

XX Anniversary of TDLS Conference 1995 – 2015



ABSTRACTS OF PAPERS
10th International Conference on
Tunable Diode Laser Spectroscopy

July 6 - 10, 2015
Moscow Russia

<http://tdls.gpi.ru/>



Organized by:

Connecticut College
New London, Connecticut USA

A.M. Prokhorov General Physics Institute
Russian Academy of Sciences, Moscow, Russia

Moscow Institute of Physics & Technology
Moscow, Russia

P.N. Lebedev Physical Institute
Russian Academy of Sciences, Moscow, Russia

Conference Chairs

Professor A. W. Mantz

Connecticut College
Department of Physics and Astronomy
270 Mohegan Avenue
New London, CT 06320-4196 USA
Phone: +1 (860) 439-5030
e-mail: awman@conncoll.edu

Professor A. I. Nadezhdinskii

A.M. Prokhorov General Physics Institute
Russian Academy of Sciences
38 Vavilov Street
Moscow 119991 Russia
Phone: +7 (499) 135-8281
e-mail: nad@nsc.gpi.ru

International Advisory Committee

Christof Janssen, UPMC Sorbonne University, Paris, France

Didier Mondelain, University Joseph Fourier, Grenoble, France

Alexander Rodin, Moscow Institute of Physics and Technology, Moscow, Russia

Trevor Sears, Brookhaven National Laboratory, Upton, NY, USA

Frank Tittel, Rice University, Houston, USA

Virginie Zéninari, University of Reims Champagne-Ardenne, Reims, France

Co-organizers:

- § **Space Research Institute of the Russian Academy of Sciences (Moscow, Russia)**
- § **Institute for Spectroscopy of the Russian Academy of Sciences (Troitsk, Russia)**
- § **Council on Spectroscopy of the RAS (Moscow, Russia)**
- § **Council on Analytical Chemistry of the RAS (Moscow, Russia)**

Sponsors:



Nanoplus Gerbrunn, Germany



Eblana Photonics Dublin, Ireland



DLS Lab Moscow, Russia



Dalian Actech Dalian, China

TDLS 2013 Conference Schedule

	JUL 6 MON	JUL 7 TUE	JUL 8 WED	JUL 9 THU	JUL 10 FRI
10:00 10:30	Registration				Optional Lab tours*
10:15 10:30	Opening Remarks				
10:30 11:30	A.Nadezhdinskii Russia L1	V.Zeninari France L4	D.Lisak Poland L7	I.Vinogradov Russia L10	
11:30 12:30	D.Mondelain France L2	M.Marangoni Italy L5	M.Bolshov Russia L8	H.Nakagawa Japan L11	
12:30 14:00	Lunch				
14:00 14:30	Poster Session A	Poster Session B	A.Pogany Germany O1	Poster Session C	
14:30 15:00			L.Hildebrandt Germany O2		
15:00 15:30			O.Anoshin Russia O3		
15:30 16:00					
16:00 17:00	F.Harren Netherlands L3	C.Janssen France L6	A.Farooq Saudi Arabia L9	I.Trofimov USA L12	
17:00				Closing Remarks	

*Optional Laboratory tours.

Spaces are limited, and there may be a charge for transportation.

Choices of possible sites to visit: Institute for Spectroscopy (Troisk), Moscow Institute of Physics and Technology, Space Research Institute, P.N.Lebedev Physical Institute, A.M.Prokhorov General Physics Institute.

Invited lectures

L1

Analytical Applications of Tunable Diode Laser Spectroscopy

A.Nadezhdinskii

A.M.Prokhorov General Physics Institute of RAS, Vavilov str. 38, 119991 Moscow, Russia

NAD@nsc.gpi.ru

Tunable Diode Laser Spectroscopy (TDLS) has been started several decades ago [1] when first high resolution molecular spectrum was recorded using diode laser. During its history TDLS passed the same steps as atomic and molecular spectroscopy: measurements of spectral line frequency, intensity, pressure broadening and shift for different molecules. Nowadays the most popular area of TDLS is analytical applications (see [2] of International TDLS conferences during last 20 years and selected papers of these conferences published in special issues).

Different TDLS applications have different requirements. The applications classification and optimization will be done based on dominant noise mechanism. There are three fundamental noise mechanisms in TDLS: PD noise, photocurrent shot noise, and DL quantum noise. For System with Topography Reflector (TR) DL Radiation is directed to TR (wall, grass, tree, etc.). Small part of scattered DL radiation is collected by receiving optics. PD noise dominates for this application and requirement is minimum Noise Equivalent Power (NEP). NEP = 1 pW was achieved. For heterodyning in Near IR spectral range photocurrent shot noise is dominating one. Heterodyne signal is also noise. It can be measured in units of photocurrent shot noise, because they have similar dependences of experimental parameters. Achieved level of heterodyne signal is 0.1 % of photocurrent shot noise for 10 min averaging. Two above mentioned applications deal with small signal detection and need significant molecular absorbance. For trace molecules detection requirement is minimum NEA (Noise Equivalent Absorbance). Achieved level $5 \cdot 10^{-8}$ corresponds to minimum detectable molecular concentration at ppt (parts per trillion) level.

Several TDLS based analytical systems were developed at GPI. These developments and tests will be discussed. A system with TR (altitude up to 5 km) can detect location of leakage from pipelines and determine leakage rate. For Near IR heterodyne spectrometer Sun light spectrum passed through atmosphere was recorded for the first time. CH₄ and CO₂ profiles in atmosphere were retrieved, wind speed was detected. TDLS complex for airplane laboratory can measure a concentration of CH₄, CO₂, H₂O, as well as isotope content of water vapor. TDLS complex for screening medical diagnostics was installed and tested at Moscow city clinical hospital #12. TDLS system developed demonstrated remote (more than 150 m) detection of explosives. TDLS complex (more than 15 instruments) was developed and installed to control hydrides (PH₃, AsH₃, NH₃, SiH₄, GeH₄) purification process.

REFERENCES

- [1] E. Hinkley, Appl.Phys.Lett., 16, pp. 351 (1970).
- [2] TDLS.gpi.ru, Spectrochimica Acta Part A, 52, #7 (1996); 55, #10 (1999); 58, #9 (2002); 60, #14 (2004); 63, #5 (2006); Applied Physics B, Volume 90, Issue 2, 2008; Volume 100, Issue 2, 2010; Volume 109, Issue 3 (2012).

THE NEAR IR WATER VAPOR ABSORPTION BY CRDS: EMPIRICAL LINE LIST AND CONTINUUM

D. Mondelain^{1,2}, *A. Campargue*^{1,2}, *P. Čermák*^{1,2,3}, *S. Kassı*^{1,2}, *S. N. Mikhailenko*^{4,5},
S. Vasilchenko^{1,2,6}

¹ *Univ. Grenoble Alpes, LIPhy, F-38000 Grenoble, France*

² *CNRS, LIPhy, F-38000 Grenoble, France*

³ *Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics,
Comenius University, Mlynská dolina F2, 842 48 Bratislava, Slovakia*

⁴ *Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, SB,
Russian Academy of Science, 1, Akademician Zuev square, 634021, Tomsk, Russia*

⁵ *Math. Physics Department, Tomsk Polytechnic Univ. 30, Lenin av., 634050, Tomsk, Russia*

⁶ *Laboratory of Molecular Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, SB,
Russian Academy of Science, 1, Akademician Zuev square, 634021 Tomsk, Russia*

The importance of water vapor in radiative budget and in climate change is directly linked to the dominant contribution of water vapor to the total atmospheric absorption. Moreover, the atmospheric transparency windows are used for atmospheric remote sensing and for quantifying the contribution of geophysical elements with spectrally large optical signature like surface albedoes, clouds and aerosols. In the mid- and near-infrared atmospheric windows, water vapor lines and water continuum both contribute to absorption and require accurate determination for atmospheric applications.

During the last years, we have used Cavity Ring Down (CRD) spectroscopy to study the water vapor absorption spectrum. We have at our disposal a set of CRD spectrometers coupled to different laser sources allowing us to cover the 5850 – 8337 cm⁻¹ region with high sensitivity (minimum detectable absorption coefficient as low as 2×10⁻¹¹ cm⁻¹) and dynamic range (about 4 orders of magnitude). Recently, we have also developed a new CRD spectrometer working around 4250 cm⁻¹.

An empirical line list for “natural” water vapor at 296 K was constructed in the 5850–8337 cm⁻¹ region [1,2] by gathering separate CRDS line lists, complemented with literature data for the strongest lines. The list includes more than 42000 transitions of four major water isotopologues (H₂¹⁶O, H₂¹⁸O, H₂¹⁷O and HD¹⁶O). The obtained line list is believed to correct a number of insufficiencies of the HITRAN2012 list in the region.

We have also used the CRDS technique to investigate the water vapor continuum in the 1.6 and 2.3 μm windows [3,4]. The self-continuum cross sections, C_s , were retrieved from the quadratic dependence of the spectrum base line level measured for different pressures, after subtraction of the local water monomer lines contribution. These C_s values are found in reasonable agreement with the latest version of the MT_CKD model but in disagreement with recent FTS measurements. Additional measurements on the foreign-continuum cross sections and temperature dependence of the self-continuum cross sections will also be presented.

1 S. Mikhailenko, D. Mondelain, S. Kassı and A. Campargue A, JQSRT, 140, 48–57 (2014).

2 A. Campargue, S. Mikhailenko, B. Guillo Lohan, E.V. Karlovets, D. Mondelain and S. Kassı, JQSRT, 157, 135–152 (2015).

3 D. Mondelain, S. Manigand, S. Kassı and A. Campargue, J. Geophys. Res. Atmos., 119, 5625–5639 (2014).

4 D. Mondelain, S. Vasilchenko, P. Čermák, S. Kassı and A. Campargue (submitted).

L3

Laser-based trace gas detection within biology and human health science

Frans J.M. Harren

*Life Science Trace Gas Facility, Institute of Molecules and Materials,
Radboud University, P.O. Box 9010, NL-6500 GL, the Netherlands*

E-mail address: F.Harren@science.ru.nl

There is a growing interest to develop laser systems (Quantum Cascade lasers, Optical Parametric Oscillators) in the mid-infrared wavelength region for trace gas detection, with applications in environmental sciences, biology, agriculture and medical sciences. Nowadays, such lasers provide relatively high output power and narrow linewidth and emit at any desired wavelength within the infrared wavelength. Accurate detection of specific gases becomes into reach thanks to the infrared fingerprint absorption spectrum of molecular gases in this wavelength region and the exact tuning capabilities of lasers. When the lasers are combined with sensitive spectroscopic techniques, such as photoacoustic spectroscopy or Integrated Cavity Output Spectroscopy (ICOS), gases can be determined extremely sensitive under atmospheric conditions.

Here, the performance of OPOs and Quantum cascade lasers for trace gas sensing is demonstrated with off-axis ICOS, and an improved detection configuration is demonstrated using a three-mirror configuration. The system was used for the detection of the important gaseous plant hormone ethylene; the latter was emitted from apples, stored under controlled atmosphere conditions. With a similar system we demonstrate the gas exchange of plants of Nitric Oxide, absorbed within the plant by healthy tissue and emitted under pathogen attack.

Within microbiological/medical related research there is an increasing interest in the development of sensitive and selective methods for breath analysis for reliable and non-invasive monitoring of lung diseases. Here we will focus on *Pseudomonas Aeruginosa* (PA) bacteria; these bacteria a relatively harmless to healthy persons, but not for Cystic Fibrosis (CF) patients. We present the real-time monitoring of hydrogen cyanide (HCN) production from *P. aeruginosa* strains *in vitro*, using laser-based photoacoustic spectroscopy. Simultaneously, the production of ammonia (NH₃) was measured, and the influence of different factors (medium, temperature, and antibiotics treatment) was assessed. Both reference strains and clinical isolates of patients with CF were studied, and compared to other pathogens commonly present in lungs/airways of CF patients.

L4

BROADLY TUNABLE MID-INFRARED QCL-BASED SOURCES FOR SPECTROSCOPY AND APPLICATIONS

Virginie ZENINARI

*Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR 7331 CNRS, Université de Reims
Faculté des Sciences, Moulin de la Housse, BP 1039, 51687 Reims Cedex 2 – France
virginie.zeninari@univ-reims.fr*

Laser spectrometers based on tunable diode lasers provide good results for gas sensing and spectroscopic measurements in terms of sensibility and selectivity thanks to the characteristics 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 that enhances selectivity. Finally, 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 ($\sim 10 \text{ cm}^{-1}$) that prevents from monitoring complex species with broad absorption spectra in the infrared region or realizing spectroscopic studies on a whole vibrational spectroscopic band of a molecule of atmospheric interest such as water vapor, carbon dioxide or methane.

In a first part I will present one way to obtain a broader tuning range that is to implement a semiconductor laser in an external cavity system. A commercial external-cavity quantum cascade laser emitting at $10.5 \mu\text{m}$ will be used to demonstrate photoacoustic gas sensing of heavy molecules such as butane and the possibility to measure spectroscopic parameters of carbon dioxide on a whole vibrational band [1]. Then developments of a lab-made external cavity - quantum cascade laser emitting at $7.5 \mu\text{m}$ and its applications to detection of acetone and POCl_3 in gas phase will be demonstrated [2]. In a second part I will present new and original developments on coherent quantum cascade laser array mounted in external cavity [3]. Finally I will present recent commercial developments on quantum cascade laser arrays that permit to develop broadly tunable mid-infrared sources without active mechanical system [4]. One of these sources operating in pulse mode is currently under study in our lab.

References

- [1] D. Mammez, C. Stoeffler, J. Cousin, R. Vallon, M.H. Mammez, L. Joly, B. Parvitte, V. Zeninari, Photoacoustic gas sensing with a commercial external-cavity quantum cascade laser at $10.5 \mu\text{m}$, *Infrared Physics and Technology* 61, pp. 14-19 (2013) <http://dx.doi.org/10.1016/j.infrared.2013.07.002>
- [2] D. Mammez, R. Vallon, B. Parvitte, M.H. Mammez, M. Carras, V. Zeninari, Development of an external-cavity quantum cascade laser spectrometer at $7.5 \mu\text{m}$ and applications to gas detection, *Applied Physics B*, 116 (4), pp. 951-958 (2014) <http://dx.doi.org/10.1007/s00340-014-5782-5>
- [3] R. Vallon, B. Parvitte, G. Maisons, M. Carras, V. Zéninari, Coherent quantum cascade laser array at $8.2 \mu\text{m}$ in extended-cavity system, *Optics InfoBase Conference Papers LACSEA*, (2014) <http://dx.doi.org/10.1364/LACSEA.2014.LM4D.2>
- [4] <http://eosphotronics.com> or <http://mirsense.com>

FREQUENCY COMB CALIBRATED SPECTROSCOPY IN THE MID-INFRARED

*D. Gatti¹, N. Coluccelli¹, A. Castrillo², T. Sala¹, M. Cassinerio¹,
G. Galzerano¹, L. Gianfrani², P. Laporta¹, M. Marangoni¹*

¹ *Istituto di Fotonica e Nanotecnologie - CNR and Dipartimento di Fisica - Politecnico di
Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy*

² *Dipartimento di Matematica e Fisica - Seconda Università di Napoli,
Viale Lincoln 5, 81100 Caserta, Italy
marco.marangoni@polimi.it*

The fine, discrete, stable, reproducible and controllable spectral structure of a frequency comb, as well as the possibility to get it referenced to a primary microwave standard, make optical frequency combs ideal tools to obtain on one side precision and absolute frequency calibration in the spectroscopic detection of individual absorption lines, and on the other side to develop a new class of spectrometers where broadband coupling of combs to passive optical cavities allows extreme sensitivity to be conjugated with spectral resolution, broad spectral coverage and fast acquisition times. In this work we will give particular emphasis to the first field and in particular to the development of comb-assisted spectrometers operating in the mid-infrared spectral region, i.e the region of utmost interest for fingerprinting and sensing of molecular targets.

The referencing to a frequency comb of a mid-infrared quantum-cascade-laser used as a probe of the molecular absorption laser is not trivial since commercial comb synthesizers lie in the near-infrared region. Solving this problem requires nonlinear optical schemes to be developed: two of them will be reviewed here, as based on difference- and sum-frequency-generation processes (DFG and SFG, respectively). Experimental results will be reported on CO₂ spectroscopy at 4.3 μm by SFG-lock to an Er-comb (1.55 μm) [1], on NH₃ spectroscopy at 9.1 μm by SFG-lock to a Tm-comb (1.95 μm) [2], on N₂O spectroscopy at 8.6 μm by DFG-lock to an Er-comb [3].

- [1] D. Gatti, A. Gambetta, A. Castrillo, G. Galzerano, P. Laporta, L. Gianfrani, and M. Marangoni, "High-precision molecular interrogation by direct referencing of a quantum-cascade-laser to a near-infrared frequency comb," *Opt. Express* 19, 17520-17527 (2011)
- [2] A. A. Mills, D. Gatti, J. Jiang, Ch. Mohr, W. Mefford, L. Gianfrani, M. Fermann, I. Hartl, and M. Marangoni, "Coherent phase lock of a 9 μm quantum cascade laser to a 2 μm thulium optical frequency comb," *Opt. Lett.* 37, 4083-4085 (2012)
- [3] A. Gambetta, M. Cassinerio, N. Coluccelli, E. Fasci, A. Castrillo, L. Gianfrani, D. Gatti, M. Marangoni, P. Laporta, and G. Galzerano, "Direct phase-locking of a 8.6- μm quantum cascade laser to a mid-IR optical frequency comb: application to precision spectroscopy of N₂O," *Opt. Lett.* 40, 304-307 (2015)

L6

ATMOSPHERIC AND LABORATORY HIGH RESOLUTION SPECTROSCOPY OF OZONE USING FTIR AND TDL TECHNIQUES

C. Janssen, C. Boursier, H. Elandaloussi, P. Jeseck, M. Minissale, Y. Té, T. Zanon

LERMA, Observatoire de Paris, PSL Research University, CNRS, UMR 8112, F-75014, Paris, France

Sorbonne Universités, UPMC Univ Paris 6, UMR 8112, LERMA, F-75005 Paris, France

Atmospheric remote sensing of ozone is of major concern for understanding atmospheric change and the climate system (eg Global Atmospheric Watch (GAW) / Global Climate Observation System (GCOS) programs of the World Meteorological Organization (WMO)). Ozone remote sensing depends on reliable spectroscopic data on this important trace gas. We review the literature and present recent results of ground based atmospheric FTIR (Fourier Transform InfraRed) measurements using the Paris-FTS (Fourier Transform Spectrometer) instrument [1], that illustrate the limitations of spectroscopic data provided by current data bases [2, 3] in the medium infrared region [4].

New measurement strategies, which cope with these requirements, and first results based on high resolution FTIR and TDL systems are presented. While the FTS provides broad spectral coverage for multi-spectral comparisons, the TDL (Tunable Diode Laser) systems allow for very high spectral resolution. TDLS systems are therefore ideally suited for line-shape and pressure shift studies. We present an interferometrically stabilized TDL spectrometer [5] and a free running QCL (Quantum Cascade Laser) for ozone line intensity, pressure-shift and time-resolved kinetic studies.

- [1] Y. Té, P. Jeseck, S. Payan, I. Pepin, C. Camy-Peyret, *Rev. Sci. Instr.* 81, 103102 (2010).
- [2] L. Rothman *et al.* *J. Quant. Spectrosc. Radiat. Transfer.* 130, 4–50 (2013).
- [3] N. Jacquinet-Husson *et al.*, *J. Quant. Spectrosc. Radiat. Transfer.* 112, 2395–2445 (2011).
- [4] Y. Té, P. Jeseck, C. Boursier, and C. Janssen, *J. Molec. Spectrosc.* to be submitted
- [5] A.Valentin, *Spectrochim. Acta A*, 52, 823 (1996).

ALTERNATIVE METHODS OF CAVITY ENHANCED ABSORPTION SPECTROSCOPY

D. Lisak *, *A. Cygan*, *P. Wcisło*, *S. Wójtewicz*, *P. Masłowski*, *R. Ciuryło*

Institute of Physics, Faculty of Physics, Astronomy, and Informatics, Nicolaus Copernicus University, Grudziądzka 5, 87-100 Toruń, Poland

* dllisak@fizyka.umk.pl

The photon lifetime in the optical cavity, commonly measured from the exponential light decays in cavity ring-down spectroscopy (CRDS), is directly related to the spectral width of the cavity resonant modes. This phenomenon is exploited in a relatively new technique called cavity mode-width spectroscopy (CMWS) [1-3] in which absorption spectrum can be retrieved by precise measurements of half-widths of the cavity modes. Qualitative analysis of CRDS and CMWS methods reveals their complementarity in terms of achievable accuracies at different levels of intra-cavity absorption [2]. For low absorptions the best precision is expected with the CRDS technique [4], where the ring-down decays are long enough to be accurately measured. In the opposite case of high absorption and short ring-down time, the cavity modes become broad and the precision of CMWS should be enhanced.

Absorption is always associated with dispersion, manifested as shifting of the resonant modes in the cavity-enhanced experiment. Measurement of dispersion mode shifts provides another possibility for very accurate quantitative spectroscopy. Since frequency is a physical quantity that can be measured most accurately, direct measurement of absolute or differential mode frequencies to obtain absorption coefficient in cavity mode dispersion spectroscopy (CMDS) should eliminate potential problems with nonlinearities of detection system and minimize contribution of systematic instrumental errors of measured spectra.

Typical mode widths of the cavities used in high-sensitivity cavity-enhanced absorption spectroscopy are at kHz level. Therefore a laser used in CMWS must be extremely narrow spectrally and precisely tunable. We demonstrate system which enables measurements of mode widths and their relative positions with sub-Hz precision.

These new cavity-enhanced techniques should be especially useful in applications that require high accuracy of weak absorption measurements, such as gas spectroscopy for atmospheric monitoring and gas metrology, Doppler thermometry, as well as fundamental study of spectral line shapes. Direct comparison of spectra obtained with various cavity-enhanced techniques allows to identify source of potential systematic instrumental errors at sub-percent level of accuracy required in modern applications.

[1] K. Nakagawa *et al.*, *Opt. Commun.* **107**, 369 (1994).

[2] A. Cygan *et al.*, *Opt. Express* **21**, 29744 (2013).

[3] D. A. Long *et al.*, *Appl. Phys. B* **114**, 489 (2014).

[4] S. Wójtewicz *et al.*, *J. Quant. Spectrosc. Radiat. Transfer* **130**, 191 (2013).

MEASUREMENTS OF TEMPERATURE AND WATER VAPOR CONCENTRATION BY ABSORPTION SPECTROMETRY WITH DIODE LASERS

*V.V.Liger¹, Yu.A.Kuritsyn¹, V.R.Mironenko¹, M.A.Bolshov¹
Ya. Ya. Ponurovskii², O.M. Kolesnikov³*

¹*Institute for Spectroscopy RAS, 5 Fizicheskaya str., 142190 Troitsk, Moscow, Russia*

²*A.M. Prokhorov General Physics Institute, 38 Vavilov str., 119991 Moscow, Russia*

³*N.E. Zhukovsky Central Aerohydrodynamic Institute, 140180 Zhukovsky, Moscow reg.,
Russia*

Tunable Diode Laser Absorption Spectrometry (TDLAS) is now the most applicable technique for diagnostics of the combustion. The technique is based on the registration of the transient absorption spectra of a target molecules and fitting of the experimental spectra by the simulated ones constructed using the spectroscopic databases. The temperature is inferred from the ratio of the intensities of the absorption lines with different low energy levels. In case of relatively low total pressure (< 1 atm) the absorption lines are narrow, so that one can select a spectral range with several resolved or slightly overlapping absorption lines within a tuning range of a single DFB laser ($\sim 1.5\text{--}2$ cm^{-1}). For such a case the fitting can be adequately performed. The efficiency and potentials of the developed H_2O sensor is tested by detection of the parameters of the hot tail of combustion in the mixing supersonic flows at reduced pressure (250 – 400 Torr).

Two algorithms of data processing were compared. The first algorithm is based on the fitting of the transient experimental spectra by the simulated ones, using temperature as a parameter. Another approach is based on the simulation of the set of spectra with the interval $\Delta T = 50$ K and calculation of the correlation function with the experimental spectrum. Temperature is inferred from the maximum of the correlation function.

In case of high gas pressure (> 1 atm) the H_2O absorption lines are broadened which makes the selection of the resolved lines within the narrow tuning range of a single DFB laser very problematic. The alternative approach for the high pressure sensing of the hot zones is the use of two DFB lasers radiating in different spectral ranges. This approach extends the possibility to select the optimal strong absorption lines from different spectral ranges. Different combinations of the excitation wavelengths are theoretically examined with the emphasis on the attainable precision of the temperature evaluation.

The new TDLAS system for the measurements of the temperature up to 2500 K and gas pressure up to 3 atm is developed. The peculiarities of the optical scheme, electronic system for TDLs tuning and data recording will be presented.

The efficiency of the developed technique was exemplified in the first set of the experiments in Zhukovsky Central Aerohydrodynamic Institute (TsAGI).

L9

QUANTUM CASCADE LASER SENSORS FOR CHEMICALLY REACTING FLOWS

A.Farooq, E.Essebbar, U.KC, M.B.Sajid, A.E.Alquaity, E.F.Nasir

Chemical Kinetics and Laser Sensors Laboratory, Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia
aamir.farooq@kaust.edu.sa

Quantum cascade laser (QCL) technology has evolved significantly over the last decade. Thermoelectrically cooled, narrow linewidth, and mode-hop-free QCLs are now available over a wide range of wavelengths (4 – 14 μm). These lasers have revolutionized sensor technology by providing access to the fundamental vibrational bands of a number of molecular species.

This talk will present some recent applications of QCLs in chemically reacting flows for the detection of trace species and for the measurement of reaction rate coefficients.

- (i) Hydrogen peroxide (H_2O_2) is measured near 8 μm using an external-cavity QCL and the sensor is utilized to measure the rate coefficient of hydrogen peroxide thermal decomposition [1].
- (ii) Pulsed cavity ringdown spectroscopy (CRDS) is applied near 10.5 μm to measure trace levels of ethylene (C_2H_4) with high time-response [2].
- (iii) Acetylene (C_2H_2) is detected near 13.7 μm using a distributed feedback QCL and the sensor is utilized to understand the role of C_2H_2 in soot formation.
- (iv) Carbon dioxide (CO_2) is measured in the fundamental vibrational band near 4.3 μm to study rate coefficients of $\text{CO} + \text{OH}$ and $\text{CO} + \text{O}$ elementary reactions.

References:

- [1] M.B.Sajid, E.Essebbar, T.Javed, C.Fittschen, and A.Farooq, *IJCK*, 46, 275 – 284 (2014)
- [2] A.E.Alquaity, E.Essebbar, and A.Farooq, *Optics Express*, 23, 7217-7226 (2015)

DIODE LASER SPECTROSCOPY FOR THE STATIONERY LANDING PLATFORM OF THE EXOMARS-2018 MISSION

I. Vinogradov^{1,2}, A. Rodin^{2,1}, V. Barke¹, A. Fedorova¹, N. Ignatiev¹, O. Korablev¹, Yu. Lebedev¹, O. Roste¹, O. Benderov², D. Churbanov², A. Klimchuk², V. Krasnopolsky², N. Pereslavytseva², V. Semenov², D. Shaposhnikov², A. Ushakov², A. Kalyuzhnyi³, A. Nadezhdinskiy⁴, M. Spiridonov⁴, Ya. Ponurovskiy⁴, G. Durry⁵, L. Joly⁵, J. Cousin⁵, N. Amarouche⁶, L. Labadie⁷, M. Sornig⁷, R. Thomson⁸, P. Moiseev⁹.

¹Space Research Institute of the Russian Academy of Sciences (IKI RAS), 117997, 84/32 Profsoyuznaya str., Moscow, Russia; ²Moscow Institute of Physics and Technology (MIPT), Institutsky dr. 9, Dolgoprudny, Moscow Region, Russia; ³Special Design Bureau of Space Device Engineering of IKI RAS, 249100, Tarusa, Kaluga Region, Russia; ⁴Prokhorov General Physics Institute of the Russian Academy of Sciences (GPI RAS), 119991, Vavilov str., 38, Moscow, Russia; ⁵GSMA, UMR CNRS 7331, Université de Reims, BP 1039, 51687 Reims, Cedex 2, France; ⁶Division Technique de l'Institut National des Sciences de l'Univers, CNRS, 92195 Meudon Cédex, France. ⁷I. Physikalisches Institut, Universität zu Köln, Köln, Germany; ⁸Scottish Universities Physics Alliance (SUPA), Institute of Photonics and Quantum Sciences, Heriot-Watt University, Edinburgh, United Kingdom; ⁹SPE Astron Electronics Ltd., Veselaya str., 2, Orel, Russia.

An experiment “M-DLS” (Multi-channel Martian Diode Laser Spectrometer) have been proposed [1] for the stationery Landing Platform of the ExoMars-2018 mission for long term studies of chemical and isotopic composition, structure and dynamics of the Martian atmosphere using IR laser and heterodyne spectroscopy.

The M-DLS instrument is targeted for studies of:

- Chemical and isotopic composition of atmosphere near the Martian surface, its diurnal and seasonal variations during one Martian year,
- Integral chemical and isotopic composition of the Martian atmosphere at low scales of altitude at the stationery Landing Platform location, and its variations in respect to local time at the light time of a day,
- Thermal and dynamic structure of the lower Martian atmosphere and its variations in local time during the day-light time.

Periodic measurements of molecular absorption spectra will be carried out in the M-DLS analytical channels (see Fig.1), including:

- Active measurements in a single volume multi-component Integrated Cavity Output Spectroscopy (ICOS) cell which will be linked to the ambient atmosphere by a specialized gas sampling system,
- Passive heterodyne measurements of the atmospheric transmission by direct Sun observations at various zenith angles, with the use of a proprietary miniature Sun tracking telescope.

Measurements will take place in series of narrow-band (2 cm^{-1}) intervals near the telecom wavelengths of 1.39, 1.56, 1.60 microns, and near 2.64, 2.78, 3.27 microns with high spectral resolution of $\sim 0.0003 \text{ cm}^{-1}$, providing for detailed contour resolution and Doppler wind measurements. Long effective optical paths of $\sim 10^{3-4}$ m order, which are specific both for ICOS cell and for direct observations of the Sun from the landing point, will result in high precision of relative absorption measurements in the line contour.

We will measure content variations of CO_2 , H_2O , CO , CH_4 molecules, of isotopic ratios D/H , $\text{O}^{18}/\text{O}^{16}$ in water vapor and of $\text{C}^{13}/\text{C}^{12}$, $\text{O}^{18}/\text{O}^{16}$ in CO_2 with accuracy of 0.1..1.0%%, and probably of $\text{O}^{17}/\text{O}^{16}$ and $\text{C}^{13}\text{O}^{18}/\text{C}^{12}\text{O}^{16}$, and we will estimate temperature and pressure vertical profiles, water vapor contents and wind velocity projection to the direction of Sun. Continuous, highly accurate (expected sensitivity ~ 70 ppt) measurements near the surface and in the atmospheric column at the fixed point of landing will contribute to the campaign for search of methane in the Martian atmosphere.

With numerous engineering and photonic solutions implemented for the first time in space applications, M-DLS experiment opens a unique opportunity to monitor Martian atmosphere with unprecedented accuracy. Further implications of the approach for future Lunar, Venusian and other planned missions is a promising area of infrared instrumentation development.

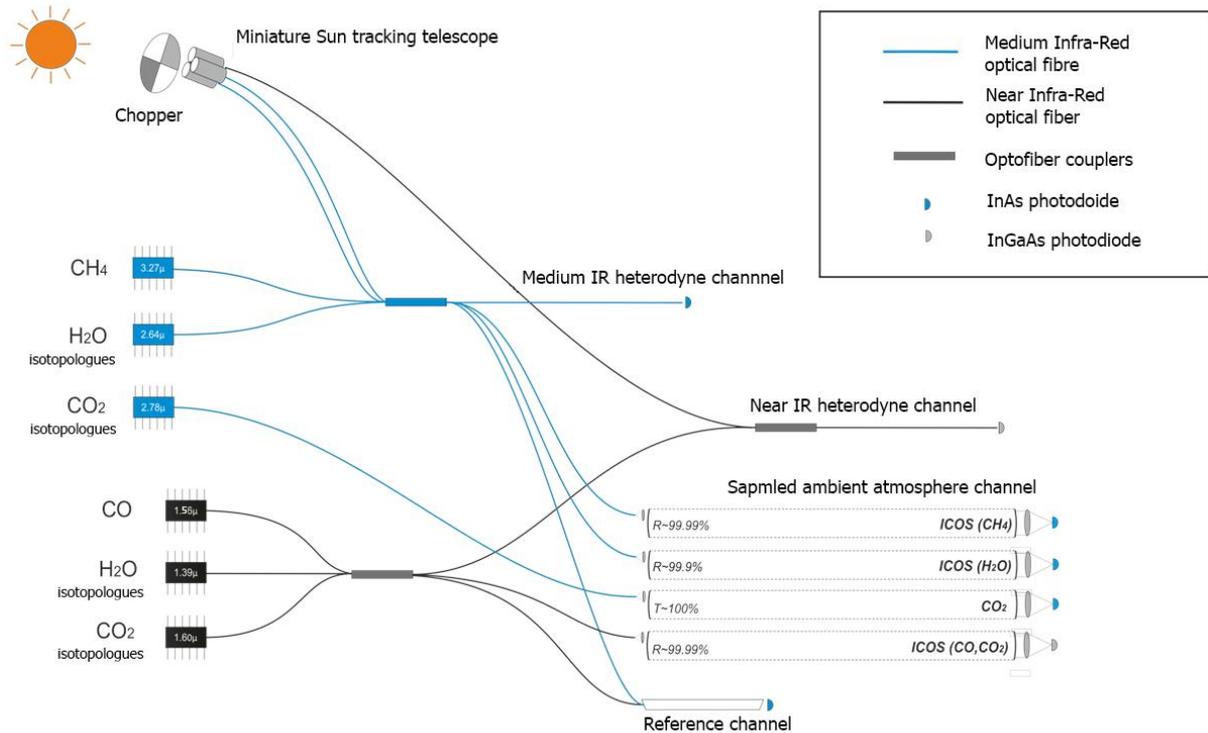


Fig.1 Optical scheme of the M-DLS instrument. DFB-laser output and sunlight, passed through the atmosphere, are distributed through the analytical and reference optical channels via single mode optical fiber system.

References:

- [1] I. Vinogradov, V. Barke, A. Klimchuk, V. Krasnopolsky, A. Rodin, N. Amarouche, O. Benderov, D. Churbanov, J. Cousin, G. Durry, A. Fedorova, I. Filatov, M. Gerasimov, N. Ignatiev, A. Ignatov, L. Joly, A. Kalyuzhnyi, L. Labadie, Yu. Lebedev, A. Nadezhdinskii, N. Pereslavl'tseva, Ya. Ponurovskiy, O. Roste, M. Sornig, M. Spiridonov, R. Thomson, A. Titov M-DLS – a multichannel diode laser spectrometer for Martian studies. The 40th COSPAR Scientific Assembly, 2-10 August, 2014, Moscow, Russia, report #B0.2-0038-14STW-L-118.

Scientific capabilities and measurement sensitivities of the infrared laser heterodyne spectroscopy

H. Nakagawa¹, Y. Kasaba¹, H. Sagawa², S. Aoki³, I. Murata¹, K. Takami¹, G. Sonnabend⁴, M. Sornig⁵, M. Kagitani¹, T. Sakanoi¹, J. Kuhn⁶, J. Ritter⁶, and S. Okano⁶

1. Tohoku University, Aramaki Aza Aoba 6-3, Aoba-ku, Sendai, Miyagi, 980-8578, Japan.
2. Kyoto Sangyo University, Motoyama, Kamigamo, Kita-ku, Kyoto, 603-8555, Japan.
3. Istituto di Astrofisica e Planetologia Spazialia, Istituto Nazionale di AstroFisica, Italy
4. Radiometer Physics GmbH, Meckenheim, Germany
5. German Aerospace Center (Deutsches Zentrum für Luft -und Raumfahrt), Germany
6. University of Hawaii Institute for Astronomy, USA

A new IR laser heterodyne instrument with ultra-high spectral resolution ($R > 10^6$) in 7-12micron is developed for continuous monitoring of planetary atmosphere using dedicated telescope at Mt. Haleakala, Hawaii. Here we introduce the scientific capabilities and measurement sensitivities of the IR heterodyne spectroscopy.

Ultra-high resolution spectroscopic measurement in the mid-IR is one of the most powerful tool to explore the planetary atmospheres with several key capabilities: (1) fully resolved molecular features to address the atmospheric temperature profiles, abundance profiles of the atmospheric compositions and their isotopes, (2) direct measurement of the mesospheric wind and temperature with high precision, (3) sensitive detection of minor trace gases, and (4) its small beam size capabilities to allow global mapping[1]. The instrument is set on the Coude focus of the Tohoku 60cm-telescope at Mt. Haleakala to demonstrate the feasibility[2]. The dedicated use of the telescope provides continuous operation, for understanding the variable nature and evolutions of the planetary atmospheres. One of the most important advantages of this instrument is that several room-temperature type quantum cascade lasers (QCLs, 100mW output for each in 7.7, 8.0, 9.6, and 10.3 micron) are installed as a local oscillator to allow many molecules of atmospheric and astronomical interest in the mid-infrared to be observed. Thanks to its tuneability, we can cover a wide range in the mid-IR region.

The scientific capabilities and measurement sensitivities are specifically investigated by the radiative transfer model: Advanced Model for Atmospheric TeraHertz Radiation Analysis and SimUlation (AMATERASU) that is being developed in the framework of the NICT [3]. Good temperature retrieval is achieved from surface to 30km on Mars with better than 10K precision and 10km vertical resolution, and from 70km to 80km on Venus with better than 5K precision and 2km vertical resolution. Wind retrieval is achieved from 80km to 90km with 40m/s uncertainty and 10km vertical resolution. The local wind and temperature is directly derived from the CO₂ non-LTE emission at the middle atmospheres with 11m/s in velocity and 12K in temperature accuracies. Detection of trace gases is performed without any ambiguity by migrating with terrestrial absorptions.

References to a Journal publication:

- [1] Sonnabend *et al.*, *JQSRT*, **109**, 1016-1029, 2008.
- [2] Sakanoi, *et al.*, *Proc. SPIE*, 9147, Ground-based and Airborne Instrumentation for Astronomy V, 91478D, doi:10.1117/12.2055877, 2014.
- [3] Baron *et al.*, *J. NiCT*, **55**, 109, 2008.

Quantum Cascade Lasers in Bio-Medical Applications.

Igor Trofimov

AKELA Laser Corporation

1095 Cranbury South River Road, Jamesburg, New Jersey 08831, USA

Igor.Trofimov@akelalaser.com

Recent advances in Quantum Cascade (QC) laser technology have revitalized interest in the mid-infrared (mid-IR) spectral range for bio-medical applications. The mid-IR spectral range hosts the strongest absorption lines of molecules due to their fundamental vibrations. Mid-IR spectral analysis of complex biological systems has a potential to detect, quantify, and monitor minute changes in biochemistry of tissues due to disease. It can be performed with high sensitivity (better than part per billion) and extraordinary specificity. It does not require exogenous labels or dyes, and in many cases enables in-situ and non-invasive diagnostics. Furthermore, targeted excitation of specific molecules can be used for photo-excitation of desirable chemical processes in cells and tissues and for precision laser surgery.

Despite high expectations, mid-IR methods have not entered mainstream medical practice mainly because the only light sources suitable for these applications are the unique scientific installations such as the synchrotron and the free electron laser. The development of QC lasers promised finally to put mid-IR into the frontline of modern diagnostics, disease research, and drug discovery. They are already being demonstrated for breath analysis [2], medical imaging [3] and surgery [4].

I will review the state of the art in QC laser technologies for bio-medical applications and will discuss challenges and limitations.

References:

[1] Faist, J.; Capasso, F.; Sivco, D. L.; Sirtori, C.; Hutchinson, A. L.; Cho, A. Y. *Science* 1994, 264, 553–556.

[2] Katharina Wörle, Felicia Seichter, Andreas Wilk, Chris Armacost, Tim Day, Matthias Godejohann, Ulrich Wachter, Josef Vogt, Peter Radermacher, Boris Mizaikoff, *Breath analysis with broadly tunable quantum cascade lasers. Anal Chem* 2013; 85(5):2697-2702.

[3] Niels Kröger, Alexander Egl, Maria Engel, Norbert Gretz, Katharina Haase, Iris Herpich, Bettina Kränzlin, Sabine Neudecker, Annemarie Pucci, Arthur Schönhals, Jochen Vogt, and Wolfgang Petrich, *Quantum cascade laser-based hyperspectral imaging of biological tissue, Journal of Biomedical Optics* 19(11), 111607 (November 2014)

[4] http://engineering.jhu.edu/ece/research-projects/vivo-laser-tissue-ablation-using-6-1-um-quantum-cascade-laser/#.VRs3rfnF_Cc

**METROLOGY IN ABSOLUTE CARBON DIOXIDE AND WATER
VAPOR GAS CONCENTRATION MEASUREMENTS USING
TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY**

*Andrea Pogany¹, Alexander Klein¹, Javis Nwaboh¹, Bernhard Buchholz¹, Olav Werhahn¹,
Volker Ebert^{1,2}*

¹*Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany,
email: andrea.pogany@ptb.de*

²*Technical University Darmstadt, Petersenstr. 32, 64287 Darmstadt, Germany*

Water vapor (H₂O) and carbon dioxide (CO₂) are common components of the atmosphere, which are often monitored using spectroscopic methods. In certain applications the limited availability or stability of bottled gas standards restricts the possibility of in-field calibration of monitoring instruments with certified gas standards. In these cases absolute, self-calibrating spectroscopic measurements are preferred, based on calculating the concentration of the analyte(s) from the measured absorption spectrum and physical properties of the gas sample and the optical set-up according to the Beer-Lambert law. Absolute measurements rely on accurate spectral line parameters, most importantly the line strengths of the probed transitions.

In the first part of our presentation we give an overview on our activities in H₂O and CO₂ [1] line strength measurements by tunable diode laser absorption spectroscopy (TDLAS). We present line strengths of 9 H₂O and 2 CO₂ lines measured using the same experimental set-up and identical data evaluation procedure. We present measured line strengths in the $5 \cdot 10^{-23}$ - $2 \cdot 10^{-20}$ cm/molecule range and discuss differences between the experiments originating from the different analytes, light sources and magnitudes of the line strength. The measured line strengths have relative expanded uncertainties (k = 2, 95 % confidence level) of 1.0-2.5 %.

Many of these lines have recently been used in our research group for absolute gas concentration measurements. The application examples include airborne humidity measurements[2], quantification of H₂O and CO₂ impurities in zero gas standards[3], humidity measurements in combustion engines[4,5] as well as in natural gas[6]. We analyse uncertainties of these measurements and discuss the possibility of achieving metrological traceability. We compare the different experiments and evaluate general capabilities. Expanded uncertainties of our measured concentrations in the presented examples are typically in the range of 1-4 %.

The work has been conducted within the EMRP projects MACPoll, METEOMET and EUMETRISPEC. The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

References:

- [1] Pogány, A., Ott, O., Werhahn, O. & Ebert, V. *JQSRT* **130**, 147–157 (2013)
- [2] Buchholz, B., Bese, N. & Ebert, V. *Appl. Phys. B* **116**, 883–899 (2014)
- [3] Pogány, A., Wagner, S., Werhahn, O., Ebert, V. *Appl. Spectrosc.* **69**, 257–268 (2015)
- [4] Witzel, O. *et al. Appl. Phys. B* **109**, 521–532 (2012)
- [5] Klein, A., Ebert, V. *58th Ilmenau Scientific Colloquium* 8–12 (2014)
- [6] Nwaboh, J. A., Werhahn, O., Ebert, V. *Mol. Phys.* **112**, 2451–2461 (2014)

RECENT PROGRESS IN SINGLE-MODE INTERBAND CASCADE LASERS

L. Hildebrandt¹, J. Scheuermann¹, M. von Edlinger¹, L. Nähle¹, M. Fischer¹, J. Koeth¹, R. Weih², M. Kamp² and S. Höfling^{2,3}

¹*nanoplus Nanosystems and Technologies GmbH, Oberer Kirschberg 4, 97218 Gerbrunn, Germany. e-mail: lars.hildebrandt@nanoplus.com*

²*Technische Physik and Wilhelm Conrad Röntgen Research Center for Complex Material Systems, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany.*

³*School of Physics and Astronomy, University of St. Andrews, North Haugh, St. Andrews, KY16 9SS, United Kingdom.*

Interband cascade lasers (ICLs) give access to the mid-infrared wavelength region [1] and many new fields of applications have been realized (e.g. [2]). It is of great interest to further improve the performance characteristics of single-mode ICL devices and to also increase the accessible wavelength range of operation, so that more applications can benefit from this novel device technology.

We present our latest results on fabricated single-mode distributed feedback ICL devices with application-grade performance. Tuning ranges of individual devices as well as the overall wavelength coverage will be discussed. As shown in Fig.1, single-mode operation has been achieved from 2.8 up to 5.2 μm with setup limited signal to noise ratios around 30 dB. Continuous wave operation at room temperature with milliwatts of output power, suitable for TLAS applications was achieved for the entire wavelength range.

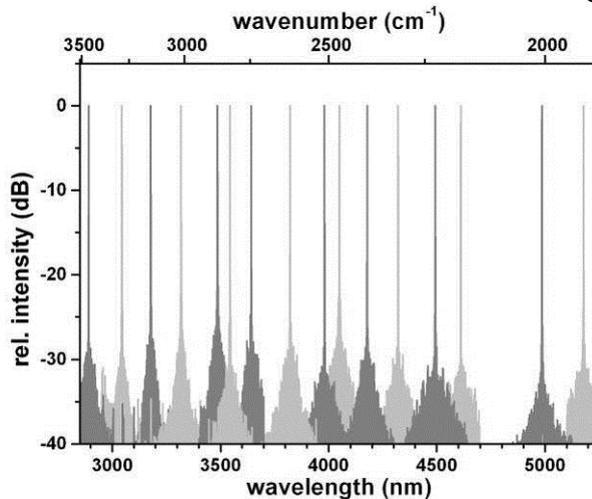


Fig.1 Spectra of various DFB ICLs operating in cw mode at room temperature. The devices show setup limited signal to noise ratio of around 30 dB.

- [1] I. Vurgaftman, W. W. Bewley, C. L. Canedy, C. S. Kim, M. Kim, C. D. Merritt, J. Abell, and J. R. Meyer, , IEEE J. Sel. Top. Quantum Electron. 19, 1200210 (2013).
- [2] S. Lundqvist, P. Kluczynski, R. Weih, M. v. Edlinger, L. Nähle, M. Fischer, A. Bauer, S. Höfling, and J. Koeth, Appl. Opt. 51, 6009 (2012).

APPLICATION OF TDLS COMPLEXES DEVELOPPED TO CONTROL IMPURITIES DURING GASES PURIFICATION

O.S. Anoshin, A.P. Kotkov, N.D. Grishnova, A.I. Skosyrev, D.M. Polezhaev, A.Yu. Suhanov

Scientific-industrial enterprise "Salut", 603950, Larina Str. 7, Nizhnii

Novgorod, Russia. saluthps@mail.ru

Ya.Ya. Ponurovskii

A.M. Prokhorov General Physics Institute of RAS

Vavilova str. 38, 119991 Moscow, Russia, ponur1960@yandex.ru

Subject of present paper is impurities control during gases purification. These impurities are important high purity gases usage for electronics and opto-electronics applications. TDLS technique was selected to control impurities content. Based on previous investigations list of impurities to be controlled was determined: H₂O, CH₄, C₂H₄, C₂H₂, and NH₃. The list is based on two motivations: impurities that are difficult both for removing during purification process and for detecting.

To detect above mentioned impurities at GPI was developed family of TDLS complexes. Impurity concentration in the sample under investigation in analytical cell is determined by comparison of its absorbance with the reference cell absorbance. Set of gas cells with optical path 0.1 – 22 m was developed, manufactured, and tested. TDLS complexes can record above mentioned impurities spectra with spectral resolution ~ 0.001 cm⁻¹.

Dependence of impurity line shape as function of impurity and main components concentrations was investigated. It was found that impurity line shape is substantially determined by main component itself and its pressure. With gas mixture pressure increase line broadening and its red shift were observed. For low pressures the line integral intensity is proportional to pressure (molecules number density). After some pressure level, its saturation and even reduction can be found.

Based on these investigations optimal pressures were determined for different impurities in different gases. For correct impurity concentration measurement it is necessary to have the same impurity line shape both for analytical and reference cells. To meet this requirement reference cell has to be filled with gas mixture of gas under investigation and impurity to be analyzed with the same pressure as in analytical cell.

Sometimes for impurity concentration below 10 ppm, absorbance of main component to be analyzed can play significant role. It is necessary to take into account and subtract from gas mixture spectra spectrum of gas itself. High purity gases spectra were measured.

TDLS complexes were calibrated using calibrated gas mixtures. To produce these calibrated gas mixtures high purity components were used.

TDLS complexes and measurement methods developed were used and tested for several gases purification processes. Tests showed that the measurement range of impurity concentrations for the developed techniques amounted to the value of 10¹ to 10⁻⁴% vol.

Poster session A

A1

DL SPECTROMETER FOR HIGH ACCURATE MEASUREMENTS

S.Kataev, A.Nadezhdinskii, Ya.Ponurovskii, Yu.Shapovalov, M.Spiridonov,

D.Stavrovskii

A.M. Prokhorov General Physics Institute, RAS, Moscow, Russia

Accuracy is one of recent challenges for Tunable Diode Laser Spectroscopy (TDLS). Several TDLS applications require measurement accuracy at and below 0.1 % level (see L1).

Diode Laser (DL) spectrometer for high accurate measurements was developed. DL radiation using fiber optics was split in 5 beams. These beams pass five optical channels and are recorded by five Photodiodes (InGaAs). Optical channels contain: calibrated FP etalon, calibrated Circle Fiber Interferometer (CFI), reference cell ($L1 = 183.42(8)$ cm), analytical cell ($L2 = 183.50(4)$ cm), and multipass cell ($L3 = 1519(1)$ cm). The spectrometer reconfiguration for different experimental tasks is doing by program of the spectrometer operation (no changes in optics). This provides very stable and reproducible signals of the spectrometer operation.

To pump cells Turbo pumping station HiCube 80 Eco (10^{-7} mBar) is using. To measure gas pressure, 3 pressure sensors are used: EDWARDS Wide range Gauge (10^{-9} мБар – 1000 мБар), EDWARDS Active Strain Gauge) (0 – 1000 mBar), and Setra model 764 (0 – 1000 Torr). 3 thermoresistors measure each cell temperature located in the middle and both side of the cell. Pressure and temperature sensors were calibrated with respect to state etalons of 1 category at ROSTEST. Diode laser frequency tuning, PD and preamplifier nonlinearity, DL spectrum influences were investigated and analyzed.

Results of this analysis for spectral line integral intensity are presented in Table 1.

Table 1 Error budget for spectral line integral intensity measurement

	Value	Error %
L, cm	183.5	0.022
DT, °C	20 - 25	0.017
P, mBar	100	0.036
CO ₂ sample purity, %	99.99	0.010
Subtotal		0.046
PD non-linearity		0.023
Dv, cm ⁻¹	0.8	0.015
Baseline		0.010
Optical zero		0.010
DL Spectrum, MHz	0.5	0.014
Subtotal		0.034
Total		0.058

Conclusion: for present spectrometer and CO₂ gas sample, spectral line integral intensity can be measured with 0.06 % accuracy. Several tests (see separate posters) were performed to prove above mentioned accuracy.

A2

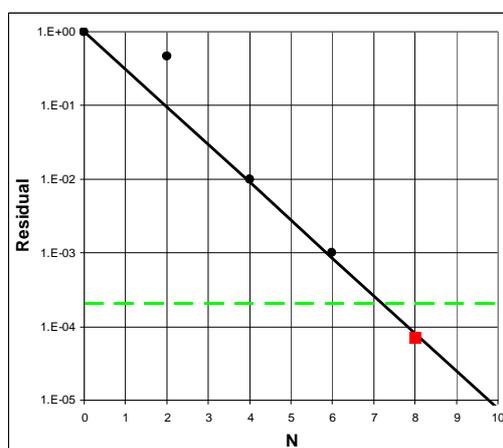
Fitting of high accurate experimental data

A.Nadezhdinskii

*A.M.Prokhorov General Physics Institute of RAS, Vavilov str. 38, 119991 Moscow, Russia
NAD@nsc.gpi.ru*

Accuracy level 0.06 % was recently achieved in TDLS (see A1). Next step is high accurate experimental spectral line shape fitting. Software developed can fit experimental line shape using soft and hard collisions models with following fitting parameters: S – integral intensity, ν – line frequency, L – broadening width, D – Doppler width, and B – narrowing width [1]. All parameters can be fixed or used in fitting.

Recent experimental accuracy improvement requires reanalysis of fitting procedure. Fitting has several goals: to fit experimental line shape with experimental accuracy (residual is measure) and to determine line parameters having physical meaning. For different parameters in fitting, residual looks like N order derivative of line shape with N = 2, 4, 6, 8 for following parameters included in fitting S and ν , L, D, B, soft-hard, respectively.



Black solid circles are dependence of residual amplitude vs N (parameters in fit).

Green dashed constant – spectrometer accuracy.

Red square is difference between soft and hard. This difference was obtained by modeling for CO₂ line under investigation.

Addition of each next fitting parameter improves residual by order of magnitude. So, fitting procedure is correct.

Hence, 5 fitting parameters mentioned above are enough to fit line shape to achieve experimental accuracy $2 \cdot 10^{-4}$. I don't think that anybody in the world has this accuracy level.

Recently pCqSDHC profile was recommended [2] having 9 fitting parameters. This approach is wrong. No more than 5 parameters have to be used in fitting. Otherwise fitting parameters correlation will take place, and fitting parameters will have no physical meaning. Moreover, to obtain parameters having physical meaning correct line shape model has to be used.

1. ABSTRACTS OF PAPERS of 9-th International Conference on Tunable Diode Laser Spectroscopy, Moscow, 2013, p.39

2 J. Tennyson, P. Bernath, A Campargue and etc. Recommended isolated-line profile for representing high-resolution spectroscopic transitions (IUPAC Technical Report). 10.2014

DIODE LASER SPECTROSCOPY OF H₂¹⁶O SPECTRA BROADENED BY N₂ and He in 1.39 μ REGION

*K.Yu.Osipov^a, V.A.Kapitanov^a, A.E.Protasevich^a,
A.A.Pereslavytseva^{b,c}, Ya.Ya.Ponurovskii^b*

^a *V.E.Zuev Institute of Atmospheric Optics SBRAS, Tomsk, Russia*

^b *A.M.Prokhorov General Physics Institute of RAS, Moscow, Russia*

^d *Moscow Institute of Physics and Technology (State University), Moscow, Russia.*

Experimental spectra of pure water vapor and its mixtures with N₂ and He were measured in a pressure range (4–19 for pure H₂O and 70–630 mBar for H₂O diluted in N₂ and He) by the diode laser spectrometer between 7184 and 7186 cm⁻¹. The noise equivalent absorption cross-section of the all observed spectra varied from 1.2 to 4.3*10⁻²⁴ cm²/molec allowing signal to noise ratio from 10 for weak (intensity on the order of 5*10⁻²⁵ cm/molec at 296 K) to 3000 for strong (intensity on the order of 6*10⁻²² cm/molec) spectral lines respectively. The Voigt, Galatry, and Speed-dependent Voigt (SDV) profiles were used to fit the experimental spectra. This region includes 7 absorption lines of H₂O and one HDO line according to the new line lists of H₂O. Line positions, intensities, line shift, collisional broadening and narrowing coefficients for 6 spectral lines were retrieved by multispectral fitting procedure assuming the linear pressure dependence. The spectral parameters of the doublet ($\nu_1+\nu_3$; 660 < 661; 661 < 660) at 7185.596 cm⁻¹ were determined for the first time (fig 1).

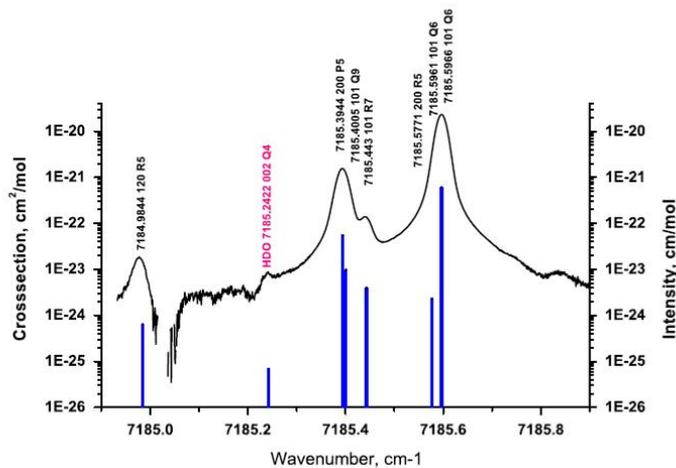


Fig 1. Experimental spectra of pure H₂O vapor at low pressure and lines identification.

DEVELOPMENT OF H₂O SENSOR FOR MEASUREMENTS OF GAS FLOW PARAMETERS AT A TOTAL PRESSURE ABOVE 1 ATM

V.V.Liger¹, Yu.A.Kuritsyn¹, V.R.Mironenko¹, M.A.Bolshov¹
Ya. Ya. Ponurovskii², O.M. Kolesnikov³

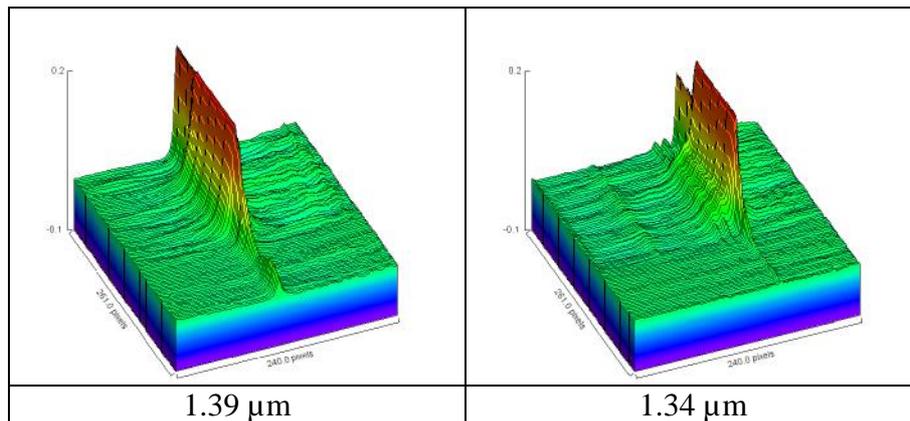
¹ *Institute for Spectroscopy RAS, 5 Fizicheskaya str., 142190 Troitsk, Moscow, Russia*

² *A.M. Prokhorov General Physics Institute, 38 Vavilov str., 119991 Moscow, Russia*

³ *N.E. Zhukovsky Central Aerohydrodynamic Institute, 140180 Zhukovsky, Moscow reg., Russia*

Tunable Diode Laser Absorption Spectrometry (TDLAS) is now widely used for diagnostics of combustion processes in different engines and propulsion facilities. The design of a TDLAS sensor depends on real conditions in a hot zone. For low total pressures (below 1 atm) the absorption lines of a test molecule are relatively narrow, which makes possible to use a single TDL for detection of several lines within the spectral range of fast TDL tuning (1-2 cm⁻¹). At higher pressures (above 1-1.5 atm) the lines are widened and the scheme of a sensor with a single TDL is no more possible. The alternative approach for high pressure sensing of the hot zones is the use of two DFB lasers radiating in different spectral ranges. The different combinations of the absorption lines of H₂O molecule from different spectral ranges are discussed in the presentation with the emphasis on the attainable uncertainties in the temperature evaluation.

The construction of the developed sensor is described. The combination of two TDLs generating in the 1.39 and 1.34 μm wavelength ranges was tested. In the laboratory experiments the cell with stable and adjustable temperature and pressure was used. The performance of the sensor was checked for two temperatures (600 and 900 K) and 3 pressures (1, 2, 3 atm). Reasonable agreement between the temperatures measured by a thermocouple and TDLAS for all three pressures was obtained.



The results of the first set of the experimental testing of the developed sensor at the propulsion system in N.E.Zhukovsky Central Aerohydrodynamic Institute (TsAGI) are presented. The dynamics of the H₂O absorption spectra during one run is shown in 3D picture. The temperature and concentration of H₂O molecules in the hot supersonic flow of air were then evaluated from line intensities using fitting technique.

A5

Studies of $^{238}\text{UF}_6$ and $^{235}\text{UF}_6$ $\nu_1+\nu_3$ band spectra with a quantum cascade laser (QCL): fine structure of a Q-branch and enrichment measurements

Sh. Nabiev, V. Semenov, D. Stavrovskii, P. Men'shikov, L. Men'shikov, G. Grigor'iev
National Research Center "Kurchatov Institute",
1, Kurchatov sq., Moscow, 123182 Russia
E-mail: Nabiev_SS@nrcki.ru, semenov.v.m@gmail.ru

Absorption spectra of the Q-branch $\nu_1+\nu_3$ vibrational band of pure uranium hexafluoride (UF_6) have been recorded in the 1290 – 1292.5 cm^{-1} spectral region with a QCL-based tunable laser spectrometer at various pressures (10 – 70 Torr), $T=23^\circ\text{C}$ and optical path length $L=30$ cm previously [1]. Samples of various isotopic abundance have been considered (0.7%; 2 %; 5 %; 20 % and 90% of ^{235}U). As it was mentioned in [1], noticeable fine structure of absorption spectra has been discovered. Present report is focused on detailed analysis of the fine structure and also presents results of measurements UF_6 spectra at $T=30..+20^\circ\text{C}$ in liquid nitrogen cooled cell with $L=230$ cm.

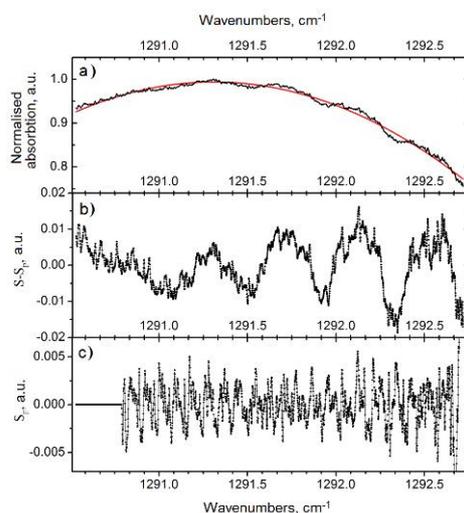


Fig.1. a - $^{238}\text{UF}_6$ (S) spectra and its 2nd order polynomic fit (S_p); b –residual $S-S_p$; c – result of high pass filtering of $^{238}\text{UF}_6$ spectra (S_f). $T=23^\circ\text{C}$

Fine structure of each spectrum (Fig.1 a,b,c), consist of broad features (HWHH ~ 0.2 cm^{-1} ; fig 1, b) and sharp peaks (HWHH ~ 0.02 cm^{-1} ; fig 1, c). All these features are alike for both isotopomers and demonstrate pressure broadening and isotopic shift of 0.59 cm^{-1} (the same value as for the $\nu_1+\nu_3$ vibrational band). A theoretical estimation has been made in order to identify this fine structure. Periodical broad structure (Fig. 1, b) has been interpreted for the first time as a reflection of hot band transitions in a Q-branch. Previously unknown anharmonicity parameters X_{21} , X_{31} , X_{32} and combinations of $X_{i1} + X_{i3}$ ($i = 4, 5, 6$) have been estimated. Two algorithms of isotopic ratio measurements are presented. Both algorithms can process original spectra (fig.1 a) and both levels of its fine structure (fig.1 b and c).

[1] A.Babichev, G.Grigoriev, Sh.Nabiev, A. Nadezhdinskii et al. $^{238}\text{UF}_6$ and $^{235}\text{UF}_6$ spectra and enrichment measurement in mid IR spectral range. Abstracts of TDLS 2013, Moscow, Russia, p.26.

NEAR INFRARED CAVITY RING-DOWN SPECTROSCOPY WITH A DFB DIODE LASER FOR MONITORING CARBON DIOXIDE

*Feng Zhu,¹ Aysenur Bicer,¹ James Bounds,¹ Alexandre A. Kolomenskii,¹
Vassilios Kelessides,² Mahmood Amani,² and Hans A. Schuessler^{1,3}*

¹*Department of Physics and Astronomy, Texas A&M University, College Station, TX 77843-4242, USA*

²*Petroleum Engineering Program, Texas A&M University at Qatar, Doha 23874, Qatar*

³*Science Department, Texas A&M University at Qatar, Doha 23874, Qatar*

We utilize the near infrared continuous wave cavity ring-down (CRD) spectroscopy with a distributed feedback diode laser to monitor carbon dioxide at the wavelength around 1600 nm. With the high reflectivity mirrors ($R \sim 99.996\%$), we built a high finesse cavity ($\sim 70,000$). We detected ~ 520 ppmv carbon dioxide in ambient air with the data acquisition time of few minutes; the detection limit of the current setup is about ~ 60 ppmv. We separate the gas from liquid with a hollow fiber porous membrane, and analyze the carbon dioxide of different isotopic content, as is shown in Fig. 1.

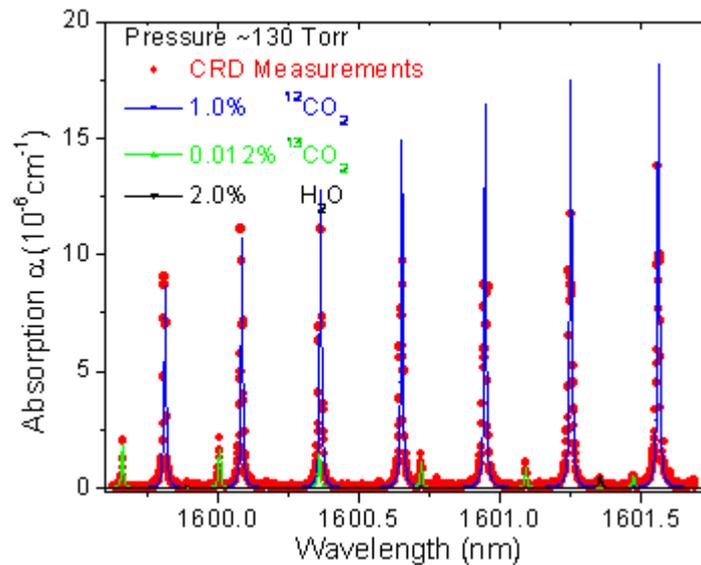


Fig. 1. Measured ring-down spectra (red dots) of the separated CO_2 gas from tap water and comparison with simulation results from HITRAN database (blue for $^{12}\text{CO}_2$, green for $^{13}\text{CO}_2$, and black for H_2O).

This research is supported by the Robert A. Welch Foundation grant No. A1546 and the NPRP 6-465-1-091 grant from the Qatar National Research Fund.

RECENT PROGRESS IN SINGLE-MODE INTERBAND CASCADE LASERS

L. Hildebrandt¹, J. Scheuermann¹, M. von Edlinger¹, L. Nähle¹, M. Fischer¹, J. Koeth¹, R. Weih², M. Kamp² and S. Höfling^{2,3}

¹*nanoplus Nanosystems and Technologies GmbH, Oberer Kirschberg 4, 97218 Gerbrunn, Germany. e-mail: lars.hildebrandt@nanoplus.com*

²*Technische Physik and Wilhelm Conrad Röntgen Research Center for Complex Material Systems, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany.*

³*School of Physics and Astronomy, University of St. Andrews, North Haugh, St. Andrews, KY16 9SS, United Kingdom.*

Interband cascade lasers (ICLs) give access to the mid-infrared wavelength region [1] and many new fields of applications have been realized (e.g. [2]). It is of great interest to further improve the performance characteristics of single-mode ICL devices and to also increase the accessible wavelength range of operation, so that more applications can benefit from this novel device technology.

We present our latest results on fabricated single-mode distributed feedback ICL devices with application-grade performance. Tuning ranges of individual devices as well as the overall wavelength coverage will be discussed. As shown in Fig.1, single-mode operation has been achieved from 2.8 up to 5.2 μm with setup limited signal to noise ratios around 30 dB. Continuous wave operation at room temperature with milliwatts of output power, suitable for TLAS applications was achieved for the entire wavelength range.

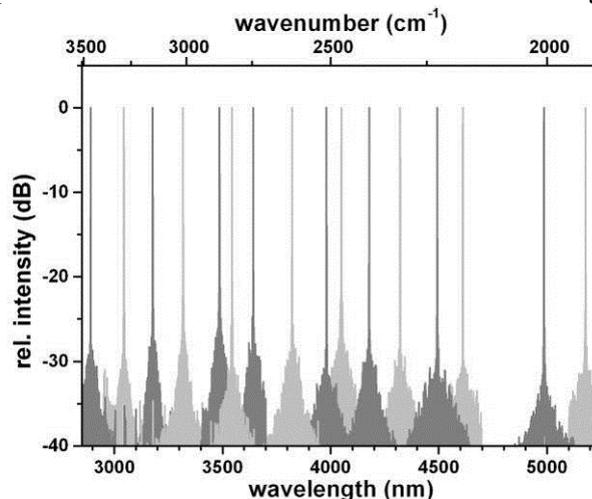


Fig.1 Spectra of various DFB ICLs operating in cw mode at room temperature. The devices show setup limited signal to noise ratio of around 30 dB.

- [1] I. Vurgaftman, W. W. Bewley, C. L. Canedy, C. S. Kim, M. Kim, C. D. Merritt, J. Abell, and J. R. Meyer, , IEEE J. Sel. Top. Quantum Electron. 19, 1200210 (2013).
- [2] S. Lundqvist, P. Kluczynski, R. Weih, M. v. Edlinger, L. Nähle, M. Fischer, A. Bauer, S. Höfling, and J. Koeth, Appl. Opt. 51, 6009 (2012).

ATOMIC SPECTROSCOPY IN MULTILAYER GAS CELLS

A.Ch. Izmailov

Institute of Physics, Azerbaijan National Academy of Sciences, Javid av. 33, Baku, Az-1143,
AZERBAIJAN

e-mail: azizm57@rambler.ru

It is very important to elaborate effective methods of ultrahigh-resolution spectroscopy which allow to analyze a structure of spectral lines hidden by the Doppler broadening because of a thermal motion of atoms or molecules [1]. Recently new methods of sub-Doppler spectroscopy were elaborated, which were based on the optical pumping of the atomic ground (or metastable) level during transits of atoms of a rarefied gas between walls of a thin cell, whose characteristic transverse dimension D was much greater than its inner thickness L . Article [2] presents review of given methods, which were well-tested by tunable diode lasers.

However, comparatively weak absorption signals in thin cells (with a submillimeter gas layer) reduce their effectiveness. Therefore the new cell with a series of successive plane-parallel thin gas layers was suggested in paper [3]. In such a cell, the monochromatic probe light beam travels along the central axis z through the opening 3 of the atomic velocities selector 2 (Fig.1). The spatially separated pumping beam (which may be even broadband) irradiates the region 1 of the cell out of the selector. Such a cell is the compact analog of many plane-parallel beams of optically pumped atoms (or molecules), whose divergence in the probe region is determined by the small dimensional ratio $2Dl / (D_1 - D_2) \ll 1$ of splits (with the thickness Dl) carved perpendicular to the axis z in the selector material 2.

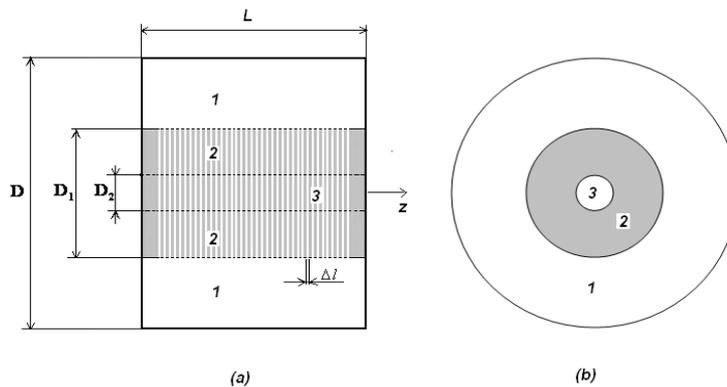


Fig.1. Scheme of the multilayer gas cell in two orthogonal projections (a) and (b).

My presentation will demonstrate that proposed multilayer cells are much more effective for applications in high-resolution atomic (molecular) spectroscopy than usual (hollow) gas cells.

- [1] W. Demtröder, *Laser Spectroscopy: Basic Concept and Instrumentation* (Springer, Berlin, 2003).
- [2] A.Ch. Izmailov, *Azerbaijan Journal of Physics: Fizika*, V.17, N1, Section En, pp. 3-28 (2011). (free access in the Internet: <http://physics.gov.az/index1.html>)
- [3] A.Ch. Izmailov, *Optics and Spectroscopy*, V.115, N4, pp. 463-468 (2013).

GAS DETECTION WITH AN A COHERENT EXTERNAL-CAVITY QUANTUM CASCADE LASER ARRAY

*R. Vallon*¹, *B. Parvitte*¹, *G. Maisons*², *M. Carras*², *V. Zeninari*¹

*1 Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR 7331 CNRS, Université de Reims
Faculté des Sciences, Moulin de la Housse, BP 1039, 51687 Reims Cedex 2 – France*

*2 III-V lab, Route Départementale 128, F-91767 Palaiseau Cedex – France
raphael.vallon@univ-reims.fr*

In the framework of the French Research Agency project called COCASE, GSMA and III-V Lab has developed a coherent quantum cascade laser array to obtain high power emission. The principle of this source consists in the fabrication of multi-stripes arrays in order to obtain high power source. 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. The main characteristic of this kind of source is that in far-field an anti-symmetrical signature is obtained with at least two lobes. Far-field emission can be simulated and compared with experiments [1-2]. The source has no modes switching, no multi-modal behavior and supermode operation is active along the current range thus there are no coherence loss.

In a second part the developed source will be used to demonstrate gas detection. GSMA is a pioneer group regarding the development of infrared spectrometers based on cutting-edge tunable lasers [3]. Results obtained with this source mounted in an external cavity system will be presented. A grating is aligned with one lobe of the source. Thus a Littrow-configuration is designed that permit to obtain a wide tunability of the source. Finally the source emitted in pulse operation was used to detect acetone. Preliminary results will be presented. Next step will consist to obtain cw emission and thus a powerful broad laser source. 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-002 called “COCASE”.

References

- [1] G. M. de Naurois, M. Carras, G. Maisons, and X. Marcadet, "Effect of emitter number on quantum cascade laser monolithic phased array", *Optics Letters* 37, 425-427 (2012)
- [2] G.M. de Naurois, M. Carras, B. Simozrag, O. Patard, F. Alexandre, and X. Marcadet, "Coherent quantum cascade laser micro-stripe arrays", *AIP Advances* 1, 032165 (2011)
- [3] V. Zeninari, A. Grossel, L. Joly, T. Decarpenterie, B. Grouiez, B. Bonno, and B. Parvitte, "Photoacoustic spectroscopy for trace gas detection with cryogenic and room-temperature continuous-wave quantum cascade lasers", *Central European Journal of Physics* 8, 194-201 (2010).

MEASUREMENT OF PRESSURE BROADENING OF Ar AND Kr ABSORPTION LINES NEAR 811 nm WITH A DIODE LASER

A. K. Chernyshov¹, P. A. Mikheyev^{1,2}, N. I. Ufimtsev¹, E. A. Vorontsova^{1,2} and V. N. Azyazov^{1,2}

¹*P.N. Lebedev Physical Institute of RAS, Samara branch, 443011, Russia;*

²*Samara State Aerospace University, 443086, Samara, Russia*

chak@fian.smr.ru

Optically pumped all-rare-gas laser (OPRGL) with unique properties [1, 2] comparable to a diode pumped alkali laser (DPAL) was recently proposed. To study this promising laser system it is necessary to have a reliable diagnostics for the active medium. A set of the pressure self- and foreign-broadening coefficients is needed for measurements of the number density of metastable atoms and temperature in rare gas discharge plasma by means of spectroscopy. However, literature analysis had shown that pressure broadening coefficients for rare gas lines in mixtures which are of interest for OPRGL laser are surprisingly hard to find. Laser spectroscopy setup displayed in fig. 1 was employed for measurement of pressure broadening coefficients for argon or krypton in an RF discharge. A MQW-diode laser (L808P030, Thorlabs) with an original short external cavity was used as a source of probing radiation [3]. The obtained coefficients for argon 811.5 nm line reduced to 300 K are: $\chi_{\text{Ar-Ar}} = (2.8 \pm 0.1) \times 10^{-10} \text{ s}^{-1} \text{ cm}^3$ for self-broadening and $\chi_{\text{Ar-He}} = (3.2 \pm 0.2) \times 10^{-10} \text{ s}^{-1} \text{ cm}^3$ for broadening in helium. For krypton 811.3 nm line the values of pressure broadening coefficients are: $\chi_{\text{Kr-Kr}} = (2.4 \pm 0.2) \times 10^{-10} \text{ s}^{-1} \text{ cm}^3$ and $\chi_{\text{Kr-He}} = (3.1 \pm 0.2) \times 10^{-10} \text{ s}^{-1} \text{ cm}^3$.

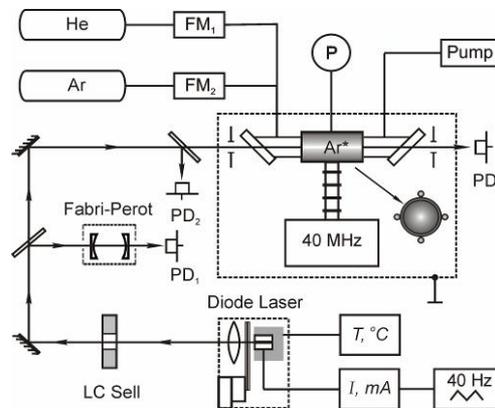


Fig.1 Experimental setup: P is the pressure transducer, FM - flowmeters, PD - photo diodes, LC - liquid crystal cell. Inside the discharge assembly (grounded dashed square) is the cross section of the discharge tube with four electrodes.

[1] J. Han and M. C. Heaven, *Opt. Lett.*, 37(11), 2157-59 (2012).

[2] A. V. Demyanov, I. V. Kochetov and P. A. Mikheyev, *J. Phys. D: Appl. Phys.*, 46, p. 375202 (2013).

[3] A. K. Chernyshov, E. A. Chernyshova, *Phys. of Wave Phenomena*, 19(2), 89-91 (2011).

A11

Isotope ratio measurement by absorption of diode laser emission in ambient air carbon dioxide at ~ 1.6 μm

I.V.Nikolaev¹, V.N.Ochkin¹, S.N.Tskhai¹, A.A.Zaytsev^{1,2}

¹*Lebedev Physical Institute, Russian Academy of Sciences, Leninsky pr. 53, 119991 Moscow, Russia*

²*Moscow Institute of Physics and Technology (State University), Institutskii per. 9, 141700 Dolgoprudnyi, Moscow region, Russia*

The spectral range of 1.6 μm is convenient to measure CO_2 concentration by absorption spectroscopy from a viewpoint of low cost and available equipment. However, it has a very low cross-section of absorption and need a long optical pass for sensitive measurement.

We develop the method of $^{13}\text{CO}_2/^{12}\text{CO}_2$ measurement in exhaled air by absorption of 2 μm diode laser radiation in the Herriot cell at atmospheric pressure using linear regression analysis [1]. Here we present the method application to the $^{13}\text{CO}_2/^{12}\text{CO}_2$ measurement in a resonant cell filled by ambient air ($\sim 0.03\%$ CO_2).

The resonator is consisted of two mirror with reflection of 0.9999 and separated by 45 cm. Optical path is estimated about 5 km. Two spectral lines were chosen for measurement $^{12}\text{CO}_2$: $2n_1+2n_2+n_3$ (R0), $\nu = 6228.689985 \text{ cm}^{-1}$, and $^{13}\text{CO}_2$: $n_1+4n_2+n_3$ (P16), $\nu = 6228.433041 \text{ cm}^{-1}$. A precision of the measurements obtained by Allan variance plot (fig.1) was 0.3 ‰ at 3000 s acquisition time.

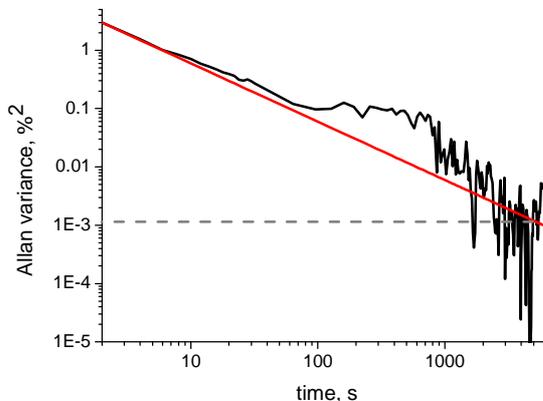


Fig.1. dC^{13} Allan variance plot

The isotope ratio in laboratory air of $d^{13}\text{C} = -8.2 \pm 0.3\text{‰}$ was obtained.

The work was supported by the Russian Scientific Foundation (project 14-12-00784).

References

[1] S.N. Andreev, E.S. Mironchuk, I.V. Nikolaev, V.N. Ochkin, M.V. Spiridonov, S.N. Tskhai, *Appl Phys B* 104, pp.73–79, (2011)

THE RESEARCH OF COMBUSTION TEMPERATURE AND GAS CONCENTRATION DISTRIBUTIONS USING TDLAS METHOD

Zhi-rong Zhang^{1*}, Feng-zhong Dong^{1,2+}, Hua Xia¹, Xiao-juan Cui¹, Peng-shuai Sun¹, Tao Pang¹, Bian Wu¹, Luo Han¹ and Yu Wang¹

¹ Anhui Provincial Key Laboratory of Photonic Devices and Materials, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei, Anhui 230031, China

² School of Environment Science and Optoelectronic Technology, University of Science and Technology of China, Hefei, Anhui 230026, China

*zhangzr@aiofm.ac.cn +fzdong@aiofm.ac.cn

Combustion is the most common, typical and direct energy conversion method. The construction of temperature and gas concentration fields could characterize the combustion position, and evaluate the combustion regime and the released heat quantity, therefore it is very important for combustion scientific research and optimization control for combustion efficiency. The recent research has been conducted by combining tunable diode laser absorption spectroscopy (TDLAS) data with mathematical algorithms to determine the temperature and gas concentration distributions of specific chemical species for combustion diagnosis.

When light permeates an absorption medium, the intensity of the transmitted light is related to the absorber's concentration according to Lambert Beer's law. Based on the number of the scanned gas absorption lines and the optical paths, the integrated coefficient value can be obtained by the photonic detector, namely the projection data. A pair of H₂O wavelengths near 1395nm was selected. The flat flam furnace "CT" models of temperature and water vapor concentration distributions were created by superimposing two Gaussian peaks on a paraboloid to simulate the combustive conditions encountered in practice, as depicted in Fig. 1. The temperature measurements with TDLAS are consistent with the thermocouple point measurement results. By using the Fluent 12.0 software, the concentration and temperature distributions results have been obtained as the theoretical analysis and simulations.

Thanks to the National Natural Science Foundation of China (11204320).

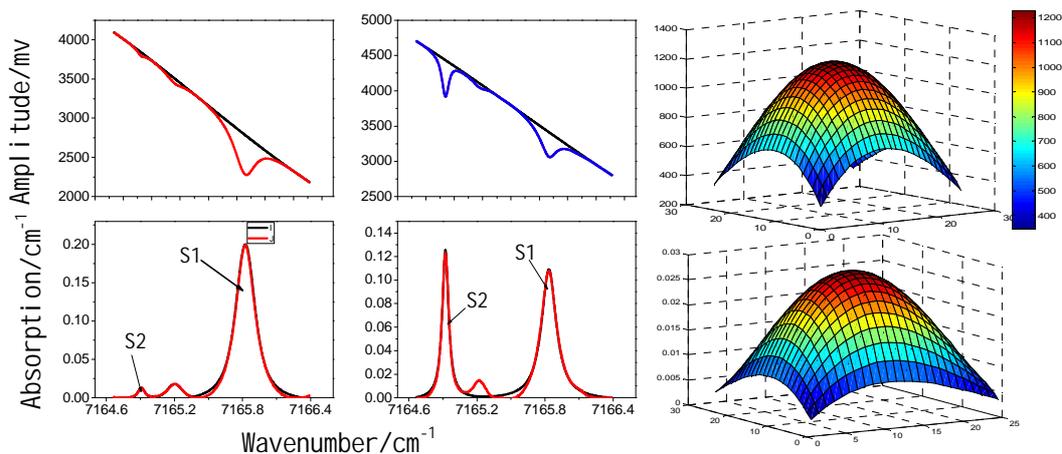


Fig.1. The absorption signals (left) and temperature (right upper) water vapor concentration (right lower) distributions with 4x4 grid configuration

LABVIEW AND FPGA-BASED DFB LASER FREQUENCY STABILIZATION SYSTEM

T.B. Eom¹, S.H. Suh¹, J.Y. Lee¹, J.A. Kim¹, J.W. Kim¹

¹Korea Research Institute of Standards and Science, 209 Gajeong-Ro, Yuseong-Gu, Daejeon, 305-340, Korea, tbeom@kriss.re.kr

Gauge block is the very important standard to transfer the length unit to industry. The absolute length of the gauge block is determined by interferometry. This interferometer requires multiple frequency stabilized laser sources generally. Traditionally multi-wavelength interferometry with 2 or 3 lasers stabilized to the absorption lines of atoms or molecules is used world-widely. So we developed the new frequency stabilized laser sources which of frequency can be stabilized at the rubidium (Rb) and cesium (Cs) absorption lines. The system uses digital locking technology with a unique filtering technique and a proportional-integral-derivative (PID) servo loop in conjunction with saturation absorption spectroscopy. Fig. 1 shows the schematic for obtaining the multiple wavelengths of which frequencies are stabilized. The system consists of five parts: a distributed feedback (DFB) lasers with driver, an absorption cell, a field programmable gate array (FPGA, NI-PXI-7842) module with real-time CPU (RT, NI PXIe-8101), A board for interfacing with FPGA module and DFB laser driver, and computer. The FPGA has several analog-digital converters (ADC) and digital-analog converters (DAC), and 3 M programmable gate array. The current and temperature of DFB lasers are controlled by DACs of FPGA module. The temperature of DFB laser can be adjusted from 0 °C to 40 °C. As a result its wavelength can be tuned over about 2 nm. The absorption signal detected by photo-diode is coupled to an ADC of FPGA module. To lock the laser frequency to one of Rb or Cs absorption peaks by the saturation spectroscopy technique, the laser frequency is modulated at 1.0 kHz by adding a small sinusoidal signal to the laser input current and the 1st or 3rd and 2nd derivative signals of absorption are calculated by RT (These are performed by FPGA). The former is used as error signal for frequency stabilization and the latter is used for checking frequency locking at absorption peak. The error signal (1st or 3th derivative) after software-based PID servo loop is then fed to a laser input current. One of several absorption peaks can be automatically selected. The system can control two lasers at the same time. This process is controlled by computer.

Fig. 2 shows the saturated absorption signal of Rb D2 line, 1st derivative and 2nd derivative. We had stabilized the frequencies at D1 and D2 of Rb and D1 and D2 of Cs. The system achieves the frequency stability of about 10^{-9} at any absorption line.

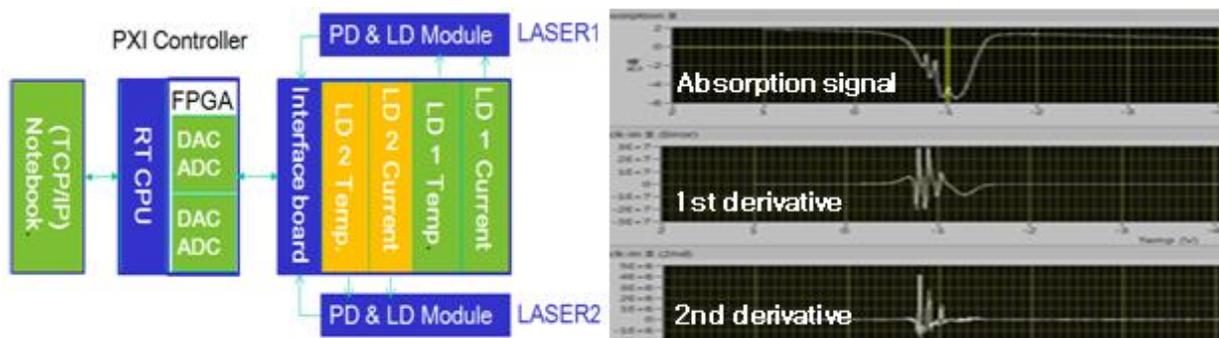


Fig.1 Control system based on FPGA and RT9.

Fig.2 Derivative signals.

APPLICATIONS OF SHORT-TERM FOURIER TRANSFORM IN TUNABLE DIODE LASER SPECTROSCOPY

Alexandre Lytkine

Light Peaks Inc., 420-233 Beecroft Road, North York, ON, Canada M2N 6Z9
e-mail: info@lightpeaks.ca

The short-term Fourier transform (STFT) is a useful tool for signal processing and real-time noise reduction [1]. The method capability for spectral analysis of signal segments may be valuable for many applications in TDLS (see an example of noise analysis in Fig. 1).

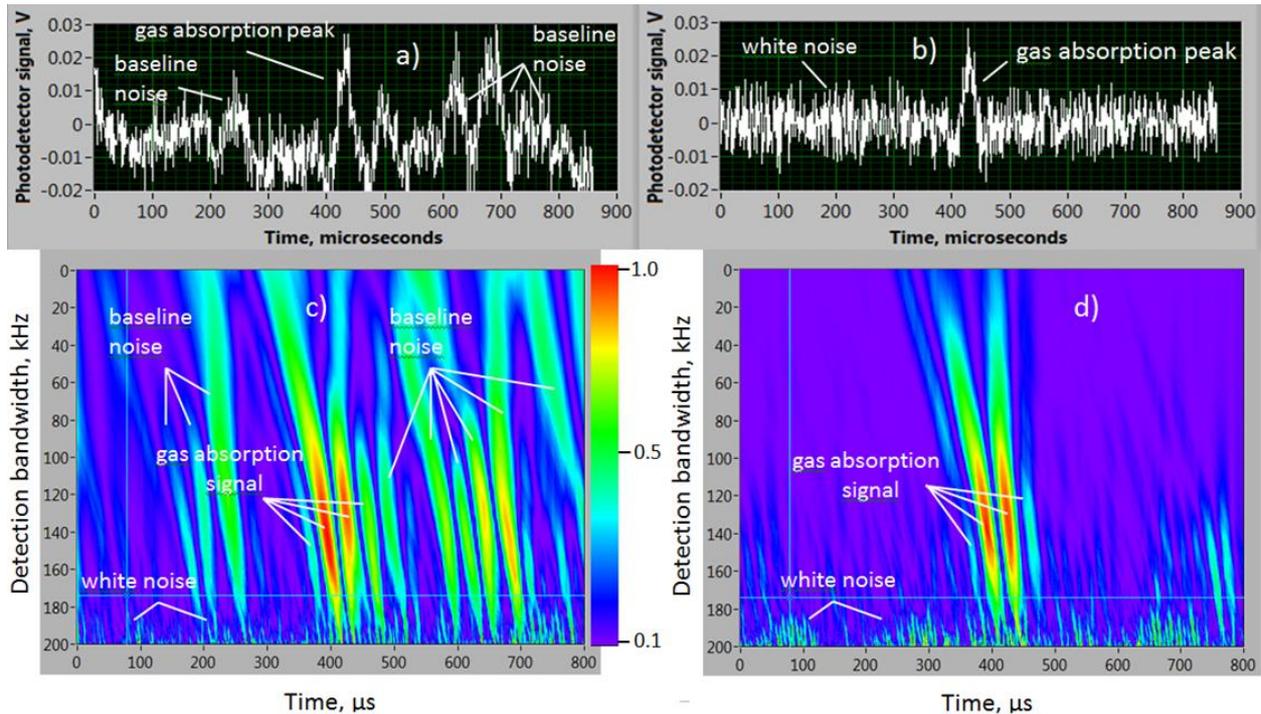


Fig.1. A real (a) and simulated (b) detector signals of a VCSEL-based spectrometer and corresponding STFTs (c-d) calculated over bandwidths varied from 200 kHz to 5.4 Hz. Signal a) is the second derivative of a 1-kHz VCSEL scan (50 averages) through an O₂ absorption feature at 13084.2 cm⁻¹ (764.28 nm). Maximum laser power was 0.5 mW. The levels of high-frequency noise (white noise in Fig.1) and baseline irregularities (baseline noise in Fig.1a,c) are typical for this type of lasers. Signal b) is a computer simulation of the real signal (absorbance 10⁻⁴) but with no baseline noise. As one can see in c), in the bandwidths less than 80 kHz the target gas signals and baseline noise are of the same magnitude while the STFT of the signal b) is practically free of noise. In the bandwidth range between 80 and 180 kHz, the baseline irregularities seen in Fig. 1c may cause significant measurement errors and drifts.

The TDLS applications of SFFT may include an optimization of optical and electrical designs of laser spectrometers, detection limit evaluation, noise reduction and real-time drift control.

Acknowledgements: The work is supported through the NRC-IRAP and SR&ED programs.

[1] Kaita Ito and Manabu Enoki, *J. Acoustic Emission*, **25**, 247-252 (2007).

A15

APPLICATION OF TDLS COMPLEX TO CONTROL ACETYLENE IMPURITY DURING HIGH PURITY PHOSPHINE PRODUCTION

D.M. Polezhaev, A.Yu.Suhanov A.P. Kotkov, N.D. Grishnova,
Scientific-industrial enterprise "Salut", 603950, Larina Str. 7, Nizhnii
Novgorod, Russia. saluthps@mail.ru
A.I. Nadezhdinskii, Ya.Ya. Ponurovskii
A.M.Prokhorov General Physics Institute of RAS
Vavilova str. 38, 119991 Moscow, Russia, ponur1960@yandex.ru

The report presents the results of the method development for determining acetylene (C_2H_2) impurity during production of the high purity phosphine (PH_3). To determine C_2H_2 concentration, DL spectrometer manufactured in GPI with diode laser 1530 nm was used. As an analytical cell, single-pass cell with a path length of 1 m was used.

The absorption spectra of acetylene and phosphine in 1528 – 1533 nm spectral range with the DL spectrometer were recorded. C_2H_2 analytical spectral line was selected. The spectral line shape of acetylene in the mixtures of acetylene-helium and acetylene-phosphine was studied depending on the pressure of the mixture. It was shown that a mixture with a phosphine has much greater acetylene line broadening than mixture with helium. C_2H_2 spectral line integral intensity with pressure increasing is increased only to a certain pressure value of the mixture. After 50 kPa of PH_3 - C_2H_2 mixture, integral intensity decreases. This fact indicates the presence of acetylene interaction with phosphine. Based on these experiments, optimal pressure for the sample analysis was determined.

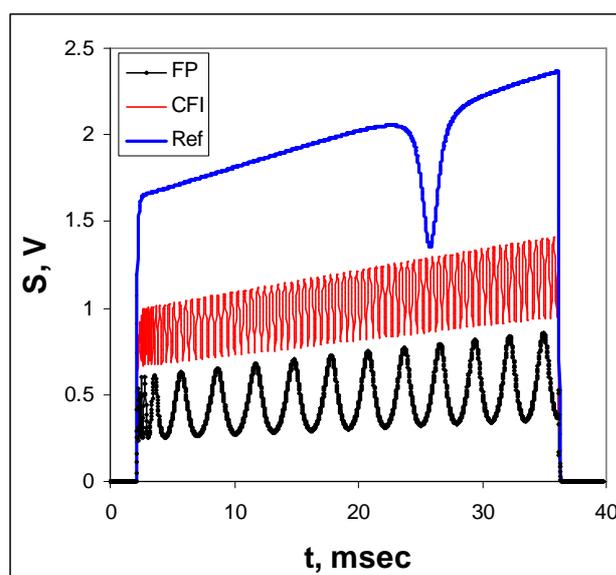
DL-spectrometer was calibrated by the "added-found" method and a comparison with the results of gas chromatographic analysis in a range of C_2H_2 concentration 5 - 0,005 % vol.

DIODE LASER FREQUENCY TUNING CALIBRATION AND TESTS

A.Nadezhdinskii

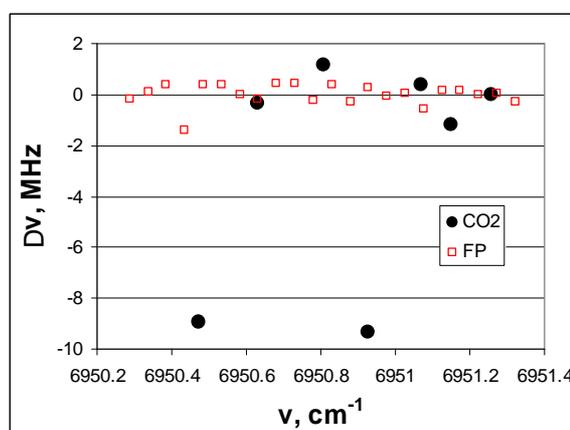
A.M. Prokhorov General Physics Institute, RAS, Moscow, Russia

Diode laser (DL) is excited by periodical trapezoidal current pulses. This provides periodical DL frequency tuning.



To check DL frequency accuracy, tests were performed. DL frequency tuning was determined using CFI signal. Two spectra with known spectral line positions were recorded in spectral range $6950.2 - 6951.4 \text{ cm}^{-1}$: FP etalon and CO_2 . Right Fig. presents difference of line positions as measured and determined by FP etalon and CO_2 . Free spectral range of calibrated FP etalon (open squares) is $0.049287(6) \text{ cm}^{-1}$, and difference has STD $1.4 \cdot 10^{-5} \text{ cm}^{-1}$. For 5 CO_2 lines (close circles) similar STD $2.6 \cdot 10^{-5} \text{ cm}^{-1}$ was found in agreement with HITRAN 2012 frequencies accuracy estimation in this spectral range [$10^{-4} - 10^{-5} \text{ cm}^{-1}$]. There are 2 lines having significantly larger difference (local resonances?). Present tests improved DL frequency tuning accuracy to 0.003 % level.

Signals from three spectrometer channels are used to calibrate, control, and test DL frequency tuning. DL frequency tuning was determined by signals from Fabry Perot etalon (FP) and Circle Fiber Interferometer (CFI). Free spectral ranges of FP and CFI were calibrated with accuracy 0.012 and 0.015 %, respectively. Spectral line in reference channel (Ref) is used to stabilize DL frequency tuning cycles. Stability of reference line position is $1.2 \cdot 10^{-6} \text{ cm}^{-1}$. Reproducibility of DL frequency tuning is $6 \cdot 10^{-6} \text{ cm}^{-1}$ ($8 \cdot 10^{-4} \%$ for 0.8 cm^{-1} tuning).



B2

DL SPECTROMETER: INTEGRAL INTENSITY TEST

A.Nadezhdinskii

A.M. Prokhorov General Physics Institute, RAS, Moscow, Russia

Diode Laser (DL) spectrometer for high accurate measurements was developed (A1). Test of its frequency tuning accuracy was performed (B1). Test of spectral line integral intensity measurements is subject of present paper.

Isolated CO₂ line 6953.467 cm⁻¹ (P20e of 00031-00001 band) was selected to be used in the test. Cell #2 (L = 183.50(4) cm) was filled with pure CO₂ (purity better than 99.98 %) at different pressures. Simultaneously with spectra recording gas pressure and temperature were measured. Accuracy of pressure and temperature measurements is 0.02 % and 0.05 °C, respectively. Five measurement series were performed during period of 20 days. Experimental spectra were fitted by software developed (A2 Hard). Results of fitting are shown in Fig.1.

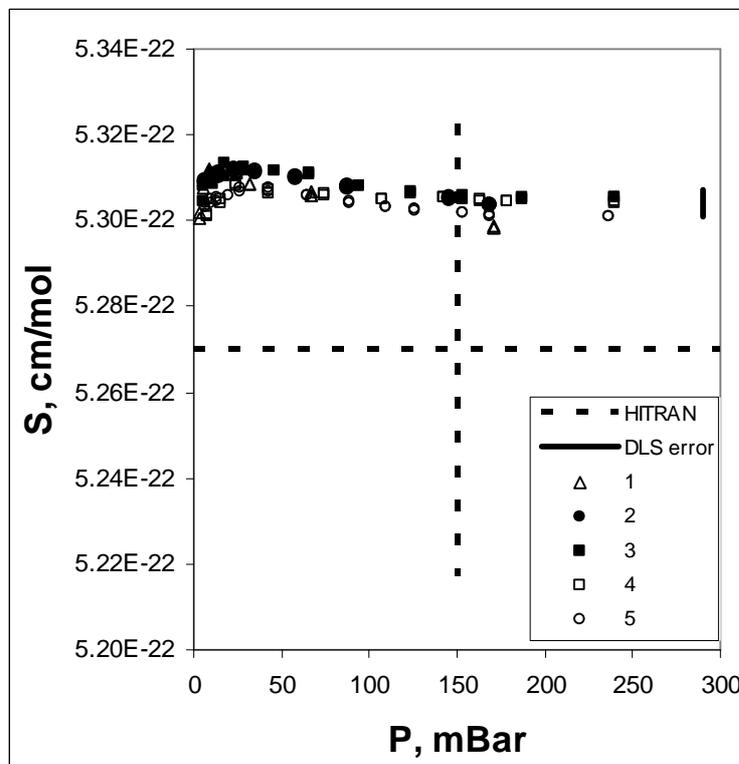


Fig.1 Measurements of analytical line integral intensity

Horizontal dashed constant is HITRAN integral intensity for analytical line. HITRAN accuracy estimation for this line is 1 – 2 %. Vertical dashed line corresponds 1 %. Our data can confirm HITRAN accuracy estimations. The reverse is not valid.

Spread of experimental data in Fig.1 is in agreement with vertical bar - our accuracy estimation (0.06 % - A1).

The test purpose: for isolated line integral intensity has to be constant.

Test result: integral intensity of analytical line is constant within 0.08 %.

However, reproducible pressure dependence of experimental results can be observed. Its physical origin will be discussed.

B3

METHANE CONCENTRATION SPACIAL AND ALTIUDE PROFILES IN ARCTIC, MEASUREMENTS USING TDLS COMPLEX OF AIRPLAN – LABORATORY “ROSHYDROMET”

A. Kuzmichev^{1,2}, A. Nadezhdinskiy², Ya. Ponurovskiy², D. Stavrovskii², Y. Shapovalov², V. Zaslavskii², V. Khattatov¹, V. Galaktionov¹,

¹*Federal State Budgetary Institution “Central aerological observatory”, Dolgoprudny
Moscow Region, Russia;*

²*A.M.Prokhorov General Physics Institute of RAS, Moscow, Russia
askuzmichev@gmail.com*

ROSHYDROMET has program of environment monitoring. According to this program monitoring campaign was performed during June 2014 using airplane – laboratory “ROSHYDROMET”. The campaign goal: investigation of the ability to identify pollution from industrial centers of Europe in the Yamal-Nenets Autonomous District. Part of this campaign was measurement of greenhouse gases special and altitude distribution.

To obtain methane distribution, TDLS complex [1] of airplane – laboratory was used. CH₄ concentration was measured using the complex channel with 1650 nm diode laser.

The campaign results will be presented.

As example, Fig.1 shows results obtained June 24, 2014.

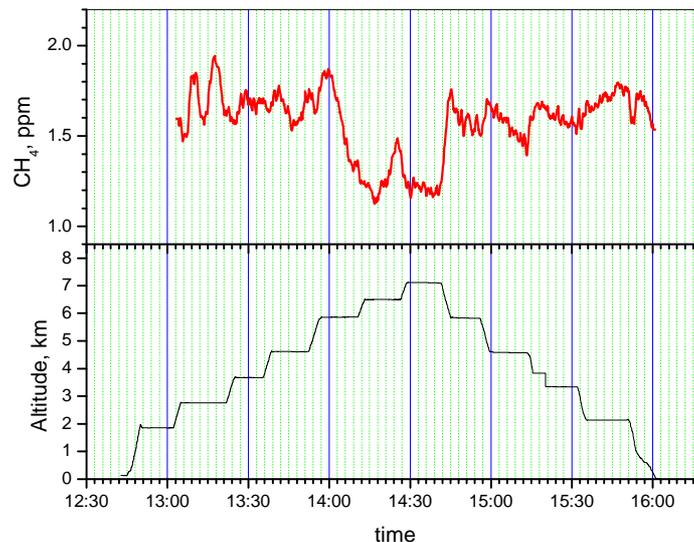


Fig.1 Results of June 24, 2014

[1] A. I. Nadezhdinsky, Ya. Ya. Ponurovsky, Y. P. Shapovalov, I. P. Popov, D. B. Stavrovsky, V. U. Khattatov, V. V. Galaktionov, A. S. Kuzmichev, "Preliminary results of an aircraft system based on near-IR diode lasers for continuous measurements of the concentration of methane, carbon dioxide, water and its isotopes", Appl. Phys. B (2012) 109:505–510

CONCEPT OF TDL BASED SPECTROMETER FOR LOCAL AND COLUMN GREENHOUSE GASES MONITORING

A. Klimchuk¹, V. Semenov¹, I. Mihailov¹, A. Ushakov¹, A. Rodin^{1,2}

¹Moscow Institute of Physics and Technology, Moscow, Russia

²Space Research Institute, RAS, Moscow, Russia

In this paper we present a concept of TDL based spectrometer for local and column greenhouse gases monitoring in particular for CO₂, CH₄, N₂O and O₂. The optical scheme of spectrometer's single gas monitoring channel is shown in figure 1 for CO₂ as an example.

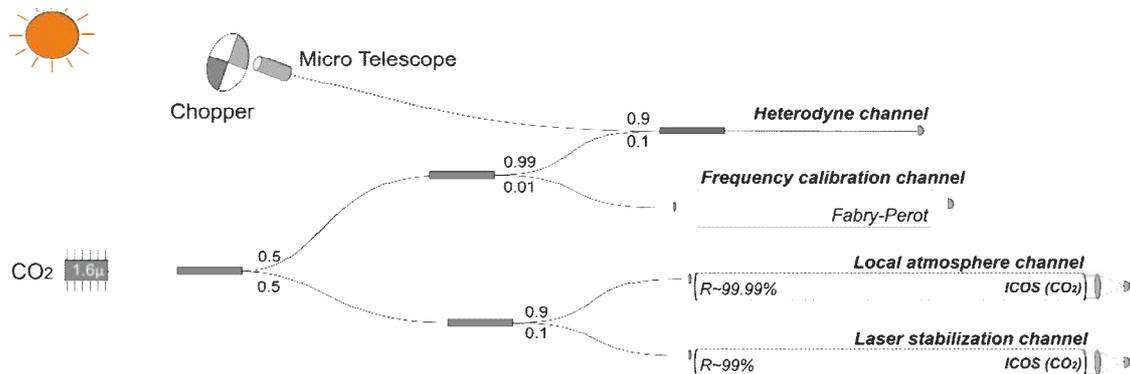


Figure 1. The optical scheme of spectrometer's single channel for monitoring CO₂.

For each gas monitoring the laser radiation is divided into four channels.

One of the channels is used for monitoring CO₂ abundance in the local atmosphere. This channel is presented by off-axis integrated cavity output spectroscopy (OA ICOS). Mirrors with reflection coefficient $R \sim 99.99\%$ are used in order to achieve effective optical path equal to 1500 meters for high sensitivity CO₂ monitoring. Measurements will be conducted at a pressure of 100 mBar and a compact diaphragm pump will be used.

Reference gas spectra will be used for diode laser frequency stabilization. These spectra will be recorded in specified channel, which is also based on OA ICOS technique. Mirrors reflection coefficients are equal to $\sim 99\%$ in this case. A frequency scale calibration will be provided by Fabry-Perot (FP) etalon in third channel. The same FP- etalon will be used for each gas measurements.

The last channel is presented by heterodyne spectroscopy and will be used for average column and vertical profiling measurements of greenhouse gases. The intermediate frequency bandwidth is 10 MHz. The spectral coverage is provided by laser wavelength sweep with 100 kHz frequency. Signal registration will be carried out by high-speed electronics without principal nonlinear elements in analog signal path.

Present concept incorporates channels for local and column monitoring of CO₂ (1.605 μ), CH₄ (1.65 μ), O₂ (1.27 μ), N₂O (2.25 μ) and can be easily extended to H₂O (1.39 μ), CO (2.33 μ), etc. measurements.

Studies of the temperature and pressure dependence of the methane absorption spectra in NIR with a tunable diode laser spectrometer

Sh. Sh. Nabiev, D.B. Stavrovskii, V. Semenov, Ya.Ya. Ponurovskii, G.Yu. Grigor'iev

*National Research Center "Kurchatov Institute",
1, Kurchatov sq., Moscow, 123182 Russia
E-mail: Nabiev_SS@nrcki.ru, semenov.v.m@gmail.ru*

During last years transportation of liquid natural gas (LNG) is growing to very large scale. Besides of all profits storage and transport of LNG may involve a relatively large environmental risk. Practically all LNG equipment operates at very low temperature -162°C . At this temperature storage tank on a ship or on land could be burst and the contents spill out onto the ground or water surface. To make models of LNG vapor plume and hazards it is necessary to know parameters of plume such as density and temperature of methane. In laboratory and field experiments it is difficult to measure these parameters by usual sensors. Most popular optical sensors can't be used because of fast saturation of absorption bands of methane. We have tried to measure density and temperature of cold methane by tunable diode laser spectroscopy of hot bands which are transparent enough even at high density of CH_4 .

The absorption spectra of a hot band multiplet of pure methane (CH_4) and its mixture with nitrogen (CH_4+N_2 , 5% of CH_4) have been recorded in the $6062.2\text{-}6063.9\text{ cm}^{-1}$ spectral range using tunable diode laser spectrometer. The lasing linewidth (HWHH) was at least 10^{-4} cm^{-1} . A liquid nitrogen cooled analytical cell with an optical path $L=235\text{ cm}^{-1}$ have been used in order to study the temperature dependence of absorption spectra. CH_4 and CH_4+N_2 spectra have been recorded in the temperature range $\Delta T = -127 - +23^{\circ}\text{C}$. Additionally, CH_4 spectra have been studied at $T=+23^{\circ}\text{C}$ in the pressure range $\Delta P=0.35\text{-}25\text{ kPa}$. Spectra of CH_4+N_2 are presented on fig. 1 as an example.

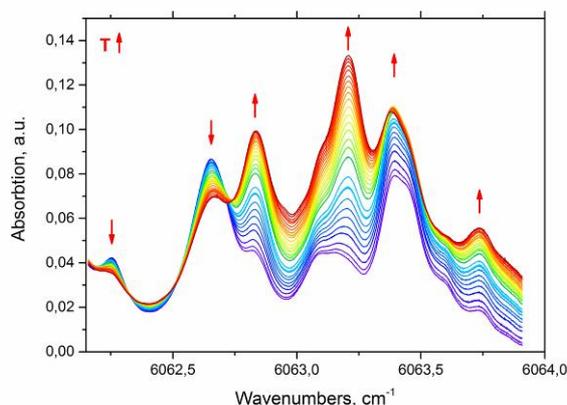


Fig. 1. Absorption spectra of CH_4+N_2 mixture (5% of CH_4) in temperature range $\Delta T = -127 - +23^{\circ}\text{C}$. Evolution of spectral bands with temperature growth is shown with arrows.

Recorded spectra demonstrate a good agreement with calculations, which was based on HITRAN-2012 database. Special software has been developed in order to fit an experimental spectrum with a model one. The software is based on LabVIEW engine, Levenberg-Marquardt algorithm and data from spectral databases (HITRAN, <http://spectra.iao.ru/>). Possibility of temperature and CH_4 -concentration measurements in is CH_4+N_2 mixture is demonstrated.

B6

TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY USED AS MOISTURE ANALYZER IN ACETYLENE GAS

S.E.Bhandarkar¹, V.M.Raut²

*^{1&2} Associate Professor, Department of Chemistry, Government Vidarbha Institute of Science
and Humanities , Amravati- 444604,(M.S.), India*

E-Mail : subodhmv@gmail.com, vivekmraut@gmail.com

Abstract

From the point of view of supplier and consumer the removal of water from Acetylene gas is of considerable costs. Reducing dehydration costs however is a tradeoff between the reduction of “gas quality” and increased maintenance. Water in excess amounts results in component corrosion, lowers the calorific value of the gas and increases the energy consumption for compression and transportation. The embodiment of this method is a process analyzer and sampling system designed to continuously measure the water concentration in acetylene gas.

GE Sensing and Inspection Technologies is in the process of developing a hygrometer for measuring water vapor in acetylene gas by utilizing TDLAS (tunable laser diode absorption spectroscopy). The system offers advances in long-term stability and speed of response. The tunable laser diode absorption spectroscopy analyzer is based on the Lambert-Beers principle that fundamentally relates the concentration of an analyte in a gas matrix to the absorption of tunable diode laser radiation by the sample gas. The system is attractive for monitoring moisture in acetylene gas because the wetted parts are inert and intrinsically safe thereby assuring long-term operation with infrequent maintenance. Test data that compares a TDLAS hygrometer to humidity standard is presented.

Key Wards : Tunable Diode Laser Absorption Spectroscopy, Acetylene Gas, Moisture

B7

DETERMINATION OF AMMONIA IN NAGPUR CITY USING TDLAS OPEN PATH SYSTEM

V.W.Banewar¹, A.R.Raut²

^{1&2} Associate Professor, Department of Chemistry, Government Vidarbha Institute of Science and Humanities , Amravati- 444604,(M.S.), India

E-Mail : banewar@gmail.com, arunrautchem12@gmail.com

Abstract :

Gaseous ammonia is the third most abundant nitrogen compound and the most abundant alkaline trace gas in the atmosphere. Ammonia plays an important role in aerosol formation, as the principal neutralizing agent for atmospheric acids, it is thought to be a major influence on regional air quality, acid deposition, atmospheric visibility. The main source of atmospheric ammonia is agriculture, industries, landfills, household products, biomass burning, motor vehicles, etc

This work demonstrates the use of the NIRTDL system for the measurement of ammonia gas in Nagpur city. Open-path, in-situ measurement techniques avoid the problems associated with wall losses and memory effects. In addition, they enable the continuous, real-time measurements of gas-phase species that are necessary to study aerosol formation and deposition rates. The high spectral resolution and tunability of diode lasers permit open-path measurements of components in a complex mixture. The high spectral resolution and tunability of the diode laser provide unequivocal identification with a very high degree of discrimination against interfering species, while frequency modulation techniques yield sensitivities in the range of ppbv-m.

Key Words : TDLAS, Ammonia , Nagpur City.

B8

Technical possibility for atmosphere CO₂ purification to get climate recovery

Tamara Tulaikova, Svetlana Amirova

*Moscow Institute of Physics and Technology, Department of Aero-physics and Space
Research, Institute per. 9, Dolgoprudny, 141700 Moscow region, Russia.*

E-mail: tulaikova@gmail.com

The novel approach for free atmosphere CO₂ purification is proposed. The proposed method includes two simple stages. The first stage involves the injection of alkaline reagents into natural clouds in order to increase their pH up to 10 – 11 to get high CO₂ absorption in rainy droplets. Precipitation enhancement can be applied during the second stage, and the acoustical method in particular. Our calculations indicated a considerable increase in the gas/water interface for all rain droplets with a perfect purification effect. The small diameters of the droplets provided fast gas saturation in comparison with time in flight during rains. In this work, two example chemical reagents are discussed in the context of cloud dynamics, and simple mechanisms for alkali introduction into clouds are provided.

The possibilities of DLS for sensitive atmosphere environmental monitoring during the method application at under-cloud purified volume will be considered. Algorithm for measurements during the fast artificial processes of purification and cooling of the atmosphere will be offered for the purpose of discussion and further optimization.

The estimations obtained during the study indicated a positive outlook for the proposed method and its utilization could offset annual carbon emission. The application of this method on the global scale was analyzed for the whole Earth for its surface area with an average annual layer of precipitation is approximately 1 m. The calculations were done for the ration of global annual emission in comparison with the removed carbon mass in presented method, and it can deduce the minimal Earth's surface (%) to apply the method considering the compensation of annual CO₂ emission as a result. As a result such future technology can compensate for annual carbon emission by method application at 0.42% – 0.14% of our planet surface then $pH = 10 - 10.8$. The other advantage of proposed approach is the very good response of plants to the precipitation which is modified in this method. We received a strong vegetation growth by enriched watering in the photos which will be presented.

References

1. Tamara Tulaikova, Svetlana Amirova. "The effective possibility for atmosphere CO₂ purification", 2012, Lap-Lambert, Germany, ISBN 978-3-8454-7851-7.
2. S.Amirova, T.Tulaikova. *Science Discovery*. "One possibility for atmosphere CO₂ purification to get climate recovery". Special Issue: New Technical Ideas for Climate Recovery. Vol. 3, No. 2-1, 2015, pp. 1-6. doi: 10.11648/j.sd.s.2015030201.11

LINE INTENSITY MEASUREMENTS AND LINE PROFILE STUDY OF THE R6 MULTICOMPONENT OF CH₄ NEAR 1.64 μm FOR THE FRENCH/GERMAN CLIMATE MISSION MERLIN

*R. Vallon*¹, *T. Delahaye*², *H. Tran*², *B. Parvite*¹, *V. Zeninari*¹

*1 Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR 7331 CNRS, Université de Reims
Faculté des Sciences, Moulin de la Housse, BP 1039, 51687 Reims Cedex 2 – France*

*2 Laboratoire Interuniversitaire des Systèmes Atmosphériques, UMR 7583 CNRS, Université
Paris-Est Créteil, 61 avenue du Général de Gaulle, 94010 Créteil Cedex – France
raphael.vallon@univ-reims.fr*

Climate change is one of the greatest challenges presently facing mankind, and methane is one of the most powerful anthropogenic greenhouse gases. For a better understanding of future climate trends, it is necessary to apply precise space-based measurements in order to obtain a global view on the complex processes that control atmospheric methane concentration. In this context, a satellite dedicated to the measurements of atmospheric methane is under joint development by the French and German space research centers (CNES and DLR). The so-called MERLIN mission (MEthane Remote LIdar mission, 2019) aims at providing global information on atmospheric methane concentration (methane column density) with a relative uncertainty less than 2% and with a spatial resolution of 50 km along the measurement track under cloudy and variable-solar illumination conditions. The main data product will be the column-weighted dry-air mixing ratio of CH₄.

Such spectroscopic monitoring of gases in the atmosphere of Earth, requires a precise description of absorption lines shapes that goes beyond the usual Voigt profile (VP). In the case of methane, the differences between the measured profiles and those given by the VP can be very important [1], making the VP completely incompatible with the reliable detection of sources and sinks from space. These differences are due to various collisional effects between molecules that are neglected by the VP: collisional interference between the lines (line-mixing), collision-induced velocity changes (Dicke narrowing effect) and speed dependence of the collisional broadening and shifting.

In this work, we present results on the modeling of methane lines in the 1.64 μm region and the associated spectroscopic parameters taking into account all of these collisional effects. These results are obtained by simultaneously fitting the model parameters to high-resolution tunable diode laser spectra recorded at GSMA, Reims. This work will be continued with the study of air-broadened spectroscopic parameters.

References

[1] H. Tran, J.-M. Hartmann, G. Toon, L.R. Brown, C. Frankenberg, T. Warneke, P. Spietz, F. Hase, « The 2n₃ band of CH₄ revisited with line mixing: Consequences for spectroscopy and atmospheric retrievals at 1.67μm », *Journal of Quant. Spectrosc. Radia. Trans.* 111, 1344-1356 (2010), <http://dx.doi.org/10.1016/j.jqsrt.2010.02.015>

B10

TRACE GAS MONITORING WITH IR LASER-BASED DETECTION SCHEMES

A.R.Rau¹, M.P.Wadekar²

^{1&2} Associate Professor, Department of Chemistry, Government Vidarbha Institute of Science and Humanities, Amravati- 444604, (M.S.), India

E-Mail : arunrraut02@gmail.com, murliwadekar@gmail.com.

Abstract

In recent years, laser-spectroscopic sensing devices have attracted a lot of interest as they enable high detection sensitivity (down to sub-ppb concentrations) and selectivity (including differentiation between isotopomers and isomers), multi-component capability and large dynamic range (several orders of magnitude in concentration) and generally neither sample-preparation nor - preconcentration are required. However, the laser source characteristics in terms of available wavelengths, tunability, linewidth, power, operation temperature, etc., as well as the combination with appropriate sensitive detection schemes are crucial for the success of laser-based sensing. As the fundamental molecular absorption ranges lie in the mid-infrared, emphasis is on lasers in the range between ca. 3 and 15 μm . Available sources include CO- and CO₂-lasers, lead salt diode lasers, quantum cascade lasers and nonlinear optical systems (optical parametric oscillators (OPOs) and difference frequency generation (DFG)). Most common detection methods include direct absorption in multipass cells (eventually combined with wavelength modulation), photoacoustic and cavity ringdown spectroscopy. Within the frame of a previous measurement campaign we demonstrated field sensing with an unattended mobile CO₂-laser-photoacoustic system employed for time-resolved street traffic emission and in collaboration with an industrial partner, we performed a feasibility study for online sensing of acetylene (C₂H₂) contaminants in an ethylene (C₂H₄) carrier gas flow. A current project focuses on the detection of methylamines in human breath as possible tracers for liver or renal diseases. First spectroscopic studies on air samples containing given concentrations of di- or tri-methylamine with a near-IR diode laser cavity ringdown and a mid-IR DFG absorption spectrometer will be discussed. A further project is aimed at laser spectroscopic analyses of doping agents used by athletes in sports. CO₂ and N₂O isotopomers are in progress and will be discussed in a separate presentation.

INTAGRATED CAVITY OUTPUT SPECTROSCOPY USING REFLECTION

I.V.Nikolaev, V.N.Ochkin, S.N.Tskhai

*P. N. Lebedev Physical Institute, Russian Academy of Sciences, Leninsky pr. 53, 119991
Moscow, Russia*

e-mail: primobaler@mail.ru

We present a new method of measuring weak absorption based on the widespread ICOS technique. In this method we use three-channel scheme in which we detect the radiation incident on and reflected from the cavity, as well as the radiation transmitted through the cavity. This approach allows compensating noises related with mismatching of the laser radiation with the eigenmodes of the cavity. It leads to a significant decrease of the integration time. We use the linear regression procedure to calculate the absorption spectrum.

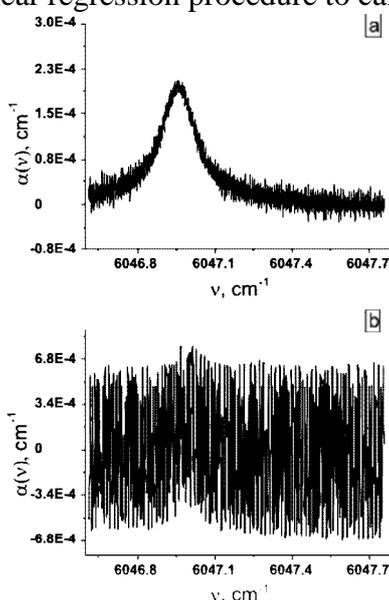


Fig1. Absorption spectra obtained by a) R-ICOS technique b) ICOS technique respectively

The method is developed for measuring methane concentration in atmospheric gases with natural content of methane, as well as in gases with increased methane concentration. The reflectivity of cavity mirrors was 99%. The background concentration of methane (a $\sim 1.6 \cdot 10^{-6} \text{ cm}^{-1}$) was measured during $320 \mu\text{s}$, and the sensitivity was $2 \cdot 10^{-8} \text{ cm}^{-1}$ using an integration time of 20 s.

Nonlinearity of the detected signal allows us to measure concentrations in samples with increased concentrations of the absorber when it is impossible to use the standard ICOS technique.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (project no 14-02-00553-a).

B12

LIGHT EMITTING DIODES FOR COMPACT CARBON DIOXIDE DETECTION DEVICES

*D.M. Kabanau^a, V.V. Kabanov^a, Y.V. Lebiadok^a, G.I. Ryabtsev^a, P.V. Shpak^a,
Yu.P. Yakovlev^b*

*^a B.I. Stepanov Institute of Physics, National Academy of Sciences of Belarus,
Nezalezhnasti Ave. 68, 220072 Minsk, Belarus, ryabtsev@ifanbel.bas-net.by*

*^b A.F. Ioffe Physicotechnical Institute, Russian Academy of Sciences, Polytechnicheskaya ul.
26, 194021 St. - Petersburg, Russia*

We present results of application of developed light emitting diodes (radiation wavelength is in the range of 3-5 μm) to the carbon dioxide concentration measurement devices. The light emitting diodes (LED) are based on the InAs/InAsSb/InAsSbP heterostructure [1]. Spectrum of LED with maximal output power at the wavelength 4.6 μm is presented in Fig.1. For the detection of LED radiation the InAs/InAs_{0.94}Sb_{0.06}/InAs_{0.88}Sb_{0.12}/InAsSbP/InAs photodiode [3] was used.

The peculiarities of LED application in the compact devices for carbon dioxide detection are discussed in the report.

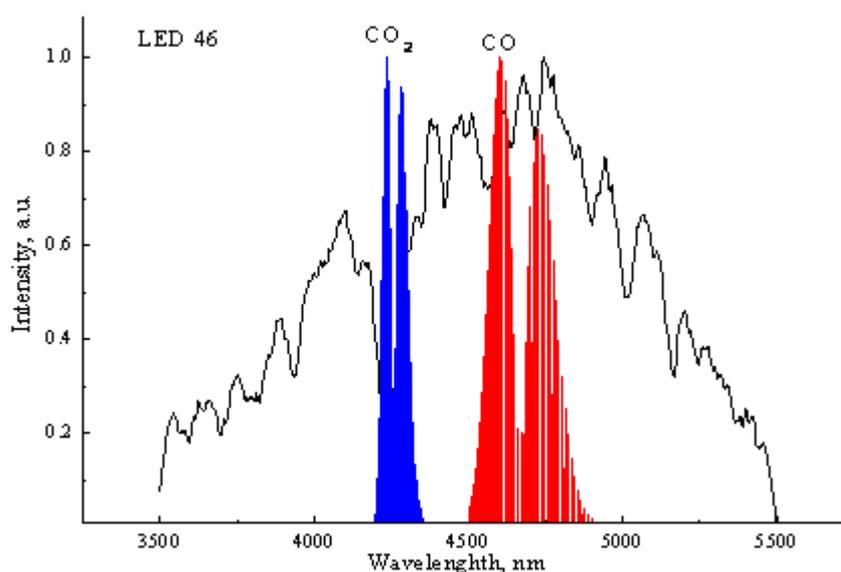


Fig.1 LED-46 radiation spectrum (experimentally obtained in the air) and CO and CO₂ absorption spectra from HITRAN [2]

References:

- [1] A.S. Golovin, A.A. Petukhov, S.S. Kizhaev, and Yu.P. Yakovlev, Technical Physics Letters, 37, 497-499 (2011).
- [2] L.S. Rothman et al., J. Quant. Spectr. Rad. Trans., 110, 533 (2009).
- [3] A.N. Imenkov et al., Semiconductors, 47, 701-706 (2013).

B13

TDLAS ANALYSIS OF STABLE ISOTOPES IN METHANE AND CARBON DIOXIDE

Teemu Kaariainen and Albert Manninen

*VTT Technical Research Centre of Finland Ltd, Tekniikantie 1, Espoo, Finland Indicate
Contact: teemu.kaariainen@vtt.fi*

Real-time measurement of isotopes has become a valuable tool in environmental and medical sciences. Variations in isotopic ratios are connected with different sources and sinks of the gas. For example, anthropologically produced CO₂ is typically enriched in the heavier carbon isotope, whereas biogenic processes tend to deplete heavier isotopes [1]. CO₂ isotopes in human breath can be used as a diagnostics tool to determine various medical conditions. For example, monitoring of heavy carbon in breath air after ingestion of ¹³C-labelled compounds can be used to diagnose *Helicobacter pylori* infection, exocrine pancreatic insufficiency or gastric emptying disorders [2]. Isotopic ratios of CH₄ could be used to determine the biogas-to-natural gas ratios in energy gas mixtures.

Recently developed mid-infrared (IR) laser sources have enabled isotope selective measurements of the fundamental ro-vibrational transitions for these gases. These transitions are orders of magnitude stronger than more commonly used near-infrared overtone transitions. This enables more precise measurement with more compact instrumentation.

To address the demand for instrumentation, TDLAS analyzer was developed. Stable isotopes of CO₂ atmospheric levels and pure CH₄ can be accessed with a single field capable instrument by merely changing the laser. CO₂ isotopic ratios are measured with an ICL operating at 4,3 μm and diode laser operating at 3,3 μm is used for CH₄. Higher CO₂ concentrations, such in exhaled breath, can be compensated by dilution with synthetic air.

This project has been partially funded by the European Metrology Research Programme (EMRP) ENV52 project HIGHGAS (Metrology for high-impact greenhouse gases) [3] and ENG54 project Biogas (Metrology for biogas) [4].

References

- [1] Pataki, D. E., et al. "Urban ecosystems and the North American carbon cycle." *Global Change Biology* **12.11**, 2092-2102 (2006).
- [2] Braden, B., et al. "¹³C-breath tests: current state of the art and future directions." *Digestive and liver disease* **39.9**, 795-805 (2007).
- [3] EMRP project ENV52-HIGHGAS (Metrology for high-impact greenhouse gases), available at: <http://www.euramet.org/>
- [4] EMRP project ENG54-Biogas (Metrology for Biogas), available at: <http://www.euramet.org/>

Laser calorimetry spectroscopy: a novel approach for in-liquid dissolved gas detection and measurement

S Maity¹, Nagapriya K S¹, S Sinha², Prashanth R³ and S Poonacha¹

¹ GE Global Research, GE India Technology Centre, Bangalore 560066, India

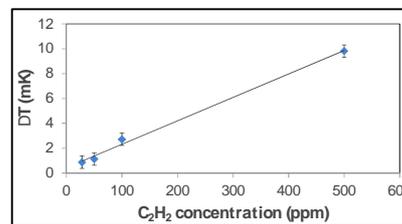
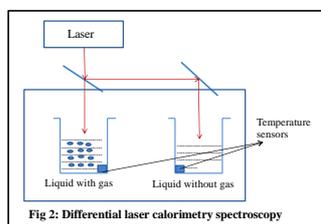
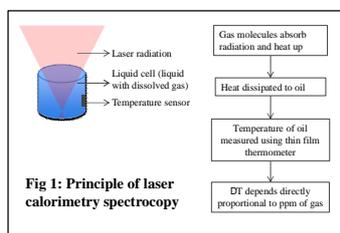
² RGSi, Bangalore 560027, India

³ Department of Electrical Communication Engineering, Indian Institute of Science, Bangalore 560012, India

Analysis of dissolved gases in liquids is of prime importance in a wide array of fields like transformer health monitoring, food and beverage industries (e.g. measuring amount of ethanol in wine), oil and gas industry (measuring dissolved gases in down hole condition, etc.). Conventional chemical and electrical sensing and analysis cannot be used due to harsh environmental conditions, high EMC/EMI.

Optical analysis is preferred due to its specificity and its non-interfering nature. However, optical spectroscopies suffer from need for line of sight, and if measured in liquid, the liquid should be transparent or substantially transparent to the radiation (wavelengths) used. For liquids like water or oil, finding a wavelength where the gas absorbs strongly while the liquids do not absorb is very difficult. Usually the absorbance of the liquid is much stronger than absorbance of the gas. Therefore conventionally, gases are extracted out from the liquids and then analyzed, either using an optical method or using GC. However, accuracy of dissolved gas concentration from such extracted technique has inherent problems of temperature and pressure dependent partition function. There is, therefore, an overwhelming need for in-liquid dissolved gas analysis.

A novel technique laser calorimetry spectroscopy (LCS) [1,2], which is a combination of laser absorption spectroscopy and calorimetry, for the in-liquid detection of gases dissolved in liquids is presented here. The technique involves determination of concentration of a dissolved gas by irradiating the liquid with a specific wavelength of light where the interested gas to be detected absorbs, heats up, radiates to the surrounding liquid, causing a change in temperature. The change in temperature (T) is measured (fig 1) and is a measure of the gas concentration. The T change due to the absorbance of the liquid is eliminated (or substantially eliminated) by using a differential T measurement (using a reference virgin liquid) (fig 2). Since most gases that need to be detected have their fundamental vibrational modes in the MIR region, QCLs and ICLs have been used for the measurements. Using LCS,



we have been able to detect ppm levels of gases (like C_2H_2 and CO_2) without extracting them from the liquid (fig3).

[1] S Maity, Nagapriya K S, and S Sinha, *US Patent App.* 13/950,733 (2013).

[2] S Maity, Nagapriya K S, S Poonacha, and Prashanth R, *US Patent App.* 14/134,525 (2013).

Poster session C

C1

Line shape models analysis for high accurate experimental data

A.Nadezhdinskii

*A.M.Prokhorov General Physics Institute of RAS, Vavilov str. 38, 119991 Moscow, Russia
NAD@nsc.gpi.ru*

Accuracy level 0.06 % was recently achieved in TDLS (see A1). Next step was high accurate experimental spectral line shape fitting (see A2). It was shown that only for correct line shape model fitting parameters have physical meanings. Line shape models analysis for high accurate experimental data is objective of present paper.

To test line shape models, isolated spectral line is necessary. Isolated spectral line (6953.467 cm^{-1}) of CO_2 molecule was selected for present investigation. It is very convenient for experiment: purity, sample preparation, etc.

Spectral line is convolution of Doppler and impact profiles.

For Doppler profile two limit solutions of kinetic equations were found by I.Sobel'man: soft (infinite number of collisions to achieve velocity relaxation - diffusion approach) and hard (one collision for relaxation of molecule velocity). With this respect CO_2 demonstrates something intermediate between soft and hard.

For impact profile (collisions duration \ll time between collisions) Lorentz shape is using. Lorentz shape parameters depend on molecular velocity (speed dependence). It results in line asymmetry. For CO_2 asymmetry is high enough.

In general one more profile has to be included in convolution: profile describing correlation between phase and velocity changes during collision. For CO_2 cross sections of velocity and phase changes are close to each other. Hence, both changes take place on the same trajectories, subject for correlation.

So, CO_2 molecule is not good to check correct line shape model.

However, CO_2 molecule is good to estimate different models applicability for high accurate spectral line measurements for different pressure ranges.

C2

FIBER OPTIC METHANE SENSOR USING DIODE LASER NEAR INFRARED RANGE

*S.Kataev², A.Kulakov¹, A.Nadezhdinski², Dm.Pleshkov¹,
Ya.Ponurovskii², Yu.Shapovalov², M.Spiridonov², V.Zaslavskii²*

¹*PETROLIGHT, Ltd, Moscow, Russia*

²*A.M. Prokhorov General Physics Institute, RAS, Moscow, Russia
ponur1960@yandex.ru.*

Methane concentration monitoring in hazard areas is an important task for many applications (coal, oil, natural gas industries, etc.). Minimum CH₄ concentration in the air when explosion is possible is 5 % and its measurement below 3 % is necessary. Additional requirement for some applications: no even low voltage electricity is allowed in hazard area. It means that all information transfer from control point to hazard area and back has to be done by light. Distance between control point and hazard area can be around 50 km. The sensor has to operate in hard environment conditions with high sensitivity and performance: temperature from -30 to 50 °C, high humidity and dust.

Fulfilling these requirements is a subject of present paper. The sensor under consideration was developed. Its block-scheme is shown in Fig.1.

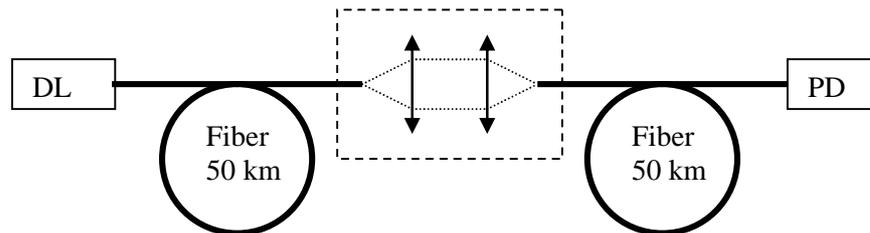


Fig.1 Block-scheme of methane sensor developed

NEL DL (1.651 μ) was used as a light source. Its radiation was transferred by 50 km single mode fiber cable to hazard area (dashed rectangular). To model it, a glass box ($V = 8$ liters) was used during tests. Analytical cell ($L = 5$ cm) was installed inside the box. After passing the analytical cell, DL radiation was focused in the other 50 km single mode fiber cable to transfer it to PD located at the control point.

During the tests carried out the glass box was filled with a known amounts of methane. Minimum detectable concentration (3 σ) was 60 ppm at 50 ms response time. The results of experiments demonstrated a feasibility of CH₄ remote sensing with the above mentioned requirements.

LINE PROFILE MODEL TESTING ON CO₂ “QUASI”-ISOLATED SPECTRAL LINES OF 30013-00001 BAND

K.Osipov¹, V.Kapitanov¹, Yu.Ponomarev¹, A.Protasevich¹, Ya.Ponurovskii²

¹*V.E. Zuev institute of atmospheric optics SB RAS, Tomsk, Russia
osipov@iao.ru*

²*A.M. Prokhorov General Physics Institute, RAS, Moscow, Russia
ponur1960@yandex.ru.*

CO₂ lines absorption spectra measurements in 30013-00001 band at spectral range (6237-6244 cm⁻¹) within the pressures up to 1 atm were performed on 2-channel high-resolution diode laser spectrometer with a signal-to-noise (S/N) ratio up to 3000. The selected spectral range includes 6 relatively strong lines which can be considered as isolated. This fact is the best suitable situation thorough the task of line shape profile testing. 4 theoretical models were used for the description of line shape: usual Voigt, Hard-collisional (Rautian), Soft-collisional (Galatry), and Speed-dependent Voigt (Boone). LabView based software developed was used for the testing of current line shape models. This software performed the nonlinear least-squares fit of the model spectrum to the experimental spectra recorded at each pressure individually. For all 6 measured spectral line is shown that the use of Rautian and Galatry line shape models leads to a significant deviation from linear pressure dependence of the narrowing coefficient while coming to the high pressures range. Most appropriate for the common description of whole experimental spectra in entire range of pressures (up to 1 atm.) is the Speed-Dependent (Boone) profile.

C4

CO₂ AND CH₄ CONCENTRATIONS MEASUREMENT NEAR NOVAYA ZEMLYA USING TDLS COMPLEX OF ROSHYDROMET AIROPLANE - LABORATORY

A.Kuzmichev^{1,2}, A.Nadezhdinskiy², Ya.Ponurovskiy², D.Stavrovskii², Y.Shapovalov², V.Zaslavskii², V.Khattatov¹, V.Galaktionov¹,

¹*Federal State Budgetary Institution "Central aerological observatory", Dolgoprudny Moscow Region, Russia;*

²*A.M.Prokhorov General Physics Institute of RAS, Moscow, Russia
askuzmichev@gmail.com*

ROSHYDROMET has program of environment monitoring. According to this program monitoring campaign was performed during February 2015 near Novaya Zemlya using ROSHYDROMET airplane – laboratory. The campaign goal: investigation of possibilities of identification of results of associated oil gas burning on torches of the oil derricks located in Khanty-Mansi Autonomous Area, also around the Kalchinsky oil field of the Tyumen region and near the city of Berezniki of the Perm area.

Besides data on distribution of soot in the troposphere, the full-fledged assessment of scales of pollution required receiving existential profiles of methane and carbon dioxide. To measure CO₂ and CH₄ TDLS complex [1] of airplane – laboratory was used. Results of altitude distributions of methane and carbon dioxide will be presented.

Scheme of this campaign is presented in Fig.1.



Fig.1 Trajectory of Feb.28, 2015 flight

[1] A. I. Nadezhdinsky, Ya. Ya. Ponurovsky, Y. P. Shapovalov, I. P. Popov, D. B. Stavrovsky, V. U. Khattatov, V. V. Galaktionov, A. S. Kuzmichev, "Preliminary results of an aircraft system based on near-IR diode lasers for continuous measurements of the concentration of methane, carbon dioxide, water and its isotopes", Appl. Phys. B (2012) 109:505–510

**VERTICAL CONCENTRATION PROFILING AND WIND
MEASUREMENTS BASED ON GROUND-BASED NIR HETERODYNE
SPECTRO-RADIOMETRY**

A.Yu. Klimchuk^{1,3}, A.V. Rodin^{1,2}, A.I. Nadezhdinskiy³, D.V. Churbanov¹, M.V. Spiridonov³

¹*Moscow Institute of Physics and Technology, Moscow, Russia*

²*Space Research Institute, RAS, Moscow, Russia*

³*A.M.Prokhorov General Physics Institute, Moscow, Russia*

A compact, lightweight heterodyne NIR spectro-radiometer suitable for ground-based atmospheric sounding by direct spectro-radiometry of Sun spectrum with spectral resolution $\sim 5 \cdot 10^7$ has been used for precise measurements and vertical profiling of methane and carbon dioxide. Highly stabilized DFB laser was used as a local oscillator, while single mode quartz fiber Y-coupler served as a diplexer. Radiation mixed in the single mode fiber was detected by quadratic detector using *p-i-n* diode within the bandpass of ~ 10 MHz. Wavelength coverage of spectral measurement was provided by sweeping the local oscillator frequency in the range of $1,1 \text{ cm}^{-1}$. With the exposure time of 15 min, the absorption spectrum of the atmosphere over Moscow has been recorded with S/N ~ 250 .

We retrieved methane vertical profile using Tikhonov method of smooth functional, which takes into account *a priori* information about first guess profile. The reference to model methane profile means that the regularization procedure always selects *a priori* values unless the measurements contradict this assumption.

The retrieved methane profile demonstrates higher abundances in the lower scale height compared to the assumed model profile, well expected in the megalopolis center. The retrievals sensitivity is limited by 10 ppb, with the exception of the lower part of the profile where the tendency to lower values is revealed. Thus the methane abundance variations may be evaluated with relative accuracy better than 1%, which fits the requirements of greenhouse gas monitoring.

The CO₂ abundance has also been retrieved with the accuracy 3 ppm sufficient for analyzing regional sources of greenhouse gases. CO₂ absorption line was also used to estimate the value of a zonal wind by Doppler shift of the line center. The estimating value of zonal wind is 28.9 ± 4.7 m/s which is corresponding to a global atmospheric reanalysis data ERA-Interim.

PULSED CRDS SENSOR FOR SENSITIVE AND ULTRA-FAST SPECIES DETECTION

*Awad B.S. Alquaity, Et-touhami Es-sebbar, Aamir Farooq**

Clean Combustion Research Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia

**aamir.farooq@kaust.edu.sa*

Study of transient combustion systems like shock tubes, internal combustion engines, and gas turbines requires high time resolution sensors capable of performing sensitive measurements. High-sensitivity sensors can be utilized to measure concentrations of trace species, such as HO₂ and H₂O₂, essential for low-temperature chemistry [1–4]. These species and other combustion radicals have been difficult to measure using currently available measurement techniques [4–6]. Ability to measure minuscule concentrations at very fast rates can be quite useful in the measurement of reaction rate coefficients. In this work, we have developed a novel, highly sensitive ultra-fast sensor based on pulsed cavity ringdown spectroscopy (CRDS) and deployed it for making *in situ* species time-history measurements in shock tube chemical kinetic experiments.

The diagnostic is demonstrated by monitoring trace concentrations of ethylene in the mid-IR region near 949.47 cm⁻¹. Each ringdown measurement is completed in less than 1 μs and the time period between successive pulses is 10 μs. The high sensitivity diagnostic has a noise-equivalent detection limit of 1.08 × 10⁻⁵ cm⁻¹ which enables detection of 15 ppm ethylene at fuel pyrolysis conditions (1845 K and 2 bar) and 294 ppb ethylene under ambient conditions (297 K and 1 bar). To our knowledge, this is the first successful application of the cavity ringdown method to the measurement of species time-histories in a shock tube and demonstrates the potential of CRDS for transient species detection in unsteady combustion experiments.

References

1. C.K. Westbrook, "Chemical kinetics of hydrocarbon ignition in practical combustion systems," *Proc. Combust. Inst.* **28**, 1563–1577 (2000).
2. M.P. Burke, M. Chaos, Y. Ju, F.L. Dryer, S.J. Klippenstein, "Comprehensive H₂/O₂ kinetic model for high-pressure combustion," *Int. J. Chem. Kinet.* **44**, 444–474 (2012).
3. H. Guo, W. Sun, F.M. Haas, T. Farouk, F.L. Dryer, Y. Ju, "Measurements of H₂O₂ in low temperature dimethyl ether oxidation," *Proc. Combust. Inst.* **34**, 573–581 (2013).
4. N. Kurimoto, B. Brumfield, X. Yang, T. Wada, P. Diévar, G. Wysocki, et al., "Quantitative Measurements of HO₂/H₂O₂ and Intermediate Species in Low and Intermediate Temperature Oxidation of Dimethyl Ether," *Proc. Combust. Inst.* **35** (2014).
5. B. Brumfield, W. Sun, Y. Wang, Y. Ju, G. Wysocki, "Dual modulation Faraday rotation spectroscopy of HO₂ in a flow reactor," *Opt. Lett.* **39**, 1783–6 (2014).
6. R.K. Hanson, D.F. Davidson, "Recent advances in laser absorption and shock tube methods for studies of combustion chemistry," *Prog. Energy Combust. Sci.* (2014).

QUANTIFYING METHANE IN AMBIENT AIR WITH MID-INFRARED DUAL FREQUENCY COMB SPECTROSCOPY

*Feng Zhu,¹ Aysenur Bicer,¹ Ruqayyah Askar,¹ James Bounds,¹
Alexandre A. Kolomenskii,¹ Mahmood Amani,² and Hans A. Schuessler^{1,3}*

¹*Department of Physics and Astronomy, Texas A&M University, College Station, TX 77843-4242, USA*

²*Petroleum Engineering Program, Texas A&M University at Qatar, Doha 23874, Qatar*

³*Science Department, Texas A&M University at Qatar, Doha 23874, Qatar*

We build a mid-infrared dual frequency comb spectrometer for the detection of methane in ambient air. Two mid-infrared frequency comb sources based on femtosecond Er:fiber oscillators are produced through difference frequency generation with periodically poled MgO-doped lithium niobate crystals and stabilized at slightly different repetition rates at about 250 MHz. Using a multipass cell of ~580 m path length, we performed dual frequency comb spectroscopy in the spectral range between 2900 cm^{-1} and 3150 cm^{-1} with 0.07 cm^{-1} resolution, and achieved the sensitivity about $7.6 \cdot 10^{-7} \text{ cm}^{-1}$ with 80 ms data acquisition time.

After the FFT and the up conversion from RF to MIR, the normalized spectra can be retrieved from signal and reference spectra. With an 80 μs apodizing window, the RF resolution is 12.5 kHz. Thus the up converted MIR resolution is ~2.1 GHz or 0.07 cm^{-1} , which is sufficient to resolve the absorption features in ambient air (see Fig. 1).

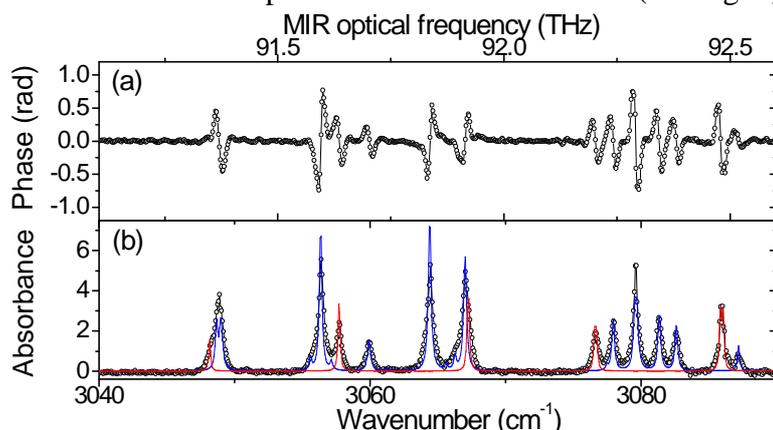


Fig. 1. Normalized methane and water vapor spectra: (a) phase, (b) absorption (black, open circles) compared with simulations from the HITRAN database (red for methane, blue for water) shown in a narrow range 3040~3090 cm^{-1} .

We determined the methane concentration as ~1.5 ppmv in the ambient air of the laboratory, and the detection limit as ~60 ppbv for the current setup.

This research is supported by the Robert A. Welch Foundation grant No. A1546 and the award NPRP 6-465-1-091 from the Qatar National Research Fund.

C8

COMPARATIVE STUDY BY TDLAS & DOAS FOR DETERMINATION OF NO₂ AND PAN IN THE ATMOSPHERE WITH LUMINOL CHEMILUMINESCENCE

V.M.Raut¹, S.E.Bhandarkar²

^{1&2} Associate Professor, Department of Chemistry, Government Vidarbha Institute of Science and Humanities, Amravati- 444604, (M.S.), India

E-Mail : vivekmraut@gmail.com, subodhvmv@gmail.com

Abstract

Nitrogen dioxide and peroxyacetyl nitrate (PAN) are important atmospheric trace gas species associated with photochemical air pollution. Peroxyacetyl nitrate is formed by photochemical oxidation of non methane hydrocarbons in the presence of NO₂. The TDLAS is an absorption technique using lead salt diode infrared lasers as sources. The sample is drawn into a multipass cell that is used to increase the optical path length to 153.5 m, thereby increasing the sensitivity of detection. By luminol chemiluminescence an instrument has been designed and constructed for the simultaneous determination of nitrogen dioxide and peroxyacetyl nitrate (PAN) in atmospheric samples. The instrument's design is based on separation by fast gas chromatography (GC) with a capillary column.

The chemiluminescent reaction between NO₂ or PAN and luminol takes place at the gas-liquid interface on the surface of a solid support. The chemiluminescent emission at 425 nm is detected with a photon counting module. The instrument is controlled by computer with a WINDOWS 2007 operating system.

The instrument was operated during the Nagpur City. Results for NO₂ from this fast GC method were compared with results from a co-located differential optical absorption spectrometer (DOAS) and a tunable diode laser absorption spectrometer (TDLAS). The results support the application of the new luminol-based instrument for atmospheric measurements. This could result in significant differences when the heavy traffic and NO₂ concentrations were highly variable over short time scales.

Key Words : TDLAS, DOAS, NO₂, PAN, luminal.

LAST ADVANCES IN SIMULATION AND DESIGN OF HELMHOLTZ PHOTOACOUSTIC SENSORS

V. Zéninari, R. Vallon, C. Risser, B. Parvitte

*Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR 7331 CNRS, Université de Reims
Faculté des Sciences, Moulin de la Housse, BP 1039, 51687 Reims Cedex 2 – France
virginie.zeninari@univ-reims.fr*

Photoacoustic (PA) spectroscopy is a well-established technique and numerous gas sensors designs have been imagined and implemented. The mass deployment of PA gas sensors is often hampered by the systems' overall size and weight but the technique also possesses favorable detection characteristics when the system dimensions are scaled to a micro-system design. In the framework of the ANR project MIRIADE, the favorable downscaling behavior of PA cells is explored by the miniaturization of PA sensors [1].

The detection limit of PA gas sensors is highly dependent on the efficiency of sound generation in the PA cell. In order to take advantage of the enhancement of the acoustical signal, PA cells are often used in resonant mode. The frequency response of the cell is directly dependent on the resonator shape and size. □ In order to optimize the miniaturized PA sensor, one must be able to accurately predict the frequency response which can be obtained analytically only for simple cell geometries. For more complex cells, electric analogy can also be used to investigate the cell response but finite element method (FEM) presents the ease of use of a computational calculation and has already demonstrated its capabilities for the simulation of PA cell characteristics. In a previous work we have already shown that the resolution of the equations of pressure acoustics using FEM software allows the accurate determination of the frequency response (resonant frequency, quality factor and peak amplitude at resonance) of a macroscopic Helmholtz resonant PA cell [2].

This paper will present a comparative study between experimental characterizations and FEM simulations using Comsol Multiphysics ® that has been carried on several PA cells of decreasing dimensions. This study will show that, as expected, the equations of pressure acoustics are not accurate enough for small resonant cells. A more complex description based on thermoacoustics must be used. The “Thermoacoustics” module of Comsol Multiphysics ® especially designed for small elements is used and simulations show a satisfactory agreement with experimental data for miniaturized cells. The influence of several parameters such as mesh quality will be demonstrated.

Acknowledgments: This work is funded by the ANR ECOTECH project #ANR-11-ECOT-004 called “MIRIADE”.

References

- [1] A. Glière, J. Rouxel, M. Brun, B. Parvitte, V. Zeninari, S. Nicoletti, “Challenges in the design and fabrication of a lab-on-a-chip photoacoustic gas sensor”, *Sensors* **14**, 957-974 (2014) <http://dx.doi.org/10.3390/s140100957>
- [2] B. Parvitte, C. Risser, R. Vallon, V. Zeninari, “Quantitative modelization of photoacoustic signal”, *Appl. Phys. B* **111**, 383-389 (2013) <http://dx.doi.org/10.1007/s00340-013-5344-2>

C10

MONITORING OF AIR QUALITY IN A PASSENGER CAR CABIN WITH COMPUTER-CONTROLLED LASER SPECTROMETERS

Andrei Lytkine, Alexandre Lytkine

*Light Peaks Inc., 420-233 Beecroft Road, North York, ON, Canada M2N 6Z9
e-mail: info@lightpeaks.ca*

We employed portable laser spectrometers controlled by a laptop computer [1] for real-time measurements of CO₂, O₂ and H₂O concentrations in a passenger car cabin. In a series of experiments, a spectrometer based on a 2012-nm VCSEL was connected to the car climate control system to detect CO₂ levels in the air forced into the car cabin. The location and speed of the car were recorded by a GPS tracker. We have found a strong correlation between the CO₂ concentrations and car speed while the car was driven on city streets with frequent stops on traffic lights (Fig. 1-2). Sharp CO₂ concentration peaks are caused by the “clouds” of air pollutants resulted from traffic accelerations following the intersection stops or decelerations.

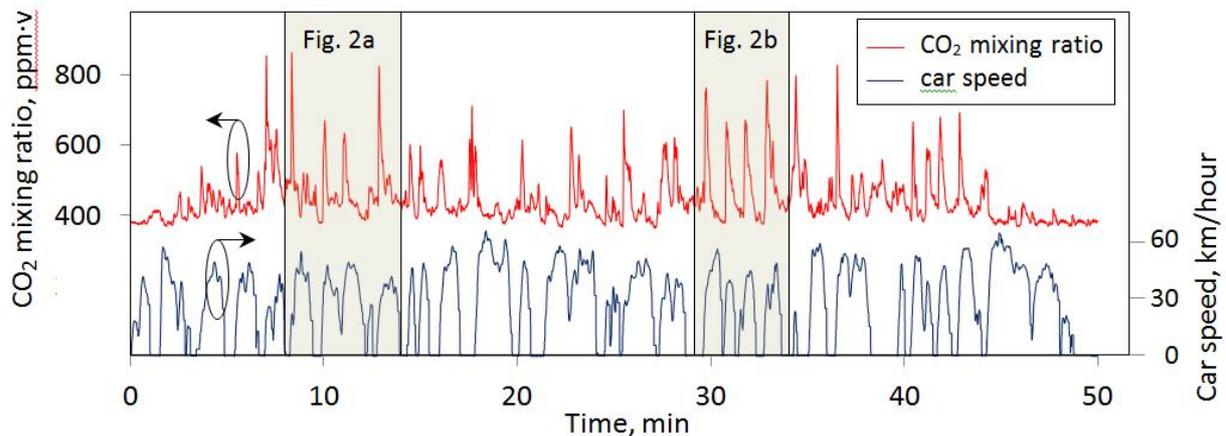


Fig.1. CO₂ concentrations in the inflow air measured simultaneously with the car speed.

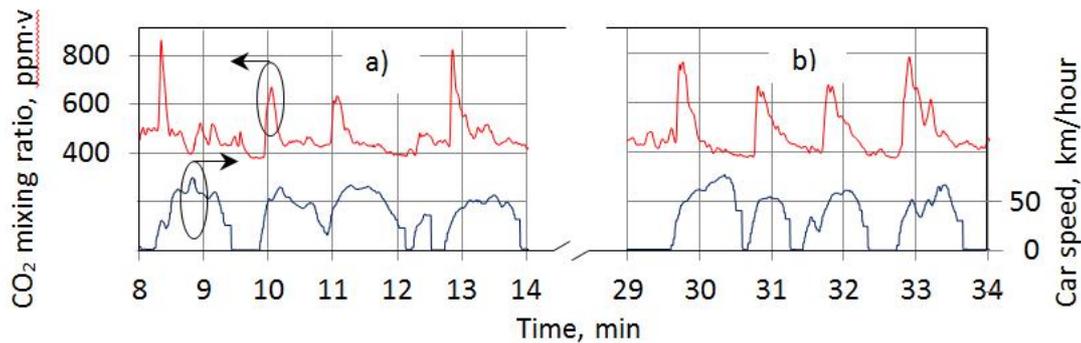


Fig. 2. Expanded view of the 8-14 min (a) and 29-34 min (b) time intervals shaded in Fig. 1. The indoor levels of traffic-related air pollutants can be estimated using CO₂ as a tracer gas.

Acknowledgements: The project was supported by the NRC-IRAP and SR&ED programs.

[1] <http://www.lightpeaks.ca/products/portablegasdetectors>

ON-LINE MONITORING OF BREATH GAS CO₂ AND O₂ CONCENTRATION WITH LASER ABSORPTION SPECTROSCOPY

Zong-ling Ding*, Jin Sun and Qun Yang

School of Physics and Material Science, Anhui University, Jiu Long Road 111, Hefei, Anhui,
China, 230601

*E-mail: zlding@ahu.edu.cn

With the development of modern medical science and interdisciplinary, the early major diseases diagnostic technique has obtained the constantly breakthrough and innovation. Especially for the major diseases diagnosis of respiratory marking gas detection technology has been rapid development. It provides the important help for the early diagnosis and screening for certain diseases. Medical research shows that the normal human exhaled gases include the N₂, O₂, CO₂, H₂O and also other hundreds ppm (parts-per-million, 10⁻⁶) or even ppb (parts-per-billion, 10⁻⁹) trace gases [1,2]. These gases concentrations have the quantitative relationship between the content in the blood and the variety disease information, such as: exhaled breath of trace ammonia and nitrogen oxides have been related to the kidney or liver dysfunction; carbon disulfide, acetylene, alkanes for nervous system diseases; and also, there are high alkane concentration in the lung cancer and early stage breast cancer breath. Therefore, the medical early diagnosis, treatment technology may have a significant impacts through the respiratory gas composition diagnosis measurement.

Carbon dioxide (CO₂) and oxygen (O₂) are two essential human breath gases. The O₂ gas concentration is higher than CO₂ gas concentration in the normal air. And also, the inhalant O₂ has reduced and converted to CO₂. It has very important significance for understanding of the human breath with monitoring of O₂ and CO₂ concentrations, simultaneously. This paper introduced the TDLAS technology which combined with the homemade long path cell to detect the two gases in laboratory. Meanwhile, we use the wavelet transform processing to obtain the corresponding both harmonic signals to calculate the breath concentrations. The measurement results agreed well with the literature reference values. It also proved that the laser absorption spectroscopy is feasible and reliable to use in the early diagnosis in medical field. The figure 1 shows the processed CO₂ gas signals.

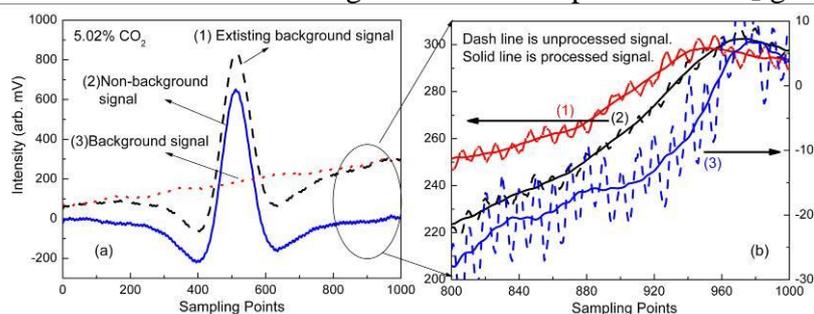


Figure 1 The CO₂ absorption signal (left) 2F signal and (right) processed signals

References:

- [1] Pauling, L.; Robinson, A.B.; Teranishi, R.; Cary, P. Quantitative analysis of urine vapor and breath by gas-liquid partition chromatography. *Proc. Natl. Acad. Sci. USA* **1971**, *68*, 2374–2384.
- [2] O'Neill, H.; Gordon, S.M.; O'Neill, M.; Gibbons, R.D.; Szidon, J.P., A computerized classification technique for screening for the presence of breath biomarkers in lung cancer. *Clin. Chem.* **1988**, *34*, 1613–1618.

METROLOGY IN ABSOLUTE CARBON DIOXIDE AND WATER VAPOR GAS CONCENTRATION MEASUREMENTS USING TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY

*Andrea Pogany¹, Alexander Klein¹, Javis Nwaboh¹, Bernhard Buchholz¹, Olav Werhahn¹,
Volker Ebert^{1,2}*

¹*Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany,
email: andrea.pogany@ptb.de*

²*Technical University Darmstadt, Petersenstr. 32, 64287 Darmstadt, Germany*

Water vapor (H₂O) and carbon dioxide (CO₂) are common components of the atmosphere, which are often monitored using spectroscopic methods. In certain applications the limited availability or stability of bottled gas standards restricts the possibility of in-field calibration of monitoring instruments with certified gas standards. In these cases absolute, self-calibrating spectroscopic measurements are preferred, based on calculating the concentration of the analyte(s) from the measured absorption spectrum and physical properties of the gas sample and the optical set-up according to the Beer-Lambert law. Absolute measurements rely on accurate spectral line parameters, most importantly the line strengths of the probed transitions.

In the first part of our presentation we give an overview on our activities in H₂O and CO₂ [1] line strength measurements by tunable diode laser absorption spectroscopy (TDLAS). We present line strengths of 9 H₂O and 2 CO₂ lines measured using the same experimental set-up and identical data evaluation procedure. We present measured line strengths in the 5·10⁻²³-2·10⁻²⁰ cm/molecule range and discuss differences between the experiments originating from the different analytes, light sources and magnitudes of the line strength. The measured line strengths have relative expanded uncertainties (k = 2, 95 % confidence level) of 1.0-2.5 %.

Many of these lines have recently been used in our research group for absolute gas concentration measurements. The application examples include airborne humidity measurements[2], quantification of H₂O and CO₂ impurities in zero gas standards[3], humidity measurements in combustion engines[4,5] as well as in natural gas[6]. We analyse uncertainties of these measurements and discuss the possibility of achieving metrological traceability. We compare the different experiments and evaluate general capabilities. Expanded uncertainties of our measured concentrations in the presented examples are typically in the range of 1-4 %.

The work has been conducted within the EMRP projects MACPoll, METEOMET and EUMETRISPEC. The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

References:

- [1] Pogany, A., Ott, O., Werhahn, O. & Ebert, V. *JQSRT* **130**, 147–157 (2013)
- [2] Buchholz, B., Bese, N. & Ebert, V. *Appl. Phys. B* **116**, 883–899 (2014)
- [3] Pogany, A., Wagner, S., Werhahn, O., Ebert, V. *Appl. Spectrosc.* **69**, 257–268 (2015)
- [4] Witzel, O. *et al. Appl. Phys. B* **109**, 521–532 (2012)
- [5] Klein, A., Ebert, V. *58th Ilmenau Scientific Colloquium* 8–12 (2014)
- [6] Nwaboh, J. A., Werhahn, O., Ebert, V. *Mol. Phys.* **112**, 2451–2461 (2014)

TUNABLE Y-JUNCTION LASERS FOR GAS SENSING APPLICATION

Thanh-Nam Tran^{}, Saroj Kumar Patra, Kjetil Haddeland and Bjørn-Ove Fimland*

*Department of Electronics and Telecommunications
Norwegian University of Science and Technology
NO-7491 Trondheim, Norway
^{*}nam.tran@ntnu.no*

GaSb-based semiconductor diode lasers are promising candidates for mid-infrared lasers in the wavelength region of 2-5 μm , whose applications include the light sources needed for trace-gas sensing systems based on tunable diode-laser absorption spectroscopy (TDLAS). Among edge-emitting laser structures, Y-junction structure is an interesting alternative, thanks to its wide tunable range and simple fabrication process. Most of widely tunable monolithic laser structures benefit from passive gratings and phase sections, requiring regrowth of the laser structures [1]. The regrowth, however, is difficult due to the reactive nature of AlGaAsSb which is used for cladding layers in GaSb-based laser diodes. In addition to not requiring regrowth, the Y-junction lasers offer easier processing, but have a complex waveguide junction structure and reduced side mode suppression ratio (SMSR). The SMSR can be improved by adding gratings or a third waveguide to the structure [1].

The Y-junction structure consists of a straight and an S-bend cavity, in which the bent section creates the length difference between two cavities for mode beating. The bending loss in the bent section, however, limits the performance of the device. In this work, we have characterized the bending loss of the S-bend waveguide lasers with different configurations. Depicted in figure 1, the L-I characteristics of those lasers show that the loss in the bent section decreases with the increase of bend radius. The results then will be used for the optimization of Y-junction laser.

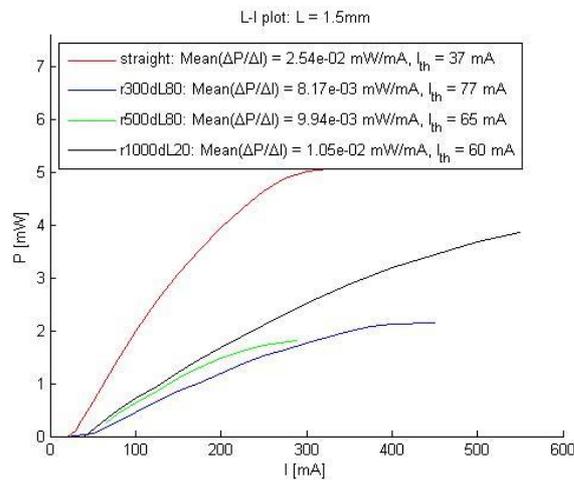


Figure 1: L-I characteristics of different S-bend waveguide lasers where r [μm] is bend radius and dL [μm] is the length difference between S-bend and straight waveguide lasers.

[1] J. Buus, M.-C. Amann, and D. J. Blumenthal, *Tunable laser diodes and related optical sources*, 2nd edition. SPIE PM. Wiley-Interscience (2005).

APPLICATION OF TDLS COMPLEX TO CONTROL WATER CONTENT DURING AMMONIA PURIFICATION

A.I. Skosyrev, O.S. Anoshin, A.P. Kotkov, N.D. Grishnova

Scientific-industrial enterprise "Salut"

603950, Larina Str. 7, Nizhnii Novgorod, Russia. saluthps@mail.ru

Ya.Ya. Ponurovskii

A.M.Prokhorov General Physics Institute of RAS

119991, Vavilova str. 38, Moscow, Russia, ponur1960@yandex.ru

A subject of present paper is DLS method applying for water (H₂O) determination in ammonia (NH₃). To determine the water content in ammonia TDLS complex was developed at GPI with 1392 nm diode laser.

TDLS complex contains reference and two analytical channels. Reference channel was used for DL frequency stabilization and as a channel for comparison. In analytical channels a single-pass and multi-pass cells (optical path lengths 0.8 m and 20 m, respectively) were used.

High resolution absorption spectra of H₂O and NH₃ in 1392 nm spectral range were obtained, and water analytical spectral line was selected.

Mixtures of H₂O:Ar and H₂O:NH₃ were prepared with water concentration range from 10⁻³ to 10⁻¹ % vol..

The influence of the pressure of argon and ammonia for water absorption spectral line shape in the pressure range from 1 to 100 kPa was investigated.

It has been established for H₂O:NH₃ gas mixtures that the major effect on the shape of the water spectral line exerts ammonia pressure. With pressure increasing occurs line broadening and red shift. For low pressures the line integral intensity is proportional to pressure Bouguer-Lambert law. After some pressure level, its saturation and even reduction can be found. This change of the absorption line shape is due to the interaction of ammonia with water. It does not allow the determination of water content in ammonia for pressures above 20 kPa.

By the "added-found" method and comparing the data obtained by the analysis of the hygrometer GE MTS-6, and the "dew point" device with a cooled silver mirror, DLS complex was calibrated with H₂O concentration in the range from 10⁻³ to 10⁻¹ % vol. Detection limit of water determination was obtained 2·10⁻² % vol. for the cell with optical path length of 0.8 m and 1·10⁻³ % vol. for multi-pass cell with an optical path length of 20 m.

Developed equipment and the method of determining the water content of the ammonia were used in the process of ammonia purification by low-temperature distillation.

To determine the water content in the high purity ammonia a method with an water impurity concentration from ammonia distillation column was developed. Using this concentration achieved level of water detection in high purity ammonia is 1·10⁻⁵ % vol.

Authors index

<i>A.Alquaity</i>	13, 55	<i>K.Haddeland</i>	62
<i>M.Amani</i>	26, 56	<i>L.Han</i>	32
<i>N.Amarouch</i>	14	<i>F.Harren</i>	7
<i>S.Amirova</i>	43	<i>L.Hildebrandt</i>	19, 27
<i>O.Anoshin</i>	20, 63	<i>S.Höfling</i>	19, 27
<i>S.Aoki</i>	16	<i>N.Ignatiev</i>	14
<i>R.Askar</i>	56	<i>A.Izmailov</i>	28
<i>V.Azyazov</i>	30	<i>C.Janssen</i>	10
<i>V.Banewar</i>	42	<i>P.Jeseck</i>	10
<i>V.Barke</i>	14	<i>L.Joly</i>	14
<i>O.Benderov</i>	14	<i>T.Kaariainen</i>	48
<i>A.Bicer</i>	26, 56	<i>D.Kabanau</i>	47
<i>S.Bhandarkar</i>	41, 57	<i>V.Kabanov</i>	47
<i>M.Bolshov</i>	12, 24	<i>M.Kagitani</i>	16
<i>J.Bounds</i>	26, 56	<i>A.Kalyuzhnyi</i>	14
<i>C.Boursier</i>	10	<i>M.Kamp</i>	19, 27
<i>B.Buchholz</i>	18, 61	<i>Y.Kasaba</i>	16
<i>A.Campargue</i>	6	<i>V.Kapitanov</i>	23, 52
<i>M.Carras</i>	29	<i>S.Kassi</i>	6
<i>M.Cassinerio</i>	9	<i>S.Kataev</i>	21, 51
<i>A.Castrillo</i>	9	<i>V.Kelessides</i>	26
<i>P.Čermák</i>	6	<i>V.Khattatov</i>	38, 53
<i>A.Chernyshov</i>	30	<i>J.A.Kim</i>	33
<i>D.Churbanov</i>	14, 54	<i>J.W.Kim</i>	33
<i>R.Ciuryło</i>	11	<i>A.Klein</i>	18, 61
<i>N.Coluccelli</i>	9	<i>A.Klimchuk</i>	14, 39, 54
<i>J.Cousin</i>	14	<i>J.Koeth</i>	19, 27
<i>X.Cui</i>	32	<i>O.Kolesnikov</i>	12, 24
<i>A.Cygan</i>	11	<i>A.Kolomenskii</i>	26, 56
<i>T.Delahaye</i>	44	<i>O.Korablev</i>	14
<i>Z.Ding</i>	60	<i>A.Kotkov</i>	20, 35, 63
<i>F.Dong</i>	32	<i>V.Krasnopolsky</i>	14
<i>G.Durry</i>	14	<i>T.Kuhn</i>	16
<i>V.Ebert</i>	18, 61	<i>A.Kulakov</i>	51
<i>M.von Edlinger</i>	19, 27	<i>Yu.Kuritsyn</i>	12, 24
<i>H.Elandaloussi</i>	10	<i>A.Kuzmichev</i>	38, 53
<i>T.Eom</i>	33	<i>L.Labadie</i>	14
<i>E.Essebbar</i>	13, 55	<i>P.Laporta</i>	9
<i>A.Farooq</i>	13, 55	<i>Yu.Lebedev</i>	14
<i>A.Fedorova</i>	14	<i>Y.Lebiadok</i>	47
<i>B.Fimland</i>	62	<i>J.Lee</i>	33
<i>M. Fischer</i>	19, 27	<i>V.Liger</i>	12, 24
<i>V.Galaktionov</i>	38, 53	<i>D.Lisak</i>	11
<i>G.Galzerano</i>	9	<i>Al.Lytkine</i>	34, 59
<i>D.Gatti</i>	9	<i>An.Lytkine</i>	59
<i>L.Gianfrani</i>	9	<i>G.Maisons</i>	29
<i>G.Grigoriev</i>	25, 40	<i>S.Maity</i>	49
<i>N.Grishnova</i>	20, 35, 63	<i>A.Manninen</i>	48

<i>M. Marangoni</i>	9	<i>H.Schuessler</i>	26, 56
<i>P.Maslowski</i>	11	<i>V.Semenov</i>	14, 25, 39, 40
<i>L.Men'shikov</i>	25	<i>S.Sinha</i>	49
<i>P.Men'shikov</i>	25	<i>D. Shaposhnikov</i>	14
<i>I.Mihailov</i>	39	<i>Yu.Shapovalov</i>	21, 38, 51, 53
<i>S.Mikhailenko</i>	6	<i>P.Shpak</i>	47
<i>P.Mikheyev</i>	30	<i>A.Skosyrev</i>	20, 63
<i>M.Minissale</i>	10	<i>G.Sonnabend</i>	16
<i>V.Mironenko</i>	12, 24	<i>M.Sornig</i>	14, 16
<i>P.Moiseev</i>	14	<i>M.Spiridonov</i>	14, 21, 51, 54
<i>D.Mondelain</i>	6	<i>D.Stavrovskii</i>	21, 25, 38, 40, 53
<i>I.Murata</i>	16	<i>S. Suh</i>	33
<i>Sh.Nabiev</i>	25, 40	<i>A.Suhanov</i>	20, 35
<i>A.Nadezhdinskii</i>	5, 14, 21, 22, 35, 36, 37, 38, 50, 51, 53, 54	<i>J.Sun</i>	60
<i>K.Nagapriya</i>	49	<i>P.Sun</i>	32
<i>L. Nähle</i>	19, 27	<i>K.Takami</i>	16
<i>H.Nakagawa</i>	16	<i>Y.Té</i>	10
<i>E. Nasir</i>	13	<i>R.Thomson</i>	14
<i>I.Nikolaev</i>	31, 46	<i>H.Tran</i>	44
<i>J.Nwaboh</i>	18, 61	<i>T.Tran</i>	62
<i>V.Ochkin</i>	31, 46	<i>I.Trofimov</i>	17
<i>S.Okano</i>	16	<i>S.Tskhai</i>	31, 46
<i>K.Osipov</i>	23, 52	<i>T.Tulaikova</i>	43
<i>T.Pang</i>	32	<i>N.Ufimtsev</i>	30
<i>B.Parvitte</i>	29, 44, 58	<i>A.Ushakov</i>	14, 39
<i>S.Patra</i>	62	<i>R.Vallon</i>	29, 44, 58
<i>A.Pereslavl'tseva</i>	14, 23	<i>S.Vasilchenko</i>	6
<i>Dm.Pleshkov</i>	51	<i>I.Vinogradov</i>	14
<i>A.Pogany</i>	18, 61	<i>E.Vorontsova</i>	30
<i>D.Polezhaev</i>	20, 35	<i>M.Wadekar</i>	45
<i>Yu.Ponomarev</i>	52	<i>Y.Wang</i>	32
<i>S.Poonacha</i>	49	<i>P.Wcislo</i>	11
<i>Ya.Ponurovskii</i>	14, 12, 20, 21, 23, 24, 35, 38, 40, 51, 52, 53, 63	<i>R.Weih</i>	19, 27
<i>R.Prashanth</i>	49	<i>O.Werhahn</i>	18, 61
<i>A.Protasevich</i>	23, 52	<i>S. Wójtewicz</i>	11
<i>A.Rau</i>	45	<i>B.Wu</i>	32
<i>A.Raut</i>	42	<i>H.Xia</i>	32
<i>V.Raut</i>	41, 57	<i>Yu.Yakovlev</i>	47
<i>C.Risser</i>	58	<i>Q.Yang</i>	60
<i>J.Ritter</i>	16	<i>T.Zanon</i>	10
<i>A.Rodin</i>	14, 39, 54	<i>V.Zaslavskii</i>	38, 51, 53
<i>O.Roste</i>	14	<i>A.Zaytsev</i>	31
<i>G.Ryabtsev</i>	47	<i>V.Zeninari</i>	8, 29, 44, 58
<i>H.Sagawa</i>	16	<i>Z.Zhang</i>	32
<i>M.Sajid</i>	13	<i>F.Zhu</i>	26, 56
<i>T.Sakanoi</i>	16		
<i>T.Sala</i>	9		
<i>J. Scheuermann</i>	19, 27		

Table of contents

TDLS 2013 CONFERENCE SCHEDULE	4
INVITED LECTURES.....	5
<i>L1</i>	5
<i>L2</i>	6
<i>L3</i>	7
<i>L4</i>	8
<i>L5</i>	9
<i>L6</i>	10
<i>L7</i>	11
<i>L8</i>	12
<i>L9</i>	13
<i>L10</i>	14
<i>L11</i>	16
<i>L12</i>	17
ORAL SESSION	18
<i>O1</i>	18
<i>O2</i>	19
<i>O3</i>	20
POSTER SESSION A.....	21
<i>A1</i>	21
<i>A2</i>	22
<i>A3</i>	23
<i>A4</i>	24
<i>A5</i>	25
<i>A6</i>	26
<i>A7</i>	27
<i>A8</i>	28
<i>A9</i>	29
<i>A10</i>	30
<i>A11</i>	31
<i>A12</i>	32
<i>A13</i>	33
<i>A14</i>	34
<i>A15</i>	35
POSTER SESSION B.....	36
<i>B1</i>	36
<i>B2</i>	37
<i>B3</i>	38
<i>B4</i>	39
<i>B5</i>	40
<i>B6</i>	41
<i>B7</i>	42
<i>B8</i>	43
<i>B9</i>	44
<i>B10</i>	45
<i>B11</i>	46
<i>B12</i>	47
<i>B13</i>	48
<i>B14</i>	49
<i>Poster session C</i>	50
<i>C1</i>	50
<i>C2</i>	51
<i>C3</i>	52
<i>C4</i>	53
<i>C5</i>	54
<i>C6</i>	55
<i>C7</i>	56

<i>C8</i>	57
<i>C9</i>	58
<i>C10</i>	59
<i>C11</i>	60
<i>C12</i>	61
<i>C13</i>	62
<i>C14</i>	63
AUTHORS INDEX	64
TABLE OF CONTENTS	66

NOTES