ABSTRACTS OF PAPERS

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Tunable Diode Laser Spectroscopy

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- **Connecticut College, New London, Connecticut USA**
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- **ETH Zurich, Institute of Quantum Electronics, Zurich, Switzerland**

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TDLS 2013 Conference Schedule

	Monday June 17	Tuesday June 18	Wednesday June 19	Thursday June 20	Friday June 21
9:45-10:00	**Welcome Address**	**FREE DAY**			
10:00-11:00	**A. Mantz** Abstract L1		**C. Janssen** Abstract L5	**W. Chen** Abstract L9	**G. Grigoriev** Abstract L13
11:00-12:00	**Yu. Ponomarev** Abstract L2		**A. Rodin** Abstract L6	**M. Belovolov** Abstract L10	**M. Sigrist** Abstract L14
12:00-14:00	**LUNCH**				**CLOSING**
14:00-16:00	**Poster Session A**	**FREE DAY**	**Poster Session B**	**Poster Session C**	
16:00-17:00	**A. Vicet** Abstract L3		**Yu. Kuritsyn** Abstract L7	**V. Khattatov** Abstract L11	
17:00-18:00	**Ya. Ponurovskii** Abstract L4		**F. Tittel** Abstract L8	**A. Kotkov** Abstract L12	

Invited lectures

L1

High Resolution Molecular gas Phase Spectra at Temperatures Between 50 and 296 Kelvin

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Solar system outer planet atmospheres are colder than the earth's atmosphere, and accurate modeling of atmospheric conditions requires temperature dependent molecular absorption line parameters useful at temperatures between 296 K and 80 K, in the specific case of Titan, a moon of Saturn. The objective of this research is to provide suitable parameters for modeling some molecules in the Earth atmosphere as well as Titan where methane and other hydrocarbons are relatively abundant. In order to achieve uniform cell temperatures and cell temperature stability better than 0.01 Kelvin the cells were designed to use copper exclusively. Copper absorption cells with path lengths of 20 centimeters, or 12.45 meter and 21 meter path length Herriott designs with all copper construction, including gold coated mirrors, were cooled by closed cycle refrigerators to as low as 20 Kelvin. Cells with 12.5 meters or less absorption path utilize a CTi Model 22 Cryodyne refrigerator with 8 Watts cooling capacity at 77 Kelvin, but for the larger 21 meter cell, a CTi model 1050 Cryodyne refrigerator with 80 Watts cooling capacity at 77 Kelvin is incorporated into the design. We used lead salt Tunable diode lasers (TDL) controlled by a stepping Michelson Interferometer with a frequency stability of approximately 2 parts in 10^8 [1] a near infrared diode laser referenced to a frequency comb (FC) with a frequency stability of 1 part in 10^{13} [2], and a Bruker 125 HR Michelson interferometer (FTIR) covering the mid and near infrared spectral region with a frequency stability of 2 parts in 10^8 [3] to record the data reported here.

Line shapes, temperature dependences of pressure parameters, and line mixing will be reported. Also, spectral simplification resulting from low temperatures allows the recording and analysis of larger hydrocarbon molecules of interest to Astronomers. Significantly, the power law dependence for the pressure broadening parameter temperature dependence no longer applies when including spectra recorded over the temperature range 296 K to 80 K; in order to properly model the temperature dependence a quadratic term needs to be added to the normal power law relation. Observations regarding simplification of spectra will also be discussed.

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L2

TDLS of methane and its applications to study of methane emissions from natural structures to the atmosphere

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We present results of the development of photo-acoustic spectrometers (PAS) with tunable diode lasers.

A two channel PAS with a photo-acoustic detector in the form of a ring type (Helmholtz) resonator provides threshold sensitivity 2x 10 $^{-9}$ cm $^{-1}$ Hz $^{-1/2}$ W when the signal to noise ratio equals 1. A TEC-100 diode laser with an outer resonator generates a continuous single-frequency radiation within 6030 – 6300 cm $^{-1}$ spectral range. We demonstrate the applications of this PA TDLS to study of high-resolution absorption spectrum of CH_4 near 1,65 ($2\nu_3$ band) and study the broadening and shifting of the overlaping spectral lines induced by collisions with noble atoms and molecules with uncertainty less than 2 % for absorption cross sections, broadening and shift coefficients [1,2].

The TDLS with multipass optical cavity designed in DLS department of GPI RAS and modified by us we have applied efficiently to:

- detection of CH_4 emission by natural structures (coal, gas hydrates) to the atmosphere [3, 4];
- monitoring of methane emission by biological systems.

The results of corresponding laboratory and field measurements are demonstrated.

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L3

QUARTZ ENHANCED PHOTOACOUSIC SPECTROSCOPY WITH NEW ANTIMONIDE COMPOUNDS

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We present in this paper measurements made by quartz enhanced photoacoustic spectroscopy (QEPAS) with antimonide laser diodes emitting at 2.3 µm and 3.3 µm. Since its invention in 2002 [1], this technique has shown a large range of applications with compact and cheap setups, based on the use of a commercial quartz tuning fork (QTF) as an efficient acoustic transducer excited by a sound wave generated by molecular absorption.

These measurements are dedicated to environmental purposes, such as methane detection and ethylene control. Two demonstrators are presented: a laboratory bench (fig 1) and a compact setup (fig 3). The detection limits of the demonstrators were evaluated: for example, measurements of methane diluted in dry nitrogen led to a threshold detectivity of 100 ppbv at 3.38 µm [2] (fig 2). Some key points of the QEPAS setup will be evaluated and discussed.

Some new laser structures were developed for reaching long wavelengths, dedicated to those spectroscopic applications. They were grown by molecular beam epitaxy on GaSb substrates. We will present a new generation of photonic crystal based lasers inspired by the concept of coupled cavities [3], photonic crystal based DFB lasers and new DFB lasers, based on the Ga(In)AlAsSb/InGaAsSb material system.

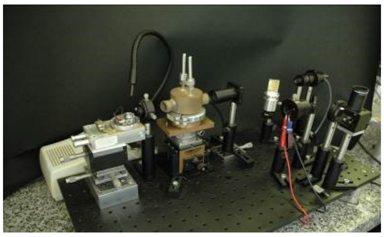

Fig 3. QEPAS setup, laboratory version.

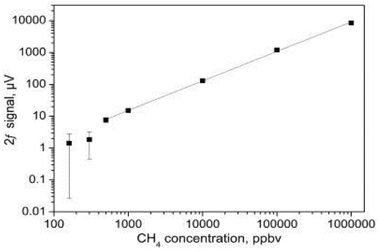

Fig 3. 2f QEPAS signal, CH_4-N_2, l = 3,38 µm.

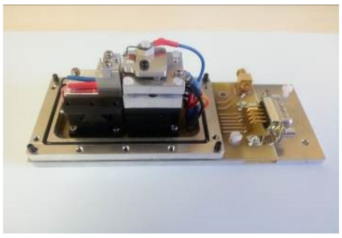

Fig 3. Compact QEPAS setup.

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L4

DEVELOPMENT OF NEW METHODS OF THE DIODE LASER SPECTROSCOPY AND THEIR APPLICATIONS FOR DETECTION MOLECULE IN GAS MIXTURES AND MEASUREMENTS OF THE ISOTOPIC COMPOSITION

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The department of diode laser spectroscopy (A.M.Prokhorov General Physics Institute of RAS) deals with diode laser (DL) spectroscopy and trace molecules detection over 30 years. Dozens of unique DL gas analyzers and spectrometers have been created this period. They have been made on the basis of DL in the near and mid IR ranges for different applications. Instruments developed demonstrated very reliable operation both for Lab and field environment. The instruments parameters achieved are comparable or better than best results obtained at the moment. Recent technology achievements of manufacturing near IR diode lasers with fiber output makes it possible to create compact, mobile DL gas analyzers with high sensitivity and speed performance.

Present paper describes the set of DL instruments developed. It also considers new techniques to measure molecules concentration in different buffer gases. Isotopic composition measurement for various molecules both in near and mid IR range will be also considered.

Following TDLS instruments will be described in details:

1. A set of the TDLS instruments (more than 12) to measure impurities H_2O, (NH_3, C_2H_4, CH_4, CO_2, H_2S) concentration during the rectification process of high-purity hydrides (GeH_4, SiH_4, PH_3, AsH_3, NH_3) [1-3]. The TDLS instruments set was installed in Scientific industrial enterprise “Salut” (Nizhny Novgorod). It is using for continuous long-term monitoring of hydrides’ purification processes.
2. The aircraft based TDLS complex to measure concentrations of greenhouse gases: CO_2, CH_4 as well as humidity and its isotopic content ($H_2{}^{16}O$, $H_2{}^{18}O$, HDO, $H_2{}^{17}O$) [4].
3. The multi-component DL gas analyzer for medical screening diagnostics

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L5

HIGH-RESOLUTION IR LASER SPECTROSCOPY OF OZONE ISOTOPOMERS USING A DIODE LASER STABILISED BY A NEW INTERFEROMETRIC PHASE FREQUENCY EMISSION CONTROL

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Accurate high-resolution spectroscopic data are of an ever-increasing importance for atmospheric and climate observation and research. Existing molecular spectroscopic data often lack the required accuracy for future observational missions [1]. The LPMAA has developed a high resolution laser spectrometer for direct molecular absorption spectroscopy [2–4], which can fulfill the high requirements on spectroscopic data (position, intensity, shift, ….) for future satellite missions [1]. Here we describe a recent upgrade of the interferometer, which improves on the resolution of the wavelength stepping mechanism.

Interferometer control is maintained by means of a frequency stabilized HeNe laser ($u_r = 2\times10^{-9}$ over 1 h). The operation principle is based on the interferometer condition

$$D = k_d l_d = k_{\mathrm{HeNe}} l_{\mathrm{HeNe}} , \qquad (1)$$

where D is the mean optical path difference, k_d and k_{HeNe} are interference orders of the laser diode and the HeNe laser, respectively, and where λ_d and λ_{HeNe} are corresponding wavelengths. IR tuning is achieved by incrementing or decrementing the path difference by small amounts DD through changing k_{HeNe} of the control laser, keeping the interferometer order of the diode laser constant, which requires adjustment of the emission wavelength l_d:

$$DD/D = Dl_d/l_d = Dk_{\mathrm{HeNe}}/k_{\mathrm{HeNe}} . \qquad (2)$$

Using typical numbers (l_d = 10 µm), k_d and k_{HeNe} are on the order of 1 and 13×10^5, respectively. The HeNe interference order can be changed and controlled in integer fractions of 64 ($\Delta k_{\mathrm{HeNe}}/k_{\mathrm{HeNe}} = 1/64/(1.3 \times 10^6)$), allowing a spectral resolution of $\Delta\nu_d/\nu_d = \Delta\lambda_d/\lambda_d = 1.2 \times 10^{-8}$. At 1000 cm^{-1} (or 10 µm), which corresponds to tuning steps of 1.2×10^{-5} cm^{-1}. This number should be compared to typical Doppler (FWHM) line-widths of about 2×10^{-3} cm^{-1}.

We demonstrate operation and control of the Michelson interferometer using newly developed control electronics based on a FPGA board (LABVIEW, QuasarConcepts, France). The tuning characteristics and the frequency stability of a lead salt laser diode at 10 µm, is investigated. As an application, we have recorded the direct absorption spectrum of several lines of the ozone isotopologue $^{16}O^{16}O^{18}O$ in the ν_1-ν_3 spectral region.

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L6

HIGH RESOLUTION INFRARED HETERODYNE SPECTROSCOPY FOR SPACE RESEARCH AND PLANETARY ASTRONOMY

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High resolution spectroscopic observations in the infrared spectral range provide very powerful tool for studies of the atmospheres of the Earth and other planets, including their chemical and isotopic composition, structure, thermal regime and dynamics. Since pioneering studies lead by T.Kostiuk [1], ultra-high resolution infrared heterodyne spectroscopy remains the only method allowing for direct measurements of wind field in planetary atmospheres by remote sensing. However, due to numerous implementation problems, first of all, high requirements to optics alignment and local oscillator stability, this method is only represented by few instruments to date [2]. Major step in the infrared heterodyne spectroscopy was an implementation of quantum-cascade lasers (QCL) in THIS instrument [3] with continuous wavelength coverage from 8 to 12 μm. Mid- and shortwave infrared ranges, however, remain unavailable for the existing heterodyne instruments. This range is particularly attractive for several reasons, including negligible thermal emissivity of the instrument entrance optics, availability of efficient transparency windows and weak ro-vibrational overtone lines, unsaturated along observation paths in the dense atmospheres, potential capability to reach higher spectral resolution up to $\lambda/\delta\lambda\sim10^8$.

We present the current status of IVOLGA project, implying the development of a series of near- and mid-infrared heterodyne spectrometers based on waveguide optics and tunable lasers. The first and simplest solution has been implemented in the near-infrared spectral range used for optical communications, based on commercial components [3]. The use of tunable diode laser with dynamical frequency stabilization as local oscillator, and single mode optical fiber coupler for wave front combining has allowed us to build a compact, lightweight instrument for field and spacecraft applications, including wind measurements and monitoring of greenhouse gases. Sensitivity of the instrument is limited by shot noise and geometric aperture of heterodyne receiver $\Omega S \sim \lambda^2$. These theoretical limitations constrain implications of the near-infrared heterodyne spectroscopic measurements to solar occultations.

In the thermal infrared, heterodyne spectro-radiometry provides capability to observe extended sources by both spacecraft instruments and ground-based telescopes. Further development of our conception implies the use of integrated optical chips with embedded single mode waveguides and couplers. In order to overcome geometric limit of the radiometric efficiency, we develop entrance optics based on deformed wispering-gallery microresonators coupled with waveguides. A combination of classical heterodyne technique with the latest achievements of photonics give rise to a new generation of spacecraft and telescopic instruments for high resolution infrared spectroscopic observations.

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L7

MEASUREMENTS OF GAS FLOW PARAMETERS BY ABSORPTION SPECTROMETRY WITH DIODE LASERS

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Tunable Diode Laser Absorption Spectrometry (TDLAS) is a powerful tool for contactless measurements of gas concentration and temperature in hot zones. The technique we used is based on the registration of the experimental transient absorption spectra of water molecules and fitting of the experimental spectra by the simulated ones constructed using the spectroscopic databases [1]. Wavelength scale, frequency, temperature, pressure, baseline and the concentration of water molecules were the parameters of the fitting. The advantages and limitations of the developed technique will be discussed in the talk with the emphasis on the problems of the experimental spectra fitting and different fitting algorithms.

The efficiency of the developed technique was exemplified by the measurement of the temperature and water vapor concentration in the hot zone of plasma-assisted combustion in air-fuel supersonic flow. The combustion is ignited and sustained by the pulsed electric discharge in experimental aerodynamic tube, characterized by rather strong fluctuations, vibrations and different optical and electrical noises. The flow parameters were: Mach number = 2, total pressure 150-300 Torr. Air was used as the oxidant, hydrogen or ethylene were used as the fuel.

The mean temperature of the hot tail of the combustion zone varied within 800-1200 K for hydrogen and 700-1000 K for ethylene, the water concentration varied within 10-20 Torr. The high signal-to-noise ratio enabled to obtain the temporal profile of both parameters with the resolution of ~ 1 ms.

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L8

Mid-Infrared semiconductor laser based trace gas sensor technologies: recent advances and applications

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Abstract: Recent advances in the development of ultra-sensitive sensor technology based on mid–infrared semiconductor lasers for the detection of trace gas species and their application in industrial process control and environmental monitoring will be reported.

1. Introduction

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

2. Laser absorption spectroscopic techniques

The architecture and performance of four sensitive, selective and real-time gas sensor systems based on mid-infrared semiconductor lasers will be described [1]. High detection sensitivity at ppbv and sub-ppbv concentration levels requires sensitivity enhancement schemes such as tunable laser diode absorption spectroscopy (TDLAS) [2, 3] and wavelength modulation spectroscopy (WMS), photo-acoustic absorption spectroscopy (PAS) or quartz-enhanced-PAS (QEPAS) [2-4]. These spectroscopic methods can achieve minimum detectable absorption losses in the range from 10-8 to 10-11 cm-1/√Hz.

3. Specific examples of TDLAS and QCL based sensor systems

TDLAS was performed using an ultra-compact, innovative multi-pass gas cell with an effective optical path length of 57.6 m capable of 459 passes between two spherical mirrors separated by 12.5 cm. A 3.36 µm CW TEC DFB GaSb based laser diode operating at 9.5 ˚C was used as the excitation source [5-7]. For an interference free C2H6 absorption line located at

2976.8 cm-1 a minimum detection limit of 130 pptv with a 1 s. acquisition time was achieved. A new state-of-the-art integrated electronic control and data acquisition module was implemented that allowed further significant size reduction without loss of sensor performance.

A QEPAS based sensor capable of ppbv level detection of CO, a major air pollutant, was developed. We used a 4.61 μm high power CW DFB QCL that emits a maximum optical power of more than 1W in a continuous-wave (CW) operating mode [5, 6]. For the R6 CO line, located at 2169.2 cm-1, a noise-equivalent sensitivity (NES, 1σ) of 2 ppbv was achieved at atmospheric pressure with a 1 s. acquisition time. Furthermore, high performance (> 100 mW) 5.26 µm and 7.24 µm CW TEC DFB-QCL (mounted in a high heat load (HHL) package) based QEPAS sensors for atmospheric NO and SO2 detection will be reported [8, 9]. A 1σ minimum detection limit of 3 ppb and 100 ppb was achieved for a sampling time of 1 s. using interference free NO and SO2 absorption lines located at 1900.08 cm-1 [10,11] and 1380.94 cm-1 respectively [12]. Specific examples include C_2H_6, NH_3, NO, CO, SO_2, CH_4, and N_2O.

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L9

Challenges and opportunities for photonic sensing of key atmospheric short-lived species

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Chemically reactive atmospheric species play a crucial role in tropospheric processes that dominate regional air quality and global climate change. Contrary to long-lived species (such as greenhouse gases), real time *in situ* sensing of such short-lived atmospheric molecules represents a real challenge due to their very high reactivity resulting in short lifetimes (of around 1-100 seconds) and ultra-low concentrations that measure in parts per billion by volume (ppbv) to parts per quadrillion by volume (ppqv).

In this talk, we will overview our recent progress in the instrumental developments for *in situ* trace gas monitoring of nitrous acid (HONO), nitrate radical (NO_3) and nitrogen dioxide (NO_2) with the help of advanced photonic technologies (such as quantum cascade laser, difference-frequency generation parametric source, light emitting diode in conjunction with long optical path length enhanced absorption spectroscopy). The experimental arrangements, their applications to field observation and smog chamber study will be presented.

Acknowledgments. This work is mainly supported by the IRENI program of the Région Nord-Pas de Calais. The financial supports from the French national research agency (ANR) under the NexCILAS (ANR-11-NS09-0002) and the CaPPA (ANR-10-LABX-005) contracts are acknowledged.

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L10

NOVEL OPTICAL FIBERS AND SENSORS FOR DIODE LASER SPECTROSCOPY IN NEAR- AND MID-INFRARED REGIONS

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Optical fibers give an additional advantages for remote sensing as flexible transmission and sensing media. We present recent achievements in fiber optics and fiber based lasers, which can improve the powerful efficiency of the diode laser spectroscopy devices in near- and mid-infrared regions. The most significant achievements are as follows.

1. New fibers for gas sensor applications:

- Novel single-mode photonic crystal optical fibers on the base of SiO_2 can have a very large mode field area of ~ 8600 μm^2 corresponding to a core mode field diameter of 105 μm, which increase the coupling efficiency with the outer receiving optics in the devices for remote sensing of optical fields and spectra [1].
- Hollow-core photonic crystal fibers (PCF) with large mode field effective area are suitable for in-line gas sensor monitoring and detection due to more effective interaction between light and gas in the holes (like in cell) which can be as high as 95 % [2,3].
- The light transmission through a new silica negative curvature hollow core fiber (NCHCF) in a spectral range from 2,5 to 7,9 μm was demonstrated [4].

2. New fiber lasers:

- Bismuth-doped glasses and optical fibers are new active optical materials for the optical amplification and lasers operating in the spectral range 1000 – 1700 nm [5].
- Tunable single-frequency diode lasers with a fiber Bragg-grating external cavity have been proposed for spectroscopy and gas analysis for selected absorption lines. This approach has been applied to detection of R7 line of the methane at $\lambda = 1{,}645\ \mu m$ [6] and ammonia at $\lambda = 1{,}52\ \mu m$ [7].
- All-fiber DFB lasers based on doped fibers demonstrate single-frequency wide tunability in the range of up to 40 nm [8]. These fiber lasers can be advantageous for TDLS than DFB laser diodes.

The advantages and disadvantages of the above fiber optic techniques for the high resolution spectroscopy studies will be discussed.

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L11

AIRCRAFT-LABORATORY FOR MONITORING OF TRACE GASES IN THE ATMOSPHERE

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The aircraft-laboratory Yak-42D "Atmosphere" created in Federal State Budgetary Institution Central Aerological Observatory of Russian Federal Service for Hydrometeorology and Environmental Monitoring is intended for measuring the following parameters of atmosphere and underlying surface:

•Thermodynamic parameters of atmosphere (air temperature, pressure, density and humidity, wind speed, turbulence and turbulent fluxes);
•Gas and aerosol structure of atmosphere;
•Radiation in atmosphere and from surface, radiation balance in atmosphere;
•Radioactive pollution of atmosphere and underlying surface;
•Microstructure of atmospheric clouds and participation;
•Atmospheric electricity.

This complex allows monitoring of changes in chemical composition, including the monitoring of pollutants and greenhouse gases in the atmosphere control of the stratospheric aerosol layer and the ozone layer of the atmosphere. To solve these problems requires systematic airborne measurements of spatial and temporal distributions of gases and aerosols on various scales, and altitudes in the free atmosphere. Airborne sensing of gaseous and aerosol composition of the atmosphere will identify as early as possible climate factors that may lead to changes in regional and global scales, and are associated either with the natural fluctuations in climate-parameter, or by anthropogenic influences.

On board of the aircraft-laboratory, among other instruments for monitoring of greenhouse gases, established tunable diode laser spectrometer on the basis of diode lasers of a near-IR range for measurement of the altitude profiles of CO2, CH4, H2O and its isotopes [1].

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L12

Results on application of VIH method in technology of production of high-purity volatile inorganic hydrides

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Volatile inorganic hydrides (VIH), i.e., arsine, phosphine, ammonia, silane, germane, are used for production of epitaxial layers and heterostructures on the basis of silicon, germanium and semiconductor compounds A3B5 by the method of chemical deposition from the gas phase. For production of epitaxial layers (EL) the high-purity VIH are required with the grade of 6N-7N since the impurities substantially degrade the target properties of EL.

For ultra purification of VIH, mainly, the method of low-temperature rectification is used. In the process of purification the "light" fractions (LF) and the "heavy" fractions (HF) are separated from the main substance which contains more and less volatile impurities, respectively, as compared with the purified substance. The conducted investigations indicated that actually there are the most hard to remove impurities in each hydride which are limiting the process of purification. These are carbon dioxide (CO2), ammonia (NH3) and water (HO2) in arsine, acetylene (C2H2) in phosphine, methane (CH4) and HO2 in ammonia, ethylene (C2H4) and carbon dioxide (CO2) in monosilane.

A series of gas analyzers for measurement of concentration of impurities in the process of production of high-purity hydrides has been developed at the GPI RAS on the basis of diode lasers (DL) with output of radiation via optical fibers generating in the near IR-range.

The behavior of the limiting impurities during purification of VIH by rectification was studied at the "NPP "Salyut" with the use of DL-gas analyzers. It made it possible to optimize the conditions for purification and to reduce the expenses on production of high-purity volatile inorganic hydrides.

At the present time the developed equipment and techniques of analysis are being used while fabricating commercial set-ups for purification.

L13

POSSIBILITIES AND PERSPECTIVES OF TDLS APPLICATION IN NUCLEAR INDUSTRY

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Nuclear industry enterprises pay great attention to the problems of industrial safety and environmental protection. Undoubtedly, the safety aspect concerns first and foremost the non-dissipation of nuclear pollution in any form. Use is made of various filters for aerosol entrapment, systems and methods of liquid radioactive waste handling, systems for exhaust gas capture. But along with radioactive material hazards, nuclear technologies pose a threat of chemical pollution of working areas and surrounding environment. In addition to personnel protection and ecological challenges, there are also problems of non-prolifiration assurance and safegurd control. Diode laser spectroscopy methods can be useful for the solution of all the said problems. The report discusses first of all problems of uranium hexafluoride sublimation production which envisages a sequence of processes with a potential risk of gaseous emissions, and problems of reprocessing of waste uranium hexafluoride and spent nuclear fuel. Gaseous emissions may contain UF_6, hydrogen fluoride HF, nitrogen oxides NOx, $^{14}CO_2$ and a number of other gases detectable with TDLS methods. Several examples of such kind of investigations will be given.

L14

Quantum cascade laser spectroscopy in biomedical and forensic science

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1. Introduction

The sensing of trace species by lasers is attractive as laser-based sensing combines several key features of interest, notably high sensitivity and selectivity of detection, multi-component capability, quantitative data, compact size, often no need for sample preparation or pretreatment, and on-line capability. Hitherto, many impressive results, both in gas and liquid phase, have been reported (see e.g. [1]) employing different kinds of sources such as quantum cascade lasers (QCLs), optical parametric oscillators (OPOs), difference frequency generation (DFG), and lead salt diode lasers, and various kinds of detection schemes including multipass transmission, photoacoustic and cavity ring-down techniques. Here we report on two recent examples in the field of glucose sensing and drug detection using QCLs.

2. Glucose sensing in human tissue

Hitherto, diabetic patients need to prick their finger several times every day to control their blood glucose level because no reliable non-invasive glucose sensing devices are currently available. Today, there is a great need for such a glucose monitor. It would not only easy the life of some 366 millions of diabetes patients worldwide but also enable to control the glucose concentration continuously.

Unlike in the near-IR where glucose only exhibits weak absorption but suffers from various spectral interferences with other constituents in blood and tissue, the glucose absorption around 10 µm is strong but water interference and the related short light penetration depth into human skin are the major challenges. We implemented a mid-infrared photoacoustic system to track glucose in the interstitial fluid in human skin. The setup has been recently described in detail [2,3]. Briefly, it consists of an external cavity QCL tunable between 1010 and 1095 cm $^{-1}$ which is coupled (with or without infrared fiber) into a specially designed photoacoustic (PA) cell of only 78 mm ^{3} volume. The cell is pictured in Fig. 1. It is equipped with a microphone to pick up the PA signal as well as with a sensor for relative humidity (RH) and temperature T. To avoid too high humidity (as is often encountered in in vivo measurements, a constant flow of N_2 is applied. The cell can be used both for measurements on aqueous glucose solutions (in that case in combination with a thin diamond window as interface between air volume and sample) or directly in contact with skin (as shown in Fig. 2).

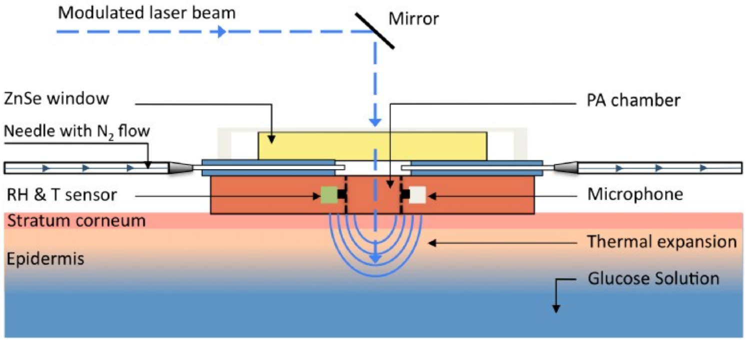

Fig. 1: Photoacoustic cell for glucose measurements. The arrangement depicted here is employed for measurements on human skin samples (Stratum corneum) in contact with an aqueous glucose solution. The diffusion of glucose into the skin sample from the bottom as well as the thermal expansion of the heated volume due to laser absorption are indicated.

In the latter case, epidermal skin samples were brought into contact with aqueous glucose solutions with concentrations between 0.1 and 10 g/dl resulting in a variation of the glucose concentration in the skin samples via passive diffusion. We achieved a detection limit for glucose in skin of 100 mg/dl (SNR=1). Although this limit is still high, it nevertheless lies within the physiological range of 30-500 mg/dl of glucose concentrations in blood. An important result is the direct time-resolved observation of glucose diffusion into skin. First promising PA studies on the skin of healthy volunteers after a so-called oral glucose tolerance test and simultaneous blood glucose measurement with a conventional device will be reported.

3. Drug sensing in human saliva

We explore the potential of laser-based spectroscopic sensing for doping agents and drugs in body fluids. An earlier example concerned ephedrine, a doping substance used by athletes in sports. With a pulsed DFG system in the 3.4 μm range and a home-built multipass cell to vaporize urine samples spiked with ephedrine, we managed for the first time to differentiate between ephedrine and the isomer pseudoephedrine even at concentrations of 25 μg/ml close to the allowed concentration in sports [4].

In a current project named IrSens we are developing a platform for the detection of drugs like cocaine in human saliva together with other groups in Switzerland. There is a great need for alternative sensors as most of today's roadside tests of drivers under the influence of drugs like cocaine are only qualitative and quantitative blood tests are still necessary for the confirmation of positive results.

In a first step we investigated the numerous possible spctral interferences with other compounds often present in saliva of drug users such as potential diluents, soft drinks, alcohol, caffeine, pain killers, masking substances like mouthwash, etc. and saliva consituents. We used an FTIR spectrometer to cover a broad spectral range and attenuated total reflection (ATR) as detection scheme. As most appropriate wavelength with strong cocaine absorption but minimum interference we identified the range around 1750 cm^{-1} [5]. In order to reduce the strong water background absorption we use either a drying technique or a simple one-step method to extract cocaine from saliva into a weakly absorbing diluent. We also developed a special cell for transmission measurements with a pathlength of 5 mm and a volume of only 1.5 ml. As source we now use a QCL at the selected wavelength of 1750 cm^{-1}. With both the ATR and the transmission method we achieve a detection limit of < 1 μg/ml. This is still considerably above the required limit of ~ 20ng/ml, but in a range encountered in saliva of drug users where peak cocaine concentrations of up to 500 μg/ml have been observed after smoking cocaine [6]. Since our extraction method is also feasible with microfluidics and waveguides, current studies are aimed at further lowering the detection limit by using microfluidics and waveguides as a first step towards a lab-on-a-chip device.

4. Acknowledgements

We thank J. Luginbühl and E. Reichmann from the University Children's Hospital Zurich for the supply of skin samples, J. Faist and Y. Bonetti of ETH Zurich for a specially developed QCL and P. Wägli from EPF Lausanne for his help with microfluidics. The financial support from GlucoMetrix NIB & Non Invasive Diagnostics GmbH, the Swiss NanoTera Initiative and ETH Zurich is gratefully acknowledged.

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Poster session A

A1

DL frequency quantum noise

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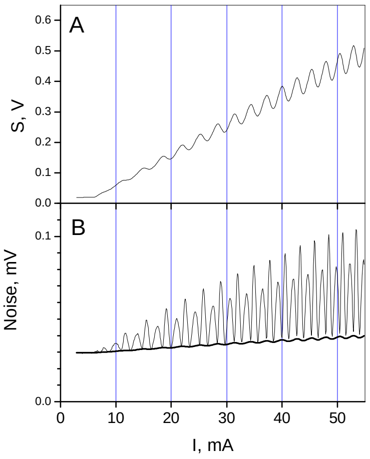
Some time ago DL intensity quantum noise was investigated [Abstracts of 8th International Conference on Tunable Diode Laser Spectroscopy TDLS 2011, p.38, 49, 61 see also these posters: http://www.dls.gpi.ru/rus/conf/TDLS2011/Posters/PostersDLS11.html B1, C1, D1]. DL noise was measured as function of excitation current value. Four quantum noise mechanisms dominating at different excitation currents were identified: excitation current shot noise, Poison noises of electrons and photons, electromagnetic field quantum noise. Data obtained were analyzed using corrected rate equations of DL operation. There are 4 parameters: threshold current, photons number at the threshold, life times of electrons and photons. This approach was tested on several DLs: near, mid IR, and QCL. The parameters either are determined directly (first two) or are in agreement with estimations.

Subject of present paper is to do similar investigation for DL frequency noise.



DL frequency noise can be measured by several techniques.

Fig.1 Recorded signal (A) and its noise (B) when FP etalon was installed in laser beam

DL frequency noise will produce intensity noise on fringes slopes. If both signal and noise dependences are known DL frequency noise can be determined.

DL frequency noise can be measured using high Q interferometer. It can be also measured using fitting of narrow molecular line.

All three techniques mentioned above were used to determine DL frequency noise spectral density. Comparison of results obtained will be presented.

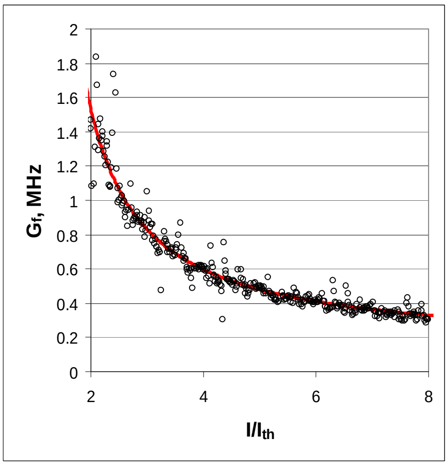


Fig.2 DL frequency noise spectral density as function of excitation current

DL frequency noise spectral density determines width of DL spectrum. In present case it is between 0.2 – 2 MHz.

When DL intensity noise parameters were determined (see above) and DL frequency tuning by current was measured, there are no free parameters to calculate DL frequency quantum noise (solid curve). It is determined by photons and electrons Poison noise.

A2

TDLS accuracy analysis

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Accuracy is one of recent challenges for Tunable Diode Laser Spectroscopy (TDLS). Several TDLS applications require measurement accuracy at level of 0.1 % or even better. At this accuracy level several fundamental physical laws as well as error mechanisms have to be considered – subject of the present paper.

Correct absorption law obtained from Maxwell equations has to be used.

$$W_L(n) = W_0(n)\exp\left[-\frac{s(n)NL}{\sqrt{1+4pcN}}\right]$$

Absorbance is determined by molecules number density - N. Denominator describes influence of rest gas polarization on DL radiation absorption by particular molecule (χ is molecular polarizability). The dependence is not linear. For methane correction is 0.05 % for 1 Bar. Gas under investigation is not ideal (pressure is not proportional to N, second virial coefficient). For CO_2 correction is 0.56 % for 1 Bar.

DL radiation has coherent component with some width and broad spontaneous emission. Recorded transmission is convolution of real gas transmission with DL spectrum. Both effects lead to optical zero problems. Recorded transmission is result of dividing some signal by reference one – baseline problem. If high accurate measurements are under consideration DL frequency tuning has to be calibrated with high accuracy. Next problem is photo detector linearity.

All experimental parameters (optical length – L, pressure – P, temperature – T, sample purity) have to be determined with required accuracy. Everything mentioned above was analyzed, calibrated, and measured.

	Value	Error	Error %
L, cm	99.95	0.05	0.05
T, ^oC	20 - 25	0.1	0.03
P, mBar	0 - 100	0.07	0.07
CO_2 sample purity, %	99.98	0.02	0.02
PD non-linearity			0.02
v, 10^{-3} cm^{-1}		0.03	0.04
Optical zero			0.04
Baseline			0.01
DL Spectrum, MHz	2.5		0.07
Total			**0.13**

Final accuracy estimate is 0.13 %. It is in agreement with experimental results obtained (see separate presentations).

A3

HETERODYNING OF A BROADBAND RADIATION IN A NEAR INFRARED REGION USING DIODE LASER

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The heterodyne is widely used technique for astronomical observations and atmospheric monitoring. Traditionally mid and far infrared spectral regions were used for these applications. Development of a near infrared heterodyne receiver is a subject of this paper. The main problem of heterodyning in the near infrared range is the stringent requirements for alignment of the incident radiations fronts.

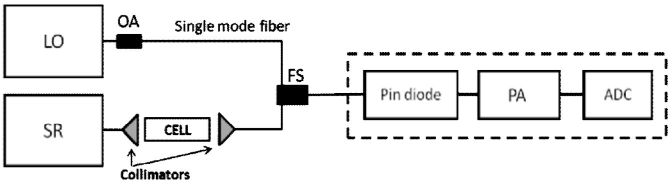

Figure 1.Schematic of setup. LO - local oscillator. SR - source of radiation, OA - optical attenuator, FS - fiber beam splitter, PA – preamplifier, ADC - Analog-to-digital converter.

The DFB-laser was used as a local oscillator (LO), λ=1.357 μ. The optical attenuator (OA) was used to control the incident to the photodiode power of LO. The other DFB laser excited by current below threshold was used as a source of radiation (SR). The fiber optic beam splitter (FS) based on single-mode silica fiber was used to align fronts of both LO and SR radiations. Both signals were detected by photo-detector (pin-diode). A Cell with H_2O could be placed between the source of radiation and the fiber splitter. The fiber collimators were used to adjust the radiation. The signal of photo detector was amplified by preamplifier (PA) with a feedback factor R=240 kOhm and a bandwidth 1MHz.

During experiment LO frequency radiation was changed by changing diode laser excitation current. The heterodyne signal gives an additional contribution to noise dispersion.

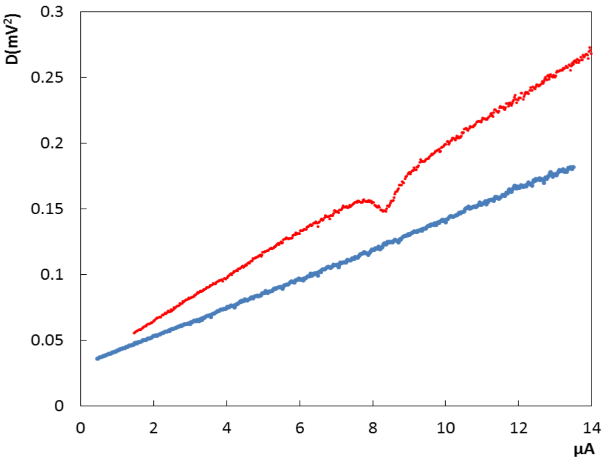

Figure 2. Depends of noise dispersion from a photocurrent in a case of shutting off SR (blue points) and in case of shutting on SR (red points).

Noise dispersion value was averaged for 10 seconds to obtain present S/N ratio.

First only LO radiation reached the photo detector (blue points in figure 2). It is due to photocurrent shot noise. Then SR was switched on. Additional noise can be observed (red points in figure 2). Minimum detectable heterodyne signal achieved was 1.4% of the shot noise. The water absorption line recorded by heterodyne in the near infrared can be easily observed.

A4

$^{238}UF_6$ AND $^{235}UF_6$ SPECTRA AND ENRICHMENT MEASUREMENT IN MID IR SPECTRAL RANGE

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Possibility to measure UF_6 enrichment using TDLS technique was considered in [1]. In this paper spectra of UF_6 sample with natural isotopes abundance were recorded. Specially developed QCL to measure UF_6 enrichment was investigated in [2]. Investigation of $^{238}UF_6$ and $^{235}UF_6$ cross sections using TDLS is subject of present paper.

Spectra of UF_6 v_1+v_3 band Q branch were recorded in mid IR for samples having enrichment 0.7 % (N - natural abundance) and 90 % (E - enriched) and several pressures (left graph in Fig.1).

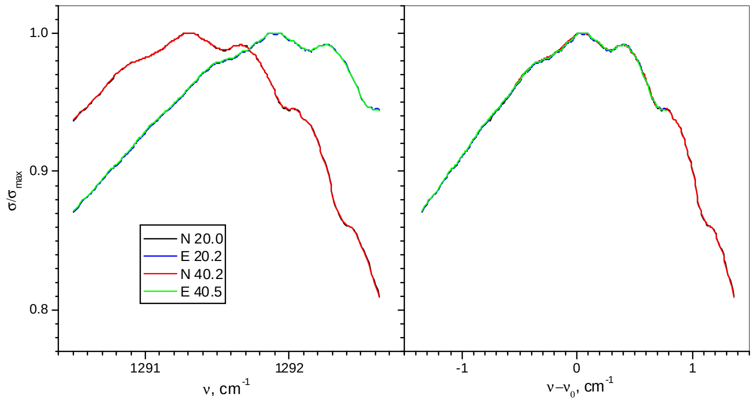

Fig.1 Normalized cross sections of samples under consideration.

Cross section shape is determined by UF_6 molecule vibration and rotation. Involving of U atom in vibration motion results in isotope shift (left graph) – 0.59(1) cm^{-1}. After taking into account this shift, spectra of both samples coincided totally (std = 0.027 %). Remained fine structure is determined by rotation of UF_6 molecule. This fine structure is the same for both isotopes because U atom is located in center of spherical top molecule and doesn’t participate in UF_6 molecule rotation.

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A5

WATER VAPOR CONTENT CONTROL DURING AMMONIA PURIFICATION

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TDLS based instrument was developed to control trace humidity during low temperature rectification process of ammonia. DL with fiber output (pig-tail) and emission wavelength 1.39 μm was used. The device contained one reference and three analytical channels. Analytical channels measured humidity in upper, lower and middle part of low-temperature rectification column. The analytic channels included cells with different optical lengths from 0.7 to 15 m [1].

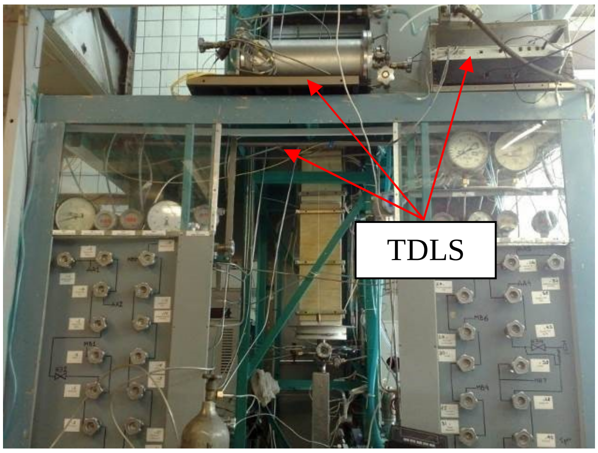

Fig.1 View of ammonia rectification column and TDLS instrument to control humidity

To achieve reliable humidity measurements, long term training (up to several hours) with pure ammonia of the inlet tubes and optical cells is necessary.

The TDLS instrument developed was calibrated. It was tested for long term measurements of trace humidity during ammonia low temperature rectification.

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A6

TDLS STUDY OF THE FIRST OVERTONE LINE OF HF BROADENED BY Ar, Kr, Xe AND N_2

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One of the promising approaches to detection of HF traces formed on interaction between UF_6 and atmospheric water vapors [1] in atmosphere is the TDLS method featuring high sensitivity (≤ppb) and prompt real-time data acquisition which is of primary importance from the viewpoint of atmospheric monitoring in the vicinity of nuclear fuel cycle (NFC) facilities [2]. The detected symptoms of the HF concentration increase in atmosphere may be useful for IAEA inspectors’ practical work for detection of latent operations on uranium enrichment facilities or those using other undeclared nuclear technologies [3]. Meanwhile, there are a number of problems to be solved on tackling the tasks of HF detection with TDLS methods. The precise detection of HF concentrations demands the exact data not only on the position of the HF analytical line center but also on its contour profile under the experimental conditions. However, the width, shift and shape of the line profile are known with much less accuracy. This inaccuracy may introduce an essential systematic error into HF concentration measurements in real atmosphere [4].

This paper discusses the results of a study of HF overtone line contours broadened by different gases (Ar, Kr, Xe, F_2, N_2) over the pressure range of 5-95 kPa. Use was made of a TDLS system similar to the one described in [4] which incorporated a diode laser with distributed feedback and a fiber radiation outlet, oscillating in the vicinity of wavelengths $\lambda=1.283\ \mu m$ (line 2-0 R0 of HF), and “Hamamatsu” InGaAs photodiodes.

Determined are collision broadening coefficients, Dicke narrowing and the analyzed HF line shift with the use of Voigt, Rautian and Galatry profiles. Broadening coefficients derived with the use of the Voigt profile are shown to be more than by 10% smaller than those obtained with the Rautian and Galatry profiles.

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[2] Sh.Sh. Nabiev, A.I. Nadezhdinskii, et all, Atomic Energy, 105, 280-289 (2008).
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[4] Sh.Sh. Nabiev, S.V. Ivanov, Ya.Ya. Ponurovskii, Atmospheric and Oceanic Optics, 24, 864-871 (2011)

A7

THE 9 MICROMETER QUANTUM CASCADE LASER TUNABLE BY QUANTIZING MAGNETIC FIELD

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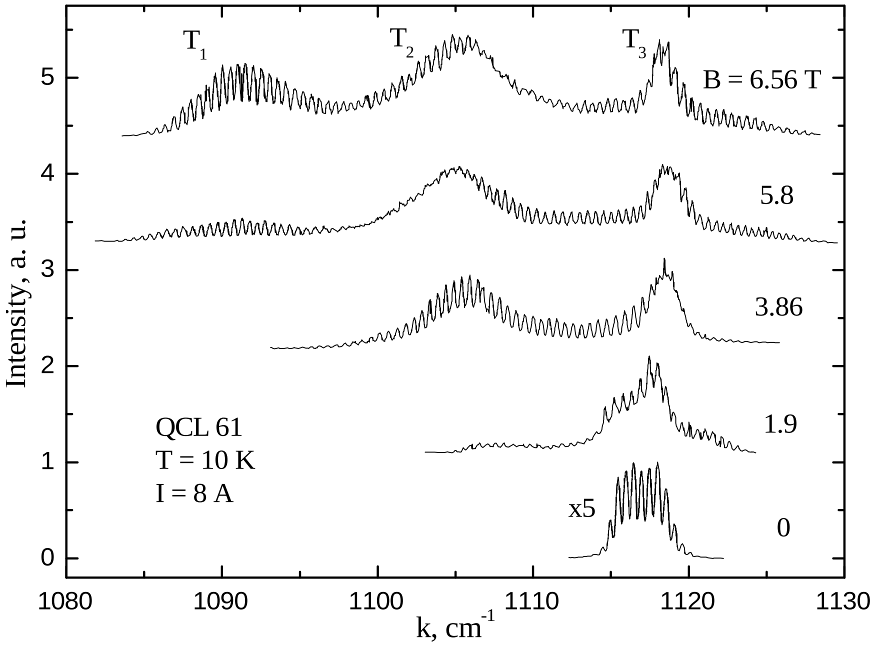
The influence of moderate quantizing magnetic field on the GaInAs/AlInAs quantum cascade laser emission spectra (λ ~ 9 μm) was studied at temperature near 10 K [1]. The active region consists of four quantum wells, and the 2 LO-phonon depletion of lower laser level takes place. It was found that the spectra broaden (up to 5 meV or 40 cm^{-1}) and split into three generation bands (T_1, T_2 and T_3) when magnetic field increases up to 7 T (see Figure). Herewith up to 80 laser longitudinal modes ($\Delta k = 0.5$ cm^{-1}) in all bands are simultaneously observed, and integral emission intensity of the laser increases by 70 times. With magnetic field the T_1 and T_2 bands have the negative slopes -4 and -1,5x10^{-4} cm^{-1}/T, respectively. For the T_3 band the slope is positive +1,5x10^{-4} cm^{-1}/T. The emission spectra bands are explained by magnetic quantizing of laser levels to the spin-split Landau levels. The emission intensity increase is mainly due to the phonon resonance adjustment in magnetic field. The magnetic field broadening effect can be used in the external cavity quantum cascade lasers tunable by relatively small magnetic field.



1. I. I. Zasavitskiy, D.A. Pashkeev, E. V. Bushuev, G. T. Mikaelyan. Quantum Electronics, **43**, (2013).

A8

Lineshape models testing: Measurements for CH4 spectral line 6105.6257 cm^{-1} (R9F1, R9F2) of 2v3 band broadened by N_2 and Ne

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The experimental spectra of CH_4 absorption lines in the spectral region of 6105-6107 cm^{-1} have been measured in binary mixtures with N_2 and Ne by a high-resolution photo-acoustic laser spectrometer [1]. Lineshape models, including Dicke narrowing [2] and speed dependent effects [3] were used for CH_4 spectral line (ν_0 = 6105.62573 cm^{-1}) fitting. Using the complicated line profile models (including the effects the speed dependence and collisional narrowing effect together) remains the systematic residuals of about 1 %, which seem to indicate that these models are still oversimplified. More refined models are thus needed.

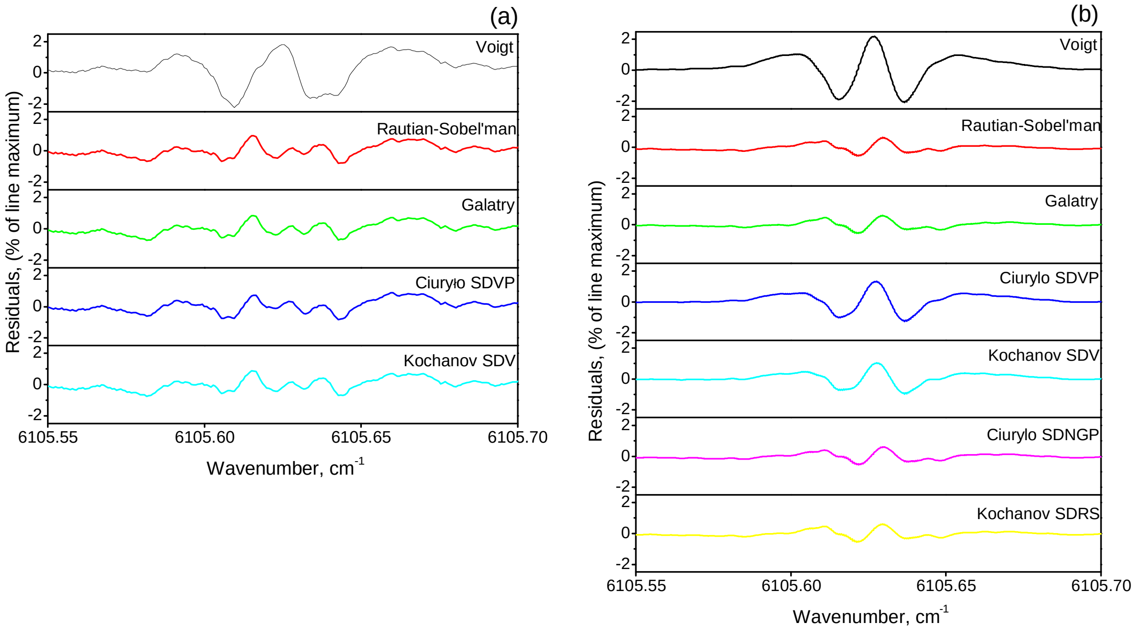

Fig.1 Experimental residuals of the methane spectra broadened by: N_2 (a) and Ne (b) for a different line profiles

References to a Journal publication:
[1] V.A.Kapitanov, K.Yu.Osipov, A.E.Protasevich, Yu.N. Ponomarev, J. Quant. Spectrosc. Radiat. Transfer 113 (2012) 1985-1992.
[2] S.G. Rautian, I.I. Sobel'man, Uspekhi fizicheskikh nauk 90 (1966) 209−236.
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A9

A PHOTOACOUSTIC SPECTROMETER COMBINED WITH A COMMERCIAL EC-QCL AT 10 µm AND APPLICATION TO GAS DETECTION

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Laser spectrometry techniques based on semiconductor lasers are well suited for gas monitoring, taking advantage of the characteristics of the laser sources implemented. Among these techniques, photoacoustic (PA) spectrometry provides better result when a powerful source is implemented. That is why a PA spectrometer has been associated with a commercial external cavity – quantum cascade laser (EC-QCL) from Daylight Solutions emitting about 100 mW at 10.5 µm. In addition to the strong emitted power, such a laser system provides a wide tuning range. This enables to record a whole absorption band of a small molecule as well as spectra of complex molecules.

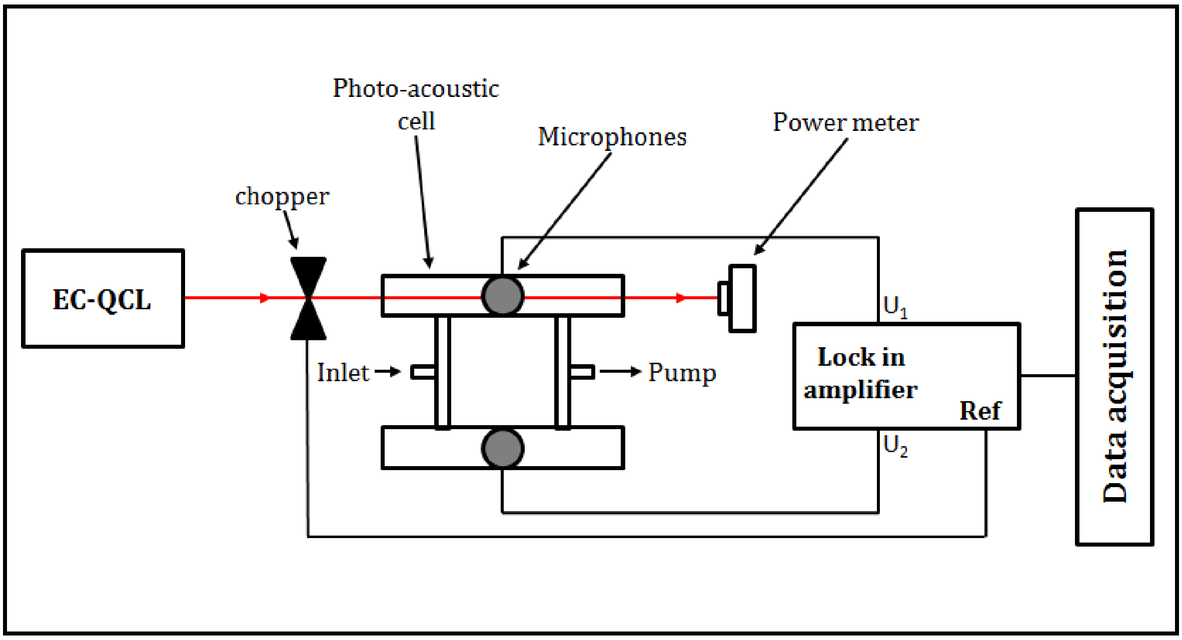

Fig. 1: Scheme of the photoacoustic spectrometer combined with the commercial EC-QCL source.

A10

Tunable Diode Laser Spectroscopy of methane for the MERLIN lidar mission

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In the framework of the MERLIN research program, a high-resolution spectroscopic study is developed on methane around 1.6 µm. MERLIN that means “MEthane Remote sensing LIdar missioN” is a Franco-German Lidar mission for Methane monitoring from space. The two national space agencies CNES and DLR are responsible for mission programmatic and satellite development. The space segment is a micro-sat e.g. 100 kg & 100 W, embarking a pulsed Lidar operating in “Integrated Path Differential Absorption technique” using surface scattering. CNES provides the spacecraft (e.g. Evolutions platform) and is responsible for overall mission integration. DLR provides the Lidar payload that is based on a pulsed Optical Parametric Oscillator laser emitting at 2 wavelengths around 1.645 µm. One of these wavelengths is called “on”. In this case the target of this laser source is the R6 manifold of the 2ν3 band of methane. The second wavelength is called “off” and no methane or water wapor may absorb at this wavelength.

Molecular spectroscopy of methane in the targeted region is crucial. First the “off” wavelength may be clear of methane and water vapor. At the moment when looking at standard databases such as HITRAN the region seems free of this gases. Preliminary results obtained with a tunable diode laser spectrometer will demonstrate that this region contains a lot of weak methane lines that may perturb the measurement if the wavelength is chosen for “off”.

In a second part, there is a key role of spectroscopic information on Weighting Function (*WF*):

$$WF(p,T) = \frac{\sigma_{on}(p,T) - \sigma_{off}(p,T)}{\left(1 + \frac{M_{H_2O}}{M_{air}} \rho_{H_2O}(p,T)\right) \cdot g \cdot M_{air}}$$

Thus, accurate absorption cross sections at 2 wavelengths is necessary. The CH_4 R6 manifold permits to obtain substantial relaxation of requirements on laser frequency and platform stability but requires accurate knowledge in all pressure & temperature conditions to avoid bias. First spectroscopic results obtained for R6 manifold of methane at 1.6 µm will be presented.

Acknowledgments : This work is funded by CNES R&T research program “MERLIN”.

A11

Can 500 m range be measured by a 15 ns diode pulsed lidar with ~1cm accuracy?

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Abstract

Portable eye-safe rangefinder based on 15 ns (~4.5 m) pulsed diode-laser and single-photon counter was capable to measure distance with accuracy better than 1 cm due to suggested signal processing.

Summary

The portable eye-safe rangefinder systems are of growing interest due to capability to achieve full 3D map of any objects (roads, bridges, industrial buildings etc.) from aircrafts. But applications of these systems is limited to low accuracy generally poor than 10 cm.

According to the laser rangefinder theory the spatial resolution of the laser radar is equal to the half of pulse duration and this value is generally greater than 10 cm. In this study a wave form analysis have been implemented to improve the range resolution. The estimated distance measurements accuracy was less than 1/500 of pulse length (1 cm for 15 ns pulse). This approach was examined by the full eye-safe (1 □J/pulse) laser rangefinder based on AlGaAs diode laser (it emits 15 ns / 4.5 m pulse, 2.5 kHz repetition) and Single Photon Avalanche Diode as detector which operates in Geiger mode. The lidar's range step for detecting electronics was equal to 5 cm. Backscattering photons were collected by 10 mm aperture. Nevertheless we have measured both the range and dynamics of atmospheric transmission along 2000 m trace at night and 800 m at day time. A building wall at the trace end is used as the target in the urban monitoring. To improve the range resolution we have calculated the pulse gravity center by Gaussian curve fitting of the histogram. The accuracy of the distance measurements can be improved by factor of 500 for 15 ns laser pulse. Remarkably that range measurement begins from very short distance (30 cm) and reached up to 2000 m from radar. We supposed that this instrument combined with GPS can be used both effectively as compact eye-safe rangefinder and backscattering lidar in topography profile, speleology, miner-safety system, balloon or superlight unmanned air platform height measurement and in ecological monitoring applications.

A12

BROADLY TUNABLE VERTICAL EXTERNAL CAVITY SURFACE EMITTING LASERS FOR HYDRO-CARBON ANALYSIS AT 3.3 µm

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Broadly tunable Vertical External Cavity Surface Emitting Lasers (VECSEL) with emission wavelengths in the mid-infrared 3300-2200 cm^{-1} range have been realized [1,2]. Due to the very short external cavity, emission occurs only from one single longitudinal resonance mode. By changing the external cavity length using a piezo actuator, the resonance modes and thus the emission wavelength can be shifted. This single TEM_{00} emission mode can be continuously tuned over a range of up to 3% or ~100 cm^{-1} around the design wavelength, see also figure 1. The emitted beam has a quasi perfect Gaussian-shaped radial-symmetric far-field, with a divergence half angle < 3.5°. The devices are operated in pulsed mode, with 5 ns pulse width and a duty cycle of up to 0.1% and an output peak power of up to 25 mW_p. They are thermoelectrically stabilized with passive air cooling.

A device tunable in the range of 2925 – 2970 cm-1 has been integrated into a basic absorption spectroscopy setup, with a 5 cm absorption path length and no reference signal. The full spectrum as shown in figure 2 was recorded with 0.5 Hz. The gas mixture consists at least of methane and butane at unknown ratios. Currently, the laser is being integrated into a professional spectroscopic setup using a much longer path length and a reference path. We anticipate the simultaneous detection of multiple hydro-carbons at ppm level.

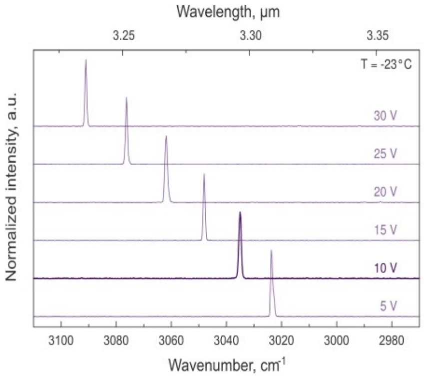

Fig. 1: Superimposed laser emission for multiple cavity lengths. The emission wavelength is shifted mode-hop free from 3090 cm^{-1} to 3020 cm^{-1}.

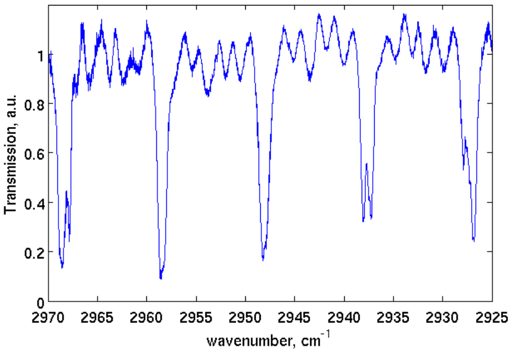

Fig. 2: Early spectroscopic measurement of methane using a 5 cm absorption path length. The fringes are due to the interferences of the cell's windows.

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A13

GAS CONCENTRATION EXTRACTION BASED ON LINE SHAPE ANALYSIS

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We present a method for optical measurements of gas concentrations based on line shape analysis instead of on absorption magnitude. The background to the approach is that the broadening and shift of molecular absorption lines are dependent on the species of the buffer gas molecules in the gas mixture (apart from on the temperature and pressure). The line shape is thus, as well known, buffer gas dependent. We have used this approach as a means to determine the concentration of, e.g., oxygen in a buffer gas mixture, by performing line shape analysis on an absorption line of water vapor in the 935-nm band. As seen in Fig. 1, the width and position of the water vapor line depends on the concentration of oxygen in the gas mixture; the latter can therefore be indirectly measured. The main advantages of the approach are that gases lacking absorption lines can be measured, and the gas concentration can be retrieved even in the case that the path length of light-gas interaction is unknown, e.g., in the application of gas in scattering media absorption spectroscopy.

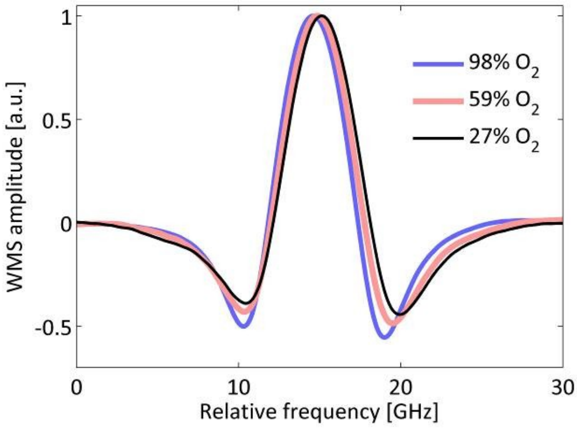

Fig.1 $2f$ WMS absorption signal of a water vapor line as broadened by different concentrations of oxygen in the gas mixture.

A14

OPTICAL POROSIMETRY STUDY OF POROUS MEDIA USING FREQEUCNY DOMAIN PHOTON MIGRATION METHOD AND GAS IN SCATTERING MEDIA ABSORPTION SPECTROSCOPY

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We present the latest results of measurements using the Frequency-Domain Photon Migration (FDPM) method and Gas in Scattering Media Absorption Spectroscopy (GASMAS) to study the porosity of porous media, such as wood and ceramics [1]. The FDPM method is utilized to retrieve the mean optical path length (MOPL) of the porous medium, while the GASMAS technique can measure the path length through the pores (pore path) by measuring the known-concentration oxygen absorption signal. The relative optical porosity is defined as the ratio between the pore path and the MOPL, which gives significant information about the structures of the porous media and extremely important for understanding their properties. An example of the relationship between the relative optical porosity and the physical porosity is given in Fig.1 [2]. By utilizing a proper nonlinear model, the physical porosity of the porous sample could be given by our optical method.

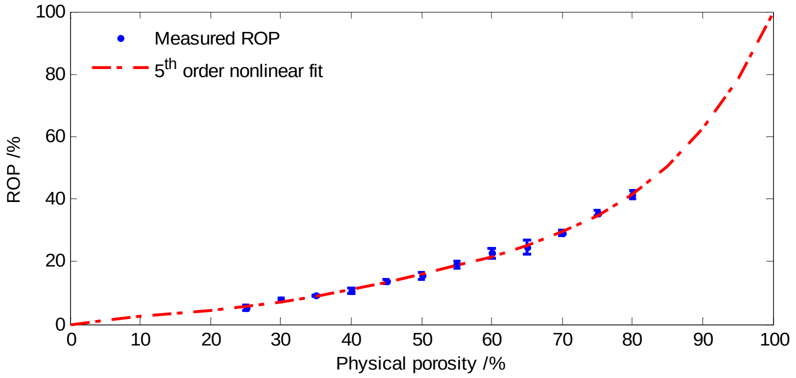

Fig.1 Relative optical porosity (ROP) *vs* physical porosity of porous ceramic samples.

[1] L. Mei, S. Svanberg, and G. Somesfalean, Combined optical porosimetry and gas absorption spectroscopy in gas-filled porous media using diode-laser-based frequency domain photon migration, Optics Express **20,** 16942 (2012).

[2] L. Mei, G. Somesfalean and S. Svanberg, Optical Characterization of Micro-porous Ceramics Using Tunable Diode Laser, in *Proc. SPIE* **8570** (2013).

A15

MINIATURIZED RESONANT PHOTOACOUSTIC CELL AS A LASER-SPECTROSCOPY TOOL FOR DETECTION OF ALCOHOL IN ATMOSPHERIC AIR

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The miniaturized spectroscopic hardware based on wavelength-tunable semiconductor lasers is a promising line of development for the photoacoustic (PA) gas-detection technique. Recent progress in the field can be associated with miniaturized PA cells optimized to the best gas-detection performance for an acoustic resonance of cell [1]. The volume of acoustic cavity for these cells is substantially smaller than 1 cm^3. Despite the reduced sizes, the cells are not worse in the performance as compared to non-miniaturized ones. The noise-limited minimal detectable absorption for the cells is down to ~ 10^{-9} $cm^{-1}W\ Hz^{-1/2}$. Development of a laser-spectroscopy gas sensor (such as a device shown in Fig.1), which includes a miniaturized PA cell in combination with an infrared current-modulated laser diode or quantum cascade laser, is of great interest for commercial purposes due to the compactness, simplicity and low cost of the equipment.

In the presentation we analyze advantages and drawbacks associated with application of the miniaturized PA cells to detection of alcohol vapor in atmospheric air with the help of semiconductor lasers operated in near- and mid-infrared wavelength ranges. We present experimental results on laser photoacoustic detection of alcohol in air at a sub-ppm concentration level. Potential capabilities of the miniaturized laser-spectroscopy PA hardware for low-cost high-sensitivity alcohol detection are discussed.

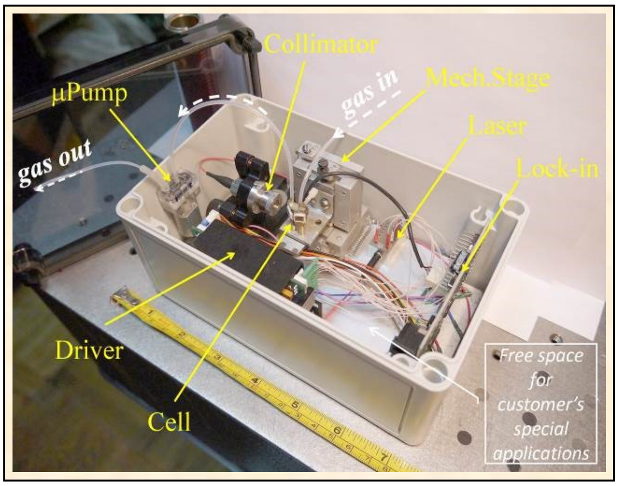

Fig.1 A recently developed photoacoustic gas sensor [1] based on a near-infrared fiber-pigtailed DFB laser diode and a miniature resonant PA cell (the volume of acoustic cavity of cell is ~ 5 mm^3). The sensor is enclosed in a box with the sizes of 18x11x9 cm. Some key sensor parts (cell, lock-in, mechanical stages, laser mount) are our original components.

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

A16

ON POTENTIAL OF COMBINATION OF FREQUENCY MODULATION AND OPTICAL FEEDBACK LOCKING IN CAVITY-ENHANCED ABSORPTION SPECTROSCOPY

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The highest sensitivities for absorption measurements close to a shot noise limit were demonstrated in noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS) [1]. However, routine demonstrations of NICE-OHMS absorption sensitivities remain to be a challenge.

An alternative approach of a combination of laser frequency modulation (FM) at high frequency of 121 MHz, equal to a free spectral range of a high finesse V-shaped cavity, with optical feedback (OF) locking of a near-IR distributed feedback laser diode at 1529.18 nm to the cavity and further detection of the transmitted optical beam at the frequency of 121 MHz, where shot noise predominates, has been reported for application in cavity enhanced absorption spectroscopy (CEAS) [2]. We will describe a model for the description of the FM signals and discuss experimental data recorded in the setup of frequency modulation and optical feedback cavity-enhanced absorption spectroscopy (FM-OF-CEAS). A noise-equivalent absorption (NEA) sensitivity of $2.1\text{x}10^{-11}$ $\text{cm}^{-11}\text{Hz}^{-1/2}$ was estimated for typical FM spectra recorded with an effective beam path length of 4133 m and a cavity finesse of 10469. This NEA sensitivity was a factor of 11.7 above the shot-noise limit for a laser power of 10 µW observed on the V-shaped cavity output. The full potential of FM-OF-CEAS based upon near-IR and mid-IR lasers with shot-noise limited absorption sensitivity is believed yet to be realised.

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[2] V.L. Kasyutich, M.W. Sigrist, Appl. Phys. B, DOI 10.1007/s00340-013-5338-0.

Poster session B

B1

Spectral line fitting for high accurate experimental data

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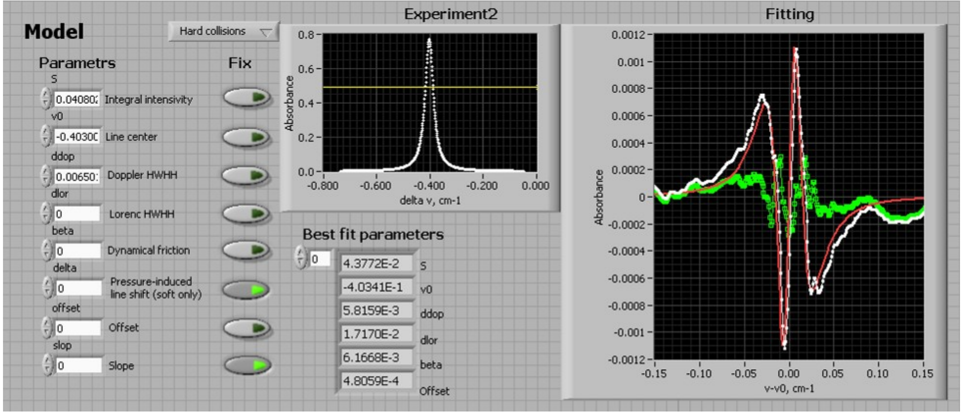
Accuracy is one of recent challenges for Tunable Diode Laser Spectroscopy (TDLS). Several TDLS applications require measurement accuracy at level 0.1 %. This accuracy level was recently achieved in TDLS (see A2).

Next step is experimental spectral line shape fitting by some model profile. At the moment three model profiles are in use: Voigt, Galatry, and Rautian. Traditionally residual is measure of fitting quality. After fitting, some spectral line parameters can be obtained. Subject of present paper is to analyze what information can be obtained from such fitting for high accurate data. What is obtained parameters meaning and accuracy.

For high accurate spectral data fitting special software was developed (Fig.1).



Model Hard collisions

Parametrs / Fix

S: 0.04080: Integral intensivity
v0: -0.4030C Line center
ddop: 0.00650: Doppler HWHH
dlor: 0 Lorenc HWHH
beta: 0 Dynamical friction
delta: 0 Pressure-induced line shift (soft only)
offset: 0 Offset
slop: 0 Slope

Best fit parameters: 0

4.3772E-2 S
-4.0341E-1 v0
5.8159E-3 ddop
1.7170E-2 dlor
6.1668E-3 beta
4.8059E-4 Offset

Fig.1 Spectral line shape fitting software interface.

The software developed can use all model profiles mentioned above to fit experimental data. There are 8 fitting parameters than can be fixed or used in fitting procedure. In present paper we’ll consider role of each parameter. After experimental data fitting presented in Fig.1 residual demonstrate (white points in right graph) line asymmetry at level 0.1 %. Difference between Galatry and Rautian is within experimental accuracy (residual is not measure of fitting quality). After taking into account line asymmetry (see B2) residual is at the level of 0.02 %.

B2

Spectral line asymmetry

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Accuracy is one of recent challenges for Tunable Diode Laser Spectroscopy (TDLS). With presently achieved accuracy level (see A2) investigation of variety of new physical effects is possible. Present paper deals with spectral line asymmetry.

Using fitting procedure developed for spectral line fitting for high accurate experimental data (see B1), spectral line asymmetry can be easily observed. In residual it looks like third derivative of line shape (Fig.1). Due to asymmetry line center location has to be corrected.

There are at least 3 mechanisms of line asymmetry: correlation of DL frequency and intensity noises, Lorentz profile asymmetry, and asymmetry due to line mixing. All three mechanisms were observed experimentally. Asymmetry due to correlation of DL frequency and intensity noises dominates at low pressures. For overlapping lines having line mixing, asymmetry is due to line mixing. For isolated line for pressures when line shape is determined by pressure broadening, asymmetry is due to asymmetry of Lorentz profile. Fig.1 presents normalized residual for isolated CO_2 line for pressures between 15 and 30 mBar.

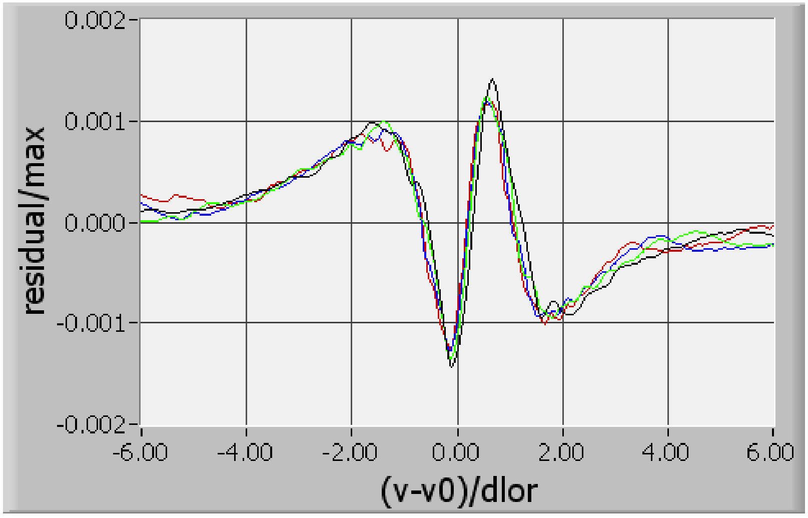

Fig.1 Normalized residual for isolated CO_2 line at pressures between 15 and 30 mBar

Origin of this asymmetry type is velocity dependence of broadening and shift. In present paper role of different intermolecular potentials will be analyzed and compared with asymmetry experimental data obtained.

B3

MEASUREMENTS OF CH_4, CO_2 AND H_2S CONCENTRATIONS FOR MEDICAL SCREENING DIAGNOSTICS

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The possibility of medical screening diagnostics using TDLS was considered decades ago [see for example 1]. The goal of present work was to test this approach in clinic environment. Two-channel Diode Laser Spectrometer (DLS) developed for this purpose was used. DLS incorporates two diode lasers operating at 1.60 and 1.65 mkm to measure CH_4, CO_2 and H_2S. Chernin multi-pass cell (optical path 39 m) was used to measure molecules under consideration concentrations. The patient exhaled breath was directed to the cell and concentrations of molecules under consideration (markers) were measured simultaneously and continuously. This instrument was tested in Moscow City Clinical Hospital №12. 78 patients with known diagnoses passed these measurements. As example we are presenting results of CO_2 and CH_4 measurements (Fig.1).

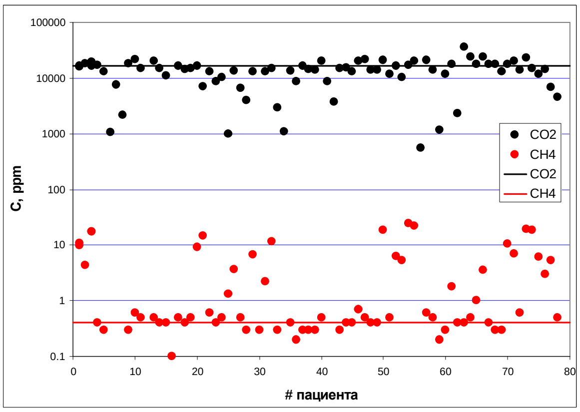

Fig. 1 Result of human breath measurements

One can see normal (constant value) and abnormal (orders of magnitude difference) behavior due to particular diseases – subject of medical screening diagnostics.

References:

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B4

MEASUREMENT OF NATURAL GAS HUMIDITY IN GAS PIPELINES

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Water vapor content in natural gas is an important parameter because a condensation of water in gas pipelines can damage equipment of pumping stations. Many pipelines are operated in harsh climatic conditions with ambient temperature from -50 to +50^{O}C. In this temperature range the saturated vapor pressure of water varies from 0.05 to 150mbar. Taking into account that pressure in gas pipelines is 30-100bar, and that measurements are carried out at a reduced pressure close to 1bar, the device have to be able to measure water vapor content within 0.5 to 5000 ppmv range.

In the near-infrared region of spectrum, water vapor can be measured in four ranges – 1.87, 1.39, 1.15, and 0.94µm. However, the measurement of water in natural gas is complicated by the fact that the spectrum of water is masked by the spectrum of methane, although one transparency micro-window can be found at 5327.4 см$^{-1}$ in 1.87µm region. The exception is 0.94µm region, where absorption of methane and other hydrocarbons is negligible (fig. 1).

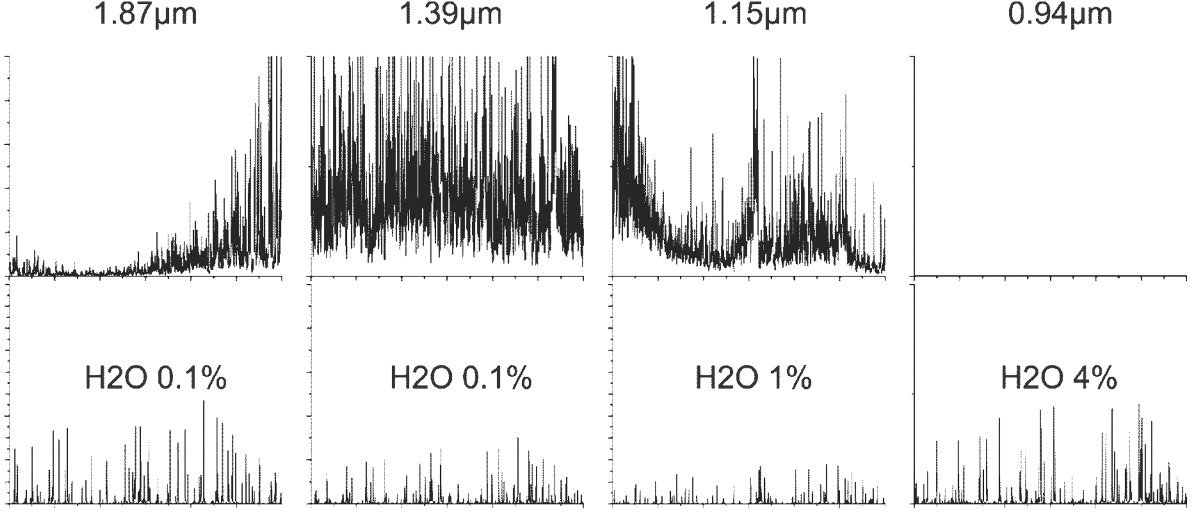

Fig. 1. Methane and water spectra. Upper spectra correspond to 100% methane. In all spectra full scale absorption coefficient is 5*10^{-3}cm^{-1}.

Device to measure humidity of natural gas in a range from 0.1 to 10000 ppmv has been made. This device consists of a fiber-coupled 937nm DFB laser, Herriott-type multipass cell with optical path length 18m, low pressure reference cell, diode laser controller, and data acquisition board. A technique described in [1] was used to process the spectra recorded and to measure water vapor content in natural gas.

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B5

METHANE IMPURITY CONTROL DURING HIGH-PURITY AMMONIA RECTIFICATION

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TDLS instrument to control methane impurity during ammonia low temperature rectification process was developed. DFB pig-tail DL (NEL) operating near 1.65 mkm was used. The instrument contains two analytical and one reference channels. In reference channel cell with calibrated methane concentration was installed. Reference channel was used to stabilize DL frequency tuning and to calibrate data obtained by analytical channels.

Two analytical channels measured methane concentration at bottom and upper parts of rectification column. It was done using optical cells having 3 cm, 1.4 m, and 15.2 m optical length. Minimum detectable CH_4 concentration was found to be 10^{-3} % for 0.3 sec averaging time. It was determined by DL baseline drift and interference of methane and ammonia absorption features in spectral range under consideration.

For the purification process control under consideration minimum detectable concentration is not main problem. More important is real time control of some impotant impurities removing during purification process. In present paper methane concentration during ammonia purification was measured using TDLS instrument developed, FTS, and Gas Chromatography (Fig.1).

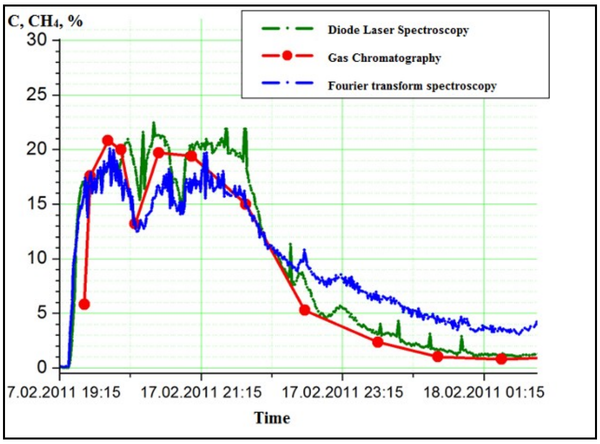

Fig.1 Long-term methane measurements during ammonia purification

B6

IR HETERODYNE SPECTROMETER BASED ON 1.55 MICRON DIODE LASER AND NbN HOT ELECTRON BOLOMETER OPTICAL MIXER

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Sergey Maslennikov[a]*, Alexander Schurakov*[a]*, Alexander Semenov*[a]*, Aleksandr A. Verevkin*[d]*,*
Boris M. Voronov[a]*, Artem Klimchuk*[b]*, Oleg Benderov*[b]*, Alexander V. Rodin*[b,e]*,*
Alexander I. Nadezhdinsky[c]*, and Gregory N. Gol'tsman*[a]

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In astrophysics, high resolution IR range observations are needed to study and fully understand processes that have been going on in the Universe since the Big Bang. High resolution and sensitivity in the IR spectrum range would allow low concentration molecules detection, isotope analysis and Doppler measurements of the velocity field. To fulfill this task, we have developed the IR heterodyne spectrometer utilizing a 1.55-micron DFB fiber-coupled laser as the Local Oscillator (LO) and the fiber-coupled Hot-Electron-Bolometer mixer based on a NbN superconducting thin film. The mixer is capable for both the detection and down-conversion of the high frequency incident radiation. Its operation is based on electron heating effect in thin superconducting films and is described elsewhere [1]. For laboratory test purposes another DFB-laser with significantly attenuated power is used to simulate the signal source. Varying its power with a tunable optical attenuator we are able to investigate both sensitivity of the system and its dynamic range.

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B7

BROAD BAND CAVITY RING-DOWN SPECTROSCOPY USING A DIODE LASER

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A broad band multimode diode laser and a high finesse optical cavity were employed to measure the cavity ring down time [1] as a function of NO_2 concentration. The laser emitted approximately 50 modes contained in a Gaussian-like envelope centered at 411 nm with a FWHM of approximately 1 nm. The laser emission covered 100's of FSR and excited a large number of cavity modes. This made the apparatus less susceptible to vibrations since slight changes to the cavity length due to vibrations merely shifted the cavity resonances to other wavelengths where the laser was emitting [2,3]. This aspect combined with the fact that cavity ringdown spectroscopy (CRDS) does not require external calibration standards makes the device well suited for field based applications.

CRDS was conducted on several NO_2 concentrations (100, 200 , 300, and 400 ppb) fed through the cell at 1 liter/min. The laser diode was operated in CW mode was chopped at a frequency of 50 kHz using an AOM. The cavity ringdown cell was 22 cm long; the mirrors had a reflectivity of 99.97%. The close spacing of the energy levels in NO_2, and the large width of the absorption features at 1 atmosphere resulted in very broad absorption features [3]. As a result, the absorption cross-section could be treated as having a constant value of ~ 6.0 × 10-19 cm^{-2} [4] over the laser's wavelength range.

The sensitivity of the detector was determined from the standard deviation of 50 sets of CRD times recorded with a 1 liter/min. flow of Zero Air. Each set of CRD data was an average of 51,200 decays. The average ring down time was 2.251 μs, with a standard deviation of 0.020 μs (0.89%), corresponding to a sensitivity of approximately 7.5 ppb. The measured values of the NO_2 concentration were found to be approximately in agreement with the specifications of the mixture.

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[4] A.C. Vandaele, C. Hermans, P.C. Simon, M. Carleer, R. Colins, S. Fally, M.F. Mérienne, A. Jenouvrier, and B. Coquart, "Measurements of the NO2 absorption cross-sections from 42000 cm-1 to 10000 cm-1 (238-1000 nm) at 220 K and 294 K," J. Quant. Spectrosc. Radiat. Transfer 59, 171-184 (1998).

B8

THE COMPARISON OF TWO SPEED-DEPENDENT VOIGT LINE PROFILE MODELS

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Numerical calculations of the ratio of line width (FWHM) and maximum value of two speed-dependent Voigt line profiles (Kochanov's SDV [1] and Berman's SDVP [2-4]) to the respective values of their speed-independent analogues are performed in the high-pressure limit. The intercomparison demonstrates considerable disagreement between different speed-dependent models (see Fig.1).

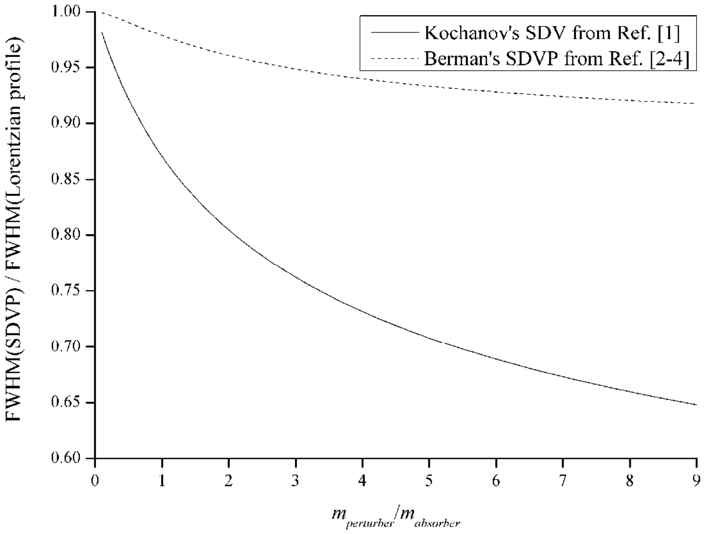

Fig.1 The high-pressure limit ratio of FWHM of two speed-dependent Voigt line profiles to the FWHM of their speed-independent analogues as a function of mass ratio $m_{perturber}/m_{absorber}$. The calculations were made using Van der Waals interaction potential in the case when line shift was fixed to zero.

Acknowledgements
The author is grateful to Igor V. Ptashnik for interest to the work and useful comments.

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[4] R.Ciuryło, Phys. Rev. A, 58, 1029-1039 (1998).

B9

Development and tests of a coherent quantum cascade laser array for gas detection

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In the framework of the ANR project called COCASE, GSMA and III-V Lab develop a coherent quantum cascade laser array to obtain high power emission. This source will be combined to a photoacoustic spectrometer devoted to trace gas detection [1]. In such a spectrometer the sensitivity limit is directly proportional to the laser power.

The principle of this source consists in the fabrication of multi-stripes arrays for high power QCL. The paper will present multi-stripes dimensioning and modelling, thermal and optical considerations. The number of emitters has been tested from 2 up to 32. N supermodes are obtained for N stripes and highest order is attended for all configurations. In nearfield up to 64 µm of active region are achieved [2]. The main characteristic of this kind of source is that in farfield an anti-symmetrical signature is obtained with at least two lobes. This result can be confirmed by Finite Element Modelling simulation. We will present far-field emission measured with a 32 emitters array around 7.8 µm. In this case 2 lobes on each part of the laser axis may be observed and there is no light in front of the source.

This source has no modes switching, no multi-modal behavior and supermode operation is active along the current range thus there are no coherence loss. This first time monolithic QCL phased array up to 32 emitters permits to increase the power of the source. The next step will be to obtain a cw emission. Then the technological robustness of the source will be useful when implemented in photoacoustic spectrometers where signal is proportional to absorbed power.

Acknowledgments: This work is funded by the ANR ASTRID project #ANR-11-ASTR-0027 called “COCASE”.

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B10

Tests of the characteristics of a 10 µm quantum cascade laser for gas remote detection by heterodyne spectroscopy

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Heterodyne sensing consists in mixing an unknown signal with the signal from a local oscillator. This superimposition creates a beat note in the RF range. The analysis of this phenomenon enables to determine the spectrum of the unknown source. This type of setup may be developed for atmospheric gas remote sensing [1].

In this work, the local oscillator is a quantum cascade laser (QCL). Its characteristics directly impact the sensitivity of the sensor. The tests realized to determine the QCL characteristics will be presented. First, the impact of the power supply on the QCL intensity noise was assessed by comparing it to CO_2 laser shot noise. In a second time, the oscillator frequency noise is measured from beat note stability between QCL and CO_2 laser. In this case, the power supply stability is again decisive. Indeed, the driver current noise increases the QCL frequency noise and then so broadens its linewidth [2]. The experimental setup is sketched in Fig. 1.

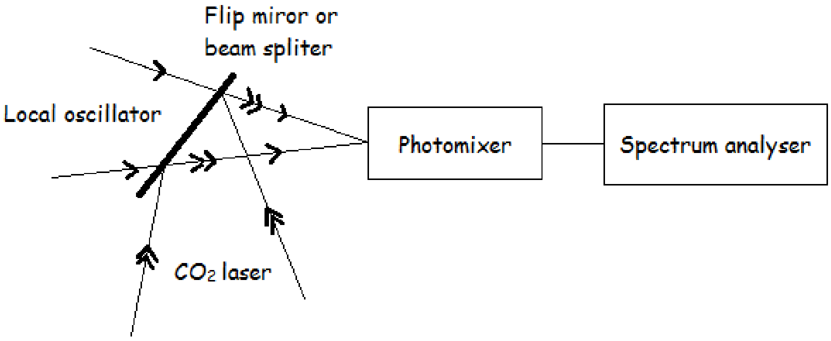

Fig. 1: Sketch of QCL tests setup

Acknowledgments:

The authors are indebted to the Délégation Générale de l’Armement and the Centre National de la Recherche Scientifique for financial support of the PhD of Marie-Hélène Mammez.

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B11

SPECTROSCOPIC TEMPERATURE DIAGNOSTICS OF GAS FLOW AT THE OUTPUT OF SINGLET OXYGEN GENERATOR

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Temperature of gas flow after singlet oxygen generator (SOG) is measured by different spectroscopic techniques. The main method is analyzing of atmospheric band of molecule oxygen luminescence (transfer , P – branch). The technique of diode laser spectroscopy to measure water line absorption shape ( ) is used for verification. Doppler width of experimental line shape is determined. Both spectroscopic techniques were applied to the same point of gas flow. The measurements were conducted in subsonic part of gas flow. The results show good agreement between both techniques.

B12

TDLS CO_2 SENSOR FOR MAINSTREAM CAPNOGRAPHY

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The monitoring of the CO_2 concentration value in exhaled air becomes more and more important. Next a continuous respiration monitoring, several health problems, e.g. hyperventilation or hyperthermia of a patient can be detected. The common sensor technology to measure the CO_2 concentration is infrared spectroscopy at a wavelength of 4.26 microns [2]. However, the need of different optical filters in the system and frequent calibration are the main disadvantages of this technique. We developed and present a 2.5 cm TDLS probe (Fig. 1, top) which measures the carbon dioxide absorption at 2 microns. The main limiting problem for such a reduced optical cell size are interference fringes which cannot be avoided and whose free spectral range is in the range of the HWHM of the absorption line (Fig. 2, top). A microcontroller board in combination with advanced signal processing for fringe rejection is able to eliminate the fringes from the absorptions spectrum. This method is based on analyzing the Fourier domain of the absorption line and is able to reduce the effect of the fringes by a factor of 30. In Measurements, we achieved a resolution of < 300 ppm (Fig. 2, bottom).

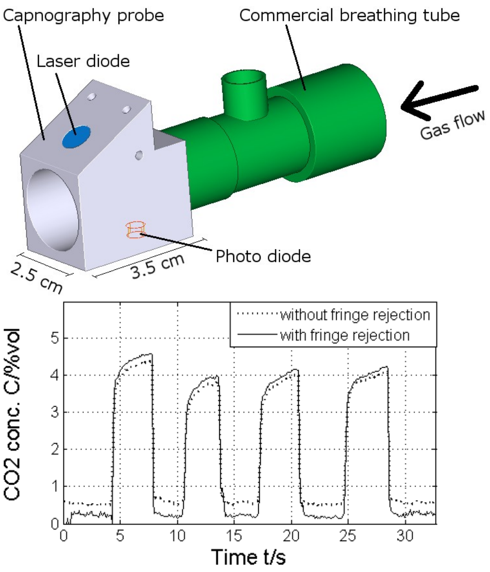

Fig. 1, top: capnography probe for connection on breathing tube; bottom: CO2 concentration while breath test without (dotted line) and with (solid line) fringe rejection method

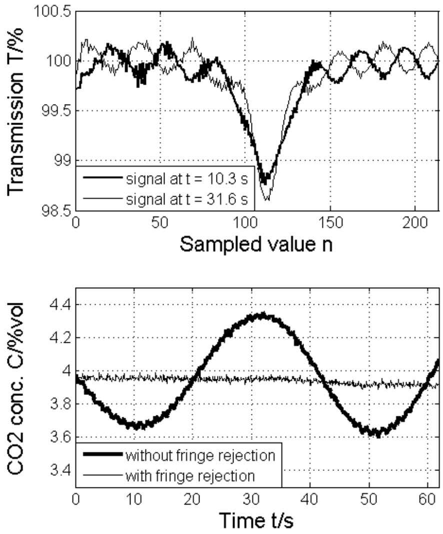

Fig. 2, top: absorption signal with "moving" fringe, plotted at t=10.3 s and 31.6 s; bottom: CO_2 concentration evaluated by curve fit without (bold line) and with fringe rejection method (normal line)

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B13

Environmental Monitoring of Gaseous Nitrous Acid (HONO) By Quantum Cascade Laser Absorption Spectroscopy

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Gaseous nitrous acid (HONO), known as a very important source of the hydroxyl free radical (OH) in the atmosphere, affects directly the atmospheric oxidant capacity [1]. Accurate real time assessment of HONO concentration is crucial for understanding the HONO chemistry: its formation / role in OH-radical production, and hence tropospheric chemical processes, which might have a severe impact on air pollution models and global environmental change. In this presentation, we report on the instrumental development for monitoring HONO trace in the atmosphere based on a quantum cascade laser (QCL) operating at 8 μm combined with a multipass cell of ~158 m effective path-length. The instrument was employed for daytime and nighttime monitoring of HONO concentration variation. Details in the developed QCL-based HONO sensor and its application for environmental HONO monitoring (Fig. 1) will be presented and discussed.

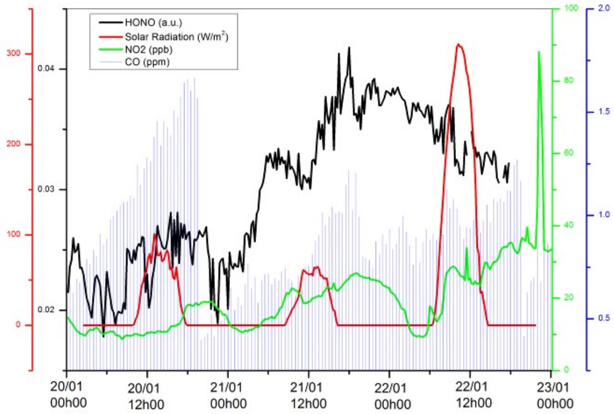

Figure 1 Preliminary observation results of HONO concentration variation in a snowy period in January 2013 in Dunkirk – France.

Reference
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B14

BACKGROUND MERCURY AND OXYGEN DETECTION USING DIFFERENTIAL ABSORPTION LIDAR SYSTEM WITH ULTRALVIOLET WAVELENGTH AROUND 253.7 NM

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** These two authors contributed equally much to this work; Email: liang.mei@fysik.lth.se.*

In the present work, we demonstrate a newly developed differential absorption lidar system (DIAL) in Guangzhou, China, which was employed to monitor the background mercury at the campus of South China Normal University (SCNU) located in Guangzhou. The absorption line for mercury is due to the transition between the ground $^1S_0$ state and the excited $^3P_1$ state, corresponding to an absorption line around 253.7 nm (vacuum wavelength). DIAL measurements on atmospheric oxygen lines were also performed for system verification. Strong oxygen absorption lines are situated close to the mercury absorption line (See Fig.1). Since the oxygen concentration is well known, expected performance can be predicted. A 24-hour continuous monitoring of the atomic mercury background is performed, and a background concentration around 12 ng/m^3 below the altitude of 110 m is obtained on January 11th, 2013 (Temperature 14 ˚C). A typical atomic mercury differential absorption curve is given in Fig.1 [1]. The system will be integrated in a mobile platform for mercury monitoring in different places of China.

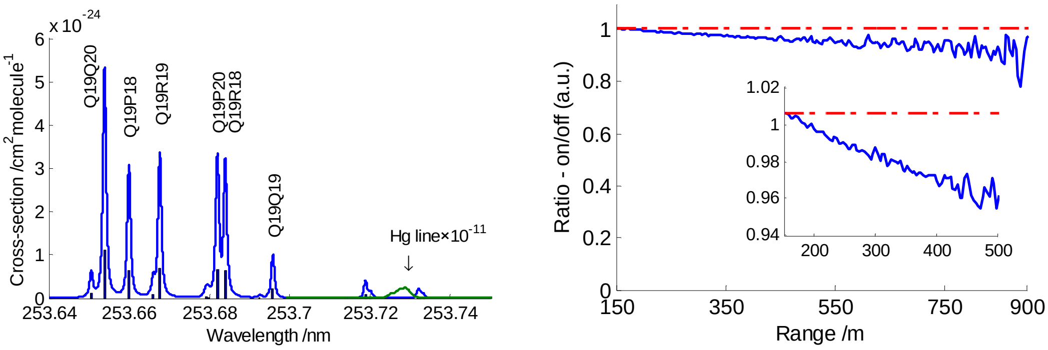

Fig.2 Left: Atomic mercury and Oxygen molecular absorption spectrum; Right: Typical atomic mercury differential absorption curve (average for one hour).

[1] Liang Mei, Guangyu Zhao, Sune Svanberg, Differential Absorption Lidar System Employed for Background Atomic Mercury Vertical Profiling in South China, in manuscript.

B15

$H_2{}^{16}O$ spectrum structure and spectral line profile at 1.39 m region. Multispectrum fitting procedure of overlapped lines broadened by water, air, and noble gases.

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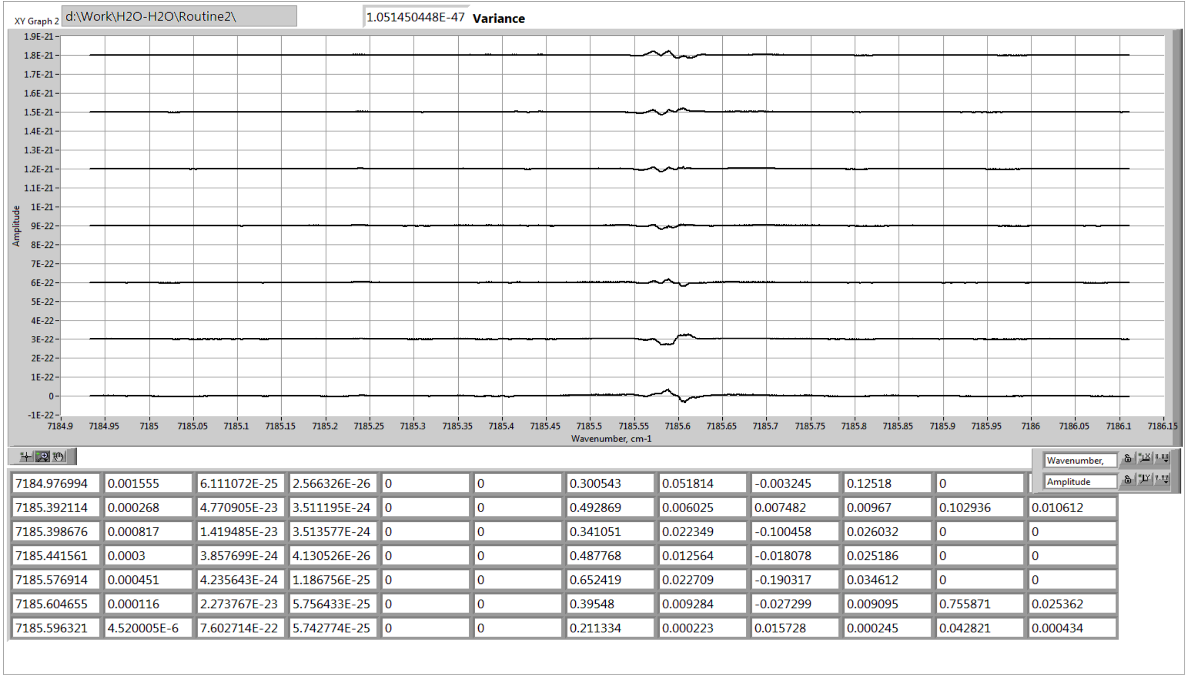
The absorption spectra of pure H_2O with mixtures of broadening gases N_2, Ar, Xe, He, Ar and air have been measured in 1.39 mμ spectral region by high resolution spectrometer based on diode laser (DFB NEL, Japan) [1]. For the processing of pure water spectra and it's mixtures with a different broadening gases in a wide pressure range we used a multispectrum fitting procedure developed at IAO. The program is based on a relatively simple Rautian-Sobel'man line profile [2,3] and linear pressure dependence of the line profile parameters. H_2O measured spectra bulk processing results in the retrieving of such line parameters: zero-pressure line center positions, intensities, self-broadening and self-shift coefficients of pure water, broadening and shift coefficients for other gases which are describes the experiment with the minimum residuals in a wide pressure range.



d:\Work\H2O-H2O\Routine2\

1.051450448E-47 **Variance**

7184.976994	0.001555	6.111072E-25	2.566326E-26	0	0	0.300543	0.051814	-0.003245	0.12518	0	
7185.392114	0.000268	4.770905E-23	3.511195E-24	0	0	0.492869	0.006025	0.007482	0.00967	0.102936	0.010612
7185.398676	0.000817	1.419485E-23	3.513577E-24	0	0	0.341051	0.022349	-0.100458	0.026032	0	0
7185.441561	0.0003	3.857699E-24	4.130526E-26	0	0	0.487768	0.012564	-0.018078	0.025186	0	0
7185.576914	0.000451	4.235643E-24	1.186756E-25	0	0	0.652419	0.022709	-0.190317	0.034612	0	0
7185.604655	0.000116	2.273767E-23	5.756433E-25	0	0	0.39548	0.009284	-0.027299	0.009095	0.755871	0.025362
7185.596321	4.520005E-6	7.602714E-22	5.742774E-25	0	0	0.211334	0.000223	0.015728	0.000245	0.042821	0.000434

Fig.1. Multispectrum fitting procedure output result. Pure H2O spectra experimental residuals in a wide pressure range and retrieved line parameters of the model.

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B16

APPLICATION-ORIENTED DESIGN OF MONOMODE INTERBAND CASCADE LASERS FOR SPECTROSCOPY IN THE MID-INFRARED

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The mid-infrared wavelength region, especially between 3 and 5 µm is of high interest for Tunable Laser Absorption Spectroscopy (TLAS). Interband Cascade Laser (ICL) [1] can provide monomode cw emission at room temperature in this wavelength range [2, 3]. We present the simulation, design and manufacturing of distributed feedback (DFB) laser devices based on this concept. The focus was set on devices that target specific, technologically and industrially relevant, wavelengths with low energy consumption. Finally devices ready for application from 3 to 5 µm are presented. As shown in Fig. 1 cw operating temperatures up to 40 °C and tuning ranges of 11 nm with Side Mode Suppression Ratios (SMSR) around 30 dB were achieved.

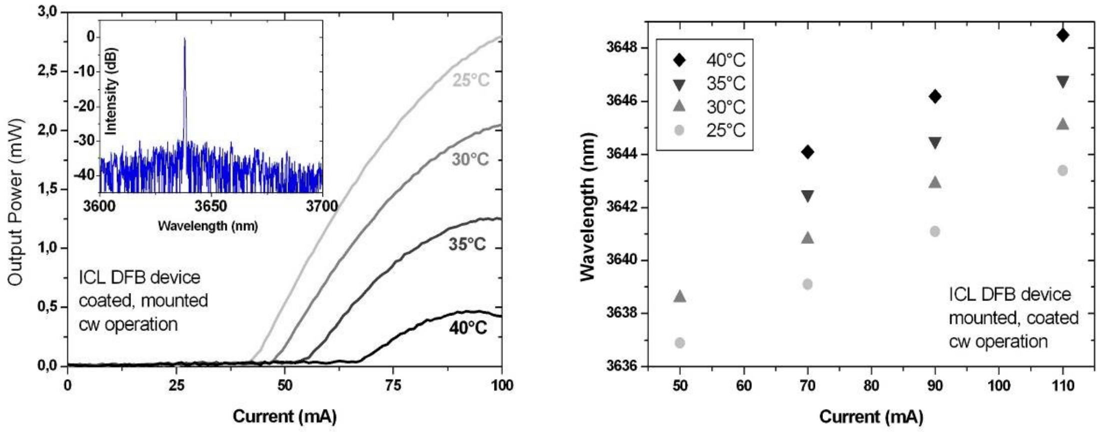

Fig. 1 L-I characteristics (left), spectrum (inset) and tuning behavior (right) of an ICL DFB device mounted on TO-style header emitting around 3.64 µm for methane detection

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B17

A NEW WMS-TDLAS LIDAR FOR NON INVASIVE GAS SENSING IN MODIFIED ATMOSPHERE PACKAGES

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We present a newly developed instrument for oxygen sensing in closed containers such as the Modified Atmosphere food packages widely used in the food industry. Those packages can have very small transparent regions free from printed graphics thus preventing any measurement with a standard transmission mode Absorption Spectroscopy setup. Our instrument, using a tunable VCSEL source operating in the 760nm oxygen absorption band, is based on a close range LIDAR scheme.

While digitally performing Wavelength Modulation Absorption Spectroscopy on the backscattered light from the bottom of the package under exam, the device is able to overcome the need for an optical interaction path length measurement thanks to an integrated imaging system which measures the distance of the effective backscattering target through triangulation techniques.

Reaching down in the low 10^{-5} absorbance unit region, the optical design of the instrument needed to be accurately optimized to minimize both stray interference fringing as well as influence from stray backscattered light from the uneven, partially scattering package material, which is beyond the designer's control.

From a software point of view, a novel absorbance fitting algorithm as well as image processing techniques for the optical path evaluation were developed.

Fig.1 WMS LIDAR oxygen detection in closed Modified Atmosphere Packages. (courtesy of L Pro srl)

Poster session C

C1

Doppler profile investigation

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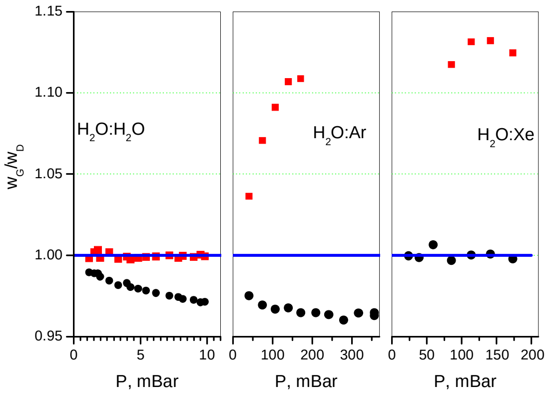
Accuracy is one of recent challenges for Tunable Diode Laser Spectroscopy (TDLS). With presently achieved accuracy level (see A2) investigation of variety of new physical effects is possible. Present paper deals with spectral line Doppler profile investigation.

No collisions: Doppler profile is determined by molecules Maxwell distribution and its width can be calculated - $\Delta\nu_D$. Collisions presence leads to Dicke narrowing. Shape of Doppler profile in presence of collisions is determined by kinetic equation solution. I.Sobel'man found two limit solutions of this equation: soft and hard. Soft (diffusion kinetic equation approximation) – the molecule velocity relaxation needs a lot of collisions. Hard - molecule velocity relaxation needs only one collision. Reality is between these two limit cases. In literature soft and hard are known as Galatry and Rautian profiles. Traditionally Gaussian component of these profiles is fixed. It is not correct.

Using fitting procedure (see B1), $\Delta\nu_G$ was included in the fitting procedure. There was no difference between soft and hard if residual is measure of the procedure. However, for correct model $\Delta\nu_G$ has to be equal to $\Delta\nu_D$.



To test this approach, shapes of water line 7185.597 cm^{-1} were measured and fitted (Fig.1).

Fig.1 Pressure dependence of normalized Gaussian width for 3 model gas mixtures
Black circles – hard
Red squares – soft
Horizontal line – prediction for correct model

Left – water self broadening. It is dipole-dipole interaction. For this interaction scattering probability has pole at 0 angles. It is model for soft collisions model.

Right – heavy atom. It is "model" for hard collisions model.

Middle – example of intermediate situation.

Difference between soft, hard, and 1 can be used as measure of collisions number required for velocity thermolization.

C2

Investigation of isolated CO_2 line shape

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Accuracy is one of recent challenges for Tunable Diode Laser Spectroscopy (TDLS). With presently achieved accuracy level (see A2) investigation of variety of new physical effects is possible. Present paper deals with analysis of high accurate CO_2 line shape measurements.

Isolated CO_2 line (6953.46708 cm^{-1} due to HITRAN) was selected as analytical one. High accurate TDLS spectra were recorded. Using the procedure developed (see B1) experimental data were fitted using both soft and hard models. Soft (diffusion kinetic equation approximation) – the molecule velocity relaxation needs a lot of collisions. Hard - molecule velocity relaxation needs only one collision. Reality is between these two limit cases. Question: what is meaning of line parameters obtained by such fitting?

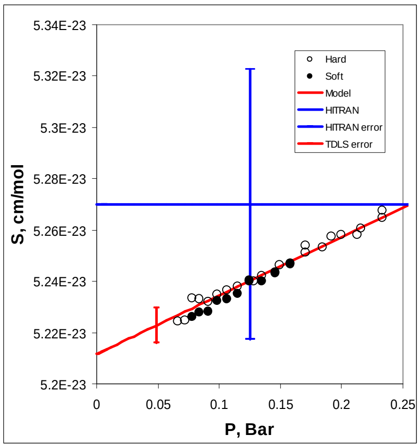


Fig.1 Pressure dependence of the line spectral intensity
Horizontal line and vertical segment are HITRAN value and its error.

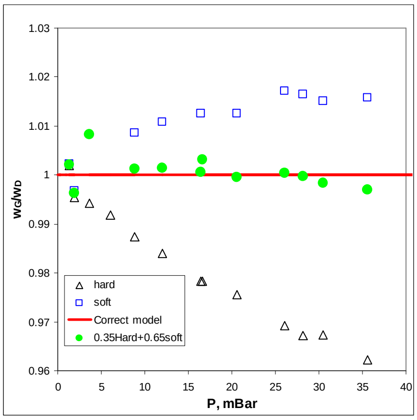
Both soft and hard are giving similar results being in agreement with HITRAN within its accuracy.

Pressure dependence of integral line intensity can be observed. Conclusion: at present experimental accuracy level this isolated line can not be considered as isolated one – line mixing.

Gauss and Lorentz as well as narrowing parameters are different for soft and hard models.

Fig.2 Pressure dependence of normalized Gauss width obtained from fitting using hard and soft models

For correct model w_G/w_D has to be 1 (red constant). Empirical linear combination of hard and soft models is presented by solid circles. Using the same linear combination, dramatic improvement of both collision broadening and narrowing coefficients was observed and will be presented. Possible meaning of numbers in empirical model will be discussed.



C3

BROADENING AND SHIFT OF $H_2{}^{16}O$ LINES NEAR 1.392 m

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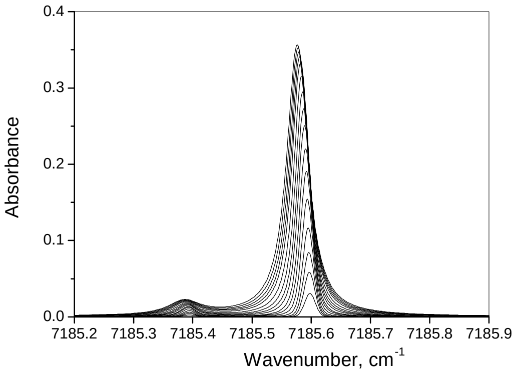
Investigation of pressure broadening and shift of the $H_2{}^{16}O$ lines is subject of present paper. Water vapor spectra were recorded by of three-channel Diode Laser Spectrometer (DLS) [1]. The analytical channel consisted of a set of vacuum optical cells 20-200 cm long. The reference channel was used for DL frequency cycles stabilization and for absolute frequency scale calibration. The channel had a 20 cm^{-1} long vacuum cell with water vapor at low pressure and at temperature 23 ^0C. The third channel was used for DL frequency scale linearization. The spectra were recorded in spectral range 7184 - 7186 cm^{-1} using DFB pig-tail diode laser (NEL) using multichannel 16-bit input/output board (NI PCI-6052E). Date sampling rate for three channels in use was 111 kHz. Fabry-Perot etalon and fiber interferometer with free spectral ranges D* = 0.049268(2) $см^{-1}$ and 0.006495(7) $см^{-1}$, respectively, were used to calibrate DL frequency tuning. Accuracy of line centers determination was $2.5*10^{-5}$ cm^{-1}. Signal-to-noise ratio after 20 averaging of recorded spectra was 2 10^4.



Spectra of water vapor and gas mixtures H_2O : N_2, Ar, He, Xe, and air were recorded at different pressures. Gas mixtures were prepared in advance. Measurements were performed after several days after gas mixtures preparation to be sure about gas mixture homogeneity. As example figure presents recorded spectra for gas mixture H_2O:Xe=1,47 % for following experimental parameters: L = 2 m, P = 0 – 400 mBar.

Rautian-Sobel'man and Galatry line shape models were used for experimental data fitting. Universal Rautian asymptotic line shape model [2] was used for H_2O:Xe gas mixture. Set of spectral line parameters was obtained from the fitting and will be presented.

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C4

TUNABLE DIODE LASER SPECTROSCOPY (TDLS) BASED COMPLEX FOR THE AIRPLAN LABORATORY

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Federal Agency for Hydrometeorology of the Russian Federation creates the flying laboratory on the basis of the passenger airplane Yak-42D for geophysical monitoring of environment, including continuous aircraft vertical concentrations measurements of greenhouse gases in the troposphere. Within the frame of this project General Physics Institute of the Russian Academy of Science developed airborne TDLS based complex to measure altitude profiles of green-house gases (CO_2, CH_4, H_2O) and H_2O isotopes content.

TDLS complex contains 3 near IR diode lasers operating near 1.39, 1.6, and 1.65 mkm to measure H_2O, CO_2, and CH_4 respectively. The complex was integrated aboard in standard 19-inch rack. Air samples, taken from an aircraft pipeline were injected into the Chernin optical cell [1]. Using inflow and pressure stabilization systems, laminar air flow in Chernin cell was achieved at rate of 80 liter/min and reduced pressure 50 mBar. Above mentioned parameters are enough to detect water vapor isotopes narrow absorption lines [2].

Modulation-correlation technique [2, 3] was used to record absorption spectra and to process measurement of greenhouse gases concentration. Time of single measurement is about 30 milliseconds. Results obtained in real time are transfering to the airborne central computer. Sensitivity of TDLS measurements was estimated: 20-30 ppm for water, 3-4 ppm for CO_2, 20-25 ppb for CH_4.

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C5

HOMODYNE NOISE OF A BROADBAND RADIATION IN A NEAR INFRARED REGION

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The additional noise mechanism has been found during heterodyne measurements of a broadband radiation in near IR (see A3). This noise was recorded in case when only broadband radiation was detected. This mechanism identification is a subject of the present paper.

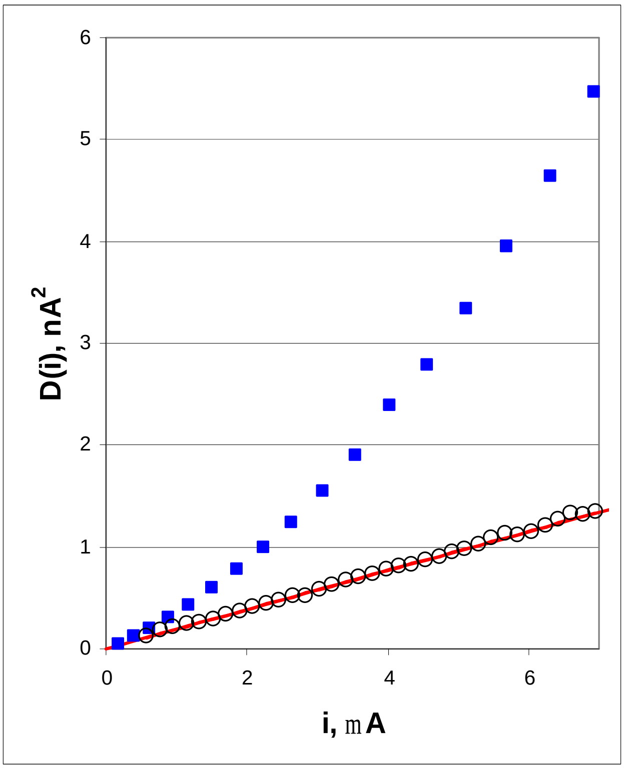

Fig.1 Dependence of photocurrent dispersion as a function of its value

Black open circles – detection of DL emission above the threshold (coherent radiation); solid blue squares - detection of DL emission below the threshold (broadband radiation)

For coherent DL radiation the noise observed is due to photocurrent shot noise (red line in Fig.1). For broadband radiation detection, in addition to the shot noise (first term in Eq.1) the heterodyne noise of broadband spectral components has to be considered (second term in Eq.1). Dispersion of the photocurrent noise (B is a bandwidth):

Eq.1
$$D(i) = eiB + \frac{i^2}{\Delta v} B$$

Here Δv – broadband radiation spectrum width. Due to Eq.1 the shot noise has a linear dependence of photocurrent. Broadband radiation noise has a square dependence of photocurrent. This dependence can be observed at Fig.1 proving that the excess noise is due to heterodyne noise of components of the broadband radiation spectrum.

C6

REMOTE SENSING OF METHANE WITH SOLAR OCCULATION TECHNIQUE USING NEAR INFARED HETERODYNE RECEIVER

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Near infrared heterodyne receiver has been developed, which uses a distributed feedback diode laser as a tunable local oscillator, for detecting methane in the atmosphere at 1.65 μ. The main problem of heterodyning in the near infrared range is the stringent requirements to alignment of the incident radiation fronts. Single mode silica fiber Y-coupler was used as a diplexer to solve this problem. Radiation mixed in a fiber was detected by a amplitude detector using two ***p-i-n*** diodes. The amplifier bandwidth was 2.5 MHz. Wavelength coverage of spectral measurement was provided by sweeping local oscillator frequency over 1.5 cm^{-1} spectral range. The receiver noise level is demonstrated to be 0.05% of the shot-noise level for averaging time ~ 12 minutes. Using Sun observations, atmospheric methane absorption line has been recorded. Achieved spectral resolution is constrained by local oscillator line width and stability, and constitutes about 2 MHz, which corresponds to resolving power of $\lambda/\delta\lambda \sim 10^8$.

The simplicity of the proposed scheme opens a perspective to use it for ultra-high resolution spectroscopy in various applications. In particular, it allows solar occultation observations of CO_2, CO, CH_4 and other gases from both spacecraft and ground-based platforms, as well as Doppler measurements of stratospheric winds.

C7

Determination of ethylene content in monosilane using TDLS

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Low temperature rectification is effective method of monosilane (SiH_4) ($T_{boiling}$ = -111.6 ^{0}C) purification. For monosilane purification under consideration, ethylene (C_2H_4) ($T_{boiling}$ = -103.5 ^{0}C) is the most difficult to remove impurity.

Traditional technique (gas chromatography with flame ionization detector) enables one to detect ethylene in inert gases up to level of 10^{-6} %. Investigations performed showed that because of chemical interaction between C_2H_4 with SiH_4 molecules ethylene in monosilane is labile impurity. For monosilane sample with low C_2H_4 concentration ($<10^{-3}$ %) during gas chromatography analysis part ethylene will be transferred to ethane (C_2H_6) and only ethylene part will reach detector. As result gas chromatography analysis is incorrect. Development of ethylene content determination in monosilane was objective of present paper.

For determination C_2H_4 content in monocilane TDLS was exploited. Pig-tail DFB DL with wavelength 1.62 μ (6172 cm^{-1}) was used as light source. C_2H_4 absorption coefficient near 6172 cm^{-1} is 0.08 cm^{-1}/atm. By fiber splitter DL radiation was split into three beams (one reference and two analytical channels). Reference channel contains reference cell filled with gas mixture of SiH_4 and C_2H_4: L = 80 cm, total P = 0.3 atm, C_2H_4 concentration - 1%. In analytical channel multy pass cell was used with optical path 40 m.

Ethylene and monosilane spectra were recorded in spectral range 6160-6180 cm^{-1}, for different pressures. Spectra obtained were analyzed and pressure dependence of ethylene line shape in monosilane was determined. Using investigations performed, method to measure C_2H_4 concentration in SiH_4 using TDLS was developed with detection limit ~10^{-4} %.

This method was tested during monosilane purification. Experiments performed demonstrated effectiveness of method developed to control ethylene impurity behavior during monosilane purification process. Using this method, samples of high purity monosilane were obtained.

C8

EXTERNAL-CAVITY QUANTUM CASCADE LASER AROUND 7.5 µm FOR THE DETECTION OF VARIOUS GASES

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Laser spectrometers based on semiconductor lasers provide good results for gas sensing in term of sensibility and selectivity because of the characteristic of these sources. Indeed, they commonly deliver power from 1 mW to #100 mW without the need for cryogenic cooling. Distributed feedback (DFB) configuration provides narrow linewidth which enhance selectivity. Besides, the development of quantum cascade lasers enables to reach the fundamental absorption bands of molecules in the mid-infrared region.

The main limitation of these sources is their low tuning range (~ 10 cm^{-1}) which prevents from monitoring complex species with broad absorption spectra in the infrared region. One way to obtain a broader tuning range is to implement a semiconductor laser in an external cavity system. We present the latest developments of a home-made external cavity - quantum cascade laser at 7.5 µm and its applications to gas sensing.

Aknowledgements:

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C9

Towards a miniaturized Helmholtz photoacoustic sensor for atmospheric gas detection

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Optical gas sensors are now indispensable for various aspects in our modern society particularly for high sensitivity trace detection. However, available optical gas sensors are bulky, complex, and expensive. Consequently they are not suitable for mass deployment. Among the possible advancements, the miniaturization of the gas sensor and the associated cost reduction are the main ways for mass deployment in many application areas with very high socio-economic implications as climate change and air quality controls.

Photoacoustic (PA) detection is a technique that can be used to detect trace levels of gases using optical absorption and subsequent thermal perturbations of the gases. A macroscopic cell design (V # 10 cm^3) that use the Helmholtz resonance was previously developed. As the technique has favorable detection characteristics when the system dimensions are scaled down, the realization of an integrated µ-PA cell design would be of great interest to generalize the use of such sensors. In the framework on the ANR ECOTECH project MIRIADE we aim at demonstrating the feasibility of a fully integrated optical gas sensor including a mid-IR source and a Helmholtz resonant µ-PA sensor.

In order to optimize the cost of development for such sensors, we must be able to accurately predict the response of the sensor. The classical description is used where the acoustical response of the PA cell is obtained by writing the pressure wave as the expansion over the eigenmodes of the cell. COMSOL Multiphysics ® is used to solve the Helmholtz equation in Pressure acoustics mode in order to obtain the eigenmodes, to normalize them and to calculate the thermal and viscosity losses. Even if this solution is sufficient for the macroscopic cell, the Helmholtz resonance is highly dependent on losses in the capillaries, and pressure acoustics in not necessarily well adapted due to strong coupling between pressure and temperature variations. Thus a thermoacoustics frequency domain study was developed for size reduction of the cell using the Acoustics module of COMSOL. The results are the demonstration that the evaluation of a photoacoustic cell response can be accurately done using Finite Element Modelling simulation for resonance frequencies, quality factors and for the amplitude of the generated pressure wave.

Acknowledgments : This work is funded by ANR ECOTECH project #ANR-11-ECOT-004 called “MIRIADE” (2012-2014). Christophe Risser acknowledges the Aerovia start-up for his Ph.D funding and Justin Rouxel acknowledges CEA for his one.

C10

ANALYSIS OF RANDOM NOISES AND LONG TERM DRIFT FOR TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY SYSTEM

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Tunable diode laser absorption spectroscopy (TDLAS) technology provides promising advantages of high sensitivity, fast response and highly specific in situ trace gas monitoring. To achieve adequate sensitivity for field applications of coal self-ignite alarming and harmful gas spilling detection, and meanwhile in order to be adaptable for the use of common installed communication-band single-mode fiber cable for beam transportation, near-infrared laser source has to be used. To satisfy these requirements TDLAS system requires long optical path to improve the sensitivity. For instance, for coal self-ignite alarming of CO field monitor, its sensitivity and resolution of ppm-level is strictly required by the State Regulations of Coal Mine Safety.

In this report we will briefly summarize our most recent progress made on developing a TDLAS system with novel miniaturized multi-pass cells for CO detection. The random noises and the slow drift, which limit the sensitivity and the long-term stability of the TDLAS system are critically analyzed and evaluated experimentally. Using a balanced optical path we have achieved six times suppression of drift amplitude. The CO concentration measurement using a multi-pass cell has shown that the sensitivity better than 0.36ppmv could be achieved with two balanced optical paths with an integration time of 20 seconds.

Acknowledgement: This work is mainly supported by national 863 high technology project (Grant No. 2007AA06Z420).

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C11

Measurement of positive gain in active media of oxygen-iodine laser with travelling microwave discharge

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The positive gain of active media of I+O_2-laser with travelling microwave discharge has been investigated. Pure oxygen and oxygen-helium mixture have been used for discharge at rate 1 mmol/s. The active media is made by nozzle array 10*50 mm^2. Excited oxygen passes via subsonic nozzles, while iodine with buffer gas (nitrogen or helium) passes via supersonic conic nozzles with half-angle of 10 degrees. Tunable diode laser 6025 Vortex (New Focus Inc.) is used for measurements of active media absorbance (positive gain). In-resonator technique of absorbance measurements is applied. Positive gain of (4-6)*10^{-6} cm-1 was obtained during the experiments.

C12

TDLS FRINGE REJECTION METHOD FOR FRINGES WITH FSR IN THE RANGE OF THE ABSORPTION LINE HWHM

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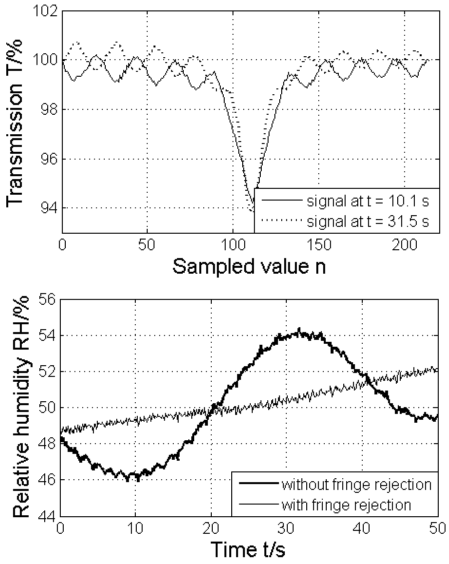
In TDLS systems interference fringes are in most cases a limiting factor for the concentration resolution. Especially when the optical path length is reduced to a few centimeters, fringes with a FSR comparable to the HWHM of the absorption line occur (e.g. water vapor at 1.854 microns: HWHM≈35 pm; fringe with 2 cm resonator length: FSR≈86 pm). A frequently used method to eliminate fringes is the use of vibrating components in the optical path (e.g. lenses), but this method leads to a more complex system design and a lower measurement rate. There are some arithmetical fringe rejection methods posted in the literature, but none of them is able to handle fringes with FSR in the range of the HWHM. Hodgkinson and Tatam summarize the different techniques [1].

We introduce an arithmetical method to eliminate interference fringes, whose FSR is in the range of the HWHM (Fig. 1, top). By transforming a Lorentzian shaped absorption line into the Fourier domain, it forms a decreasing straight trend in logarithmic scale (Fig. 1, bottom). An occurring interference fringe is represented as an isolated peak in the Fourier spectrum if the width of the measurement window is chosen well. We interpolate this peak and reconstruct the absorption line without fringe by means of the inverse Fourier transform. The resulting absorption line is evaluated by a simple curve fit. For a water vapor probe (laser wavelength 1.854 µm) with 2 cm optical cell length and the signal of Fig. 1, the influence of the fringe on the absorption is reduced from 0.7% to 0.021%, means the influence on the concentration decreases from 6.5% to 0.2% relative humidity.



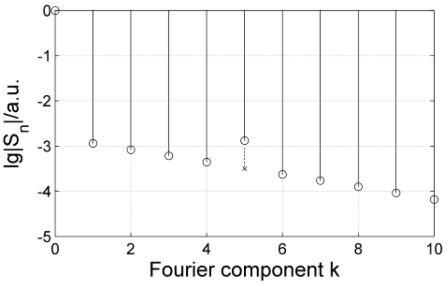


Fig. 1, left top: absorption signal including interference fringe;
left bottom: relative humidity while moving fringe test without (bold line) and with (normal line) fringe rejection
right: Fourier spectrum of absorption line including fringe (solid circles) and interpolated component (dotted cross)

[1] J. Hodgkinson, R. P. Tatam, Optical gas sensing: a review, Measurement Science and Technology 24, no. 1, (2013) 59pp.

C13

A PORTABLE ANALYZER FOR CO_2 ISOTOPIC COMPOSITION MEASUREMENTS USING A NOVEL MULTIPASS CELL DESIGN

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The CO_2 isotope ratios are of great interest for diverse applications such as medical, environmental, and climate research. Quantum cascade laser absorption spectroscopy has shown its potential to measure the CO_2 isotope ratios with very high precision. In recent studies, we have successfully demonstrated long-term remote measurements at ambient air concentrations.[1,2]

Here, we report on the development of a highly compact laser absorption spectrometer suitable for medical and environmental applications. The device employs a new multipass cell consisting of a diamond turned, 80 mm diameter copper cylinder with a toroidal surface carved into the plane of the recirculating light beam.[3] Since, the light beam is refocalized at each reflection from the toroidal surface, a minimal aberration of the laser beam is achieved. The cell geometry allows for a small detection volume of 40 ml, combined with a robust and easy optical alignment. Furthermore, the optical path in the cell can be adjusted from 16 cm to more than 4 m. Using this cell, we have demonstrated $\delta^{13}C$ and $\delta^{18}O$ measurements with a precision significantly below 0.1 ‰.

To obtain a small footprint of the optical set up (30 x 13 cm^2), we employed for the first time quantum cascade technology for both, the laser and the detector. The cw quantum cascade laser (QCL) packaged in an HHL housing emits at 2310 cm^{-1}, while the quantum cascade detector's (QCD) absorption is optimized for this spectral range. In this configuration, the concentrations of the four most abundant, stable CO_2 isotopes can be simultaneously analyzed. We demonstrate the suitability of this compact CO_2 isotope sensor for high precision and fast response measurements, as required for medical (*e.g.* for human breath analysis) and environmental applications.

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[2] B. Tuzson, J. Mohn, M.J. Zeeman, R.A. Werner, W. Eugster, M.S. Zahniser, D.D. Nelson, J.B. McManus, L. Emmenegger, Appl. Phys. B 92, 451 (2008).
[3] B. Tuzson, M. Mangold, H. Looser, A. Manninen, L. Emmenegger, Opt. Lett. 38, 257 (2013).

C14

MULTI-WAVELENGTH MEASUREMENT OF AEROSOL OPTICAL ABSORPTION COEFFICIENT WITH A PHOTOACOUSTIC SPECTROMETER

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Atmospheric aerosol absorption capacity is a critical parameter determining its direct [1] and indirect effect [2] on climate. Accurate measurement is highly requested for study of the radiative budget of the Earth. Photoacoustic spectroscopy (PAS) technique, observes aerosols on their natural suspended state, is commonly recognized as one of the best candidates to measure the optical absorption coefficient (OAC) of aerosols [3]. A multi-wavelength (405 nm, 532 nm, 780 nm) PAS based on a cylindrical acoustic resonator was developed. The acoustic resonator was operated on the first longitudinal mode, which had a resonance frequency of ≈1600Hz, a quality factor of ≈ 21. In order to calibrate the PAS, the specific absorption coefficient of NO_2 is calculated with the emission spectrum of the laser at 532nm and the absorption cross section of NO_2 provided by the HITRAN 2008 database [4] and described in detail for the first time, to our knowledge. A sensitivity of 1.3 Mm^{-1} for aerosol OAC measurement, which corresponded to an black carbon mass density of 130 $ng \cdot m^{-3}$ assuming an efficiency for optical absorption of 10 $m^2 \cdot g^{-1}$ [5], was demonstrated. OACs of atmospheric nigrosin aerosol and ambient aerosol at suburb of Hefei city were measured, at the mean time, absorption cross section and absorption Ångström exponent (AAE) were also determined for characterization of the component of the ambient aerosol.

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C15

COLLINEAR PHOTOFRAGMENTATION AND ATOMIC ABSORPTION SPECTROSCOPY FOR DETECTION OF KCl

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Detection of KCl and similar molecules using direct absorption measurement is a difficult task as the molecular spectra at UV wavelengths is broad and interfering absorption caused by other molecules is evident. It was shown that much more selective and sensitive measurement will be achieved using a UV pulse to dissociate K atom from KCl molecule and atomic absorption spectroscopy to detect the temporally increased atomic concentration. [1] Atomic spectroscopy yields to increased sensitivity and selectivity due to narrow linewidth of atomic spectrum.

In this work, we describe the use of collinear photofragmentation and atomic absorption spectroscopy (CPFAAS) in detection of KCl at ppm level concentrations in laboratory scale measurements having interaction lengths from 1 cm to 50 cm. Wavelength locking of the tunable diode laser and calibration of the measurement is discussed.

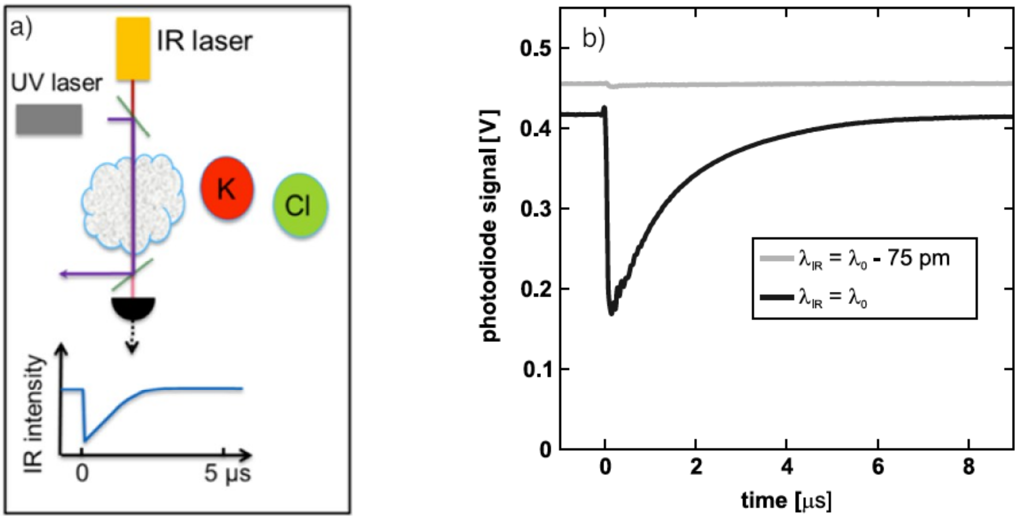

Fig.1 a) Principle of collinear photofragmentation and atomic absorption spectroscopy (CPFAAS). b) Transmission transients of a wavelength tunable diode laser at resonance with K atom absorption line and with 75 pm offset. UV pulse is launched at t = 0.

[1] T. Sorvajärvi, J. Saarela, and J. Toivonen, "Optical detection of potassium chloride vapor using collinear photofragmentation and atomic absorption spectroscopy," Optics Letters 37, 4011-4013 (2012).

C16

Single mode tunable semiconductor lasers with FBG

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In present paper results of development and investigation of diode lasers with FBG (Fiber Bragg Grating) will be presented (Fig.1).

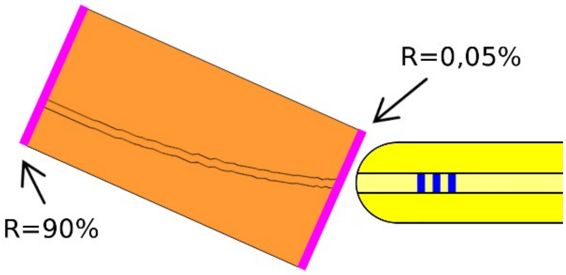

Fig.1 Scheme of DL with FBG.

InGaAs/GaAs and InGaAsP/InP heterostructures grown by MOS hydride epitaxy were used [1]. Length of DL crystal was 600 – 1000 μ, stripe width 3 μ. Laser modules with FBG for spectral range 635 - 1650 nm were developed. Details of DL modules structure (Fig.1) will be discussed. For spectral range 1300 - 1650 nm laser power was up to 150 mW. Stable single mode operation with line width less than 1 MHz was obtained for all spectral range under consideration. Mechanisms of both discrete and continuous modules tuning will be considered.

Laser frequency is determined by FBG period - Λ and effective optical distance between FBG and 90 % mirror. Continuous laser frequency tuning can be achieved within FBG reflection spectrum by changing laser temperature and excitation current [2]. Continuous frequency tuning range 0.15 – 1 nm depends on the grating in use selectivity. Laser frequency continuous tuning alternative is changing fiber reflective index (Fig.2). In present case FBG temperature was changed.

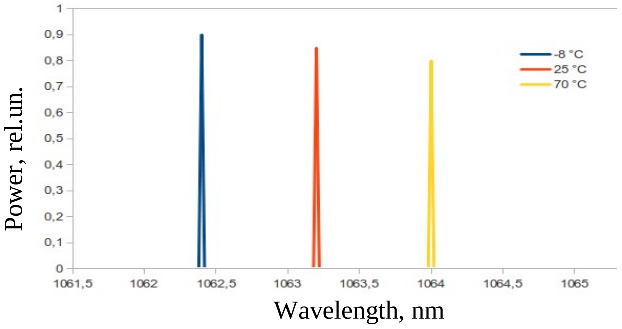

Fig.2. Emission spectra for -8, 25, and 70 °C.

For 150 and 20 mW emission power tuning was found to be 0.1 and 1.5 nm respectively.

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