a relative frequency instability of 3×10^{-13}, limited by the reference used in the Allan deviation measurement.

[1] S.A. Diddams et al. *Nature* **445**, 627-630, (2007)
[2] M.J. Thorpe et al., *Science* **311**, 1595-1599, (2006)
[3] M.C. Stumpf et al., *Appl. Phys. B* **99**(3), 401-408, (2010)
[4] S. Schilt et al., *Proc.* CLEO-2011, Baltimore, USA; May 1-6, 2011, paper CFK3
[5] J. Alnis et al. *Phys. Rev. A* **77**, 053809, (2008)

P3

OPTICAL FEEDBACK LOCKING OF A QUANTUM CASCADE LASER TO A HIGH FINESSE OPTICAL CAVITY FOR DETECTION OF CH_4 AND N_2O IN AIR USING CAVITY-ENHANCED ABSORPTION SPECTROSCOPY

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Quantum cascade lasers (QCLs) are relatively new sources of mid-infrared radiation. If combined with optical-cavity-enhanced absorption techniques they are well suited to the application of in-field sensing, being compact, sensitive and with low power consumption.

Optical feedback cavity-enhanced absorption spectroscopy (OF CEAS) is an evolution of cavity ring-down spectroscopy (CRDS) that is well suited for use with QCLs. Optical feedback is generated using a V-shaped cavity, which allows only light from within the optical cavity to return to the QCL. As the QCL scans across each cavity mode the emission frequency is locked and the laser linewidth narrows. This increases the intracavity intensity, improving the signal-to-noise ratio. The light intensity exiting the cavity is measured to calculate the sample absorption coefficient and a spectrum may be obtained, see Fig. 1.

Results will be presented of measurements of ambient air and standard samples at atmospheric and reduced pressures. The $^{13}C/^{12}C$ isotope ratio measured in methane by OF CEAS will be compared with results using isotope ratio mass spectrometry (IRMS) and a commercial CRDS based instrument. For this entirely thermoelectrically cooled system, and after an averaging time of 1 s, the minimum detectable absorption coefficient is ~1 × 10^{-8} cm^{-1}, corresponding to a few ppb of CH_4 and N_2O at atmospheric pressure [1].

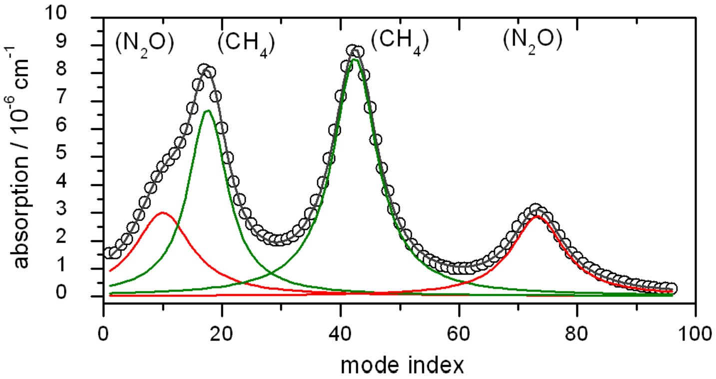

Fig.1 Absorption spectrum of atmospheric air recorded at 1275 cm^{-1} / 7.84 μm under ambient conditions using OF CEAS. Visible are two N_2O and two CH_4 absorption lines.

References

[1] D. J. Hamilton, A. J. Orr-Ewing, Appl. Phys. B, DOI 10.1007/s00340-010-4259-4 (2010).

P4

60 MHz resolution atmospheric spectroscopy of O_3, N_2O, H_2O, CH_4, and CCl_2F_2 with a ground-based external cavity quantum cascade laser heterodyne radiometer

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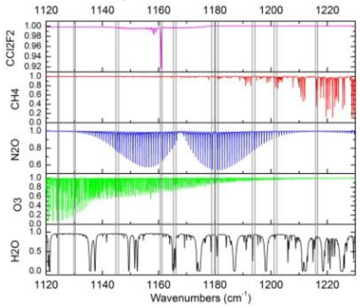
We present 60 MHz resolution (0.002 cm^{-1}) atmospheric transmission spectroscopy results for five molecular species (O_3, N_2O, H_2O, CH_4, and CCl_2F_2) obtained with a widely tunable external cavity quantum cascade laser heterodyne radiometer (EC-QC-LHR) that operates from the ground and uses the sun as background radiation. The local oscillator is an external cavity quantum cascade laser (EC-QCL) configured as in Ref. [1] and exhibits a tuning range of 118 cm^{-1} centered at 1179 cm^{-1} (8.68 μm). Within the overall tuning range, narrow ~1 cm^{-1} wide mode-hope-free tuning spectral micro-windows can be selected. Based on simulated atmospheric absorption shown in Fig. 1, several specific micro-windows were chosen to establish the EC-QC-LHR capabilities. Experimental spectra acquired within four spectral micro-windows are shown in Fig. 2. They clearly demonstrate that true absorption lineshapes can be fully resolved with the EC-QC-LHR instrument. This allows for enhanced determination of pressure, altitude, and temperature profiles [2]. Preliminary evaluation of two data sets (Fig. 2d) acquired at different solar elevation angles confirm stronger absorption due to an increased path within the atmosphere that is expected close to either dawn or sunset. High resolution spectra over the selected narrow windows were obtained with scan times as short as 3 minutes. Heterodyne detection performance was assessed to be about twenty times lower than the ideal shot noise limited case, which given the phase front distortion in the atmosphere (turbulence), represents a satisfactory performance level.

The experimental arrangement and results from the campaign as well as the influence of the acquisition time on signal to noise ratio will be described. Differences between atmospheric LHR performance and gas cell measurements in the laboratory will be discussed. Merits of EC-QC-LHR compared to high resolution Fourier Transform Spectrometer will also be presented.

1)



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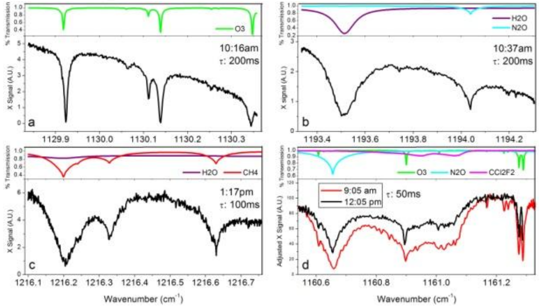

Figure 1) HITRAN simulation at zenithal elevation and standard atmospheric conditions overlaid with mode-hop-free tuning micro-windows and 2) Experimental spectra taken at noted time with lock-in integration time, τ.

[1] G. Wysocki, R. F. Curl, F. K. Tittel, R. Maulini, J.M. Bulliard, and J. Faist, *Appl. Phys. B* **81**, 769-777 (2005).
[2] D. Weidmann, W. J. Reburn, and K. M. Smith, *Appl. Opt.* **46**, 7162-7171 (2007).

Acknowledgements: The authors wish to acknowledge financial support from the US National Science Foundation through the Engineering Research Center MIRTHE and the UK NERC (research grant number NE/H002383/1).

P5

INFRARED LINE INTENSITIES OF FORMALDEHYDE FROM SIMULTANEOUS MEASUREMENTS BY DIODE-LASER AND FOURIER TRANSFORM SPECTROSCOPIES

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Formaldehyde (H_2CO) is an important intermediate compound in the degradation of the volatile organic compounds (VOCs), including methane, in the terrestrial troposphere. Its observation using optical remote sensing in the infrared range relies on the 3.6 and 5.7 μm absorption bands. Band and individual line intensities have been reported in both ranges [1].

With the present work, we aim to also derive infrared line intensities for formaldehyde, however relying on pure rotation line intensities and the known electric dipole moment to determine the particle density. Indeed, because formaldehyde polymerizes or degrades easily, the gas phase may contain polymerization or degradation products. Spectra of H_2CO diluted in 10 hPa of N_2 were therefore simultaneously recorded in 3.6 μm and the $20 - 60$ cm^{-1} ranges, respectively using a tunable diode-laser and a Bruker IFS125HR Fourier transform spectrometers.

[1] A. Perrin, D. Jacquemart, F. Kwabia Tchana, N. Lacome, J. Quant. Spectrosc. Radiat. Transfer, 110, 700-716 (2009), and references therein.

P6

Room Temperature CW Distributed Feedback Quantum Cascade Laser coupled with Optical Feedback Cavity Enhanced Spectroscopy for trace gas analysis in the Mid-IR region.

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Recent developments on distributed feedback quantum cascade lasers (DFB-QCL)[1] and high sensitivity optical methods (e.g. Optical Feedback Cavity Enhanced Absorption Spectroscopy, OF-CEAS [2,3]) make absorption spectroscopy an excellent tool for analysis of atmospheric pollutants.

We have demonstrated that the sensitivity to optical feedback presented by a continous wave DFB-QCL laser working at 4.46 μm is fully compatible with an OF-CEAS, V-shape cavity set up [4]. This technique exploits optical feedback to induce laser frequency self-locking to cavity resonances, resulting in a higher efficiency of light injection and strong cavity transmission, which compensates for low light sensitivity, especially when using room-temperature MCT detectors in the mid-IR. In addition, spectral data points correspond to cavity modes, which are uniformly spaced and offer a spectral resolution of 150 MHz (0.005 cm^{-1}) for a 1m long V-shape cavity with a spectral definition in the 10 kHz range. We obtained a noise equivalent absorption coefficient below 3?10^{-9} cm^{-1} for 1 s averaging of spectra composed by 100 independent points, corresponding to a bandwidth-normalized detection limit of 3?10^{-10} cm^{-1}/√Hz. At 4.46 μm, this yields a detection limit of 35 pptv for N_2O at 50 mbar, corresponding to 4?10^{7} molecules/cm^{3}.

We will present results of atmospheric gas trace spectra at 4.46μm and demonstrate the potential of such sensor for detection of N_2O traces. Features and first results concerning a newly developed spectrometer that measures few ppbv levels of HCHO at 5.7 μm at the exit of a plasma discharge reactor used in air depollution processes [5] will also be presented.

References

[1] Carras M., Maisons G., Simozrag B., Garcia M., Parillaud O., Massies J., and Marcadet X.: Room-temperature continuous-wave metal grating distributed feedback quantum cascade lasers, Appl. Phys. Lett. 96, 161105 (2010)

[2] Morville J., Romanini D., and Chenevier M.: Laser device coupled to a cavity by optical feedback for detecting gas traces, Patent FR2830617 (11/04/2003) and WO03031949 (17/04/2003), Univ. J. Fourier, 2003.

[3] Morville J., Kassi S., Chenevier M., and Romanini D.: Fast, low-noise, mode-by-mode, cavity-enhanced absorption spectroscopy by diode-laser self-locking, Appl. Phys., B 80, 1027-1038, 2005.

[4] Maisons G., Gorrotxategi Carbajo P., Carras M., Romanini D.: Optical-feedback cavity-enhanced absorption spectroscopy with a quantum cascade laser, Opt. Lett., 35, 3607, 2010

[5] Rousseau A., Allegraud K., Guaitella O. : R?acteur de couplage catalyseur /d?charge de surface pour le traitment de polluants atmosph?ric. N°FR07.04900

P7

Study of CH4 multiplet spectra under foreign gas pressure variation using TDLS techniques.

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The results of the experimental researches of N_2– and Ne– pressure induced line profile parameters of multiplets of the methane $2\nu_3$ band are presented. The methane absorption spectra were recorded by two channel photoacoustic or spectrometric techniques with tunable near IR diode lasers. The spectra of CH4 in binary mixtures with N2 and He were measured with a high resolution better than 30 MHz. Spectra processing was performed using the developed in IAO software, in which simultaneous fitting procedure of synthetic spectra to recorded ones under various pressures. The program uses known models of spectral line profiles (Voigt, Rautian-Sobelman, Rosenkranz). It is based on the linear dependence of spectral lines parameters on pressure at which spectrum is recorded. The retrieved line profile parameters (intensities, and coefficients of broadening, shifting and narrowing) were compared with known literature data.

This work is supported by the program of RAS, project 3.9.4. (experiment) and “Bruker Ltd” (design of the software), grant RFFI, project № 10-05-00764-a.

P8

3-5 µm Continuously Tunable Single Mode VECSEL

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Single mode continuously tunable mid-infrared Vertical External Cavity Surface Emitting Lasers (VECSEL) have been realized [1]. Emission wavelength is 3-5 µm with a total mode-hop free tuning range >100 nm. Due to the ~100 µm short cavity length, only one longitudinal mode can develop. While the presented design is for low temperatures, above room temperature operation has already been achieved using a long cavity length [2].

The schematics of our devices are shown in figure 1. IV-VI semiconductors such as PbTe are used for the active region. The top Bragg mirror is curved using a 5 pairs of λ/4 wavelength thick Si\SiO. It is transparent for the 1.55 µm pump beam. The generated laser light is emitted through the bottom mirror. The cavity length can be altered with a piezoelectric crystal. By changing the cavity length, the resonance condition changes and the emission wavelength is continuously shifted.

Figure 2 shows spectra obtained for different drive voltages. The emission wavelength is shifted mode-hop free corresponding to the cavity length. A total tuning range of >100 nm is achieved. The output power of the single mode VECSEL is >50 mW_p, and the absorbed threshold power is <1 W_p for 300 ns pulse width and 9 kHz repetition frequency. While the here presented spectra were measured at 100 K, thermoelectric stabilized devices offering >10 mW_p output power have been realized as well.

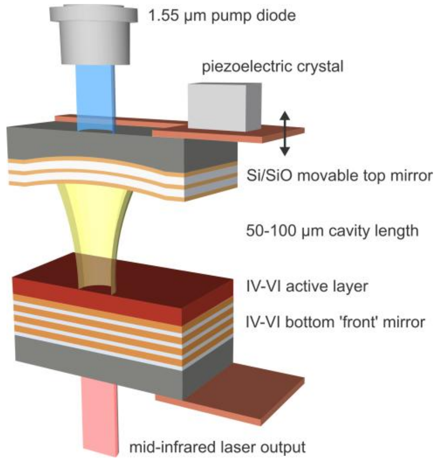

Fig. 1: Schematics of the VECSEL setup. Generated laser light is emitted through the 'front' mirror at the bottom.

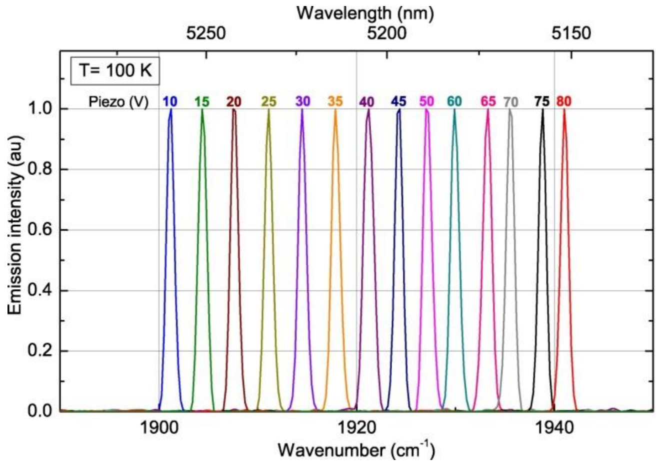

Fig. 2: Superimposed normalized spectra for different piezo actuation voltages. The emission wavelength shifts mode-hop free corresponding to the piezo actuation voltage.

[1] A. Khiar, M. Rahim, M. Fill, F. Felder, F. Hobrecken, H. Zogg, Appl. Phys. Lett. 97, 151104 (2010)
[2] M. Rahim, A. Khiar, F. Felder, M. Fill, H. Zogg, Appl. Phys. Lett. 94, 201112 (2009)

P9

Mid-Infrared Quantum Cascade Laser based Trace Gas Technologies: Recent Progress and Applications in Health and Environmental Monitoring

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This talk will focus on recent advances in the development of sensors based on infrared (IR) semiconductor lasers for the detection, quantification, and monitoring of trace gas species as well as their applications to medical diagnostics, environmental monitoring, industrial process control, and security. The development of compact trace gas sensors, in particular based on quantum cascade (QC) and interband cascade (IC) lasers, permits the targeting of strong fundamental rotational-vibrational transitions in the mid-IR, that are one to two orders of magnitude more intense than overtone transitions in the near-IR [1].

The architecture and performance of several sensitive, selective, and real-time gas sensors based on mid-infrared semiconductor lasers will be described. High detection sensitivity at ppbv (parts per billion in volume) and sub-ppbv concentration levels requires sensitivity enhancement schemes such as multipass optical cells, cavity absorption enhancement techniques, or quartz enhanced photo-acoustic absorption spectroscopy (QEPAS) [1,2]. These three spectroscopic methods can achieve minimum detectable absorption losses in the range from 10^{-8} to 10^{-11} $\mathrm{cm}^{-1}/\sqrt{\mathrm{Hz}}$.

Two recent examples of real world applications of field deployable PAS and QEPAS based gas sensors will be reported, namely the monitoring of ammonia concentrations in exhaled human breath analysis and urban environments. The monitoring of ammonia (NH_3) in exhaled human breath using a laser spectroscopic technique can provide fast, non-invasive diagnostics for patients with liver and kidney disorders [3]. The exhaled NH_3 concentration measurements are obtained with QEPAS using a compact mid-IR, continuous wave (CW), high performance, distributed feedback (DFB) QCL. The QEPAS technique is very suitable for real time breath measurements due to the fast gas exchange inside an ultra-compact gas cell. The minimum detectable NH_3 concentration that is achieved with a thermoelectrically cooled, 24mW, CW, DFB QCL operating at 10.34 µm (965.35 cm^{-1}) is ~ 6 ppbv (with a 1 sec time resolution). An amplitude modulated photo-acoustic spectroscopy (AM-PAS) technique was employed to monitor atmospheric NH_3 at sub-ppb concentration levels using a 67mW, 10.34 µm CW-TEC Daylight Solutions EC-QCL based sensor platform.

References:

[1] R. F. Curl, F. Capasso, C. Gmachl, A. A. Kosterev, B. McManus, R. Lewicki, M. Pusharsky, G. Wysocki, and F. K. Tittel,” Quantum cascade lasers in chemical physics” *Chem. Phys. Lett.*, **487**, 1 (2010)

[2] L. Dong, A.A. Kosterev, D. Thomazy and F.K.Tittel, ”QEPAS spectrophones: design, optimization and performance”, *App. Phys. B* **100**, 627-635 (2010)

[3] T. Risby and F.K. Tittel, “Current status of mid-Infrared quantum and interband cascade lasers for clinical breath analysis”. *SPIE Optical Engineering*, **49**, 111123-111123-14 (2010)

P 10

Infrared Laser Spectroscopic Analysis of Surgical Smoke

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Several surgical instruments (harmonic scalpels, high-speed drills and saws, lasers and electroknives) generate heat and cause tissue pyrolysis, which produces what is usually referred to as *surgical smoke* [1].

In a recent study we investigated the chemical composition of surgical smoke – collected during minimally invasive surgery at the University hospital Zurich – by infrared laser spectroscopy with a difference frequency generation (DFG) based spectrometer (2817– 3144 cm^{-1}, $\langle_{\min} = 8.7\times10^{-7}$ cm^{-1}) [2] and with a distributed feedback (DFB) laser diode at 2323.6 nm for carbon monoxide (CO) detection ($\langle_{\min} = 3.1\times10^{-8}$ cm^{-1}, $c_{\min} = 250$ ppb CO).

With the DFG spectrometer, in addition to water vapor, we detected methane in most samples (<0.1–9.1 ppm), and rarely ethane (<0.1–2 ppm) and ethylene (<5–10 ppm) (Fig. 1 a,b). More interestingly, we found traces of the employed anesthetic (sevoflurane) at concentrations of up to 450 ppm in the abdominal cavity of the patient (Fig. 1 a). For comparison, the recommended exposure limit for halogenated anesthetics is 2 ppm. Since surgeons occasionally release smoke from the patient's peritoneum to restore good visibility, vapors of the anesthetic are released into the operation room. With the DFB laser diode we detected CO in four out of six samples at concentrations between 0.3 and 3.2 ppm (Fig. 1 c), well below the recommended exposure limit of 30 ppm.

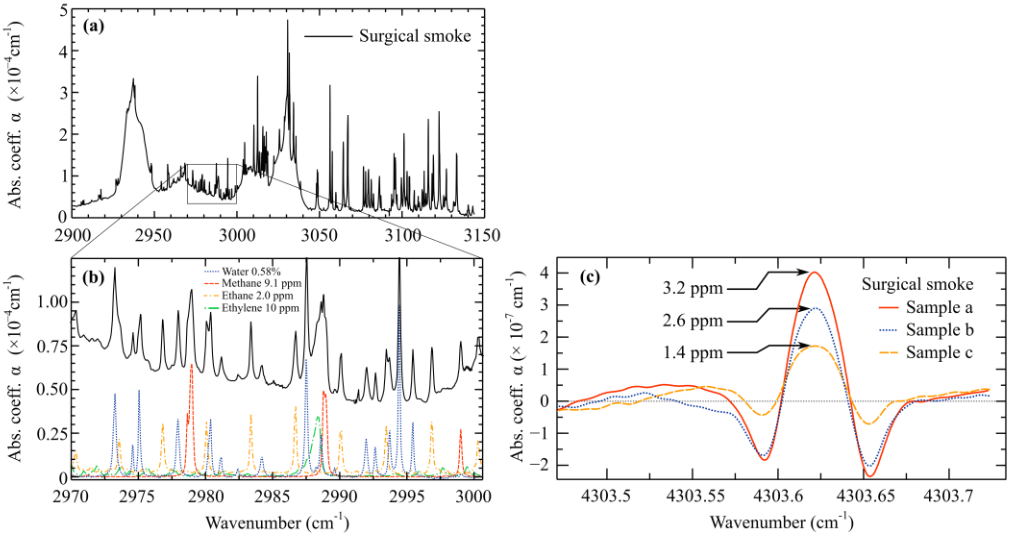

Fig.1. (a,b) Surgical smoke spectrum measured with the DFG spectrometer (the four broad peaks are due to sevoflurane). **(c)** CO absorption line (wavelength modulation).

References
[1] W. Barrett and S. Garber, *Surg. Endosc.* **17**, 979–987 (2003).
[2] M. Gianella and M.W. Sigrist, *Appl. Opt.* **50**, A11–A19 (2011).

P11

CO_2 and N_2O isotopic ratio measurements by QCL spectroscopy - recent developments and environmental applications

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Isotope ratios of greenhouse gases are excellent tools to study their sources and sinks, because the involved relevant chemical reactions and biochemical processes lead to characteristic isotopic fractionation. For example, the distinct CO_2 isotopic signatures of respiration, photosynthesis and fossil fuel burning can be used for the apportionment of CO_2 fluxes at various scales. Similarly, the intramolecular distribution of ^{15}N in N_2O can be used to study bacterial nitrification and denitrification processes in soils and aquatic systems, which are the main sources of atmospheric N_2O.

The development of QCL based spectrometers and their ongoing improvement have led to instruments with a precision below 0.1 ‰ for isotope ratio measurements of both CO_2 and N_2O [1, 2]. To reach this precision, N_2O can be sampled using an automated, liquid nitrogen free preconcentration unit [3]. While improvements in calibration and validation procedures are ongoing, several studies already illustrate the power of combining precision and high time resolution for a range of environmentally and technically relevant topics.

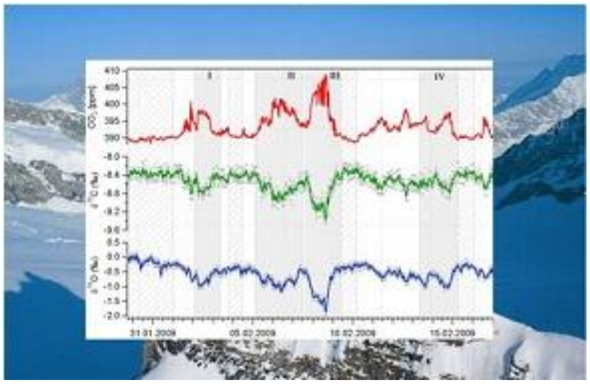

Fig. 1 Continuous measurements of $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 at Jungfraujoch (3580 m a.s.l.) reveal sources and residence time in the atmospheric boundary layer of the air masses. [4]

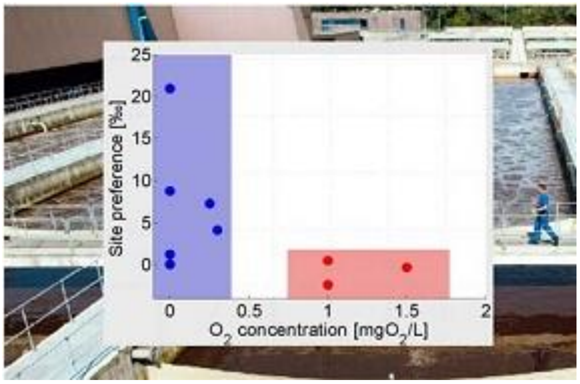

Fig. 2 N_2O production under denitrifying conditions (blue), and under nitrifying conditions (red). Reduction of N_2O release is relevant because N_2O frequently dominates the total greenhouse gas emissions during waste water treatment.

[1] B. Tuzson et al., Applied Physics B: Lasers and Optics, 92(3) 1-8 (2008).
[2] H. Wächter et al., Optics Express, 16(12) 9239-9244 (2008).
[3] J. Mohn et al., Atmos. Meas. Tech., 3, 609–618 82010).
[4] B. Tuzson et al., Atmos. Chem. Phys., 11, 1685–1696, (2011)

P12

GAS IN SCATTERING MEDIA ABSORPTION SPECTROSCOPY BASED ON FREQUENCY-MODULATED CONTINUOUS-WAVE TECHNIQUES

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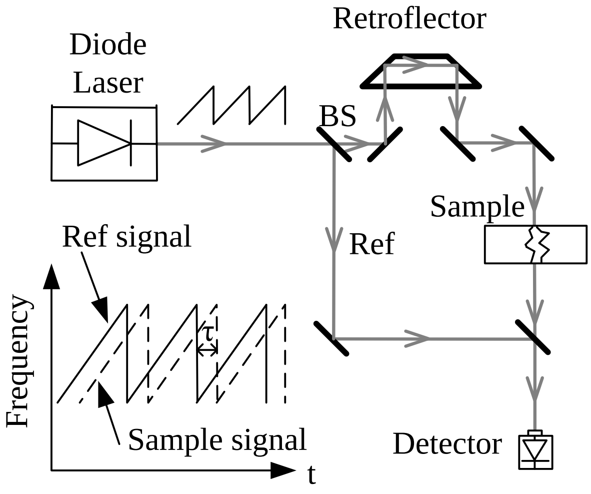
The presence and exchange of gases in scattering media can be assessed by narrow-band absorption spectroscopy using tunable diode lasers. According to Beer-Lambert’s law, the absorption signal not only depends on the concentration, but also on the path-length that the light has travelled. Two methods have been used to evaluate the path-length in scattering media: a relative one based on the mean equivalent path-length, which is defined as the equivalent open-path distance which yields the same absorption [1]; and another absolute method which employs time-resolved spectroscopy, also called time-of-flight spectroscopy, where a short-pulsed laser beam is used to measure the decay curve of the light passing through the scattering medium [2].
In the present work a Frequency-Modulated Continuous-Wave (FMCW) technique, well known in the telecommunication field, is used to evaluate the optical path-length in the scattering media. The basic principle of the FMCW technique is presented in the figure to the right. The laser frequency is modulated by a ramp signal and a Michelson interferometer setup is used to obtain the beat frequency between the reference and the sample beam. Due to the scattering in the sample, the light will pass through different path-lengths and will then induce corresponding beat frequencies with the reference beam. By analyzing the beat frequency in the detected signal we can evaluate how the light passes through the scattering medium. By combination with the absorption spectroscopy signal we can obtain the gas concentration in the sample when the laser is scanned across an absorption line. Proof-of-principle experiments on polystyrene foam are reported.



Reference

[1]. M. Sj?holm, G. Somesfalean, J. Alnis, S. Andersson-Engels, and S. Svanberg, Optics Letters **26**, 16 (2001).

[2]. G. Somesfalean, M. S. holm, J. Alnis, Claes af Klinteberg, S. Andersson-Engels, and S. Svanberg, Applied Optics **41**, 3538 (2002).

P13

HIGH PRECISION MEASUREMENTS OF CARBON ISOTOPE RATIO AT ATMOSPHERIC PRESSURE IN HUMAN BREATH USING A 2 μm DIODE LASER

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The analysis of the $^{13}CO_2/^{12}CO_2$ isotope ratio is being widely used in geology, volcanology, criminology, medicine, and many other fields. The constant extension of the range of its applications stimulates the development of novel experimental techniques capable of high measurement precision and accuracy. The spectral measurement techniques are usually based on comparison between the absorption data obtained for individual molecular lines at gas pressures reduced to 10-100 Torr to prevent spectral lines overlapping. The aim of this work is to demonstrate the technique of measuring the $^{13}CO_2/^{12}CO_2$ isotope ratio at atmospheric pressure with precision and reproducibility high enough to meet the needs of medical practice.

The light source used is a VCSEL laser diode (*Vertilas*) emitting some 0.5 mW of power near 2.007 μm. A Herriott multipass cell with total optical path length of 24 m was used. The procedure used to analyze the spectra recorded is based on multivariate linear regression from simulated spectra of the $^{13}CO_2$, $^{12}CO_2$, and H_2O molecules. The spectra of these molecules were calculated from HITRAN-2008 database in the approximation of Voigt line profile. Certain corrections of intensities, pressure broadening, and pressure-induced shift parameters from HITRAN-2008 were required to obtain minimum fitting residual. Data from pressure and temperature sensors mounted in the multipass cell were taken into account in calculations of these simulated spectra.

The proposed technique of determining the concentration of gas components at atmospheric pressure does not involve measuring the intensities of individual lines. This allows carrying out measurements on complex spectrum with overlapped lines directly, and thus one do not need to solve the inverse problem of extracting the contribution of individual spectral lines. In this approach, use can be made of relatively low-level passive temperature stabilization, for possible temperature variations are recorded by the sensors and are taken into account in spectra simulations. In other words, it is necessary to measure the temperature in the sample cell, rather than stabilize it. Furthermore, with this approach there is no need for the use of a reference cell with a calibrated gas mixture.

The δ-value precision determined by means of the Allan deviation plot with an averaging time of 3 minutes amounted to 0.07 ‰. The precision level necessary for medical breath tests (0.5 ‰) can be achieved with an averaging time of 3 seconds. The standard deviation of the δ-value measured for 16 hours was no more that 0.2 ‰, no special measures being taken to thermally and mechanically isolate and stabilize the experimental setup.

Acknowledgements. This work was partially supported by the Russian Foundation for Basic Research (RFBR Grants 10-02-01111-a and 11-08-01127-a).

Part 3 Poster presentations

Poster session A

A1

TDLS system to measure CO_2:N_2 gas mixtures with 0.12 % accuracy

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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 %. In [1] we've considered possibility to achieve this level. Present paper is next step.

Green house gases in atmosphere measurements require accurate gas mixture standards. International inter-comparison campaign is performing to achieve this goal. As result accurate instruments are necessary for the campaign. Additional requirement – primary standard: after development no calibrations.

Instrument for high accurate gas mixture measurement with TDLS was optimized and developed, as well as software of the instrument operation and calibration procedures. After this moment no calibration of the instrument is necessary. The instrument was developed for VNIIM – organization responsible for gas mixture standards in Russia. Using calibrated gas mixtures the instrument developed tests of accuracy achieved were performed (Fig.1).

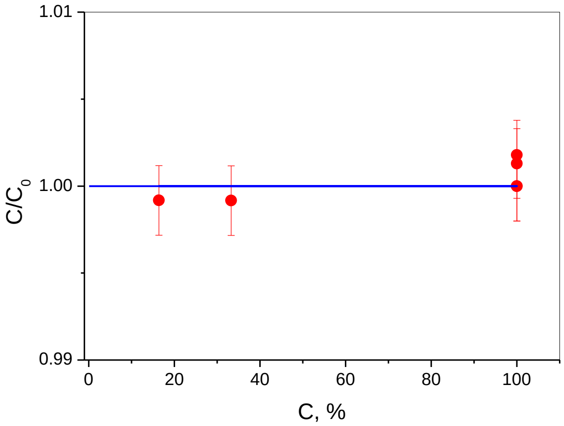

Fig.1 Calibrated gas mixtures measurements

Accuracy achieved - 0.12 % is in agreement with accuracy estimate -0.15 %. Based on achieved accuracy and analysis performed, TDLS can be considered as high accurate gas mixtures primary standard.

[1] L.Konopelko, A.Nadezhdinskii, Accuracy in TDLS. TDLS as gas mixtures primary standard, Abstracts of TDLS 2009, Zermatt, Switzerland, p.76.

A2

DL frequency accurate calibration

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Accuracy is one of recent challenges for Tunable Diode Laser Spectroscopy (TDLS). In present paper DL frequency tuning accuracy will be considered and analyzed.

Motivations: Traditional spectroscopy – accurate measurements of molecule under investigation spectral line frequency and intensity. Spectral line shape – accurate measurements of spectral line shift, broadening, and shape (see B2). TDLS based primary gas mixture standard – accurate measurement of impurity concentration in gas mixture under investigation (see A1).

Mechanisms of DL frequency tuning errors were identified and analyzed. DL frequency calibrating procedure minimizing errors under consideration was proposed. DL frequency tuning calibration was developed using both FP calibrated and fiber etalons. Fiber etalon calibration refer to calibrated FP etalon was developed and tested with 6 10^{-5} relative accuracy. FP etalon was calibrated with 4 10^{-5} relative accuracy (Fig.1).

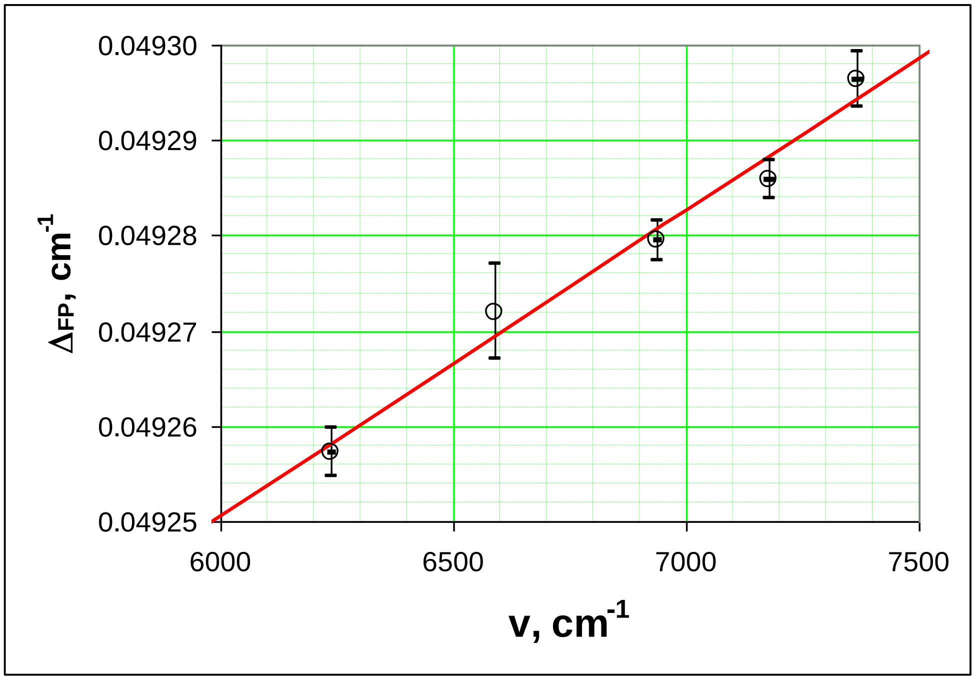

Fig.1 Spectral dependence of calibrated FP etalon free spectral range

Conclusion: for accurate measurements, each FP etalon has to be calibrated and its spectral dependence has to be taken into account.

Absolute accuracy of DL frequency tuning calibration below 10^{-4} cm^{-1} was demonstrated.

A3

Water channel of TDLS complex for the airplane-laboratory

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Russian state program to develop airplane-laboratory started some time ago. It contains TDLS complex [1]. Refer to program plan water channel of TDLS complex was developed subject of present paper. Goals of TDLS complex water channel are following: to measure during flight humidity, isotopes abundance, and atmosphere turbulence parameters.

Spectral range 7182-7184 cm^{-1} was selected as analytical one for above mentioned goals solution. This spectral range is covering by excitation current tuning of NEL diode laser in use. H_2O spectral line (7182.940 cm^{-1}) (see D2) is using for humidity and atmosphere turbulence parameters measurements. Spectral range 7182.8-7184 cm^{-1} is using to measure water molecules isotopes abundance ($H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, and HDO) (see C2).

Using fiber splitters DL radiation was directed to three modules. Reference module contains cell with low pressure water vapor to stabilize DL frequency tuning. Vacuum Chernin matrix optical system (L = 39 m) is using to measure humidity and water molecules isotopes abundance. Part of DL radiation is directed through airplane window to measure humidity variation in open atmosphere to determine turbulence parameters (see B3).

Fig.1 View of vacuum Chernin matrix optical system and module of electronics developed

Atmosphere air sampling system contains inlet module, air heating module (to heat cold collected air), air sample under investigation pressure stabilizer, and vacuum pump. This system provides laminar air flow through Chernin matrix optical system at rate of 0.2 liter/sec at reduced pressure 48 mBar. Both gas pressure inside cell and its temperature are measuring in real time of data recording.

[1] V.Galaktionov, V.Khattatov, A.Nadezhdinskii, Ya.Ponurovskiy, D.Stavrovskii, I.Vyazov, V.Zaslavskii, TDLS complex development for airplane-laboratory “Atmosphere”, Abstracts of TDLS 2009, Zermatt, Switzerland, p.44.

A4

OPTICAL FEEDBACK LOCKING OF A QUANTUM CASCADE LASER TO A HIGH FINESSE OPTICAL CAVITY FOR DETECTION OF CH_4 AND N_2O IN AIR USING CAVITY-ENHANCED ABSORPTION SPECTROSCOPY

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Quantum cascade lasers (QCLs) are relatively new sources of mid-infrared radiation. If combined with optical-cavity-enhanced absorption techniques they are well suited to the application of in-field sensing, being compact, sensitive and with low power consumption.

Optical feedback cavity-enhanced absorption spectroscopy (OF CEAS) is an evolution of cavity ring-down spectroscopy (CRDS) that is well suited for use with QCLs. Optical feedback is generated using a V-shaped cavity, which allows only light from within the optical cavity to return to the QCL. As the QCL scans across each cavity mode the emission frequency is locked and the laser linewidth narrows. This increases the intracavity intensity, improving the signal-to-noise ratio. The light intensity exiting the cavity is measured to calculate the sample absorption coefficient and a spectrum may be obtained, see Fig. 1.

Results will be presented of measurements of ambient air and standard samples at atmospheric and reduced pressures. The $^{13}C/^{12}C$ isotope ratio measured in methane by OF CEAS will be compared with results using isotope ratio mass spectrometry (IRMS) and a commercial CRDS based instrument. For this entirely thermoelectrically cooled system, and after an averaging time of 1 s, the minimum detectable absorption coefficient is $\sim 1 \times 10^{-8}$ cm^{-1}, corresponding to a few ppb of CH_4 and N_2O at atmospheric pressure [1].

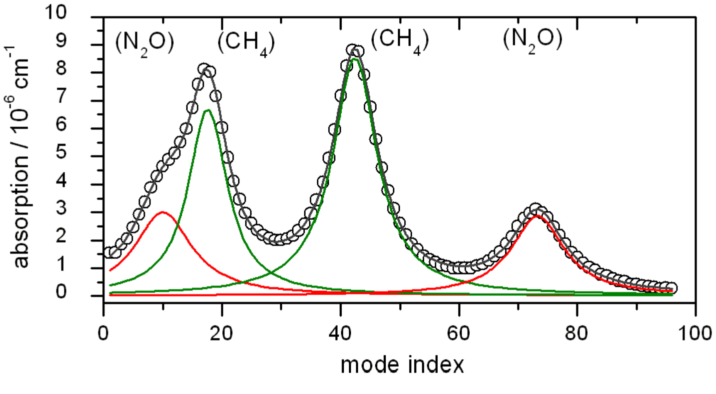

Fig.1 Absorption spectrum of atmospheric air recorded at 1275 cm^{-1} / 7.84 μm under ambient conditions using OF CEAS. Visible are two N_2O and two CH_4 absorption lines.

References
[1] D. J. Hamilton, A. J. Orr-Ewing, Appl. Phys. B, DOI 10.1007/s00340-010-4259-4 (2010).

A5

60 MHz resolution atmospheric spectroscopy of O_3, N_2O, H_2O, CH_4, and CCl_2F_2 with a ground-based external cavity quantum cascade laser heterodyne radiometer

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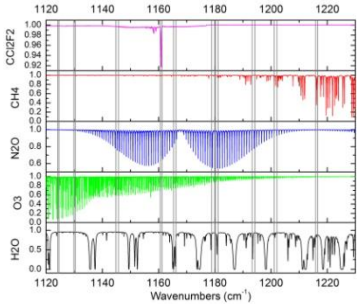
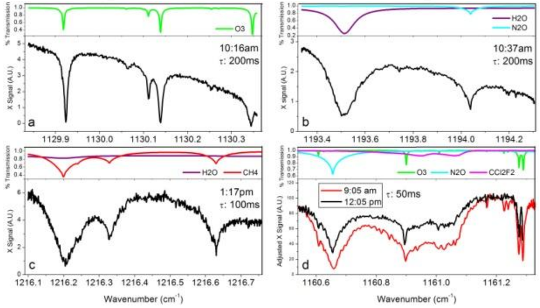
We present 60 MHz resolution (0.002 cm^{-1}) atmospheric transmission spectroscopy results for five molecular species (O_3, N_2O, H_2O, CH_4, and CCl_2F_2) obtained with a widely tunable external cavity quantum cascade laser heterodyne radiometer (EC-QC-LHR) that operates from the ground and uses the sun as background radiation. The local oscillator is an external cavity quantum cascade laser (EC-QCL) configured as in Ref. [1] and exhibits a tuning range of 118 cm^{-1} centered at 1179 cm^{-1} (8.68 μm). Within the overall tuning range, narrow ~1 cm^{-1} wide mode-hope-free tuning spectral micro-windows can be selected. Based on simulated atmospheric absorption shown in Fig. 1, several specific micro-windows were chosen to establish the EC-QC-LHR capabilities. Experimental spectra acquired within four spectral micro-windows are shown in Fig. 2. They clearly demonstrate that true absorption lineshapes can be fully resolved with the EC-QC-LHR instrument. This allows for enhanced determination of pressure, altitude, and temperature profiles [2]. Preliminary evaluation of two data sets (Fig. 2d) acquired at different solar elevation angles confirm stronger absorption due to an increased path within the atmosphere that is expected close to either dawn or sunset. High resolution spectra over the selected narrow windows were obtained with scan times as short as 3 minutes. Heterodyne detection performance was assessed to be about twenty times lower than the ideal shot noise limited case, which given the phase front distortion in the atmosphere (turbulence), represents a satisfactory performance level.

The experimental arrangement and results from the campaign as well as the influence of the acquisition time on signal to noise ratio will be described. Differences between atmospheric LHR performance and gas cell measurements in the laboratory will be discussed. Merits of EC-QC-LHR compared to high resolution Fourier Transform Spectrometer will also be presented.



1)



2)

Figure 1) HITRAN simulation at zenithal elevation and standard atmospheric conditions overlaid with mode-hop-free tuning micro-windows and 2) Experimental spectra taken at noted time with lock-in integration time, τ.

[1] G. Wysocki, R. F. Curl, F. K. Tittel, R. Maulini, J.M. Bulliard, and J. Faist, *Appl. Phys. B* **81**, 769-777 (2005).
[2] D. Weidmann, W. J. Reburn, and K. M. Smith, *Appl. Opt.* **46**, 7162-7171 (2007).

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A6

Room Temperature CW Distributed Feedback Quantum Cascade Laser coupled with Optical Feedback Cavity Enhanced Spectroscopy for trace gas analysis in the Mid-IR region.

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Recent developments on distributed feedback quantum cascade lasers (DFB-QCL)[1] and high sensitivity optical methods (e.g. Optical Feedback Cavity Enhanced Absorption Spectroscopy, OF-CEAS [2,3]) make absorption spectroscopy an excellent tool for analysis of atmospheric pollutants.

We have demonstrated that the sensitivity to optical feedback presented by a continous wave DFB-QCL laser working at 4.46 μm is fully compatible with an OF-CEAS, V-shape cavity set up [4]. This technique exploits optical feedback to induce laser frequency self-locking to cavity resonances, resulting in a higher efficiency of light injection and strong cavity transmission, which compensates for low light sensitivity, especially when using room-temperature MCT detectors in the mid-IR. In addition, spectral data points correspond to cavity modes, which are uniformly spaced and offer a spectral resolution of 150 MHz (0.005 cm^{-1}) for a 1m long V-shape cavity with a spectral definition in the 10 kHz range. We obtained a noise equivalent absorption coefficient below 3?10^{-9} cm^{-1} for 1 s averaging of spectra composed by 100 independent points, corresponding to a bandwidth-normalized detection limit of 3?10^{-10} cm^{-1}/√Hz. At 4.46 μm, this yields a detection limit of 35 pptv for N_2O at 50 mbar, corresponding to 4?10^{7} molecules/cm^{3}.

We will present results of atmospheric gas trace spectra at 4.46μm and demonstrate the potential of such sensor for detection of N_2O traces. Features and first results concerning a newly developed spectrometer that measures few ppbv levels of HCHO at 5.7 μm at the exit of a plasma discharge reactor used in air depollution processes [5] will also be presented.

References

[1] Carras M., Maisons G., Simozrag B., Garcia M., Parillaud O., Massies J., and Marcadet X.: Room-temperature continuous-wave metal grating distributed feedback quantum cascade lasers, Appl. Phys. Lett. 96, 161105 (2010)

[2] Morville J., Romanini D., and Chenevier M.: Laser device coupled to a cavity by optical feedback for detecting gas traces, Patent FR2830617 (11/04/2003) and WO03031949 (17/04/2003), Univ. J. Fourier, 2003.

[3] Morville J., Kassi S., Chenevier M., and Romanini D.: Fast, low-noise, mode-by-mode, cavity-enhanced absorption spectroscopy by diode-laser self-locking, Appl. Phys., B 80, 1027-1038, 2005.

[4] Maisons G., Gorrotxategi Carbajo P., Carras M., Romanini D.: Optical-feedback cavity-enhanced absorption spectroscopy with a quantum cascade laser, Opt. Lett., 35, 3607, 2010

[5] Rousseau A., Allegraud K., Guaitella O. : R?acteur de couplage catalyseur /d?charge de surface pour le traitment de polluants atmosph?ric. N°FR07.04900

A7

Multi-mode diode laser correlation spectroscopy using gas-filled porous materials for path length enhancement

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A straight forward method to improve sensitivity in diode laser absorption spectroscopy for point monitoring is by employment of multi-pass gas cells to increase the optical path length. Three typical embodiments have been developed: (a) White and Herriot cells; (b) cavity enhanced techniques; (c) use of integrating spheres as sampling cells.

An alternative approach can be based on the gas in scattering media absorption spectroscopy (GASMAS) [1, 2] by using gas-filled porous materials as multi-pass cells. In GASMAS, the equivalent pathlength in porous materials can easily be increased to one order of magnitude larger compared with the physical length, which implies promising applications of scattering materials for pathlength enhancement. In the present work, this new approach was applied to multi-mode diode laser correlation spectroscopy (MDL-COSPEC) [3]. Compact and robust multi-pass cells made of polystyrene foam and Al_2O_3 ceramic with open pores were employed in proof-of-principle measurements of oxygen detection. Figure 1 shows a typical signal pair and a sample of recorded signal pair magnitudes acquired during 20 s. Figure 2 shows the Allan variance analysis rendering the stability of the system.

By using porous scattering materials as multi-pass cells, the compactness and sensitivity of the MDL-COSPEC system can be improved. This approach is particularly helpful for multi-species detection, where employment of several gas cells is required. Due to the general high-power capability of MDLs, the sensitivity can be greatly enhanced by using porous media with large thicknesses.

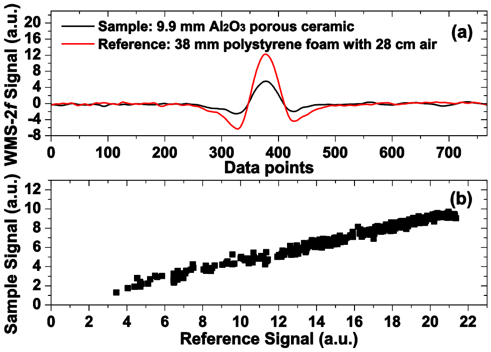

Fig. 1 (a) Typical O_2 signal pair; (b) recorded signal pair magnitudes acquired during 20 s due to random multi-mode absorptions.

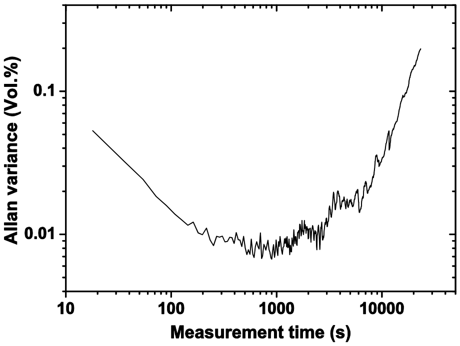

Fig. 2 Allan variance rendering the stability of the O_2 detection system.

References:

[1] M. Sjöholm, G. Somesfalean, J. Alnis, S. Andersson-Engels, and S. Svanberg, Opt. Lett. **26**, 16 (2001)

[2] G. Somesfalean, M. Sjöholm, J. Alnis, C. Klinteberg, S. Andersson-Engels, and S. Svanberg, Appl. Opt. 41, 3538 (2002)

[3] G. Somesfalean, M. Sjoholm, L. Persson, H. Gao, T. Svensson, and S. Svanberg, Appl. Phys. Lett. **86**, 184102 (2005)

A8

Frequency noise properties of free-running room temperature 4.6-µm quantum cascade lasers

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Narrow-linewidth lasers exhibiting a high spectral purity have important applications in various research fields, such as high-resolution spectroscopy, coherent optical communications or time and frequency metrology, to name a few. Quantum cascade lasers (QCLs) are already widely used in mid-infrared spectroscopy and trace gas sensing and show promising properties for frequency metrology applications, owing to their expected narrow intrinsic linewidth (that results from their linewidth-enhancement factor $\alpha_H \approx 0$).

We have recently investigated the frequency noise properties of commercial free-running singlemode QCLs emitting in the 4.6-µm wavelength range and operated in CW mode near room temperature. Since optical frequencies, and thus frequency noise, cannot be directly accessed, our frequency noise measurements were performed by converting the laser frequency fluctuations into intensity variations using the side of the carbon monoxide R14 absorption line (at 2197cm^{-1}) as a frequency discriminator, in standard single-pass direct absorption spectroscopy (1 cm long gas absorption cell filled with pure CO at 20 mbar).

The laser frequency noise power spectral density (PSD) provides much more information about the laser noise than a linewidth measurement and a simple formula can be used to retrieve the laser linewidth from the frequency noise PSD [1]. The frequency noise measured in our QCLs reveals a nearly perfect $1/f$-behavior from 3 Hz up to 10 kHz Fourier frequencies and $1/f^{3/2}$ at higher frequencies, with a noise level of 2x10^8 Hz^2/Hz at 100 Hz and below 10^2 Hz^2/Hz at 10 MHz. The upper limit for the white frequency noise level inferred from our measurement lies below 100 Hz^2/Hz, corresponding to ~300 Hz instantaneous linewidth. However, the real laser linewidth observed in a reasonable time scale is strongly broadened by the $1/f$-type noise, leading to a calculated linewidth of 650 kHz at 15 ms observation time, which is in good agreement with the spectral width of the heterodyne beat signal between the two identical QCLs observed in a complementary experiment. The measured frequency noise is a factor of 100 lower than the one previously reported by Bartalini et al. [2], obtained with a similar laser (4.3 µm DFB) but operated at 77 K (instead of 277 K for ours). Our results show that a servo-loop bandwidth of a few hundreds of kHz should be sufficient to significantly reduce the QCL linewidth using Pound-Drever-Hall (PDH) stabilization to a high-finesse reference Fabry-Perot cavity. Finally, preliminary results of such a PDH stabilization to a Fabry-Perot cavity with 5 MHz resonance width will be presented.

[1] G. Di Domenico et al., Applied Optics, Vol. 49, No. 25, pp. 4801-4807, 2010
[2] S. Bartalini et al., Phys. Rev. Lett., Vol. 104, pp. 083904, 2010

A9

NEW INTENSITY MEASUREMENTS OF H_2O AROUND 850 NM USING TUNABLE ECDL SPECTROSCOPY

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This study reports new laboratory measurements of water vapor intensities using tunable external cavity diode laser (ECDL) spectroscopy around 850 nm. The ECDL used was a Toptica Photonics DL100 in Littrow configuration. The experimental setup is basically the same as that used in our previous study (see [1] for details). Here, particular care was taken about baseline stability and mode-hop free scanning up to 30 GHz (approximately 1 cm^{-1}) for each individual line in order to improve line surface precision. In addition to the experimental setup presented in ref. 1, a new compact grating spectrometer with a CCD-array detector (Ocean Optics, HR2000+ with 0.3 nm spectral resolution) was used to check that residual spontaneous emission of the ECDL is negligible. It was found that this is an indispensable step each time the central wavenumber of the scan is changed.

Concerning theoretical modeling of the water lines, we have reduced the residuals using a modified Voigt profile by adjusting, during the non-linear least-squares fitting (NLSF) procedure, also the Gaussian width (that is usually fixed to the theoretical value). Comparisons of our new data to our previous intensity values and those found in the most recent version of HITRAN database (HITRAN2008 [2]) will be presented. Line intensities in the 9500 - 14500 cm^{-1} region were taken from R. Tolchenov and J. Tennyson [3].

In a next step, these measurements will be used to determine theoretical line profiles for H_2O near infrared lines that include pressure-narrowing and speed-dependent effects. These effects are important to consider for the modeling of the radiative transfer in the Earth's atmosphere.

[1] N. Ibrahim, P. Chelin, J. Orphal, and Y.I. Baranov, JQSRT **109**, 2523–2536 (2008).
[2] L.S. Rothman, et al., JQSRT **110,** 533–572 (2009).
[3] R. Tolchenov and J. Tennyson, JQSRT, **109**, 559–568 (2008).

A10

SPECTROSCOPY OF ACETYLENE AT HIGH TEMPERATURE: APPLICATION TO ATMOSPHERIC AND COMBUSTION MEDIA.

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In the last decades, laser spectroscopic techniques have been greatly improved, in particular their applications to atmospheric monitoring [1-4] and combustion diagnostics [5-6]. To retrieve the C_2H_2 abundance in some of these media, N_2-broadenings of C_2H_2 lines coefficients and their temperature dependencies are needed.

Using a tunable diode-laser spectrometer [7] adapted with a home made high temperature absorption cell [8], we have measured the N_2-broadening coefficients of absorption lines in the $\nu_4+\nu_5$ band of acetylene located around 1330 cm^{-1}.

The experimental determination of N_2-broadening coefficients was performed by fitting to the experimental profile of each line recorded at each temperature, the theoretical Voigt, Rautian and Galatry models. The latter take into account the Dicke effect, a narrowing due to the molecular confinement.

From these values of broadening, we have determined temperature dependencies of these coefficients and compared these results with our previous studies made at low temperature using the same technique [9-10].

[1] J. Rudolph, D.H. Ehhalt and A. Khedim, J. Atmos. Chem., 2, 117-124 (1984).
[2] W. Macy Jr., Icarus, 41(1), 153-158 (1980).
[3] S.J. Kim, T.R. Geballe, K.S. Noll and R. Courtin, Icarus, 17, 522-532 (2005).
[4] M. Burgdorf, G. Orton, J. van Cleve, V. Meadows and J. Houck, Icarus, 184, 634-637 (2006).
[5] Z.S. Li, M. Linvin, J. Zetterberg, J. Kiefer and M. Aldén, Proceeding of the Combustion Institute, 31(1), 817-824 (2007).
[6] J. Kiefer and P. Ewart, Progress in Energy and Combustion Science (2010) – in press.
[7] M. Lepère, G. Blanquet, J. Walrand and J.-P. Bouanich, J. Mol. Spectrosc., 180, 218–226 (1996).
[8] L. Fissiaux, N. Sanzahrov, J.-Cl. Populaire and M. Lepère, "High Temperature infrared absorption cell used for diode-laser spectroscopy", poster presented during the *8th International Conference on Tunable Diode Laser Spectroscopy (July 11th to 15th, Zermatt, Switzerland).*
[9] M. Dhyne, L. Fissiaux, J.-Cl. Populaire and M. Lepère, J. Quant. Spectrosc. Radiat. Transfer, 110 (6-7), 358-366 (2009).
[10] M. Dhyne, P. Joubert, J.-Cl. Populaire and M. Lepère, J. Quant. Spectrosc. Radiat. Transfer, 112 (6), 973-989 (2010).

A11

HIGH TEMPERATURE INFRARED ABSORPTION CELL USED FOR DIODE-LASER SPECTROSCOPY

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The determination of the infrared spectroscopic line parameters at high temperatures is particularly important in remote sensing of high temperature sources such as flames, combustion processes [1], exhaust plumes and stellar atmospheres [2]. For example, the knowledge of spectral line parameters of hydrocarbon gases at high temperatures is important for the in situ determination of the concentration of these gases in combustion systems. The main source of these parameters is the database HITEMP [3], essentially composed by theoretical results.

In our laboratory, we have developed an absorption cell for infrared spectroscopy studies of gas mixtures at high temperature (from room to 500 K). In order to demonstrate the feasibility, the characteristics and the interest of this cell, allene (C_3H_4), ethane (C_2H_6) and mono-deuterated ethylene (C_2H_3D) spectra have been recorded by diode-laser spectroscopy. When the gas temperature increases, lines of vibrational hot bands appear in the spectra, while the absorption of fundamental bands decreases. In this work, we present the set-up of our high temperature absorption cell and some examples of recorded spectra, putting in evidence the cell characteristics.

[1] Lin W.F., Wang J.T., Savinell R.F., J. Electrochem. Soc., 144, 1917-1923 (1997).
[2] Jones H.R.A., Viti S., Tennyson J., Barber B., Pickering J.C., Blackwell-Whtiehead R., Champion J-P., Allard F., Hauschildt P. H., Jørgensen U.G., Ehrenfreund P., Stachowska E., Ludwig H-G., Pavlenko Y.V., Lyubchik Y., Kurucz R.L., in *High Resolution Infrared Spectroscopy in Astronomy*, edited by H.U. Käufl, R. Siebenmorgen, and A.F.M. Moorwood, Springer, Berlin, 2005, p. 477-483.
[3] Rothman L.S., Gordon I.E., Barber R.J., Dothe H., Gamache R.R., Goldman A., Perevalov V.I., Tashkun S.A., Tennyson J, J Quant Spectrosc Radiat Transfer, 111, 2139-2150 (2010).

A12

A NEW OPEN-PATH CH_4 GAS ANALYZER FOR EDDY COVARIANCE FLUX MEASUREMENT

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We present a new commercially available open-path methane analyzer, LI-7700 [1]. The instrument uses a vertical-cavity surface-emitting laser (VCSEL) operating at 1.651 µm, in a multipass Herriott optical cell configuration with an optical pathlength of 30m. Methane number density is measured using wavelength modulation spectroscopy (WMS) with 2f detection, providing RMS noise below 5 ppb at 10 Hz.

The instrument is insensitive to variations in optical power due to mirror contamination or other factors over a wide range of conditions. Field maintenance is minimized by a self-cleaning mechanism to remove dirt on the lower mirror. Condensation on the mirrors is controlled by a radiation shield and slightly heating both mirrors when necessary.

The combination of fast response (up to 40 Hz), low weight (5.2 kg), low power (8W in steady state) and low maintenance requirements makes it suitable for long term deployment in remote areas with solar-powered operation, and simplifies installation at hard-to-reach sites.

[1] http://www.licor.com/env/products/gas_analyzers/LI-7700/LI-7700.jsp

Poster session B

B1

Diode Laser Quantum Noise

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Fundamental TDLS limit achieved for trace molecules absorption detection is determined by DL radiation quantum noise [1, 2].

Four DL quantum noise mechanisms were introduced in present paper:

1. Excitation current shot noise.
2. Electrons Poisson noise.
3. Photons Poisson noise.
4. Quantum noise of electromagnetic field.

They were analyzed based on solution of rate equations proposed.

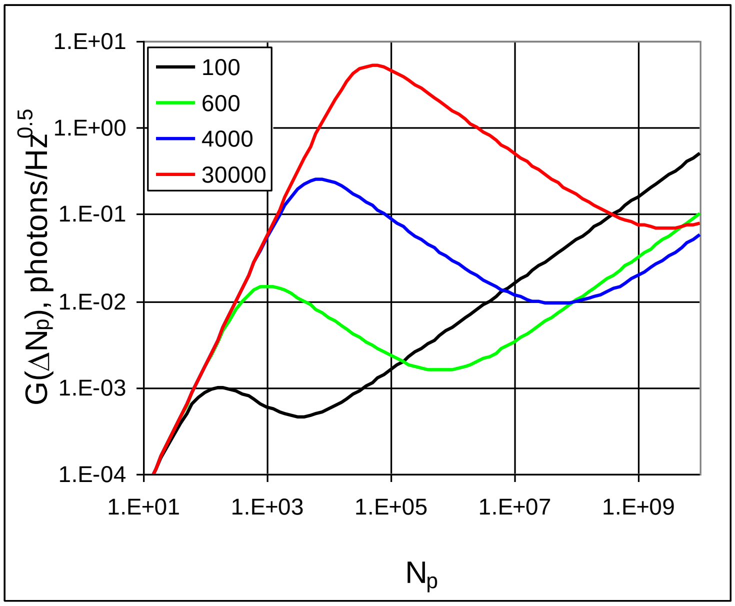

Fig.1 Photons number noise spectral density.

Fig.1 shows final photons number noise spectral density taking into account all noise mechanisms under consideration as function of photons number N_p. Photons number at threshold $N_p(I_{th})$ is parameter. Dominant noise depends on DL in use and experiment set up. Based on analysis performed both DL and TDLS operation mode in use can be optimized.

Comparison with experiment will be presented in C1 and D1.

[1] A.Nadezhdinskii, Fundamental Noises in TDLS, Abstracts of TDLS 2009, Zermatt, Switzerland, p.43.
[2] http://www.dls.gpi.ru/rus/conf/TDLS2009/Posters/B1_Fundamental%20noises%20in%20TDLS.pdf

B2

Accurate measurements of CO_2 line

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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 %. In [1, 2, see also A1] we've considered possibility to achieve this level. Measurements of green house gases in atmosphere require accurate measurement of their absorption. CO_2 was selected as molecule under investigation. Isolated CO_2 P(20) 00031-00001 line was selected as analytical one.

Accuracy of measurements was analyzed. TDLS technique was developed for molecule under investigation absorbance measurement with accuracy better than 0.1 %. More than 200 spectra of CO_2 sample (more than 99.98 %) were recorded for pressure range 1 – 900 mBar. Rautian and Voigt profiles were used to fit experimental spectra. Line intensity was also calculated by experimental spectra direct integration. Results obtained using different data processing techniques were compared (for example Fig.1).

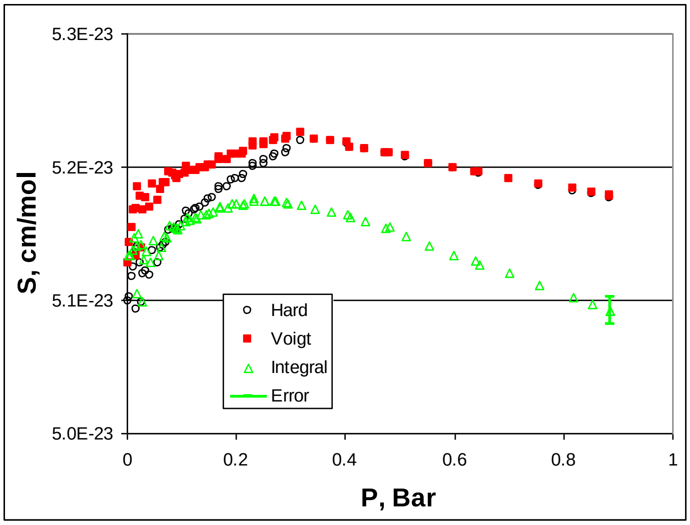

Fig.1 Pressure dependence of line intensity

Observed difference is significantly larger experimental error. Pressure dependence means that line can not be considered as isolated one even for low pressures. Effect of non ideal CO_2 gas behavior was observed. It was corrected using second virial coefficient B = -123 cm^3/mol.

Table 1 Line parameters

S	$5.172(33)10^{-23}$ cm/mol
γ_{self}	0.1003(2) cm^{-1}/Bar
δ_{self}	0.01109(2) cm^{-1}/Bar

Line parameters were determined (Table 1). They were compared with HITRAN 2008 being in agreement within 2 %. Declared HITRAN accuracy is 1-2 %.

[1] L.Konopelko, A.Nadezhdinskii, Accuracy in TDLS. TDLS as gas mixtures primary standard, Abstracts of TDLS 2009, Zermatt, Switzerland, p.76.
[2]http://www.dls.gpi.ru/rus/conf/TDLS2009/Posters/D2_TDLS%20primary%20standart.pdf

B3

ATMOSPHERIC TURBULENCE INVESTIGATION USING TDLS

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Russian state program to develop airplane-laboratory started some time ago. It contains TDLS complex [1]. Atmosphere turbulence is important parameter of atmosphere monitoring. Atmosphere turbulence module development and testing is subject of present paper.

Part of DL radiation of TDLS complex water channel (see A3) is directed to turbulence module under consideration. This radiation passes airplane window, is reflected by mirror located at some distance from window, and detected by PD inside airplane. Recorded signal processing gives humidity in open atmosphere out of airplane. Humidity variation during airplane flight gives information about atmosphere turbulence. Humidity variation analysis by Allan plots gives information atmosphere turbulence parameters.

Turbulence module under consideration prototype was developed. It contains NEL DL with fiber output operating near water analytical line (7182.940 cm^{-1}). Distance between DL and PD (closely spaced) and mirror was 50 cm. The prototype was installed on vehicle. GPS navigator was also installed to determine coordinates of driving car. Results of one of test drives are presented in Fig.1. Left – drive trajectory, right –humidity variation.

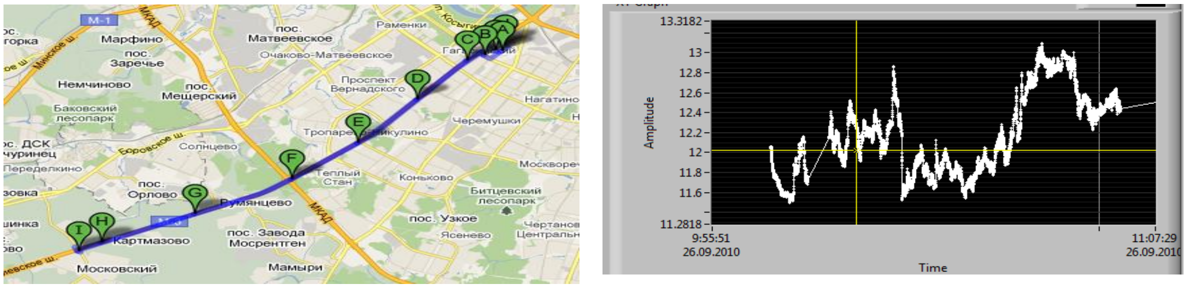

Fig.1 Results of one of test drives

Humidity variation was analyzed using Allan plots to determine characteristic humidity inhomogeneity dimension. In present case it was found 3-5 meters due to dense traffic conditions on the highway during test.

[1] V.Galaktionov, V.Khattatov, A.Nadezhdinskii, Ya.Ponurovskiy, D.Stavrovskii, I.Vyazov, V.Zaslavskii, TDLS complex development for airplane-laboratory “Atmosphere”, Abstracts of TDLS 2009, Zermatt, Switzerland, p.44.

B4

LINE SHAPE OF NEAR INFRARED DFB AND VCSEL DIODE LASERS UNDER THE INFLUENCE OF BACK REFLECTIONS

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Near infrared diode lasers are a key component in many optical sensing techniques, including tunable diode laser spectroscopy. Both VCSEL and DFB type lasers are commonly used. In most cases, a well-defined, narrow line width is desired. Depending on the application, back reflections of a certain fraction of the emitted light to the laser diode may be inevitable and can influence the width and the shape of the spectral line.

We present results of self-homodyne line width measurements of several VCSEL and DFB type lasers for different diode currents and for different degrees of back reflections to the laser diode. The evolution of the line shape with increasing diode current turned out to be different for the VCSEL and DFB lasers. While we observed a broadening of the line width for the VCSELs, all investigated DFB lasers showed a decrease of line width with increasing current (Fig. 1).

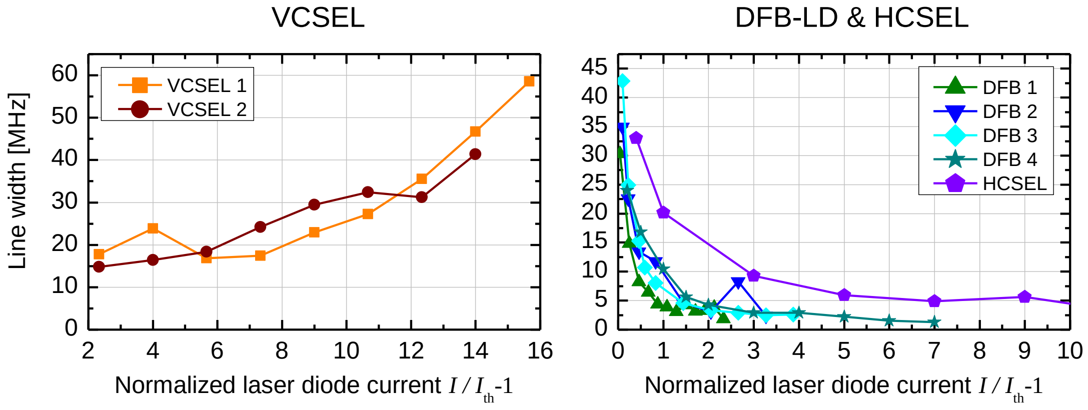

Fig. 1: Measured FWHM line widths of VCSEL and DFB lasers over laser diode current. The current axis is normalized to the respective threshold current.

Under the influence of back reflections, the VCSELs reproducibly showed a considerable line width narrowing for back reflection ratios larger than -20 dB. The DFB lasers, in contrast, showed erratic variations of the line widths depending on the phase of the back reflected beam.

B. Lins gratefully acknowledges partial funding of the Erlangen Graduate School in Advanced Optical Technologies (SAOT) by the German Research Foundation (DFG) in the framework of the German excellence initiative.

B5

N_2 – AND Ne– PRESSURE INDUCED LINE PROFILE PARAMETERS OF THE METHANE R(9) MULTIPLET OF THE $2\nu_3$ BAND. MULTISPECTRUM FIT OF OPTOACOUSTIC SPECTRA WITH OVERLAPPED ABSORPTION LINES.

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The results of the experimental researches of N_2– and Ne– pressure induced line profile parameters of the R(9) manifold of the methane $2\nu_3$ band are presented. The methane absorption spectra were recorded by Optoacoustic method using tunable diode laser. Spectra processing was performed using the developed in IAO program, in which simultaneous fitting procedure of synthetic spectra to spectra, recorded under various pressures, was realized. The program uses known models of spectral line profiles (Voigt, Rautian-Sobelman, Rosenkranz) and is based on the linear dependence of parameters from pressures at which spectrum are recorded. The retrieved line profile parameters (intensities, and coefficients of broadening, shifting and narrowing) were compared with known literature data.

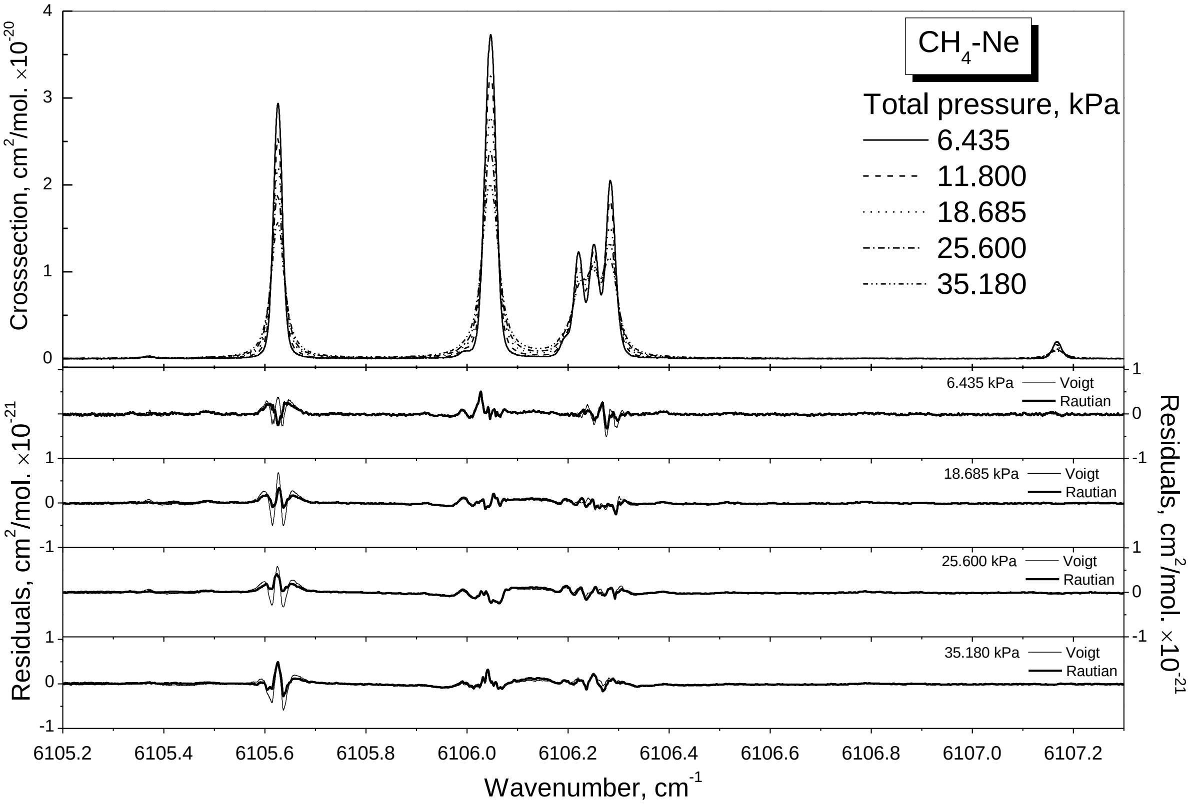

Fig.1. Absorption spectra of the $2\nu_3$ band R(9) manifold of CH_4, broadened by Ne with the obs-calc residual from fitted Voigt and Rautian line shapes.

This work is supported by the program of RAS, project 3.9.4. (experiment) and “Bruker Ltd” (design of the software), grant RFFI, project № 10-05-00764-a.

B6

DETECTION OF MOLECULAR HYDROGEN BY THE S(1) TRANSITION OF THE 1 – 0 QUADRUPOLE BAND USING OFF-AXIS CAVITY ENHANCED ABSORPTION SPECTROSCOPY (OA-CEAS)

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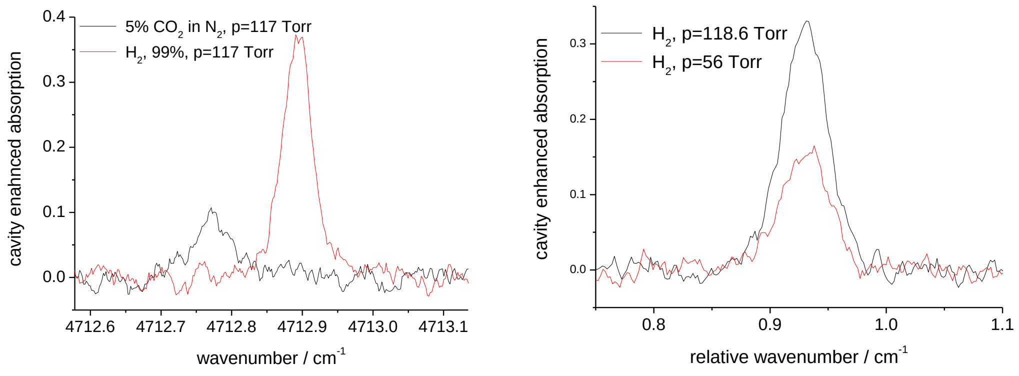
The quadrupole spectrum was first measured by Herzberg in 1949 [1] and later by Rank et al [2] who were the first to measure the fundamental band. There are many applications for hydrogen detection such as in fuel cells and hydrogen storage technologies. This preliminary work describes the first laser spectroscopic measurement of molecular hydrogen by the S(1) transition of the 1 – 0 fundamental vibrational quadrupole band at 4712.89 cm^{-1} (2.122 μm). A tunable near-infrared DFB diode laser was used with off-axis cavity-enhanced absorption spectroscopy (OA-CEAS) to detect the weak H_2 S(1) transition with a linestrength at 293 °K of 3.36×10^{-26} cm/molecule. The detection limit was of the order 0.16 % for 200 scan averages within 2 s. This was limited by photodetector noise as the laser power injected into the cavity was only ~2 mW. Higher laser power and longer effective pathlength should lead to detection limits of the order of 2 ppm for this cavity.



a) b)

Fig. 1. Cavity enhanced absorptions for 5% CO_2 in N_2 and 99% H_2 at 117 Torr (a); cavity enhanced absorptions of molecular hydrogen with the measured Doppler linewidths of 1.4±0.1 GHz (full width at half maximum) at 56 Torr and 118.6 Torr.

References to a Journal publication:
[1] G. Herzberg, *Can. J. Phys.* A28, 144 (1950)
[2] U. Fink, T.A. Wiggins, D.H. Rank, *J.Mol. Spec* 18, 384-395 (1965)

B7

CO_2 and N_2O isotopic ratio measurements by QCL spectroscopy - recent developments and environmental applications

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Isotope ratios of greenhouse gases are excellent tools to study their sources and sinks, because the involved relevant chemical reactions and biochemical processes lead to characteristic isotopic fractionation. For example, the distinct CO_2 isotopic signatures of respiration, photosynthesis and fossil fuel burning can be used for the apportionment of CO_2 fluxes at various scales. Similarly, the intramolecular distribution of ^{15}N in N_2O can be used to study bacterial nitrification and denitrification processes in soils and aquatic systems, which are the main sources of atmospheric N_2O.

The development of QCL based spectrometers and their ongoing improvement have led to instruments with a precision below 0.1 ‰ for isotope ratio measurements of both CO_2 and N_2O [1, 2]. To reach this precision, N_2O can be sampled using an automated, liquid nitrogen free preconcentration unit [3]. While improvements in calibration and validation procedures are ongoing, several studies already illustrate the power of combining precision and high time resolution for a range of environmentally and technically relevant topics.

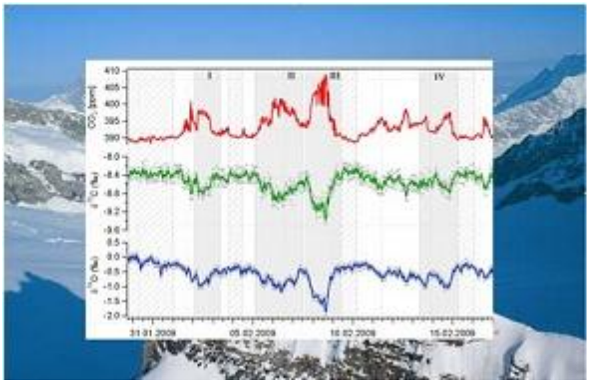

Fig. 1 Continuous measurements of $\delta^{13}C\text{-}CO_2$ and $\delta^{18}O\text{-}CO_2$ at Jungfraujoch (3580 m a.s.l.) reveal sources and residence time in the atmospheric boundary layer of the air masses. [4]

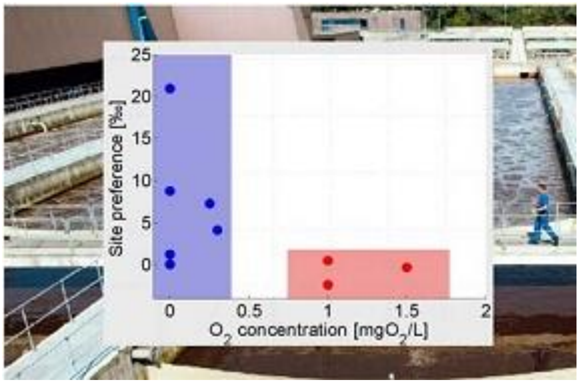

Fig. 2 N_2O production under denitrifying conditions (blue), and under nitrifying conditions (red). Reduction of N_2O release is relevant because N_2O frequently dominates the total greenhouse gas emissions during waste water treatment.

[1] B. Tuzson et al., Applied Physics B: Lasers and Optics, 92(3) 1-8 (2008).
[2] H. Wächter et al., Optics Express, 16(12) 9239-9244 (2008).
[3] J. Mohn et al., Atmos. Meas. Tech., 3, 609–618 82010).
[4] B. Tuzson et al., Atmos. Chem. Phys., 11, 1685–1696, (2011)

B8

WIDELY TUNABLE QUANTUM CASCADE LASER FOR SPECTROSCOPIC APPLICATIONS.

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Quantum cascade lasers (QCL) are very adapted sources for laser spectrometers as they are reliable, powerful, with narrow linewidth and can operate in continuous wave at room temperature. All that makes the laser spectrometers based on these QCL lasers good tools for trace gas sensing. Nevertheless, the spectral range over which these lasers can be tuned is limited: ~15 cm^{-1} for a distributed feedback (DFB) QCL. As a consequence, only a few absorption lines can be monitored with these laser spectrometers.

The Laser team from Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA) in Reims is developing a new external cavity quantum cascade laser in Littrow configuration emitting in the mid-infrared to phase gas molecular species measurements. This configuration has been chosen because it needs only two optical elements (a lens for collimation and a diffraction grating) and enable spectral tuning in single-mode emission on the whole gain curve of the QCL chip. Such a large spectral range would give us the possibility to perform multi-species gas monitoring in the mid-infrared.

First results were obtained with QCL chips emitting around 4.5 µm and based on a bound-to-continuum design. The front and back faces are respectively anti-reflexion and high-reflexion coated. The chips and the coatings have been developed by III-V lab in Palaiseau. We reached ~25 cm^{-1} tuning range by simple rotation of the diffraction grating with a chip whose gain curve was not wide. Other experiments are currently realised with QCL chips emitting around 7.8 µm.

Acknowledgments:

The Authors are indebted to the *Délégation Générale de l'Armement*, particularly Mr Desruelle, and the *Région Champagne-Ardenne* for financially supporting of the PhD of Dominique Mammez and for experiments funding.

B9

NOISE PROPERTIES OF AN OPTICAL FREQUENCY COMB STABILIZED TO THE 10^{-13} LEVEL

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Optical frequency combs (OFC) have revolutionized the domain of optical frequency metrology in the last decade by enabling to directly link optical and microwave frequencies. An OFC can be viewed as a huge number of equally-spaced singlemode lasers that are phase-coherently linked together and constitute a frequency ruler over a spectrum which can span as much as one octave. The optical frequency of each comb mode is determined by only two radio-frequencies, the comb repetition rate f_{rep} and the carrier-envelope offset f_{ceo} (global offset of the comb modes from exact harmonics of f_{rep}). Apart from frequency metrology, OFCs have found new applications in high resolution spectroscopy and trace gas sensing during the last years [1-2], as they constitute a versatile spectroscopic tool, combining an excellent accuracy, a high spectral purity and at the same time a broad spectral coverage.

In this work, we will discuss the frequency control and noise properties of highly stabilized OFCs. We will compare a state-of-the-art diode-pumped solid-state Er:Yb:glass oscillator (ERGO) developed and fully stabilized in our laboratories [3-4] with a commercial Er-fiber comb. We will show how the CEO frequency noise of our comb is improved compared to the fiber comb of similar servo-loop bandwidth, leading to a 20-fold reduction of the CEO contribution to the fractional frequency instability of a 1.5-μm comb line (contribution of 10^{-15} at 1 s integration time in our comb versus 2×10^{-14} in the fiber comb).

Traditionally, an OFC is used as an optical frequency synthesizer in high-resolution spectroscopy: the two comb frequencies (f_{rep} and f_{ceo}) are referenced to a microwave frequency standard (atomic clock) to generate absolute optical frequencies. In such a case, the fractional frequency instability of a comb line corresponds in the best case to that of the reference frequency, which is in the order of 10^{-13} at 1 s integration time for the best ones (active H-masers). We will show a fractional frequency instability of our comb at the level of 2×10^{-12} (@1 s) when referenced to a H-maser, experimentally measured from the Allan deviation of the beat signal between a comb line and a 1.56-μm ultrastable laser. An improved stability can be achieved by using the comb in the reverse direction, *i.e.* from optical to microwave. Today, ultra-narrow linewidth (<1 Hz) lasers locked to ultrastable high-finesse Fabry-Perot cavities can achieve a fractional frequency stability in the 10^{-15} range (@1 s) [5] and an OFC locked to such an optical frequency standard can transfer the high relative stability of the laser to a microwave signal, leading to an all-optical ultrastable microwave oscillator. We will present our OFC locked to a cavity-stabilized ultrastable laser, with preliminary ultrastable microwave generation showing a relative frequency instability of 3×10^{-13}, limited by the reference used in the Allan deviation measurement.

[1] S.A. Diddams et al. *Nature* **445**, 627-630, (2007)
[2] M.J. Thorpe et al., *Science* **311**, 1595-1599, (2006)
[3] M.C. Stumpf et al., *Appl. Phys. B* **99**(3), 401-408, (2010)
[4] S. Schilt et al., *Proc.* CLEO-2011, Baltimore, USA; May 1-6, 2011, paper CFK3
[5] J. Alnis et al. *Phys. Rev. A* **77**, 053809, (2008)

B10

3-5 µm Continuously Tunable Single Mode VECSEL

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Single mode continuously tunable mid-infrared Vertical External Cavity Surface Emitting Lasers (VECSEL) have been realized [1]. Emission wavelength is 3-5 µm with a total mode-hop free tuning range >100 nm. Due to the ~100 µm short cavity length, only one longitudinal mode can develop. While the presented design is for low temperatures, above room temperature operation has already been achieved using a long cavity length [2].

The schematics of our devices are shown in figure 1. IV-VI semiconductors such as PbTe are used for the active region. The top Bragg mirror is curved using a 5 pairs of $\lambda/4$ wavelength thick Si\SiO. It is transparent for the 1.55 µm pump beam. The generated laser light is emitted through the bottom mirror. The cavity length can be altered with a piezoelectric crystal. By changing the cavity length, the resonance condition changes and the emission wavelength is continuously shifted.

Figure 2 shows spectra obtained for different drive voltages. The emission wavelength is shifted mode-hop free corresponding to the cavity length. A total tuning range of >100 nm is achieved. The output power of the single mode VECSEL is >50 mW_p, and the absorbed threshold power is <1 W_p for 300 ns pulse width and 9 kHz repetition frequency. While the here presented spectra were measured at 100 K, thermoelectric stabilized devices offering >10 mW_p output power have been realized as well.

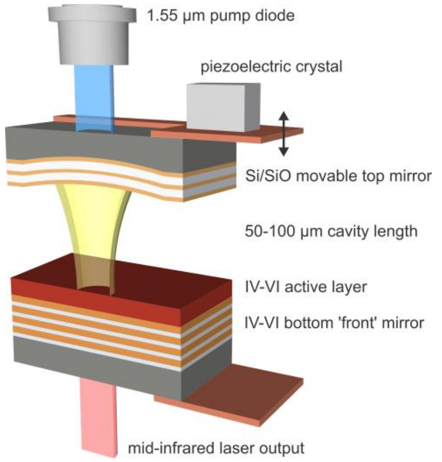

Fig. 1: Schematics of the VECSEL setup. Generated laser light is emitted through the 'front' mirror at the bottom.

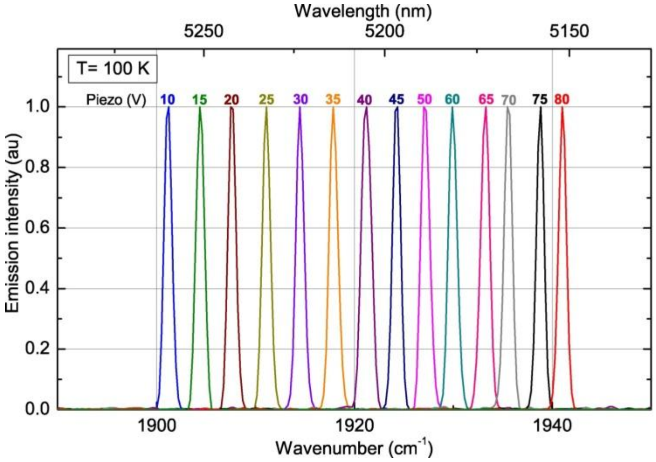

Fig. 2: Superimposed normalized spectra for different piezo actuation voltages. The emission wavelength shifts mode-hop free corresponding to the piezo actuation voltage.

[1] A. Khiar, M. Rahim, M. Fill, F. Felder, F. Hobrecken, H. Zogg, Appl. Phys. Lett. 97, 151104 (2010)
[2] M. Rahim, A. Khiar, F. Felder, M. Fill, H. Zogg, Appl. Phys. Lett. 94, 201112 (2009)

B11

Spatially resolved *in situ* Measurements of Absolute CO Profiles in Atmospheric Laminar Counterflow Diffusion Flames

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The light emitted by flames via chemiluminescence (CL) offers a low-cost, completely passive and highly interesting possibility to realize an active control and optimization of technical combustion processes [1]. One of the molecular species responsible for CL emission is exited CO_2^* [2] which is extremely difficult to be absolutely quantified. Carbon monoxide ,CO, which is the direct precursor for CO_2^* is therefore an interesting target species to be studied in order to understand, simulate and model the underlying chemical side paths of CL species and precursors. However, CO is also an important chemical indicator for the combustion completeness and a key atmospheric pollutant of major interest. Spatially resolved CO profiles in laminar model flames – especially if determined absolute - are highly important data essential to test, validate and optimize flame chemistry models. Therefore we developed a new tunable diode laser absorption spectrometer (TDLAS) [5] for the quantitative, calibration free and spatially resolved in situ measurements of CO in important model and test flames like the Tsuji [3] counter flow burner. To ensure homogeneous, well defined, physic-chemical boundary conditions along the absorption path with step like changes when leaving the flame we had to modify the Tsuij burner head by including N_2 purged slots on both ends of the flame in order to suppress curved end flames at edges of the burner head [4]. Furthermore we employed N_2 ro-vibrational coherent anti-Stokes Raman (CARS) spectroscopy with a spatial resolution of 65 µm to determine highly accurate, spatially resolved, absolute temperature profiles.

The paper will present a new, scanning TDL spectrometer utilizing a distributed feedback diode laser near 2300nm to analyze the only 60 mm long, atmospheric, laminar, non-premixed CH_4/air flames and determine absolute, spatially resolved CO concentrations (and their strain dependence) by translating the burner with a DC motor through the laser beam at a resolution of 0.1 mm. By development of a multiple Voigt line Levenberg-Marquardt fitting algorithm, the use of highly efficient optical disturbance correction algorithms for treating transmission and background emission fluctuations and careful fringe interference suppression we achieved a fractional optical resolution of up to 2.3×10^{-4} OD (1σ) in the flame (T up to 1965K) which permitted CO signal to noise ratios of more than 80. These lead to temperature dependent CO detection limits for the R20 line at 4324.4 cm^{-1} of 250 to 2000 ppm at peak CO concentrations up to 42000 ppm.

[1] N. Docquier, S. Candel, Progress in Energy and Combustion Science 28, (2002) 107 - 150.
[2] H. Najm, P. H. Paul, C. J. Mueller, P. S. Wyckoff, Combustion and Flame 113, (1998) 312-332.
[3] H. Tsuji, I. Yamaoka, Proceedings of the Combustion Institute, (1971) 723-731.
[4] S. Wagner, B.T. Fisher, J.W. Fleming, V. Ebert, Proc. Combust. Inst. 32 (2009) 839-846.
[5] C. Schulz, A. Dreizler, V. Ebert, J. Wolfrum , "Combustion Diagnostics" in Springer Handbook of Experimental Fluid Dynamics , Editors C. Tropea, J. Foss, A. Yarin , pp (2007) 1241-1316.

Poster session C

C1

Experimental investigation of Diode Laser Quantum Noise

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Fundamental TDLS limit achieved for trace molecules absorption detection is determined by DL radiation quantum noise [1, 2]. Four DL quantum noise mechanisms were introduced and analyzed (see B1). Technique was developed to investigate stationary and noise characteristics of different diode laser types (Fig.1). Results for two diode types are presented in the paper NIR DL and QCL.

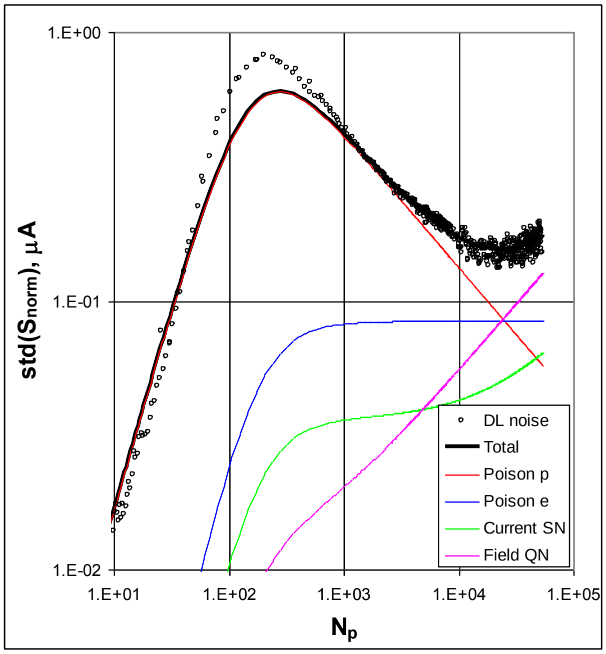

Fig.1 Normalized noise std of DL under investigation (NIR DL) as function of photons number – N_p (black circles)

Noise model parameters were determined by comparison with experimental data. Noises due to different noise mechanisms are shown in Fig.1 by color curves. Parameters obtained are in agreement with theory prediction.

Field quantum noise and excitation current shot noise were determined as dominant ones for NIR DL and QCL, respectively. Further comparison with experiment will be presented in D1.

[1] A.Nadezhdinskii, Fundamental Noises in TDLS, Abstracts of TDLS 2009, Zermatt, Switzerland, p.43.
[2] http://www.dls.gpi.ru/rus/conf/TDLS2009/Posters/B1_Fundamental%20noises%20in%20TDLS.pdf

C2

TDLS SPECTROSCOPY OF WATER ISOTOPOMERS NEAR 1.39 μ

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Accurate measurement of greenhouse gases is significant goal with respect to global warming. Water is one of the most important greenhouse gases. Measurement of water molecules isotopes abundance ($H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, and HDO) gives additional information of atmosphere monitoring. Accurate data of analytical spectral lines are needed for such monitoring. Currently available information (HITRAN 2008 [1]) is not enough accurate for goal under consideration. Accurate measurement of $H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, and HDO lines parameters is subject of present paper.

To record water sample spectra 3-channel diode laser spectrometer was used. The spectrometer contains NEL diode laser with fiber output operating in selected spectral range near 1.39 μm. In analytical channel 200.0(2) cm cell was installed. Both gas pressure in cell and its temperature were measured. Water sample with natural abundance was used for investigation. Cell with low pressure water vapor was installed in second channel to stabilize DL frequency tuning. Third channel contains FP etalon to calibrate DL frequency tuning. Example of spectra obtained is shown in Fig.1 (black curve in upper graph). Observed lines belong to $H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, and HDO.

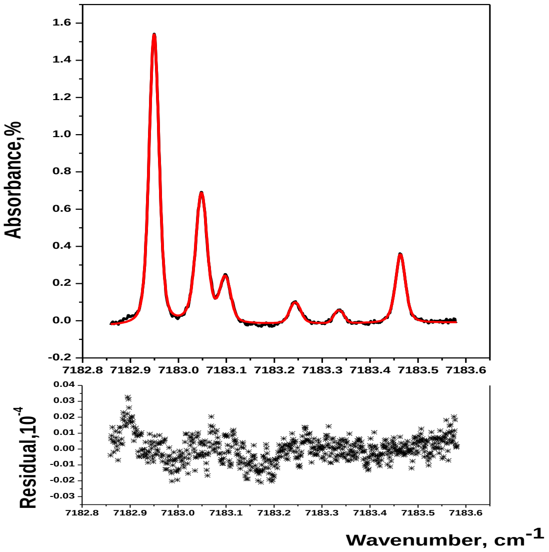

Fig. 1 Recorded water sample spectrum (23°C and 13.16 mBar) and its fitting

Spectra obtained were fitted (red curve in upper graph) using hard collision model profile. Residual is shown in lower graph. Using fitting, analytical lines parameters were determined and will be presented.

[1] http://www.cfa.harvard.edu/hitran/

C3

ATMOSPHERE CONSTITUENTS SPECTRA MODELING UP TO 25 KM ALTITUDE

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Measurement of atmosphere constituents altitude distribution is important component of atmosphere monitoring (atmosphere physics and chemistry, global warming, etc.). Central aerological observatory of Russia has airplane-laboratory M55 (22 km altitude) [1]. Due to Russian state program airplane-laboratory based on Jak-42d (9.1 km altitude) is under development [2]. To optimize instruments operation to be installed on airplane-laboratories modeling of atmosphere constituents spectra up to 25 km altitude is necessary subject of present paper.

Software "line-by-line" was developed to model atmosphere constituents' spectra. Software developed is using molecular spectral data from HITRAN 2008 [3] as well as atmosphere models available. Using software developed several atmosphere constituents (H_2O, CO_2, CO, CH_4, etc.) spectra altitude dependences were modeled. As example, modeling of water vapor altitude dependence is presented (Fig.1).

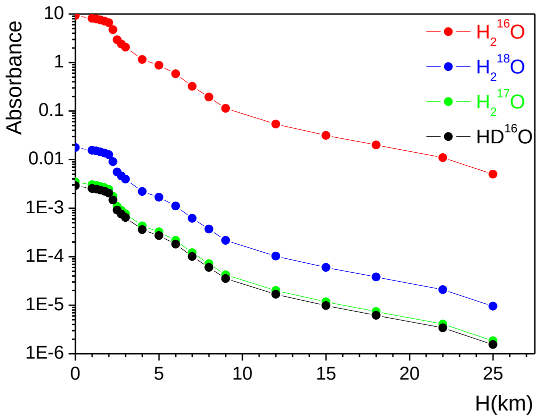

Fig.1 Altitude dependence of H_2O isotopologies absorbance near 1.39 μ

Modeling presented was performed up to 25 km altitude for L = 39 m, P = 10 mBar, T = 296 K. Modeling results presented consider measurement of H_2O isotopologies ($H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, and HDO) subject of H_2O isotope abundance determination using instruments installed on airplane-laboratories under consideration.

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

[1] http://www.aviaport.ru/directory/aviation/m55
[2] http://www.aviaport.ru/directory/aviation/jak42d/
[3] http://www.cfa.harvard.edu/hitran/

C4

RELATIVE INTENSITY NOISE (RIN) OF NEAR INFRARED DFB AND VCSEL DIODE LASERS UNDER THE INFLUENCE OF BACK REFLECTIONS

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[b] *Erlangen Graduate School in Advanced Optical Technologies (SAOT), Friedrich-Alexander-Universität Erlangen-Nürnberg, Paul-Gordan-Str. 6, 91052 Erlangen*

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VCSELs and DFB lasers are two types of diode lasers commonly used for tunable diode laser spectroscopy (TDLS). Depending on the setup and the details of application, back reflections of a certain fraction of the emitted light to the laser diode may occur. These back reflections can cause an increase of relative intensity noise (RIN) of the laser and lead to a reduced sensor performance.

We present our comparison of relative intensity noise (RIN) of near infrared VCSEL and DFB type diode lasers. To exclude the often strong influence of different commercial diode laser controllers, measurements have been performed with a simple, battery powered current source. RIN has been analyzed in the frequency range up to 200 kHz for different diode currents for a range of laser diodes (Fig. 1). Additionally, we present measurement results for the RIN if the laser diodes are subject to back reflection for different reflection ratios between -40 dB and -1 dB. Under the influence of back reflections, an increase of RIN could be observed for both investigated VCSELs and for some of the DFB laser diodes.

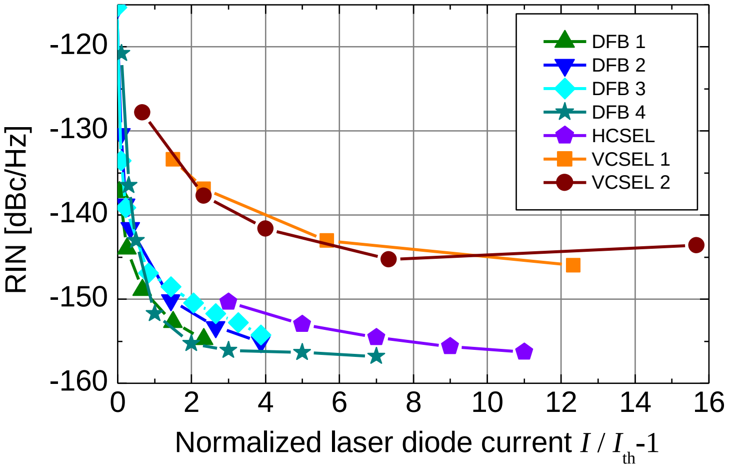

Fig. 1: Relative intensity noise over laser diode current for different laser diodes operated with a battery current source. The current axis is normalized to the respective threshold current.

B. Lins gratefully acknowledges partial funding of the Erlangen Graduate School in Advanced Optical Technologies (SAOT) by the German Research Foundation (DFG) in the framework of the German excellence initiative.

C5

Fast Wavelength Scan Faraday Rotation Spectroscopy For Sensitive Detection of OH Radicals at 2.8 µm

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The hydroxyl (OH) free radical plays a central role in atmospheric chemistry due to its high reactivity with trace molecular species. Because of its very short life time and very low concentration in the atmosphere, interference-free high sensitivity *in-situ* OH monitoring by laser spectroscopy represents a real challenge. Faraday rotation spectroscopy (FRS) takes advantage of the magnetic circular birefringence observed in the vicinity of Zeeman split transitions in paramagnetic species. This makes FRS capable of enhancing the detection sensitivity and completely eliminating interference from the diamagnetic species in the atmosphere (CO_2, H_2O). We report on the recent development of a FRS instrument operating at 2.8 µm for OH radical detection suitable for real time OH detection in environmental photoreactor chambers. In the present work we utilize a 15Hz laser frequency scan rate to perform FRS spectral scanning. As compared to our previous work that was based on a slow step-like point-by-point frequency tuning [1], the signal-to-noise ratio has been improved by a factor of 1.5 with an optimum average time of ~50 s. This provided a 1σ detection limit of ~5.5×10^8 radicals/cm^3. The instrument configuration and results of the system performance tests will be presented in details.

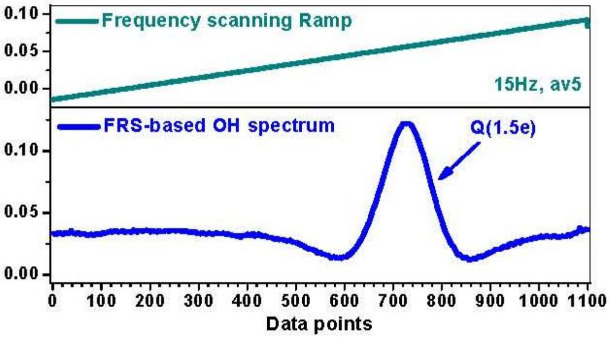

Figure 1 Fast wavelength scan FRS spectrum of OH radical

Acknowledgments. This work is supported by the IRENI program of the Région Nord-Pas de Calais. W. Zhao thanks the IRENI program for the postdoctoral support. The support of the Groupement de Recherche International SAMIA between CNRS (France), RFBR (Russia) and CAS (China) is acknowledged. G. Wysocki acknowledges the invited professorship support from the Université du Littoral Côte d'Opale and the US NSF CAREER award CMMI-0954897.

References

[1] W. Zhao, G. Wysocki, W. Chen, E. Fertein, D. Le Coq, D. Petitprez, W. Zhang, "Sensitive and Selective Detection of OH Free Radical using Faraday Rotation Spectroscopy at 2.8 µm", Opt. Express, **19**, 2493-2501 (2011)

C6

HIGH SENSITIVITY DIFFERENTIAL ABSORPTION SPECTROSCOPY OF METANE IN THE 1.26 - 1.70 µm SPECTRAL RANGE FOR PLANETOLOGY APPLICATIONS

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In absence of a satisfactory theoretical modeling of the CH_4 spectrum, accurate and exhaustive experimental data in low temperature conditions are essential to study the atmosphere of Titan and of the giant outer planets. For instance, the transparency windows, corresponding to the weak absorption regions between the strong absorption bands, allow to access to the lower atmosphere composition and to the albedo of these planets.

We present a high sensitivity near infrared spectrometer for the study of methane by differential direct absorption spectroscopy (DAS) at liquid nitrogen temperature (LNT) [2]. It is based on a cooled absorption cell (142 cm long) coupled with a set of about 80 fibered DFB diodes permitting to continuously cover the 1.26 – 1.70 µm spectral region. A noise equivalent absorption (NEA) on the order of $\alpha_{min} \approx 5\times10^{-8}$ cm^{-1} could be achieved in a double pass configuration.

With this instrument we have exhaustively studied the strong absorption bands of natural methane (Figure 1), $^{13}CH_4$ and CH_3D. The study of the minor isotopologues – CH_3D particular – is very important as they may have a dominant contribution in the $^{12}CH_4$ transparency windows that we studied separately by CRDS at LNT. This will be illustrated in the case of CH_3D in the 1.28 and 1.58 µm methane windows at room temperature and 80 K. The DAS spectra of CH_3D allowed to identify all the transitions of CH_3D present in the CRDS spectra of methane in natural isotopic abundance.

Fig 1

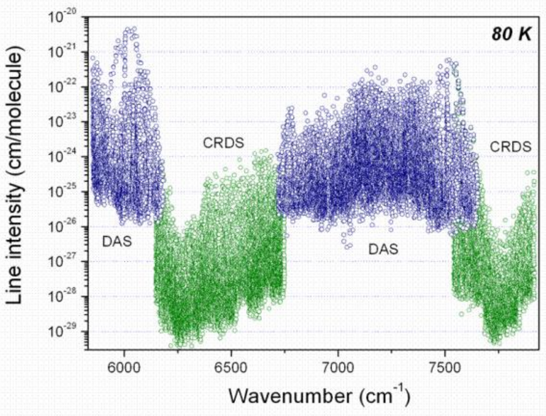

Fig.1 Overview of our line lists of “natural” methane. The tetradecad and the icosad regions were recorded by DAS while the 1.58 µm and 1.28 µm windows were

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[2] S. Kassi, B. Gao, D. Romanini, A. Campargue, Phys. Chem. Chem. Phys., 10, 4410-4419 (2008)

C7

NITRIC OXIDE DETECTION BASED ON FARADAY ROTATION SPECTROMETRY

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Nitric Oxide (NO) is known as an atmospheric pollutant, as well as an indicator of airway inflammation and next-generation devices are needed to monitor NO in a more robust and simpler way. Here we propose a simple setup (Fig. 1) based on continuous wave quantum cascade lasers (QCL) using Faraday Rotation Spectroscopy (FRS) [1]. This technique allows sensitive and selective detection of paramagnetic molecules or radicals, such as NO, NO_2, O_2, OH^-. Since FRS is not sensitive to abundant molecules such as H_2O or CO_2, it represents an excellent tool for detection NO in exhaled breath. To enhance the sensitivity of the system FRS is combined with a multipass cell with an internal optical path length of 70 m. At the moment, a detection limit of 9 ppbv (part per billion by volume $=1:10^9$) of NO in N_2 is achieved, using the $Q_{3/2}(3/2)$ transition (at 1875.81 cm^{-1}), which has the strongest Faraday effect (field strength up to 200 Gauss, modulation frequency 9 kHz). Improvements by using differential detection schemes (reduce laser intensity noise) and integrated cavity output spectroscopy (ICOS) are under investigation.

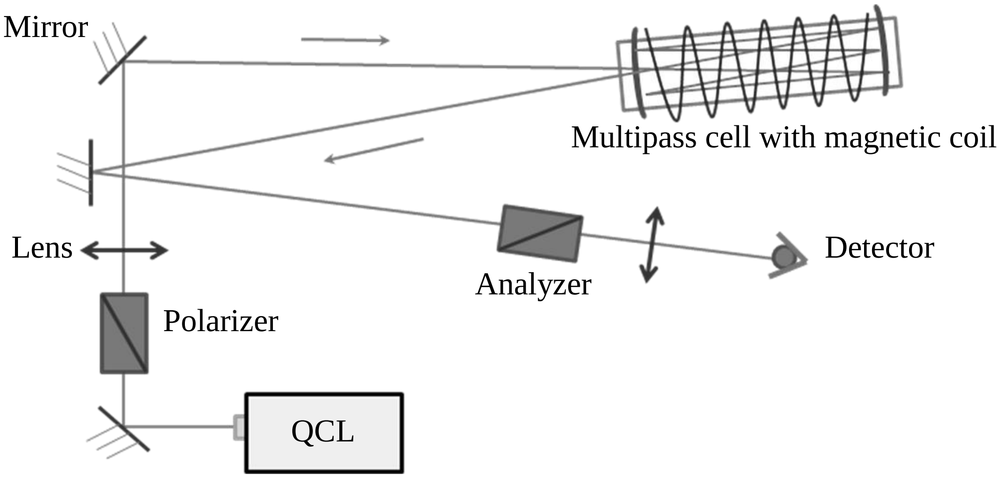

Fig. 1 Schematic diagram of the QCL based FRS experimental setup

References:

[1] R.Lewicki, J.Doty, R.Curl, F.Tittel, and G.Wysocki: PNAS, vol. 106, no. 31, 12587-12592 (2009)

C8

Tunable diode laser measurements of self- and pressure-shifts coefficients of CO_2 around 2.05 µm

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Atmospheric carbon dioxide (CO_2) is one of the main contributors to the greenhouse effect. A global monitoring of CO_2 from space is foreseen as a key issue to quantify its sources and sinks at a regional scale and to better predict future levels of CO_2 and their effect on climate change. Differential Absorption Lidar (DiAL) is a promising and novel spectroscopic technique for remote sensing CO_2 spatial and temporal concentration distribution with a high level of accuracy. However, a precise knowledge of spectroscopic parameters of CO_2 molecular transitions and their dependence with temperature and pressure is required for reducing the uncertainty on DiAl measurements. Hence, to support remote sensing of carbon dioxide in the troposphere, we report on the accurate determination of self- and air-pressure-induced shift coefficients for eight absorption lines belonging to the R branch of $(2001)_{III} \leftarrow (0000)_I$ band of CO_2 at 2.05 µm. Purposely, a high-resolution tunable diode laser absorption spectrometer (TDLAS) coupled to a cryogenically cooled optical cell was implemented. From these measurements, we have further determined the temperature-dependencies of the pressure-induced shift coefficients.

Acknowledgments:

The authors are most grateful to Thomas Decarpenterie and Pierre Von der Heyden for their technical help. Jing Song Li would like to thank the INSU-CNRS postdoctoral fellowship program.

C9

DESIGN OF A COMPACT AND VERSATILE MULTIPASS CELL FOR QCL-BASED TRACE GAS ANALYSIS

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Breath air analysis for medical purposes, and environmental and industrial monitoring, demand for sensitive, selective, and inexpensive real-time trace gas analyzers. Infrared laser spectroscopy is the most promising technique capable of measuring low concentrations at high precision and high temporal resolution with cost-efficient instrumentation.

In this work, a laser spectroscopic instrumentation is designed for measurements of CO_2 and N_2O. A versatile cell allows direct absorption and photoacoustic modes of operation. The sample cell comprises an easily adjustable, star-like multipass configuration and a transverse, longitudinal photoacoustic resonator. The multipass configuration is used both, to enhance the sensitivity of the direct absorption method by providing over three meters of optical path, and to generate a planar excitation source for the photoacoustic resonance. A continuous wave, room temperature quantum cascade laser (cw RT QCL), emitting near 2240 cm^{-1}, is used as a light source.

Newly developed software, written in LabView, is used for fully automated instrumentation control, data acquisition and analysis. Real-time and fast (100 Hz) data fitting is based on spectral parameters of the Hitran-database. To demonstrate the performance of the instrumentation, the concentrations of N_2O and $^{13}CO_2$ were measured in ambient air. Using the direct absorption technique, 1 Hz precisions of 0.1 ‰ and 0.4 ‰ were obtained for $^{13}CO_2$ and N_2O, respectively. In comparison, the 1 Hz precision of 3 % for $^{13}CO_2$ was achieved with the photoacoustic technique, and is adequate for applications that require wavelength independent detection and low cost instrumentation.

The planned implementation of the latest generation cw RT QCL, emitting near 2310 cm^{-1}, is expected to significantly improve the performance of the photoacoustic method, whose signal is proportional to the incident light power. In addition, the new laser will allow simultaneous measurements of $^{12}CO_2$, $^{13}CO_2$ and $^{18}O\text{-}CO_2$, which creates new possibilities for stable-isotope-ratio applications.

C10

INFRARED LINE INTENSITIES OF FORMALDEHYDE FROM SIMULTANEOUS MEASUREMENTS BY DIODE-LASER AND FOURIER TRANSFORM SPECTROSCOPIES

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Formaldehyde (H_2CO) is an important intermediate compound in the degradation of the volatile organic compounds (VOCs), including methane, in the terrestrial troposphere. Its observation using optical remote sensing in the infrared range relies on the 3.6 and 5.7 μm absorption bands. Band and individual line intensities have been reported in both ranges [1].

With the present work, we aim to also derive infrared line intensities for formaldehyde, however relying on pure rotation line intensities and the known electric dipole moment to determine the particle density. Indeed, because formaldehyde polymerizes or degrades easily, the gas phase may contain polymerization or degradation products. Spectra of H_2CO diluted in 10 hPa of N_2 were therefore simultaneously recorded in 3.6 μm and the $20 - 60$ cm^{-1} ranges, respectively using a tunable diode-laser and a Bruker IFS125HR Fourier transform spectrometers.

[1] A. Perrin, D. Jacquemart, F. Kwabia Tchana, N. Lacome, J. Quant. Spectrosc. Radiat. Transfer, 110, 700-716 (2009), and references therein.

C11

OPTICAL FEEDBACK CAVITY ENHANCED ABSORPTION SPECTROSCOPY:
FROM THE NEAR- TO THE MID-INFRARED

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We present two Optical Feedback Cavity Enhanced Absorption Spectroscopy (OF-CEAS) experiments for trace gas detection. First, we discuss the refinement of a near-infrared system based on a telecoms DFB diode laser centered at 1.53 µm and demonstrate it on measurements of pressure induced changes in the line shapes of CO_2 transitions. We then compare this to measurements in the mid-infrared, with a system based on a distributed feedback quantum cascade laser at 5 µm. The relative merits of working with feedback locked cavity enhanced systems in both regions will be contrasted.

C12

Fiber-coupled high-speed in-situ TDLAS-Laser Hygrometer for Engine Applications

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The development of modern internal combustion engines is characterized by the need to increase the efficiency and reduce emissions. One important route to minimize NO_x production in engines and emission is the addition of significant amounts of product gas of the combustion to the next cylinder charge. This so called exhaust gas recirculation (EGR) which plays a major role in the development of low emission, high efficiency engines. However, in order to achieve good results the EGR has to be adapted and optimized at the individual operating points of the engine. Furthermore a solid understanding of the mixing processes inside the engine end especially near the spark plug are essential to understand EGR problems e.g. associated with too large amounts of EGR or too high humidity values in the flue gas. Sampling techniques are rather problematic for EGR studies especially if H_2O is the target molecule due to the modification of the gas sample.

Thus we started to develop different fiber coupled diode laser spectrometers to measure the H_2O concentration in-situ, i.e. directly in the combustion chamber of the engine. H_2O plays an important role in EGR optimization, but is also assumed to correlate well with other active EGR gas ingredients like CO_2. Tunable Diode Laser Absorption Spectroscopy (TDLAS) based in-situ H_2O measurements have been successfully realized in several applications [1] but also can be adapted to other motor-related or EGR-gas species such as CO_2, CO or hydrocarbons. TDLAS is ideal for processes that are otherwise difficult to access with traditional methods [2]. Compared to extractive methods, e.g. high speed gas extraction using rapid-closing valves, TDLAS offers the potential of an self-calibrating, spatially resolved high speed in-situ technique with measurement intervals up to the µsec range.

Here we report on a newly developed, fiber-optic, µsec-fast in situ laser hygrometer capable of measuring water vapor directly inside a transparent engine. A 1.4µm diode laser is used and current tuned over an individual ro-vibrational absorption line with 4 kHz rep rate. A new, compact, fiber optic interface ensures optical access into the engine through a standard quartz ring typically used in transparent engines. Within the engine we achieve an in-cylinder absorption path of about 8 cm. The transmitted laser light is captured using a free space InGaAs detector positioned directly behind the quartz ring. All free space air paths are purged with N_2 to suppress parasitic water absorption outside the engine. The high speed laser modulation permits a time resolution of 250µs, which corresponds to 3° crank angle resolution at 2000 rpm. Direct TDLAS based on our own LabView data evaluation software [3] allows the extraction of absolute H_2O vapor concentrations. First successful measurements in a towed optical engine at $p_{max} = 4.5$ bar are presented. At 250 µsec resolution we reached a detection limit of 0.02 Vol% at 1 bar and average moisture contents of 1.2 Vol% H_2O. Details of the spectrometer will be explained and future extensions of the technique be discussed.

1. S. Hunsmann, K. Wunderle, S. Wagner, U. Rascher, U. Schurr und V. Ebert, Applied Physics B: Lasers and Optics **92**, 393-401 (2008).
2. H. Teichert, T. Fernholz und V. Ebert, Appl. Opt. **42**, 2043-2051 (2003).
3. C. Schulz, A. Dreizler, V. Ebert, J. Wolfrum , "Combustion Diagnostics" in Springer Handbook of Experimental Fluid Dynamics , Editors C. Tropea, J. Foss, A. Yarin , pp 1241-1316 (2007)

Poster session D

D1

INTER-COMPARISON OF DIFFERENT DIODE LASER TYPES

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Fundamental limit of trace molecules detection due to DL quantum noise was achieved. Different noise types due to electron and photon quantum nature were analyzed (see B1): excitation current shot noise, Poison noise of electrons, Poison noise of photons, electro-magnetic field quantum noise. Technique of DL investigation was developed (see B1, C1).

A lot of diode lasers were investigated. In present paper results obtained will be presented for seven different diode laser types (both near and mid IR DLs, both DFB and FP different DL type's chips, different DL types with fiber output, QCL) of different suppliers (NEL, Anritsu, Sensor Unlimited, Laser Components, Hamamatsu).

When trace resonance molecular absorption is considered NEA (Noise Equivalent Absorbance or relative photocurrent noise) is subject of analysis. Fig 1 presents NEA as function of excitation current above threshold for different diode lasers under consideration. Results of operation current in use are presented for optimal bandwidth B = 120 kHz.

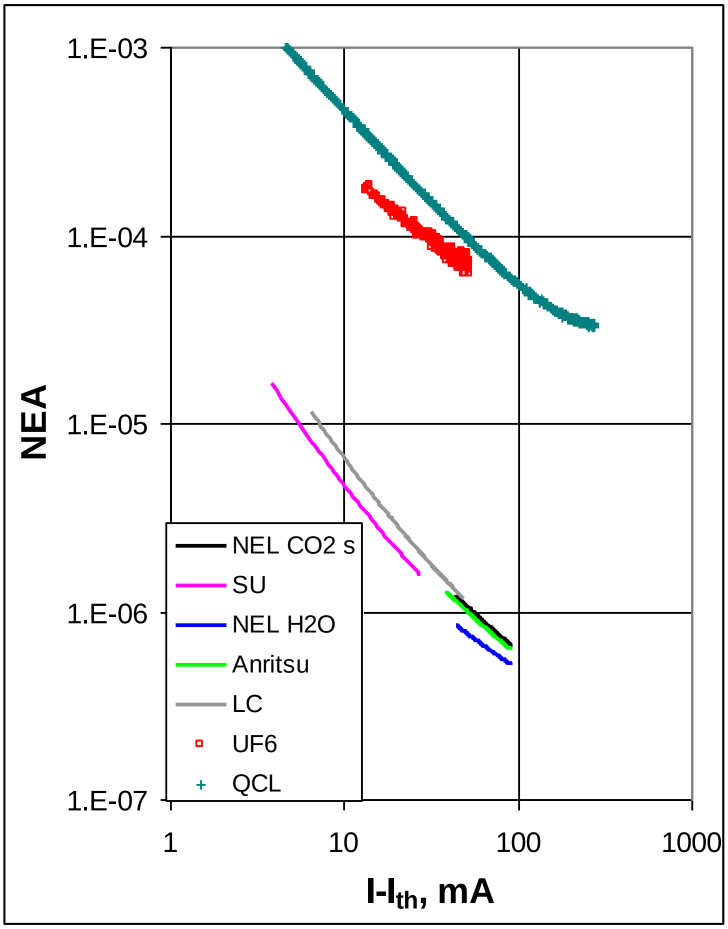

Fig.1 NEA as function of excitation current above threshold for different diode lasers under consideration.

Different DL types have different mechanisms of limitation. Near IR: Poison noise and electro-magnetic field quantum noise for small and high excitation currents, respectively. Mid IR $A^{IV}B^{VI}$ – PD noise. QCL – PD noise + excitation current noise.

D2

PRESSURE BROADING AND SHIFT OF H_2O LINE NEAR 1.39 μ

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Purpose of present paper was line shape investigation of 000-101 2_{12} - 3_{13} H_2O line. This line was selected as analytical one for water channel of airplane-laboratory TDLS complex.

To record water spectra 3-channel diode laser spectrometer was used. The spectrometer contains NEL diode laser with fiber output operating in selected spectral range near 1.39 μm. In analytical channel 100.0(1) cm cell was installed. Cell with low pressure water vapor was installed in second channel to stabilize DL frequency tuning. Third channel contains FP etalon (D^*=0.049286(2) cm^{-1}) to calibrate DL frequency tuning. Gas mixtures of water vapor in air (1.15%) and xenon (2.54%) were prepared and used in experiment. Both gas pressure in cell and its temperature were measured during spectra recording. Example of spectra obtained for different pressures is shown in Fig.1.

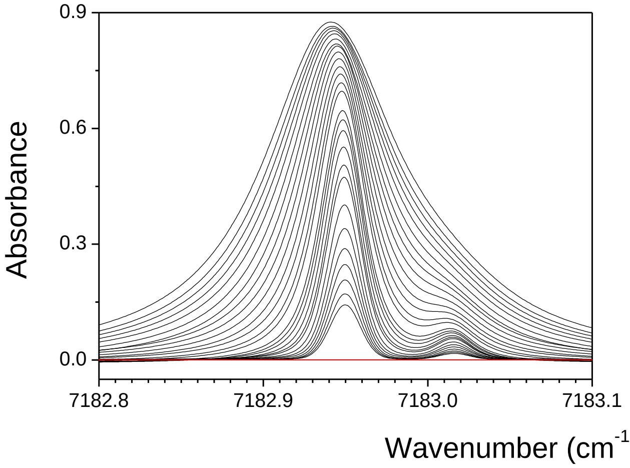

Fig. 1 H_2O:Xe gas mixture spectra for different pressures (2-700 mBar)

Additional weak line (101 2_{02} - 2_{21}) can be observed near analytical one. Software developed processed data in real time to obtain spectra (Fig.1). Simultaneous fitting of both lines was also performed in real time using hard collision model (Rautian-Sobel'man). Lines asymmetry was observed for H_2O in xenon. Pressure broadening and shift coefficients were determined and compared with HITRAN-2008 [1].

[1] http://www.cfa.harvard.edu/hitran/

D3

Investigation of quantum cascade laser developed to measure UF_6 enrichment

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UF_6 enrichment measurement is very important goal of IAEA safeguards. In frame of activity of IAEA working group for TDLS implementation in IAEA safeguards, QCL development for UF_6 enrichment measurement was considered as very important step [1]. Thanks to IAEA German support program such QCL module was developed and supplied to IAEA by Laser Components (Germany) (Fig.1).

Fig.1 QCL module view.

IAEA requested GPI to investigate this QCL module with respect to UF_6 enrichment measurement. In present paper results of this investigation will be presented. Comparison of results obtained for QCL and for other DL types will be considered in D1.

To investigate QCL parameters test software set was developed to investigate temperature stabilization, threshold, frequency tuning, noise, baseline, etc.

Temperature stabilization quality test of QCL module supplied was totally negative. QCL module was redesign to achieve satisfactory temperature stabilization performance.

QCL quantum efficiency and threshold were measured. Threshold time dependence was observed. From this dependence QCL life time was estimated – 5 years.

QCL frequency temperature and current tuning was calibrated. QCL DFB chip provides frequency tuning acceptable for UF_6 enrichment measurements.

QCL noise, NEA (Noise equivalent Absorbance), and Baseline were investigated. New noise and Baseline mechanisms typical for only for QCL were identified. Parameters under consideration can be improved by optimization of setup and operation mode.

Conclusion: present QCL module with some additional modification and optimization of setup and operation mode is acceptable for UF_6 enrichment measurements.

[1] G.Grigoriev, A.Lebrun, A.Mantz, L.Mechold, A.Nadezhdinskii, N. Peter – Stein, V.Ryzhikov, F.Tittel, M.Zendel, Status of the Tunable Diode Laser Spectroscopy Contribution to International Safeguards Verifications, Abstracts of TDLS 2009, Zermatt, Switzerland, p.21.

D4

Mid-Infrared Quantum Cascade Laser based Trace Gas Technologies: Recent Progress and Applications in Health and Environmental Monitoring

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This talk will focus on recent advances in the development of sensors based on infrared (IR) semiconductor lasers for the detection, quantification, and monitoring of trace gas species as well as their applications to medical diagnostics, environmental monitoring, industrial process control, and security. The development of compact trace gas sensors, in particular based on quantum cascade (QC) and interband cascade (IC) lasers, permits the targeting of strong fundamental rotational-vibrational transitions in the mid-IR, that are one to two orders of magnitude more intense than overtone transitions in the near-IR [1].

The architecture and performance of several sensitive, selective, and real-time gas sensors based on mid-infrared semiconductor lasers will be described. High detection sensitivity at ppbv (parts per billion in volume) and sub-ppbv concentration levels requires sensitivity enhancement schemes such as multipass optical cells, cavity absorption enhancement techniques, or quartz enhanced photo-acoustic absorption spectroscopy (QEPAS) [1,2]. These three spectroscopic methods can achieve minimum detectable absorption losses in the range from 10^{-8} to 10^{-11} $cm^{-1}/\sqrt{Hz}$.

Two recent examples of real world applications of field deployable PAS and QEPAS based gas sensors will be reported, namely the monitoring of ammonia concentrations in exhaled human breath analysis and urban environments. The monitoring of ammonia (NH_3) in exhaled human breath using a laser spectroscopic technique can provide fast, non-invasive diagnostics for patients with liver and kidney disorders [3]. The exhaled NH_3 concentration measurements are obtained with QEPAS using a compact mid-IR, continuous wave (CW), high performance, distributed feedback (DFB) QCL. The QEPAS technique is very suitable for real time breath measurements due to the fast gas exchange inside an ultra-compact gas cell. The minimum detectable NH_3 concentration that is achieved with a thermoelectrically cooled, 24mW, CW, DFB QCL operating at 10.34 µm (965.35 cm^{-1}) is ~ 6 ppbv (with a 1 sec time resolution). An amplitude modulated photo-acoustic spectroscopy (AM-PAS) technique was employed to monitor atmospheric NH_3 at sub-ppb concentration levels using a 67mW, 10.34 µm CW-TEC Daylight Solutions EC-QCL based sensor platform.

References:

[1] R. F. Curl, F. Capasso, C. Gmachl, A. A. Kosterev, B. McManus, R. Lewicki, M. Pusharsky, G. Wysocki, and F. K. Tittel," Quantum cascade lasers in chemical physics" *Chem. Phys. Lett.*, **487**, 1 (2010)

[2] L. Dong, A.A. Kosterev, D. Thomazy and F.K.Tittel, "QEPAS spectrophones: design, optimization and performance", *App. Phys. B* **100**, 627-635 (2010)

[3] T. Risby and F.K. Tittel, "Current status of mid-Infrared quantum and interband cascade lasers for clinical breath analysis". *SPIE Optical Engineering*, **49**, 111123-111123-14 (2010)

D5

Broad band tunable external cavity quantum cascade laser system for detection of hazardous chemicals

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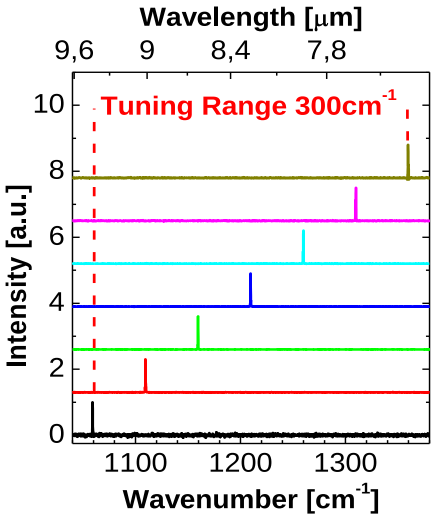
Due to the terrorist threat there is a strong demand for reliable tools for CBRNE detection. Especially the trace detection of explosives is in the focus of interest. In addition, fast detection of dangerous concentrations of pesticides or chlorinated hydrocarbons in drinking water is another example where high sensitivity techniques are needed. As many chemical compounds of interest exhibit very broad characteristic “fingerprint” absorption bands in the mid-infrared spectral range, spectroscopic sensing is an attractive approach towards the detection of hazardous substances. Since the spectral structures are very broad a source with broad spectral tunability is mandatory.

Quantum cascade lasers are robust, compact and wavelength-versatile semiconductor lasers and therefore ideal illumination sources for this type of spectroscopy. In order to achieve a tunable laser source, the QCL can be integrated into an external cavity setup.



Tuning range of external cavity quantum cascade laser system operating at 300 K.

By carefully adjusting the multiple quantum well structure building the active region of the QCL, the emission wavelength can be tailored over a large spectral range. By using more sophisticated quantum well sequences very broad gain curves can be realized. In this study we present results obtained with different designs of the active region. We compare (i) bound-to-bound, (ii) bound-to-continuum (b-to-c) and (iii) b-to-c hetero-cascading active region with emphasis on the spectral tuning and the beam propagation properties. With the hetero-cascading active layer we achieve a tuning range of 300 cm^{-1} in the 7 to 10 µm wavelength range.

The laser system is used for stand-off detection of traces of explosives. Traces of TNT (trinitrotoluene) and PETN (pentaerythritol tetranitrate) as well as various non-hazardous substances such as flour or skin cream on different substrate-materials were analyzed by illuminating them with the EC-QC laser and collecting the diffusely backscattered light. By tuning the EC-QCL across the characteristic absorption spectra we were able to detect the explosives with excellent discrimination against other non-hazardous substances.

The work is funded under the programme "Research of Civil Security" by the German Federal Ministry of Education and Research (BMBF), contract numbers FKZ 13N4543 and FKZ 13N11034.

D6

HIGH PRECISION MEASUREMENTS OF CARBON ISOTOPE RATIO AT ATMOSPHERIC PRESSURE IN HUMAN BREATH USING A 2 μm DIODE LASER

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The analysis of the $^{13}CO_2/^{12}CO_2$ isotope ratio is being widely used in geology, volcanology, criminology, medicine, and many other fields. The constant extension of the range of its applications stimulates the development of novel experimental techniques capable of high measurement precision and accuracy. The spectral measurement techniques are usually based on comparison between the absorption data obtained for individual molecular lines at gas pressures reduced to 10-100 Torr to prevent spectral lines overlapping. The aim of this work is to demonstrate the technique of measuring the $^{13}CO_2/^{12}CO_2$ isotope ratio at atmospheric pressure with precision and reproducibility high enough to meet the needs of medical practice.

The light source used is a VCSEL laser diode (*Vertilas*) emitting some 0.5 mW of power near 2.007 μm. A Herriott multipass cell with total optical path length of 24 m was used. The procedure used to analyze the spectra recorded is based on multivariate linear regression from simulated spectra of the $^{13}CO_2$, $^{12}CO_2$, and H_2O molecules. The spectra of these molecules were calculated from HITRAN-2008 database in the approximation of Voigt line profile. Certain corrections of intensities, pressure broadening, and pressure-induced shift parameters from HITRAN-2008 were required to obtain minimum fitting residual. Data from pressure and temperature sensors mounted in the multipass cell were taken into account in calculations of these simulated spectra.

The proposed technique of determining the concentration of gas components at atmospheric pressure does not involve measuring the intensities of individual lines. This allows carrying out measurements on complex spectrum with overlapped lines directly, and thus one do not need to solve the inverse problem of extracting the contribution of individual spectral lines. In this approach, use can be made of relatively low-level passive temperature stabilization, for possible temperature variations are recorded by the sensors and are taken into account in spectra simulations. In other words, it is necessary to measure the temperature in the sample cell, rather than stabilize it. Furthermore, with this approach there is no need for the use of a reference cell with a calibrated gas mixture.

The δ-value precision determined by means of the Allan deviation plot with an averaging time of 3 minutes amounted to 0.07 ‰. The precision level necessary for medical breath tests (0.5 ‰) can be achieved with an averaging time of 3 seconds. The standard deviation of the δ-value measured for 16 hours was no more that 0.2 ‰, no special measures being taken to thermally and mechanically isolate and stabilize the experimental setup.

Acknowledgements. This work was partially supported by the Russian Foundation for Basic Research (RFBR Grants 10-02-01111-a and 11-08-01127-a).

D7

Parametric Oscillator-based real-time Breath Monitoring by Off-Axis Integrated Cavity Output Spectroscopy

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Trace gases are distinctive indicators of biological processes occurring in plants, animals and humans. An excellent method for highly sensitive and selective detection of these volatile organic compounds is mid-infrared laser spectroscopy, where many molecules have strong distinctive absorption patterns. To capture the dynamics of the gas concentrations and detect multi-component gas samples we use a fast scanning near infrared diode laser with a mode-hop-free wavelength coverage tuning range (up to 5 cm^{-1}) at a speed of up to 100 THz/s. This tunable diode laser light is amplified in a fiber amplifier and converted to the mid-infrared wavelength region with a single resonant Optical Parametric Oscillator (OPO). The OPO is used as a passive converter and has several advantages in comparison other sources of coherent radiation in the mid-IR region. Continuous tuning coverage between 2.5 - 4 μm, narrow linewidth (100 MHz), and continuous wave output radiation power of 1.2 W. In combination with Off Axis Integrated Cavity Output Spectroscopy, these advantages are used to build a rapid and sensitive trace gas detector for gases such as ethane, methane, acetone at the sub-ppbv level concentrations at sub-second time scale. The fast subsecond response time of the system is able to show quantitatively methane, ethane (C_2H_6), water, CO_2 and acetone (C_3H_6O) in single exhalations of human breath at the low part per billion levels.

D8

HYBRID INTEGRATION OF DOUBLE QUANTUM CASCADE LASERS FOR TUNABLE MIDINFRARED LASER SOURCES

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This work presents the development of a technique for hybrid mounting of a Quantum Cascade Laser (QCL) pair. Electrical and optical properties of the used singlemode Distributed Feedback (DFB) QCLs were characterized. In order to evaluate the quality of the performed mounting technique, the thermal behavior was determined.

The realization of an integrated system of two separately operated DFB QCLs achieves the appropriation of singlemode emission on two distinct wavelengths from the same focal point. The hybrid packaging technique allows close positioning of the emitting active regions on top of each other, through the combination of episide-up and episide-down laser mounting (see Fig. 1). This enables us to use both lasers in the same optics, resulting in a compact and simple system design.

For the demonstration of spectroscopy application, the detection of carbon dioxide (CO_2) as a trace gas in ambient air has been shown. In the implemented experiment one laser was emitting on 2230cm^{-1}, where CO_2 is absorbing, the other one on 2200cm^{-1} as reference. Similarly, the combination of two laser chips also would permit gives rise for the detection of different gases in a single optical system. The developed hybrid mounting technique facilitates the combination of QCLs with particular selectable wavelengths.

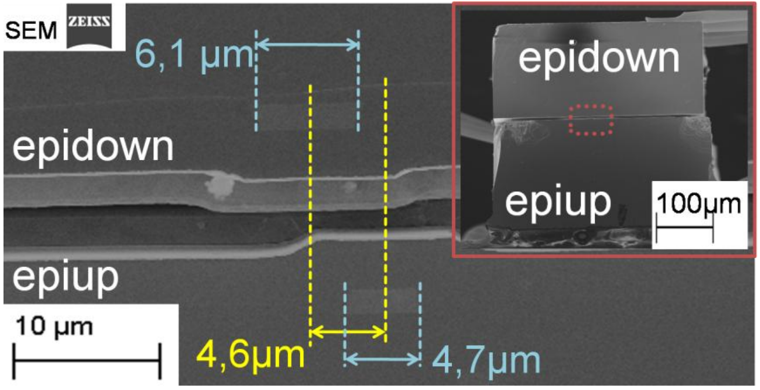

Fig. 1: SEM image of the front facet of the double laser device: The width of the active region of the two lasers is indicated, as well as their horizontal separation corresponding to the positioning error during the hybrid mounting. Insert: Front view if the mounted chip.

D9

The application of TDLS to evaluate Metal Organic Frameworks (MOFs) in new industrial products.

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TDL Sensors Ltd has begun developing a laser based monitoring system to evaluate a newly emerging class of industrially important materials. These metal organic frameworks (MOFs) are currently being implemented in the next generation of products and processes. These applications include safe gas storage, gas delivery and the purification of feed gases.

MOFs consist of metal nodes and organic linker molecules that form extended frameworks with large interior surface areas and volumes. As porous materials they have performance levels often exceeding established materials such as zeolites or activated carbon.

An overview is to be presented on the approach taken to overcome the challenges in developing instrumentation for performance evaluation in a variety of applications. Such as a wide dynamic range for high concentration removal in textile filters to the high level of sensitivity needed for the removal of contaminants for ultra high purity feed gases for the semiconductor and solar industries.

This work is undertaken as part of the Framework 7 project – NanoMOF.

D10

Chirped Laser Dispersion Spectroscopy for Remote Chemical Sensing

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Laser absorption spectroscopy (LAS) has become one of the most popular technologies for quantitative chemical detection in a variety of fields including atmospheric monitoring [1], industrial process control [2], security or bio-medical studies [3]. The measurement of an absorption signal requires small changes in sample transmission to be determined from a several order of magnitude greater background (the total photodetected laser power). Thus any intensity noise or transmission fluctuations cause significant measurement errors in LAS. In contrast the measurement refractive index change inherent to molecular absorption remains theoretically independent from the intensity fluctuations. In this paper a new method of chemical detection based on molecular dispersion sensing will be described. The new technology takes a full advantage of the coherent nature of laser radiation and combines the advantages of direct LAS (e.g. simplicity, robustness and calibration-free operation), with a precision and noise suppression capability that have been primarily known for indirect, zero-baseline spectroscopic sensing methods (e.g. photoacoustics or Laser induced fluorescence).

This work has been focused on remote detection of the optical dispersion observed around molecular ro-vibrational transitions in the mid-infrared spectral region.A recently introduced chirped laser dispersion spectroscopy (CLaDS) technique [4] is used to perform open-path remote chemical sensing. In the presented setup light from a frequency-chirped quantum cascade laser (QCL) is split into two frequency-shifted beams using an acousto-optical modulator. These two beams are recombined into a single dual-frequency beam using the Mach-Zender interferometer configuration. The dual-frequency beam is sent towards a retro-reflector allowing for path-integrated remote sensing of molecules. Returning light is collected with a telescope and focused on a fast photodetector. The CLaDS signal is measured using optical heterodyne detection and FM-demodulation. The dispersion signal is encoded into an instantaneous frequency of the heterodyne beatnote, thus it exhibits high immunity to intensity fluctuations. The prototype instrument was populated with a distributed feedback (DFB) QCL which operates around 2210 cm^{-1} (4.52µm) and can probe the most intense nitrous oxide (N_2O) ro-vibrational transitions. Preliminary performance tests provided a (1σ) minimum N_2O detection limit of ~1ppbv/$Hz^{1/2}$ for a 100m optical path length. In this paper we will present performance, discuss main limitations and show CLaDS suitability to remote sensing of chemicals in gas phase.

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REFERENCES:

1. D. D. Nelson, et al.," Spectrochim. Acta, Part A **60**, 3325-3335 (2004).
2. E. Schlosser, et al.," Spectrochim. Acta, Part A **58**, 2347-2359 (2002).
3. G. Duxbury, et al.," Chem. Soc. Rev. **34**, 921-934 (2005).
4. G. Wysocki, and D. Weidmann," Opt. Expr. **18**, 26123-26140 (2010).

D11

DEVELOPMENTS IN BROADBAND CAVITY ENHANCED DETECTION

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Cavity enhanced absorption measurements have been made of several species that absorb light between 1.5 and 1.7 µm using both a supercontinuum source (SC) and superluminescent light emitting diodes (SLEDs). The broadband spectrometer we have developed consists of an optical enhancement cavity of relatively high finesse, containing mirrors of reflectivity ≥99.98%, and a Fourier transform interferometer. Spectra are recorded of butadiene, isoprene and acetone, important biomarker molecules with broad, unstructured transitions that are difficult to detect selectively with conventional narrowband, diode laser CEAS. Using the fibre-coupled near-infrared SLED, which emits ~10 mW of radiation between 1.6 and 1.7 µm, we are able to express a minimum detectable absorption coefficient of 1.5×10^{-8} cm^{-1} over 4 minutes of acquisition time. This sensitivity is sufficient that we can clearly detect atmospheric methane with our system. Higher detection sensitivities are achieved using the SC source, with a minimum detectable absorption coefficient of 4×10^{-9} cm^{-1} over the same length of acquisition time. In addition, we show that two SLEDs can be coupled together to increase the wavelength coverage to ~200 nm, allowing measurements to be made simultaneously on acetylene, CO_2 and butadiene, enabling varying concentrations of different species within a gaseous mix to be monitored.

We also demonstrate the use of a Digital Supermode Distributed Bragg Reflector (DS-DBR) laser, a novel source which combines the wide coverage of a broadband source with the high resolution of a diode laser, in conjunction with an optical enhancement cavity. With a range from 1.56 to 1.613 µm, the DS-DBR allows us to probe transitions up to 50 nm apart. As a result of this property, we are able to measure CO_2 transitions arising from both $^{12/13}CO_2$ isotopes and with similar initial rotational quantum numbers without the need to change the experimental setup or conditions, thereby reducing the temperature dependence of the isotope ratio. This method for accurate determination of the CO_2 isotope ratio has obvious applications in the urea breath test and diagnosis of *H. pylori* infection.

D12

MEASUREMENT OF NH_3 AND CO_2 ISOTOPOLOGUES IN HUMAN BREATH USING AN EXTERNAL-CAVITY TUNABLE QUANTUM CASCADE LASER AND PHOTO-ACOUSTIC DETECTION

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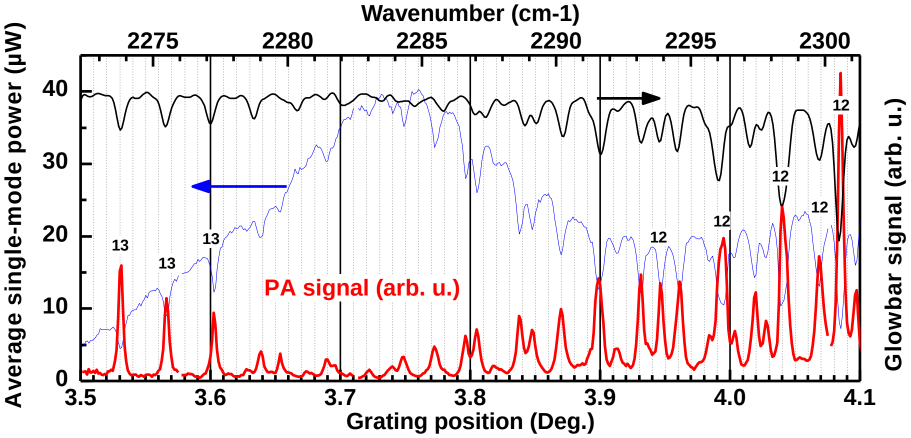
We demonstrate the versatility of an external-cavity (EC) quantum-cascade laser (QCL) using all-refractive-optics in the Littrow configuration with photo-acoustic (PA) detection. The cavity is straightforward to align for practically any emission wavelength. We have successfully used the cavity with QCL active regions emitting at wavelengths centered both at λ_1=11.3µm and λ_2=4.35µm. These configurations were used for ammonia detection near 11.3µm and CO_2 isotopologue recognition in human breath near 4.35µm.

Ammonia detection was accomplished using a 200-cascade QCL active region that emits more than 10W pulse power at 11.3µm and room temperature in multimode operation with uncoated facets [1]. EC performance and NH_3 sensitivity both with and without an AR-coated facet at λ_1=11.3µm will be discussed.

CO_2 detection was based on the same EC configuration using a QCL active region that emits up to 3W pulse power at 4.35µm and room temperature. One facet was AR coated, reducing its reflectivity to 0.6% to avoid Fabry-Perot mode lasing. Mode-hop-free wavelength tuning was achieved within the tuning range of $2255cm^{-1}$ to $2320cm^{-1}$. In this range the absorption lines of $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$ have comparable intensity and sufficient spacing to be resolved from each other. The single-mode laser power, averaged over both duty cycle and acoustic modulation, is depicted in the figure's blue curve. (In this measurement, a peak power of only 10mW was used.) Absorption due to atmospheric CO_2 within the EC resonator is clearly visible and is compared to an FTIR glowbar measurement. The red line in the figure shows the output from the PA cell detecting CO_2 in human breath. Absorption lines due to both $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$ are visible and indicated in the figure.



[1]. O. Fedosenko et al., J. Cryst. Growth (in press).

Poster session E

E1

Frequency tuning of fiber pigtail diode laser

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Fiber pigtail DL modules are now widely used in TDLS. In present paper some aspects of their usage in trace molecules detection and high accurate measurements will be considered.

The module under consideration contains: DL, micro lens connecting DL to single mode fiber, optical isolator (OI), and fiber connector (FC). Part of DL radiation reflected (scattered) by FC can achieve DL active area even after passing OI. This radiation forms additional optical feedback. This feedback is very small in comparison with DL DFB. However, even in this case it can lead to significant changes of DL radiation (Fig.1).

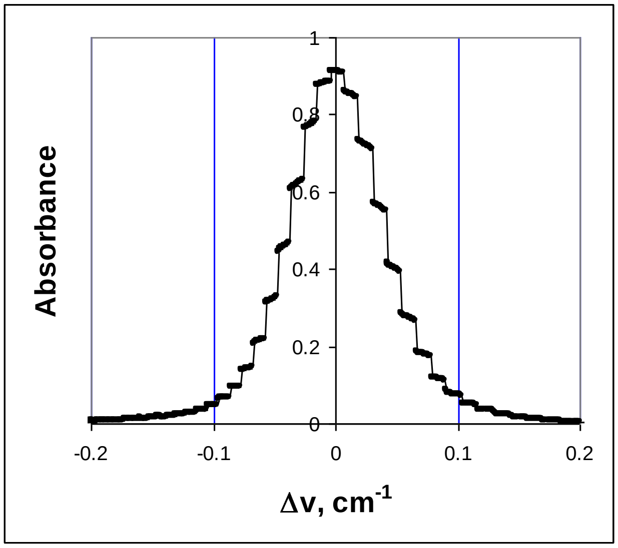

Fig.1 Low pressure water vapor line was recorded by NEL DL with FC/PC

Stepwise absorbance changes can be observed. They are due to DL frequency tuning change in presence of additional feedback. Such frequency tuning of DL results in presence of significant baseline. Both are not acceptable for trace molecule detection and high accurate line shape measurements.

Model was developed and analyzed to describe frequency tuning of DL with additional feedback. 4 DL modules having different additional feedback were investigated. Results obtained were compared with modeling performed. DL line width influence on frequency tuning in presence of additional feedback was investigated.

Suppression strategy of undesirable effect under consideration was developed and demonstrated.

E2

Behavior of the CH_4 and H_2O impurities in process of the high-purity ammonium rectification

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High purity hydrides (NH_3, AsH_3, PH_3, SiH_4, GeH_4) are important components of modern electronics and optoelectronics technologies. Real time impurities in hydrides control is the key element of purification process optimization. During rectification impurities are concentrated at bottom (Heavy Fraction - HF) and upper (Light Fraction - LF) parts of rectification column.

High purity NH_3 is component of modern photo detectors manufacturing. NH_3 purification process control is subject of present paper. CH_4 and H_2O were selected as important representatives of LF and HF impurities. Two DLs operating near 1.65 and 1.39 μ were used to detect CH_4 and H_2O, respectively.

CH_4 and H_2O analytical spectral lines pressure broadening by NH_3 was investigated.

The system to control above mentioned impurities during NH_3 purification process contains 3 cells with optical lengths 3 cm, 1.4 m, and 15.2 m (White multipath cell). Reference channels contain cells with low pressure methane and water vapor. They were used for diode lasers frequency tuning stabilization using molecule under detection line position.

Results of system developed usage to control NH_3 purification process will be presented. Minimum detectable concentrations were found to be 10^{-3} % for CH_4 and 10^{-4} % for H_2O for 0.3 s averaging time.

E3

C_2H_4 detection in SiH_4 purification using TDLS

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SiH_4 is main source to produce Si of highest purity necessary for modern electronics. Requirements for SiH_4 purity: concentration of electrically active impurities (B, P, As, Al) $< 10^{-9}$ %, and for gaseous impurities $< 10^{-5}$ -10^{-6} %. To produce high purity SiH_4 low temperature rectification is using.

Volatile hydrides (diboran, arsine, phosphine) sources of electrically active impurities have physical – chemical properties close to SiH_4. As result it is difficult both to remove and control them during rectification process. Due to the problem mentioned above SiH_4 purification efficiency can be controlled by C_2H_4 having in purification process under consideration separation factor close to 1 (1,26).

Present paper presents results of methodology and instrument development to control C_2H_4 during SiH_4 purification. Scientific-industrial enterprise "Salut" SiH_4 purification column was subject of investigation. The TDLS instrument under consideration was developed by DLS department of A.M.Prokhorov General Physics Institute. C_2H_4 was detected using DL operating near 1.63 μ.

Spectra of both pure SiH_4 (C_2H_4 concentration $< 5*10^{-6}$ %) and pure C_2H_4 (99.99%) were recorded in spectral range 6158.5-6181.5 cm^{-1}. Spectral range 6173.45 – 6173.7 cm^{-1} was selected as analytical one. C_2H_4 spectral line pressure self-broadening as well as broadening by SiH_4, Ar, N_2 was investigated.

TDLS system to control C_2H_4 concentration during SiH_4 purification process was developed. Results of developed TDLS system operation will be presented.

E4

Infrared Laser Spectroscopic Analysis of Surgical Smoke

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Several surgical instruments (harmonic scalpels, high-speed drills and saws, lasers and electroknives) generate heat and cause tissue pyrolysis, which produces what is usually referred to as *surgical smoke* [1].

In a recent study we investigated the chemical composition of surgical smoke – collected during minimally invasive surgery at the University hospital Zurich – by infrared laser spectroscopy with a difference frequency generation (DFG) based spectrometer (2817– 3144 cm^{-1}, $\langle_{\min} = 8.7\times10^{-7}$ cm^{-1}) [2] and with a distributed feedback (DFB) laser diode at 2323.6 nm for carbon monoxide (CO) detection ($\langle_{\min} = 3.1\times10^{-8}$ cm^{-1}, $c_{\min} = 250$ ppb CO).

With the DFG spectrometer, in addition to water vapor, we detected methane in most samples (<0.1–9.1 ppm), and rarely ethane (<0.1–2 ppm) and ethylene (<5–10 ppm) (Fig. 1 a,b). More interestingly, we found traces of the employed anesthetic (sevoflurane) at concentrations of up to 450 ppm in the abdominal cavity of the patient (Fig. 1 a). For comparison, the recommended exposure limit for halogenated anesthetics is 2 ppm. Since surgeons occasionally release smoke from the patient's peritoneum to restore good visibility, vapors of the anesthetic are released into the operation room. With the DFB laser diode we detected CO in four out of six samples at concentrations between 0.3 and 3.2 ppm (Fig. 1 c), well below the recommended exposure limit of 30 ppm.

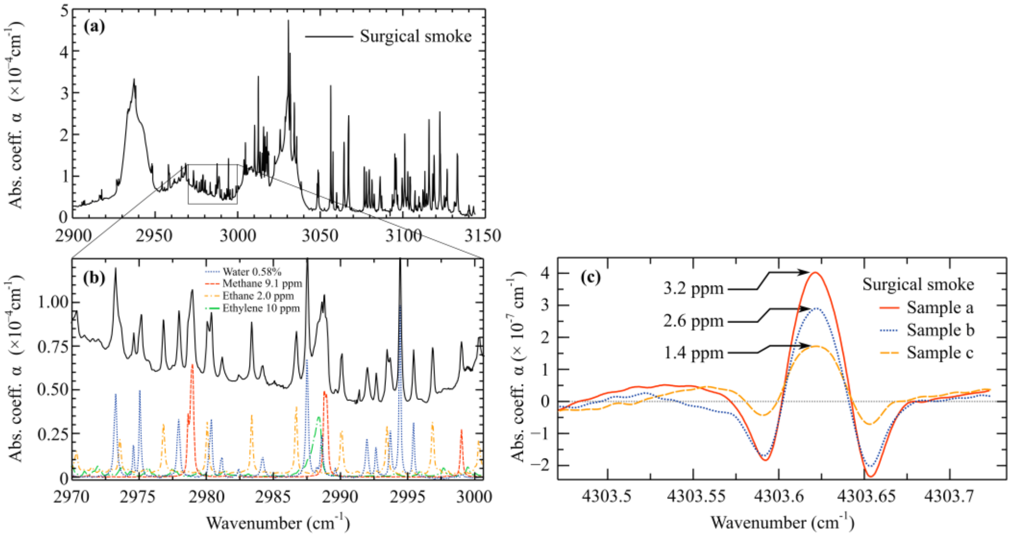

Fig.1. (a,b) Surgical smoke spectrum measured with the DFG spectrometer (the four broad peaks are due to sevoflurane). **(c)** CO absorption line (wavelength modulation).

References
[1] W. Barrett and S. Garber, *Surg. Endosc.* **17**, 979–987 (2003).
[2] M. Gianella and M.W. Sigrist, *Appl. Opt.* **50**, A11–A19 (2011).

E5

OH radical measurements using wavelength modulated Off-Axis Integrated Cavity Output Spectroscopy (WM-OA-ICOS)

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It is well known that the hydroxyl (OH) free radical plays an important role in both combustion chemistry and atmospheric chemistry. There is a considerable interest in instrumental development for *in situ*, real time concentration measurements of OH radicals.

In this work, we demonstrate the feasibility of OH radical detection by means of wavelength modulation enhanced off-axis integrated cavity output spectroscopy (OA-ICOS) using a distributed feedback (DFB) diode laser operating near 1435 nm. A detectivity of ~10^{10} radicals/cm^3 was achieved by probing the OH line at 6965.1939 cm^{-1} with a line intensity of 6.5E-21 cm^{-1}/(molecule cm^{-2}). Figure 1(a) shows an OH absorption spectrum obtained with OA-ICOS approach, in comparison with a 1f WM-OA-ICOS spectrum of OH (b) that offered an enhancement factor of ~12 in the SNR. Experimental instrument detail and the preliminary measurement results will be presented and discussed.

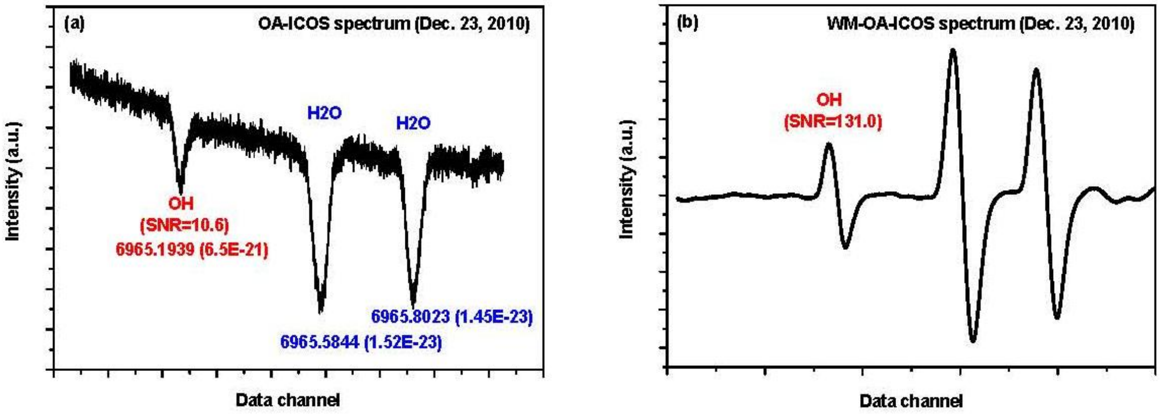

Figure 1 OH radical absorption spectra using : (a) OA-ICOS, (b) WM-OA-ICOS

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E6

HIGH RESOLUTION PHASE SHIFT CAVITY RINGDOWN SPECTROSCOPY TECHNIQUE FOR TRACE GAS DETECTION

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A technique of phase shift cavity ringdown spectroscopy (PS-CRD) has been proposed for the first time in [1]. In [2] this technique was used for measurements of molecular oxygen absorption of in visible spectral region, a ring dye laser pumped by Ar+ laser being used as a radiation source. Subsequently, this approach was widely used in systems based on LEDs [3, 4] and on DLs [5] to measure NO_2 trace concentrations in the atmosphere. A sensitivity of such systems is in the range from a few ppmv to fractions of ppbv, however concentration measurements are performed with low spectral resolution.

Since the PS-CRD technique requires a modulation of DL intensity, the use of DLs to record the absorption spectra with high resolution is connected with certain difficulties. The problem is that the modulation of the injection current leads simultaneously both to the intensity modulation, and to the modulation of the diode laser wavelength. As a result the spectral resolution degenerates considerably, and the recorded absorption corresponds to the spectral range of about 1 cm^{-1}.

Our proposed approach allows us to realize all the advantages of phase-shift measurements while maintaining high spectral resolution. The experimental setup consists of a DL emitting at a wavelength of 640 nm, a high-finesse multipass cell with the high-reflective mirrors (R = 0.99995), and a photomultiplier tube. The DL injection current was modulated at 12 kHz, and a phase shift of radiation transmitted through the cell was measured. High resolution spectra can be obtained after processing the detected signal and the solutions of integral equations.

First experimental results on the absorption spectra of water in the spectral region near 640 nm were obtained. There is a good agreement between the experimental spectra with those calculated using the HITRAN-2008 database. Currently, this technique provides a spectral resolution of 10^{-3} cm^{-1} and a sensitivity of the absorption coefficient measurement of $7*10^{-11}$ cm^{-1} at a time of registration about 10 minutes.

Acknowledgements. This work was partially supported by the Russian Foundation for Basic Research (RFBR Grants 10-02-01111-a and 11-08-01127-a).

References

[1] J.M. Herbelin, J.A. McKay, M.A. Kwok, R.H. Ueunten, D.S. Urevig, D.J. Spencer, and D.J. Benard, Appl. Opt., v19, 144-147, (1980).
[2] R. Engeln, G. von Helden, G. Berden, G. Meijer, Chem. Phys. Lett., v262, 105-109, (1996).
[3] P.L. Kebabian, K.D. Annen, T.A. Berkoff, and A. Freedman, Meas. Sci. Technol., v11, 499–503 (2000).
[4] P.L. Kebabian, S.C. Herndon, and A. Freedman, Anal. Chem., v77, 724–728, (2005).
[5]. V.L. Kasyutich, P.A. Martin, and R.J.Holdsworth, Meas. Sci. Technol. v17, 923-931 (2006).

E7

ETHYLENE DETECTION QUANTUM CASCADE LASER BASED OFF-AXIS INTEGRATED CAVITY OUTPUT SPECTROSCOPY

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Ethylene plays an important role in many aspects of plant growth and development. Among its effects are promoting fruit ripening and revealing stress responses in plants. In horticulture, the ethylene production needs to be controlled during shipments, which requires fast, simple and sensitive gas detectors. Here, we propose the combination of a Quantum Cascade Laser (QCL) with off-axis alignment integrated cavity output spectroscopy (OA-ICOS) for the detection of ethylene. To access the strongest absorption properties of ethylene, a pulsed QCL is used. This laser allows system integration, thus ensuring fast and sensitive measurements. OA-ICOS takes advantage of long path absorption spectroscopy, thereby eliminating the common problems of resonance with other cavity-based absorption techniques and reducing the complexity of the setup [1]. Application of this technique aims for the development of a detector platform for the detection of trace gasses at the sub part-per-billion volume ($1{:}10^9$) level. This will provide advanced and compact spectroscopic gas sensors for the future research of different volatiles.

References:

[1] Joshua B. Paul, Larry Lapson, James G. Anderson, Applied Optics, 40, 27, 4904-4910

E8

A COMPARATIVE ANALYSIS OF METHANE SENSING IN DIFFERENT FREEUENCY MODULATION USING LASER SPECTROSCOPY

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Methane monitoring is very important for study in Atmospheric changes, chemical facilities, gas plants, and for safety in industrial environments, because of Methane is a combustible, explosive and is also acts as a greenhouse gases. For comparative study of methane detection sensitivity using frequency modulation, a wide band emission spectra and commercially low cost mid-infrared range (3.32 µm) InAsSbP LED and InAs/InAsSbP (sensible for 3-3.8 µm) is used for the methane detection. For this experiment LED is biased through quasi continuous wave (QCW) mode regarding that precision electronics is being made. Mid-Infrared spectral region is an effective tool for monitoring atmospheric trace-gas species; it has many other advantages such as high sensitivity, high reliability, and molecular selectivity. This technique has sensitivity 5% of Low Explosive Level (LEL) for methane capable to detect in PPM or sub PPM level. As LED's characteristic is associated with temperature. As temperature rises, absorption coefficient is changes with the frequency due to the intensity fluctuation. Intensity fluctuation causes the detection sensitivity. To control the LED's and PD's temperature, LED and PD has a thermal resistor and thermo electric cooler.. Source and detector has been connected by a synchronous cable for synchronization and lock in card also being used to minimize ambient noise. Source has been modulated with different frequency in QCW mode. A comparative result has been discussed due to frequency modulation in difference quantities.

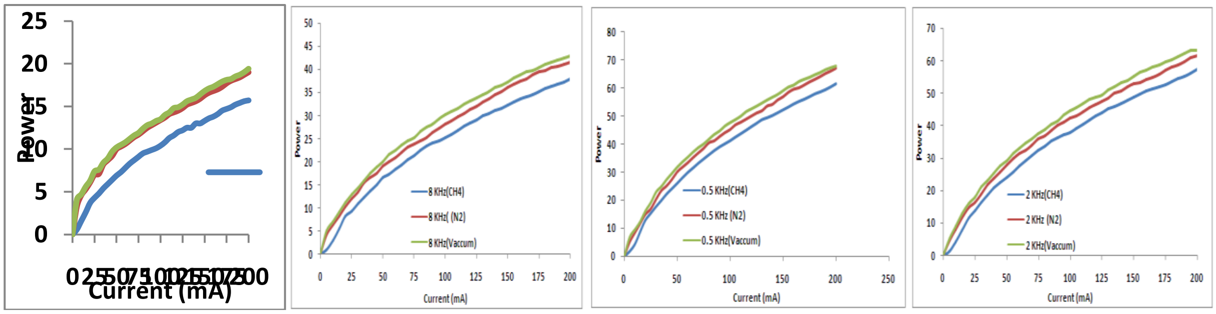

Fig 1: Different detection sensityvity of sensor at different freequency modulation

Reference:

1. "Design of portable optical sensor for methane gas detection" –C Massie, G Stewart, G McGregor Sensor and actuators B 113 2006 830-836
2. "Measurement of methane gas concentration using an infrared LED"-H Okajima, S. Kakuma, K. Uchida, K Noda SICE-ICASE Int. Joint Confr 2006
3. Non Dispersive Infra Red Methane Absorption Model"- Y. Wu, D Li, W Cheng and R Li-978-1-4244-7050-1/10 2010 IEEE

E9

GAS IN SCATTERING MEDIA ABSORPTION SPECTROSCOPY BASED ON FREQUENCY-MODULATED CONTINUOUS-WAVE TECHNIQUES

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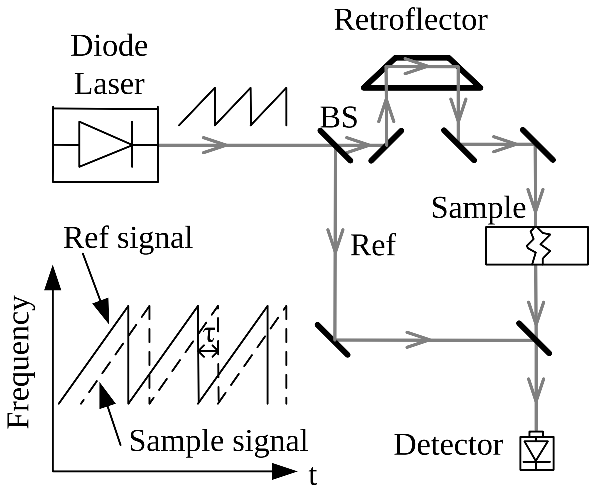
The presence and exchange of gases in scattering media can be assessed by narrow-band absorption spectroscopy using tunable diode lasers. According to Beer-Lambert's law, the absorption signal not only depends on the concentration, but also on the path-length that the light has travelled. Two methods have been used to evaluate the path-length in scattering media: a relative one based on the mean equivalent path-length, which is defined as the equivalent open-path distance which yields the same absorption [1]; and another absolute method which employs time-resolved spectroscopy, also called time-of-flight spectroscopy, where a short-pulsed laser beam is used to measure the decay curve of the light passing through the scattering medium [2].

In the present work a Frequency-Modulated Continuous-Wave (FMCW) technique, well known in the telecommunication field, is used to evaluate the optical path-length in the scattering media. The basic principle of the FMCW technique is presented in the figure to the right. The laser frequency is modulated by a ramp signal and a Michelson interferometer setup is used to obtain the beat frequency between the reference and the sample beam. Due to the scattering in the sample, the light will pass through different path-lengths and will then induce corresponding beat frequencies with the reference beam. By analyzing the beat frequency in the detected signal we can evaluate how the light passes through the scattering medium. By combination with the absorption spectroscopy signal we can obtain the gas concentration in the sample when the laser is scanned across an absorption line. Proof-of-principle experiments on polystyrene foam are reported.



Reference

[1]. M. Sj?holm, G. Somesfalean, J. Alnis, S. Andersson-Engels, and S. Svanberg, Optics Letters **26**, 16 (2001).

[2]. G. Somesfalean, M. S. holm, J. Alnis, Claes af Klinteberg, S. Andersson-Engels, and S. Svanberg, Applied Optics **41**, 3538 (2002).

E10

TDLAS-BASED OPEN-PATH LASER HYGROMETER USING REFLECTIVE SCATTERING TARGETS FOR WATER VAPOR MEASUREMENTS

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Owing to the worldwide climate change, northern hemisphere permafrost e.g. on Svalbard and elsewhere is in danger to melt and cause increased emission of carbon greenhouse gases (CO_2/CH_4) stored in the soil [1,2]. This can lead to a positive feedback to climate change which would significantly worsen the problem [1]. This gas emission and its spatial distribution needs to be studied in detail, which is often hampered by adequate field qualified instrumentation. For this purpose we plan to realize field instrumentations to study the water vapor distribution in the soil-/air boundary-layer. Further measurements regarding the emission of carbon dioxide and methane are also planned.

Therefore we plan to develop a new light-weight and transportable tunable diode laser absorption spectrometer (TDLAS) to enable absolute water vapor measurements in areas that are difficult to access. Based on low-cost industrially available components like a distributed feedback (DFB) diode laser and robust fiber optics the setup comprises a joint sender/receiver side and a separate low cost reflector as a scattering target. This retro-reflecting target allows the setup of simple mono-static TDLAS instruments which ensure easy installation and maintenance free operation in harsh environment and under varying climate conditions. First demonstration measurements with such a mono-static setup demonstrate the large dynamic range of the spectrometer. For absorption path length of up to 2m, hence laser target separation of 1 m, low concentrations (200 ppmv) as well as high concentrations (13000 ppmv) could be measured without gas sampling or sensor calibration. With a time resolution of 5.4 Hz (aiming at Eddy correlation measurements above 10 Hz) we achieved a detection limit of up to 19 ppm·m for the H_2O 211-110 line at 7299.431 cm^{-1}. Fractional optical resolutions of up to $2.1x10^{-4}$ OD_e (1σ) and a signal to noise ratio of more than 900 were attained. The presented spectrometer is a promising alternative to extractive measurement methods or techniques which require frequent adjusting since it avoids extraction artifacts as well as calibration and reduces expenditure on personnel and equipment. Currently measurements are prepared to realize a 1D spatially resolved water measurement by combining scatter targets, rapid beam scanning and 1D reconstruction by means of Abel inversion.

[1] S.Zimov, E.Schuur, and F.Chapin, Science **312,** *1612-1613* (2006).
[2] E.Schurr, J.Vogel, K.Crummer, H.Lee, O.Sickmann and T.Osterkamp, nature **459,** *556-559* (2009).

E11

CAVITY-ENHANCED RESONANT PHOTOACOUSTIC SPECTROSCOPY WITH OPTICAL FEEDBACK CW DIODE LASERS: A NOVEL TECHNIQUE FOR ULTRA-TRACE GAS ANALYSIS AND HIGH-RESOLUTION SPECTROSCOPY

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Cavity-enhanced resonant photoacoustic spectroscopy with optical feedback cw diode lasers (OF-CERPAS) is introduced as a novel technique for ultra-trace gas analysis and high-resolution spectroscopy [1]. In the scheme, a single-mode cw diode laser (3 mW, 635 nm) is coupled into a high-finesse linear cavity and stabilized to the cavity by optical feedback. Inside the cavity, a build-up of laser power by a factor of 8000 occurs. Absorbing gas phase species inside the cavity are detected with high sensitivity by the photoacoustic effect using a microphone embedded in the cavity. To increase sensitivity further, coupling into the cavity is modulated at a frequency corresponding to a longitudinal resonance of an organ pipe acoustic resonator (f = 1.35 kHz, Q ≈ 10). The technique has been characterized by measuring very weak water overtone transitions near 635 nm. Normalized noise-equivalent absorption coefficients are determined as $\alpha \approx 4.4 \times 10^{[illegible]}$ cm^{-1}s$^{1/2}$ (corresponding to 1 s integration time) and 2.6×10^{-11} cm$^{[illegible]}$ s$^{1/2}$ W$^{[illegible]}$ (corresponding to 1 s integration time and 1 W laser power). These sensitivities compare very favourably with existing state-of-the-art techniques. As an advantage, OF-CERPAS is a "zero-background" method which increases selectivity and sensitivity, and its sensitivity scales with laser power.

Reference:

[1] M.Hippler, C.Mohr, K.A. Keen and E.D. McNaghten, J. Chem. Phys. 133, 044308 (2010)

E12

External Cavity Quantum Cascade Laser with Active Wavelength Control

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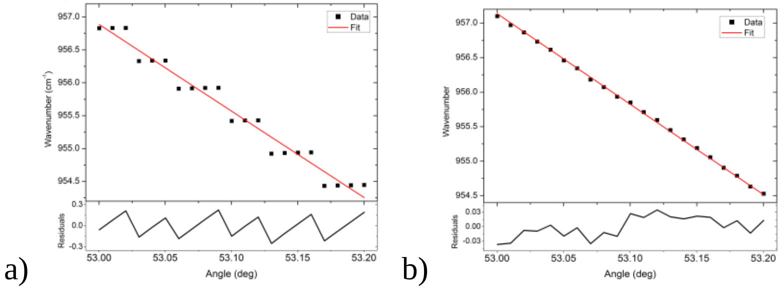
Tunable single-mode lasers are critical for applications in spectroscopic sensing of trace chemicals in gas phase. Semiconductor lasers are of particular importance because they provide a small footprint, relatively high output powers, and often exhibit broad gain profiles. To take advantage of the latter and provide broadband wavelength tuning, the semiconductor gain chip can be incorporated into an external cavity laser (ECL) configuration. However due to unwanted laser frequency pulling effects the precision of wavelength setting is insufficient for high resolution spectroscopic sensing applications. Thus we developed an active wavelength setting technique to provide precise control of the ECL operating wavelength.

In this work, we use our folded cavity Littrow-type ECL system based on a quantum cascade laser (QCL) gain media operating at 10 μm [1]. According to the grating equation, $2d\sin(\theta)=m\lambda$ (d-the groove spacing; m-the diffraction order), the wavelength (λ) favored by the grating feedback is determined by the angle between the grating normal and the optical axis of the incident beam (θ). In an ECL cavity, there are two additional wavelength selecting resonant structures: the Fabry Perot (FP) cavity of the chip itself and the FP mode of the external cavity. By tuning only one of the three wavelength-selecting elements (e.g. the grating) mode-hops and mode-pulling effects will occur. This causes the grating equation to inaccurately predict the actual operating wavelength. Such an effect is shown in Fig. 1a. The residuals from the grating equation fit clearly show ~0.5 cm^{-1} mode-hops between the longitudinal FP modes of the laser chip cavity. Our method actively synchronizes all three wavelength-selective elements by performing modulation of the resonant structures and phase-sensitive detection of the relative spectral alignment. The process consists of two active feedback loops: one locks the chip FP mode onto the EC FP mode, and the second performs lock of the EC FP mode onto the grating filter maximum. This process is automated using two proportional-integral controllers. Residuals from the active wavelength setting process shown in Fig. 1b are an order of magnitude smaller than without an active control. The wavelength setting error of 0.06 cm^{-1} (3σ) is below an average linewidth of pressure broadened molecular transitions at atmospheric pressure. Therefore, this process has applications in atmospheric trace-gas detection by obviating the experimental need for using wavemeters or other frequency calibration standards (e.g. etalons). Moreover, besides the mid-IR QCLs this process is applicable to most external cavity semiconductor laser systems without significant modifications to the laser module.



a) b)

Figure 1a) ECL output frequency with respect to grating angle without active wavelength locking and b) with active wavelength locking. Residuals from fitting the data by the grating equation are plotted below.

[1] T. Tsai, and G. Wysocki, *Appl. Phys. B* **100**, 243-251 (2010).

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Poster session F

F1

High temperature, robust Herriott cell for sensitive NH_3 spectroscopy to optimize NO_x removal

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Ammonia plays an important role in the NO_x removal in combustion processes. However, a too high concentration of NH_3 results in unconverted ammonia that pollutes the environment and damages the combustion plant. Today's available ammonia sensors are either not suitable for high temperature applications that are common in combustion processes or do not have the needed accuracy to control the ammonia concentration. We present a robust and cost-efficient extractive gas sensor suitable for detection of NH_3 with a precision of 50 ppb.

To control the injected ammonia concentration, the sensor should have a low detection limit (< 50 ppb) and a fast response time (< 20 seconds). A suitable technique is tunable diode laser absorption spectroscopy (TDLAS) in the near infrared range. However, since the absorption of ammonia is very small in this region, we have to use a Herriott multipass cell to achieve the required lower detection limit [1, 2]. To obtain a fast response time the cell volume was minimized and the cell, including gas lines, need to be heated to prevent adsorption of NH_3 and condensation of water along the gas path. Moreover, the cell should be cheap, robust and operate over a large temperature range.

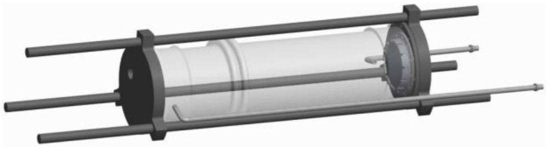

Fig. 1: The Herriott cell. The base is formed by three rods, the mirrors are mounted on two flanges and the gas compartment is a flexible bellow.

The laser source is a commercially available DFB infrared laser emitting near 1.5 μm. The laser is mounted on the frame close to the heated cell and a lens is used to obtain a beam waist in the hole of the first mirror. Using a gas mixing setup having two mass flow controllers the cell has been tested. Measurements show a standard deviation of 12 ppb NH_3. The presented multipass cell is very attractive for industrial applications because of the robust and cost efficient design that will allow better ammonia control in NO_x removal applications.

References:

[1] Herriott, D., Kogelnik, H. and Kompfner, R. "Off-Axis Paths in Spherical Mirror Interferometers," Appl. Opt. 3, 523-526 (1964).
[2] Bartlome, R., Baer, M. and Sigrist, M. W. "High-temperature multipass cell for infrared spectroscopy of heated gases and vapors," Review of Scientific Instruments 78, 013110-013116 (2007).

F2

THE RETRIEVING OF THE LINE PROFILE PARAMETERS OF THE CH_4 R(5) MULTIPLET $2\nu_3$ BAND ABSORPTION SPECTRA BROADENED BY N_2

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The experimental results of methane R(5) $2\nu_3$ band multiplet spectral line profiles, broadened by N_2, are presented. Methane absorption spectra were recorded using two-channel photometric spectrometer based on tunable diode laser. The feature of spectra, recorded with such methodic, is the complicated baseline behavior. Spectra were processed using developed at IAO program, in which simultaneous fitting procedure of synthetic spectra to spectra recorded under various pressures was implemented. The program uses known models of spectral line profiles (Voigt, Rautian-Sobelman, Rosenkranz) and is based on the linear pressure dependence of line profile parameters. The retrieved line profile parameters (intensities, and coefficients of broadening, shifting and narrowing) were compared with known literature data.

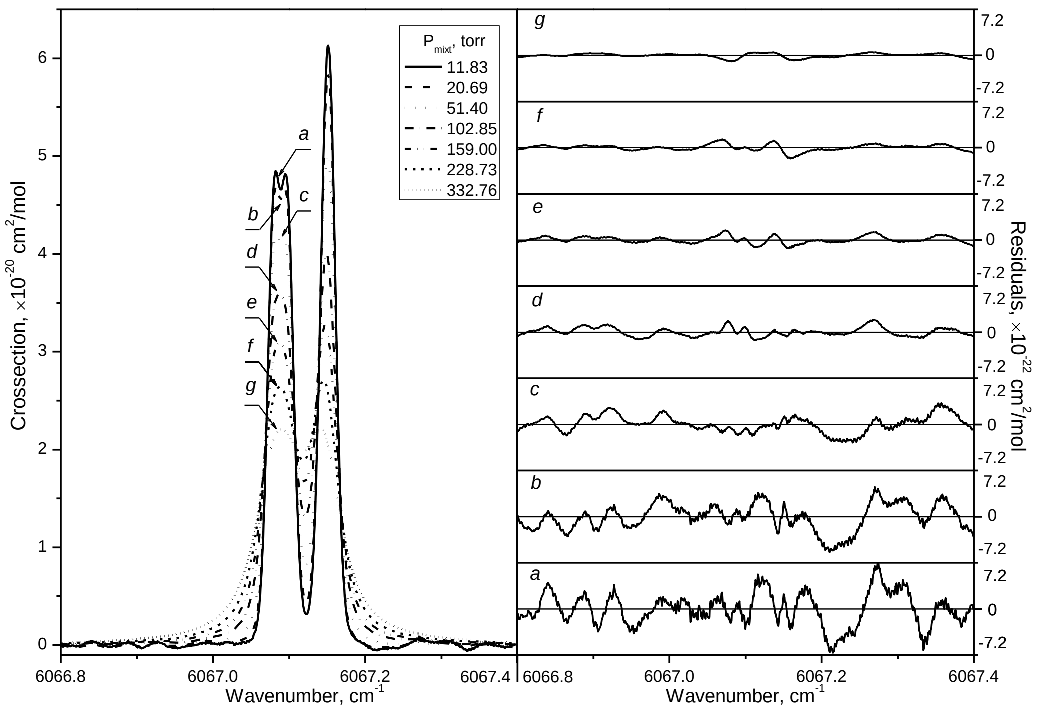

Fig 1. Some of measured absorbance spectra of the $2\nu_3$ band R(5) manifold of CH_4 broadened by N_2 (left panel) and obs-calc residuals from simultaneously fitted Rosenkranz line shapes (Pine A.S., 1997) (right panel).

This work is supported by the program of RAS, project 3.9.4. (experiment) and “Bruker Ltd” (design of the software), grant RFFI, project № 10-05-00764-a.

F3

APPLICATION OF A CURRENT-MODULATED LASER DIODE IN COMBINATION WITH MINIATURIZED RESONANT PHOTOACOUSTIC CELLS FOR SPECTROSCOPIC MEASUREMENTS IN GASES

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The miniaturized spectroscopic hardware provided with tunable semiconductor lasers is a promising line of development for the photoacoustic (PA) trace-gas detection technique. Recent progress in the field can be associated with miniaturized resonant PA cells, the design of which is optimized to the best gas-detection performance for an acoustic mode of internal cell cavity [1]. The volume of internal cavity for such cells can be smaller than 1 cm^3 (see Fig.1). Despite the reduced sizes, the cells are not worse in the performance as compared to non-miniaturized ones. The measured minimal detectable absorption for the cells is better than ~ 10^{-8} cm^{-1}W Hz$^{-1/2}$. The cells are adapted to a linearly polarized, collimated and modulated laser beam. Development of a spectroscopic gas analyzer, which includes these PA cells in combination with near-infrared current-modulated laser diodes, is of great interest for commercial purposes due to the compactness, simplicity and low cost of the equipment. But, one should take into account the spectral broadening for the modulated laser beam.

In the report we discuss aspects associated with application of a standard near-infrared single-mode laser diode for absorption spectroscopy measurements in gases. In experiments we study the spectral broadening for the beam to be generated by the laser diode when the diode current is modulated at frequencies (TTL-like amplitude modulation at 1 ÷ 20 kHz) typical for acoustic resonances of miniaturized cells. The spectral laser-beam widths are estimated and analyzed as functions of the diode current and modulation frequency.

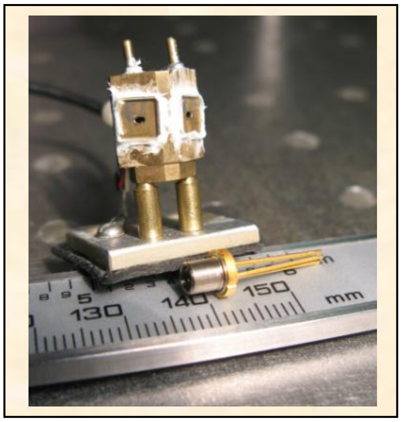

Fig.1 A standard commercially available single-mode near-infrared DFB laser diode (a 5.6 mm can package) and our recently developed resonant PA cell. The cell has the internal volume ~ 5 mm^3 and aperture d = 0.8 mm. This cell is provided with Brewster windows and can be applied inside the laser cavity.

References:
[1] http://www.micepas.basnet.by

F4

AN EFFECTIVE TDLS SETUP USING HOMEMADE DRIVING MODULE FOR EVALUATION OF PULSED QCL

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TDLS using QCL are becoming popular [1], whereas more details accompany each device is still anticipant for users. We present here an effective TDLS setup mounted on a 30×60 cm optical breadboard using only a few parts as shown in Fig 1(a); the purpose of this setup is for the evaluation of our homemade pulsed QCL chips and modules to meet the wide range of requirements of end-users. In this setup a homemade pulse driving module was adopted; this compact driver have rich practical utilities and >3A driving ability with pulse width range from tens of ns to a few μs to meet the demands of both inter-pulse and intra-pulse schemes [2]. A commercial 10m white cell for FTIR spectrometer originally was used in the system; the wide beam feature of this gas cell makes the system quite stable and easier to operation. In this setup various characteristics of the QCL chips and modules related to TDLS applications have been evaluated in detail, Fig 1(b) shows a measured absorption features of N_2O around 7.75 μm using a homemade DFB-QCL[3] in intra-pulse scheme.

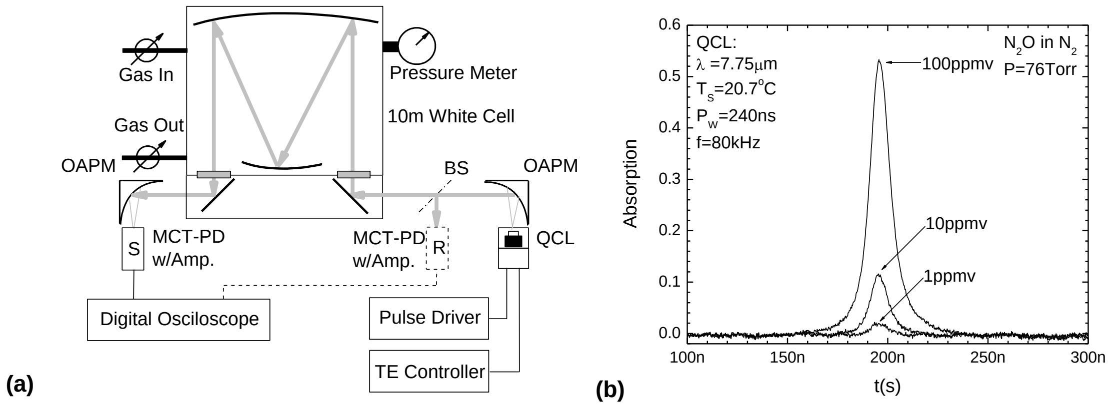

Fig.1 (a): Schematic drawing of the TDLS setup; (b): Measured absorption of N_2O around 7.75 μm using a homemade DFB-QCL in intra-pulse scheme.

[1] F. K. Tittel, Y. Bakhirkin, A. A. Kosterev, and G. Wysocki, The Review of Laser Engineering **34**, 275, (2006)
[2] J.Manne, W.Jäger, and J.Tulip, Appl. Phys. B, **97**, 334, (2009)
[3] G.Y. Xu, A. Z. Li, Y. Y. Li, L. Wei, Y. G. Zhang, C. Lin, and H. Li, Appl. Phys. Lett., **89**, 161102, (2006)

F5

Nitrous Acid Trace Detection using Continuous-Wave Quantum Cascade Laser Absorption Spectroscopy at 8 µm

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Gaseous nitrous acid (HONO), one of the main hydroxyl (OH) free radical sources in the atmosphere, plays a significant role in the atmosphere, especially in the polluted troposphere. Understanding the HONO sources and sinks would allow better estimation of the OH radical budget. HONO concentration measurement in the atmosphere requires high sensitivity, good temporal and spatial resolution. Tunable diode laser spectrometry (TDLS) provides advantage in terms of sensitivity and spatial resolution for *in situ* real time quantification of trace HONO. In this paper, we report on the development of a TDLS instrument for HONO detection, based on a continuous wave, room temperature operation quantum cascade laser （QCL） emitting near 1254.6 cm^{-1}. Fig. 1 shows an absorption spectrum of 95 ppm HONO scanned with a high rate of 2.5 kHz. Preliminary results relative to HONO concentration measurement and calibration, sensitivity and selectivity (spectral interference with CH_4, NO_2) issue, as well as fast wavelength sweep approach will be discussed.

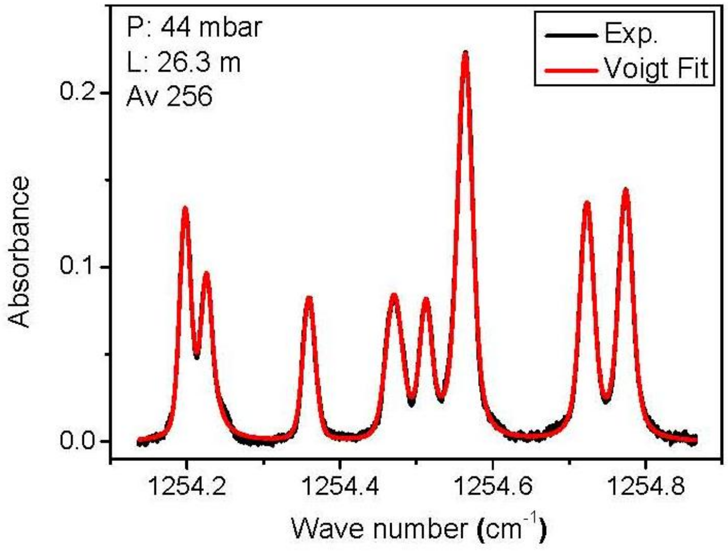

Figure 1 HONO absorption spectrum at a pressure of 44 mbar in a multipass cell of 26.3 m.

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F6

4.6 μm-BAND DIFFERENCE FREQUENCY GENERATION IN LiNbO$_3$ RIGDGE WAVEGUIDE FOR TRACE GAS DETECTION

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The mid-infrared (IR) wavelength region is attractive for highly sensitive gas detection. We have demonstrated mid-IR difference frequency generation (DFG) using periodically poled LiNbO$_3$ (PPLN) waveguide (WG) [1]. DFG using PPLN WG is a promising because it can achieve efficient conversion from mature near-IR laser diodes (LD), which can generate CW output at room temperature [1]. Incidentally, the detection of N_2O is attracting much interest because it has a large green house effect despite its small concentration in the atmosphere. In this study, we newly constructed a stable 4.6 μm-band DFG source using a lens-coupled PPLN WG module and DFB-LDs for a pump and a signal. We also performed N_2O gas detection using wavelength modulation spectroscopy (WMS). Stable wavelength modulation can be obtained by using current modulation of a signal (or pump) laser based on telecom-band DFB-LD technology. The new design of the DFG source and WMS method enables us to improve sensitivity compared with the previous work [2].

The PPLN ridge WG was fabricated by using the direct bonding method [1]. A 50-mm-long WG was assembled in the lens-coupled fiber pigtail module. A 1.06-μm DFB-LD amplified by an Yb-doped fiber amplifier and a 1.39-μm DFB-LD were used as a pump and a signal, respectively. A White cell with a 16-m optical path was used in the detection. The WMS was performed at a pressure of 13.3 kPa. Figure 1 shows an example of the WMS 2f spectra. By using current modulation of the signal LD, stable WMS spectra were obtained. Figure 2 shows WMS 2f signal intensity as a function of N_2O concentration. We found that the detection limit was 35 ppb, which corresponds to one-tenth of the atmospheric N_2O concentration. These results suggest that this DFG source based on a PPLN WG is useful for a high-sensitivity in-situ trace gas sensor.

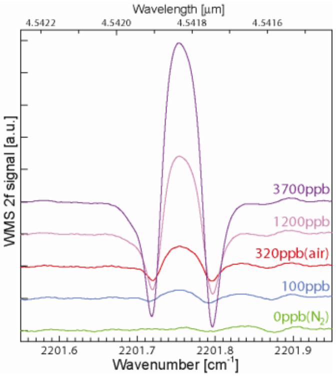

Fig. 1. WMS 2f spectra of N_2O.

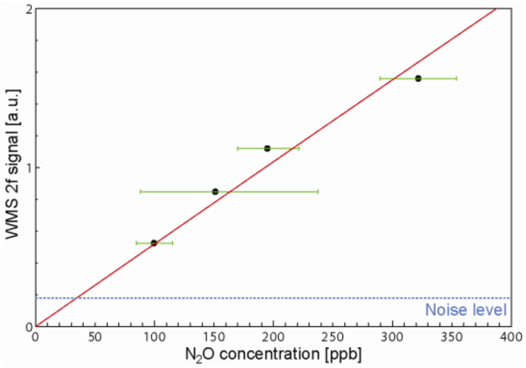

Fig. 2. WMS 2f signal versus N_2O concentration.

References
[1] O. Tadanaga, Y. Nishida, T. Yanagawa, H. Miyazawa, K. Magari, T. Umeki, K. Yoshino, M. Asobe, and H. Suzuki, Electron. Lett. 42, 988 (2006).
[2] T. Yanagawa, O. Tadanaga, Y. Nishida, K. Magari and M. Asobe, Electron. Lett. 45, 369 (2009).

F7

INTEGRATED NIR AND MIR SENSING PLATFORM FOR GASES AND LIQUIDS (IRSENS): GOALS AND INTERMEDIATE RESULTS

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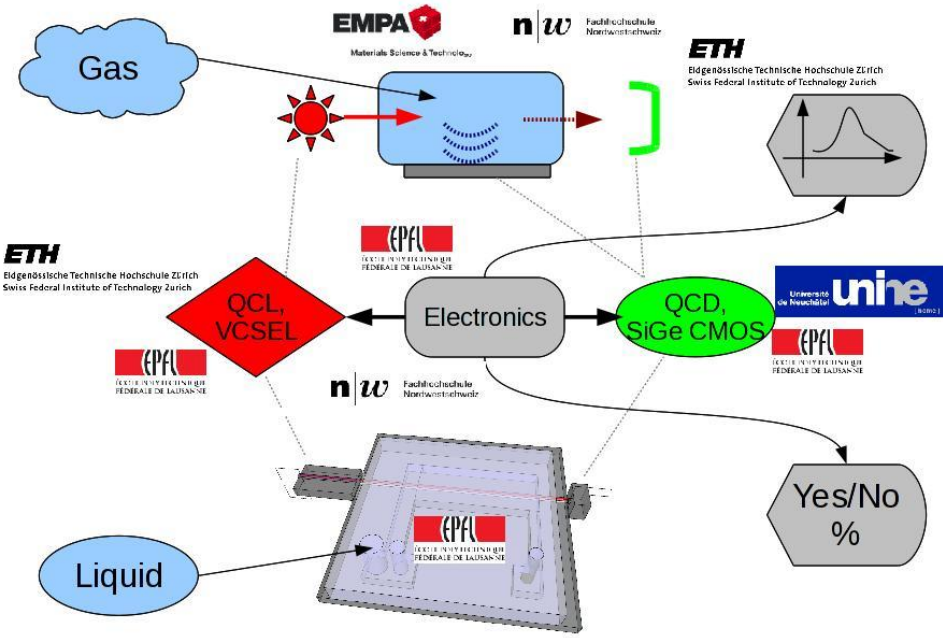
Tunable infrared semiconductor lasers have become commercial products, and they represent core elements of a multitude of systems aimed at specific measurement needs. However, there exist few attempts yet to integrate them into general-purpose gas or liquid phase measurement platforms for monitoring or in-the-field applications.

In this project[1], various source and detector types in the near- and mid-infrared range are combined with optical waveguide and bench systems together with gas and microfluidic cells, to build a versatile and portable platform with small power and space requirements and capable of measuring various selected trace species with fingerprints in a large wavelength range from 2 to 10 micrometers and beyond. The project was launched in the scope of the Swiss Nano-Tera[2] research framework and is based on the collaboration of several research institutes, aggregating expert knowledge about infrared sources and detectors, signal processing, microfluidics, microoptics, gas and liquid spectroscopy.

Design considerations, and intermediate results from the first generation of central parts of the project are presented.



[1] http://www.nano-tera.ch/projects/80.php
[2] http://www.nano-tera.ch

F8

HIGH TEMPERATURE INVESTIGATIONS OF METHANE FOR THE CALCULATION OF THE TEMPERATURE DEPENDENCE OF SPECTRAL PARAMETERS

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For gas sensing applications in high temperature environments, such as aeroengine exhaust, solid oxide fuel cells and flames, it is important to have accurate knowledge of the temperature dependence of the spectral parameters used for laser gas composition measurements. Here we present methane spectral measurements for a number of spectral manifolds, taken using direct tunable diode laser spectroscopy, for a temperature range of 50-850°C. The R(4) manifold is of particular interest in this work, as the individual transition assignments vary between the HITRAN2008 database [1], based on the work of Frankenberg [2], and the GOSAT database [3]. Comparative spectra will be shown using parameters from both databases, as will temperature dependence calculations for the self- and nitrogen-broadening parameters. Studies of the R(4) manifold have previously been carried out at high temperatures [4], however, only the HITRAN transitional assignments were used. Furthermore, two 'hot' lines have been found in the R(4) manifold that are not present in the work of Gharavi and Buckley [4]. This is because they interrogated a much smaller wavelength range in their work, as they were operating at pressures of ~0.1 bar compared to the atmospheric pressure measurements taken in this work. We provide linestrength and position values for these new transitions.

[1] L.S. Rothman, I.E. Gordon, A. Barbe, D. Chris Benner, P.F. Bernath, M. Birk, V. Boudon, L.R. Brown, A. Campargue, J-P Champion, K. Chance, L.H. Coudert, V. Dana, V.M. Devi, S. Fally, J-M. Flaud, R.R. Gamache, A. Goldman, D. Jacquemart, I. Kleiner, N. Lacome, W.J. Lafferty, J-Y. Mandin, S.T. Massie, S.N. Mikhailenko, C.E. Miller, N. Moazzen-Ahmadi, O.V. Naumenko, A.V. Nikitin, J. Orphal, V.I. Perevalov, A. Perrin, A. Predoi-Cross, C.P. Rinsland, M. Rotger, M. Simeckovo, M.A.H. Smith, K. Sung, S.A. Tashkun, J. Tennyson, R.A. Toth, A.C. Vandaele and J. Vander Auwera, J. Quant. Spectrosc. Ra. Vol. 110, pp 533-572 (2009).
[2] C. Frankenberg C, T. Warneke, A. Butz, I. Aben, F. Hase, P. Spietz and L.R. Brown, Atmos. Chem. Phys., Vol. 8, pp 5061-5075 (2008)
[3] A.V. Nikitin, O.M. Lyulin, S.N. Mikhailenko, V.I. Perevalov, N.N. Filippov, I.M. Grigoriev, I. Morino, T. Yokota, R. Kumazawa and T. Watanabe, J. Quant. Spectrosc. Ra., Vol. 111, pp2211-2224 (2010).
[4] M. Gharavi and S.G. Buckley, J. Mol. Spec., Vol.229, pp78-88, (2005)

F9

COMPACT, LIGHT WEIGHT, HIGH PRECISION WATER VAPOR SENSOR FOR PLANETARY EXPLORATION BY FREQUENCY MODULATION USING LASER SPECTROSCOPY

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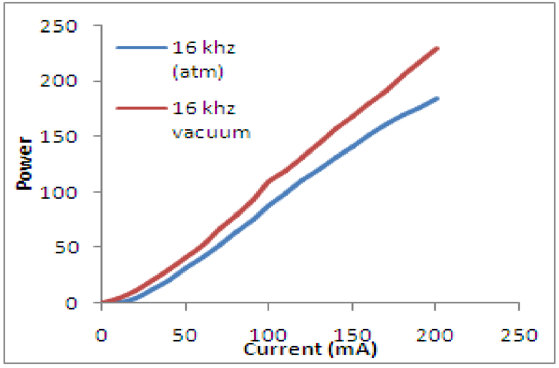
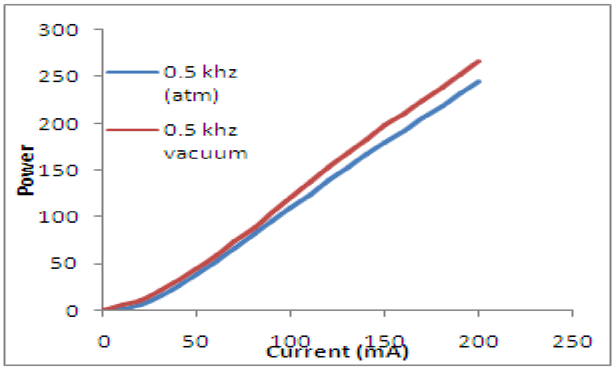
For planetary exploration, the challenges remain in its high precision, harse environment, size and weight for uploading onto payload. We have designed & developed a proto type of trace water vapor sensor with the sensitivity at PPT level. A near infrared LED (1854nmGaInAsSb/AlGaAsSb heterostructure lattice matched to GaSb substrate) around the absorption overtone lines of water vapor at 1854 nm using in house multi reflection optical holder and a suitable photodiode (GaInAsSb/GaAlAsSb) are being used to detect water vapor accurately. The instrument is being tested from ambient to vacuum having compact electronics attached. Using precision electronics, frequency modulation has been done and effect of sensing water vapor with its different isotope with different frequency modulation has been notified. A noticeable change in sensing due to different frequency modulation of LED current in quasi continuous mode has been discussed. Experiment has been done in different temperatures like -20^{0}C to +20^{0}C and interpreted its effect on water sensing. Noise has been suppressed by maximum level using filter circuit, synchronous cable between source and detector, lock in card. Although system has been calibrated with HITRAN database and tried to make error less as long as possible.





Reference:

1. The HITRAN database 2000 to 2008.
2. P.T.Mosely, J.O.W.Norris, D.E.Williams (Eds.), Technique and Mechanisms in Gas Sensing, Adam Hilger, Bristol, 1991, pp.134-259.
3. R.M.Biefeld, A.A.Allerman and S.R.Kurtz, recent advance in mid infrared emitters.Mat.Sci.Engg.B51, 1, (1998).

F10

Stand-Off detection of explosives using a combination of Pulsed Laser Fragmentation and MIR absorption spectroscopy

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In this contribution we want to introduce a combination of Pulsed Laser Fragmentation (PLF) and MIR absorption spectroscopy for the Stand-Off detection of nitro-based explosives. This method indirectly identifies nitro-based explosives via the detection of traces of NO and NO_2 which are generated by PLF in the UV and VIS spectral range. For the conventional direct detection of explosives a single laser source is usually required for each molecular species to be detected. In contrast, the indirect analysis is capable to detect various species of explosives using only two Quantum Cascade Lasers (QCL) at 1600 and 1900 cm^{-1}, which are related to absorption lines of NO_2 and NO respectively. The ratio between the concentrations of NO and NO_2 makes the distinction between energetic and non-energetic materials possible [1-3]. Furthermore, PLF enables to detect low vapor pressure explosives which only release very small amounts of their natural molecules under ambient air conditions.

In the current experiment the beams of a frequency doubled/tripled Nd:YAG Laser and two pulsed DFB-QCLs are aimed at an explosive sample. The Nd:YAG laser beam generates a plume of NO_x fragments next to the sample whereas the backscattered MIR radiation passes the plume and is attenuated due to the absorption of NO and NO_2. Finally, the backscattered MIR radiation is collected by a gold coated telescope and analyzed by a thermoelectrically cooled IR detector using Lock-In technique. The distance between the detector and the sample is currently restricted to 2m due to the dimensions of the optical table. For future field measurements distances of up to 20m are envisaged.

This work is part of a cooperative project with the name “OPTIX” which is funded by the Seventh Framework Programme of the European Union [4]. The objective of this project is the combination of Laser Induced Breakdown Spectroscopy, Raman Spectroscopy and MIR absorption spectroscopy for the reliable Stand-Off detection of explosives [5].

[1] C. Bauer, P. Geiser, J. Burgmeier, Appl. Phys. B 85, 251-256 (2006)
[2] C. Bauer, A.K. Sharma, U. Willer, Appl. Phys. B 92, 327-333 (2008)
[3] Jens-Uwe Guenther, Christian Bohling, Mario Mordmueller, Proc. SPIE 7838, 783807 (2010)
[4] http://www.fp7-optix.eu/
[5] Sara Wallin, Anna Pettersson, Henric Östmark, Anal Bioanal Chem 395, 259–274 (2009)

F11

Development of a TDLS-based Ambient Water Vapour Sensor for Aeroengine Intake Temperature Determination

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The development of a TDLS-based sensor for determining the temperature of ambient water vapour is described. For the purposes of ground testing, aeroengine intake temperature is typically measured using platinum resistance temperature detectors but under certain conditions these devices become unreliable and an alternative is needed. The sensor requirements are to measure gas temperature over the range of 0-40°C with an absorption path determined by the intake cross section, whilst recording continuously in a harsh environment. Wavelength modulation spectroscopy (WMS) with balanced detection is used to interrogate two water vapour absorption features near 1430nm. The lines can both be accessed by a single DFB laser current scan, yet have good spectral isolation and temperature sensitivity[1-3].

The use of autobalanced noise cancellers[4-6] for stand alone two-line ratio thermometry sensors is investigated. When used in conjunction with second harmonic detection in WMS, the detector bandwidth and dynamic range need to be optimised to ensure any temperature calibration is not susceptible to long-term drift and changing optical conditions. Initial calibration and testing is performed in an environmental chamber with temperature and humidity control.

References:
[1] J. Shao, L. Lathdavong, P. Kluczynski, S. Lundqvist, O. Axner, Applied Physics B, 97, 727-748 (2009)
[2] X. Zhou, X. Liu. J. B. Jeffries, R. K. Hanson, Measurement Science and Technology, 14, 1459-1468 (2003)
[3] J. T. C. Liu, G. B. Rieker, J. B. Jeffries, M. R. Gruber, C. D. Carter, T. Mathur, and R. K. Hanson, Applied Optics, 44(31), 6701-6711 (2005)
[4] K. L. Haller and P. C. D. Hobbs, Proceedings of SPIE, 1435, 298-309 (1991)
[5] X. Zhu and D. T. Cassidy, Applied Optics, 34(36), 8303-8308 (1995)
[6] P. C. D. Hobbs, Applied Optics, 36(4), 903-920 (1997)

F12

A PULSED QUANTUM CASCADE LASER BASED WAVELENGTH MODULATION SPECTROSCOPY FOR OPEN-PATH GAS SENSING

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Quantum cascade (QC) lasers have been extensively used in closed path configurations for gas sensing applications.[1-3] The biggest challenge in utilizing these lasers (either pulsed or cw) for open-path spectroscopy lies in obtaining a proper background subtraction to retrieve absorption information. Open path spectroscopy is important since it can provide integrated absorption measurements over long distance and consequently can be used for atmospheric monitoring of different molecules. Here, we report the results of wavelength modulation spectroscopy (WMS) with a pulsed QC laser which can open new avenues for sensitive open -path gas sensing. Pulsed WMS has many advantages over its continuous wave (cw) counterpart. The pulsed QC laser is much easier to fabricate than the cw QC laser. Pulsed QC lasers are typically used with 1-2% duty cycle so the power consumed is a small fraction of that in a cw device. Moreover, high frequency pulses of light with relatively higher intensity are much easier to detect than modulated cw light.[4] Additionally, this technique is independent of laser characteristics. The implementation of such new mid-infrared laser technologies into industrial trace gas analyzers holds great promise.

A pulsed QC laser operating at 957 cm^{-1} was used which provides an output power of ~5mW at 2% duty cycle. The laser is excited with short current pulses at a repetition rate of 500 kHz. First, the QCL was characterized and operating parameters were optimized for gas sensing applications. CO_2 or water vapour spectral lines were used for all these measurements. A linear sub-threshold current ramp at 20Hz was added to the excitation pulse train which resulted in a ~2.5 cm^{-1} frequency scan. We utilized demodulation approach to catch the envelop of the pulses and thus avoiding high speed electronics. We then combine the ramp with a sine modulation at 10kHz, and detect the second harmonic signal using a in-house designed and built phase locked loop (PLL) detection circuit.

[1] J. Faist and F. Capasso, "Quantum cascade laser," Science **264**, pp. 553-556, 1994.

[2] Y. A. Bakhirkin, A. A. Kosterev, R. F. Curl, M. G. Allen, and F. K. Tittel, "Off-axis integrated cavity output spectroscopy for nitric oxide detection in human breath using a quantum cascade laser," in *Frontiers in Optics*, OSA Technical Digest (CD) (Optical Society of America, 2003), paper MNN6.

[3] Y. A. Bakhirkin, A. A. Kosterev, C. Roller, R. F. Curl, and F. K. Tittel, "Mid-Infrared Quantum Cascade Laser Based Off-Axis Integrated Cavity Output Spectroscopy for Biogenic Nitric Oxide Detection," Appl. Opt. **43,** pp. 2257-2266, 2004.

[4] A. Lytkine et al, "Range-resolved gas concentration measurements using tunable semiconductor lasers." App. Phys. B **90**, 339-343, 2008.

Part 4 Authors index

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