ABSTRACTS OF PAPERS

5th International Conference on

Tunable Diode Laser Spectroscopy

July 11-15, 2005
Florence, Italy

We wish to thank the following for their contribution to the success of this conference: Ente Cassa di Risparmio di Firenze, European office of Aerospace Research and Development, AFOSR, and our Sponsors

Organized by:

Connecticut College, New London, Connecticut USA
General Physics Institute, Russian Academy of Sciences, Moscow, Russia

Local Organization by:

National Institute of Applied Optics, Florence, Italy

Benefactors:

ENTE CASSA DI RISPARMIO DI FIRENZE

European Office of Aerospace Research and Development AFOSR

Supported and Sponsored by:

Canberra Aquila, Inc.	**http://www.aquilagroup.com/**
Laser Components Group	**http://www.laser-components.com/**
Alpes Lasers SA	**http://www.alpeslasers.com/**
Southwest Sciences, Inc.	**http://swsciences.com/**
Toptica Photonics	**http://www.toptica.com/**
INP-Greifswald	**http://www.inp-greifswald.de/**
Cascade Technologies, Ltd.	**http://www.cascade-technologies.com/**
Nanoplus	**http://www.nanoplus.com/**
Los Gatos Research, Inc.	**http://www.lgrinc.com/**
Aculight Corporation	**http://www.aculight.com/**
Campbell Scientific, Inc.	**http://www.campbellsci.com/**
Norsk Elektro Optikk AS	**http://www.neo.no/**
EKIPS Technologies	**http://www.breathmeter.com/**
Unisearch Associates, Inc.	**http://www.unisearch-associates.com/**
Aerodyne Research, Inc.	**http://www.aerodyne.com/**
Vertilas GmbH	**http://www.vertilas.com/**
Gestione Societa Italiana Lavorazioni Ottiche (SILO)	**http://www.silo.it/**
Sacher Lasertechnik Group	**http://www.sacher.us/**
Scienza Industria Technologia	**http://www.scintec.it/**
Fraunhofer Institut fuer Physikalische Messtechnik	**http://www.ipm.fhg.de/**
Vescent Phtotonics, Inc.	**http:// www.vescentphotonics.com /**
Siemens	**http:// www.siemens.com /**
Aero Laser	**http://www.aero-laser.de/**

Conference Chairs

Professor A. W. Mantz
Connecticut College
Department of Physics and Astronomy
270 Mohegan Avenue
New London, Connecticut 06320-4196 USA
Phone: +1 (860) 439-5030
Fax: +1 (860) 439-5011
E-mail: awman@conncoll.edu

Professor A. I. Nadezhdinskii
General Physics Institute
Russian Academy of Sciences
38 Vavilov Street
Moscow 119991 Russia
Phone: +7 (095) 135-8281
Fax: +7 (095) 135-8281
E-mail: nad@nsc.gpi.ru

Organizer for the Industrial Developments Session

Dr. Peter Werle
National Institute of Applied Optics
Largo Enrico Fermi 6
50125 Florence, Italy
E-mail: PWWerle@inoa.it

Local Organizers

Chair: Dr. Francesco D'Amato	**Istituto Nazionale di Ottica Applicata** **Largo E. Fermi 6, 50125 Firenze, Italy**
Dr. Piero Mazzinghi	**Istituto Nazionale di Ottica Applicata** **Largo E. Fermi 6, 50125 Firenze, Italy**
Dr. Peter Werle	**Istituto Nazionale di Ottica Applicata** **Largo E. Fermi 6, 50125 Firenze, Italy**

International Advisory Committee

Claude Alibert (France)
Paul Davies (United Kingdom)
Armin Lambrecht (Germany)
A. R. W. McKellar (Canada)
Frank Tittel (USA)
Peter Werle (Italy)
Mark Zahniser (USA)

Claude Camy-Peyret (France)
Alan Fried (USA)
Muriel Lepere (Belgium)
Claude Thiebeaux (France)
Hiromichi Uehara (Japan)
Gisbert Winnewisser (Germany)

Conference Web Page: http://tdls.conncoll.edu
E-Mail: tdls@conncoll.edu

TDLS 2005 Conference Schedule

<table>
<tr><th></th><th>11 July</th><th>12 July</th><th>13 July</th><th>14 July</th><th>15 July</th></tr>
<tr><td>9:00</td><td>Capasso</td><td rowspan="20">Industrial session</td><td>Laurila</td><td>Martin</td><td>Chen</td></tr>
<tr><td>9:30</td><td rowspan="2">Kerstel</td><td rowspan="2">Tanaka</td><td rowspan="2">Gianfrani</td><td>Fischer</td></tr>
<tr><td>9:45</td><td>Dyroff</td></tr>
<tr><td>10:00</td><td>Rossi</td><td>Inguscio</td><td>Velichanskii</td><td>Fried</td></tr>
<tr><td>10:30</td><td>Coffee break</td><td>Coffee break</td><td>Coffee break</td><td rowspan="19">END OF MEETING</td></tr>
<tr><td>11:00</td><td>Hering</td><td rowspan="8">Poster session B</td><td rowspan="8">Poster session C</td></tr>
<tr><td>11:30</td><td>Alibert</td></tr>
<tr><td>11:45</td><td>Brown</td></tr>
<tr><td>12:00</td><td>Yang</td></tr>
<tr><td>12:15</td><td>Duxbury</td></tr>
<tr><td>12:30</td><td>Zeninari</td></tr>
<tr><td>12:45</td><td>Mazzinghi</td></tr>
<tr><td>13:00</td><td>Lunch</td><td>Lunch</td><td>Lunch</td></tr>
<tr><td>14:30</td><td rowspan="4">Poster session A</td><td rowspan="6">Optional excursion (dinner included)</td><td>Mizaikoff</td></tr>
<tr><td>15:00</td><td>Kosterev</td></tr>
<tr><td>15:15</td><td>Camy-Peyret</td></tr>
<tr><td>15:30</td><td>McCann</td></tr>
<tr><td>16:00</td><td rowspan="2">Coffee break</td></tr>
<tr><td>16:30</td><td></td><td rowspan="2">Poster session D</td></tr>
<tr><td>18:00</td><td rowspan="2">Conference reception in Historic Florence</td><td rowspan="2">Conference Dinner at Castello Mediceo di Cafaggiolo</td></tr>
<tr><td>18:30</td><td></td></tr>
</table>

Contents

Part 1. Invited Lectures

L-1 New nonlinear optical quantum cascade lasers from the mid- to far-infrared
Federico Capasso and Mariano Troccoli

L-2 Water isotope ratio measurements with near-infrared DFB diode lasers
Eric Kerstel

L-3 Trace gas detection by means of optically enhanced diode laser photoacoustic spectroscopy
Alessandro Rossi

L-4 TDLS based ultra sensitive trace gas detection for environmental and biomedical applications
Peter Hering

L-5 Improving sensitivity in on-line heavy metals detection using diode lasers in the UV spectral range
Toni Laurila

L-6 Infrared diode laser spectroscopy of transient species produced by UV-laser photolysis
Keiichi Tanaka

L-7 The impact of semiconductor lasers on precision atomic and molecular spectroscopy
Massimo Inguscio

L-8 In situ process analysis with NIR diode lasers
Philip Martin

L-9 Chemical and isotopic analysis by means of near-IR diode laser spectrometry: applications to Earth Sciences
Livio Gianfrani

L-10 Tunable diode laser spectroscopy of alkali atoms
Vladimir Velichansky

L-11 Fiberoptic infrared chemical sensors based on quantum cascade lasers
Boris Mizaikoff

L-12 Tunable fiber laser spectroscopy and application to trace gas detection
Weidong Chen

L-13 Lead-salt and difference frequency generation IR spectrometers: performance comparisons and common requirements for ultra sensitive airborne measurements
Alan Fried

L-1

New nonlinear optical quantum cascade lasers from the mid- to far-infrared

Federico Capasso and Mariano Troccoli

Division of Engineering and Applied Sciences

Harvard University, Cambridge MA 02138

Alexey Belyanin, Department of Physics, Texas A&M University

College Station, TX 77843

capasso@deas.harvard.edu

After a brief review of giant optical nonlinearities associated with intersubband transitions in quantum wells we will discuss their application to new coherent light sources for the mid-ir and far ir based on the integration within a single quantum well structure of a nonlinear optical element and a quantum cascade laser active region which serves as an internal optical pump for the latter. The nonlinear optical element can be a second harmonic or difference frequency generator, a Raman region where Stokes or Antistokes stimulated Raman scattering are generated, etc. The internal optical pumping makes it possible to achieve high conversion efficiency by using the extremely large intersubband resonant nonlinearities. Experiments will be presented for second harmonic generation and Raman. Our mid-ir (λ = 9 μm) Raman lasers exhibit high conversion efficiency (30%) with up to 60 mW of optical power. Raman Lasers have potential as widely tunable room temperature far-ir sources for spectroscopy.

L-2

Water isotope ratio measurements with near-infrared DFB diode lasers

Erik Kerstel

Center for Isotope Research

Department of Physics, University of Groningen

Nijenborgh 4, 9747AG, Groningen, The Netherlands

e.r.t.kerstel@rug.nl

Isotope ratio mass spectrometers routinely achieve impressive measurement precisions and high throughput. In spite of this, a number of fundamental and practical problems remain. These are most notable in the case of isotope ratio measurements on water, arguably the most important molecule in the environment. Optical techniques to measure stable isotope ratios are able to address at least some of these issues; particularly, in relation to sample pretreatment and the difficulty of *in-situ* measurements.

We show that distributed feedback diode laser emitting in the OH-stretching overtone band of water near 1.39 μm are an excellent choice to build both laboratory-based and on-line, *in-situ* isotope ratio analyzers. This will be illustrated with optical isotope ratio measurements in applications from earthbound to the atmospheric: from laboratory based ice-core and biomedical water isotope analyses to *in-situ* water isotope measurements in the upper troposphere and lower stratosphere.

L-3

Trace gas detection by means of optically enhanced diode laser photoacoustic spectroscopy

Alessandro Rossi [1], Roberto Buffa [1], Mario Scotoni [2], Davide Bassi [2], Salvatore Iannotta [3] and Andrea Boschetti [3]

[1] Università di Siena, Dipartimento di Fisica, I-53100 Siena, Italy

[2] Università di Trento, Dipartimento di Fisica, I-38050 Povo-Trento, Italy

[3]Istituto di Fotonica e Nanotecnologie, CNR-ITC

Sezione di Trento, I-38050 Povo-Trento, Italy

The photoacoustic technique is an interesting detection method in IR spectroscopy, because of its peculiar characteristics: sensitivity proportional to the probe light power, large dynamic range, constant sensitiveness versus probe light frequency and very low background signal. Diode laser-based photoacustic detectors fit very well the needs of a portable device, but the low probe light power limits the sensibility to tens of ppm for molecules with a transition line intensities of about 10^{-22} $cm^{-1}/(mol\ cm^{-2})$. In order to investigate the possibility to build a portable trace-gas detector with a sub-ppm sensibility, we have coupled a diode laser photoacoustic system with a build-up cavity. The detector is tunable in the range of 1.57-1.64 μm, were transition lines of many molecules (ethylene, methane, ammonia, carbon dioxide, water…), interesting for in-field detection applications, are present. In order to improve the mechanical stability, the acoustic and the optical cavity are made out of a mono-block piece of brass. From measurements taken by the device, we can deduce a build-up cavity gain factor of 100.

L-4

TDLS based ultra sensitive trace gas detection for environmental and biomedical applications

Manfred Mürtz [1], Daniel Halmer [1], Markus Horstjann [1], Sven Thelen [1], Peter Hering [1,2]

[1] *Institut für Lasermedizin, Universität Düsseldorf, Germany*

Email: muertz@uni-duesseldorf.de or hering@uni-duesseldorf.de

[2] *Research center caesar, Bonn, Germany, hering@caesar.de*

Monitoring emission rates and ambient concentrations of trace gases is of big interest in life sciences and several other fields. Infrared spectroscopic techniques have proven to be powerful tools for this purpose. Major activities are directed towards transportable sensors with sub-ppb sensitivities for mixtures containing several compounds. In the past decade Quantum Cascade Lasers (QCLs) have enabled themselves as reliable sources of laser light in the mid-infrared region with high optical output power and narrow line width. They are continuously tunable with laser current and temperature and are very small in size, making them compact, powerful devices.

In our laboratory, QCLs emitting near λ=5µm are used to monitor nitric oxide (NO), which has been found to play a major role in many endogenous processes in the human body. Two different approaches are pursued: Faraday Modulation Spectroscopy (FAMOS) based upon magneto-optic rotation [1], and Cavity Leak-Out Spectroscopy (CALOS), which boosts sensitivity by using an external resonator [2]. In this talk we report on our advances in extremely sensitive and specific analysis of NO and other trace gases by means of these infrared laser-spectroscopic techniques. An example for recent measurements of biogenic NO is the analysis of UVA-induced NO release from human sweat samples. Moreover, we demonstrate simultaneous detection of ^{14}NO and ^{15}NO, which enables interesting isotopic tracer studies with ^{15}N-labeled substances [2].

Where the FAMOS approach is limited to NO and other open-shell molecules, the CALOS technique also enables rapid analysis of various VOCs, CO, OCS, etc. on the parts-per-trillion level. Currently we are exploring this technique for the quantitative real-time detection of breath constituents and for the analysis of plant emissions. A prominent example is ethane which is considered as the most important volatile marker of free-radical induced lipid peroxidation and cell damage in most organisms.

We discuss the performance of CALOS and FAMOS with QCLs and other mid-infrared laser sources and we present ongoing and future applications in environmental and life sciences.

[1] H. Ganser, M. Horstjann, C. V. Suschek, K. D. Kröncke, V. Kolb-Bachoven, P. Hering, M. Mürtz, On-line monitoring of biogenic nitric oxide with a QC-laser based Faraday modulation technique, *Appl. Phys. B* 78, 513-517 (2004)

[2] D. Halmer, G. von Basum M. Horstjann, P. Hering, M. Mürtz, Time resolved simultaneous detection of ^{14}NO and ^{15}NO via mid-infrared cavity leak-out spectroscopy, Isotop. Environ. Health Stud., in press (2005)

L-5

Improving sensitivity in on-line heavy metals detection using diode lasers in the UV spectral range

T. Laurila, R. Oikari, and R. Hernberg

Optics Laboratory, Tampere University of Technology

P.O. Box 692, FI-33101 Tampere, Finland

The ultraviolet (UV) spectral region is of great importance for analytic spectroscopy because the resonance lines of most of the elements and electronic transitions of molecules lie in the UV. The absorption cross sections of electronic transitions are larger than the ones of ro-vibrational transitions in the infrared. On the other hand, the demand for compact and easily operable high-resolution instruments for real-time diagnostics is rapidly increasing in a variety of applications. Semiconductor based UV light sources have great potential in that sense. The expanding wavelength range of the diode laser technology increases the coverage of detectable species. Compact UV light sources will have a great impact on several analytical applications, e.g., medical fluorescence measurements and biological agent detection. Diode lasers' capability for direct modulation schemes enables the realization of sensitive measurement systems.

The emission of toxic metals from waste incineration, industry and traffic is an increasing hazard for human health. The governmental regulations for monitoring toxic metal levels call for new highly sensitive on-line measuring techniques. However, as the shortest commercial diode laser wavelength today is around 370 nm, frequency conversion with non-linear optics is still in many cases the only way by which the absorption region of metal atoms can be reached using diode lasers. In this work we have generated 60 nW UV light in the range 320-327 nm with a frequency-doubled external cavity diode laser (ECDL) based on a transmission grating [1,2]. The system has been used for the spectral analysis of atomic copper, cadmium and indium near 325 nm. The developed light source has been applied to a recently developed on-line heavy metal analyzer [3,4]. Compared to a hollow-cathode light source in the analyzer we have demonstrated substantial improvement of the reference device with the diode laser based light source.

References

[1] T. Laurila, T. Joutsenoja, R. Hernberg, and M. Kuittinen, Applied Optics **41**, 5632-5637 (2002).

[2] T. Laurila and R. Hernberg, Applied Physics Letters **83**, 845-847 (2003).

[3] R. Oikari, V. Häyrinen, T. Parviainen, and R. Hernberg, Applied Spectroscopy **55**, 1469-1477 (2001).

[4] R. Oikari, L. Botti, and R. Hernberg, Applied Spectroscopy **56**, 1453-1457 (2002).

L-6

Infrared diode laser spectroscopy of transient species produced by UV-laser photolysis

Keiichi Tanaka

Department of Chemistry, Faculty of Sciences, Kyushu University, Hakozaki, Higashiku, Fukuoka 812-8581 Japan

Infrared diode laser spectrometer in the mid-infrared region of 600 – 2500 cm^{-1} was applied to observe the rotationally resolved infrared spectra of the free radicals produced by ultraviolet excimer laser photolysis. The short lived transient species were detected with a time-resolved technique selectively from stable long lived species, sometimes in a supersonic jet expansion where the reactive species can survive under the collision-less condition thanks to the ultra cold temperature. The technique has been applied to observe the radicals, including vinyl $H_2C=CH$, propargyl $H_2C=C=CH$ [1], cyanomethyl $H_2C=CN$ [2], and silylene SiH_2. For example, propargyl was produced by the 193nm UV photolysis of allene, and the ν_6 band observed at 687 cm^{-1} was assigned to the CH_2-wagging band, which has the anomalously large vibrational change in the A rotational constant due to the interaction with the ν_{10} CH_2-rocking vibrational state.

The same technique has been applied to observe the jet cooled $Fe(CO)_x$ [3-5], $Co(CO)_x$ (x=1,2), FeNO, CoNO, and Co(CO)(NO) produced in a supersonic jet expansion by excimer laser photolysis of $Fe(CO)_5$, $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$. The rovibrational lines of FeCO of the ν_1 (CO str.) band were split into triplet due to the spin-spin interaction in the $^3\Delta$ electronic ground state. The hot band lines of ν_1 from the ν_2 bending state were also observed. The rotational lines of the hot band were split into sextet due to the vibronic interaction with a $^3\Delta$ electric excited state as well as the spin-spin interaction. The jet-cooled spectra of the ν_3 band of $Fe(CO)_2$ split into triplet in the $^3\Sigma_g^-$ electronic ground state. One of the spin components was missing for each rovibrational line due to the spin statistics of the C and O nuclei confirming that $Fe(CO)_2$ has a linear structure with $D_{\infty h}$ symmetry.

Similarly, the infrared spectra of CoCO and $Co(CO)_2$ have been observed to determine their electronic and molecular structure. The electronic structures of CoCO and $Co(CO)_2$ in the ground state are $^2\Pi_i$ and $^2\Pi_g$, and both radicals have the linear structures, but $Co(CO)_2$ may be a quasi-linear molecule with very low frequency bending (CCoC) vibration.

The rotational spectra of these radicals have also been observed in the millimeter-wave region [6-8] with the combination of supersonic jet and UV laser photolysis to confirm their assignments and to have more detailed molecular constants.

[1] *J. Chem. Phys.* **103** 6450 (1995)
[2] *J. Chem. Phys.* **104** 1839 (1996)
[3] *J. Chem. Phys.* **106** 2118 (1997)
[4] *Chem. Phys. Lett.* **218** 285 (1997)
[5] *J. Chem. Phys.* **111** 3970 (1999)
[6] *J. Chem. Phys.* **106** 6820 (1997)
[7] *J. Chem. Phys.* **107** 2728 (1997)
[8] *J. Chem. Phys.* **120** 3604 (2004)

L-7

The impact of semiconductor lasers on precision atomic and molecular spectroscopy

S. Borri, P. Cancio, P. De Natale, G. Giusfredi, D. Mazzotti, V. Krachmalnicoff, M. Inguscio

Istituto Nazionale di Ottica Applicata, European Laboratory for Non-Linear Spectroscopy and Dipartimento di Fisica-Università di Firenze, Via Carrara 1, 50019 Sesto Fiorentino (Firenze), Italy.

An overview will be given of applications of semiconductor lasers to sensitive and precise atomic and molecular spectroscopic measurements recently performed in Firenze, Italy. Results will be shown for high sensitivity frequency modulation techniques applied to CW nitrogen-cooled Quantum-Cascade-Lasers for trace molecular detection. Semiconductor lasers have also proven to be key sources for precise atomic spectroscopy, and spectroscopic results with an achieved accuracy of about 1 kHz for the measurement of absolute atomic helium (both ^{4}He and ^{3}He) frequencies around 1.08 μm wavelength will be shown. It will be discussed how such high-precision measurements in simple atoms may also be used to perform sensitive tests of the quantum electrodynamics (QED) theory, to achieve a better determination of the fine structure constant, α and to get information on the nucleus, through ^{3}He hyperfine structure. Phase-locking of diode laser sources to an optical-frequency-comb generator (OFS) have allowed to achieve such high precision in absolute frequency measurements and have also recently allowed to extend the OFS itself to the infrared range, for application to molecular frequency metrology.

L-8

In situ process analysis with NIR diode lasers

P. A. Martin

School of Chemical Engineering and Analytical Science,
University of Manchester, Manchester, M60 1QD, UK

Philip.Martin@manchester.ac.uk

Near-infrared diode laser spectroscopy is starting to be more widely used in industrial process analysis and environmental applications due to its advantages of robustness and ease of use. Although the high sensitivities of mid-infrared diode laser and quantum cascade laser spectroscopy are difficult to achieve in the near-infrared due to the intrinsically weaker line intensities the practical advantages of room temperature operation, ease of optical integration and ruggedised components outweigh the sensitivity issues in many situations. This presentation will illustrate recent work in this area carried out in Manchester.

One application area is in situ monitoring of atmospheric pressure chemical vapour deposition processes. An example is the deposition of tin oxide layers on glass based on the oxidation of dimethyltin dichloride $(CH_3)_2SnCl_2$ which is used in high volume production for low-emissivity glazing. NIR diode laser spectroscopy around 1665 nm was used to monitor methane evolving from the gas phase reaction. The NIR beam could be passed directly through the walls of the glass reactor. Spatial measurements of methane concentrations near the surface of the growing layer resulted in correlations with film properties such as thickness. Further work has resulted in time -resolved and spatially-resolved measurements of HCl and HF in the growth of tin oxide films for photovoltaics.

A portable NIR diode laser spectrometer will also be described for the remote sensing of vehicle emissions. It detects carbon monoxide and carbon dioxide absorptions around 1580 nm with a single DFB laser and has been used successfully for screening studies of 'gross polluting' vehicles. Current work has increased sensitivity by detecting CO at 2320 nm.

Finally, a summary will be given of the European project ASSYST (Advanced Laser Sensor Systems for Leading Edge Manufacturing) which is concerned with developing multispecies and multipoint diode laser sensor systems across a range of industrial sectors.

L-9

Chemical and isotopic analysis by means of near-IR diode laser spectrometry: applications to Earth Sciences

Livio Gianfrani

Dipartimento di Scienze Ambientali della Seconda Università di Napoli

Via Vivaldi 43 – I-81100 Caserta, Italy

In the last decade, the accurate determination of stable isotope abundance ratios has been widely recognized as a powerful tool for quantitative studies of complex environmental processes, exploiting fractionation effects occurring in a variety of physical, chemical and biological processes. Nowadays, quick and reliable field analysis of isotope ratios in simple molecules seems to be the last challenge of which researchers in Earth sciences could enormously benefit in the near future. Similarly, new instruments for in-situ, accurate, sensitive, selective and fast chemical analysis of gaseous species are urgently needed.

Recent advances in the field of semiconductor laser technology and laser spectroscopy have made possible to satisfy the demand of advanced analytical instrumentation, at least for some relevant molecules. In particular, the spectral window around 2 μm-wavelength has emerged as one of the most advantageous for diode-laser-based diagnostic of the environment, for two main reasons: relevant molecules, such as H_2O, CO_2, N_2O, and NH_3, exhibit relatively strong absorption features and high quality diode lasers, of the distributed feedback (DFB) type, are commercially available.

I will report on concentration measurements of H_2O, CO_2 and NH_3, with high precision and accuracy, by means of diode lasers around 2 μm-wavelength. I will also show the fruitful use of high precision absorption spectroscopy to the accurate determination of stable isotope ratios. In particular, I will present recent results on the accurate measurement of the $^{13}C/^{12}C$ ratio in carbon dioxide at 2.008 and 2.053 μm [1].

Applications in Ecology, for soil respiration studies [2], and Geochemistry, for monitoring of volcanic activity, will be discussed. Regarding the latter application, I will show the successful demonstration of field operation of a diode laser spectrometer that is able to provide accurate values of the $^{13}CO_2/^{12}CO_2$ isotope ratio in volcanic gases [3]. This parameter is of the utmost importance in geochemical monitoring of active volcanic areas, its variations being studied as indicator of impending eruptions.

References

[1] G. Gagliardi, A. Castrillo, R. Iannone, E. R. Th. Kerstel, and L. Gianfrani, Applied Physics B, 77, 119-124 (2003).

[2] L. Gianfrani et al., Applied Spectroscopy, 58, 1051-1056 (2004).

[3] A. Castrillo, G. Casa, M. van Burgel, and L. Gianfrani, Optics Express, 12, 6515-6523 (2004).

L-10

Tunable diode laser spectroscopy of alkali atoms

V. L. Velichansky

Lebedev Institute of Physics, Leninsky prosp.53, Moscow 119991 Russia

vlvlab@fsl1.lpi.troitsk.ru

Alkali atoms were the first objects probed with the technique of diode laser spectroscopy. Supprisingly they still provide challenging problems for high resolution spectroscopy and tunable lasers. The report will cover the following issues:

- The early works carried out with solitary diode lasers (Cs atomic beam, selective specular reflection, the first paper on Doppler-free spectroscopy).
- The first papers on extended cavity diode lasers (ECDL) operated at liquid nitrogen temperature. The first Doppler free spectra (potassium) taken with ECDL.
- Evolution of extended cavity diode lasers. Two approaches: strong feedback from low-Q cavity versus low feedback from high - Q cavity. A possibility to combine strong feedback and high- Q cavity.
- Diode lasers coupled to whispering gallery modes of quartz microspheres.
- Compact ECDLs with double loop of thermal stabilization and improved regime stability.
- Doppler-free single photon spectroscopy of Cs, 85,87Rb, 39,41K. Different types of saturartion: pumping to the excited level, pumping to another hf sublevel of the ground state, velocity selective polarization and alignment. Collision of different saturation mechanisms in crossover resonances.
- Laser cooling of alkalies. Requirements for the DLs. Frequency stabilization against Doppler-free, Zeeman-tunable resonance peak on cycling transition.
- Two photon doppler-free spectroscopy and cascade transitions in Cs (6S-6P-6D and 6S-6P-8D).
- The techniques of power amplification.
- Two photon spectroscopy in _ configuration of Rb and Cs.
- Different techniques in generation of bichromatic radiation: two mode laser, high frequency current modulation of travelling wave amplifier, modulation of slave laser in injection locking, phase locking of independent diode lasers.
- Lambda resonance and compact atomic clocks and magnetometers.

L-11

Fiberoptic infrared chemical sensors based on quantum cascade lasers

B. Mizaikoff

Georgia Institute of Technology,

School of Chemistry and Biochemistry

Applied Sensors Laboratory

Atlanta, GA 30332-0400, U.S.A.

boris.mizaikoff@chemistry.gatech.edu

Optical chemical sensor technology in the mid-infrared (MIR) spectral range (3-20 μm) is gaining importance in process monitoring, environmental analysis and the biomedical field due to the increasing demand for versatile and robust sensor technology with inherent molecular specificity. Interfacing IR-transducers with continuous measurement or surveillance situations becomes increasingly feasible with the advent of appropriate waveguide technology (e.g. MIR transparent optical fibers and planar waveguides), protective surface coatings (e.g. DLC), and the availability of advanced light sources such as room-temperature operated quantum cascade lasers (QCLs).

Efficient infrared sensor systems take advantage of the unique properties of quantum cascade lasers as a light source. The use of single mode distributed feedback (DFB) QCLs allows for the creation of wavelength-tailored waveguides matched to the laser emission frequency. A new generation of IR sensing platform based on integrated waveguide technology for gas phase and liquid phase analysis will be discussed and selected application examples for liquid phase and gas phase sensing utilizing mid-infrared fiberoptic chemical sensor technology in combination with QCLs will highlight today's state-of-the-art.

Integrated mid-infrared sensing system for trace level (ppb) gas analysis combining quantum cascade lasers with an emission frequency of 10.3 μm with a frequency matched photonic bandgap hollow core waveguide have been developed, demonstrating the first sensing application of photonic bandgap fibers [1]. The photonic bandgap fiber simultaneously acts as a wavelength selective waveguide and miniaturized gas cell. The laser emission wavelength corresponds to the vibrational C-H stretch band of ethyl chloride gas. This sensing system enables the detection of ethyl chloride at concentration levels of 30 ppb (v/v) with a response time of 8 s probing a sample volume of only 1.5 mL in a transmission absorption measurement within the photonic bandgap hollow core waveguide.

Furthermore, the first mid-infrared evanescent field absorption measurements with InGaAs/AlInAs/InP DFB QCLs coupled to free-standing thin film planar silver halide waveguides will be discussed, detecting 80.7 μg of solid urea precipitate and 10.8 μg of acetic anhydride solution after deposition at the planar silver halide waveguide surface [2].

References

[1] C. Charlton, B. Temelkuran, G. Dellemann, and B. Mizaikoff, *Appl. Phys. Lett.,* accepted for publication (2005).

[2] C. Charlton, A. Katzir, and B. Mizaikoff, *Anal. Chem.,* accepted for publication (2005).

L-12

Tunable fiber laser spectroscopy and application to trace gas detection

W. Chen*, *J. Cousin

Laboratoire de Physicochimie de l'Atmosphère, Université du Littoral Côte d'Opale

189A, Av. Maurice Schumann, 59140 Dunkerque, France

S. Kassi, D. Romanini

Laboratoire de Spectrométrie Physique, Université J. Fourier de Grenoble

140 rue de la Physique, 38402 St Martin d'Hères, France

Application of continuous-wave (cw) tunable erbium doped fiber laser to high-resolution molecular spectroscopy is reported. The laser is widely tunable in the near-infrared region of 1542-1600 nm by temperature tuning. The laser linewidth is less than MHz. This ultranarrow linewidth is highly desirable for ultra-sensitive spectroscopic detection using high-finesse cavity.

High-resolution spectra of C_2H_2 and N_2O have been obtained near 1.544 μm with a minimum measurable absorption coefficient of about 10^{-7} cm^{-1} for direct absorption spectroscopy associated with a 100-m long multipass cell and 10^{-10} cm^{-1} for cw cavity ring down spectroscopy (CRDS), respectively. Measurements of N_2O concentration have been performed as well with high dynamic range varying from 100% purity to sub ppm by using CRDS technique.

L-13

Lead-salt and difference frequency generation ir spectrometers: performance comparisons and common requirements for ultra sensitive airborne measurements

Alan Fried, Dirk Richter, Petter Weibring, and James G. Walega

The National Center for Atmospheric Research, Boulder, Colorado 80301

www.apol.ucar.edu

&

Chad Roller and Frank Tittel

Rice University, Houston, Texas, 77005

Tunable infrared absorption spectroscopy employing lead-salt diode lasers as well as other infrared laser sources continues to provide atmospheric researchers an important means of acquiring measurements of numerous trace gases in the atmosphere. Since many of these gases are present in the atmosphere at mixing ratios in the 1 to 1000 parts-per-trillion (ppt) range, the specific measurement approach requires extremely low limits of detection. Airborne measurements are particularly useful for atmospheric studies, and such measurements further require instruments with fast response times (seconds to minutes) and instruments that are immune to severe vibrations and variable sampling conditions of temperature, pressure, relative humidity, and aircraft accelerations.

The present talk will discuss an airborne tunable diode laser absorption spectrometer based on a cryogenically cooled lead-salt diode laser operating at 3.5 microns to acquire ambient measurements of the important trace gas formaldehyde (CH_2O). This system has been developed and continuously refined over the past 10 years, and 1 detection limits for CH_2O in the 30 to 40 ppt range are now routinely achieved during airborne operation employing 30-second integration times. The approaches to achieve this performance during our most recent airborne campaign in the summer of 2004 will be discussed. In addition, an overview of a new room temperature operation difference frequency generation (DFG) system developed in our laboratory for airborne CH_2O measurements will also be presented. This system is significantly smaller, lighter, and has demonstrated even lower limits of detection than the lead-salt instrument in our laboratory. Common features and requirements with the lead-salt system will be given, including performance comparisons between the two systems. A more detailed discussion of the new DFG instrument will be provided by a companion poster paper by Weibring et al. at this same conference.

Part 2. Industrial Session

I-16 LasIR™ – the next generation
A. Chanda, G. I. Mackay, G. Bell, S. Dwight, H. Gamble, F. Zibapour and J. R. Robbins

I-17 VCSEL-based methane monitoring for industrial applications
David Bomse

I-18 A new generation TDL analysers from NEO for process applications
Peter Kaspersen, Ove Bjorøy, Ivar Linnerud and Viacheslav Avetisov

I-19 State-of-the-art of diode-laser based gas analysis in process industries
Michael W. Markus

I-1

Quo Vadis TDLS ?

Johannes Kunsch

Laser Components GmbH, Olching, Germany

The good news first: Tunable Diode Laser Spectroscopy (TDLS) has managed to turn from a "promising technology" into an "established technology" in the industry within the last two years. In the fall of 2004 the first company announced the sale of their 1.000th TDLS instrument in history [1]. This historic event is nearly exclusively based on NIR wavelengths. Key gases are O_2, NH_3, CH_4 and water vapour. Recent results are closely linked with improvements in lifetime and a reliable supply of specially tailored lasers. Many of them are derived from telecom developments and sometimes even telecom spare parts are used for gas analysis. [2] This paper highlights the changes in commercial applications of TDLS that have happened since 2003.

In reality light and shadows are close by. In 2003 at Zermatt the following warning was issued: "Quantum Cascade technology is experiencing a hype these days. But if we cannot create a breakthrough for this technology within the next 18 months, the tables might turn." Unfortunately, the heralded became true. Sales numbers of commercial QC laser based systems are stagnating. The biggest obstacle so far has been the difficult supply of lasers. However, the summary of the OPTAM conference held in October 2004 in Duesseldorf has been that QC lasers get a second chance in industrial applications. This optimism is based on the fact that laser manufacturers (that even compete in certain areas) are teaming up to commercialize QC technology. For example, Nanoplus and LASER COMPONENTS GmbH and Alpes Lasers SA and LASER COMPONENTS GmbH do cooperate on developing and marketing QC lasers. Despite all progress of room temperature cw-operation of QC lasers the focus with industrial applications is still on pulsed operation. The reasons are rather simple: First, good experimental results have been achieved by pulsed technology. [3] Second, pulsed QC lasers are easier to supply and third: Lifetime indications of pulsed QC are promising.

Finally, one historic pattern should not be omitted. TDLAS is a complicated and diversified application. It is rather unlikely, that a new type of laser will make a commercial breakthrough single handedly. It is more likely, that this will be achieved by less demanding and broader applications. Consequently, the QUANTA®-OEM QC laser head has been designed not just to meet the technical demands of the spectroscopic community. It has also been designed for opening up potential wider markets with its cost advantages, plug and play features and its universal interface. The latest marketing campaign of LASER COMPONENTS GmbH has been "Rent a QC laser" in order to widen the user community.

[1] C. HEINLEIN: Gas analysis with tuneable diode lasers in demanding process environments, VDI Berichte **1863**, 4. Konferenz über Optische Analysenmesstechnik in Industrie und Umwelt, VDI Verlag GmbH, Düsseldorf (2004) 217-219

[2] M. G. ALLEN: Gas analyzers in the near- and mid-IR, Abstracts of 4th International Conference on Tunable Diode Laser Spectroscopy, Zermatt (2003), 42

[3] D.D. NELSON, J.H. SHORTER, J.B. MCMANUS, M.S. ZAHNISER: Sub part-per-billion detection of nitric oxide in air using a thermoelectrically cooled mid-infrared quantum cascade laser spectrometer, Appl. Phys.B **75** (2002), 343-350

I-2

VCSELs in the 1.3–2.0 µm wavelength range for TDLS application

M. Ortsiefer, R. Shau, J. Rosskopf, S. Baydar, K. Windhorn and E. Rönneberg

VERTILAS GmbH, Garching, Germany

The availability of both high performance and well-priced laser diodes and related systems is one of the preconditions for broadly established TDLS applications. In this context, long-wavelength vertical-cavity surface-emitting lasers (VCSELs) are expected to considerably expand the range of applications due to their unique device charatceristics as well as their potential for simplified manufacturing. VCSELs show longitudinal singlemode emission, small power consumption, high efficiencies and can be tested on wafer level. All of these advantages do not hold for conventional edge emitters. However, the development of long-wavelength VCSELs with suitable performance has been challenged by several technological drawbacks. During the past few years, VERTILAS has been pioneering the Buried Tunnel Junction (BTJ)-VCSEL technology which resembles a breakthrough for long-wavelength VCSELs. The BTJ-VCSELs exhibit high performance characteristics and offer a convenient way to detect a large number of absorption lines with easy to handle, room temperature cw operating laser diodes [1]. Up to now, the lasers can be employed to detect near infrared active gases in the wavelength range from 1.3-2.0 µm. This wavelength range comprises most of the relevant greenhouse gases and industrial pollutants (CH_4, CO, CO_2, H_2O, H_2S, NH_3,…).

BTJ-VCSELs are grown in a twofold Molecular Beam Epitaxy (MBE) process. The subsequent processing is done on a full wafer scale. By altering material composition and layer thicknesses, customer specific wavelengths throughout the entire range are accessible with the mature InGaAlAs/InP semiconductor compound system [2]. At 1.55 µm wavelength, typical threshold currents, threshold voltages and cw output powers at room temperature are 1 mA, 0.9 V and 1.5 mW, respectively. For longer wavelengths, the output power decreases but is still ~0.5 mW at 2 µm wavelength. The measured spectral linewidth is as small as 20-30 MHz. VCSELs from VERTILAS are available on a large variety of housings including diffferent sizes, windows with AR-coatings, fiber pigtail or temperature controlled submounts for a wavelength tuning of ~0.1 nm/°C. The lasers show high side mode suppression ratios well beyond 30 dB for both transverse and polarization modes with a small beam divergence around 15°. Mode-hopping free current tuning is achieved together with high tuning rates of ~0.6 nm/mA and tuning ranges of 3-5 nm which is particularly useful for simultaneous measurements of more than one absorption line or even multiple species. Furthermore, the small active volume size allows for current tuning even in the MHz range with a sufficient wavelength tuning range.

[1] G. Totschnig, M. Lackner, R. Shau, M. Ortsiefer, J. Rosskopf, M.-C. Amann and F. Winter, *Meas. Sci. Technol.*, **14**, 472-478, 2003

[2] C. Lauer, M. Ortsiefer, R. Shau, J. Rosskopf, G. Böhm, E. Rönneberg, F. Köhler and M.-C. Amann, *IEEE Photon. Technol. Lett.*, **16**, 2209-2211, 2004

I-3

DFB laser diodes for tunable diode laser spectroscopy at wavelengths beyond 2.3 µm

J. Koeth, M. Fischer, M. Legge, J. Seufert and R. Werner

nanoplus Nanosystems and Technologies GmbH, Gerbrunn, Germany

Distributed feedback (DFB) lasers are widely used in a variety of applications based on tunable diode laser spectroscopy. Although recent progress in semiconductor laser manufacturing and system design has brought this technique to sophisticated detection limits as low as a few ppm there is still an ever growing need for even higher sensitivity. One way towards this goal is to get access to molecular rotational-vibrational modes at lower photon energies where many molecules of interest exhibit higher absorption probabilities. However, so far mainly laser diodes with emission below 2.3 µm have been employed in tunable diode laser spectroscopy due to the lack of suitable coherent light sources emitting at higher wavelengths. Many gases and liquids (e.g. HF, CO_2, NO, H_2O) exhibit pronounced absorption features in the wavelength range beyond 2.3 µm, which lays the ground for an improved detection sensitivity. E.g. the absorbance for water is by a factor of 12 higher at a wavelength of 2630 nm as compared to the prominent absorption line at 1877 nm and for CO_2 the increase in oscillator strength at 2700.3 nm even amounts to a factor of 40 with respect to the absorption line at 2004 nm [1]. The fabrication of DFB lasers emitting at wavelengths beyond 2.3 µm became possible with a specialized technology which employs lateral metal Bragg gratings within the waveguide structure of the semiconductor laser diode. This concept can be applied to vitually all compound semiconductor material systems. Using this technology, single mode emitting laser devices with emission wavelengths as high as 2.8 µm were successfully processed. The lasers work in cw operation at room temperature. Side mode suppression ratios exceeding 30 dB and output powers of a few mW guarantee excellent spectral selectivity for a wide range of spectroscopic applications. As an example Fig. 1 shows the spectrum and the light-output curve of a DFB laser emitting at a wavelength of 2744 nm.

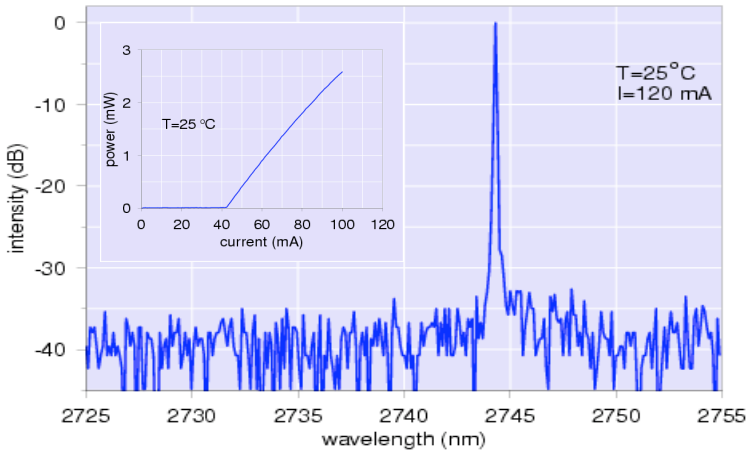


Fig. 1 Spectrum and light output curve (inset) of a DFB laser emitting at 2744 nm.

[1] HITRAN96 database

I-4

Quantum-cascade lasers for TDLS

Stéphane Blaser, Yargo Bonetti, Lubos Hvozdara and Antoine Muller

Alpes Lasers SA, Neuchâtel, Switzerland

The market of IR applications shows an increased interest of industry to base developments on quantum-cascade (QC) lasers, since they are the only solid-state lasers that can access the mid-infrared region of the spectrum where toxic gases and vapors have their tell-tale absorption features. Nowadays numerous applications can be approached using QC lasers as powerful mid-infrared light sources, such as chemical sensing or trace gas measurements for process development, environmental science, forensic science, liquid detection spectroscopy; non-invasive medical diagnostics for breath analyzer or glucose dosage; remote sensing for leak detection, exhaust plume measurement or combat gas detection; optical wireless communications or lidar. For chemical sensing by optical spectroscopy, several detection techniques were already been demonstrated using QC lasers, such as photo-acoustic, TILDAS, cavity ringdown, absorption spectroscopy, heterodyne detection scheme or cavity enhanced spectroscopy.

Alpes Lasers is the leading QCL manufacturer. The state-of-the-art of commercially available QC lasers will be reviewed. Devices operating in pulsed mode at room-temperature ranging from 4.3 to 11.8 μm with 3GHz linewidth will be presented. High-resolution spectroscopy requires tunable single-frequency light sources with very narrow linewidth (< 3.5 MHz); this can be achieved using QC lasers operating in continuous-wave (CW) mode. This can be obtained using commercial cryogenic devices available from 4.3 to 9.1 μm. CW operation on TE-cooler up to –20°C has been demonstrated [1]. Alpes Lasers aims at producing commercial devices for NO detection (5.26 μm). In this direction, Alpes Lasers reports the realization of a single-frequency QC laser with CW operation up to +30 °C at a frequency of $\tilde{\nu}$ ~ 1840 cm^{-1}, corresponding to a wavelength of ~5.4 μm [2]. Processing is done using standard lithography in ridge waveguides mounted junction-up. The active laser region is based on a bound-to-continuum design, which allows for generation of broad gain. The high performances were achieved with a low active region doping and a thick electroplated gold deposition, resulting in a characteristic temperature of T_0 = 155 K in CW, which is comparable with typical values in pulsed mode, with a threshold current density of j_{th} = 2.05 kA/cm^2 at 300K. A single-mode emission is observed over the entire investigated temperature and current ranges, with a side-mode suppression ratio > 25 dB.

[1] T. Aellen, S. Blaser, M. Beck, D. Hofstetter, J. Faist, and E. Gini, *Appl. Phys. Lett.,* **83**, 2003

[2] S. Blaser, D. Yarekha, L. Hvozdara, Y. Bonetti, A. Muller, M. Giovannini, J. Faist, *Appl. Phys. Lett.,* **85**, 2005

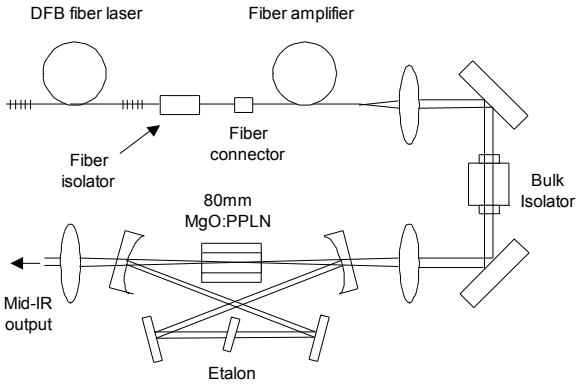
I-5

Room temperature cw PPLN optical parametric oscillator for mid-infrared spectroscopy

Angus Henderson and Ryan Stafford

Aculight Corporation, Bothell, Washington, USA

Single frequency, continuous wave PPLN optical parametric oscillators (OPOs) are highly attractive for spectroscopic applications requiring widely, continuously tunable mid-infrared output. Extended mode-hop-free tuning of these devices has been demonstrated using tunable pump sources such as diode lasers and, more recently, fiber lasers [1]. The practicality of OPOs pumped by such sources is limited by the high powers required to exceed oscillation threshold, and the need for heating of the nonlinear material above 100°C to avoid photorefractive damage. We report the first demonstration of stable, continuous wave, room temperature operation of a singly resonant PPLN OPO using 5% MgO–doped PPLN. The crystal used was of 80mm length, 60% longer than previously used in such CW devices, allowing reduction of oscillation threshold.



Configuration of single frequency DFB-fiber laser pumped CW OPO

The pump source consists of a distributed feedback fiber laser and a fiber amplifier. The DFB fiber laser produces 10 mW of single frequency output, in a linear polarization. The output wavelength, centered on 1083nm, can be tuned continuously a total of 0.5nm by temperature variation and/or piezoelectric strain of the DFB fiber. The seed is amplified using a polarization-maintaining amplifier, producing up to 10W of single longitudinal and transverse mode, linearly polarized output. The pump beam passes through a faraday isolator, and is mode-matched into a bow-tie ring cavity OPO using a single lens. The cavity consists of four mirrors, which are highly reflective at 1.8 m, and highly transmissive at pump and idler (1.08/2.7 m respectively). The cavity design is designed to mode-match a cavity signal beam waist to the pump beam, which is focused to a beam radius of 80 m at the center of the crystal. The nonlinear crystal is poled with a fan-out structure across its width, such that the poling period varies from 31.3…32.3 m. This allows wavelength to be tuned without varying the crystal temperature, by translating the crystal laterally.

[1] M. E. Klein, P. Gross, K-J. Boller, M. Auerbach, P. Wessels and C. Fallnich, "Rapidly tunable continuous wave optical parametric oscillator pumped by a fiber laser", Opt. Lett. **28**, 920-922 (2003).

I-6

Distributed feedback diode lasers and tunable femtosecond fiber lasers for spectroscopy

J. Posthumus, A. Deninger and W. Kaenders

TOPTICA Photonics AG, Martinsried, Germany

Recent technological developments allow TOPTICA Photonics to build distributed-feedback diode lasers at virtually any wavelength between 760nm and 1600nm. These devices provide mode-hop free scanning across nanometers and are ideal laser sources for spectroscopy, gas sensing, LIDAR seeding, THz generation, etc. In another activity, a new femtosecond fiber laser has been developed that is widely tunable (575nm–2μm) thanks to non-linear processes. It may be used as a powerful universal light source for spectroscopic applications and can be nicely combined with TOPTICA's diode technology. Traditional high-resolution diode lasers work with an external cavity that couples light back into the laser diode. For example TOPTICA's diode lasers **DL100** have linewidths of about 1 MHz and power levels of up to 150mW. The frequency of such lasers is very stable and their tuning range is typically 10nm. The series covers the wavelength ranges 375nm–450nm and 625nm–1850nm. For even higher powers, it is necessary to amplify the diode laser. The tapered amplifier, which is a single-pass semiconductor device, preserves the high beam quality whilst boosting the powers up to 1 W. The series **TA100** covers the range 730nm–1100nm. Building upon this technology is the series **SHG100**, which provides powers of up to 200mW in the 375nm–540nm range from the principle of frequency doubling in an external cavity. Other products interesting for spectroscopy are lasers that were especially developed for Raman spectroscopy, high resolution Fabry-Perot interferometers, multi-pass cells for absorption spectroscopy **(**Herriott cell) and wavelength meters. The ultimate resolution available is 10 MHz (relative accuracy almost 10^{-8}) in the range 350nm–1100nm. Infrared wavemeters extend the range to 2250nm at an accuracy of 10^{-6}.

A distributed-feedback (**DFB)** laser diode is quite different, it has the wavelength selecting grating inside the laser diode itself. Scanning via pump current is fast, but the tuning range is limited to tens of GHz. Scanning via diode temperature is slow (tens of seconds), but mode-hop free tuning ranges can be as high as 1200 GHz, i.e. more than 2 nm. In combination with TOPTICA's low-noise driving electronics and temperature control the diodes have a linewidth of 2–4 MHz, tuning rates of 1–2 GHz/mA and 25 GHz/°C. Individual diodes are wavelength-selected with very high precision (0.1nm) and can be packaged according to customer requirements. Popular wavelengths are 766nm, 780nm, 795nm, 852nm and 895nm, but also 935nm and 1360nm, which are usually available ex-stock. Even so, virtually any wavelength within the range 760nm–1600nm is possible. Output powers reach 100mW in the near infrared.

The FemtoFiber Scientific (**FFS**) laser system is made of reliable telecom components. The active medium is an Erbium doped fiber, which is pumped directly by fiber-pigtailed laser diodes. The highly stable FFS delivers 180 mW average power in sub-100 fs pulses at a central wavelength near 1560 nm. The high peak powers of 20kW allow efficient frequency doubling to 780nm. As a unique feature, the FFS is available with a highly non-linear fiber, permitting the generation of tunable broadband output in the wavelength range 950nm–2μm with power levels of 100mW. By varying the chirp of the laser pulses that enter the non-linear fiber, it is possible to concentrate the power in particular wavelength regions. Again this output may be compressed to ultrashort pulses (25 fs) and subsequently frequency doubled. Like that most wavelengths between 575 and 950nm are also covered. We conclude therefore that a single FFS laser system can provide virtually any wavelength in the 575nm–2μm range.

I-7

Compact 1 W tunable Littman-Metcalf diode laser for high resolution spectroscopy

Sandra Stry and Joachim Sacher

Sacher Lasertechnik Group, Marburg, Germany

The combination of high power, small linewidth and fast tuneability is essential for many fields in high resoution spectroscopy [1-3]. Precise monitoring of trace gases using in situ optical absorption techniques is important for various environmental and medical application. Examples are quantitative measurements of atmospheric polutants and the analysis of endogenous biomarkers in exhaled breath. Both applications needs an ultra sensitive detection technique as the cavity ring down or cavity leak-out spectroscopy. To achieve high sensitivity the infrared wavelength range is very attractive. Considering the boundary conditions of the spectroscopy technique, the only cw laser source for the mid-infrared wavelength region are devices based on nonlinear frequency conversion, like optical parametric oscillation (OPO) of difference-frequency mixing Requirements for such a laser system used are extensive: a modehop free tuning range of several GHz, with a linewidth in the regime of lower than 1 MHz with an output power of several 100 mW. We report a new principle of using high power laser diodes directly in an external Littman-Metcalf cavity configuration to combine the high power of these diodes with the excellent properties of this kind of external cavity (low linewidth and high tuneability)[4]. The very compact design offers an output power of up to 1000 mW and an excellent beam quality with a beam propagation factor of $M^2 < 1.2$ in both directions. This laser system operates single mode with a modehop free tuning range of up to 100 GHz without current modulation and a side mode suppression better than 50 dB. The determined linewidth of this laser system via a heterodyne experiment with a low power Littman laser system, is below 500 kHz in 1 ms. Advanced applications require a large tuning range which can only be achieved by motorized systems. Examples are the online monitoring of several trace gases within a sample probe or the indication of a special gas species within a non none gas mixture. A large coarse tuning range guarantees the detection of a great number of absorption lines with the use of only one laser system. The coarse tuning range of our high power Littman-Metcalf laser is above 20 nm. For a difference frequency laser system this results in a tuning range of more than 250 nm at 3 µm. Within this tuning range no realignment of the cavity is required. An encoder at the stepper motor provides the position of the tuning motor. To reach the exact wavelength position of a absorption line the laser can be fine tuned via a piezoelectric transducer which allows a modehop free tuning over several tenth of GHz. We developed an easy computer controlled locking tool which gives the opportunity to find the absorption line automatically. The combination of high power with advanced tuneability in a compact setup offers the potential that such a laser system can be used in various applications.

[1] C. E. Wieman and L. Hollberg, "Using diode lasers for atomic physics," Rev. Sci. Instrum. 62, 1-20 (1991).

[2] M. Mürtz, D. Kleine, S. Stry, H. Dahnke, P. Hering, J. Lauterbach, K. Kleinermanns, W. Urban, H. Ehlers, D. Ristau, *Ultra-Sensitive Trace Gas Monitoring with CW Ring-Down Spectrometer*, Atmospheric Diagnostic, Special Issue 4, 61-67 (2002).

[3] S. Stry, P. Hering, M. Mürtz, "Portable difference-frequency laser-based cavity leak-out spectrometer for trace-gas analysis", Appl. Phys. B 75, 297-303 (2002).

[4] L. Ricci, M. Weidenmüller, T. Esslinger, A. Hemmerich, C. Zimmermann, V. Vuletic, W. König, T. W. Hänsch, "A compact grating-stabilized diode laser system for atomic physics.", Opt. Commun. 117, 541 (1995).

I-8

Electronically tunable, waveguide external-cavity semiconductor lasers

M. H. Anderson, S. R. Davis and S. D. Rommel

Vescent Photonics, Inc., Denver, CO, USA

We have designed and demonstrated a new waveguide external-cavity semiconductor laser (WECSL) using grating feedback in Littrow configuration in a planar optical-waveguide form factor. An innovative giant electro-optic effect capable of changing the effective index by $\Delta n_{eff} = 0.02$ forms the basis for extended synchronous tuning of both the optical path delay (OPD) and lasing wavelength. The waveguide is coupled to commercially available laser diodes with either microlenses or direct butt coupling. The light from the laser then passes through an OPD tuning element and a beamsteering element before encountering a blazed reflection grating bonded to the end facet of the waveguide resulting in an entirely electro optic and monolithic device. The unused facet from the laser diode provides a non-steering output and another steering output can be taken from the grating.

The WECSL can be designed to tune over 100 nm ranges for applications such as distributed fiber sensing or detection of multiple trace-gas species. Alternatively, for sensing of a single trace-gas specie, the center frequency of the WECSL can be adjusted during manufacturing to tune over a smaller range anywhere inside the gain profile of the laser diode. In addition to providing electronic tuning in a environmentally robust package, the WECSL design reduces manufacturing costs of external-cavity tunable diode lasers while maintaining their primary benefits such as spectral linewidth, side-band suppression ratio, and continuous mode-hop-free tuning range.

We are currently developing WECSLs at 670 nm and 1824 nm for NOx detection, a device at 1380 nm for water-vapor spectroscopy, and an extended-range tuning device at 1550 nm for distributed fiber sensing.

In this paper we will discuss the giant electro-optic effect and several WECSL designs. We will also discuss the performance of prototype devices.

I-9

Lasers and laser source modules for TDLS

Lars Mechold

Laser Components GmbH, Olching, Germany

The product range of LASER COMPONENTS GmbH is well adapted to the needs of the spectroscopic community. Markets for TDLAS applications are growing and all activities are focused on improving the laser production as well as new developments. The 760 nm SM-VCSEL from AVALON PHOTONICS is the workhorse for many instrument producers worldwide This cell phone sized source module is trimmed for real time spectroscopy with excellent stability. The design is universal and custom settings can be made via the analogous interface. Despite the module being developed for real-time measurements by using detectors with appr.100 MHz bandwidth, it also works well with slow detectors like pyroelectrics. In these cases pulse width and / or pulse repetition rate is modulated via the interface. Together with InfraTec Gmbh a special pyroelectric laser detector will be launched into the market.. One of the main tasks is the measurement of molecular oxygen under various conditions. It is less known that aside from single emitters also laser arrays are offered which allow for simultaneous monitoring of oxygen concentration and spatial fluctuations. Spectroscopic absorption diagnostics based on diode laser emission especially from 1250 - 1750 nm has been the focus of interest for some time now. Specially tailored DFB lasers are used at many locations for concentration measurement of ammonia, water vapour and methane, to name just the main applications. The traditional core business of LASER COMPONENTS GmbH is the infrared region. Many users around the world have been working with our in-house manufactured lead salt diode laser for 13 years. Based on this technology the wavelength range from 3 to almost 25 µm can be completely covered, all spectral positions are possible. A delivery within 8 weeks or less is guaranteed. Last but not least over 200 individual lasers can be selected from our extensive internet library of stocked tuneable diode lasers. The selection process of single mode lasers could be significantly enhanced by the introduction of reference gas testing. In the DEGAS instrument of Fraunhofer IPM our lasers proved mode stability over many cycles of warm up and rapid cool down [1]. Therefore, when it comes to small number applications lead salt lasers are definitely an alternative to the widely discussed QC lasers.

Based on discussions at Zermatt 2003 the QUANTA®-OEM QC laser based radiation source has been designed. To increase the number of customers and to lower the entry barrier for spectroscopy based absorption diagnostics more services were introduced to the market: An application laboratory has been installed to support customers with their investigations and to carry out feasibility studies using TDLAS. Based on our lean production structure custom laser assemblies are possible. One of the recent successes is the introduction of QC Lasers in TO housings which are now gaining more and more acceptance. Furthermore, QC laser heads can be rented to carry conduct feasibility studies before a purchase. Latest developments have been dealing with laser source module for the THz range.

[1] K. Sassenscheid, 4. Konferenz über Optische Analysenmesstechnik in Industrie und Umwelt, Düsseldorf, *VDI Berichte* **1863**, 171 (2004).

I-10

Electronics and signal processing components for TDLS

Antonio Chiarugi

Scienca Industria Technologia srl., Pisa, Italy

In the last years gas sensors based on tuneable diode laser absorption spectroscopy have attracted a growing attention of the industrial world for leak-detection, pollution monitoring, quality control. These applications require instruments that can obtain high sensibility and reliability but that must be also very sturdy and easy to use. During several years of activity designing and producing gas sensors, S.I.T has developed increasingly compact, versatile, and multi-functional electronic components to control and monitor each process involved in a absorption measurement using tuneable diode laser.

We present our newly developed laser-diode systems controller LDC1, which has demonstrated its capabilities in a lot of different applications. This electronic module is been used in instruments mounted on the chimney of industrial plants for pollution monitoring, on small vehicles for leak-detection from methane distribution pipelines, on stratospheric aircraft for scientific purpose [1]. This controller is designed to be interfaced with a computer, so that every functionality can be fully managed via software, and it is also possible to monitor all the parameters describing its performance. The electronic module is composed by three boards, that can be used also separately :

- A Laser Driver Board, for laser-diode power supply, that can be configured to supply variable currents in a wide range. The user can set and monitor the current value by computer.
- A Temperature Controller Board with Peltier cell, PID temperature controller, and NTC temperature sensor (10k), for stabilizing the laser diode temperature. Also in this case the user can set and check the temperature value via software.
- A Signal processing Board designed for the acquisition and elaboration of photodiode signal in measure that use various techniques, from direct absorption, to wavelength modulation spectroscopy or two tone modulation spectroscopy.

LDC1 offers also auxiliary inputs and outputs (both analogue and digital) to perform other tasks, as monitoring or managing other sub-devices. The laser diode controller LDC1 is available in PC104 format, a widespread standard in the industry and it is very compact and robust. We present in detail its main features and how this controller can be applied for various in-situ TDLS applications.

[1] F. D'Amato, P. Mazzinghi, F. Castagnoli: "Methane analyzer based on TDL's for measurements in the lower stratosphere: design and laboratory tests", Appl. Phys. B75, 195-202 (2002).

I-11

QC laser gas sensor platform
From high end to low cost volume applications

E. Normand, I. Howieson, M. McCulloch and R. Cooper

Cascade Technologies Ltd, Glasgow, United Kingdom

Since they were first demonstrated at Bell Laboratories in 1994, Quantum Cascade (QC) Lasers have been gaining acceptance as the mid-infrared (IR) source of choice. Their shift out of the laboratory into real world applications has been accelerated by the step change in performance that these devices can deliver in fields as diverse as range finding, electronic counter measures, Free Space optical telecoms and chemical sniffing. It is in this last field, chemical sniffing, that perhaps the biggest opportunities can be found as the combination of QC lasers and recent gas sensor developments promise to deliver superior levels of spectroscopic performance in terms of detection and selectivity. This will open up huge markets in environmental monitoring, health and safety, security, defence and medical diagnostics.

I-12

Lasers and laser systems for medical diagnostics

Patrick J. McCann

Ekips Technologies, Inc., Norman, OK, USA

Progress continues to take place at Ekips Technologies on the development of laser spectrometer instrumentation designed for medical diagnostic applications. A leading medical application involves real-time measurement of exhaled nitric oxide (eNO) to assess airway inflammation in asthmatic patients. Real-time eNO breath tests require an NO sensitivity of better than 10 ppb with an integration time of about one second. In addition, laser tunability should be sufficient for simultaneous measurement of exhaled carbon dioxide (eCO_2) since it offers an internal calibration feature for timing breath collection and calculating lower airway eNO concentrations. Such measurements are possible in the 5.2 μm spectral range with widely-tunable IV-VI semiconductor lasers. This presentation will review recent success in the development of liquid-nitrogen-free cryogenic cooling systems for both the IV-VI laser and the HgCdTe detector. Such laser/detector systems allow continuous operation without the need for frequent liquid nitrogen refills, an essential requirement for clinical deployment. Further improvements in instrumentation have also been made possible by development of customized electronics for performing second harmonic laser absorption measurements thus eliminating the need for bulky function generators and lock-in amplifiers. Progress on the development of user-friendly instrument control and data acquisition software will also be described. These hardware and software advances enable the fabrication of turn-key mid-IR laser absorption spectrometers with a bench-top form factor suitable for use by both allergy and asthma clinicians as well as biomedical researchers. This platform instrument combined with commercially available IV-VI semiconductor lasers will facilitate future research on measuring biologically important gas phase molecules.

I-13

Novel instrumentation for trace gas measurements in the field

Doug Baer, Manish Gupta, Tom Owano, Robert Provencal, Ken Ricci and Anthony O'Keefe

Los Gatos Research Inc., Mountain View, California, USA

We present the development, testing and deployment of new compact, rugged and inexpensive gas analyzers for atmospheric monitoring, industrial process control, and scientific applications. These commercial instruments operate autonomously and report measurements with high sensitivity, accuracy, and specificity in real time. Examples of commercial instruments, operating in the field, that combine near-infrared diode lasers or mid-infrared quantum cascade lasers with Off-Axis Integrated Cavity Output Spectroscopy (Off-Axis ICOS) methods will be presented.

I-14

TDL trace gas analyzer for environmental measurements

Steven D. Sargent and Bertrand D. Tanner

Campbell Scientific, Inc., Logan, Utah, USA

The TGA100A Trace Gas Analyzer measures trace gas concentration in an air sample using tunable diode laser absorption spectroscopy (TDLAS). This technique provides high sensitivity, speed, and selectivity. The TGA100A is a rugged, portable instrument designed for use in the field. It includes a temperature-controlled, weather-tight fiberglass enclosure to allow it to be used without additional shelter. Its simple optical design makes it easy to adjust and maintain alignment. It uses a single-pass, 1.5 m sample cell to optimize the frequency response for trace gas flux measurements by the eddy covariance method. Its optical source is a lead-salt diode laser that is cryogenically cooled either with liquid nitrogen or with a closed-cycle refrigeration system. The laser is operated in quasi continuous-wave mode, with a spectral scan sequence that includes a linear ramp of the injection current to provide the spectral scan, as well as a brief subthreshold pulse to measure the detector dark response followed by a temperature stabilization pulse. This scan sequence is repeated 500 times per second. The trace gas concentration is calculated for each scan, and then digitally filtered using either a moving average with the averaging time set by the user, or a digital filter optimized for high frequency response. A recent electronics and software upgrade integrates all control, measurement, and computation functions into the custom-designed electronics package, eliminating the need for a separate computer to be attached. Data can be output to a Campbell Scientific datalogger by digital interface, to a PC by Ethernet interface, or as analog signals. This recent upgrade also allows the user to alternate spectral scans between two or three nearby absorption lines. This feature is used primarily to measure isotope ratios such as $\delta^{13}C$ and $\delta^{18}O$ in carbon dioxide, but can also be used to measure different gases such as carbon dioxide and nitrous oxide.

I-15

High sensitivity QCL trace gas monitors for environmental and industrial monitoring

D. D. Nelson, S. C. Herndon, J. B. McManus, J. H. Shorter and M. S. Zahniser

Aerodyne Research, Inc., Billerica, Massachusetts, USA

We describe our dual laser Quantum Cascade Laser (QCL) spectrometers and present trace gas measurement results obtained with them. These commercial instruments are being produced in two versions: 1) a standard version suitable for most laboratory and industrial environments and 2) an aircraft version suitable for deployment on a wide variety of aircraft platforms.

Both versions employ the same basic optical design. The aircraft version is more modular (to accommodate a variety of aircraft installations), utilizes PXI computers and data acquisition cards and is especially designed to be lighter and more rugged. For both versions, the data acquisition method uses rapid sweep, direct absorption spectroscopy which provides sensitive, multi-species trace gas detection and absolute molecular concentrations without calibration. We implement this approach using *TDLWintel*, our Windows-based data acquisition and analysis program.

We will present several recent applications of these instruments to environmental and industrial trace gas monitoring. For example, we will discuss the deployment of one of these spectrometers during July 2004 aboard NOAA's P3 aircraft as part of the New England Air Quality Study (NEAQS). Tropospheric concentrations of formaldehyde (HCHO) and formic acid (HCOOH) were measured continuously using a single laser which was scanned across absorption features due to each of the molecules. This campaign represented the first flight-based measurement of any species using a TE-cooled pulsed quantum cascade laser for mid-IR absorption spectroscopy. Formaldehyde and formic acid were detected under a variety of conditions including in the New York city outflow plume, in the plumes of electric power plants and in a plume generated by last summer's Alaskan forest fires which was detected near Hudson Bay.

We will also discuss applications of these instruments to the measurement of light duty and heavy duty vehicle emissions. We have used three separate approaches to addressing this issue with the dual laser QC instruments. In the first two approaches, the instrument is mounted in a mobile laboratory and operated with the lab in motion. The approaches include: 1) random vehicle emissions sampling (fleet emissions) while driving in traffic, 2) specific individual vehicle sampling while chasing the vehicle, and 3) specific vehicle sampling with a stationary instrument using a sampling tube over which the vehicle drives. Detected species include NO, NO_2, CO, HCHO, NH_3 and N_2O.

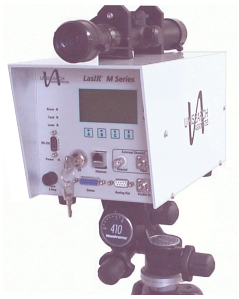
I-16

LasIR™ – the next generation

A. Chanda, G. I. Mackay, G. Bell, S. Dwight, H. Gamble, F. Zibapour and J. R. Robbins

Unisearch Associates Inc., Concord, Ontario, Canada

Unisearch has successfully manufactured and marketed worldwide the LasIR™ line of gas analyzers based on near-infrared tunable diode laser spectroscopy. The next generation of economically priced gas analyzers began to be introduced a year ago. These models are compact, rugged and efficient, and are available as portable single-channel analyzer to up to 32-channel analyzer for monitoring multiple species and locations. Front-panel keypad allows relevant operational parameters to be entered by the user. No field calibration is required. Fast, real-time in-situ measurements of gas concentrations can be made under various industrial environments. These analyzers are suitable for ambient air monitoring and for industrial process control. Measurements of various gases in the laboratory and in industrial environments will be presented and discussed.



Portable analyzer

20-channel analyzer

8-channel analyzer

I-17

VCSEL-based methane monitoring for industrial applications

David Bomse

Southwest Sciences, Inc., Santa Fe, New Mexico, USA

Single frequency, tunable and room temperature operating diode lasers have a wide array of gas sensing applications. Compared to readily available edge-emitting DFB devices, recently available VCSEL (Vertical Cavity Surface Emitting Laser) devices offer characteristics that are favorable for industrial monitoring applications. Simpler device fabrication and wafer-level device testing result in lower per laser cost. Low threshold and operating currents enable portable, battery-operated instruments. Wide wavelength tuning available by bias current tuning allows monitoring of several spectral lines which can offer wider dynamic range and sometimes multiple species detection. I will describe some of the active industrial gas sensing applications at Southwest Sciences that utilize VCSEL lasers. These include a natural gas leak detector utilizing 1650 nm VCSEL. This is a hand-held, battery-operated sensor platform that is under joint development with an instrument manufacturer, and is intended to replace the flame ionization detection. The measurement dynamic range extends from 1 ppm to 100% methane with a response time of ~2 seconds. Another project under active development is a CH_4 flux monitor that also utilizes 1650 nm VCSEL. In the context of global warming discussion, methane is receiving a growing attention and accurate accounting of methane emissions is needed. We expect the portable and accurate methane flux monitor to find applications in atmospheric monitoring, landfill monitoring and methane emission credit trading. Results from laboratory prototype instruments, and if available, data from field prototype instruments, will be described.

I-18

A new generation TDL analysers from NEO for process applications

Peter Kaspersen, Ove Bjorøy, Ivar Linnerud and Viacheslav Avetisov

Norsk Elektro Optikk AS, Lorenskog, Norway

Gas Analysers using tuneable diode laser (TDL) absorption spectroscopy in the near infrared have been widely accepted in the industry for applications where other techniques have failed to operate satisfactorily. The majority of the applications so far have been for emission control of pollutants such as HF, HCl and NH_3 where an in situ TDL measurement is superior to most other spectroscopic techniques both with respect to sensitivity, accuracy and reliability. Norsk Elektro Optikk A/S has, after servicing the market with its LaserGas range of TDL Analysers during the last 10 years, recently introduced the new LaserGas II range of instruments that offers even better reliability and serviceability than the first generation of instruments. A brief description of the new LaserGas II Analyser will be given.

Fig. 1 The LaserGas II Analyser

The new model is more compact with lower power consumption, has the capability of measuring up to three gases simultaneously, and Ethernet connection with TCP/IP. To simplify service and minimize downtime a modular design has been chosen. A service technician can do field replacements of individual electronic boards or the laser module without the need for any special test equipments or tools. It is even possible to convert an Analyser from measuring one gas type to another by replacing the laser module (and if necessary the detector). The new LaserGas II Analyser is suitable for all "traditional" applications, but due to its modularity and compact design it is specifically aimed at new applications related to process control. Some new applications in the process industry where it is used successfully is presented. These include measurements of:

- CO concentrations at low ppm levels at 1300 °C in glass furnaces,
- O_2 at pressures up to 20 bar,
- H_2O at low ppb levels in pure process gases,
- H_2S at concentrations up to 100% vol. with large self broadening effects,
- Several selected hydrocarbons, such as Propylene and Ethylene,
- O_2 for detection of leakages in small glass enclosures at concentrations < 0.1%vol.

I-19

State-of-the-art of diode-laser based gas analysis in process industries

Michael W. Markus

Siemens AG Automation & Drives, Karlsruhe, Germany

Establishing diode laser technology as a new standard for gas analytics in process industries means to meet all the up-to-date requirements on process instrumentation in terms of easy handling, robustness, high stability, maximum availability, and low cost-of ownership. Beside that, the analytical performance needed for technical relevant applications is sometimes a challenge even for a diode laser spectrometer. Presenting their first industrialized process spectrometer based on diode lasers and fibre optical devices already in the early 1990s, Siemens Laser Analytics (formerly AltOptronic) was always a driving force in this progress. With the new model LDS 6, Siemens is offering again a state-of-the-art in-situ process gas analyser based on the proven concept of a fibre coupled diode laser spectrometer having all the experience implemented from decades of gas analytics in process industries. The process gas analyzer consists of a 19" rack mounted central unit which holds the spectrometer part of the system including the frequency stabilized laser source and simple but robust in-situ cross duct sensors in a transmitter/receiver set-up. A cable consisting of optical fibres and copper wires is used to connect the central unit and the sensors in the field over hundreds of meters if necessary. With this modular concept the in-situ gas analyser can be adapted to the requirements of almost any process industry in terms of measuring conditions in the process and ambient conditions in the sensor environment. Since the central unit can be operated in a temperature range from +5…+45 °C it can be placed in any industrial environment used for electronic devices. The analyser allows an easy implementation of the laser based in-situ analysers in existing conventional analytic equipment without the need for specially trained operating personnel. Having a fibre optical beam splitter in the central unit up to three in-situ sensors can be operated independently and simultaneously by one central unit. The cross duct sensors, certified protection class IP 67, fulfill highest demands on robustness and can be operated at ambient conditions -30°C…+70°C. The sensors are optionally available in an intrinsically safe version for operation in hazardous areas incl. those for dust. Various configurations can be chosen to define the process interface by the choice of flange sizes, materials, purging modes and purging media, in order to adapt the sensors directly to gas pipes, steam boilers, incineration chambers, process ovens, gas filter, flue gas stacks, tank, silos or any other process engineering device. Not even a calibration is necessary in the field neither during commissioning nor during long-term operation. Examples are NH_3 slip control in DeNOx installations, determination of HCl or HF concentrations in flue gases, combustion control by O_2 measurements, or safety related measurements of O_2 or CO. LDS 6 showed stable, hands-off operation in the product line of a chlorine plant measuring the residual water content in pure Cl_2 with a resolution better than 0,3 ppm H_2O. Purging of the sensor heads and their process windows is necessary to get rid of the ambient air in the optical path of the spectrometer and to avoid any contamination on the process windows by the process gas. The analytical performance and availability of the signal turned out to be much better than that of any alternative method. Therefore diode laser set a new benchmark for trace moisture measurements in highly corrosive gases.

Part 3. Oral Session

P-1 Overview of Laser Diodes(FP, QCL, DFB and VCSEL) for Trace gas analysis grown by the University of Montpellier

C. Alibert, J. Angellier, D. Barate, L. Cerutti, j. Commalonga, S. Gaillard, F. Genty, A. Garnache, A. Ouvrard, Y. Rouillard, A. Salhi, E. M. Skouri, R. Teissier, A. Vicet and A Baranov

P-2 Atmospheric nitrogen oxide detection using high finesse cavity absorption spectroscopy

Steven S. Brown, Hans D. Osthoff, William P. Dube and A. R. Ravishankara

P-3 Status and prospects of mid-IR interband cascade lasers

Rui Q. Yang

P-4 Rapid passage induced saturation effects in nitrous oxide and water using a long pulse 8 micron quantum-cascade laser spectrometer

Geoffrey Duxbury, Nigel Langford, Stephen Wright and Michael McCulloch

P-5 Infrared laser spectrometry for atmospheric applications

Virginie Zeninari

P-6 Lead-salt in the stratosphere: application of an airborne TDLS in the global climate monitoring

Piero Mazzinghi

P-7 Quartz-enhanced photoacoustic spectroscopy: shrinking the spectroscopic gas sensor

A. A. Kosterev, F. K. Tittel

P-8 Balloon-borne and airborne TDLS instruments: results from SPIRALE and prospects for SIMCO

C. Camy-Peyret, D. Mondelain and V. Catoire

P-9 Recent progress in IV-VI semiconductor laser research

Patrick J. McCann

P-10 Comparison of CW absorption spectroscopy in the mid-IR spectral range using lead halcogenide and quantum cascade lasers

H. Fischer, Ch. Gurk, R. Kormann

P-11 A new concept for the sensitive in-situ measurement of atmospheric trace gases and stable isotopes based on a sample modulation multipass cell

C. Dyroff 1, A. Zahn1 and P. Werle

P-1

Overview of Laser diodes (FP, QCL, DFB, and VCSEL) for trace gas analysis grown by the University of Montpellier

C. Alibert, J. Angellier, D. Barate, L. Cerutti, J. Commalonga, S. Gaillard, F. Genty,

A. Garnache, A. Ouvard, Y. Rouillard, A. Salhi, E. M. Skouri, R. Teissier, A. Vicet and

A. Baranov

Not available at the date of printing

P-2

Atmospheric nitrogen oxide detection using high finesse cavity absorption spectroscopy

Steven S. Brown, Hans D. Osthoff, William P. Dube and A. R. Ravishankara

NOAA Aeronomy Lab, R/AL2, 325 Broadway,Boulder, CO 80305

and
Cooperative Institute for Research in the Environmental Sciences
University of Colorado, Boulder, CO 80309

High finesse cavity absorption spectroscopy (HFCAS) has become an increasingly important tool for measurements of optical extinction and concentrations of trace compounds in the atmosphere [1]. HFCAS encompasses a wide variety of techniques (e.g. cavity ring-down spectroscopy (CRDS) and cavity enhanced absorption (CEA) / integrated cavity output spectroscopy (ICOS)) and employs a variety of light sources (pulsed lasers, diode lasers and broadband sources). This presentation will briefly overview some of the applications of HFCAS to measurements in the atmosphere and will describe our instruments for visible detection of the nitrogen oxide species, NO_2, NO_3 and N_2O_5. We detect these compounds using pulsed CRDS with a sensitivity of 3×10^{-11} cm^{-1} $Hz^{-1/2}$ in extinction, or about 0.1 pptv in mixing ratio units for the NO_3 radical. These instruments have been deployed at ground sites and on mobile platforms such as towers, ships and aircraft in order to characterize the nocturnal chemistry of nitrogen oxides. Results from these field deployments will be discussed in the context of current instrument performance and anticipated future improvements.

[1] S. S. Brown: Absorption Spectroscopy in High-Finesse Cavities for Atmospheric Studies. Chem. Rev. 103 (2003) 5219-38.

P-3

Status and prospects of mid-IR interband cascade lasers

Rui Q. Yang

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California

Mid-IR type-II interband cascade (IC) lasers take advantage of the broken band-gap alignment in type-II quantum wells to reuse injected electrons in cascade stages for photon generation [1] with high quantum efficiency. Unlike intraband quantum cascade lasers, type-II IC lasers use interband transitions for photon emission without involving fast phonon scattering, making it possible to significantly lower threshold current density. Also, type-II IC lasers can have a wide wavelength tailoring range that is less limited by the conduction-band offset on the short wavelength side. Theoretical calculations [2, 3] projected the feasibility of type-II IC lasers to operate in continuous wave (cw) mode up to room temperature with high output power. Since the proposal of type-II IC lasers in 1994 [1], significant progress has been achieved toward developing high-performance mid-IR IC lasers [4-11]. Some outstanding performance features such as low threshold current densities (e.g. ~8 A/cm^2 at 80 K), high wall-plug efficiency (e.g. ~23% at 80 K), and high temperature operation (e.g. 325 K in pulsed and 230K in cw in 3.2-3.5 microns region) partially verified the advantages of type-II IC lasers. These accomplishments were achieved even though most device fabrication and packaging were in a preliminary stage and still being perfected. For applications in chemical sensing, distributed feedback (DFB) IC lasers [8] have been demonstrated stable single-mode operation in cw mode for the wavelength range from ~3.2 to 3.5 μm. These DFB IC lasers have been employed for the detection of gases [11] such as methane (CH_4), hydrogen chloride (HCl), and formaldehyde (H_2CO) [12]. One IC laser made at JPL was flown on a high-altitude balloon instrument and measured HCl profiles in the stratosphere.

We will review the recent progress of mid-IR IC lasers and address the requirements for further improvements in their performance to meet the needs of practical application.

[1] R. Q. Yang, at *7th Inter. Conf. on Superlattices, Microstructures and Microdevices*, Banff, Canada, Aug. 1994; Superlattices and Microstructures **17**, 77 (1995).

[2] J. R. Meyer, I. Vurgaftman, R. Q. Yang, and L. R. Ram-Mohan, Electronics Letters, **32**, 45 (1996).

[3] I. Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan, IEEE Photo. Tech. Lett. **9**, 170 (1997).

[4] R. Q. Yang, Microelectronics J. **30**, 1043-1056 (1999); and references therein.

[5] R. Q. Yang, *et al*., IEEE J. Quantum Electron. **38**, 559 (2002); and reference therein.

[6] R. Q. Yang, C. J. Hill, B. Yang, J. K. Liu, Appl. Phys. Lett. **15**, 2109 (2003).

[7] C. J. Hill, B. Yang, R. Q. Yang, Physica E **20**, 486 (2004).

[8] R. Q. Yang, *et al*., Appl. Phys. Lett. **84**, 3699 (2004).

[9] J. L. Bradshaw, *et al*., Physica E **20**, 479 (2004).

[10] C. J. Hill, C. M. Wong, B. Yang, R. Q. Yang, Electronics Lett. **40** (2004).

[11] R. Q. Yang, C. J. Hill, L. E. Christensen, C. R. Webster, SPIE Proc. **5624**, 413 (2005).

[12] M. Horstjann, *et al*., Appl. Phys. B **79**, 799 (2004).

P-4

Rapid passage induced saturation effects in nitrous oxide and water using a long pulse 8 micron quantum-cascade laser spectrometer

Geoffrey Duxbury, Nigel Langford, Stephen Wright and Michael McCulloch

Department of Physics, University of Strathclyde,

John Anderson Building, 107 Rottenro, Glasgow G4 0NG

Scotland, UK

The coherent transfer of population between energy levels is of great significance for many optical processes, such as laser cooling. One possible approach is to use the optical analogue [1] of the rapid passage experiments first used in NMR spectroscopy, described in detail by Ernst [2]. In optical rapid passage a time varying electric field is applied to a transition. If the rate of change of the field is greater than the rate at which energy is lost from the system, through decay or collisions, then the population follows the applied field [1,2,3].

We have recently developed a spectrometer whose tuning relies on the rapid sweep of the quantum cascade (QC) laser from high to lower frequency during the current pulse [4]. The laser radiation then passes through a variable path-length (20 - 120 m) astigmatic Herriott cell onto a wide bandwidth infrared detection system. This has enabled the direct observation of rapid passage signals in low-pressure molecular gases. In our system the rate of change of frequency, 100 - 300 MHz/ns, is much greater than the relaxation rate of the low pressure molecular gases under investigation, typically less than 10 MHz, and hence a significant fraction the population in the gas is transferred coherently between energy levels.

We will show examples of the way in which the laser power and the laser sweep rate influence coherent population transfer and hence transient power saturation, and the role of buffer gases such as nitrogen in competing with the coherent driving provided by the laser. The examples of rapid passage will be chosen from the 8 μm spectra of nitrous oxide and water. The unusual rapid passage behaviour of a Dicke narrowed water line, which lies within our tuning range, provides clear evidence for the role of velocity changing collisions in rapid passage processes.

Our calculations of the optical polarisation and of population transfer have been based upon the optical Bloch equations [1,5].These show that the intensity of the laser is sufficient to cause some coherent driving of the transitions, but that the very large degree of coherence, which is inferred from the large rapid passage signals observed in our experiments, requires also the assistance of self-focussing [6]. We also demonstrate the influence of the inhomogeneously (Doppler) broadened line on the form of the rapid passage signals.

References

[1] J. C. McGurk, T. G. Schmalz and W. H. Flygare, *J. Chem. Phys*., **60**, 4181 (1974).

[2] R. R. Ernst, *Advances in* Magnetic *Resonance*, **2**, p1 (1966).

[3] M. M. T. Loy, *Phys. Rev.* Lett. **32**, 814 (1974).

[4] M. T. McCulloch, E. L. Normand, G. Duxbury and N. Langford, *JOSA* **B** 8, 1761 (2003).

[5] R. H. Lehmberg and J. Reintjes, *Phy. Rev*. **A** 12 2574 (1975).

[6] D. Grischowsky, *Phys. Rev. Lett*, **24** 866- 869(1970).

P-5

Infrared laser spectrometry for atmospheric applications

Virginie Zéninari

Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 6089,

UFR Sciences Exactes et Naturelles, Moulin de la Housse, BP 1039,

51687 Reims, Cedex 2, FRANCE

Tel. +33.3.2691.8788 Fax. +33.3.2691.3147 Email: virginie.zeninari@univ-reims.fr

Since 1997 the Service d'Aéronomie of the CNRS-France has developed the SDLA spectrometer (Spectrométre _ Diodes Lasers Accordables), a balloon-borne spectrometer for the in situ monitoring of H_2O, CH_4 and CO_2 in the upper troposphere and the lower stratosphere [1]. The laser diodes emit respectively near 1.39 μm, 1.65 μm and 1.60 μm. To reach the scientific objectives, an accuracy better than 5 % is required in the concentration retrieval. Hence, a precise knowledge of the molecular parameters is of high importance.

The GSMA has developed a near infrared diode laser spectrometer for the laboratory study of H_2O line parameters near 1.39 μm. The spectral region ranging from 7165 to 7186 cm^{-1} which is of interest for the in situ monitoring of H_2O was studied. 23 transitions of $\nu_1+\nu_3$ and $2\nu_1$ bands have been studied [2]. The results of intensity measurements were used for the retrieval of H_2O concentration in the middle atmosphere from SDLA. Four of these lines with increasing line strengths were used to match the strong decrease in water vapor concentration with altitude. These intensity measurements have been completed by the measurements of N_2 and O_2 broadening coefficients for the 4 transitions. We demonstrate that the new set of parameters (intensity and air-broadening coefficients) drastically improves the atmospheric retrieval of H_2O [3].

A near infrared diode laser spectrometer was used in the laboratory to study CO_2 line intensities and pressure broadening coefficients near 1.60 μm. The spectral region ranging from 6230 to 6250 cm^{-1} was studied using a commercial telecommunication type diode laser. Thirteen lines of the $(30^01)_{III} \leftarrow (000)$ band of CO_2 have been studied [4]. The results of intensity measurements are compared to previous determinations and available databases. These results were used for the retrieval of CO_2 concentration in the middle atmosphere from SDLA [5].

[1] Durry G., Hauchecorne A., Ovarlez J., Ovarlez H., Pouchet I., Zéninari V., Parvitte B., Journal of Atmospheric Chemistry, 43, 175-194, (2002)

[2] Parvitte B., Zéninari V., Pouchet I. and Durry G., J. Quant. Spectros. Radiat. Transfer, 75, 493-507, (2002)

[3] Durry G., Zéninari V., Parvitte B., Le Barbu T., Lef_vre F., Ovarlez J., Gamache R.R., Journal of Quantitative Spectroscopy and Radiative Transfer, in press (2005)

[4] Pouchet I., Zéninari V., Parvitte B., Durry G., J. Quant. Spectros. Radiat. Transfer, 83, 619-628, (2004)

[5] Durry G., Amarouche N., Zéninari V., Parvitte B., Le Barbu T., Ovarlez J., Spectrochimica Acta Part A, 60, 3371-3379, (2004)

P-6

Lead-salt in the stratosphere: application of an airborne TDLS in the global climate monitoring

Piero Mazzinghi

Istituto Nazionale di Ottica Applicata, Largo Enrico Fermi 6

50125 Firenze, Italia

mazzinghi@inoa.it

This paper describes the development and operation of a tunable diode laser absorption spectrometer for the measurement of trace gases in the atmosphere or the chemical composition of the evaporated particles in the clouds. This system was successfully employed onboard the stratospheric aircraft Myasishchev M55 "Geophysica" during several measurement campaigns, from the tropics to the arctic. During flights the system operates unattended for several hours under huge changes of ambient conditions: the pressure is ranging from 1000 down to 30 mbar, while ambient temperature was found from +70°C to –90°C, in presence of strong mechanical vibrations. Typical flight measurements are performed at altitudes between 10 to 22 km and at an aircraft speed of 160 to 190 m/s.

The instrument is based on lead-salt single mode diodes, selected according to the application and gas to be investigated in the particular application. Laser diodes and the main detector are installed in a liquid nitrogen cooled dewar with a pressure control system to allow stable operation at any altitude. The multipass cell is a commercial astigmatic Herriott cell, modified to improve its mechanical stability, with an absorption path of 36 m with 182 passes between a pair of quasi-confocal, toroidal mirrors at a distance of 20 cm. The low cell volume (0.2 l) allows a short gas residence time (about 5 s) even with the limited gas flow provided by the particle analysis inlet.

Detection is based on a direct absorption scheme with fast acquisition and extended averaging over a sample period of a few s. At a scan repetition frequency of 2 kHz the software averages 5000 scans and stores the averaged waveform in the computer memory. This was found the most robust and reliable system for an instrument that must operate unattended for several hours in hostile environmental conditions. The direct absorption acquisition followed by off-line processing with lineshape fitting permits retrieval of a reliable measurement even in case of partial malfunctioning, as misalignment, laser instability or the optical noise due to interference fringes, induced by the extremely varying environmental conditions. The ultimate detection limit in absorption, reaching 10^{-5} in the laboratory and $2x10^{-4}$ in flight conditions, was found limited by the above-mentioned factors, and not by the detection scheme. The total uncertainty in the mixing ratio is about 5 %, depending on the investigated species. Usually, it is limited by the knowledge of the sample thermodynamic condition more than by the error in the number density retrieved from the absorption measurement. Measurements of H_2O and HNO_3 in cloud particles and of N_2O and CO in gas phase obtained during the measurement campaign will be also briefly discussed.

P-7

Quartz-enhanced photoacoustic spectroscopy: shrinking the spectroscopic gas sensor

***A. A. Kosterev*, F. K. Tittel**

Rice University, Laser Science Group

6100 Main St., Houston, TX 77005, USA

akoster@rice.edu

Latest progress in quantum electronics resulted in availability of compact and powerful tunable laser sources both in the near-IR and mid-IR regions. In order to take full advantage of these devices for chemical sensing applications, an equally compact absorption detection module (ADM) is required. Photoacoustic spectroscopy (PAS) based on the detection of sound generated in the media upon absorption of modulated optical radiation allows low detection limits to be reached with a small sample volume, typically starting from ~10 cm^3. However, PAS performance can be strongly degraded by ambient acoustic noise which prevents its widespread use in the design of portable gas sensors.

A novel variation of PAS called Quartz-Enhanced PAS, or QEPAS [1], allows to overcome this drawback with an additional advantage of dramatically reduced sample volume. This technique is based on a quartz tuning fork (TF) used as a resonant acoustic transducer. The TFs are designed to be used as frequency standards in electronic clocks, resonating at f~32 768 (2^{15}) Hz. QEPAS makes use of the extremely high Q-factor of these quartz vibrators, which allows the signal build-up during (1-3)_10^4 modulation periods. The largest dimension of a TF is typically <5mm, thus matching the size of a semiconductor laser source.

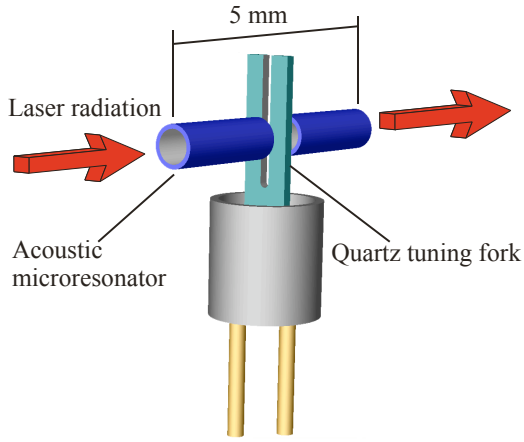


Fig. 1. QEPAS ADM.

A configuration of the QEPAS based ADM in shown in Fig. 1. Acoustic microresonator consisting of two glass tubes with a combined length equal to a half sound wavelength at 32.76 kHz is added to the TF for sensitivity enhancement.

Trace gas sensing experiments based on QEPAS were performed for a number of species both in near-IR and in mid-IR spectral regions [2]. Normalized QEPAS sensitivity achieved to date in NH_3 detection experiments is 5.4_10^{-9} $cm^{-1}W/\sqrt{Hz}$, which is comparable to or better then the sensitivity reported for conventional PAS-based ammonia sensors.

References

[1] A. A. Kosterev, Yu. A. Bakhirkin, R. F. Curl, and F. K. Tittel, *Optics Letters* **27**, 1902–1904 (2002).

[2] A. A. Kosterev, F. K. Tittel, D. Serebryakov, A. Malinovsky, and I. Morozov, to be published in *Rev. Sci. Instr.*, April 2005.

P-8

Balloon-borne and airborne TDLS instruments: results from SPIRALE and prospects for SIMCO

C. Camy-Peyret[(1)], D. Mondelain[(1)] and V. Catoire[(2)]

[(1)] LPMAA, Laboratoire de Physique Moléculaire pour l'Atmosphère et l'Astrophysique,

Paris, France

[(2)] LPCE, Laboratoire de Physique et Chimie de l'Environnement,

Orléans, France

Mid-infrared lead-salt diode laser sources are powerful tools for *in situ* measurements of trace species in the atmosphere. Two French tunable diode laser spectrometers (TDLS) which can operate in harsh balloon or aircraft environments are briefly described.

SPIRALE (SPectroscopie InfraRouge par Absorption de Lasers Embarqués) is a balloon-borne stratospheric instrument with an open multiple pass absorption cell, which has been developed by LPCE at Orléans and has already been flown on 3 occasions under stratospheric balloon. Sample results for performances obtained for O_3, CO, CH_4, NO_2 and HNO_3 will be presented.

Another experiment under development at LPMAA for operation onboard tropospheric aircraft is the instrument SIMCO (Spectrometer for Isotopic Measurements of CO_2), which is also based on a mid-infrared lead-salt diode TDLS instrument to measure with high accuracy (hopefully better than 0.5 %) the abundances of $^{12}CO_2$ and $^{13}CO_2$ as well as the $\delta^{13}C$ in carbon dioxide. A status of the project will be presented together with preliminary test results obtained in the laboratory.

P-9

Recent progress in IV-VI semiconductor laser research

Patrick J. McCann

School of Electrical and Computer Engineering

University of Oklahoma

Norman, OK 73019

Narrow bandgap IV-VI semiconductors (also known as lead-salts) are proven materials for fabrication of widely-tunable mid-IR lasers. A number of groups continue to perform research in the IV-VI semiconductor area, and recent results indicate that significant improvements in IV-VI mid-IR laser performance should be possible when new materials and processing methods are fully developed. Experimental and theoretical analysis of (111)-oriented PbSe/PbSrSe multiple quantum well (MQW) materials, for example, indicates that such structures offer attractive features for fabrication of low threshold lasers. L-valley degeneracy removal, which occurs in (111)-oriented QWs [1], can result in electrophonon resonance effects that reduce population inversion thresholds by beneficially affecting electron lifetimes in both the upper and lower lasing states. Such QW designs, which have yet to be fully explored in fabrication of IV-VI mid-IR lasers, are similar to those recently used in the fabrication of quantum cascade lasers. Improving active region heat dissipation is another area of active research. Past theoretical work has shown that sandwiching the epitaxially-grown laser structure between two copper heat sinks can increase IV-VI laser continuous wave (cw) operating temperatures into the thermoelectrically-cooled range. Recent experimental work has now provided the first experimental confirmation of improved active region heat dissipation when the growth substrate is removed and the epitaxial layer is bonded to higher thermal conductivity copper [2]. This presentation will show that it should be possible to develop a substrate-removal laser packaging technology using (111)-oriented MQW materials for fabrication of in-plane cleaved cavity lasers, and that when fully developed this new technology will enable fabrication of IV-VI mid-IR lasers with near-room-temperature cw operation.

[1] I. I. Zasavitskii, E. A. de Andrada e Silva, E. Abramof, and P. J. McCann, "Optical Deformation Potentials for PbSe and PbTe", *Physical Review B* **70**, 115302 (2004).

[2] Y. F. Li, P. J. McCann, A. Sow, C. Yao, and P. C. Kamat, “Improvement of Heat Dissipation Through Transfer of IV-VI Epilayers From Silicon to Copper”, *IEEE Photonics Technology Letters* **16**, 2433 (2004).

Support from the National Science Foundation (grant numbers DMR-9802396, DMR-0080054, and EPS-0132354) and the Oklahoma Center for the Advancement of Science and Technology (grant numbers AR021-043 and AR03-057) is gratefully acknowledged.

P-10

Comparison of CW absorption spectroscopy in the mid-IR spectral range using lead chalcogenide and quantum cascade lasers

H. Fischer, Ch. Gurk, R. Kormann

Max Planck Institute for Chemistry

Airchemistry Division

POB 3060, 55020 Mainz, Germany

hofi@mpch-mainz.mpg.de

We present results of laboratory and aircraft based comparisons of mid-infrared absorption spectroscopy using either lead chalcogenide tunable diode lasers (TDL) or quantum cascade lasers (QCL). The different lasers were operated in identical spectrometers, both in continuous wave mode, which required cryogenic cooling of the devices. First results have been obtained for CO in the 2150 cm^{-1} band. A TDL and QCL were simultaneously operated in a two laser spectrometer in the laboratory. Both lasers were tuned to probe the P(25) line of CO at 2037.025 cm^{-1}, which is about a factor 100 weaker than the strongest CO lines within this band. Overall the performance of the QCL was better by a factor 2-3 with respect to the measurement precision. This is mainly due to an overall lower noise level and much reduced laser drifts of the QCL. Similar results were obtained in the field. Airborne measurements of CO in 2003 using a TDL (R(5) line at 2165.6 cm^{-1}) and 2004 using a QCL (R(3) line at 2158.3 cm^{-1}) deployed in the single channel instrument QUALITAS, confirmed the superiority of the QCL, resulting in an improved measurement precision of the order of a factor of 2. Recently we started investigating the use of QCLs for trace gases at the sub-ppbv level. In June 2005 the three channel instrument TRISTAR, equipped with 3 QCLs for the simultaneous detection of CO, HCHO and H_2O_2, will be deployed on a jet aircraft to probe the upper troposphere/lower stratosphere. First results from this campaign will be presented at the conference.

P-11

A new concept for the sensitive in-situ measurement of atmospheric trace gases and stable isotopes based on a sample modulation multipass cell

C. Dyroff [1], ***A. Zahn*** [1] ***and P. Werle*** [1,2]

[1] *Institute for Meteorology and Climate Research, Research Center Karlsruhe, Germany*

[2] *National Institute for Applied Optics, Largo E. Fermi, 6, Florence, Italy*

Diode-laser absorption spectroscopy is an established technique among analytical methods for trace gas analysis and meanwhile finds increasingly applications in industrial gas analysis and environmental sciences [1]. A key issue in ecosystem research and atmospheric studies being conducted today is the ability to quantify small concentrations of trace gases [2]. Especially the in-situ measurement of stable isotope ratios of stable molecular species (isotopomers) is still a measurement challenge [3]. In order to meet requirements for environmental research, means have to be found to cope with the present limitations of spectroscopic systems. The implementation of a sample modulation, here based on the Stark effect in molecular spectra, within an optical multi-pass cell is a promising scheme to increase the stability of spectroscopic instrumentation required for ecosystem research and airborne atmospheric platforms. In this paper we describe this approach to reduce the influence of time dependent, unwanted background structures generally superimposed to the desired signal from the spectral feature under investigation and discuss the application of this technique to the measurement of trace gases (HCHO) and water isotopes (HDO).

[1] Werle, P., Diode-laser sensors for in-situ gas analysis, in: Lasers in Environmental and Life Sciences – Modern Analytical Methods. (Eds. P. Hering, P. Lay, S. Stry), Springer: Heidelberg 2004; Chapter 11, p. 223-243 and references therein.

[2] Fried, A., S. Sewell, B. Henry, B. P. Wert, T. Gilpin, and J. R. Drummond, Tunable diode laser absorption spectrometer for ground-based measurements of formaldehyde, J. Geophys. Res., 102, 6253-6266, 1997.

[3] Kerstel, E., Isotope ratio Infrared spectrometry (2004) in: In Handbook of stable isotope analytical techniques (Ed. Pierre A. de Groot.), Elsevier 2004; Chapter 34, p. 759-787 and references therein.

Part 4. Poster presentations

Poster Session A

A-1 Spectroscopic tests of a 2.3 μm TDL

A. R .W. McKellar

A-2 Puff by puff and total acrolein and 1,3-butadiene deliveries for 1R5F and three prototype carbon filter cigarettes using lead-salt tunable diode laser infrared spectroscopy

W. David Thweatt, Charles N. Harward, Sr., Milton E. Parrish

A-3 Simultaneous measurement of $^{12}CO_2$, $^{13}CO_2$ and $^{12}C^{18}O^{16}O$ with a NIR fiber-coupled DFB diode laser spectrometer

Steffen Lau, Rainer Engelbrecht, Katharina Salffner, Hans-Gerd Loehmannsroeben

A-4 Remote sensing of atmospheric carbon dioxide and methane using tunable diode lasers, fiber amplifiers and photon counting detectors

Michael A. Krainak, James Abshire, Graham Allan, John Burris, G. James Collatz, Amelia Gates, Randy Kawa, Haris Riris, Xiaoli Sun

A-5 CW-TDLS-LADAR concept for range-resolved open-path detection of atmospheric constituents

Ravil R. Agishev

A-6 Investigation into tunable diode laser spectroscopy for use in harsh industrial environments

K. Duffin, A. J. McGettrick, W. Johnstone, G. Stewart and D. Moodie

A-7 Small tunable diode-laser & fibre-amp based lidar for remote sensing from orbit of water vapour, cloud & aerosol profiles

Graham Allan, Michael A. Krainak, James Abshire and Amelia Gates

A-8 Simultaneous frequency stabilization of four laser diodes in the 935-nm water vapour spectrum for space application

S. Schilt, D. Werner, L. Thévenaz, R. Matthey, C. Affolderbach, G. Mileti

A-9 Gas analysis based on high speed thermal tuning of VCSEL lasers

M. Braun, S. Hartwig, J. Wöllenstein, J. Nurnus, H. Böttner, A. Lambrecht F. Volkert, A. Schubert

A-10 Quantum physics and TDLS fundamental noises

A. Nadezhdinskii

A-11 Diode laser temperature stabilization at 3_10^{-5} K level

A. Nadezhdinskii

A-12 Below 10^{-7} absorption sensitivity limited by diode laser quantum noise

A. Nadezhdinskii

A-13 Detection of trace amounts of water in ammonia by means of TDLS technique

A. Berezin, S. Malyugin, A. Nadezhdinskii, D. Namestnikov, Ya. Ponurovskii, D. Stavrovskii, Yu. Shapovalov, I. Vyazov, N. Grishnova, A. Kotkov, V. Sidorov

A-14 Measurements of the ^{13}__$_2$/$^{12}CO_2$ isotope composition using the TDLS technique

A. Berezin, S. Chernin, A. Makkaveiskii, A. Nadezhdinskii, Ya. Ponurovskii, D. Stavrovskii, Yu. Shapovalov, A. Babichev, G. Grigoriev, S. Malyugin, Sh. Nabiev

A-15 External-cavity VCSEL emitting in the 2–2.5 µm range applied to high-sensitivity intracavity laser absorption spectroscopy

A. Garnache, L. Cerutti, P. Grech, F. Genty, A. Campargue

A-16 Combining pre-concentration of air samples with cavity ring down spectroscopy

Ruth E. Lindley, Alistair M. Parkes and Andrew J. Orr-Ewing

A-17 Characterization of a 10.3-m pulsed DFB quantum cascade laser

Alexandre Lytkine, John Tulip, Wolfgang Jaeger, and Jagadeeshwari Manne

A-18 Compact tunable mid-IR spectrometer for ultra sensitive formaldehyde measurements

Petter Weibring, Dirk Richter, Alan Fried, and Jim Walega

A-19 Spectral measurement of the cesium D_2 line with a tunable heterodyne interferometer

L. Spani Molella, R.-H. Rinkleff, K. Danmann

A-20 Study of methane fluxes through Baikal lake surface using diode laser techniques

V. A. Kapitanov, I. S. Tyryshkin, N. P. Krivolutskii, Yu. N. Ponomarev

A-21 Diode laser spectroscopy of $^{13}CO_2$ and $^{16}O^{12}C^{18}O$ in the 2 µm region

B. Parvitte, V. Zéninari, T. Le Barbu, D. Courtois, G. Durry

A-22 Diode laser absorption spectrometry refined – from optical saturation and optical pumping phenomena in conventional and wavelength modulated absorption spectrometry to ultra-sensitive detection of ammonia by NICE-OHMS

Florian Schmidt, Aleksandra Foltynowicz and Ove Axner

A-23 Spectroscopic remote sensing instrument for orbital atmospheric pressure and temperature measurement

Mark Stephen, Michael Krainak, Michael Hayden

A-24 Exact calculation of beam propagation in Chernin matrix multipass optical cell

A. Berezin, S. Chernin

A-25 Characteristics of several NIR tuneable diode lasers for spectroscopic based gas sensing: a comparison

David McInerney, John Donegan, Michael Lynch, Vincent Weldon, T. Farrel, M. Todd, D. McDonald

A-26 Diode Laser System for Precision Spectroscopy of Atomic Hydrogen

J. Alnis, N. Kolachevsky, M. Fischer, Th. Udem, T.W. Hänsch

A-1

Spectroscopic tests of a 2.3 μm TDL

A. R. W. McKellar

Steacie Institute for Molecular Sciences,

National Research Council of Canada,

Ottawa, Ontario K1A 0R6, Canada

robert.mckellar@nrc-cnrc.gc.ca

For a time in 2001, relatively low-cost room-temperature InP or GaSb Fabry-Perot diode lasers were commercially available for certain wavelength ranges between 1.8 and 2.4 μm from Laser Components GmbH. We evaluated one such laser as a way to extend the range covered by mid-infrared Pb-salt diode lasers, which are typically available from 3 to 30 μm. Our laser (Model FNIR-2344-GMP) came mounted in a TO3 case. In order to use it in a usual Pb-salt laser source dewar (e.g. Laser Components L5736), it was first necessary to construct a mounting adaptor. The laser could then be used with the same current source (L5830), collection optics (L5120), monochromator (L5110), calibration etalon (5 cm solid Ge), and detectors (InSb) normally used for our Pb-salt lasers in the 4-5 μm range. The output power was huge (>5 mW) by Pb-salt standards. By varying the temperature from 200 to 315 K it was possible to obtain wavelengths from 2.25 to 2.41 μm (4150 - 4450 cm-1). Like a Pb-salt laser, the new source could be rapidly tuned with a current ramp, enabling direct observation of absorption spectra on an oscilloscope. Compared to Pb-salt lasers, the tuning was 'backwards': higher temperature and/or current gave lower wavenumbers. Current and temperature generally had similar effects on laser output – in other words, the coverage of existing modes could not be extended much by playing with I and T.

From the description so far, the new laser seems to be ideal for sensitive IR laser spectroscopy around 2.3 μm. Unfortunately, however, there were significant problems involving instability, multi-moding, and extreme sensitivity to optical feedback. Such problems also affect many Pb-salt lasers, but they were much worse for this 2.3 μm laser. Regions of 'good' tuning behavior were very limited. Overall, the new laser showed promise as a source for high resolution spectroscopy, but was not really usable unless a good mode luckily occurred in just the right place. Interesting questions remain: Would different samples be similar, or would they show large variations in spectroscopic suitability, as with Pb-salt diodes? Could some of the abundant output power be sacrificed to obtain more civilized tuning behavior, perhaps simply by coating the end face(s) to control reflectivity? When will similar devices again become commercially available?

A-2

Puff by puff and total acrolein and 1,3-butadiene deliveries for 1R5F and three prototype carbon filter cigarettes using lead-salt tunable diode laser infrared spectroscopy

W. David Thweatt [1], Charles N. Harward, Sr. [2], Milton E. Parrish [3*]

[1] Philip Morris USA Postgraduate Research Program, 4201 Commerce Road,

Richmond, VA 23234 USA

[2] Nottoway Scientific Consulting Corp., P.O. Box 125, Nottoway, VA 23955 USA

[3] Philip Morris USA Research Center, 4201 Commerce Road, Richmond, VA 23234 USA

[*] contact: milton.e.parrish@pmusa.com

Acrolein and 1,3-butadiene in cigarette smoke generally are measured using a carbonyl derivative HPLC method and a volatile organic compound (VOC) GC/MS method, respectively. However, for evaluating prototype cigarettes having filters containing carbon materials designed to reduce the deliveries of these constituents, an analytical technique having better sensitivity and real-time per puff measurement is required. This poster describes such a technique using two lead-salt tunable diode lasers (TDLs) for the simultaneous measurement in each puff of whole cigarette smoke in real time [1]. The acrolein was monitored with one TDL operating at 958.8 cm^{-1} while the 1,3-butadiene used the other TDL operating at 891.0 cm^{-1}. The dual TDL system uses a 3.3 L volume, 100 m Herriott multi-pass gas cell. Quantitation is based on the best spectral fit using molecular parameters previously determined, including infrared absorption line positions, line strengths and nitrogen-broadened half-widths for these species [2,3].

The puff-by-puff deliveries of ethylene and propylene also are determined because their absorption lines overlap the spectra of 1,3-butadiene and acrolein and these overlapping lines must be taken into account by the fit. The acrolein and 1,3-butadiene total cigarette deliveries for the 1R5F Kentucky Reference cigarette were in agreement with the HPLC and GC/MS methods, respectively. The limit of detection (LOD) for 1,3-butadiene and acrolein is less than 50 ng/puff which is adequate to determine at which puff 1,3-butadiene and/or acrolein breaks through the carbon filter for different prototype cigarettes. Breakthrough can occur on different puffs for the two primary smoke constituents of interest depending upon the cigarette design and characteristics of the carbon filter.

References

[1] S. Plunkett, M. Parrish, K. Shafer, D. Nelson, J. B. McManus, J. L. Jimenez, M. Zahniser, SPIE Proc., 3758, 212 (1999).

[2] C. N. Harward Sr., R. E. Baren, M. E. Parrish, Spectrochimica Acta Part A, 60, 3421-3429 (2004).

[3] C. N. Harward Sr., W. D. Thweatt, M. E. Parrish, "Determination of molecular parameters for molecules with overlapping infrared spectra using infrared tunable diode laser spectroscopy", poster presenting at 5th International Conference on Tunable Diode Laser Spectroscopy, Florence, Italy, July 11-15, 2005.

A-3

Simultaneous measurement of $^{12}CO_2$, $^{13}CO_2$ and $^{12}C^{18}O^{16}O$ with a NIR fiber-coupled DFB diode laser spectrometer

Steffen Lau [a], Rainer Engelbrecht [b], Katharina Salffner [a], Hans-Gerd Loehmannsroeben [a]

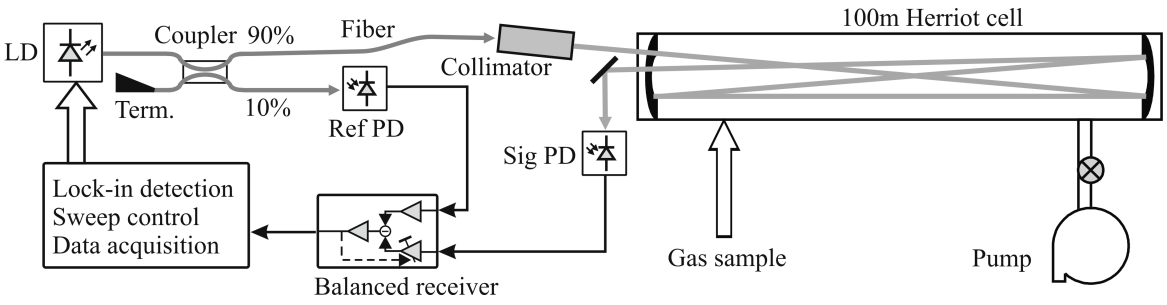
[a] *Institute of Chemistry, Physical Chemistry, University Potsdam, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam-Golm, Germany.*

[b] *Chair for Microwave Engineering (LHFT), University of Erlangen-Nuremberg, Cauerstr. 9, D-91058 Erlangen, Germany.*

Measurement of the isotopic ratios of carbon dioxide is of great interest in many environmental, medical and industrial areas like soil gas fluxes, breath gas analysis and process gas monitoring. Near-infrared (NIR) absorption spectroscopy with tunable diode lasers allows for the simultaneous detection of the three most important isotopologues of carbon dioxide ($^{12}CO_2$, $^{13}CO_2$, $^{12}C^{18}O^{16}O$). A compact and flexible fiber-optic diode laser spectrometer for isotopic sensing of CO_2 with high isotopic resolution and no interference by water vapour will be presented. In the regime of the $(30^01)_{III} \leftarrow (000)$ band of $^{12}CO_2$ around 1605 nm, the following lines are used with data from the HITRAN database:

Isotopologue	Frequency / cm^{-1}	S / cm^{-1} cm^2 $molec^{-1}$	Line
$^{12}CO_2$	6228.690	1.716×10^{-24}	R (0)
$^{13}CO_2$	6228.436	2.002×10^{-25}	P (16)
$^{12}C^{18}O^{16}O$	6228.202	1.007×10^{-26}	P (32)

A fiber-coupled DFB diode laser spectrometer with 2f WMS detection and balanced reference subtraction as described in [1] is used. Within a single frequency sweep by modulating the diode current, these three CO_2 isotopologue lines can be measured simultaneously. The collimated laser beam is fed into a Herriot-type multi-pass-cell (MPC1000S; Scienca Industira Tecnologia, Florence, Italy) with a tube length of 1.12 m, a volume of 8.25 l and a total light path of 100.9 m [2]. Gas mixtures with different CO_2 concentrations (CO_2/N_2) were filled in the multi-pass-cell with a total pressure of 60 mbar. The overall experimental precision is evaluated from complete fill-measurement-evacuation-refill cycles. Preliminary results indicate a detection limit smaller than ± 1 ‰ for $^{12}CO_2$ / $^{13}CO_2$ ratios in 0.1 % total carbon dioxide mixtures. Data for $^{12}C^{16}O_2$ / $^{12}C^{18}O^{16}O$ ratios has still to be evaluated.



[1] R. Engelbrecht, "A compact NIR fiber-optic diode laser spectrometer for CO and CO_2: analysis of observed 2f wavelength modulation spectroscopy line shapes", *Spec. Chim. Acta A* **60**, 3291-3298, (2004).

[2] G. Hoerner, S. Lau, Z. Kantor, H.-G. Loehmannsroeben, "Isotope Selective Analysis of CO_2 with Tuneable Diode Laser (TDL) Spectroscopy in the NIR", *Analyst* **129**, 772-778, (2004).

A-4

Remote sensing of atmospheric carbon dioxide and methane using tunable diode lasers, fiber amplifiers and photon counting detectors

Michael A. Krainak, James Abshire, Graham Allan, John Burris, G. James Collatz,

Amelia Gates, Randy Kawa, Haris Riris, Xiaoli Sun

NASA Goddard Space Flight Center

Greenbelt, MD USA 20771

Michael.A.Krainak@nasa.gov

Atmospheric carbon dioxide (CO_2) and methane (CH_4) are at their highest levels of the last 200,000 years [1]. Furthermore, both of these "greenhouse" gases have experienced a dramatic increase in the last 100 years. However global measurements are still difficult with fewer than 100 sites in the present global network of in-situ near-surface atmospheric CO_2 sampling sites and about half that for CH_4. In addition, significant uncertainties persist in the nature and magnitude of major sources and sinks of CO_2 and CH_4. Measurements of total column CO_2 and CH_4 from space can overcome the problems of sparse global sampling and high variability over land. Indeed, NASA recently initiated global methane measurements using the Tropospheric Emission Spectrometer (TES) instrument on AURA (http://aura.gsfc.nasa.gov/). The Orbiting Carbon Observatory (http://oco.jpl.nasa.gov/) will make global carbon dioxide measurements after its launch in 2007.

In this paper, we describe prototype laser-based active remote sensing instruments for precise measurement of atmospheric CO_2 and CH_4. In the near term, we hope to validate these instruments at a NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) tall-tower site then use them for calibration and validation of missions like AURA and OCO. In the future, we plan laser-based orbital instruments for high-precision day-night global measurements. These instruments share a general technology approach that includes tunable-diode-laser master oscillators, high-power fiber-optic amplifiers and photon-counting-detector based receivers.

Our prototype laser sounder for measuring atmospheric CO2 near the 1572 nm wavelength uses a tunable external cavity (or DFB laser diodes), an erbium fiber amplifier and InGaAs photocathode photomultiplier. We present data demonstrating close agreement between our prototype laser sounder instrument and the industry standard Licor instrument by measuring the CO2 diurnal cycle over a 206-meter open path. We present measurements of atmospheric methane with a similar instrument near 1640 nm wavelength. In addition, we present progress and developments of the erbium fiber amplifier, Raman fiber amplifier and InGaAs avalanche photodiode photon-counting detector technologies as well as gas detection algorithms.

References

[1] J. R. Petit et al., Nature, 399 (6735), 1999

A-5

CW-TDLS-LADAR concept for range-resolved open-path detection of atmospheric constituents

Ravil R. Agishev

Kazan State Technical University, 10, K. Marx St., Kazan 420111, Russia

ravil_agishev@mail.ru

Potential capabilities of continuous-wave (CW) frequency-modulated (FM) remote monitoring technique based on NIR-CW-FM room temperature diode lasers (DL) using spectroscopic modulation techniques to perform spatially-resolved measurements of trace-gas concentration over open paths with high constituent selectivity are discussed.

The use of pulsed lidar/ladar techniques for open-path range-resolved trace gas concentration measurements is already well established. An alternative approach we use is based on an energy equivalence principle whereby the high peak power, short-pulse duration and low duty-cycle of pulsed system is replaced with CW operation having low peak power over long observation periods, but with equivalent average powers.

The novel technique is in contrast to commonly used diode laser gas sensors based on WM/FM spectroscopy techniques that modulate the laser frequency by a sinusoidal signal. WMS and FMS provide real-time measurement of a wide variety of gaseous species with high sensitivity and fast time response, but do not have ranging capabilities.

The conceptual outline for a spectroscopic CW-TDL-based FM-ladar for atmospheric pollution monitoring is shown in Fig.1. It combines features of conventional methods of modulation spectroscopy and existing methods of remote sensing, together with modern techniques of optical signal transmission, reception/detection and processing.

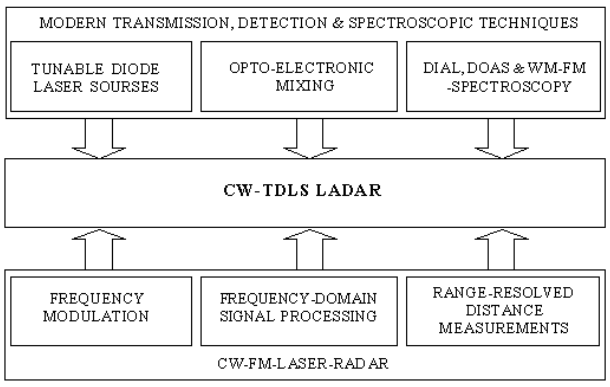


Fig. 1. CW-TDLS LADAR concept.

The approach is based on the advantages of remote monitoring techniques, such as lidar/ladar, differential absorption optical spectroscopy (DAOS) and differential absorption lidar (DIAL) with those of wavelength and frequency modulation spectroscopy. To probe the absorption profile in an open path configuration, the spectroscopic CW-FM-ladar uses aerosol backscattering.

The interaction between the optical carrier and an absorption line of the target species then converts the frequency modulation of the optical carrier into an intensity modulation of the received echo-signal. For range information, the optical carrier is frequency-modulated by a subcarrier that is, in turn, linearly frequency-modulated so the beat frequency spectrum corresponds to a range profile.

Main features, potential capabilities and applications of the novel approach for trace gas constituents detection are discussed.

A-6

Investigation into tunable diode laser spectroscopy for use in harsh industrial environments

K. Duffin [1], A. J. McGettrick [1], W. Johnstone [1], G. Stewart [1] and D. Moodie [2]

[1] The Centre for Microsystems and Photonics, The University of Strathclyde, 204 George Street, Glasgow, UK, G1 1XW

[2] OptoSci Ltd, The University of Strathclyde Incubator, 141 St James Road, Glasgow, UK, G4 0LT

Tunable diode laser spectroscopy (TDLS), using either direct or wavelength modulation detection schemes, is a well-established technique to extract gas concentration data from the overtone vibrational / rotational absorption bands in the near-infrared. At constant and known temperature and pressure, accurate measurements are made by calibration to a gas of known concentration. More recently, interest has grown in the application of TDLS over optical fibre to gas measurements in harsh industrial environments where the temperature and pressure may be varying and unknown. Both temperature and pressure influence the profile / width of the gas absorption lines and may compromise the measurement of concentration if they are unknown, particularly in cases where wavelength modulation schemes are being used. In this presentation, we report our recent investigations into the development of robust calibration algorithms to enable accurate measurements of concentration under conditions of varying / unknown pressure or temperature. In cases involving wavelength modulation spectroscopy, this implies development of techniques for the accurate recovery of the gas line transmission functions from the first derivative / harmonic signals. Experimental results and their analysis are presented for acetylene, carbon dioxide and methane in the pressure range 0.2 to 2.0 atmospheres.

A-7

Small tunable diode-laser & fibre-amp based lidar for remote sensing from orbit of water vapour, cloud & aerosol profiles

Graham Allan, Michael A. Krainak, James Abshire and Amelia Gates

NASA Goddard Space Flight Center, Greenbelt, MD USA 20771

graham.allan@gsfc.nasa.gov

The atmosphere of Mars is surprisingly dynamic, with a highly variable water vapour distribution and an unusual amount of atmospheric dust and clouds [1]. The dynamics, and forcing functions, particularly for global processes involving water vapour, aerosol, ice distributions, and the planetary boundary layer (PBL) remain largely hypothesis [2]. To fully understand these processes requires global observations with a high temporal and spatial resolution which can only realistically be obtained from an orbiting Lidar.

We are conducting the critical R&D for a small, orbital, atmospheric lidar to measure water vapour and aerosol distributions from Mars orbit during day and night, with much higher vertical and spatial resolution than those to date or planned. The optical source will be a Master Oscillator Power Amplifier (MOPA) design using a tuneable diode-laser and Nd-doped fibre amplifiers (NDFA) coupled with narow-linewidth single photon counting detectors operating in the 935 nm. This combination of technology enables Differential Absorption Lidar (DIAL) to be practical for planetary missions for the first time.

Significant work has gone into developing a breadboard instrument, identifying candidate water vapour lines to provide high sensitivity to changes in H_2O amount, but are not as strong as to be saturated in the "wetter" spring conditions on Mars (~70ppt.µm water). Absorption spectroscopy measurements are presented for both low-pressure, (Doppler broadened) and high pressure (collisional broadened) regimes. The current approach is to sweep a tuneable narrow-linewidth laser-diode's output frequency across the absorption feature of interest and derive the salient parameters from a real-time fit to the absorption profile. The same tuneable diode-laser and detectors are used to monitor transmission from three systems, a low-pressure 10 m optical cell, a 5 m open-path in a controlled environment and a 0.4 Km open-path test range.

We will present data on a sounder capable of remotely measuring total water vapour content over a 0.4 Km open path to better than one ppt.µm with a cooperative hard target. While the data shows that the system can measure water vapor content to the desired precision the long-term & absolute accuracy of the system must still ascertained. Our NDFA based laser and electro-optic receiver technology is innovative and will enable a new class of small lidars for planetary atmospheric science investigations. Our lidar approach can be generalized to measure other trace gases from orbit.

References

[1] Kahn, R.A. et al., (1992). The Martian Dust Cycle, *MARS*, H.H. Keiffer, B.M. Jakosky, C.W. Snyder and M.S. Matthews editors, Univ. of Arizona Press, Ch. 29, p. 1017.

[2] Smith M.D. (2002), The annual cycle of water vapor on Mars as observed by the Thermal Emission Spectrometer, *Journal of Geophysical Research-Planets* 107 (E11): art. no. 5115.

A-8

Simultaneous frequency stabilization of four laser diodes in the 935-nm water vapour spectrum for space application

S. Schilt, D. Werner, L. Thévenaz

Ecole Polytechnique Fédérale de Lausanne (EPFL), Laboratory of Nanophotonics and Metrology, CH-1015 Lausanne, Switzerland (stephane.schilt@epfl.ch)

R. Matthey, C. Affolderbach, G. Mileti

Observatoire de Neuchâtel, Observatoire 58, CH-2000 Neuchâtel, Switzerland (renaud.matthey@ne.ch)

Water vapour is a major atmospheric gas in terms of impact on climate and weather. Since its highly variable distribution in time and space is not covered satisfactorily with current instruments, improved water vapour measuring systems with global coverage are strongly demanded by the user community. For this reason, the European Space Agency (ESA) has been planning a satellite-borne H_2O differential-absorption lidar (DIAL) instrument. The DIAL technique offers high vertical resolution and selective gas detection by sensing the difference in light absorption at two close on-line and off-line wavelengths.

In the frame of an ESA-ESTEC supported study, we are developing a frequency detection unit (FDU) delivering four stable cw optical signals. They will be optically injected into the pulsed high-power oscillator of the transmitter laser, in order to set its spectral properties. This FDU is made of four injection seed lasers (ISL) precisely stabilized on four different wavelengths in the 935.4-nm range. Two different types of ISLs are used in the set-up: ECDL and DFB lasers. Three lasers are directly locked on three H_2O absorption lines of different strength, whereas the fourth laser wavelength lies outside of any absorption line (off-line wavelength). This off-line stabilization is achieved by an offset-locking technique. The FDU thus combines various stabilization schemes in order to grant an ISL stability better than 60 MHz over the 2-year expected lifetime of the system.

On-line stabilization is performed by wavelength modulation spectroscopy (WMS) using low-pressure water vapour reference cells. Due to severe ISL linewidth requirements, the laser modulation must be restricted to small values (only a few percents of the absorption linewidth). This constraint, associated to the limited optical pathlengths and H_2O absorption intensities, makes impossible the use of standard stabilization techniques based on third harmonic detection. A theoretical analysis of the WMS signals has thus been performed in order to define a suitable modulation/demodulation scheme for each ISL, as well as the cell parameters required to reach the target specifications. As a result, a balanced detection is used for the weakest H_2O line in order to remove the 1f-background level produced by the residual laser intensity modulation. The outputs of the model will be presented and compared with experimental results. Preliminary measurements of laser stability will also be presented.

The off-line stabilization is realised by an offset-locking between two lasers. For this purpose, an electrical filter is used to create an artificial microwave absorption line which is used to lock the beat note between the two lasers at a fixed and precisely selected value. The designed method is very similar to the WMS technique used to lock a laser on a H_2O line, but it applies to the beat note in the electrical domain. Offset-locking with frequency differences up to 19 GHz has been experimentally demonstrated with the proposed technique.

A-9

Gas analysis based on high speed thermal tuning of VCSEL lasers

M. Braun, S. Hartwig, J. Wöllenstein, J. Nurnus, H. Böttner, A. Lambrecht

Fraunhofer IPM, Heidenhofstr. 8, 79110 Freiburg, Germany

F. Volkert, A. Schubert

Infineon Technologies AG, München, Germany

Time constants for temperature stabilization or thermal tuning of miniaturized devices like vertical cavity surface emitting lasers (VCSEL) are nowadays limited by the large thermal masses of available Peltier coolers. Miniaturized MicroPelt® Peltier coolers - built by using conventional wafer based technology [1] - have essentially faster response times than conventional macroscopic Peltier coolers. By this new applications and measurement methods can be developed. VCSEL lasers have not only a wide spread in telecommunication applications but also in industrial gas analysing systems [2]. The advantages of these lasers are low cost and low power consumption, which make them very attractive for small, fast and sensitive measurement systems. Due to the small size and therefore low thermal mass they are ideally suited for the use with the MicroPelt® coolers described above. By this combination a fast thermal tuning of several nanometers in emission wavelength of the laser can be obtained. The large span can be used to cover not only one or two lines but a whole branch of an absorption band of the observed molecules with measurement rates below 1 Hz. Due to the high redundancy of the spectral information not only concentration but also other parameters like pressure or temperature can be extracted from the absorption data. The advantage of thermal tuning compared to tuning by laser current is that a larger tuning range can be obtained with less variation in laser power, for comparison a thermal tuning over 60 K results in a wavelength range of about 4 nm, whereas a tuning of 1.2 nm follows from a current variation of 2 mA for a 760 nm VCSEL.

A combination of a MicroPelt® cooler and a VCSEL laser was mounted on a commercially available Peltier cooler on a TO8 baseplate. The complete stack was sealed with a cap and an antireflection coated window. The setup was integrated in a measurement system with a heatable absorption cell of 1 m length to perform concentration measurements on gases. Measurements have been carried out on the A- band ($b^1\Sigma_g^+ \_ X\ ^3\Sigma_g^+$ (0,0) @ 13123 cm^{-1}) of O_2 for different gas concentrations and temperatures. Data evaluation is performed via multivariate analysis. HITRAN simulations have been performed for different gas concentrations, temperatures and pressures to create a basis set for data analysis. The resulting concentration values show a good stability against external influences like variations in temperature and pressure.

References

[1] H. Böttner, J. Nurnus et al., *J. of MEMS,* **13 (3)**, 414-420, 2004.

[2] I. Linnerud, P. Kaspersen, T. Jæger, *Appl. Phys. B,* **67**, 297–305, 1998.

A-10

Quantum Physics and TDLS fundamental noises

A. Nadezhdinskii

NSC of A. M. Prokhorov General Physics Institute

38 Vavilov str., 119991 Moscow, Russia

NAD@nsc.gpi.ru

In literature related to Tunable Diode Laser Spectroscopy (TDLS) frequently wrong models are using to explain experimental results. For example, many authors consider shot noise as photons number fluctuation. This assumption conflicts with fundamentals of quantum physics (see for example [1]).

In the paper brief introduction of most common models of Quantum Physics will be given related to TDLS needs. First and second quantization, as well as coherent states of electromagnetic field will be considered. Squeezed light and sub-Poisson noise will be touched. Diode laser quantum noise will be discussed.

Physical nature of DL quantum noise is related to non-commutation of a and a^+ operators of electromagnetic field (spontaneous emission). Hence, due to uncertainty principal it is impossible to measure simultaneously intensity and phase of light. Fig.1 shows diagram explaining nature of DL quantum noise (see for example [2]). Vector corresponds to stimulated emission, while circle represents spontaneous emission. Examples of different fundamental noise types in TDLS will be given.

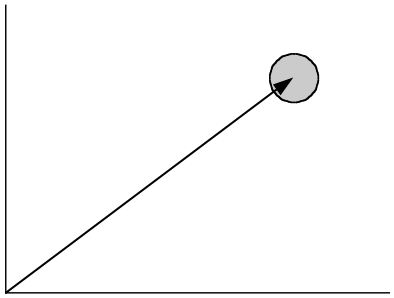


Fig.1 Influence of spontaneous emission on complex electromagnetic field

There are four main fundamental noise mechanisms limiting TDLS:

1. Photocurrent shot noise dominates for small signal (below 100 mkA) applications (diode laser based systems with topographic reflector).
2. Diode laser excitation current shot noise doesn't play important role in our systems. However, it can dominate in future for systems based on Quantum Cascade Lasers.
3. Diode laser frequency quantum noise can be important for some applications.
4. Diode laser intensity quantum noise is main fundamental mechanism of TDLS sensitivity limitations (for photocurrent higher than 100 mkA).

References

[1] J. R. Klauder and E. C. G. Sudarshan, Fundamentals of Quantum Optics, W. A. Bengamin, Inc., NY, Amsterdam, 1968.

[2] G. Morthier, P. Vankwikelberge, Handbook of Distributed Feedback Laser Diodes, Artech House, Boston, 1997.

A-11

Diode laser temperature stabilization at 3_10^{-5} K level

A. Nadezhdinskii

NSC of A. M. Prokhorov General Physics Institute

38 Vavilov str., 119991 Moscow, Russia

NAD@nsc.gpi.ru

Quality of Diode Laser (DL) temperature stabilization is important for many DL applications. Typical values reported in literature are about 1 mK. Following theory of regulation our system operation was optimized (details can be found in [1]) and temperature stabilization was significantly improved (see Fig.1).

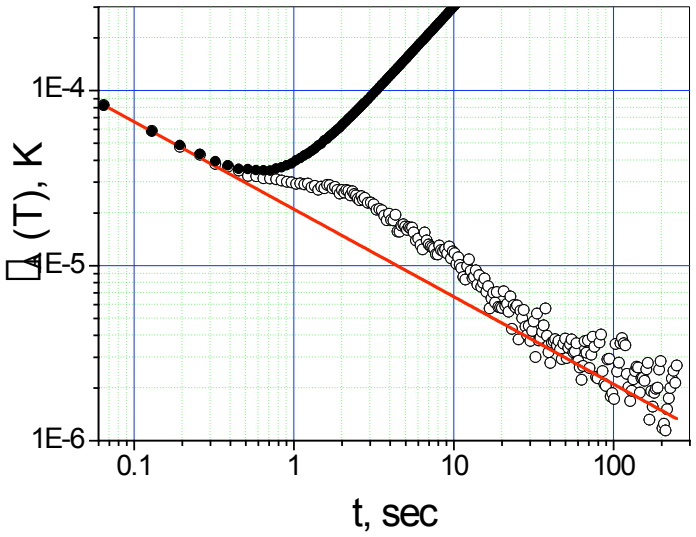


Fig.1 Allan plot of temperature with stabilization off and on (solid and open circles respectively); solid line represents 16 bit ADC white noise.

As example Allan deviation of temperature $\sigma_A(T)$ for one of DL modules is shown on Fig.1 demonstrating 0.03 mK temperature stability. Comparison of several commercially available DL modules (Sensors Unlimited, Laser Components, Anritsu, NOLATEX, etc.) will be presented.

References

[1] A. Nadezhdinskii, Diode laser spectroscopy of polyatomic molecules, Doctor of Sciences Thesis, Moscow, 1986

A-12

Below 10^{-7} absorption sensitivity limited by diode laser quantum noise

A. Nadezhdinskii

NSC of A. M. Prokhorov General Physics Institute

38 Vavilov str., 119991 Moscow, Russia

NAD@nsc.gpi.ru

In this paper results of experiment when fundamental limit of TDLS sensitivity was achieved will be presented. Origin of this limitation is related to diode laser quantum noise (see details in separate poster). Minimum detectable absorption in this experiment was found to be $6 \cdot 10^{-8}$ (see Fig.1). Comparison with best known to author results will be given.

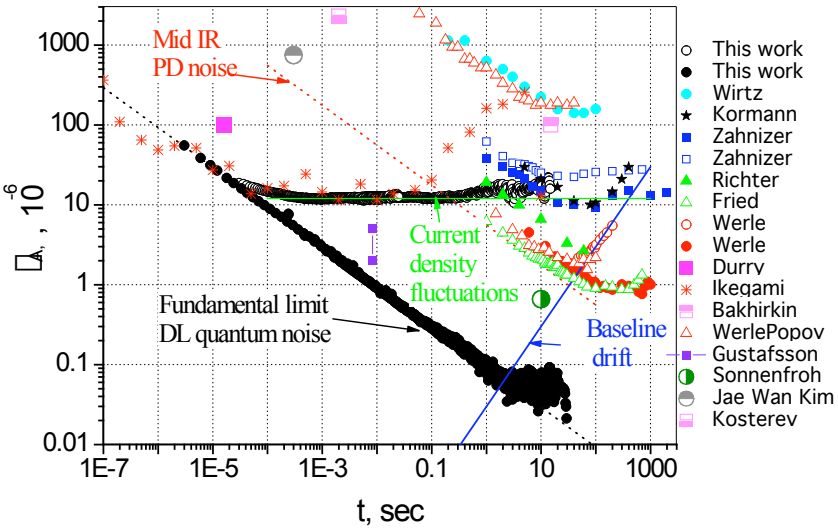


Fig.1 Allan deviation σ_A of relative photo-current noise as function of averaging time *t*.

Different physical mechanisms limiting sensitivity will be considered: photocurrent shot noise; photo diodes noise; thermal photo detectors noise; diode laser intensity quantum noise; diode laser frequency quantum noise; modes competition noise; interference in optical tract; baseline drift; flicker noise due to excitation current density fluctuations.

Fundamental limit due to diode laser quantum noise was achieved: $\mathbf{6 \cdot 10^{-8}}$ for averaging time 5 sec. Minimum detectable absorption coefficient is frequently considered (photo-acoustic and ring-down spectroscopy). For Chernin multi-pass cell in use (0.5 m × 200 passes) this parameter is equal to $\mathbf{6 \cdot 10^{-12}}$ cm^{-1} and is comparable with the best known results obtained in Stark spectroscopy.

Next sensitivity parameter widely used in literature is minimum detectable molecular concentration. For HF molecule above mentioned sensitivity corresponds to minimum detectable concentration equal to **0.8 ppt**.

A-13

Detection of trace amounts of water in ammonia by means of TDLS technique

A. Berezin, S. Malyugin, A. Nadezhdinskii, D. Namestnikov, Ya. Ponurovskii, D. Stavrovskii, Yu. Shapovalov, I. Vyazov

NSC of A.M.Prokhorov General Physics Institute of Russian Academy of Sciences, 38 Vavilov Str., 119991Moscow, Russia. E-mail: anber@nsc.gpi.ru

N. Grishnova, A. Kotkov, V. Sidorov

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

A presence of even trace amounts of water in industrial gases which serve as precursors in semiconductor industry can seriously influence a quality of final production. Usually the requirements for concentration of impurities are at ppm level or less. Such concentrations of water in ammonia could not be detected by traditional dew point technique since ammonia dew point is -33^{o}C.

The goal of present paper was to develop simple and reliable instrument to detect trace water in gaseous ammonia during real process of ammonia purification. Pigtail diode laser (Nolatech, Moscow) operated at wavelength 1.396 μm was used for ammonia probes testing at the one of the outlets of purification column. We've used our traditional DL operation mode (see separate poster). Analytical cell 0.5 m long was made of electropolished stainless steel tube, having glass windows. A small portion of laser radiation (few percents) was directed splitter into reference channel. Signal from this channel was used for DL frequency cycles stabilization and water concentration determination. A whole detection system was installed in a box that was purged by dry nitrogen, so a part of optical path between laser, annalytic cell, reference cell and detectors in both channels was almost free of atmospheric water.

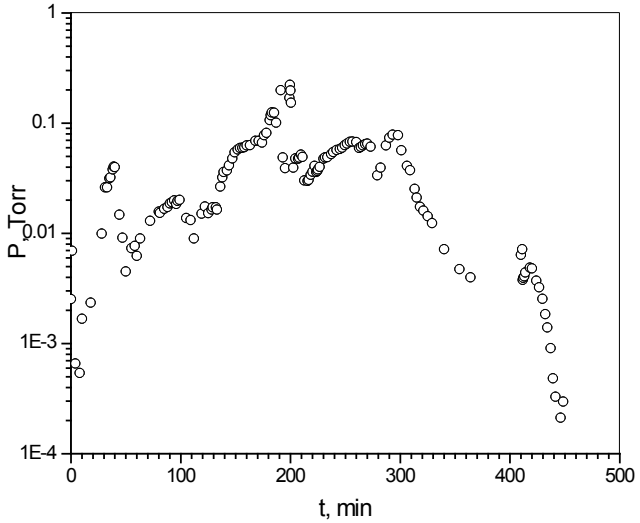


Fig. 1 Example of purification process continuous monitoring when the lower outlet of column, having the excess of water was investigated.

Fig. 1 shows example of water continuous monitoring during the process of ammonia purification. The lower outlet of column, having the excess of water was investigated. During the process under consideration its parameters were optimized based on data obtained (details will be published

elsewhere). Results presented on Fig.1 shows that optimized purification process can be finished after 450 min. This time is significantly less than it was considered traditionally.

Measurements of the $^{13}\_\__2/^{12}CO_2$ isotope composition using the TDLS technique

A. Berezin, S. Chernin, A. Makkaveiskii, A. Nadezhdinskii, Yu. Shapovalov, Ya. Ponurovskii, D. Stavrovskii

Natural Sciences Center of the A.M. Prokhorov Moscow General Physics Institute, RAS
38 Vavilov street, 119991 Moscow, Russia. E-mail: jakov@nsc.gpi.ru

A. Babichev, G. Grigoriev, S. Malyugin, Sh. Nabiev

Russian Research Center "Kurchatov Institute", 1 Kurchatov sq., 123182 Moscow, Russia

Isotopes abundance measurements are important now for variety of applications: Deposit oil fields and gas; control of an ecological situation and man-caused accidents, it is especial in connection with recent entrance into force of the Kyoto treaty; and several medical applications (for example, "breath-test", an efficient method of diagnostics of gastrointestinal tract diseases), etc. Goal of present paper was instrument development for precise absolute isotopes abundance measurements for CO_2 molecule.

Absorption lines R4 $^{12}CO_2$ and _12 $^{13}\_\__2$ located in the frequency range of 6232.7–6232.5 cm^{-1} were chosen taking into account independence of results obtained on sample temperature [1]. Fiber pigtail Anritsu DFB DL was used to cover spectral range near 1.6 _m. We've used our traditional DL operation mode (see separate poster). "Chernin" multipass cell with total optical path of 42 m was used in the instrument analytical channel. Absorption of main isotopomer spectral line was chosen close to 0.1 to reduce influence of DL electromagnetic field spectrum on results obtained [2]. To reduce instrument operation time observed spectral lines were fitted by Gaussian profile using HITRAN [3] data to determine isotopomers partial pressure. Special procedure was developed to removed baseline (see separate poster) influence on results measured. Intercomparison campaign between Mass-Spectrometer (MS) and the instrument developed (TDLS) was performed using several gas samples having different isotopes abundance (Fig. 1).

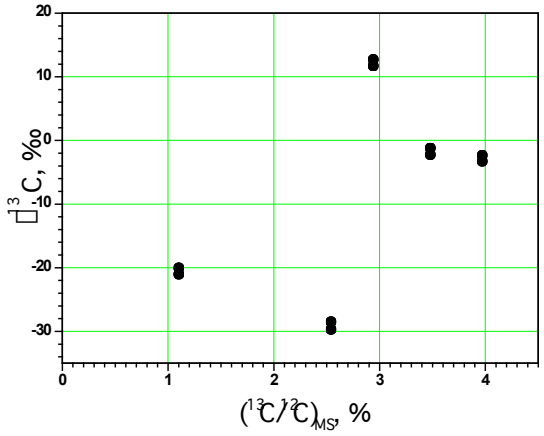


Fig. 1 Intercomparison of isotopes abundance measurements by MS and TDLS.

Two points represents spread of results obtained for different probes for the same gas sample. This spread is due to sample pressure measurement accuracy because of fitting procedure in use. Voigt profile fitting can solve this problem. Disadvantage — increasing of measurement time.

Difference between MS and TDLS results will be considered. Mainly it is due to MS memory with respect to previously measured samples.

Precision achieved for present measurement is smaller than cycle diameter on Fig.1. It is caused by DL quantum noise and is equal to 0.013 %. Analysis shows that this value can be considered as accuracy if HITRAN data are accurate enough. Achieved precision corresponds to minimum detectable absorption at level of 1.3_10^{-7}.

[1] Zahniser M. S. et.al, Abstracts of papers 4th Int. Conf. on TDLS 2003, Zermatt, Switzerland, p.104 (2003),

[2] Nadezhdinskii A. I. et.al, *Quantum electronics,* **29,** #10, 916-920 (1999).

[3] L. S. Rothman et al, The HITRAN molecular spectroscopic database, *JQSRT*, vol. **82**, numbers 1-4, 15 November–15 December (2003).

A-15

External-cavity VCSEL emitting in the 2-2.5 µm range applied to high-sensitivity intracavity laser absorption spectroscopy

A. Garnache [1], L. Cerutti [1], P. Grech [1], F. Genty [1], A. Campargue [2]

[1] *CEM2, CNRS UMR5507, Université Montpellier 2 (F)*

[2] *Laboratoire de Spectrométrie Physique, CNRS UMR5588, Université J. Fourier,Grenoble(F)*

We report the first demonstration of high-sensitivity intracavity laser absorption spectroscopy using diode-pumped Sb-based quantum-well Vertical-External-Cavity Surface-Emitting semiconductor Lasers [1] emitting in the 2-2.5µm atmospheric transparency window (CH_4, NH_3, CO_2...). A Sb-based 1/2-VCSEL structure was grown by MBE. It is composed of a AlAsSb/GaSb Bragg mirror and GaInAsSb/GaAlAsSb quantum wells [2]. The layout of our three-mirror 1m long L-shaped VECSEL is shown in Fig.1. The chip substrate is mechanically polished to form a 3° wedge [1], and is covered with a 300nm AuZn layer, to avoid Fabry-Perot effects. The cw 830nm fibre-coupled laser diode is focused on a 60µm spot diameter. The laser is operating cw above 300K with a threshold pump power <100mW, a linear polarization and a TEM_{00} beam. Wavelength tuning is achieved by a change in the chip temperature and the pump power level. A 50cm long gas cell, closed by two Brewster oriented 1cm thick CaF_2 windows, is inserted in the cavity. The pump is switched on and off by inserting an intracavity mechanical chopper (1kHz). The surrounding atmosphere is filled with N_2 to reduce by ~1/50 CH_4 and H_2O atmospheric concentrations. In order to control the generation time, an Acousto-Optic-Deflector is switched on for a short time with a delay t_g *(equivalent path length* $L_{eq}=0.45ct_g$*)* with respect to the leading edge of the laser. Thus a short slice of the laser radiation is sent to a high-resolution grating monochromator (600MHz resolution) with a Xenics extended-InGaAs photodiode linear array (512 pixels) in its focal plane. Fig.2 shows a comparison of the ICLAS-VECSEL spectrum of natural water (*P=18Torr,* t_g*=400µs or* L_{eq}*=54km*) with the stick spectrum of H_2O, HDO and NH_3 as provided by the HITRAN2004 database. The overall agreement is good but additional weak lines are observed. Further experiments performed with $^{12}CO_2$ and $^{13}CO_2$ samples have allowed for the new observation of extremely weak bands which are under analysis. A detection limit of $3.5x10^{-10}/cm$, or $10^{-10}/cmHz^{1/2}$, has been achieved on Fig.2. For gas detection application, this system can be rendered more compact by replacing the spectrograph and the AOD by a photoacoustic cell as detector.

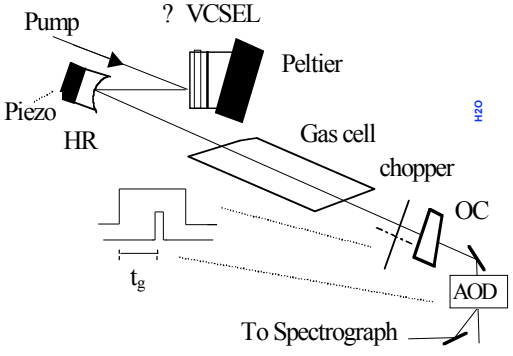


Fig. 1

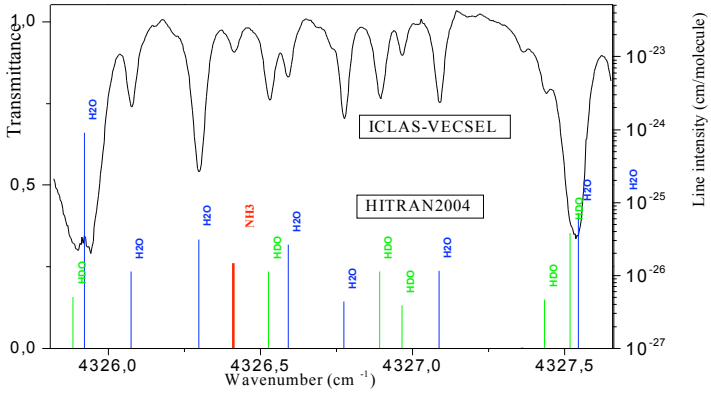


Fig. 2

[1] A. Garnache, A. A. Kachanov, F. Stoeckel, and R. Houdré, *J. Opt. Soc. Am. B*, **17** (2000), 1589

[2] L. Cerutti, A. Garnache, A. Ouvrard, and F. Genty, *J. Cryst. Growth*, **268** (2004), 128–134.

A-16

Combining pre-concentration of air samples with cavity ring down spectroscopy

Ruth E. Lindley, Alistair M. Parkes and Andrew J. Orr-Ewing

School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK, BS8 1TS

http://www.chm.bris.ac.uk/pt/laser/laserhom.htm

Cavity ring down spectroscopy (CRDS) is a highly sensitive laser absorption technique that can be used to detect gaseous species at very low concentrations (ppbv and pptv mixing ratios). The use of continuous wave diode lasers in the near infrared allows detection of a number of atmospherically important molecules via excitation of overtone and combination bands. Although these features have relatively small absorption cross-sections (typically of the order of 10^{-21} cm^2 $molecule^{-1}$ cm^{-1}) detection limits are still approaching the atmospheric concentrations of many species. In cases where the detection limit is not sufficiently low an additional pre-concentration step can be employed prior to analysis by CRDS.

Sample pre-concentration can be achieved by passing a large volume sample through a trap containing an absorbent material which retains the species of interest. The adsorbent can then be heated to desorb the trapped molecules which are transferred into a small volume ring down cavity using a carrier gas. The concentration of molecules within the cavity can then be determined using CRDS and the concentration of the original sample obtained. This combination of techniques has been shown to improve the detection limit by a factor of 34 and allowed detection of ethene (C_2H_4) at 6150.3 cm^{-1} in urban air samples at mixing ratios as low as 6 ppbv without the need for calibration.[1]

Research is now ongoing to apply this technique to a variety of species including acetylene (C_2H_2) and ammonia (NH_3), as well as improving the magnitude of pre-concentration that can be realised by further reducing the volume of the ring down cavity. The experimental set up is also being improved to produce a more robust, compact and portable system, including minimisation of free standing optics with fibre coupled equipment. This work will be presented.

Financial support from the EPSRC Portfolio Grant *LASER* and the EPSRC and Royal Society of Chemistry Analytical Trust Fund is gratefully acknowledged.

References

[1] A. M. Parkes, R. E. Lindley and A. J. Orr-Ewing, *Anal. Chem*. **76**, 7329-7335 (2004)

A-17

Characterization of a 10.3-μm pulsed DFB quantum cascade laser

Alexandre Lytkine [1], John Tulip [1], Wolfgang Jaeger [2], and Jagadeeshwari Manne [1]

[1] ECE Dept., [2] Chem. Dept., Univ. of Alberta, 9107-116 St., Edmonton, AB, Canada T6G 2V4

We have measured output parameters of a 10.3-μm pulsed distributed-feedback (DFB) quantum cascade (QC) laser manufactured by Alpes Lasers and intended for high-sensitive detection of ammonia and ethylene. The laser was mounted in an airtight housing supplied with a Peltier cooler which allowed to stabilize the laser heat sink temperature in the range between –30 and +30 ^{0}C with accuracy of 0.1 ^{0}C. The laser was excited with current pulses with duration in the 10-100 ns range, amplitude up to 9 A, and pulse repetition rate up to 1 MHz (duty cycle was kept below 2 %). The threshold current and minimum duration of the laser pulse at room temperature were 5.2 A and 8 ns (FWHM) respectively.

The laser beam was collimated with an AR-coated aspheric ZnSe lens with focal length of 11.6 mm and clear aperture of 16.5 mm. The efficiency of collimating lens was found to be close to 99% by comparing the laser power directed into the power meter by the lens and by a short (10 mm) copper tube with inner diameter corresponding to the diameter of the sensitive area of a power meter (8 mm) [1]. Near- and far-field distributions of the laser emission were recorded with an infrared camera (Electrophysics Corp., model PV320). The laser power was measured in dependence on the distance of the power meter from the laser varied in the range between 15 cm and 3 m. An increase in divergence of QC laser emission was observed at injection currents exceeding 7 A, which can be explained by the excitation of a guided mode with a divergence higher than that of the fundamental mode.

An air-spaced Fabry-Perot interferometer with free spectral range of 0.05 cm^{-1} was used to measure the tuning parameters and frequency chirp of the laser. The laser could be tuned by either temperature, injection current or pulse repetition rate with tuning rates of 8_10^{-2} cm^{-1}/K, 7_10^{-2} cm^{-1}/A and 9_10^{-4} cm^{-1}/kHz respectively. As tuning laser by a sub-threshold current applied via a bias-T provided by the manufacturer generates an additional thermal load on the laser chip, the total thermal load being substantial at high duty cycles, we scanned the laser frequency across the CO_2 absorption lines sweeping the pulse repetition rate from 200 to 700 kHz, as it was suggested in [2]. Three CO_2 absorption lines were observed in the tuning range of about 4.8 cm^{-1} achieved by changing heat sink temperature over 60 ^{0}C. The rate of the frequency chirp was equal to 10^{-2} cm^{-1}/ns (~300 MHz/ns) for laser pulse width varied from 10 to 30 ns and decreased slowly for longer laser pulses. The rate of the laser frequency chirp measured in our experiments appeared to be almost twice as big as that reported for the similar laser and measured with an FTIR spectrometer [3]. A home-made infrared diffraction-grating spectrometer will be described and the details of the spectral behaviour of the QC laser will be presented.

References

[1] Y. Bonetti, Alpes Lasers, private communications.

[2] A. Kosterev, R. Curl, F. Tittel, et al., Appl. Phys. B75, 351-357 (2002).

[3] E. Normand, G. Duxbury, and N. Langford, Optics Communications, 197, 115-120 (2001).

A-18

Compact tunable mid-IR spectrometer for ultra sensitive formaldehyde measurements

Petter Weibring, Dirk Richter, Alan Fried, and Jim Walega

The National Center for Atmospheric Research, Boulder, Colorado 80301

Mid-IR solid-state laser based spectrometers operating in the 3-4 micron wavelength region are particularly well suited for performing selective and sensitive measurements of a large variety of important atmospheric trace gases. The low abundance of many trace gases, especially in the higher layers of the troposphere, requires mixing ratio sensitivities in the low parts-per-trillion (pptv) region. For example, in high altitude airborne measurements of formaldehyde using multi-pass cells, the mid-IR laser spectrometer must not only be able to resolve a mixing ratio of equal to or better than 40 pptv, but also have acquisition times on the order of seconds to a one minute, including all overhead time needed for calibration, correction of the instrument response, and data processing. A laser source based on Difference-Frequency Generation (DFG) is a promising alternative to Quantum Cascade and Lead-Salt lasers in the 2-5 micron wavelength region and has the ability to match and exceed the performance of liquid nitrogen cooled lead salt diode lasers currently applied in airborne instruments, while providing enhanced flexibility and a more compact and robust optical architecture.

In this presentation the development and initial performance testing of a compact ultra sensitive atmospheric trace gas sensor, based on a fiber pumped difference frequency source is described. For performance testing purposes, formaldehyde is selected as a test gas due to its representative absorption cross section for species in the mid-IR wavelength region and our experience in gas handling of formaldehyde. To access formaldehyde absorption features, the system mixes the output of a DFB laser at 1562 nm and a fiber laser at 1083 nm in a periodically poled $LiNbO_3$ crystal achieving 3.5 μm wavelength radiation. The pump beams are combined by fiber optical components and launched into the crystal from a single optical fiber. The generated idler beam is focused by a single lens and launched into an astigmatic Herriott cell (100 m) and detected by peltier cooled MCT detectors. A dual-beam setup is utilized to suppress the large fast- changing common mode noise originating from temperature, phase, polarization and power fluctuations in the DFG process. By applying several strategies, including computer lock-in amplifiers, dual-beam subtraction, focus matching, thermal stabilization, active wavelength control and advanced signal processing, a typical sensitivity of 16 pptv ($A_{min}=5*10^{-7}$) is achieved for 200 s averaging during laboratory conditions. Also during favorable conditions a best effort sensitivity of 8 pptv ($A_{min}=2*10^{-7}$) was achieved. Modifications to this setup have the potential to improve this performance even further.

We will present various aspects of the spectrometer development, including DFG source characterization, detector focusing issues, thermal issues, wavelength locking, balancing schemes for dual-beam setups and procedures for performance validation.

A-19

Spectral measurement of the cesium D_2 line with a tunable heterodyne interferometer

L. Spani Molella, R.-H. Rinkleff, K. Danzmann

Max Planck Institute of Gravitational Physics

and Institute for Atom and Molecular Physics, Hannover University,

Callinstrasse 38, D-30167 Hannover, Germany

In recent years a tunable laser diode heterodyne interferometer was developed, which was used mainly to perform absorption and dispersion measurements of coherent population trapping in Cesium.

The setup involves three different phase locked lasers (one of which is used as a reference for the dispersion measurement) and allows simultaneous absorption and dispersion measurements of either the probe or the coupling laser while keeping track of the absorption of the other one [1,2]. The lasers are diode lasers with external optical feedback (ECDL); in this way the line width at the laser output is lower than 1 kHz. Since these lasers do not always offer the frequency stability needed from the setup a new laser design is under development [3] and is planned to be implemented soon.

The sample (in this case atomic cesium) is prepared in the form of an atomic beam propagating in a vacuum chamber in a direction perpendicular to that of the laser beams, in order to avoid Doppler shifts. Within the interaction area the residual magnetic field is compensated through coils that surround the vacuum tank.

With this setup several absorption and dispersion spectra within the Cs D_2 line were measured. During each measurement the coupling laser is kept fixed on one hyperfine transition (chosen via frequency modulation spectroscopy) and the probe laser sweeps through the transition of interest, usually making a sweep of 100 MHz centered at the resonant frequency. Joining together several 100 MHz sweeps one can obtain sweep ranges up to 500 MHz, thus confronting the intensities of the different spectral lines.

Among the different effects that one can resolve there are electromagnetically induced transparency and a curious dispersive feature in a coupling laser absorptive spectrum which corresponds to a huge absorption in the probe laser (if confronted with the absorption of the other lines). This absorption feature depends strongly on the polarization of the two lasers and on their relative intensity.

References

[1] M. Müller, F. Homann, R.-H. Rinkleff, A. Wicht and K. Danzmann, Phys. Rev. A, 64, 013803 (2001).

[2] M. Müller, F. Homann, R.-H. Rinkleff, A. Wicht and K. Danzmann, Phys. Rev. A, 62, 060501(R) (2000)

[3] A. Wicht, M. Rudolf, P. Huke, R.-H. Rinkleff and K. Danzmann, Appl. Phys. B, 78, 137 (2004)

A-20

Study of methane fluxes through Baikal lake surface using diode laser techniques

V. A. Kapitanov, I. S. Tyryshkin, N. P. Krivolutskii, Yu. N. Ponomarev

Institute of Atmospheric Optics, Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia

Methane is the most important representative of organic substances in the atmosphere, and its concentration significantly exceed the concentration of other organic compounds. The contribution of methane to the greenhouse effect is about 30% of that from carbon dioxide. On the global scale, natural sources of methane are wetlands, rice fields, cattle, biomass burning, and gas-hydrates.

The aim of this work is the measurements of methane concentration in air and methane flaxes through water surface of Baikal lake using a high-sensitivity laser methane detector.

The methane detector employs a GaInPAs diode laser as a source of radiation. The diode laser operates in the range from 6000 to 6080 cm^{-1} (1.645-1.666 μm), which includes rather strong absorption lines of methane. The detector was calibrated by the nitrogen-methane mixture with the methane concentration of 2.0 ppm. The detection limit (standard deviation) was 0.037 ppm, and time constant of the methane detector on the whole (with the allowance for the pump productivity and cell volume) was 99 s (spatial resolution of 450 m).

The measurements of the methane content in the atmosphere over Lake Baikal were conducted by the method of continuous air sampling from the height 2–10 m above the water level from aboard *Vereshchagin* Research Vessel in the period of August 10 through 16 of 2003 and of June 16 through 24 of 2004. Analysis of the measuring results obtained in the course of 2003 - 2004 expeditions has shown: values of methane concentrations in near-surface air all along Baikal averaged 1.9–2.0 ppm and the standard deviation did not exceed 0.1 ppm.

Obtained in the course of vessel expeditions distinctive and considerable (more than 2.4 ppm) anomalies were observed at six areas of Middle Baikal. Maximum value of air methane concentration 30 ppm was detected near open seep (Selenga entry). The distinctive and considerable (4 ppm) peak of the near-surface air methane concentration was observed near Mishicha entry, the water depth is about 1000 m.

The direct measurements of methane fluxes are very important for assessment of global fluxes of methane from water surface to the atmosphere. These measurements were carried out on vessel board for the first time.

Acknowledgments

This work was supported in part by the INTAS (grant No. 01-2309) and the Program of Basic Research of Division of Physical Science RAS (Project No. 2.10.1 “High-Resolution Spectroscopy”)

A-21

Diode laser spectroscopy of $^{13}CO_2$ and $^{16}O^{12}C^{18}O$ in the 2 µm region

B. Parvitte, V. Zéninari, T. Le Barbu, D. Courtois, G. Durry

Groupe de Spectrom_trie Moléculaire et Atmosphérique (GSMA), UMR CNRS 6089,

Faculté des Sciences, BP 1039, F-51687 Reims Cedex 2 - France

The Groupe de Spectrométrie Moléculaire et Atmosphérique is developing with the support of CNES a laser sensor for studying the Martian atmosphere. The Martian atmospheric composition and pressure conditions enable the realization of a compact instrument. The main objectives are to determine water vapor and carbon dioxide fluxes and to study boundary layer properties. The sensor will provide in situ daily, diurnally resolved measurements of near-surface H_2O and CO_2 concentration over seasonal time scales. For this instrument additional isotopic measurements of $^{13}CO_2$ and $^{16}OC^{18}O$ will provide quantitative constraints on the evolution of atmospheric composition and on the history of water on Mars.

A diode laser spectrometer was used in the laboratory to study $^{13}CO_2$ and $^{18}O^{12}C^{16}O$ line intensities and self-broadening coefficients near 2.04 µm. The spectral region ranging from 4896 cm^{-1} to 4903 cm^{-1} was studied using a commercial telecommunication-type diode laser from Nanoplus-Inc. We have studied five lines of the $(20^01)_{II} \leftarrow (000)$ band of $^{13}CO_2$ and seven lines of the $(20^01)_{II} \leftarrow (000)$ band of $^{18}O^{12}C^{16}O$. The results of intensity and self-broadening measurements are compared to available databases. These results will be used for the *in situ* sensing of carbon dioxide $^{13}CO_2$ and $^{18}O^{12}C^{16}O$ isotopes in the Martian atmosphere.

A-22

Diode laser absorption spectrometry refined – from optical saturation and optical pumping phenomena in conventional and wavelength modulated absorption spectrometry to ultra-sensitive detection of ammonia by NICE-OHMS

Florian Schmidt, Aleksandra Foltynowicz and Ove Axner

Department of Physics, Umeå University,

SE-901 87 Umeå, Sweden

florian.schmidt@physics.umu.se, aleksandra.foltynowicz@physics.umu.se, and ove.axner@physics.umu.se

Our group has been active in the field of *Diode Laser Absorption Spectrometry* (DLAS) in gaseous media for a number of years. This poster presents work performed in several fields of *Absorption Spectrometry* (AS). The first part presents a description of the influence of *Optical Saturation* (OS) and *Optical Pumping* (OP) in conventional AS under arbitrary optical thickness conditions. The second part provides an investigation of the influence of OS and OP on *Wavelength Modulation Absorption Spectroscopy* (WMAS). The third part presents preliminary results of the endeavors of our group to apply a rather new technique, *Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectroscop*y (NICE-OHMS), to ultra-sensitive detection of ammonia.

It should be well known that Beer's law is not valid when OS or OP takes place. Descriptions alternative to Beer's law exist when OS or OP takes place under optically thin conditions. However, there has so far not been any description of AS when OS or OP takes place under partly optically thick conditions. In order to deal with this, two quantities have been defined; one called the "observed" Absorbance, which refers to the measured absorbance, and another termed the "true" Absorbance, which refers to the quantity one would measure if the light solely acted as a probe of the level population. Explicit expressions are derived for how these two entities are related to each other when AS is performed with narrowband light that can induce an arbitrary degree of OS or OP in collision or Doppler broadened media under arbitrary sample optical thickness conditions.

We furthermore present the results of a theoretical description of the influence of OS and OP on WMAS-signals in the collision broadened regime, which is built upon the Fourier series-based formalism that our group has previously developed for describing WMAS. For the case of OS, it is found that the *nf*-WMAS signal on resonance decreases faster than an ordinary AS signal as a function of the laser flux when smaller-than-optimum modulation amplitudes are used, but slower when larger-than-optimum modulation amplitudes are used. For optimum (or close-to optimum) modulation amplitudes, the flux dependence of the WMAS-signal resembles that of ordinary AS.

The NICE-OHMS method combines, for the first time, several concepts that are of importance for AS; *Frequency Modulation* (FM) for noise reduction, *Cavity Enhanced* (CE) spectrometry for increased sensitivity and *Saturation Spectrometry* (SS) for improved selectivity. The NICE-OHMS technique offers therefore the potential for ultra-sensitive detection of atoms and molecules, with a sensitivity that is far beyond that achieved by established AS techniques. Some first results of sensitive detection of ammonia around 1.5 μm are presented.

A-23

Spectroscopic remote sensing instrument for orbital atmospheric pressure and temperature measurement

***Mark Stephen*[*†], *Michael Krainak*[*], *Michael Hayden*[†]**

[*] *NASA's Goddard Space Flight Center*

Mail Code 694

Greenbelt, MD 20771

[†] *University of Maryland Baltimore County*

Physics Department

Baltimore, MD 21250

We report on progress demonstrating the feasibility of a remote sensing laser instrument capable of measuring atmospheric pressure and temperature from orbit. The measurement approach uses differential optical absorption spectroscopy of O_2. The shape of absorption lines is a well-defined function of temperature and pressure. Using laser spectroscopy in the Oxygen A-band, we measure the change in shape of absorption features caused by changes in pressure and temperature. Because temperature and pressure both affect absorption linewidth, distinguishing the two effects is challenging. We discuss progress on a laser-sounding instrument with a continuous wavelength scan, yielding the entire line shape and fitted Voigt parameters. This enables unambiguous differentiation between the Gaussian broadening due to temperature and Lorentzian broadening due to pressure. We use a surface echo return to measure the average pressure and temperature of the atmospheric column of the laser path. This technique allows the use of much lower power lasers than traditional DIAL instruments require.

The laser transmitter under investigation is a ~1540 nm distributed-feed-back (DFB) diode laser seeding an erbium-doped fiber amplifier (EDFA), which is frequency doubled to ~770 nm with periodically-poled (PP) KTP. The DFB seeded EDFA forms a tunable, narrow frequency (~1 MHz), high-power laser source. In addition, the fiber-coupled design minimizes the part count and makes a very robust and lightweight transmitter that is ideal for a space-qualified instrument. The 1540 nm output is then frequency doubled to 770 nm with the use of PPKTP, a nonlinear crystal designed for high conversion efficiency. The scanning capability eliminates measurement ambiguity and should improve accuracy over much wider operating conditions. The objective of this research is to demonstrate an instrument for remote sensing of atmospheric pressure and temperature to 1 mbar and 1°C accuracy, respectively.

A-24

Exact calculation of beam propagation in Chernin matrix multipass optical cell

A. Berezin, S. Chernin

NSC of A. M. Prokhorov General Physics Institute of Russin Academy of Sciences,
38 Vavilov Str., Moscow 119991, Russia. E-mail: anber@nsc.gpi.ru

An exact solution for beam propagation based on the rules of geometric optics for Chernin four objective matrix multipass cell [1] was found and program was written that could calculate position, incoming and outcoming angles on corresponding mirror at every reflection. Chernin multipass cell consists of two sets of mirrors, one of which joins four objective mirrors and the other two field mirrors, located on radius of curvature, the same for all mirrors. The system works as consequence of White [2] optical schemes, forming pairs of lines of images on field mirror with a help of one or another pair of objectives until a matrix of images appears on field mirrors.

The program allowed change of position and orientation of every mirror comprising multipass cell, as well as position and orientation of mirror sets. The critical parameters to which an alignment was most sensitive were determined and it was found that positions and declinations of objective mirrors with respect to each other were most critical, while the distance between two sets of mirrors and their tilting as a whole were less critical. The example of calculation for a case when two sets of mirrors were located at a distance slightly less than radius of curvature.

Theoretically the number of passes in Chernin multipass cell is not limited. Practically optimal number of passes depends on mirrors' reflectivity and aberrations. This work was dedicated also to find out the limitations arising due to aberrations. It was found that aberrations in ideal Chernin optical cell are mostly compensated during beam propagation and final spot at the exit of a cell is much smaller than intermediate spots. That makes Chernin multipass cell preferable with respect to Herriott optical cell since Cernin multipass cell can operate with diverging beams.

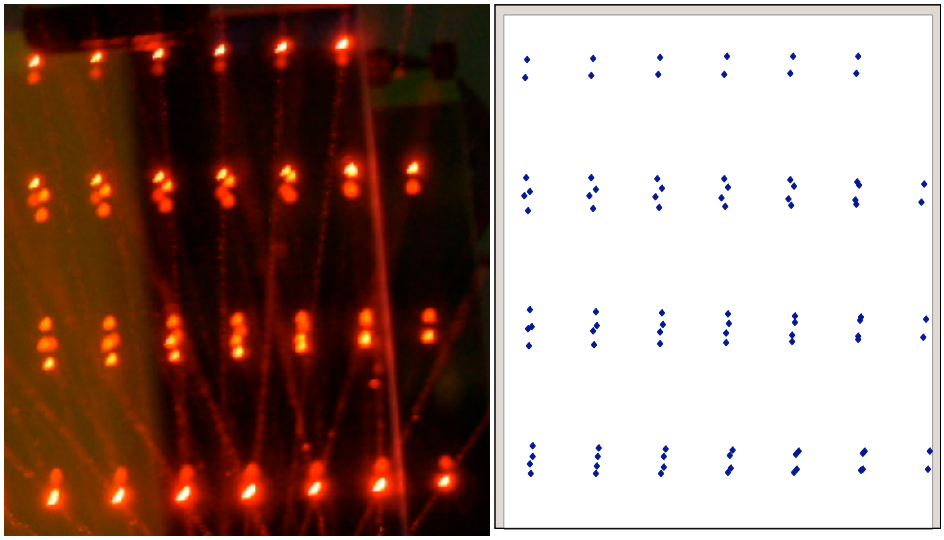


Fig. 1 Real and calculated positions of images on field mirrors in a case when a distance between two sets of mirrors was slightly less than their curvature.

[1] S. M. Chernin, E. G. Barskaya, Appl. Opt. **30** (1991) 51.

[2] J. U. White J. Opt. Soc. Am. **32** (1942) 285.

A-25

Characteristics of several NIR tuneable diode lasers for spectroscopic based gas sensing: a comparison

David McInerney, John Donegan, Michael Lynch, Vincent Weldon

Trinity College Dublin

T. Farrel, M. Todd, D. McDonald

Intune Technologies, Dublin

Tuneable laser diodes were characterized and compared for use as tuneable sources in gas absorption spectroscopy. Specifically the characteristics of widely tuneable single frequency lasers, such as sampled grating distributed Bragg reflector (SG-DBR) laser and modulated grating Y-branch (MG-Y) laser diodes, recently developed for optical communications, with operating wavelengths in the 1520 □ □ □1570 nm, are compared. The comparison also includes an external cavity laser (ECL) emitting at 935nm and a distributed feedback (DFB) laser. Characteristics investigated include, side mode suppression ratio, ease of tuning, tuning range, spectral emission linewidth, frequency stability, output power and wavelength modulation.

Widely tuneable diode lasers are capable of multi-species gas detection and are more complex than standard DFB lasers used for single-species gas sensing and have some undesirable artifacts in their operating behavior. However they present exciting opportunities for applications in absorption based multi-gas sensing regimes. Such wide wavelength tuning is not possible with conventional single frequency DFB devices whose use is typically limited to the detection of one gas.

A-26

Diode Laser System for Precision Spectroscopy of Atomic Hydrogen

J. Alnis, N. Kolachevsky,M. Fischer, Th. Udem, T.W. Hänsch

Max-Planck-Institut für Quantenoptik, 85748 Garching, Germany

Email: Janis.Alnis@mpq.mpg.de

The two-photon precision spectroscopy of the 1S-2S transition in atomic hydrogen has recently reached the precision of a few parts in 10^{-14} [1] being one of the the most precisely measured atomic transitions. The measurement had been done with a dye laser locked to the Cs atomic fountain clock using a femtosecond laser frequency comb [2].

We are now developing a diode-laser based system that will replace the dye laser and will bring the set-up one step closer to a practical atomic clock. We presently are evaluating the performance of the diode laser system.

Our new diode laser system is based on a commercial laser (Toptica TA-SHG) consisting of a grating stabilized diode laser at 972 nm followed by a 1 W tapered amplifier and a bow-tie type doubling stage that yields 200 mW at 486 nm. The blue light is doubled in a second doubling stage (Laser Physics Wavetrain delta-shape). We measured at most 20 mW at 243 nm that is comparable to the UV output of the dye laser system due to a very efficient SHG enhancement cavity.

We stabilise the diode laser on an external Fabri-Perot cavity with a finesse of 100 000 in order to reduce laser linewidth and measure the beatnote with the dye laser system. The measured beatnote signal line width is below 1 kHz FWHM.

[1] M. Fischer, N. Kolachevsky, M. Zimmermann, R. Holzwarth, Th. Udem, T.W. Hänsch, M. Abgrall, J. Grünert, I. Maksimovic, S. Bize, H. Marion, F. Pereira Dos Santos, P. Lemonde, G .Santarelli, P. Laurent, A. Clairon, and C. Salomon, M. Haas, U. D. Jentschura, and C. H. Keitel, Phys. Rev. Lett. **92**, 230802 (2004)
[2] Th. Udem, R. Holzwarth, and T.W. Hänsch), Nature, **416**, 233 (2002)

Poster Session B

B-1 A DFG source for high-sensitivity molecular spectroscopy in the 3-micron range
G. Gagliardi, P. Maddaloni, P. Malara, P. De Natale

B-2 Determination of molecular parameters for molecules with overlapping infrared spectra using tunable diode laser infrared spectroscopy
Charles N. Harward Sr., W. David Thweatt, Milton E. Parrish

B-3 Spatially resolved flame temperature measurements with blue diode laser two-line atomic fluorescence
I. S. Burns, G. Hartung, J. Hult, C. F. Kaminski

B-4 Trace oxygen detection using tunable diode lasers
Katherine A. Keen, Ruth E. Lindley, Edward D. McNaghten and Alistair M. Parkes

B-5 Sub-ppm multi-gas photoacoustic sensor
J-Ph. Besson, S. Schilt, L. Thévenaz

B-6 Fully fiber-coupled NIR diode laser absorption spectrometer for simultaneous *in situ* detection of O_2, CO, H_2O and temperature in a high-temperature rotary kiln
V. Ebert, H. Teichert

B-7 Diode laser based photoacoustic sensing using micromechanical cantilever detection
H. Cattaneo, T. Laurila, V. Koskinen, J. Kauppinen, R. Hernberg

B-8 Mid infrared laser sensors for remote detection of explosives
Wolfgang Schade, Ulrike Willer, Thomas Keune, Gerhard Holl

B-9 Rotationally resolved diode laser jet spectrum of propadienone (CH_3CCO) in the $\square_2$ band region
P. B. Davies, P. J. O'Sullivan, R. J. Livingstone and Z. Liu

B-10 Diode laser frequency tuning cycles stabilization at kHz level
A. Nadezhdinskii

B-11 Shot noise limited TDLS
A. Nadezhdinskii

B-12 Diode laser quantum noise
A. Nadezhdinskii

B-13 Ethanol vapor detection limited by diode laser frequency quantum noise
A. Berezin, S. Malyugin, T. Moskalev, A. Nadezhdinskii, D. Namestnikov, Ya. Ponurovskii, Yu. Shapovalov, D. Stavrovskii, I. Vyazov, V. Zaslavskii

B-14 Applications of Chernin four-objective multipass matrix system

A. Berezin, S. Chernin, L. Medvedev, A. Nadezhdinskii, Ya. Ponurovskii, S. Rudov, D. Stavrovskii

B-15 Use of injection locking for reducing optical feedback effects and residual amplitude modulation in wavelength modulation spectroscopy

M. Vainioa, M. Merimaab, and K. Nyholm

B-16 Observation of stark level crossing signals in $7^2D_{3/2}$ Cs applying two-step diode laser excitation

M. Auzinsh, K. Blushs, R. Ferber, F. Gahbauer, A. Jarmola, and M. Tamanis

B-17 Cavity-enhanced absorption detectors for monitoring of breath and ambient atmospheric air

V. L. Kasyutich, R. J. Holdsworth, P. A. Martin

B-18 High-speed infrared hygrometer for respiratory diagnostics

Igor Shvarchuck, Graeme Murray

B-19 Studies of kinetic processes in H_2-N_2-O_2 plasmas by IR-TDLAS

O. Gabriel, S. Welzel, R. A. B. Zijlmans, G. Lombardi, G. D. Stancu, R. Engeln, D. C. Schram, J. Röpcke

B-20 Laser sources for precision spectroscopy on atomic strontium

R. E. Drullinger, G. Ferrari, N. Poli, M. Prevedelli, F. Sorrentino, and G. M. Tino

B-21 Open path atmospheric spectroscopy using room temperature operated pulsed quantum cascade laser

M. Taslakov, V. Simeonov, H. van den Bergh

B-22 A remotely controllable optical multi-pass system

Harald Verbraak and Harold Linnartz

B-23 Non-invasive determination of porosity in pharmaceutical tablets using tunable diode laser spectroscopy

Tomas Svensson, Jonas Johansson, Stefan Andersson-Engels, Sune Svanberg and Staffan Folestad

B-24 In-situ monitoring of low ppb level moisture and other critical contaminants in ultra pure speciality gases, for electronic manufacturing

H. Beese, W. Grählert, V. Hopfe, P. Kaspersen, A. Bohman, F. Petzold, E. Wudy, P. Mackrodt

B-25 Simultaneous detection of HCl and HF by TTFMS and high frequency WMS

A. C. De Luca, G. Pesce, G. Rusciano and A. Sasso

B-26 Stratospheric carbon monoxide in tropical convections: in-situ measurements with a mid-IR airborne spectrometer

F. D'Amato, P. Mazzinghi, S. Viciani, P. W. Werle, F. Castagnoli, M. De Pas, M. Giuntini

B-1

A DFG source for high-sensitivity molecular spectroscopy in the 3-micron range

G. Gagliardi, P. Maddaloni, P. Malara, P. De Natale

Istituto Nazionale di Ottica Applicata - Comprensorio "A. Olivetti"

Via Campi Flegrei 34, I-80078 Pozzuoli (Naples), Italy

gagliardi@inoa.it

In the last decades, novel coherent radiation sources, such as difference-frequency generators (DFGs), optical parametric oscillators (OPOs) and quantum cascade lasers (QCLs) have opened new perspectives for high-resolution and high-sensitivity spectroscopy in the mid-infrared spectral region. While emission of quantum cascade lasers has been demonstrated for a number of wavelengths from 3.5 to 24 μm, the range between 2.5 and 3.5 μm seems to be difficult to access. Thanks to wide tunability, low-noise and narrow line-width, cw DFG sources proved to be valuable tools for spectroscopic applications and were successfully operated from 2 to 20 μm. So far, the main limitation has been the low generated power, typically around a few hundreds μW, while a higher power is desirable in many applications. Recent advances in the fabrication of nonlinear crystals have led to a strong improvement in optical frequency-down conversion processes. In this work, we report on development and spectroscopic use of a difference-frequency-generation (DFG) source, capable to emit between 2.9 and 3.5 μm, with a maximum power of 3.5 mW. In our setup, the signal beam comes from an erbium-fiber amplified diode laser emitting from 1545 to 1605 nm with a maximum power of 5 W (in the 1545-1570 nm interval). The pump radiation is generated by an extended-cavity diode laser with a tuning range of 1030-1070 nm, then amplified by a double-stage Yb-amplifier that delivers up to 700 mW. Coherent radiation at their difference frequency is generated by focusing the two beams, properly collimated and polarized to satisfy the quasi-phase-matching (QPM) condition, into a temperature-controlled, antireflection-coated, periodically poled $LiNbO_3$ (PPLN) crystal.

High sensitivity absorption spectroscopy of CH_4, C_2H_4 and NH_3, exhibiting fundamental bands in the 3-micron range, was carried out combining the DFG source to a high-finesse optical cavity. For this purpose, we adopted a particularly simple detection method, suitable to obtain long absorption pathlength, which is based on the so-called integrated-cavity-output scheme with off-axis alignment. Using two mirrors with reflectivity higher than 99.9%, at a relative distance of about 1 m, it was possible to approach total pathlengths of 1.5 km with an equivalent-noise sensitivity ranging from 10^{-8} to 10^{-9} $cm^{-1}/\sqrt{Hz}$. An example of simultaneous detection of $^{12}CH_4$, $^{13}CH_4$ and $^{12}CH_3D$ species in natural abundance is presented.

References

[1] P. Maddaloni, G. Gagliardi, P. Malara, P. De Natale, "A 3.5-mW continuous-wave difference-frequency source around 3 μm for sub-Doppler molecular spectroscopy", Appl. Phys. B 80, 141 (2005).

B-2

Determination of molecular parameters for molecules with overlapping infrared spectra using tunable diode laser infrared spectroscopy

Charles N. Harward Sr. [1]***, W. David Thweatt*** [2]***, Milton E. Parrish*** [3*]

[1] *Nottoway Scientific Consulting Corp., P.O. Box 125, Nottoway, VA 23955 USA*

[2] *Philip Morris USA Postgraduate Research Program, 4201 Commerce Road,*

Richmond, VA 23234 USA

[3] *Philip Morris USA Research Center, 4201 Commerce Road, Richmond, VA 23234 USA*

[*] *contact: milton.e.parrish@pmusa.com*

For many years molecules, such as carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), ammonia (NH_3), nitric oxide (NO) and nitrous oxide (N_2O), that have relatively simple IR spectra consisting mostly of single non-overlapping absorption lines, have been measured using high resolution tunable diode laser (TDL) spectroscopy systems. Our laboratory at Philip Morris USA RD&E has used TDL spectroscopy to quantitate some of these molecules in cigarette smoke using instruments purchased from Aerodyne Research, Inc. (ARI). The spectral parameters, *i.e.*, line positions, integrated line strengths, temperature dependence, and line broadening coefficients, needed for quantitation of these molecules can be found in the HITRAN database of spectral lines.

Recently, there has been increased interest in the quantitation of more complex molecules. One of these molecules, acrolein (C_3H_4O), is important for environmental monitoring and remote sensing of exhaust emissions from gasoline and diesel vehicles. Our laboratory also is interested in measuring this constituent in cigarette smoke. The molecular structure of acrolein generates a large number of overlapping infrared absorption lines within the spectral scanning range of the TDL (~ 0.5 cm-1 to 1 cm-1). Since the spectral parameters for acrolein are not in the HITRAN database, they must be determined to develop an analytical method. In addition, the quantitation of acrolein in cigarette smoke is made more difficult by the low concentration and the overlap from infrared absorption lines from other constituents in the cigarette smoke matrix. This poster presents the steps necessary for the quantitation of acrolein in a fresh puff of cigarette smoke.

B-3

Spatially resolved flame temperature measurements with blue diode laser two-line atomic fluorescence

I. S. Burns, G. Hartung, J. Hult, C. F. Kaminski

Department of Chemical Engineering, University of Cambridge,

Pembroke Street, Cambridge CB2 3RA, UK

E-mail: clemens_kaminski@cheng.cam.ac.uk

This poster describes the use of blue extended cavity diode lasers (ECDLs) to make accurate measurements of flame temperature with high spatial and temporal resolution. The technique is based on laser induced fluorescence (LIF) of seeded indium atoms. Two blue diode lasers emitting at around 410 nm and 451 nm were used respectively to probe the $5^2P_{1/2}$_$6^2S_{1/2}$ and $5^2P_{3/2}$_$6^2S_{1/2}$ electronic transitions of indium. The relative strengths of the LIF signals can be related to the temperature by an expression derived from the Boltzmann equation. The choice of indium as the probe species leads to high temperature sensitivity since the energy separation between the spin-orbit split sub-levels of the ground state is roughly equal to *kT*. One of the advantages of the two-line atomic fluorescence (TLAF) technique is that the quenching coefficients cancel out of the expression for temperature since the probed transitions have a common upper state.

The construction of custom-designed blue ECDLs with favourable mode-hop-free tuning ranges, and their application to flame spectroscopy of atomic indium, has already been described [1]. The realisation of a temperature sensor has now been achieved by sequentially probing the same point in the flame with each laser. It has been possible to achieve a substantial increase in the wavelength scanning rate of the ECDLs and this has allowed temperature measurements at rates of up to 10 kHz. Such high temporal resolution is essential for probing turbulent combustion environments. A rigorous validation of the accuracy and precision of this thermometry tool has been made by comparison both to Coherent Anti-Stokes Raman Scattering, and to Na-line reversal, which were performed in close succession in a very stable flat-flame burner.

This approach is thus superior to diode laser absorption thermometry, which is a line-of-sight method and thus only capable of measuring average temperatures in homogeneous environments. By instead employing a technique based on fluorescence, it is possible to achieve a spatial resolution defined by a cylinder 100 μm in diameter and 300 μm in length. The TLAF technique is suitable for widespread application in turbulent flames and engines, and also in particle-laden environments.

[1] J. Hult, I. S. Burns, C. F. Kaminski, 4th International Conference on Tunable Diode Laser Spectroscopy, **Abstract D6**, Zermatt, 14-18 July, 2003

B-4

Trace oxygen detection using tunable diode lasers

Katherine A. Keen, Ruth E. Lindley*, Edward D. McNaghten and Alistair M. Parkes

AWE, Aldermaston, Reading, RG7 4PR, U.K.

**School of Chemistry, University of Bristol, Cantocks Close, Bristol, BS8 1TS, U.K.*

AWE's Materials Science Research Division conduct experiments to predict the manner in which a range of materials undergo chemical and physical change as they age. These changes are sometimes evidenced by the evolution or consumption of gaseous species. We have developed a range of Tunable Diode Laser Absorption Spectroscopy (TDLAS) systems for detecting a variety of gases at trace levels. The advantages offered by these systems include compact and robust design, low cost components, portability and ease of use. Analytes of interest include CO_2, CO, CH_4, O_2, NO, N_2O, NO_2, water vapour and volatile organic compounds. The gas samples are contained in a variety of sample vessels; some are extracted from experiments and transferred to multi-pass absorption cells whilst others are examined in-situ in sealed sample vessels which have optically transparent windows. Measurements are performed at reduced internal pressures of 100 – 200 mbar where practical in order to minimize pressure broadening effects.

A current program focuses on the development of TDLAS techniques to detect molecular oxygen at concentrations in the 10 -100 ppm range. This presents a significant challenge as oxygen is not infrared (IR) active (i.e. an IR absorption spectrum is not observed). However, oxygen has a very weak electronic absorption band in the 759-764 nm region ($b^1\Sigma_g^+$ (v = 0) ← $X^3\Sigma_g^-$ (v″ = 0), $\sigma = 10^{-23}$ cm^2 $molecule^{-1}$). The small absorption cross section in this region makes detection of trace levels of O_2 extremely challenging. We aim to detect oxygen using a DFB laser which operates in this region.

At present several different approaches are being undertaken to develop a fully optimized system for trace O_2 detection, accounting for both minimum detection limits and robustness of design, to aid in materials ageing trials. An small volume (500 ml) astigmatic multi-pass absorption cell, enabling a 76 m path length, is used for TDLAS with and without lock-in detection. Cavity enhanced strategies are also being employed, with high reflectivity mirrors enabling much longer path lengths but placing much greater demand upon the robustness of alignment.

We will present a comparison of the different methods applied, stating current detection limits for O_2 at reduced pressure (within the Doppler broadening limit) and at atmospheric pressure. We will also assess the prospect for using these techniques in materials ageing experiments which require (i) extraction of gas samples for TDLAS analysis in multi-pass cells and (ii) in-situ measurements.

B-5

Sub-ppm multi-gas photoacoustic sensor

J-Ph. Besson, S. Schilt, L. Thévenaz

Ecole Polytechnique Fédérale de Lausanne (EPFL),

Nanophotonics and Metrology Laboratory

CH-1015 Lausanne, Switzerland

jean-philippe.besson@epfl.ch

The control of industrial processes represents an important field of application for infrared laser spectroscopy. The main requirements of gas sensing instruments for this kind of applications are a good selectivity, a sensitivity at ppm level or even better and continuous on-line monitoring. The capability of measuring simultaneously several species is sometimes also necessary in order to detect various potential contaminants for the process.

In this work we present the design of a new photoacoustic sensor that makes possible the simultaneous measurement of three different gases using tunable laser diodes in the NIR range. The photoacoustic cell is designed to operate in its first longitudinal acoustic mode at about 1 kHz. The sensor was developed for the control of the manufacturing process of novel low-water-content fibres used in optical telecommunications. It aims at monitoring traces of hydrogenated compounds such as H_2O, CH_4 and HCl at sub-ppm level, as the presence of these contaminants during the fabrication of the optical fibre preform results in a large attenuation of the fibre in the 1.39 μm range due to OH^- absorption.

A detection limit (*SNR* = 3) of 0.15 ppm at 1651.0 nm for CH_4, 0.2 ppm at 1742.4 nm for HCl and 24 ppb at 1368.6 nm for H_2O was achieved. The power of each laser was respectively 10 mW, 2 mW and 22 mW.

In addition, the buffer gas used in optical fibre manufacturing plays a crucial role in the photoacoustic response and needs to be included for the evaluation of the gas concentration. Therefore a proper calibration of the system must be performed taking into account the buffer gas composition. Two different buffer gases were used to compare the effect on the photoacoustic signal.

B-6

Fully fiber-coupled NIR diode laser absorption spectrometer for simultaneous *in situ* detection of O_2, CO, H_2O and temperature in a high-temperature rotary kiln

V. Ebert, H. Teichert

Physikalisch-Chemisches Institut, University Heidelberg, INF 253, D-69120 Heidelberg

contact: volker.ebert@pci.uni-heidelberg.de fax: 49-6221-545050 www.gasanalysis.org

Since the combustion of fossil fuels will remain an important energy source over the next decades, it becomes an urgent task to minimize CO_2- and pollutant emission and maximize the total efficiency of the power plants. Measurement techniques for species concentration, temperature and other parameters are vital for this task. Diode laser based absorption techniques offer great promise to improve the control loops and thus the combustion efficiency. Using telecommunication diode lasers in the near infrared we developed over the last years numerous robust *in situ* absorption spectrometers, which are capable of measuring multiple species concentrations and temperature simultaneously, and applied them to full-sized industrial combustion processes, e.g. the first simultaneous *in situ* detection of all major combustion species (CH_4, O_2, H_2O, CO_2) and temperature in the combustion chamber of a 1000MW_{th} gas-fired power plant[1], the first *in situ* detection of 3-CO in the combustion chamber of a 700 MW_{th} lignite-fired power plant[2], or the first high-sensitivity 2-CO detection in a rotary kiln using new 2.3µm DFB diode lasers[3].

Today we present a new DSP-based data acquisition system with which we could optimize our data evaluation procedures for the correction of the *in situ* disturbances, so that we are now able to measure species concentrations even in pulsating rotary kilns or coal-fired power plants with extremely fast transmission fluctuations resp. overall transmissions of the measurement path in the 10^{-3} to 10^{-5} range. For applications in batch-fired processes, like rotary kilns, where rapid stoichiometry fluctuation generate fast and strong CO peaks, which limit the overall plant throughput, we recently developed a new time-multiplexed, multi-species NIR diode laser spectrometer for CO, O_2, H_2O and gas temperature. This spectrometer is in contrast to our earlier spectrometers completely fiber-coupled. This provides first of all a much easier application in harsh industrial environments, an important factor for real world applications. Further, fiber coupling opens up the possibility for multi-point detection, i.e. simultaneous measurements at different locations, which we demonstrate by simultaneous measurements at the entrance and the exit of the post combustion chamber of the rotary kiln.

[1] V. Ebert, T. Fernholz, C. Giesemann, H. Pitz, H. Teichert, J. Wolfrum, H. Jaritz "Simultaneous Diode-Laser-Based In-situ-Detection of Multiple Species and Temperature in a Gas-fired Power-Plant", Proc. Comb. Inst. 28, 423-430 (2000)

[2] H. Teichert, T. Fernholz, V. Ebert, "In situ Measurement of CO, H_2O and Gas Temperature in a Lignite-Fired Power-Plant", Applied Optics 42, 2043-2051 (2003)

[3] V. Ebert, H. Teichert, P. Strauch, T. Kolb, H. Seifert, J. Wolfrum,"High Sensitivity In-Situ CO-Detection in a 3 MWth Rotary Kiln for Special Waste Incineration Using New 2.3 µm Distributed Feedback Diode Lasers", Proc. Comb. Inst. 30, 1611-1618 (2005)

B-7

Diode laser based photoacoustic sensing using micromechanical cantilever detection

H. Cattaneo [1], T. Laurila [1], V. Koskinen [2], J. Kauppinen [2], R. Hernberg [1]

[1] *Optics Laboratory, Tampere University of Technology*

P.O. Box 692, FI-33101 Tampere, Finland

[2] *Laboratory of Optics and Spectroscopy, University of Turku,*

FI-20014 Turku, Finland

Photoacoustic spectroscopy (PAS) is recognized as a sensitive method for trace gas analysis. Even ppt-level concentrations can be detected with efficient laser setups. Recently, PAS has been combined with tunable diode lasers. Attention has also been given to the development and improvement of the sensing element itself, and thus, novel sensing methods have been proposed [1, 2].

In this work, a novel and sensitive photoacoustic approach to detect weak pressure variations [3] has been applied to tunable diode laser spectroscopy. As a pressure sensor a micromechanical cantilever was used (see fig. 1). The position of the cantilever was measured with a compact Michelson-type interferometer.

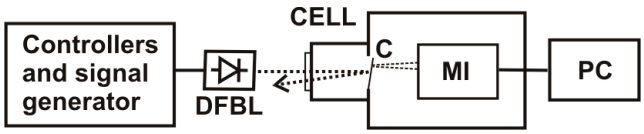


Fig. 1. Photoacoustic measurement setup: DFBL, distributed feedback laser; C, cantilever; MI, Michelson interferometer; PC, personal computer.

Our aim was to demonstrate the feasibility of this technique combined with diode lasers to detect trace gases. For that purpose the $R(18)$ rotational line of the $[00^00]_I$ _ $[30^01]_{II}$ vibrational band of CO_2 near 1572 nm was detected with a distributed feedback (DFB) diode laser. The photoacoustic cell, originally designed for a black body excitation source [1], was a cylinder with a diameter of 1 cm and a volume of 8 cm^3. The micromechanical cantilever (4 mm □ 2 mm, thickness of 5 □m) was made of silver-coated silicon and was attached to the back of the cylinder. Wavelength modulation of the laser was used to avoid the broadband absorption of the windows and cell walls. The method proved to be very sensitive and the detection limit was estimated to be 7 ppm. Expressed as a noise equivalent sensitivity this corresponds to 2.8 _ 10^{-10} $cm^{-1}WHz^{-1/2}$.

References

[1] K. Wilcken, and J. Kauppinen, Applied Spectroscopy, **57**, 1087-1092 (2003)

[2] A. Kosterev, Y. A. Bakhirkin, R. F. Curl, and F. K. Tittel, Optics Letters, **27**, 6213-6217 (2002)

[3] J. Kauppinen, K. Wilcken, I. Kauppinen, and V. Koskinen, Microchemical Journal, **76,** 151-159 (2004)

B-8

Mid infrared laser sensors for remote detection of explosives

Wolfgang Schade [1,2], Ulrike Willer [1], Thomas Keune [1], Gerhard Holl [3]

[1] Technische Universität Clausthal, Institut für Physik und Physikalische Technologien, Leibnizstrasse 4, 38678 Clausthal, Germany

[2] Technische Universität Clausthal, LaserApplikationsCentrum, Arnold Sommerfeld Strasse 6, 38678 Clausthal, Germany

Phone: +49 5323 72 2061, Fax: +49 5323 72 3318, wolfgang.schade@tu-clausthal.de

[3] Wehrwissenschaftliches Institut fuer Werk-, Explosiv-, und Betriebsstoffe (WIWEB), 53913 Swisttal, Germany

Laser optical methods are very promising for selective and sensitive non-intrusive detection of explosives under real-time conditions. With compact and portable lasers and fiber optics remote sensors can be set up which will find various applications in threat detection. In general, explosives have very low vapor pressure; therefore the analysis of different explosives in the gas phase is problematic under ambient air conditions. However, contrary to TNT or RDX the explosive TATP (triacetone-triperoxide) has a very high vapor pressure and therefore allows mid-infrared (MIR) spectroscopic sensing of evaporated compounds, e.g. peroxides with fundamental absorption bands between 7 and 8 µm. Even at room temperature conditions the concentration of peroxides in the presence of TATP is in a range that easily can be detected by MIR laser absorption spectroscopy. In combination with special fiber coupled absorption sensors or multi-reflection elements for evanescent-field spectroscopy mobile MIR sensors are developed and used for security applications.

Narrow bandwidth and tunable MIR laser radiation is generated by difference frequency generation (DFG). Two single mode diode lasers (775 and 860 nm) are used as pump and signal waves for the DFG and $AgGaS_2$ with type II phase matching as nonlinear medium [1,2]. In the present investigation the crystal cut is _ = 50° for generation of MIR laser radiation around 7.9 µm. As MIR sensor elements a simple absorption element or a multiple reflection element (evanescent field spectroscopy) are used [3].

In addition, cavity ring down experiments are in progress to enhance the sensitivity. First results will be reported at the conference for TATP detection.

This work is financially supported by the German Ministry of Defence under contract E/E210/4D065/4F101 (MoSEV).

References

[1] V. Petrov, C. Rempel, K.-P. Stolberg, W. Schade, Appl. Opt., 37, 4925 (1998).

[2] L. Wondraczek, G. Heide, G.H. Frischat, A. Khorsandi, U. Willer, W. Schade, Glass Sci Technol. 77, 68 (2004).

[3] U. Willer, D. Scheel, I. Kostjucenko, C. Bohling, W. Schade, E. Faber, Spectrochimica Acta Part A 58, 2427 (2002).

B-9

Rotationally resolved diode laser jet spectrum of propadienone (CH_3CCO) in the ν_2 band region

P. B. Davies, P. J. O'Sullivan, R. J. Livingstone and Z. Liu

Department of Chemistry, University of Cambridge,

Lensfield Rd., Cambridge CB2 1EW, UK.

The unstable molecule propadienone (methylene ketene) is the third member of the cumolenone series (H_2C_nO). In contrast with the first two members of this series, formaldehyde and ketene, no rotationally resolved infrared spectra have been reported. However, the pioneering work from the Monash microwave group has provided rotational and distortion parameters for the ground state of the molecule. In particular they demonstrated the non-rigidity of the molecule associated with the double minimum potential of the ν_{12} mode. We have generated propadienone by the pulsed thermolysis of acrylic anhydride in quartz or ceramic tubes heated to 1000^{o}C, which were an integral part of a diode laser jet spectrometer. The complete spectrum between 2123 cm^{-1} and 2133 cm^{-1} was recorded, corresponding to the absorption position for the intense C=O stretching mode reported by Chapman et al in the matrix. This mode should have the appearance of a parallel band of a near prolate top (κ = -0.998). Several series of lines were identified in the jet spectrum but the spectrum is clearly perturbed. Nevertheless using ground state combination differences it has been possible to assign 73 lines in the spectrum of K_a = 0 and 1 sub-bands. The ground state combination differences give rotational constants in good agreement with the microwave values.

B-10

Diode laser frequency tuning cycles stabilization at kHz level

A. Nadezhdinskii

NSC of A.M.Prokhorov General Physics Institute

38 Vavilov str., 119991 Moscow, Russia

NAD@nsc.gpi.ru

Diode Laser (DL) frequency stability is important for many DL applications. In [1] DL frequency cycles stabilization was proposed. It combined DL frequency tuning with tuning cycles stabilization. Now this approach is widely used in our experiments as well as by several other groups.

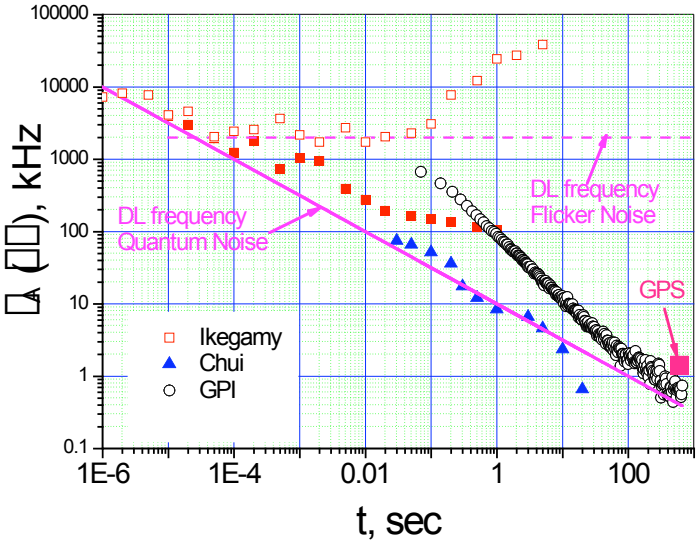


Fig. 1 Allan plot of DL frequency; solid line represents DL frequency quantum noise, dashed line – DL frequency flicker noise.

Fig. 1 shows Allan deviation of DL frequency demonstrating kHz stability close to needs of Global Position System (GPS) [2]. In present case spectral line of water vapor at low pressure (WHH 600 MHz) was used for stabilization. Comparison with experiments of traditional frequency stabilization will be presented. Dominating noise mechanisms such as DL frequency quantum noise and flicker noise due to excitation current density fluctuations will be considered.

References

[1] Yu. Kosichkin, A. Kuznetsov, A. Nadezhdinskii, A. Perov, E. Stepanov, Sov. J .Quantum Electronics, **12**, 518 (1982)

[2] R. Fox, S. Diddams, A. Bartels, L. Hollberg, Appl. Opt., **44**, #1, 113-120 (2005)

B-11

Shot noise limited TDLS

A. Nadezhdinskii

NSC of A. M. Prokhorov General Physics Institute

38 Vavilov str., 119991 Moscow, Russia

NAD@nsc.gpi.ru

Shot noise is noise of current due to the fact that electron in our experiments is particle [see separate poster]. For constant current value its spectral density can be calculated straightforward:

Eq. 1 $$G(i) = \int dt_1 \int \exp\left[j2\pi f(t_2 - t_1)\right] dt_2 \left\langle \Delta i(t_1) \Delta i(t_2) \right\rangle = ei$$

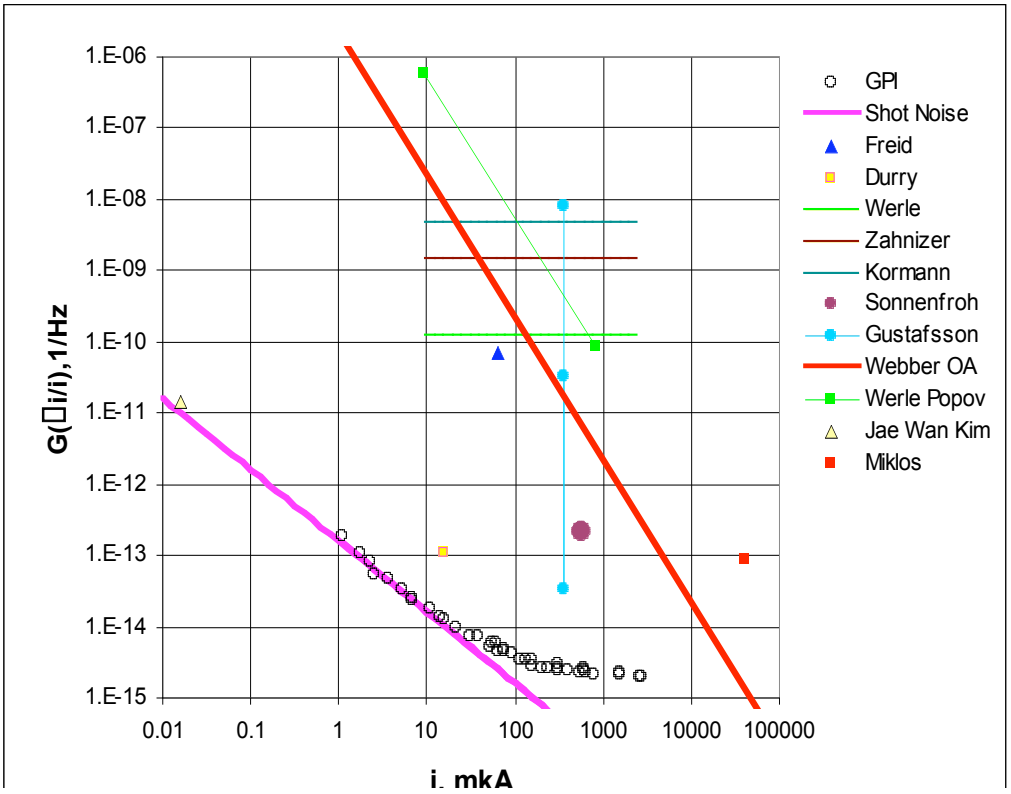


Fig. 1 Spectral density of relative photocurrent noise G(Δi/i) as function of photocurrent value

Best results known to author of measurement of spectral density relative photo-current noise are presented on Fig. 1. Traditionally information in referred papers was not enough for picture under consideration. Allan plots were used frequently to obtain necessary spectral density. Shot Noise line represents calculation using Eq. 1. Analysis of results presented will be given.

It is obvious, that shot noise dominates at small photo-current values (< 100 mkA). In our experiments it is important for systems with topography reflector [see separate poster]. For majority application diode laser quantum noise dominates [see separate poster].

B-12

Diode laser quantum noise

A. Nadezhdinskii

NSC of A. M. Prokhorov General Physics Institute

38 Vavilov str., 119991 Moscow, Russia

NAD@nsc.gpi.ru

Diode laser quantum noise is fundamental limit of possible TDLS sensitivity when trace molecule detection is considered. Spontaneous emission is physical origin of DL quantum noise (see separate poster).

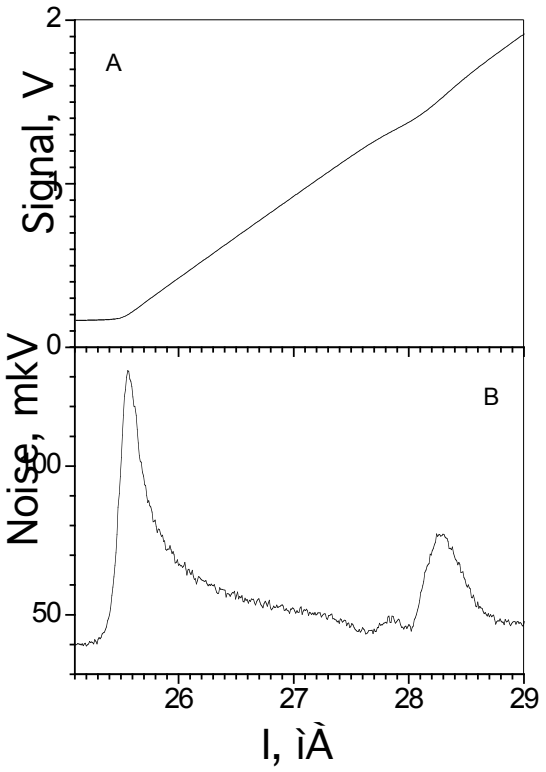


Fig. 1 Recorded signal (A) and its noise (B) as function of excitation current near diode laser threshold.

Fig.1A shows photo-diode signal as function of excitation current near diode laser threshold. Weak water vapor line at low pressure can be observed at right part of graph. Noise of recorded signal is presented on Fig1B. Several features can be mentioned: peak near threshold (typical for phase transitions); constant quantum intensity noise above threshold; presence of quantum frequency noise (maxima on spectral line slope); correlation of frequency and intensity quantum noises (asymmetry of frequency noise features). Both intensity and frequency quantum noises can limit absorption TDLS sensitivity. Correlation of frequency and intensity quantum noises produces spectral line asymmetry and has to be taken into account for accurate line shape measurements.

Software developed will be presented with several examples of diode laser noise investigations.

B-13

Ethanol vapor detection limited by diode laser frequency quantum noise

A. Berezin, S. Malyugin, T. Moskalev, A. Nadezhdinskii, D. Namestnikov, Ya. Ponurovskii, Yu. Shapovalov, D. Stavrovskii, I. Vyazov, V. Zaslavskii

NSC of A. M. Prokhorov General Physics Institute

38 Vavilov str., 119991 Moscow, Russia

NAD@nsc.gpi.ru

Aim of present paper was trace ethanol vapor detection inside moving car. To achieve this aim we had to solve several fundamentals goals being important for many TDLS applications.

Ethanol is broad band absorber as it was introduced in [1]. Ethanol spectrum has not resolved structure because of spectral lines overlapping even at low pressures. Spectra of this type could be considered as challenge for TDLS. Up to authors knowledge first successful trace broad band absorber detection was demonstrated in [2, 3]. Successful solution of this problem opens new areas of TDLS applications in complex molecules detection as well as impurity's concentration measurement in solids and liquids [4].

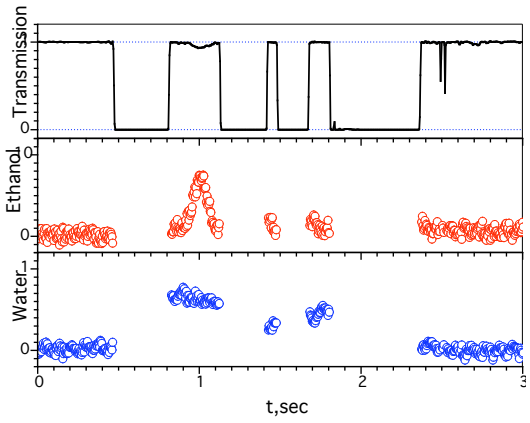


Fig. 1 Event recording of vehicle passing with imitation of drunken driver breath at front seat. Upper graph – transmission, middle and lower graphs stand for excess alcohol and water contents, respectively.

Second problem is related to TDLS selectivity. In present work trace ethanol absorption as small as 10^{-6} has to be measured in presence of water vapor having 4 orders of magnitude more intensive absorption in spectral range under consideration. This problem was also solved.

Third goal: real time molecule detection is important for many TDLS applications. In present work trace molecule detection with time resolution better than 1 ms was demonstrated.

Necessarily detection sensitivity needs achievement of fundamental limited absorption sensitivity. In present work absorption sensitivity limited by diode laser frequency quantum noise was demonstrated.

Software developed and results of test experiments will be presented (see Fig. 1).

Present work is example when obtained concentrations themselves are not representative. On other hand, ratio of different molecules concentrations determined has to be considered as measure of event under analysis.

[1] K. L. McNesby, R. T. Wainer et al.: Appl.Opt. **39**, 5006 (2000).

[2] A. Nadezhdinskii, A. Berezin et al.: Spectrochim. Acta Part A **55,** 2049 (1999)

[3] A. I. Nadezhdinskii, A. G. Berezin, O.V. Ershov: Appl. Phys. B **75,** 203 (2002)

[4] A. W. Mantz, private communication

B-14

Applications of Chernin four-objective multipass matrix system

A. Berezin, S. Chernin, L. Medvedev, A. Nadezhdinskii, Ya. Ponurovskii, S. Rudov, D. Stavrovskii

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

e-mail: stavr@nsc.gpi.ru

Chernin multipass matrix systems were designed in the last quarter of 20-th century as further development of classical White system [1, 2]. Much greater amount of passes can be realized in matrix systems due to additional one field and one or two objective mirrors, which transform string of images on field mirror surface into matrix of images. That's why matrix systems are preferable to form long optical way in small volume.

Two long-way optical cells were designed at DLS-laboratory of A. M. Prokhorov General Physics Institute. The cells are based on Chernin four-objective multipass matrix system. 300 and 40 meters optical ways were realized in volumes of 14 and 2 liters. Both cells can be evacuated and then filled with gas mixture to be necessary for experiments.

The first field of those cells application at DLS-laboratory is tunable diode laser spectroscopy (TDLS). The cells are used as a part of sensitive TDLS gas-analyzers. Limits of detection at the level of 1…10 ppt can be achieved for a lot of atmosphere pollutions, which are of great interest (green-house, toxic gases). The gas-analyzers with Chernin system cells were successfully used for methane distribution measurements in atmosphere of Moscow and Baikal Lake regions. Those analyzers were mounted on a car and on a ship. Another branch of high-sensitive TDLS gas-analyzer application is isotope ratio measurements. Experimental prototype of the $^{13}C/^{12}C$ analyzer is under investigation now at DLS-laboratory (see another abstract).

The second, unusial field of Chernin system cells application is the experimental test of the Universe optical isotropy. If the Universe is not isotropic, for example like anisotropic crystal, the fact of anisotropy can be stated in the experiment with light beams of different polarization. For sensitive measurements an extremely long optical way is desirable. 300 m cell (600 passes) was used to measure the limit of the Universe optical isotropy. The results obtained are discussed.

References

[1] Chernin, S.M., *J. Mod.Opt*., 2001, **48**, 619.

[2] White, J. U., 1942, *J. Opt. Soc. Am*., **32**, 285.

B-15

Use of injection locking for reducing optical feedback effects and residual amplitude modulation in wavelength modulation spectroscopy

M. Vainio [a], M. Merimaa [b], and K. Nyholm [b]

[a] Metrology Research Institute, Helsinki University of Technology, P.O. Box 3000,

FI-02015 TKK, Finland;

[b] Centre for Metrology and Accreditation (MIKES), P.O. Box 239, FI-00181 Helsinki, Finland

Email: markku.vainio@tkk.fi

We have studied injection locking as a way to reduce detrimental optical feedback effects and residual amplitude modulation (RAM) in wavelength modulation spectroscopy. Our experimental set-up is a diode-laser-based spectrometer, which is designed for high-precision spectroscopy of iodine (I_2) hyperfine structure. The spectrometer utilizes saturation spectroscopy with collinear geometry in an external iodine cell, and the standard third-harmonic technique is used to lock the laser frequency to the narrow hyperfine components of I_2. The set-up is developed particularly in order to measure, together with a femtosecond frequency comb generator, the absolute frequencies of various transitions of iodine near 633 nm. To obtain good frequency accuracy, special attention has been paid to minimization of frequency shifts arising e.g. from asymmetric beam profile. This has been made by using an injection-locking scheme with a microlensed diode laser as the slave laser and a stable external-cavity diode laser (ECDL) as the master laser [1].

The ECDL determines the spectral properties of the master-slave system and provides convenient frequency tuning. On the other hand, intensity of the system output beam is not notably affected by the ECDL, and the spatial and spectral purity of the beam can be independently optimized. Moreover, RAM is effectively suppressed in the injection-locking scheme, since the intensity variations of the master laser are not transferred to the slave laser.

Injection locking also significantly reduces slave laser's sensitivity to optical feedback. In practice, the feedback effects are fully suppressed as long as proper injection locking is sustained. With diode lasers reliable injection locking is normally easy to obtain over a relatively large frequency range. For instance, in our spectrometer set-up the injection locking range of approximately 2 GHz is attainable already with a seed ratio as small as 0.02.

[1] M. Vainio, M. Merimaa, and E. Ikonen, "Iodine spectrometer based on a 633-nm transmission-grating diode laser," *Meas. Sci. Technol*. (sent).

B-16

Observation of stark level crossing signals in $7^2D_{3/2}$ Cs applying two-step diode laser excitation

M. Auzinsh, K. Blushs, R. Ferber, F. Gahbauer, A. Jarmola, and M. Tamanis

Department of Physics and Institute of Atomic Physics and Spectroscopy, University of Latvia, 19 Rainis Blvd., LV-1586 Riga, Latvia

jarmola@latnet.lv

Two tunable diode lasers have been applied for stepwise excitation $6^2S_{1/2}$ → $6^2P_{3/2}$ → $7\,^2D_{3/2}$ of the $7^2D_{3/2}$ level of atomic cesium in the presence of an external dc electric field. The Stark splitting for magnetic sublevels m_F of the hyperfine F=2,3,4,5 levels of the $7^2D_{3/2}$ state, based on polarizabilities from [1], is given in Fig. 1. The experiment was aimed to detect resonance signals of two level crossings at ca. 1300 and 1800 V/cm. Cesium vapor was produced in a sealed glass cell kept at room temperature. An electric field up to E_{el} = 2400 V/cm was applied via transparent Stark electrodes separated a 2.5 mm gap. For the first step, the 852.1 nm beam of the diode laser (LD-0850-100sm laser diode), actively stabilized by the Cs atomic clock method was used to excite the $6^2P_{3/2}$ state. The laser beam $\mathbf{e_1}$ was linearly polarized along the external electric field $\mathbf{E_{el}}$ direction ($\mathbf{e_1}||\mathbf{z}$). The second laser beam $\mathbf{e_2}$, polarized as $\mathbf{e_2}||\mathbf{y}$, was sent in the counter-propagating direction to induce the $6^2P_{3/2}$ → $7^2D_{3/2}$ transition at 698.3 nm, using a Hitachi HL6738MG laser diode. The laser induced fluorescence (LIF) $7^2D_{3/2}$ → $6^2P_{1/2}$ was observed along the **z**-axis via a monochromator with 1.3 nm/mm inversed dispersion. The second laser was operating in a jittering mode within 1.2 GHz at 20 Hz repetition. The intensity I(**y**) of LIF linearly polarized along **y** axis was detected as dependent on E_{el}, see Fig. 2. The experiment reveals two resonant signals centered at the positions of m_F level crossings. The calculations performed by applying the density matrix rate equations [2] for Zeeman coherences demonstrate excellent agreement with the experimental signals, see Fig. 2.

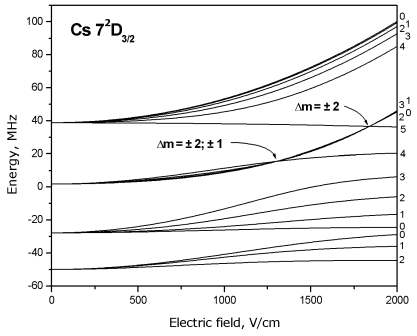


Fig. 1

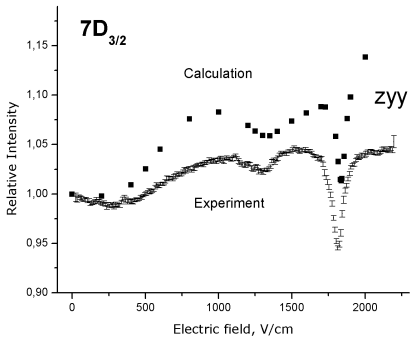


Fig.2

We acknowledge support from NATO Grant SfP-978029, EC 5th Frame Growth Grant G1MA-CT-2002-04063, Latvian Government Grants TOP-04-44 and ES-03-40, Latvian Science Council Grants 04.1308, 05.1865, the European Social Fund program.

References

[1] W. A. Van Wijngaarden and J. Li, *JQSRT* **52**, 555 (1994)

[2] Blush Kaspars, Auzinsh Marcis, Phys. Rev. A **69**, 063806 (2004)

B-17

Cavity-enhanced absorption detectors for monitoring of breath and ambient atmospheric air

V. L. Kasyutich, R. J. Holdsworth, P. A. Martin

School of Chemical Engineering and Analytical Science, University of Manchester, Manchester, M60 1QD, UK,

Philip.Martin@manchester.ac.uk

We demonstrate and characterize measurements of carbon dioxide in breath by means of wavelength-modulation off-axis cavity-enhanced absorption spectroscopy [1] using a tunable distributed feedback diode laser at *ca*. 1.6 μm and 1*f*-harmonic detection. Additionally, we present initial results for the monitoring of ambient atmospheric nitrogen dioxide concentrations using an optical off-axis cavity-enhanced absorption detector based on an intensity modulated violet diode laser at *ca*. 405 nm.

References

[1] V. L. Kasyutich et al., *Appl. Phys. B,* **75**, 755-761 (2002).

B-18

High-speed infrared hygrometer for respiratory diagnostics

Igor Shvarchuck [1,2], Graeme Murray [1]

[1] Fisher & Paykel Healthcare
15 Maurice Paykel Place, East Tamaki, Auckland, New Zealand.

[2] Physics Department, University of Auckland

38 Princes St., Auckland, New Zealand.

We present the details of a high-speed infrared hygrometer developed by Fisher & Paykel Healthcare for clinical research applications in respiratory humidification. In this context, it is desirable to be able to resolve the rapid variations in absolute humidity, temperature and flow information, within a breath cycle, during mechanical ventilation of a subject.

Tunable diode laser spectroscopy has been successfully used in the measurement of water vapour concentration in atmospheric research as well as in industrial applications (see for example [1-3]). However, the measurement of absolute humidity in respiratory gases in the context of mechanically ventilated patients presents significant technical challenges. This embodiment of the hygrometer employs a DFB diode laser running at 1.4 _m. Wavelength modulation spectroscopy is used to detect harmonic signals of an individual vibrational absorption line. Signal processing of the acquired harmonic signal does not require additional measurements of temperature or pressure, and takes into account the effects of ambient pressure changes. The response time of the instrument can be as low as 20 ms, which is essential for monitoring the humidity levels at high breath rates. Two key features of the measurement cell are its ease of sterilisation and small internal volume, which are both desirable for medical applications. The hygrometer is further combined with fast-response gas temperature probes and an ultrasonic flow meter to allow the thermodynamic properties of the humid air to be calculated.

[1] G. Durry, G. Megie, Applied Optics 39, 5601 (2000).

[2] R. D. May, J. Geophys. Res. 103, 19161 (1998)

[3] J. A. Silver, D. C. Hovde, Rev. Sci. Instrum. 65(5) 1691 (1994).

B-19

Studies of kinetic processes in H_2-N_2-O_2 plasmas by IR-TDLAS

O. Gabriel [1], S. Welzel [1], R. A. B. Zijlmans [2], G. Lombardi [1], G. D. Stancu [1], R. Engeln [2], D. C. Schram [2], J. Röpcke [1]

[1] INP-Greifswald, Friedrich-Ludwig-Jahn Str. 19, 17489 Greifswald, Germany

[2] Department of Applied Physics, Eindhoven University of Technology, P.O. Box 51, 5600 MB Eindhoven, The Netherlands

This contribution is focused on kinetic processes occurring in reactive plasmas containing a mixture of H_2, N_2 and O_2. This type of plasma is of interest for the understanding of phenomena (a) in plasma chemistry, (b) in plasma/surface interaction and also (c) in atmospheric physics. Our aim was to gain insight into the gas phase chemistry and plasma-surface interaction that take place in the formation and destruction of stable and transient molecules generated from atomic fragments issued from monomer precursors.

In order to cover a wide range of plasma conditions in terms of pressure, power, temperature, gas mixture, but also of kinetic processes, we studied two different types of plasma reactors by means of infrared tunable diode laser absorption spectroscopy (IR-TDLAS):

(i) First, a plasma expanding from a *thermal plasma source* is studied. A high density argon or nitrogen/hydrogen plasma with gas flows of typically 2 to 3 slm is created in the source, which expands into a low pressure (between 20 to 100 Pa) vessel. H_2, N_2 and/or O_2 are injected in the background. The plasma chemistry that occurred in the reactive low pressure plasma chamber is initiated by ion (Ar^+, N^+) and radical (N) fluxes [1] coming from the plasma source. Surface processes play an important role in molecule formation [2].

(ii) Further, a *planar microwave reactor* working at pressure of 1.5 mbar and power of 1.5 kW and at a flow of 0.5 slm was studied. In the microwave discharge the dissociation processes are mainly initiated by electron impact and gas-phase chemistry at the relatively high gas temperature of about 700 K. Also in this reactor the plasma-surface interactions are likely to contribute to the formation of molecules.

IR-TDLAS systems [3] were used to perform a quantitative analysis of species kinetics such as NO, NH_3 and N_2O. In N_2/H_2 plasmas with O_2 admixture the time dependent NH_3 destruction and NO formation was studied, suggesting (i) an ammonia production due to surface processes and (ii) an efficient NO production (and NH_3 destruction) caused by O_2 admixture. Based on a complementary approach for both types of plasmas the relevant chemical schemes have been identified by quantifying other by-products such as water.

References

[1] R. Engeln, S. Mazzoufre, P. Vankan, I. Bakker, and D.C. Schram, *Plasma Sources Sci. Technol.*, **11**, A100-A104 (2002).

[2] P. Van Kan, T. Rutten, S. Mazouffre, D.C. Schram, and R. Engeln, *Appl. Phys. Lett.* **81** , 418 (2002).

[3] J. Röpcke, L. Mechold, M. Käning, J. Anders, F.G. Wienhold, D. Nelson, and M. Zahniser, *Rev. Sci. Instrum.*, **71**, 3706-3710 (2000).

B-20

Laser sources for precision spectroscopy on atomic strontium

R. E. Drullinger, G. Ferrari, N. Poli, M. Prevedelli, F. Sorrentino, and G. M. Tino

Dipartimento di Fisica and LENS, Università di Firenze,

INFN Sezione di Firenze, INFM Unità di Firenze,

Polo Scientifico, 50019 Sesto Fiorentino, Italy,

Guglielmo.Tino@fi.infn.it

We present a new laser setup designed for high precision spectroscopy on laser cooled atomic strontium. The system, which is entirely based on semiconductor laser sources, delivers: 200 mW at 461 nm for cooling and trapping atomic strontium form a thermal source, 4 mW at 497 nm for optical pumping form the metastable $^3P_2$ state, 12 mW at 689 nm on linewidth less than 1 kHz for second stage cooling of the atomic sample down to the recoil limit, 1.2 W at 922 nm for optical trapping close to the "magic wavelength" for the 0-1 intercombination line at 689 nm.

The 689 nm laser was already employed to perform a frequency measurement of the 0-1 intercombination line with a relative accuracy of $2.3 \cdot 10^{-11}$ [1], and the ensemble of laser sources allowed the loading in a conservative dipole trap of multi-isotopes strontium mixtures [2].

The simple and compact setup developed represent one of the first steps towards the realization of transportable optical standards to be employed in future tests of fundamental physics on earth and in space.

References

[1] G. Ferrari, P. Cancio, R. E. Drullinger, G. Giusfredi, N. Poli, M. Prevedelli, C. Toninelli, and G. M. Tino, Phys. Rev. Lett. **91**, 243002 (2003).

[2] N. Poli, R. E. Drullinger, G. Ferrari, J. Léonard, F. Sorrentino, and G. M. Tino, submitted to Phys. Rev. A.

B-21

Open path atmospheric spectroscopy using room temperature operated pulsed quantum cascade laser

M. Taslakov, V. Simeonov, H. van den Bergh

Air and Soil Pollution Laboratory (LPAS), Swiss Federal Institute of Technology (EPFL); CH-1015 Lausanne, Switzerland

We report the application of a distributed feedback quantum cascade laser for 6 km long open path spectroscopic monitoring of ozone, water vapor and CO_2. The thermal chirp during a 200 ns long excitation pulse is used for fast wavelength scanning. Fast wavelength scanning has the advantage of not being affected by atmospheric turbulence, which is essential for long open path measurements. An almost linear tuning range of about 1.5 cm^{-1} is achieved. A line from the $\square_3$ vibrational band of the ozone spectra centered at 1049 cm^{-1} is used for ozone detection by differential absorption. The lowest column densities (LCD) of the order of 10 ppm.m retrieved from the absorption spectra for averaging times less than 1 min are comparable to the LCD measured with UV DOAS systems. The intrinsic haze immunity of mid IR laser sources is an additional important advantage of mid-IR open path spectroscopy, compared with standard UV-visible DOAS. The third major advantage of the method is the possibility to measure more inorganic and organic atmospheric species compared to the UV-visible DOAS.

The open path of 6 km is covered using average laser power of less than 0.2 mW (less than 1 W pulse power at 0.02% duty cycle – 200 ns pulse at 1000 Hz pulse repetition rate), which shows much higher efficiency of spectroscopy using narrowband laser source, compared to broadband light as Xe lamp. Laser operates at temperature 235 K achieved by water cooled Peltier element. The laser source and the IR detector are placed in the laboratory. A hollow corner cube retroreflector with a clear aperture of 35 mm disposed 3 km far from the laboratory reflects the IR beam back to the receiver. The detector is MCT type with 200 MHz bandwidth.

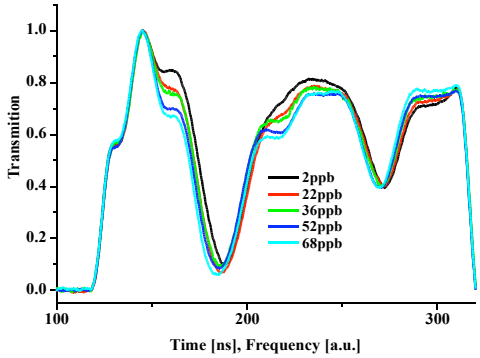


Fig. 1 Actual absorption spectra measured at 6 km open path.

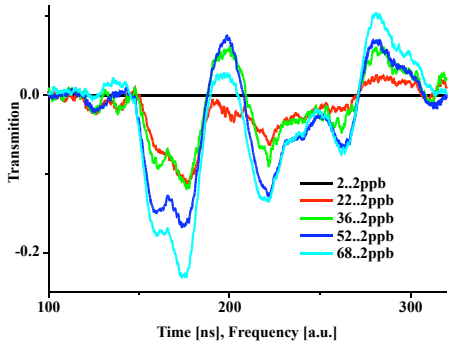


Fig. 2 Normalised absorption spectra measured at 6 km open path.

In Fig. 1 is shown a real received pulse for one minute averaging. The absorption lines of water vapor, O_3 at different concentration during the day and CO_2 are well separated from left to right. Fig. 2 shows the normalized spectra at different O_3 concentration. The day variations of absolute humidity variations are also well visible.

The low power consumption, compact size and non-cryogenic operation of the QCL based systems make them useful as autonomous field-deployable equipment.

B-22

A remotely controllable optical multi-pass system

Harald Verbraak and Harold Linnartz

Laser Center Vrije Universiteit, De Boelelaan 1083, NL 1081 HV Amsterdam

The Netherlands

In the past several optical multi-pass configurations have been proposed to improve the sensitivity of direct absorption experiments by increasing the effective path length through an absorbing medium. Well known geometries have been introduced by White [1], Welsh [2], Herriott [3,4], Perry [5], McManus [6] and Chernin [7,8] and their coworkers. Optical multi-pass configurations based upon these geometries use high quality spherical mirrors resulting in an efficient round trip refocusing that prohibit a divergence of the laser beam. Inherent to these spherical optical multi-pass systems is a rather critical alignment and as a consequence remotely controlled multi-pass systems have not been reported so far.

In this poster a planar multi-pass system is described in which the total number of passes can be varied in a defined way by using one single translation stage without the necessity of realigning the system [9]. To put this very clearly: this planar geometry is not as effective as the systems described in Refs. 1–8 in terms of effective absorption path length, but it offers a number of other advantages that are worth considering.

- The system is easily aligned.
- The system offers a possibility for remote control.
- The system allows a simultaneous multi-passing of different laser beams.
- The system can be made very flat (principally as flat as the diameter of the laser beam) which makes it very suited in experiments where space is limited.

Current applications are in reference gas cells for TDL calibration or in planar expansion experiments s in order to minimize Doppler effects.

[1] J. V. White, J. Opt. Soc. Am. 32 (1942) 285.

[2] H. L. Welsh, C. Cumming, E. J. Stansbury, J. Opt. Soc. Am. 41 (1951) 712.

[3] D. Herriott, H. Kogelnik, R. Kompfner, Appl. Opt. 3 (1964) 523.

[4] J. Altmann, R. Baumgart, C. Weitkamp, Appl. Opt. 20 (1981) 995.

[5] D. Kaur et al., Appl. Opt. 29 (1990) 119.

[6] J. B. McManus, P. L. Kebabian, M. S. Zahnisser, Appl. Opt. 34 (1995) 3336.

[7] S. M. Chernin, E. G. Barskaya, Appl. Opt. 30 (1991) 51.

[8] S. M. Chernin, J. Mod. Optic. 48 (2001) 619.

[9] H. Linnartz, Phys. Scripta 70 (2004) C24.

B-23

Non-invasive determination of porosity in pharmaceutical tablets using tunable diode laser spectroscopy

Tomas Svensson [1], Jonas Johansson [2], Stefan Andersson-Engels [1], Sune Svanberg [1] and Staffan Folestad [2]

[1] Department of Physics, Lund Institute of Technology, P.O. Box 118, SE-221 00 Lund, Sweden

[2] AstraZeneca R&D Mölndal, SE-431 83 Mölndal, Sweden

Physical properties of solids such as porosity are of great interest to the pharmaceutical industry. In this work porosity of solid pharmaceutical tablets is determined by using the fact that oxygen is dispersed in the material. This technique is referred to as GASMAS (Gas in Scattering Media Absorption Spectroscopy) and the general idea, as implied by the name, is to use gas (*e.g.* oxygen) absorption. In contrast to common absorption spectroscopy, the photon path length is in this case unknown due to massive light scattering. Full understanding of the absorption signal is therefore reached first after determination of the mean photon path length. Time- or frequency domain measurements are employed to extract these path lengths.

Diode lasers emitting light in the range where oxygen absorbs (760-765 nm) are used as light sources. These are modulated and wavelength tuned over one of the narrow oxygen absorption lines. Transmitted light is detected using a PMT. Lock-in amplification is used to detect the absorption signal.

The influence of tablet particle size and tablet density were investigated using the GASMAS technique. Comparison with mercury based porosity measurements were performed. The results show that correlation of the GASMAS signal to tablet hardness as well as particle size can be established.

B-24

In-situ monitoring of low ppb level moisture and other critical contaminants in ultra pure speciality gases, for electronic manufacturing

H. Beese [1], W. Grählert [1], V. Hopfe [1], P. Kaspersen [2], A. Bohman [2], F. Petzold [3], E. Wudy [3], P. Mackrodt [4]

[1] Fraunhofer Institut für Werkstoff- und Strahltechnik, Winterbergstrasse 28, Dresden 01277, Germany

[2] Norsk Elektro Optikk, Solheimveien 62A, Lørenskog N-1471, Norway

[3] Intega Hans J. Jehl GmbH, Bergener Ring 51, Ottendorf-Okrilla 01458, Germany

[4] Physikalisch Technische Bundesanstalt, Bundesallee 100, Braunschweig 38116, Germany

A tunable diode laser absorption spectroscopy based sensor has been designed and tested for measurements of up to 3 trace gas species simultaneously in bulk and specialized (highly reactive) gases, e.g. N_2, He, Ar, H_2, NH_3, SiH_4, HCl. Contaminants being critical for application of this ultra pure gases in microelectronics manufacturing are H_2O, O_2, (CO/CO_2), hydrocarbons. Based on spectra modeling optimal wavelength regions for DFB lasers have been identified which ensure interference free detection of said contaminants.

Further described is a dynamic gas mixing and calibration system for trace gas supply down to the upper ppt range beginning from 100% gas components.

Besides the optimization of essential parts of the VIS/NIR laser diode spectrometers, the gas cell has been designed concerning low detection limit and short response time of concentration changes. Challenging was furthermore to set-up a ruggedised design which can cope with extremely surface active and corrosive gases.

The developed sensor reaches detection limits down to the low ppb-level for moisture and low ppm-level for oxygen in inert gases at atmospheric pressure. For application in pressurized gas lines also pressures level up to 5 bar were tested with good performance. Multi point calibration performs excellent linearity over 4 decades. For moisture calibration the curves have been referenced to a permeation tube based moisture generator being calibrated with a dew point hygrometer. Based on gas-specific background correction factors almost the same detection limits were reached in “challenging gases” like ammonia.

B-25

Simultaneous detection of HCl and HF by TTFMS and high frequency WMS

A. C. De Luca, G. Pesce, G. Rusciano and A. Sasso

Università di Napoli "Federico II"

Dipartimento di Scienze Fisiche

Complesso Universitario di Monte S.Angelo

Via Cinthia - 80126 Napoli - Italy

Laser-based systems have attained an increasing attention in recent years, due to their high sensitivity and selectivity. In particular, laser sensors based on the use of diode lasers emitting in the near- and mid-IR regions [1–2], represent a mature technology to achieve high sensitivity with a relatively cheap and small systems.

In this work, we present the development of a new compact sensor, based on the use of two different diode lasers, for continuous monitoring of chloridric and fluoridric acids. The purpose of the work is to perform in-situ measurements for diagnostic of exhaust gases coming from a waste inceneritor. In particular, HCl concentration is monitored by investigating the P(4) line at 1.7 μm in the ν_2 overtone vibrational band, while HF is detected observing the absorption of the R(3) line at 1.3 μm. These lines have a line-strength of 7.8_10^{-21} cm/mol and 2.8_10^{-20} cm/mol, respectively, and both are quite far from other lines which can introduce interference effects. As detection techniques we have used two different high frequency modulation techniques: for HCl detection we used Two-Tone Frequency Modulation Spectroscopy (f_1= 800 MHz and f_2=804 MHz) while for HF we followed a simpler approach based on Wavelength Modulation Spectroscopy (f=600 kHz). The two laser beams were overlapped and sent in a 30 m-long Herriott type multipass cell. All the optical elements are fixed on a breadboard (60x75 cm^2) and they have been properly designed to reduce as much as possible mechanical instability. The calibration of acid concentrations was performed by using known concentrations of water vapor lines close to the investigated HCl and HF lines. In spite of the differences in the two detection techniques, the sensitivities found for the detection of the two molecules were quite similar. Indeed the minimum detectable concentration at a total pressure of 100 Torr resulted to be 8 ppb and 18 ppb for HCl and HF, respectively. At atmospheric pressure these values were of the order of 0.2 ppm. Finally we tested the reproducibility of our measurements by repeating about twenty times the concentration measurements within several hours: from this analysis we estimated a precision around 10%.

References

[1] G. Pesce, G. Rusciano, A. Sasso: "Laser spectroscopy of OH fundamental vibrational band based on a difference frequency generator at 3 μm" , Chem. Phys. Lett. 374 425 (2003)

[2] G. Rusciano, G. Pesce, F. Pignatiello, A. Sasso: "A DFG-based spectrometer for high-sensitivity C_2H_2 and H_2O detection" Opt. Exp. 11 3010 (2003)

B-26

Stratospheric carbon monoxide in tropical convections: in-situ measurements with a mid-IR airborne spectrometer

F. D'Amato, P. Mazzinghi, S. Viciani, P. W. Werle,

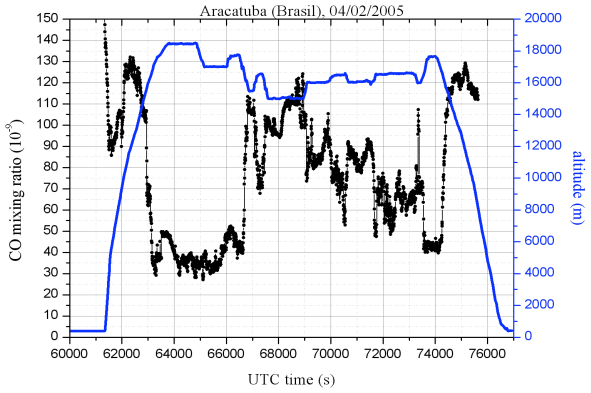
F. Castagnoli [1], M. De Pas [2], M. Giuntini [2]

INOA, Largo E. Fermi 6, 50125 Firenze, Italia, damato@inoa.it

[1] IFAC-CNR, V. Panciatichi 64, 50127 Firenze, Italia

[2] LENS, Università di Firenze, V. N. Carrara 1, 50019 Sesto Fiorentino (FI), Italia

The contribution of tropical thunderstorms to the production of NOx is one of the main goals of the European Project TROCCINOX (TROpical Convection, Cirrus, and Nitrogen OXides Experiment) [1]. A set of airborne atmospheric research instruments (including LIDAR, Gaschromatograph and other chemical and meteorological sensors) provided *in-situ* atmospheric data during a 4 weeks airborne measurement campaign over Brazil. We present the results of our in-situ measurements of carbon monoxide concentrations in the upper troposphere/lower stratosphere during the TROCCINOX-2 field campaign in Araçatuba (Sao Paulo, BR) in January-February 2005. We have operated an airborne mid-infrared lead-salt diode-laser spectrometer [2,3], where the laser has been tuned to the strongest CO absorptions in the fundamental R branch centered at 2170 cm^{-1}. The instrument was carried on board of the russian stratospheric aircraft M55 Geophysica. A first data sample of the measurements is shown below.



Flight profile of CO concentration and corresponding altitude vs. time.

This activity has been sponsored by EC through contracts EVK2-CT-2001-00122 and EVR1-2001-00020, and by ESA in the frame of the ENVISAT validation programme.

References

[1] See: http://www.pa.op.dlr.de/troccinox

[2] G. Toci, P. Mazzinghi, and M.Vannini, *Journal of Atmospheric and Oceanic Technology,* **16**, 1295-1302 (1999).

[3] M. Pantani, F. Castangnoli, F. D´Amato, M. De Rosa, P. Mazzinghi, P. W. Werle, Inf. Phys. & Technology **46**, 109-113 (2004).

Poster Session C

C-1 A tunable diode laser spectrometer for the simultaneous detection of H_2O and CO_2 in the martian atmosphere
T. Le Barbu, V. Zéninari, B. Parvitte, G. Durry

C-2 Gas detection using remote laser pointers: interpretation of results
J. Hodgkinson, B. van Well, M. Padgett and R. D. Pride

C-3 Diode laser spectroscopy measurement of oxygen A-band linestrengths
Robert J. Brecha

C-4 Photoacoustic trace gas detection with quantum-cascade lasers: application to nitric oxide
A. Elia, P. M. Lugarà, C. Giancaspro

C-5 Spectroscopic properties of long-wavelength BTJ-VCSELs
Alexandre Lytkine, John Tulip, and Wolfgang Jaeger

C-6 Methane detection with a quantum cascade laser photoacoustic spectrometer
A. Grossel, V. Zéninari, L. Joly, B. Parvitte, G. Durry, D. Courtois

C-7 Ultraviolet spectroscopy of SO_2 using diode lasers
Gabriel Somesfalean, Zhiguo Zhang, Mikael Sjöholm, and Sune Svanberg

C-8 A high precision pulsed QCL spectrometer for measurements of stable isotopes of carbon dioxide
J. B. McManus, D. D. Nelson, J. H. Shorter, R. Jimenez, S. Herndon, S. Saleska and M. Zahniser

C-9 Quantum cascade laser spectroscopy system for intra-puff measurements of the effects of iron oxide cigarette paper on CO and CO_2 deliveries
Danielle R. Crawford, Milton E. Parrish, Diane L. Gee, Charles N. Harward Sr.

C-10 No interference fringes above 10^{-6}
A. Nadezhdinskii

C-11 Diode laser based system with topographic reflector for trace molecules remote monitoring
A. Berezin, S. Malyugin, T. Moskalev, A. Nadezhdinskii, D. Namestnikov, Ya. Ponurovskii, S. Rudov, Yu. Shapovalov, D. Stavrovskii, I. Vyazov, V. Zaslavskii, E. Dianov, A. Kurkov, V. Paramonov

C-12 Tunable diode laser spectroscopy application for detection and isotope ratio measurements of UF_6 molecules
A. Nadezhdinskii, Ya. Ponurovskii, Yu. Shapovalov, D. Stavrovskii, D. Bolyasov, G. Grigor'ev, N. Gorshunov, S. Malyugin, Sh. Nabiev

C-13 Baseline in TDLS
A. Nadezhdinskii

C-14 Ratio measurement of water ortho/para nuclear spin isomers via TDLS in the vicinity of 1.392 _

S. Malugin, T. Moskalev, A. Nadezhdinskii, Ya. Ponurovskii, D. Stavrovskii

C-15 Pressure broadening and shift of I_2 near 675 nm

T. R. Dyke, J. L. Hardwick, and E. N. Wolf

C-16 Study of CH_4, C_2H_4 and air spectra with a diode laser photoacoustic spectrometer

V. A. Kapitanov, I. S. Tyryshkin, N. P. Krivolutskii, Yu. N. Ponomarev

C-17 Novel Helmholtz-based photoacoustic sensor for trace gas detection at ppm level using GaInAsSb/GaAlAsSb DFB lasers

M. Mattiello, M. Niklès, S. Schilt, L.Thévenaz, A. Salhi, D. Barat, A. Vicet, R. Werner, J. Koeth

C-18 Light directionality generated by partial coherent plane source

Mostafa Sahrai, and Habib Tajalli

C-19 A ground based remote sensing tunable diode laser - fiber amplifier instrument. Apllication to carbon dioxide detection

Haris Riris, James Abshire, Graham Allan, John Burris, G. James Collatz, Amelia Gates, Randy Kawa, Michael A. Krainak, Xiaoli Sun Arlyn Andrews, Arlyn Andrews

C-20 2.65 µm antimonide based diode lasers for vapour detection in the atmosphere of Mars

A. Vicet, A. Salhi, J. Angellier, D. Barat, Y. Rouillard, G. Durry, T. Lebarbu, A. Martinez, A. Ramdane

C-21 Line profile study by diode laser spectroscopy in the $^{12}CH_4$ □2+□4 band

D. Mondelain, P. Chelin, A. Valentin, D. Hurtmans and C. Camy-Peyret

C-22 Time resolved detection of nitric oxide from biological liquids with a quantum cascade laser

S. Thelen, D. Halmer, M. Horstjann, P. Hering, M. Mürtz

C-23 Gas analysis with quantum cascade lasers

O. Werhahn, J. Koelliker Delgado, D. Schiel

C-24 7.7-micron quantum cascade laser suitable for spectroscopy and isotopomer analysis of methane

N. Akikusa, T. Edamura, A. Sugiyama, T. Ochiai, Y. Takiguchi, H. Kan, and K. Uehara

C-25 Development of a transportable spectrometer based on an erbium fiber doped laser for multiple trace gas sensing

J. Cousin, W. Chen

C-1

A tunable diode laser spectrometer for the simultaneous detection of H_2O and CO_2 in the martian atmosphere

T. Le Barbu [a,b], V. Zéninari [a], B. Parvitte [a], G. Durry [a,b]

[a] *Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA), UMR CNRS 6089,*

Faculté des Sciences, BP 1039, F-51687 Reims Cedex 2 - France

[b] *Institut Pierre Simon Laplace (IPSL), Service d'Aéronomie, UMR 7620, CNRS-Réduit de Verri_res, B.P. 3, 91371 Verri_res-le-Buisson Cedex, France*

Laser absorption spectroscopy is highly efficient to provide in situ trace-gas measurements at high temporal and spatial resolutions and with a high selectivity in the analyzed species. It is used in the SDLA spectrometer, developed by Service d'Aéronomie with the support of the CNES and CNRS, to monitor H_2O, CH_4 and CO_2 in the middle atmosphere from stratospheric balloons. Based on the developed laser probing technique, we are developing with the support of CNES a laser sensor for studying the Martian atmosphere. The Martian atmospheric composition and pressure conditions enable the realization of a compact instrument. The main objectives are to determine water vapor and carbon dioxide fluxes and to study boundary layer properties. The sensor will provide in situ daily, diurnally resolved measurements of near-surface H_2O and CO_2 concentration over seasonal time scales.

The laboratory prototype of the sensor uses a Distributed Feedback InGaSb laser diode at 1877nm to monitor simultaneously H_2O and CO_2 over a 120cm folded path length. A diode laser spectrometer was used in the laboratory to study H_2O and CO_2 line intensities and self-broadening coefficients around 1877 nm. The spectral region ranging from 5327 cm^{-1} to 5329 cm^{-1} which is suitable for the *in situ* sensing of water vapor and carbon dioxide in the Martian atmosphere was studied. We have studied one line from the (011) ← (000) band of H_2O and two lines from the $(01^12)_I$ ← (000) band of CO_2. The results of intensity and self-broadening measurements are compared to available databases and previous experimental determinations.

C-2

Gas detection using remote laser pointers: interpretation of results

J. Hodgkinson [ac], B. van Well [b], M. Padgett [b] and R. D. Pride [a]

[a] Advantica, Loughborough, UK

[b] Dept of Physics and Astronomy, Glasgow University, Glasgow, UK

[c] Now at School of Engineering, Cranfield University, Bedfordshire, UK

j.hodgkinson@cranfield.ac.uk

There is great interest in remote gas detectors, based on tunable diode lasers, operating over distances of 10m or more[1,2,3]. These systems use a laser beam aimed through open space at a target, collecting the backscattered light and spectroscopically demodulating the signal. Applications include the detection of natural gas leaks from low-pressure distribution pipes, with a methane detector based on a tunable DFB laser emitting light at 1.65nm.

This detection geometry represents a significant step change within the gas industry from the use of pumped sampling sensors that detect gas concentrations at a single point in space. The new instruments present challenges for instrument designers and operators that cannot be fully addressed without also understanding the behaviour of the leaking gas plume.

We present results from the recently completed EC co-funded "VOGUE" project to develop a laser pointer instrument. Understanding the interaction between the laser beam and the leaking gas was a core element of this project and was used to inform both instrument design and operation guidelines.

We used a Gaussian model of leaking gas concentrations, based on a previous study of gas dispersion performed using a wind tunnel. A computer model of the instrument response was developed, taking a line integral of gas concentrations through the simulated cloud from the position of the instrument to a target position on the ground. Both positions could be changed in the model in three dimensions, as could the type of background target (using their different characteristic reflectivities).

The model enabled us to investigate trends in behaviour under controlled conditions more rapidly than would be the case when performing field tests. We report our findings concerning the optimum instrument height, pointing accuracy required, ability to "zero trace" (confirm the absence of gas) and the intuitive use of the readings to locate gas leaks. In some circumstances the apparent leak location can be ambiguous, however strategies have been developed to allow users to avoid such confusion. Conclusions drawn from the model compare well qualitatively with the results of instrument field tests.

References

[1] T. Iseki, H. Tai and K. Kimura. Meas. Sci. Technol. 11, 594-602 (2000).

[2] R. T. Wainner, B. D. Green, M. G. Allen, M. A. White, J. Stafford-Evans and R. Naper. Appl. Phys. B 75, 249-254 (2002)

[3] B. van Well, S. Murray, J. Hodgkinson, R. Pride, R. Strzoda, G. Gibson and M. Padgett, J. Opt. A, in preparation.

C-3

Diode laser spectroscopy measurement of oxygen A-band linestrengths

Robert J. Brecha

Physics Dept. and Electro-optics Program

Univ. of Dayton, Dayton, OH 45469-2314 USA

We report a set of linestrength and self-broadening measurements for the oxygen A-band at 13122 cm^{-1} using tunable diode laser absorption spectroscopy. The diode lasers are scanned over individual lines and the absorption at different pressures is recorded; from these data the linestrength for each transition is obtained. Average values for each transition are compared to those previously published, and in particular a comparison with the HITRAN 2004 database values will be presented. Our results indicate linestrengths 8% lower than HITRAN values on average, but in approximate agreement with some other published results.

C-4

Photoacoustic trace gas detection with quantum-cascade lasers: application to nitric oxide

A. Elia, P. M. Lugara, C. Giancaspro,

LIT³ INFM Regional Laboratory,

Dipartimento Interateneo di Fisica "M. Merlin", Università di Bari

Via Amendola 173, I-70126 Bari, Italy

In recent years, the development of new mid-infrared laser sources has resulted in the implementation of different spectroscopic methods for trace-gas sensing applications such as air pollution monitoring, medical diagnostics, combustion diagnostics, industrial-process control. In particular, single mode distributed feedback (DFB) quantum cascade lasers (QCLs) have become very attractive for mid-infrared gas sensing techniques thanks to tunability in the spectroscopically important region from 3 to 20 μm (fingerprint region), where many polluting gases exhibit strong fundamental rotovibrational absorption transitions. Moreover, single mode quantum cascade lasers show excellent properties in terms of narrow linewidth, average power (tens of milliwatts) and room temperature operation. In combination with these laser sources, photoacoustic spectroscopy (PAS) offers the advantage of high sensitivity (ppb detection limits), compact set-up, fast time-response and simple optical alignment.

In this work, we report on a photoacoustic trace gas sensor for the detection of nitric oxide (NO) with a detection limit of 500 parts in 10^9 by volume (ppbv). The detection and quantification of NO in ppb range play an important role in monitoring environmental pollution and in medical diagnostics. NO is formed during high temperature combustion process and it is implicated in depletion of Earth's ozone layer, generation of photochemical smog and acid rain. More recently it was demonstrated that NO is involved in many biological functions and human pathologies; it has been proved that its detection in human breath is important in non-invasive diagnoses of asthma and inflammatory lung diseases. The trace gas sensor is based on a thermoelectrically cooled DFB-QC laser operated in pulsed mode near 5.3 μm with an average laser power of 8 mW. The modulated laser beam was coupled to a resonant photoacoustic cell excited in its first longitudinal mode. The sensitivity limit of the present PA sensor for the detection of NO and its possible future improvements are surely interesting for applications in ppbv and sub-ppbv range.

C-5

Spectroscopic properties of long-wavelength BTJ-VCSELs

Alexandre Lytkine [1], John Tulip [1], and Wolfgang Jaeger [2]

[1] ECE Dept., [2] Chem. Dept., Univ. of Alberta, 9107-116 St., Edmonton, AB, Canada T6G 2V4

We have measured for the first time nonlinear current tuning coefficients and a phase shift between amplitude and frequency modulations of buried tunnel junction (BTJ) VCSELs (VERTILAS, Germany), and have studied other their spectroscopic properties, such as power and frequency stability, capability of resolving Doppler-limited absorption lines, and noise properties.

The BTJ technology enables the development of InGaAlAs/InP VCSELs in the 1.3 - 2 μm range with low threshold currents (~ 0.5 mA) and single-mode output up to 1.7 mW [1]. The suitability of BTJ-VCSELs for time-resolved TDLS and their capability of performing multi-species gas analysis have been demonstrated recently [2-3].

We have developed a bench-top BTJ-VCSEL-based spectroscope containing a 1.8-m one-pass absorption cell and a TE-cooled laser mount (THORLABS) accepting VCSELs in TO-46 packages. To date we have obtained from VERTILAS the BTJ-VCSELs emitting at 1512, 1577, and 1654 nm and intended for detecting NH_3, H_2S, and CH_4 respectively. We have implemented the methods of direct absorption and wavelength-modulation spectroscopy with fully digital signal processing. A LabVIEW-based computer code has been developed for multi-species gas analysis in time domain with averaging of $10^2 – 10^3$ single-scan absorption spectra. A digital lock-in amplifier (National Instruments) has been exploited in wavelength-modulation approach.

The 1577-nm laser was tuned continuously over a 9.61-nm (38.62-cm^{-1}) interval, the widest among tuning ranges of all the BTJ-VCSELs under study, by changing both the laser temperature and injection current in the 0-50 ^{0}C and 1.6-6.5 mA ranges respectively. The current tuning rates were found to be directly proportional to the injection current with proportionality coefficients of 0.42 and 0.55 cm^{-1}/mA^2 at 0 and 50 ^{0}C respectively. Gas mixture CO:CO_2 with a multitude of absorption lines in the tuning range of the 1577-nm laser was used to measure a phase shift between the amplitude and frequency modulations by the following method. The laser modulated with a sinusoidal waveform was tuned slowly by a DC bias until one of the absorption lines detected by the direct absorption method became twinned in the end of a laser scan. The time delay between the end of the laser scan defined by the twinned absorption line and the local maximum in the laser power resulted from the sinusoidal modulation was measured and converted into phase angle, which appeared to change from 0 to – 54 arc deg when the modulation frequency was increased from 100 Hz up to 500 kHz.

The influence of the spectroscopic properties of the BTJ-VCSELs on the results of gas concentration measurements performed with different methods will be analyzed, and the BTJ-VCSELs will be compared with edge-emitting laser diodes with regard to TDLS applications.

References

1. C. Lauer, M. Ortsiefer, R. Shau, J. Rosskopf, G. Bohm, R. Meyer, and M.-C. Amann, Physica Status Solidi (C), 1(8), 2183-2209 (2004).
2. G. Totschnig, M. Lackner, R. Shau, M. Ortsiefer, J. Rosskopf, M.-C. Amann , and F. Winter, Appl. Phys. B, 76(5), 603-608 (2003).
3. A. Lytkine, W. Jaeger, J. Tulip, Proc. of SPIE, 5594, 155-163 (2005).

C-6

Methane detection with a quantum cascade laser photoacoustic spectrometer

A. Grossel [a], V. Zéninari [a], L. Joly [a], B. Parvitte [a], G. Durry [a,b], D. Courtois [a]

[a] *Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA), UMR CNRS 6089,*

Faculté des Sciences, BP 1039, F-51687 Reims Cedex 2 - France

[b] *Institut Pierre Simon Laplace (IPSL), Service d'Aéronomie, UMR 7620, CNRS-Réduit de Verri_res, B.P. 3, 91371 Verri_res-le-Buisson Cedex, France*

The Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA, Reims, France) has developed since 1997 a photoacoustic cell based on differential Helmholtz resonance for infrared gas detection in collaboration with the Institute of Atmospheric Optics (IAO, Tomsk, Russia) [1]. This cell was used in conjunction with a near-infrared diode laser to detect methane. The main origin of this gas choice is the need of gas companies which are confronted to the leak problems of their gas distribution networks. The typical commercial methane detectors based on flame ionization present the main disadvantages to be non-specific to methane. Other pollutants such as C_2H_4, C_3H_8… may introduce false alarms.

In recent years molecular gas lasers and diode lasers have been widely used for in-situ pollution monitoring. The photoacoustic sensor described here represents an effective spectroscopic technique for detection of ambient trace gases due to its intrinsically high sensitivity, large dynamic range and comparatively simple instrumentation. The detection limit of this technique is mainly determined by the characteristics of the laser used (output power, tunability, single mode emission…) and the photoacoustic cell sensitivity. The feasibility of methane detection has been demonstrated with near-infrared diode lasers and the system has been improved significantly so as to increase sufficiently the sensitivity for sub-ppm methane detection [2].

The use of quantum cascade laser gives the possibility to improve the detection limit thanks to its high power and its emission in the methane fundamental bands. We will present the first results obtained with the association of our photoacoustic cell and a quantum cascade laser emitting in the 7.9µm region for the methane detection.

[1] V. Zéninari et al, Gas detection device, International Patent No. WO 03/083455 A1 (2003)

[2] V. Zéninari et al, Infrared Physics and Technology, 44, 253-261, (2003)

C-7

Ultraviolet spectroscopy of SO_2 using diode lasers

Gabriel Somesfalean [a), b)], Zhiguo Zhang [b)], Mikael Sjöholm [a)], and Sune Svanberg [a)]

[a)] *Department of Physics, Lund Institute of Technology, P.O. Box 118, SE-221 00 Lund, Sweden*

[b)] *Department of Applied Physics, Harbin Institute of Technology, P.O. Box 406, Harbin 150001, P. R. China*

Most atoms and molecules exhibit strong electronic transitions in the ultraviolet (UV) spectral range. Compact and low-cost diode-laser-based spectrometers would facilitate the widespread application of UV spectroscopy for in situ and remote gas measurements, which has been largely prevented so far by the size, weight, cost, and complexity of existing sources.

Presently, there are no direct diode laser cw sources available in the UV region between 200 and 350 nm. A common approach to reach new wavelengths is to use different non-linear optical frequency conversion schemes. For example, recently available blue/violet diode lasers have been successfully employed in frequency mixing with visible diode lasers to produce 254 nm for mercury spectroscopy [1].

Here, we present a scheme producing tunable UV radiation around 302 nm by sum-frequency generation in beta-barium borate employing a blue and a near-infrared diode laser [2]. The diode-laser-based spectrometer has a mode-hop-free tuning range of 50 GHz and a 6.9-nW output of UV light.

The device was used for high-resolution spectroscopic detection of sulfur dioxide (SO_2). Differential measurements of several SO_2 gas concentrations, at low pressure as well as at ambient atmospheric pressure, were demonstrated, as illustrated in Figure 1. The absorption spectrum of SO_2 in the wavelength region around 300 nm consists of a complicated and very sharp rotational line structure superimposed on the typical broader structure that is normally used in, e.g., differential absorption lidar (DIAL) measurements.

An interesting aspect of the proposed mixing scheme is that, except allowing for SO_2 detection, the two driving lasers can be made resonant with transitions in nitrogen dioxide (blue laser) and water vapor (near-infrared laser). Such a three-gas-monitoring scheme employing diode lasers has previously been demonstrated for difference-frequency generation to 3.4 μm (methane) by mixing a 760 nm (oxygen) and a 980 nm (water vapor) source [3].

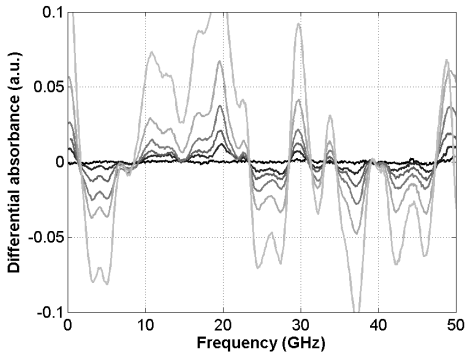


Figure 1. Differential spectra of a 2% SO_2 gas mixture measured at several gas pressures (2, 5, 10, 20, 40, and 80 mbar, respectively) [2].

[1] J. Alnis, U. Gustafsson, G. Somesfalean, and S. Svanberg, Appl. Phys. Lett. 76, 1234 (2000).

[2] G. Somesfalean, Z.G. Zhang, M. Sjöholm, and S. Svanberg, All-diode-laser ultraviolet absorption spectroscopy for sulfur dioxide detection, Appl. Phys. B, to appear.

[3] U. Gustafsson, J. Sandsten, and S. Svanberg, Appl. Phys. B 71, 853 (2000).

C-8

A high precision pulsed QCL spectrometer for measurements of stable isotopes of carbon dioxide

J. B. McManus*[*†], D. D. Nelson[†], J. H. Shorter[†],

R. Jimenez[‡], S. Herndon[†], S. Saleska[§] and M. Zahniser[†]

[†] *Aerodyne Research, Inc.*

45 Manning Road

Billerica, MA US 01821

[‡] *Harvard University*

Dept. of Earth and Planetary Sciences

20 Oxford St., Cambridge, MA, US 02138

[§] *University of Arizona*

Dept. of Ecology and Evolutionary Biology

Tucson, AZ 85721

* Corresponding author. Email: mcmanus@aerodyne.com
Phone: (978) 663-9500 Fax: (978) 663-4918

We describe a prototype instrument using a Peltier cooled quantum cascade laser for precise measurement of stable carbon ($^{13}C/^{12}C$) isotopologue ratios in atmospheric CO_2. Using novel optics and signal processing techniques in a compact instrument, we are able to detect the difference between sample and reference with a precision of 0.1‰ (2 std error of mean of 11 samples) in 10 minutes of analysis time. The standard deviation of 0.18‰ for individual 30s measurements shows that this prototype instrument already approaches the best reported literature values using continuous wave lead-salt tunable diode lasers. The application of pulsed near room-temperature quantum cascade lasers to this demanding problem opens the possibility of field worthy rapid response isotopic instrumentation and attests to the maturity of these lasers as spectroscopic sources.

C-9

Quantum cascade laser spectroscopy system for intra-puff measurements of the effects of iron oxide cigarette paper on CO and CO_2 deliveries

Danielle R. Crawford [1], Milton E. Parrish [1*], Diane L. Gee [1], Charles N. Harward Sr. [2]

[1] Philip Morris USA Research Center, 4201 Commerce Road,

Richmond, VA 23234 USA

[2] Nottoway Scientific Consulting Corp., P.O. Box 125, Nottoway, VA 23955 USA

[*] contact: milton.e.parrish@pmusa.com

The objective of this research was to generate CO and CO_2 intra-puff evolution profiles in cigarette smoke for prototypes with iron oxide cigarette papers. An analytical technique using a quantum cascade laser (QCL) high resolution infrared spectroscopy system has the necessary temporal and spectral resolution and whole smoke analysis capabilities to attempt this task. The QCL system (Figure 1) has an optimal data rate of 20 Hz and a unique puffing system, with a square wave shaped puff, that allows whole smoke to enter an 18 m, 0.3 L multi-pass gas cell in real time (0.1 sec cell response time) requiring no syringe or Cambridge filter pad. Another similar multi-pass gas cell simultaneously monitors the sidestream cigarette smoke.

Cigarettes manufactured with two types of iron oxide papers were analyzed and compared to cigarettes manufactured similarly without iron oxide in the paper. The delivery per puff determined by the QCL method agreed with FTIR results. Mainstream (MS) CO intra-puff evolution profiles for iron oxide prototype cigarettes demonstrated CO reduction when compared to cigarettes without iron oxide paper (See Figure 2). Additionally, both CO and CO_2 intra-puff evolution profiles of the cigarettes with iron oxide paper showed a skewing of the square puff profile in the initial portion of the 2 second puff not observed in the non-iron oxide prototype cigarettes. This effect also was observed for ammonia and ethylene, suggesting that physical parameters such as paper porosity and burn rate are important.

There is no evidence, to date, that the sidestream (SS) CO_2 or CO deliveries during the puffing events are being affected by the iron oxide cigarette papers. The iron oxide paper technology remains under development and is being evaluated.

Figure 1. Quad QCL with Dual Gas Cells

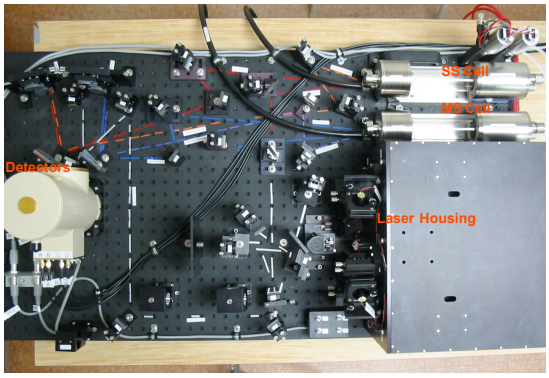
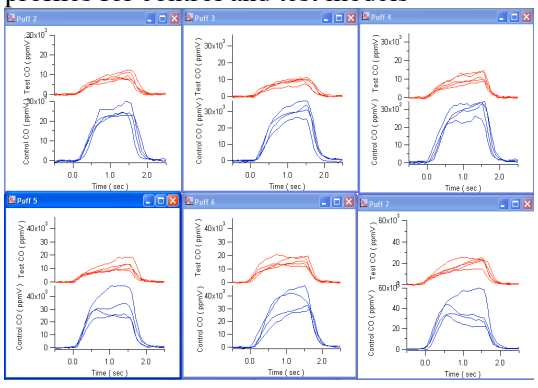


Figure 2. Differences in CO intra-puff profiles for control and test models



C-10

No interference fringes above 10^{-6}

A. Nadezhdinskii

NSC of A.M.Prokhorov General Physics Institute

38 Vavilov str., 119991 Moscow, Russia

NAD@nsc.gpi.ru

Many authors consider interference fringes as main limiting mechanism for trace molecules detection using Tunable Diode Laser Spectroscopy (TDLS). In [1] we described strategy of this problem solving. In present paper this strategy together with software developed will be presented.

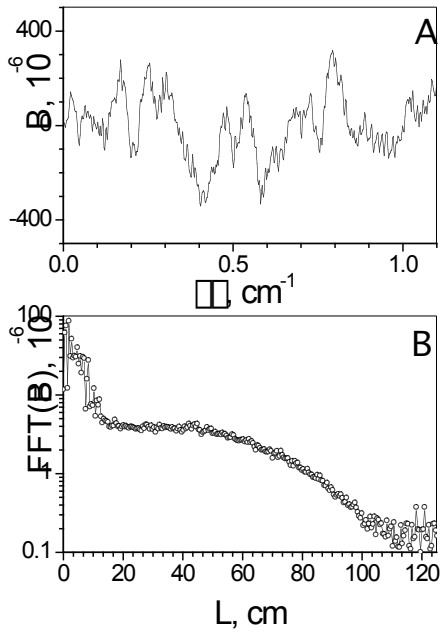


Fig.1 Example of recorded baseline signal (A) and its FFT (B).

Fig. 1A shows recorded baseline signal – B after Chernin multi-pass cell. FFT of this baseline is presented on Fig. 1B. In present experiment there were no reflecting surfaces at distances L shorter than 20 cm. FFT at L < 10 cm is due to baseline. Nature of this effect will be considered in separate poster. Broad feature in FFT spectrum is due to white noise (photo-current shot noise in this case). It is evident that in present experiment all interference fringes and optical feedback were removed below 10^{-6} level. Role of diffused scattering for high sensitivity achievement will be discussed.

References

[1] A. Nadezhdinskii, I. Zasavitskii, in "Monitoring of gaseous pollutants by tunable diode lasers", R. Grisar, H. Preier, G. Schmidtke, G. Restelli (Ed.), Proc. Int. Symposium, Freiburg, FRG 1986, D. Reidel Publ.Com., Dordrecht, 1987, p. 95–106.

C-11

Diode laser based system with topographic reflector for trace molecules remote monitoring

A. Berezin, S. Malyugin, T. Moskalev, A. Nadezhdinskii, D. Namestnikov, Ya. Ponurovskii, S. Rudov, Yu. Shapovalov, D. Stavrovskii, I. Vyazov, V. Zaslavskii

NSC of A. M. Prokhorov General Physics Institute

E. Dianov, A. Kurkov, V. Paramonov

FORC at A. M. Prokhorov General Physics Institute

38 Vavilov str., 119991 Moscow, Russia

NAD@nsc.gpi.ru

Trace molecules remote sensing using diode laser based systems with topography reflector is very attractive for different applications. Recently several groups reported about development of ground based systems [1-3]. However, a lot of applications needs helicopter or airplane based instruments. Main problem in this case is related to minimum allowed altitude of their flights (more than 80 m). Up to our knowledge, the first successful demonstration of such system was reported in our paper [4].

In present paper we'll present new instrument developed. This instrument has higher sensitivity and can be efficiently used at higher flight altitudes (up to 600 m). Results of its tests will be presented also (see Fig. 1).

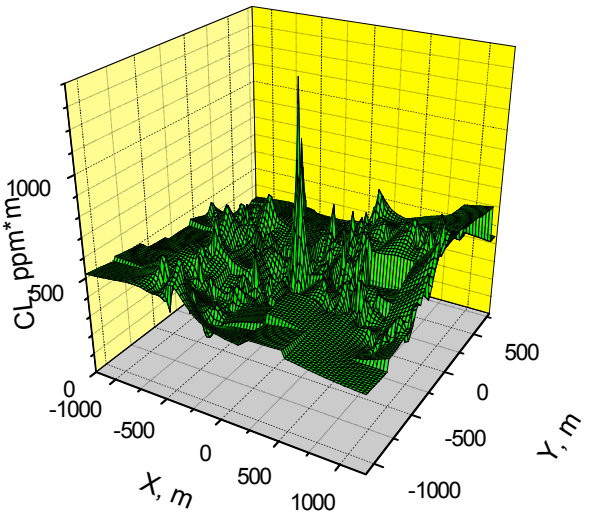


Fig. 1 Methane leakage detection from low pressure line using helicopter based instrument.

References

[1] T. Iseki, H. Tai, K. Kimura, Meas. Sci. Technol. 11, 594–602 (2000).

[2] A. Berezin, O. Ershov, A. Nadezhdinskii, Appl. Phys., B 75, 203–214 (2002)

[3] R. Wainner, B. Green, M. Allen, M. White, J. Stafford-Evans, R. Naper, Appl.Phys., B 75, 249–254 (2002)

[4] A. Berezin, O. Ershov, A. Nadezhdinskii, S. Rudov, D. Stavrovskii, T. Shubenkina, in TDLS 2003, Abstracts of papers, Zermatt, 2003, p. 86.

C-12

Tunable diode laser spectroscopy application for detection and isotope ratio measurements of UF_6 molecules

A. Nadezhdinskii, Ya. Ponurovskii, Yu. Shapovalov, D. Stavrovskii

NSC of A. M. Prokhorov General Physics Institute

38 Vavilov str., 119991 Moscow, Russia

D. Bolyasov, G. Grigor'ev, N. Gorshunov, S. Malyugin, Sh. Nabiev

Institute of Molecular Physics of RRC "Kurchatov Institute"

Kurchatov sq. 1, 123182 Moscow, Russia

Beginning of Tunable Diode Laser Spectroscopy (TDLS) more than three decades ago was related to one molecule of interest practically in all countries. It was UF6 molecule with respect to the problem of laser uranium isotopes separation. Dramatic progress in TDLS technique achieved during last decade and success of trace complex molecules detection again brought our intention to the same molecule because of IAEA needs related to Additional Protocol of Safeguards. There were three objectives of present paper:

1. To investigate if it is possible to use Tunable Diode Laser Spectroscopy (TDLS) technique for gaseous uranium hexafluoride enrichment measurement.
2. To analyze possibility to detect trace UF_6 presence in atmosphere.
3. To detect trace HF molecule concentration due to hydrolysis of uranium hexafluoride in atmosphere.

Spectra of uranium hexafluoride gas mixture were investigated using Fourier Transform Spectrometers and TDLS. Observed spectral features were identified and model spectra of different gas mixture components were developed. Optimal spectral range for measurements was determined near maximum of UF6 combination band v1+v3.

Laboratory prototype of multi channel instrument under consideration based on tunable diode lasers was built and algorithms of its operation were developed to measure gaseous UF6 isotopes ratio. Diode laser in use operated at the wavelength of $\lambda = 7.68$ μm.

Instrument was tested in measurements of real UF6 gas mixtures in Moscow and Seibersdorf. Achieved measurement accuracy was analyzed and error sources were identified. The random error in the content of isotope 235U is characterized by a std of about 0.27%. Overcoming of present experimental problems (absence of high resolution spectra of uranium hexafluoride isotopomers and low quality of Diode Laser and Photo-Diode in use) will provide at least one order of magnitude improvement of this parameter.

To investigate uranium hexafluoride in atmosphere special chamber was built. Two diode laser based instruments were used for simultaneous measurement of trace UF6 (mid IR) and HF (near IR) concentration after uranium hexafluoride injection into the chamber. Preliminary results of this experiment will be presented.

C-13

Baseline in TDLS

A. Nadezhdinskii

NSC of A. M. Prokhorov General Physics Institute

38 Vavilov str., 119991 Moscow, Russia

NAD@nsc.gpi.ru

Baseline plays key role for trace molecules detection using Tunable Diode Laser Spectroscopy (TDLS). For the first time for author knowledge it was mentioned in [1]. In our experiments, when broad DL frequency tuning was used, baseline was observed without any problem and easily can be distinguished from interference fringes. Physical nature of baseline was explained in [2]. Recently baseline was investigated carefully using new technique developed. Some results of this investigation will be presented in the paper.

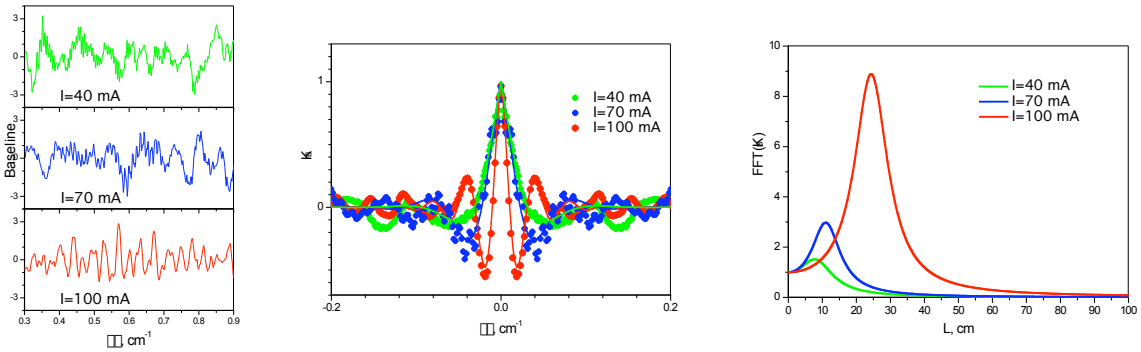


Fig. 1 Normalized baseline (left), its correlation function (mid), and FFT (right) for different values of excitation current.

Fig. 1 shows example of this investigation.

Resume: Baseline nature is related to inhomogeneity in diode laser active area and its interaction with standing electromagnetic wave. Baseline properties are determined by electron–photon subsystem behavior (relaxation oscillations and spatial diffusion).

References

[1] J. Reid, D. Labrie, Appl. Phys., B26, 203-210 (1981)

[2] A. Nadezhdinskii, I. Zasavitskii, in “Monitoring of gaseous pollutants by tunable diode lasers”, R. Grisar, H. Preier, G. Schmidtke, G. Restelli (Ed.), Proc. Int. Symposium, Freiburg, FRG 1986, D. Reidel Publ.Com., Dordrecht, 1987, p.95-106.

C-14

Ratio measurement of water ortho/para nuclear spin isomers via TDLS in the vicinity of 1.392 _

S. Malugin, T. Moskalev, A. Nadezhdinskii, Ya. Ponurovskii, D. Stavrovskii

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

e-mail: stavr@nsc.gpi.ru

Water molecule exists in two nuclear spin isomers. The hydrogen atom nuclear spins could be either parallel (total spin is 1) in ortho molecule or antiparallel (total spin is 0) in para molecule. Each spin isomer has its own system of rotational levels. Optical transitions between levels of different spin isomers are strongly forbidden. Number of ortho isomer molecules is three times greater than number of para isomer molecules in the thermal equilibrium state at room temperature.

Succesful separation of ortho and para water isomers was demonstrated [1]. Interest to further investigation of separation mechanisms is connected with feasible application of para-enriched water in medicine (EPR-thomography). The method of ortho/para ratio measurement used in [1] is based on microwave absorbtion spectroscopy in 36–38 cm^{-1} frequency interval. This technique is rather complicated and it could unlikely be used outside of physical laboratory. That's why alternative diagnostic methods are of greate interest.

This report is concerned with futher development of the method based on technique of absorbtion TDLS [2]. Distributed feedback (DFB) diode laser (DL) from Laser Components GmbH with the wavelength in the vicinity of 1.392 _m was used. The DL was pumped with trapezoidal pulses of 0.5–1 ms duration and 1–2 kHz repetition rate. Frequency tuning of the DL radiation was produced in the frequency interval 7181.0–7183.1 cm^{-1}. The interval was chosen to ensure simultaneous detection of three ortho isomer absorption lines (7181.15578; 7182.20911; 7183.01579) and one para isomer absorption line (7182.94962). These lines are strong enough for reliable ratio measurements.

Samples of water vapor under pressure from 1 to 10 Torr were placed in stainless steel optical cell with the length of 20 cm. Absorption spectra of water vapor were detected and then processed using LabVIEW-based software. Ratio factors were calculated by use of integral cross section data of HITRAN-2004 [3].

[1] V. I. Tikhonov, A. A.Volkov, Science, v.296, p.2363 (2002).

[2] A. I. Nadezdinskii, P. M. Omarova. J. Mol. Spectr., v.170, p.27 (1995).

[3] L. S. Rothman et al, The HITRAN molecular spectroscopic database, *JQSRT*, vol. **82**, numbers 1–4, 15 November–15 December (2003). http://cfa-www.harvard.edu/hitran//

C-15

Pressure broadening and shift of I_2 near 675 nm

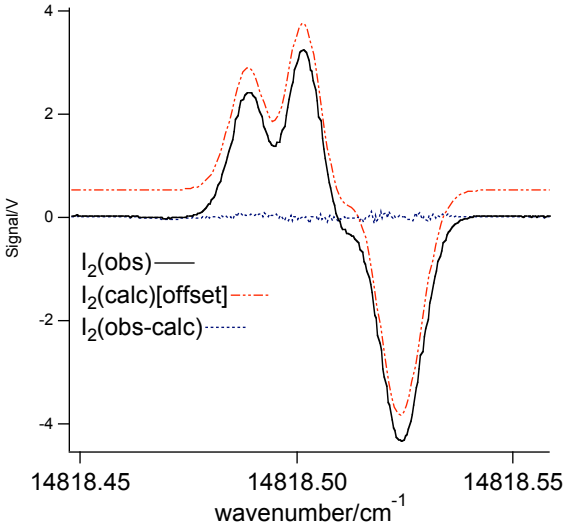
T. R. Dyke, J. L. Hardwick, and E. N. Wolf

Department of Chemistry, University of Oregon

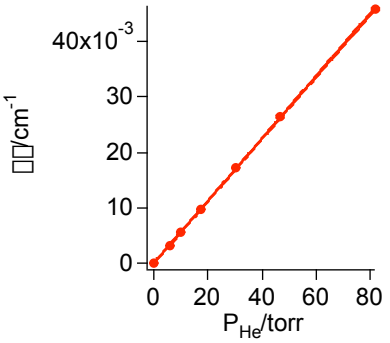
Eugene, OR 97403, USA

Pressure broadening and shift studies of lines of the B-X system of I_2 have been performed in the region between 14818 and 14819 cm^{-1} by wavelength modulation spectroscopy using a free-running Fabry-Perot diode laser. Pressure broadening and pressure shift coefficients have been determined for the noble gases as well as for H_2 and D_2.

Lines of the wavelength modulation spectrum exhibit a shape characteristic of the well-determined nuclear electric quadrupole coupling, as illustrated in Figure 1. This line shape is, in turn, very sensitive to the pressure broadening. The most reliable pressure broadening measurements for I_2 are recorded with the FWHM of the Lorentz component <0.02 cm^{-1}.



In these experiments both the laser line width and the modulation depth must be held below 0.001 cm^{-1}; otherwise, the instrument function of the spectrometer would overwhelm both the quadrupole structure and the associated pressure-induced changes. To accomplish this while maintaining the signal/noise ratio acceptably high, we have used an off-axis paraboloid to collimate the laser, eliminating the small but noticeable optical feedback produced by a collimating lens.



The pressure-broadened lines were modeled by a Voigt profile. The Lorentz component of the Voigt profile of isolated lines has a width that varies linearly with pressure, as shown in Fig. 2. Although some lines showed small systematic deviations from the Voigt line shape, no clear evidence of pressure narrowing was identified.

C-16

Study of CH_4, C_2H_4 and air spectra with a diode laser photoacoustic spectrometer

V. A. Kapitanov, I. S. Tyryshkin, N. P. Krivolutskii, Yu. N. Ponomarev

Institute of Atmospheric Optics SB RAS, 1, Akademicheskii Av., 634055, Tomsk, Russia

e-mail: yupon@iao.ru

Near-infrared diode laser spectrometer with new model of resonant photoacoustic detector (ring resonator) was designed and applied to study the spectra of atmospheric air and hydrocarbons (CH_4, C_2H_4) within 6060-6290 cm^{-1} spectral range. The use of additional multipass sell, coaxial with photoacoustic detector, provides the precise measurements of absorption line centre pressure shift. The diode laser photoacoustic spectrometer (DLPAS) has the threshold sensitivity 4E-9 $cm^{-1}\cdot W$. The diode laser TEC-100 provides the spectral resolution of 2E-4 cm^{-1}. The interference multiplex wavelength meter is used for calibrating of the wavelength scale with uncertainty 10^{-7}.

The detail description of hardware and software of DLPAS together with the results of measurements of CH_4, C_2H_4 and atmospheric air spectra are presented.

This work is particularly supported by RBRF (Project 04 – 03 – 32627).

C-17

Novel Helmholtz-based photoacoustic sensor for trace gas detection at ppm level using GaInAsSb/GaAlAsSb DFB lasers

M. Mattiello, M. Niklès

Omnisens SA, Science Park, CH-1015 Lausanne, Switzerland (marc.nikles@omnisens.ch)

S. Schilt, L.Thévenaz

Ecole Polytechnique Fédérale de Lausanne (EPFL),
Laboratory of Nanophotonics and Metrology,

CH-1015 Lausanne, Switzerland (stephane.schilt@epfl.ch)

A. Salhi, D. Barat, A. Vicet

Centre d'Electronique et de Microoptoélectronique de Montpellier (CEM2 UMR CNRS 5507),
Université Montpellier II, F-34095 Montpellier cedex 05, France (a.vicet@univ-montp2.fr)

R. Werner, J. Koeth

Nanoplus Nanosystems and Technology GmbH, Oberer Kirschberg 4,
D-97218 Gerbrunn, Germany (ralph.werner@nanoplus.com)

The mid-infrared 2-2.5 μm region is attractive for trace gas sensing due to the presence of quite strong absorption bands of several species, including CO, CH_4, NH_3 and HF, and its location in the so-called atmospheric window, where absorption from the main infrared active atmospheric compounds (H_2O and CO_2) is rather weak.

The recent developments of novel antimonide-based semiconductor laser diodes have opened new perspectives for infrared spectroscopy. The improvement of the general performances of these lasers, and particularly the realization of distributed feedback (DFB) structures enabling single-frequency and continuously tunable emission, makes them suitable for gas sensing applications.

We report here the development of a photoacoustic (PA) sensor based on GaInAsSb/GaAlAsSb DFB lasers in the 2.2-2.3 μm range. The structures, based on a three compressively strained quantum wells active region, were grown by molecular beam epitaxy on N doped GaSb substrates. The technology used for DFB fabrication is based on a patented development using a ridge-waveguide structure with a lateral metal grating for distributed feedback. This technology has successfully been applied to a variety of material systems leading to DFB lasers in a wavelength range from 760nm up to 2.8μm.

The highly divergent emission of these mid-infrared lasers makes an efficient coupling of the laser power into a resonant PA cell difficult. In order to fully benefit from the characteristics of the antimonide-based lasers and to achieve optimal power collection, we have designed a novel configuration of PA cell, based on a Helmholtz resonator. In this type of resonator, the excitation of the acoustic signal is independent of the laser beam geometry. We used this property to design a configuration that directly exploits the diverging laser emission to excite the acoustic resonance in one volume of the Helmholtz resonator, without any collecting optics. This geometry enables multiple reflections of the laser beam in this volume, in order to increase the photoacoustic signal.

This compact PA design has been used for CH_4 and NH_3 detection using different antimonide-based DFB lasers. Various laser modulation schemes and harmonic detections have been performed to improve the performances of the system and reduce the noise. A sub-ppm sensitivity has thus been demonstrated for NH_3 detection.

C-18

Light directionality generated by partial coherent plane source

Mostafa Sahrai, and Habib Tajalli

Research Institute for Applied Physics and Astronomy, Tabriz University, Tabriz, Iran

E-mail: sahrai@tabrizu.ac.ir

Tel: +98-411-3393007

Fax: +98-411-3347050

This paper investigates the partial coherent beam propagation produced by a Gaussian Shell-Model source. By introducing the new form of Cross-Spectral density function, the intensity of light beam at far zone, has been obtained. The effects of the size and coherence of the source on beam directionality has also been discussed.

C-19

A ground based remote sensing tunable diode laser - fiber amplifier instrument. Apllication to carbon dioxide detection

Haris Riris, James Abshire, Graham Allan, John Burris, G. James Collatz, Amelia Gates, Randy Kawa, Michael A. Krainak, Xiaoli Sun

NASA Goddard Space Flight Center

Greenbelt, MD USA 20771

Arlyn Andrews

NOAA Climate Monitoring and Diagnostics Laboratory,

325 Broadway, Boulder, CO 80305

hriris@pop900.gsfc.nasa.gov

Remote and point sensing technologies are important components in our efforts to understand and quantify the global distribution of greenhouse gases and atmospheric pollutants. Recent advances in tunable diode laser and high power fiber amplifier technology have made it possible to apply remote sensing techniques in the near infrared region where most atmospheric molecules exhibit overtone transitions. Application of these technologies to ground, airborne, and space instruments requires extensive development and qualification of the instrument components: laser sources, amplifiers, detectors, etc. For the near infrared region (1.5-1.6 μm) the component technology is driven by the telecommunications, aerospace and defense industries.

At NASA's Goddard Space Flight Center (GSFC) we have been leveraging the development of these technologies and applying them to environmental sensing. A ground based, remote sensing instrument is currently being developed at GSFC. The instrument uses tunable diode lasers and Erbium Doped Fiber Amplifiers (EDFA) at 1.57 μm to make differential absorption measurements of Carbon Dioxide (CO_2) in the atmosphere. Two distributed feedback lasers (DFB) act as seed lasers for a low power pre-amplifier and a high power amplifier. The lasers are modulated by external electro-optic modulators to provide 100 ns pulses at 25 kHz to the pre-amp. The repetition rate and pulse width are adjustable. The two laser wavelengths are tuned on and off a CO_2 absorption line at 1571.111 nm. A fiber-coupled photomultiplier tube at the end of a 20.3 cm diameter telescope acts as a receiver.

We have made initial differential absorption measurements with a cooperative target and demonstrated detection of atmospheric CO_2 in a 225 m open-air path. The eventual application of the differential absorption technique to a network of autonomous ground based systems or a space borne CO_2 global measurement satellite imposes stringent stability and accuracy requirements on the instrument. We have used the Allan variance [1] to quantify the stability of our TDL spectrometer and identify sources of error in our instrument.

[1] P. Werle, R. Mucke, F. Slemr, The Limits of Signal Averaging in Atmospheric Trace-Gas Monitoring by Tunable Diode-Laser Absorption Spectroscopy (TDLAS), Appl. Phys. B **57**, 131-139 (1993)

C-20

2.65 µm antimonide based diode lasers for vapour detection in the atmosphere of Mars

A. Vicet, A. Salhi, J. Angellier, D. Barat, Y. Rouillard

CEM2 UMR CNRS 5507, Place Eugène Bataillon, CC 67, Université Montpellier 2,

34095 Montpellier cedex 05, France.

G. Durry, T. Lebarbu

GSMA UMR CNRS 6089, Moulin de la Housse, Université de Reims Champagne-Ardennes,

BP 1039, 51687 Reims, France

IPSL, Institut Pierre-Simon-Laplace Service d Aeronomie, UMR 7620

B.P. 3, 91371 Verrieres-le-Buisson Cedex

A. Martinez, A. Ramdane

CNRS-LPN Laboratory for Photonics and Nanostructures
Route de Nozay, 91 460 Marcoussis, France

A few billions years ago, Earth and Mars were two similar planets starting with the same potential. It turned out that both planets develop in different ways. Mars got cold. Life appeared on Earth and, because of its geological evolution, the process and its developments seems to have been stopped on Mars. Since many years though, scientists are looking for a trace of life on the red planet. This research implies the research and study of traces of water because it is believed that the presence of this element is a mandatory condition for life to appear. Due to the actual pressure and temperature conditions on Mars (7.6 millibars, -53°C), water can not be found in liquid state, but only in solid or vapour state. Detecting traces of moisture vapour today would account for the former presence of liquid water and would be a strong argument in favour of those who defend the thesis that life actually existed on this planet.

The isotopical ratio of hydrogen and deuterium in water molecules can be assessed by absorption spectroscopy. A study of Martian meteors landed on Earth showed that the isotopic deuterium/hydrogen ratio (D/H) is about five times higher in the Martian atmosphere than on Earth. This higher ratio is due to the fact that H_2O has scattered from Mars leading to the disappearance of 90% of water molecules with hydrogen atoms.

The following work is performed within the framework of a collaboration between the CEM2, the GSMA and the CNES ("Centre National d'Etudes Spatiales"). We present new InGaAsSb/AlGaAsSb laser diodes designed for a single frequency emission around 2.65 µm. This wavelength is ideally suited for measuring water vapour isotopic ratios. The growth of the laser structure was carried out by molecular beam epitaxy (MBE) on n-GaSb substrates in a Riber Compact 21 system. The 0.8 µm-thick active region is based on two $In_{0.45}Ga_{0.55}As_{0.13}Sb_{0.87}$ 12 nm-thick compressively strained quantum wells embedded between barriers and a waveguide made from $Al_{0.25}Ga_{0.75}As_{0.03}Sb_{0.97}$. First results around this wavelength were published last year [1], accounting for a low threshold current density (152 A/cm^2 in the pulsed regime). The technological process was performed by the LPN, to obtain the single-frequency emission needed by the application.

[1] A. Salhi, Y. Rouillard, J. Angellier, P. Grech and A. Vicet, 2.61 µm GaInAsSb/AlGaAsSb type I quantum well laser diodes with low threshold, *Electronics letters vol 40 (7), pp424-425, 2004.*

C-21

Line profile study by diode laser spectroscopy in the $^{12}CH_4$ $\nu_2+\nu_4$ band

D. Mondelain, P. Chelin, A. Valentin, D. Hurtmans(*) and C. Camy-Peyret

Laboratoire de Physique Moléculaire pour l'Atmosphère et l'Astrophysique,

UMR 7092 CNRS-Université Pierre et Marie Curie,

Case 76, 4 place Jussieu,

75252 Paris Cedex 05, FRANCE

www.lpma.jussieu.fr

(*) Service de Chimie Quantique et de Photophysique (Atomes, Molécules et Atmosphères), Université Libre de Bruxelles

50 Av F.D. Roosevelt CPi 160/09

B-1050 Bruxelles, BELGIUM

We present a complete study on four methane lines for two atmospheric micro-windows (in the $\nu_2+\nu_4$ absorption band). One micro-window, centred on 2921.3 cm^{-1}, was selected in the UFTIR project (Time series of Upper Free Troposphere observations from a European ground-based FIR network) for the determination of atmospheric methane concentrations with ground-based Fourier Transform spectrometers. The other micro-window, centred on 2914.6 cm^{-1}, is suitable to quantify the NO_2 column (see the Spectroscopic Atlas of A. Meier [1]). But an important drawback of this window is the interference with the CH_4 absorption especially because the spectroscopic parameters of the $\nu_2+\nu_4$ band are not accurately known.

Thanks to our tunable diode laser (TDL) spectrometer with active wave number control and step-by-step recording mode [2], we have improved the accuracy on intensity, broadening, narrowing and pressure shift parameters of methane lines in these two micro-windows. To make our results directly useable in atmospheric models that usually assume a Voigt line shape, we have parameterised an effective broadening parameter $\gamma_{Voigt}(P)$ for each line and each gas mixture (CH_4-N_2 and CH_4-O_2). When this parameterisation is used to fit a "true" line profile, the same concentration as with more sophisticated models is retrieved from a consistent set of spectroscopic parameters in both approaches.

[1] A. Meier, G. C. Toon, C. P. Rinsland, A. Goldman, F. Hase, Spectroscopic atlas of atmospheric microwindows in the middle infra-red 2nd edition, IRF technical report 048 (2004).

[2] A. Valentin, *Spectrochim. Acta A*, **55**, 1967-1986 (1999).

C-22

Time resolved detection of nitric oxide from biological liquids with a quantum cascade laser

S. Thelen, D. Halmer, M. Horstjann, P. Hering, M. Mürtz

Universität Düsseldorf, Institut für Lasermedizin

40225 Düsseldorf, Germany

Sven.Thelen@uni-duesseldorf.de

Biological human liquids (e.g. sweat and blood) contain Nitric Oxide (NO) generating agents like nitrite. The mechanisms and kinetics in human skin - involving NO formation in sweat - that lead to skin aging, inflammation and cancerogenesis are subject to intensive studies. As those NO generating agents typically occur with a nmolar concentration, highly sensitive detection methods are required.

Since many trace gases like NO have a characteristic absorption spectrum as well as high absorption line strengths in the mid-infrared region between 3 and 10 µm, laser spectroscopic techniques are well suited for highly sensitive trace gas analysis. Aside from being able to measure very small concentrations of specific trace gases, the capability of time resolved measurements allows studying biological processes and kinetics in the human body.

Quantum Cascade Lasers (QCL) are well suited for laser spectroscopy as compact lasers in the mid-infrared region with high optical output power and narrow linewidth. We use a 5.2 µm LN_2-cooled cw-QCL with a Distributed Feedback (DFB) structure for single mode operation, the wavelength is tuneable with the laser current between 270 and 580 mA (= 1920.4 – 1922.8 cm^{-1}, P_{max} = 24 mW, = 2 MHz in 20 ms).

We use our QCL for the Faraday-Modulation-Spectroscopy (FAMOS) which is an excellent detection method for the quantitative and time resolved detection of the NO radical. Since FAMOS is based on the rotation of linearly polarized light due to a magnetic moment of the targeted molecule (Faraday effect), it specifically detects NO without interference to other molecules. FAMOS is the only method for detection of the time resolved release of gaseous NO from liquids without any gas pretreatment. We reach a detection limit of 10 ppb in 1 s averaging time, corresponding to a minimal detectable release rate of 4.5 pmol/s.

We have examined the quantitative, time resolved release of NO in human skin by UVA-challenge to gain a better understanding of the biological processes [1]. The time resolved simultaneous detection of ^{14}NO and ^{15}NO allows differing between endogenous and exogenous sources of NO. Preliminary studies with human blood have been conducted [2].

References

[1] A. Paunel et al., Enzyme-independent nitric oxide formation during UVA challenge of human skin: characterization, molecular sources, and mechanisms, Free Radical Biology & Medicine, 38, 606-615, (2005).

[2] D. Halmer et al., Time resolved detection of ^{14}NO and ^{15}NO via mid-infrared cavity leak-out spectroscopy, Isotopes in Environmental and Health Studies, submitted.

C-23

Gas analysis with quantum cascade lasers

O. Werhahn, J. Koelliker Delgado, D. Schiel

Physikalisch-Technische Bundesanstalt (PTB),

D-38116 Braunschweig, Germany

www.ptb.de

The development and availability of reliable room temperature quantum cascade laser (QCL) systems provide new possibilities for gas analysis in the fields of medical, environmental or process technology. Due to their unique characteristics in the MIR combined with micro-technical system sizes QCLs are suitable tools for nearly all relevant molecular species in practical analytics.

Based on Beer-Lambert's law, QCL gas analysers provide the possibility of absolute measurements with direct SI-traceable results. We present results on CO operating a QCL in the long-pulse mode. Interesting effects need to be addressed that are unknown in conventional TDLS. Considerations on linewidth requirements and expected measurement uncertainties compared to conventional TDLS results operating a cw-diode will be presented.

C-24

7.7-micron quantum cascade laser suitable for spectroscopy and isotopomer analysis of methane

N. Akikusa, T. Edamura, A. Sugiyama, T. Ochiai,

Y. Takiguchi, H. Kan, and K. Uehara [1]

Central Research Laboratory, Hamamatsu Photonics K.K.

5000, Hirakuchi, Hamamatsu, 434-8601, Japan

[1] *Department of Physics, Faculty of Science and Technology, Keio University*

3-14-1, Hiyoshi, Kohoku-ku, Yokohama, 223-8522, Japan

We have made a single-mode distributed-feedback quantum cascade laser (DFB-QCL) which operates around 7.7 μm and tentatively applied it to absorption spectroscopy of methane. The DFB-QCL operates as a continuous-wave mode-hop-free tunable light source at temperatures between 77 and 120 K.

The wavelength 7.7 μm falls on the Q branch of the ν_4 band of $^{12}CH_4$. Figure 1 shows the direct absorption spectrum of this branch observed by current sweep of our DFB-QCL between 200 and 500 mA at a fixed temperature of 77 K. Comparison with known spectral data shows that the tuning range is 1302.7 - 1304.4 cm^{-1}. The observed halfwidth (HWHM), 58 MHz, is very close to the Doppler width (57.2 MHz). It means that the laser linewidth is MHz order or less.

The narrow linewidth and high power up to 50 mW achieved here is suitable for high resolution linear and nonlinear absorption spectroscopy of methane. In addition, very high precision isotopomer analysis of methane by the same spectroscopic technique as demonstrated with near-infrared diode lasers[1] seems feasible.

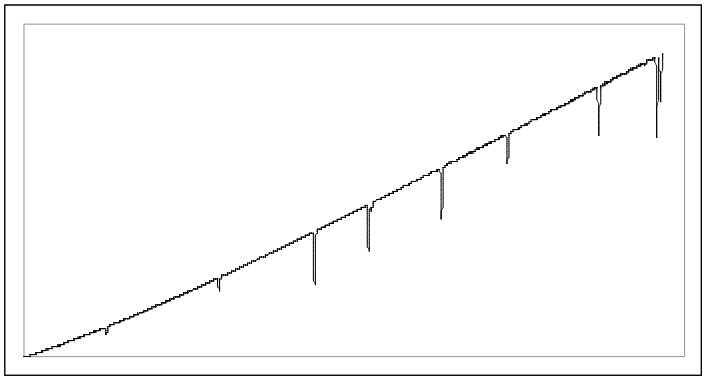


Fig. 1 Direct absorption spectrum of the Q branch of the ν_4 band of methane observed by current tuning. Sample pressure: 0.04 torr; path length: 20 cm.

References

[1] K. Uehara, K. Yamamoto, T. Kikugawa, S. Toyoda, K. Tsuji, and N. Yoshida, *Sens. Actuat. B* **90** 250-255 (2003).

C-25

Development of a transportable spectrometer based on an erbium fiber doped laser for multiple trace gas sensing

J. Cousin, W. Chen

Laboratoire de Physico-Chimie de l'Atmosphère,

UMR-CNRS 8101, Université du Littoral Côte d'Opale, 189A, Av. Maurice Schumann,

59140 Dunkerque, France,

julien.cousin@univ-littoral.fr

We present a novel spectrometer for real time and in situ trace gas sensing in near and mid-infrared. As optical pump source, an erbium doped fiber laser (EDFL) is used. This source generate near-IR continuously tunable from 1543 to 1602 nm with a power up to 1 W and a spectral linewidth less than 1 MHz. Furthermore this source will be employed to generate difference frequency with a second fiber laser (Ytterbium doped fiber laser) emitting near 1.06 µm. So this source would generate mid-IR from 2.8 to 3.3 µm with a power near 1 mW.

We present our preliminary results obtained in near-IR. Two detection schemes have been used :

1) Direct absorption in a Herriott multipass cell with 100 m optical path and a limited volume of 3.2 L ;
2) Cavity Ring-Down Spectroscopy (CDRS) with an equivalent optical path of ten kilometers.

Trace gas detection of acetylene (C_2H_2) and nitrogen protoxide (N_2O) with concentrations from some percents up to tens ppb have been achieved. Detection sensitivity is in the order of 10^{-7} cm^{-1} for direct absorption in the herriott cell and 10^{-10} cm^{-1} for CRDS.

Poster Session D

D-1 New 2318 nm distributed feedback diode lasers: spectroscopic characterization and application to sensitive monitoring of CH_4

V. Ebert, A. Awtry, J. Fleming, S. Wagner

D-2 Field measurements of N_2O and CO_2 using a pulsed quantum-cascade laser

L. Emmenegger, K. Zeyer, M. Steinbacher, J. Mohn

D-3 QCL-based sensors from 3 - 130 microns: applications to gas and solid phase chemical sensing

Mark Allen, David Cook, Brian Decker, Joel Hensley, David Rosen, Michelle Silva, Richard Wainner

D-4 Frequency modulated spectroscopy as a probe of molecular collision dynamics

M. L. Costen, A. Alagappan, K. G. McKendrick

D-5 Spectral properties and spectroscopic applications of near-IR DFB diode lasers

Jan Posthumus, Anselm Deninger, and Frank Lison

D-6 Measurement of nitrogen dioxide in cigarette smoke using quantum cascade tunable infrared laser differential absorption spectroscopy (TILDAS)

Joanne H. Shorter, David D. Nelson, Mark S. Zahniser, Milton E. Parrish, Danielle R. Crawford, Diane L. Gee

D-7 Anti personnel mine detection using laser induced breakdown spectroscopy

Wolfgang Schade, Christian Bohling, Konrad Hohmann, Dirk Scheel, Gerhard Holl

D-8 Spectroscopy of HDO in the 6.7 μm region with a quantum cascade laser spectrometer

L. Joly, B. Parvitte, L. Daumont, V. Zéninari, A. Jenouvrier, G. Durry, D. Courtois

D-9 A comparison of VCSEL and edge-emitting diode lasers when sensing nitrogen dioxide in the 660 nm region

S. N. Andreev, D. F. Baltakov, V. N. Ochkin, S. Yu. Savinov, M. V. Spiridonov, S. N. Tskhai

D-10 Instrument based on visible diode laser to detect trace NO_2 concentration with minimum detectable concentration at ppt level

A. Berezin, S. Chernin, A. Makkaveiskii, S. Malyugin, T. Moskalev, A. Nadezhdinskii, D. Namestnikov, Ya. Ponurovskii, Yu. Shapovalov, D. Stavrovskii

D-11 Statistical analysis of data series in TDLS

A. Nadezhdinskii

D-12 Tunable single-frequency diode laser at wavelength _ = 1.52 _m for ammonia concentration measurements

A. V. Gladyshev, M. I. Belovolov, S. A. Vasiliev, O. I. Medvedkov, V. P. Duraev, E. T. Nedelin, A. I. Nadezhdinskii, Ya. Ya. Ponurovskii

D-13 Optimal spectral range and operation mode for trace molecule detection with diode lasers
A. Nadezhdinskii

D-14 Measurement of water isotopomers via TDLS in the vicinity of 1.392 _
T. Kumanskaya, A. Nadezhdinskii, Ya. Ponurovskii, Yu. Shapovalov, D. Stavrovskii, I. Vyazov, A. Babichev, G. Grigoriev, C. Malugin, Sh. Nabiev, A. Ustinov

D-15 A novel technique for rapid wavelength scanning of extended cavity diode lasers
J. Hult, I. S. Burns, C. F. Kaminski

D-16 Tunable diode laser spectroscopy of the $[Ar\text{-}N_2]^+$ complex: new experimental/theoretical results
H. Verbraak, J. Bouwman, D. Verdes, H. Linnartz, J. van Stralen and F. M. Bickelhaupt

D-17 Trace gas detection of CO using a pulsed quantum cascade laser
B. W. M. Moeskops, S. M. Cristescu, F. J. M. Harren

D-18 650-kHz wide Lamb dip of the 3.3 micron band of methane with difference frequency generation and enhanced cavity
K. Anzai, H. Sasada, N. Yoshida

D-19 2.3 μm single-frequency tunable VCSEL for gas detection
A. Ouvrard, A. Garnache, L. Cerutti, F. Genty and D. Romanini

D-20 Vibrational-rotational spectroscopy of AlF: an analysis based on the non-Born-Oppenheimer effective hamiltonian
Hiromichi Uehara and Koui Horiai

D-21 Q-MACS — a compact quantum cascade laser absorption spectroscopy system for process monitoring
J. Röpcke, S. Glitsch, F. Hempel, S. Saß, K.-D. Schulz, K.-D. Weltmann, H. Zimmermann

D-22 Biological and medical applications of gas in scattering media absorption spectroscopy using tunable diode lasers
Mikael Sjöholm, Linda Persson, Mats Andersson, Gao Hong, and Sune Svanberg

D-23 Widely tunable narrrow linewidth diode laser system for coherent spectroscopy
P. Huke, R.-H. Rinkleff, S. Chepurov, A. Wicht, K. Danzmann

D-24 Electric field induced alignment – orientation conversion in Cs atoms at diode laser excitation
M. Auzinsh, K. Blushs, R. Ferber, F. Gahbauer, A. Jarmola, and M. Tamanis

D-25 Airborne measurement of CH_4 profiles during the TROCCINOX-2 campaign with the near infrared TDL instrument "ALTO"
F. D'Amato, P. Mazzinghi, S. Viciani, P. W. Werle, F. Castagnoli, M. De Pas, M. Giuntini

D-1

New 2318 nm distributed feedback diode lasers: spectroscopic characterization and application to sensitive monitoring of CH_4

V. Ebert [1], A. Awtry [2], J. Fleming [2], S. Wagner [1]

[1] Physikalisch-Chemisches Institut, University Heidelberg, INF 253, D-69120 Heidelberg

contact: volker.ebert@pci.uni-heidelberg.de fax: 49-6221-545050 www.gasanalysis.org

[2] Combustion Dynamics Section, Code 6185, Navy Technology Center for Safety and Survivability, Naval Research Laboratory, Washington, DC 20375-5342 USA

Due to their unique combination of excellent spectroscopic properties and low cost telecommunication diode lasers in the 1.3µm to 1.65µm spectral range have found wide spread applications in basic research as well as in industrial applications. However, such spectrometers always suffer from a rather low sensitivity, which in exchange requires to achieve rather high optical resolutions and thus causes new problems with optical baseline stability, fringes etc. Quantum cascade lasers in the mid IR promise much higher sensitivities but here one has to face complications due to a lack of good room temperature detectors, low availability of the lasers and their need for high-current nanosecond driving pulses, special crystal optics, and dedicated data evaluation electronics which can handle the pulsed detector signals. An excellent compromise between spectrometer sensitivity and complexity is the 2000nm-3000nm spectral range, where significant improvements in laser availability have been achieved recently and where first reliable DFB-lasers have become available[1], which will soon replace the tedious 2-3µm FP-DL, with their problematic mode-hoping behavior.

CO and CH_4 are two very important species in this spectral range, as they are needed for many applications from methane flux measurements for environmental science to active combustion control and monitoring of gas pipelines. Up to now they have been monitored nearly exclusively via the weak second overtone of the CO stretch (1.56µm)[2] or the first overtone of the asymmetric C-H-stretch at 1.65µm[3].

We report on the spectroscopic characterization of a new 2318nm DFB-Diode laser, which permits access to the 5x stronger CH_4 combination band as well as the 50x stronger first overtone of CO. We show new data on LI-curves, threshold temperature dependence, static current and temperature tuning and most important for calibration-free TDL spectrometers on dynamic wavelength tuning which was measured with a 10cm etalon at modulation frequencies from 10 Hz to 3 kHz. For absolute wavelength calibration we used CO absorption lines of the first overtone band. Finally the laser was also used for extractive species concentration measurements of CH_4 at various total pressures, which has not been realized before with a DFB laser in this spectral range.

[1] Proc. Comb. Inst. 30, 1611-1618 (2005)
[2] Applied Optics 42, 2043-2051 (2003)
[3] Appl. Phys. B 66, 511-516 (1998), Proc. Comb. Inst. 28, 423-430 (2000), Applied Optics 44, 91-102, (2005)

D-2

Field measurements of N_2O and CO_2 using a pulsed quantum-cascade laser

Lukas Emmenegger, Kerstin Zeyer, Martin Steinbacher, Joachim Mohn

Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Air Pollution / Environmental Technology, CH-8600 Dübendorf, lukas.emmenegger@empa.ch

Quantum-cascade lasers (QCLs) have passed from research to industrial production since their development 10 years ago. Applications for the detection of numerous substances have been published, and some instrumental setups are commercially available. Our work is focused on laboratory and field tests done with an instrument supplied by Aerodyne Research Inc., which employs thermoelectrically cooled cascade lasers and detectors [1].

The QCL (Alpes Lasers, Switzerland) was driven around 4.46 µm with short (~ 10 ns) pulses and a 1% duty cycle at a temperature of approximately -25 °C. Extractive samples were measured at 65 mbar in a 0.5 l astigmatic multipass absorption cell with a path length of 56 m. The data acquisition system, TDL Wintel [2] controls the electronics and laser driver, monitors the IR detector, and analyzes the spectra to derive mixing ratios based on spectral parameters from HITRAN [3]. Spectral scans are obtained by a sub-threshold voltage ramp which creates a bias temperature. The relevant parameters were chosen to allow simultaneous detection of N_2O and CO_2 at ambient concentrations.

Laboratory tests showed excellent linearity for N_2O and CO_2 in the concentration ranges 0-1000 ppb and 0-1000 ppm, respectively. As expected, there was no experimentally detectable cross-sensitivity to CO_2 or H_2O. Quantification based on HITRAN parameters differed by up to 20 % when compared to certified calibration gases. This can be overcome by regularly measuring a reference gas. After stabilization of the optical bench and the pulse electronics we obtained a minimum Allan variance corresponding to 0.12 ppb (0.05 %) or 0.56 ppm (0.19%) for N_2O and CO_2, respectively.

In a field validation, the QCL setup was compared to FTIR and GC-FID-ECD from January 19 to 26, 2005 at a site of the National Air Pollution Monitoring Network (NABEL) in Dübendorf. Accuracy and precision were determined by replicate measurement of pressurized air from a single tank. The average concentrations and standard deviations were calculated for ten time intervals of 30 minutes. Absolute differences were 1.1 % for both CO_2 (FTIR; QCL) and N_2O (FTIR; QCL; GC). Analytical precision (2 □) was comparable for QCL and FTIR but slightly better for GC. However, precision has since significantly been improved for FTIR and QCL using better strategies for background measurement and calibration. Continuous measurements showed excellent agreement between FTIR and QCL for CO_2. The evaluation of the continuous N_2O data was not meaningful because there were no significant changes in ambient air concentrations.

[1] Nelson, D. D., McManus, B., Urbanski, S. et al. (2004), *Spectrochimica Acta A*, 60, 3325–3335.

[2] Nelson, D. D., Shorter, J. H. et al. (2002), *Applied Physics B*, 75, 343–350.

[3] Rothman, L. S., Barbe, A., Benneret al. (2003), *Journal of Quantitative Spectroscopy & Radiative Transfer* 82, 5-44.

D-3

QCL-based sensors from 3 - 130 microns: applications to gas and solid phase chemical sensing

Mark Allen, David Cook, Brian Decker, Joel Hensley, David Rosen,

Michelle Silva, Richard Wainner

Physical Sciences Inc, 20 New England Business Center, Andover, MA 01810

t: 978.689.0003, f: 978.689.3232, e: allen@psicorp.com

Type I and Type II Quantum Cascade Lasers (QCL's) have now been fabricated at wavelengths spanning the range from 3 to 130 _m. This wavelength range allows spectroscopic measurements of vibrational and rotational transitions in gases, hindered rotations in liquids, and phonon-band transitions or intra-molecular interactions in solids. This poster will outline applications focused at the extrema of this wavelength range and present representative laboratory data showing sensor architectures and results.

Ultra-Sensitive Detection of Ethane. We are developing sensors using cw Type-II QCL devices in the technically important fundamental C-H stretch region near 3.4 microns for detection of various hydrocarbons. Ethane is an important trace species in a number of applications and a highly sensitive ethane monitor would prove useful for both industrial and biomedical markets. To attain sub-ppb sensitivity, we combine Wavelength Modulation Spectroscopy with Integrated Cavity Output Spectroscopy, thereby achieving high absorbance sensitivity and optical pathlengths on the order of 1 km in a compact sensor architecture.

Remote Sensing of Hidden Explosives. Crystalline solids exhibit strong, structured phonon absorption bands in the THz spectral region between 0.5 and 3 THz. Using a time-domain, broadband spectrometer, we obtain quantitative real- and imaginary-index data for a number of pure explosives and use this data to design a multi-laser, Type-I THz-QCL LIDAR system for remote detection of explosive solids based on differential reflection spectroscopy. Because clothing and many non-metallic packaging materials are essentially transparent at this wavelength, this LIDAR sensor is expected to allow stand-off detection of explosives hidden under clothing or carried in personal items.

Atomic Oxygen Sensing. Oxygen atoms are an important species in high-altitude aeronomy and astrophysics. Strong nuclear fine-structure transitions near 63 microns are now accessible using THz QCL's. We will describe the development of an absorption sensor using an external cavity-stabilized THz QCL probe laser for atomic oxygen measurements in high-speed aeronomy test facilities.

D-4

Frequency modulated spectroscopy as a probe of molecular collision dynamics

M. L. Costen, A. Alagappan, K. G. McKendrick

School of Engineering and Physical Sciences,

Heriot-Watt University, Edinburgh, UK

m.l.costen@hw.ac.uk

Frequency modulated spectroscopy is used as a sensitive high-resolution probe of the molecular scattering dynamics of a small free radical. Photolysis of ICN vapour at 266 nm is used to produce CN $A^2\Pi^+$ radicals in a range of rotational states, with sharply defined velocity and rotational angular momentum properties. The CN radicals are probed using an external cavity tuneable diode laser around 800 nm, frequency modulated at 400 MHz by an external phase modulator. The beat signals from a photoreceiver are demodulated using an I&Q demodulator, with the transient in-phase and quadrature signals digitized by a storage oscilloscope. The resulting time and frequency dependent arrays may be used to construct pure absorption spectra of individual rotationally resolved transitions as a function of delay time after photolysis. The very narrow bandwidth of the diode laser compared to the Doppler width of the lines (Δ 5 GHz) results in a very high-resolution measurement of the translational and rotational vector properties of the CN. The collisional evolution of these properties with a variety of simple collider species will be presented.

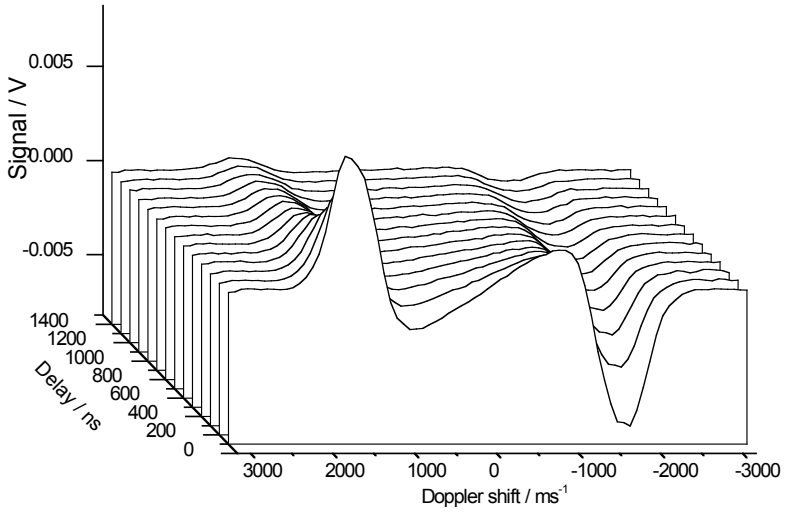


Fig.1 Example of evolution of CN $A^2\Pi^+$ (2,0) $R_1(0.5)$ transition in collisions with ICN precursor.

D-5

Spectral properties and spectroscopic applications of near-IR DFB diode lasers

Jan Posthumus, Anselm Deninger, and Frank Lison

TOPTICA Photonics AG, Lochhamer Schlag 19, 82166 Gräfelfing, Germany

Distributed feed-back (DFB) laser diodes offer a narrow line width, convenient frequency tuning and high output power. These diodes, originally developed for telecom wavelengths, have recently become available within the entire wavelength range from 730 nm to 2800 nm. Relevant wavelengths for alkali spectroscopy, plasma physics and trace gas analysis can thus be covered with compact, robust and inexpensive DFB laser systems. This includes the important resonance transitions at 763 nm (O_2), 811 nm (Ar*) and 935 nm (H_2O) as well as the D_1 and D_2 transitions of K, Rb and Cs. We studied the spectral properties, tuning characteristics and modulation behavior of continuous wave, single-mode DFB diodes, and demonstrated the suitability of DFB diodes to high-resolution spectroscopy.

The output power of the DFB lasers was between 10 and 150 mW, depending on the wavelength. All diodes emitted within a single-mode (TEM_{00}) beam profile. In the laser spectrum, the background of amplified spontaneous emission (ASE) was suppressed relative to the coherent part of the laser radiation by 40-55 dB (measured with a grating spectrometer with 60 pm resolution).

The high sensitivity of the emission frequency to temperature or current changes calls for low-noise control electronics for applications that require narrow line width and/or high frequency stability. We used a ”ColdPack” adapter (TOPTICA Photonics) to control the temperature of the laser diodes. This TO-3 sized package comprises an integrated thermistor and four thermo-electric coolers and can be used to rapidly heat or cool the diode, or alternatively stabilize the laser temperature. A long-term frequency stability of < 20 MHz (standard deviation within a 9 h measurement period) was obtained for a temperature-stabilized DFB diode, without any additional locking scheme. When locked to an atomic absorption line, a frequency stability on the 1 MHz level could be realized.

To test the performance of the DFB lasers in a spectroscopic application, Doppler free saturation spectra of the D_1 and D_2 transitions of rubidium and cesium were recorded. All hyperfine transitions and cross-over lines could be resolved. The measured half width of the Doppler-free peaks was 9 MHz [1], close to the natural line width of 6 MHz.

The line width of the DFB diodes was further examined in a heterodyne beat experiment with two identical lasers, side-of-fringe locked (bandwidth 10 kHz) to Doppler-free resonances of the D_2 transition of ^{87}Rb at 780 nm. The spectral half width of a single laser of about ~ 2.4 MHz was found to be constant for scan times between 50 ms and 10 s. Multiple sharp “needles” on the line profile indicated a much narrower instantaneous line width of the DFB diodes. The observed technical line width thus results from frequency jitter occurring on time scales much shorter than the data acquisition time. This can be related to spatial hole burning within the semiconductor cavity [2].

Tuning and modulation properties of the DFB diodes were investigated using a high resolution wavelength meter (HighFinesse-Angstrom WS/7) with an absolute accuracy of 100 MHz. In general, the frequency of DFB lasers can be tuned by varying either the operating current, or the temperature of the laser chip. Thermal tuning is comparatively slow (typically 0.5 nm/s), however extremely large mode-hop free tuning ranges can be attained. Continuous tuning of 1346 GHz (3.6 nm) over a 47 K temperature sweep was demonstrated for a DFB laser @ 895 nm. The thermal tuning rate $\Delta\nu/\Delta T$ of the DFB lasers typically amounted to 25 … 30 GHz/ K (ca. + 0.06 nm/K). Much faster frequency tuning within a smaller range can be accomplished by modulating the driver current of the laser diode. This modulation alters both the carrier density and the temperature of the semiconductor and therefore, the electrical tuning rate $\Delta\nu/\Delta I$ depends upon the modulation frequency. We measured $\Delta\nu/\Delta I$ ~ 1.3

GHz/mA at very slow modulation frequencies (0.1 Hz), and tuning rates of ~ 0.6 GHz/mA at 10 kHz modulation.

The output power of DFB diodes is sufficient for subsequent amplification in a semiconductor amplifier. We coupled the output of a 10 mW DFB diode @ 852 nm into a tapered amplifier chip and demonstrated coherent amplification of the laser radiation up to 600 mW, preserving the spectral properties of the seed laser light. The availability of a conveniently tunable, high-power laser source opens many new possibilities including non-linear frequency conversion or the usage of multiple beams for laser cooling and trapping experiments. Another application that will benefit from the large mode-hop free tuning range of DFB lasers is the generation of tunable cw Terhahertz (THz) radiation via difference frequency mixing. In particular, the possibility to individually tailor the emission wavelength of DFB laser chips with high precision will permit the realization of a dual-wavelength laser source with a difference frequency continuously tunable from 0 to > 2 THz.

[1] S. Kraft, A. Deninger, Ch. Trück, J. Fortagh, F. Lison and C. Zimmermann, Laser Phys. Lett. 2, 71 (2005).

[2] X. Pan, H. Olesen, and B. Tromborg, IEEE Photon. Tech. Lett. 2, 312 (1990).

D-6

Measurement of nitrogen dioxide in cigarette smoke using quantum cascade tunable infrared laser differential absorption spectroscopy (TILDAS)

Joanne H. Shorter [1], David D. Nelson [1], Mark S. Zahniser [1], Milton E. Parrish [2], Danielle R. Crawford [2], Diane L. Gee [2]

[1] Aerodyne Research Inc., 45 Manning Road, Billerica, MA 01821-3976 USA

[2] Philip Morris USA Research Center, 4201 Commerce Road,

Richmond, VA 23234 USA

Although nitrogen dioxide (NO_2) has been previously reported to be present in cigarette smoke, the conclusions were derived from kinetic measurements or from smoke collection methods where NO_2 was formed sometime after the puff was taken. These investigators discussed the reactivity of this species and the difficulty of selective detection in the cigarette smoke matrix. In conducting research to modify conventional cigarettes for reducing the NO levels in smoke, it is important to monitor unexpected changes in other constituents in the smoke, such as NO_2. The objective of this work was to determine if NO_2 could be detected and quantified in a fresh puff of cigarette smoke. Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS) using quantum cascade (QC) lasers has been used previously to rapidly and accurately quantify selected gaseous constituents, such as CO_2, CO, NH_3, and NO, present in single puffs in mainstream and also in sidestream cigarette smoke. NO_2 was measured in a single puff using a QC laser operating at 1604.6 cm^{-1} with a 56 m pathlength, 0.5L volume gas cell. This technique provided a temporal resolution of ~0.2 sec so the measurement was taken directly as the NO_2 was formed during the puff. The detection limit was ~5 ppbV, which is equivalent to ~ 0.4 ng in a puff volume of 35 mL.

Smoking was performed using a square-wave puff profile, 35 mL puff volume, 2 sec duration, once every minute. Experiments were conducted using 2R4F Kentucky Reference cigarettes with and without a Cambridge filter pad. NO_2 was detected only in the lighting puff of whole smoke (without a Cambridge filter pad), with no NO_2 detected in the subsequent puffs. Several lighting sources were used, and it was shown that more NO_2 was generated in the lighting puff using a match or butane lighter (29 ± 21 ng) than when using an electric lighter (9 ± 3 ng). However, in the presence of a Cambridge filter pad, NO_2 was observed in the gas phase smoke for every puff (total of 200 ± 30 ng/cigt.). This observation is most likely an artifact due to changes in the smoke chemistry taking place on the filter pad where the smoke condensate has been deposited from the previous puffs.

D-7

Anti personnel mine detection using laser induced breakdown spectroscopy

Wolfgang Schade [1,2], Christian Bohling [1], Konrad Hohmann [1], Dirk Scheel [1], Gerhard Holl [3]

[1] Technische Universität Clausthal, Institut für Physik und Physikalische Technologien, Leibnizstrasse 4, 38678 Clausthal, Germany

[2] Technische Universität Clausthal, LaserApplikationsCentrum, Arnold Sommerfeld Strasse 6, 38678 Clausthal, Germany

Phone: +49 5323 72 2061, Fax: +49 5323 72 3318, wolfgang.schade@tu-clausthal.de

[3] Wehrwissenschaftliches Institut fuer Werk-, Explosiv-, und Betriebsstoffe (WIWEB), 53913 Swisttal, Germany

The great number of mines laid worldwide requires detection methods that enable a reliable and fast detection for clearing purposes. Since many mines are cased by plastic materials, they cannot be detected by conventional geo-radars or metal detectors. Therefore, the use of a conventional manually operated mine prodder is combined with laser-induced breakdown spectroscopy (LIBS). This method is very promising because it allows analyzing solid state samples in real-time. A portable LIBS system requires a miniaturized laser which enables the generation of high power laser pulses. Therefore, a miniaturized passively Q-switched Cr^{4+}:Nd^{3+}:YAG-microchiplaser [1] is used as a seed laser for an ytterbium-fiber amplifier. Laser-pulses with duration below 1 ns, a repetition rate of up to 15 kHz and pulse energy of typically 25 µJ are emitted. For high power amplification an ytterbium fiber amplifier is used [2]. A large mode area double clad ytterbium doped optical fiber is pumped by a high power cw diode laser (P = 50 W, l = 976 nm). With the present set-up, laser pulses with a power of up to E_p = 1 mJ and a pulse duration Δt = 1 ns at a repetition rate f_{rep} = 2 to 15 kHz are generated. This corresponds to a peak power of P = 1 MW or an intensity of I = $1x10^{11}$ W/cm^2 which allows the generation of a plasma on different mine casing materials and explosives as well as drilling holes through the casing of plastic mines. The intense laser pulses are guided via optical fibers through a conventional mine prodder; its tip is sealed by a lens which focuses the laser light directly in front of the lens surface to ignite a plasma as soon as the prodder tip is in contact with the material to be inspected. The light emission of the plasma is collected by the same lens and imaged onto an ultraviolet transparent optical fiber bundle and measured by a photomultiplier (Typ Hamamatsu H5773-06). Spectral filtering is done by using band-pass filters with center wavelengths at 248 and 388 nm, respectively. The time resolved data analysis of the raw LIBS data is done by applying neural networks.

This work is financially supported by the German Ministry of Defence under contract E/E210/3D023/X5/65.

References

[1] Willer, U., Blanke, T., Schade, W., Appl. Opt., 40, 5439-5445 (2001)

[2] Limpert, J., Höfer, S., Liem, A., Zellmer, H., Tünnermann, A., Knoke, S., Voelckel, H., Appl. Phys. B 75, 477–479 (2002)

D-8

Spectroscopy of HDO in the 6.7 μm region with a quantum cascade laser spectrometer

L. Joly [a], B. Parvitte [a], L. Daumont [a], V. Zéninari [a],

A. Jenouvrier [a], G. Durry [a,b], D. Courtois [a]

[a] *Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA), UMR CNRS 6089,*

Faculté des Sciences, BP 1039, F-51687 Reims Cedex 2 - France

[b] *Institut Pierre Simon Laplace (IPSL), Service d'Aéronomie, UMR 7620, CNRS-R_duit de Verri_res, B.P. 3, 91371 Verri_res-le-Buisson Cedex, France*

Since the first realization of a quantum cascade laser (QCL) in 1994, many applications have been studied: communications (for example, high-speed digital data transmission and optical free-space high-speed links), detection and quantification of trace gases, and high-resolution spectroscopy. Spectroscopic detection sensitivities of trace gases down to one part in 10^9 (ppb) concentration level can be achieved.

We had previously demonstrated the possibility to use DFB QCL to make spectroscopic measurements of SO_2 in the 9.1 μm region [1]. We will present a spectroscopic study of the □2 band of HDO between 1480 and 1490 cm^{-1}. This study has been made using a DFB quantum cascade laser (QCL) from Alpes Lasers (Switzerland). The detection of atmospheric HDO is of high interest for geophysicists. Its measurement is used to identify the different scenarii for the injection of tropospheric water vapor in the low stratosphere in the tropical region.

Line intensities of 5 lines of HDO were determined in this region. These measurements need careful attention to correctly determine the isotope ratios in our sample. The results are compared with previous experimental determinations by Fourier-transform spectrometry and available database. The HDO spectroscopic measurements are also used to detect atmospheric HDO.

[1] L. Joly et al, Spectroscopic study of the n1 band of SO2 using a continuous wave DFB QCL at 9.1 μm, Applied Physics B: Lasers and Optics, 77, 703-706, (2003)

D-9

A comparison of VCSEL and edge-emitting diode lasers when sensing nitrogen dioxide in the 660 nm region

S. N. Andreev, D. F. Baltakov, V. N. Ochkin, S. Yu. Savinov, M. V. Spiridonov, S. N. Tskhai

P. N. Lebedev Physical Institute

53 Leninskii prosp., 119991 Moscow, Russia

max@sci.lebedev.ru

A comparison of sensitivities of VCSEL and edge-emitting lasers based gas analyzers arouses different opinions [1, 2].

Large frequency tuning range of VCSEL can improve sensitivity of gas analyzer when measuring molecules which have complex absorption spectrum with overlapped spectral lines, such as nitrogen dioxide molecule (NO_2) [3,4].

The performance of VCSEL and edge-emitting Fabry-Perot commercial diode lasers for low concentration NO_2 sensing is experimentally compared. A correlation technique with linear regression was applied to process recorded spectra and to calculate NO_2 concentration.

Detectivities of 0.3 ppm*m using the VCSEL and 3.5 ppm*m using the Fabry-Perot edge-emitting laser were determined in the 660 nm region. It should be mentioned that 660 nm is not the best region to detect NO_2, because a local minimum of NO_2 absorption coefficient is observed around 662 nm. Use of the VCSEL operating in the region 645-650 nm could improve detectivity of NO_2 by a factor of 10-15.

This work was partially supported by RFBR grant 04-02-08192.

References

[1] V. Weldon, J. O'Gorman, J. J. Perez-Camacho, D. McDonald, J. Hegarty, J. C. Connolly, N. A. Morris, R. U. Martinelli, J. Y. Abeles. Infrared Phys.&Techn., **38**, p. 325–329 (1997).

[2] J. Wang, S. T. Sanders, J. B. Jeffries, R. K. Hanson. Appl. Phys. B: Laser and Optics, **72**, p. 865–872 (2001).

[3] D. M. Sonnenfroh, M. G. Allen. Applied Optics, **35**, p. 4053–4058 (1996)

[4] A. I. Nadezhdinskii, Ya. Ya.Ponurovskii, M. V. Spiridonov, E. A. Kudryashov, 4 Int. Conf. on TDLS, p.87 (2003). See also D-10

D-10

Instrument based on visible diode laser to detect trace NO_2 concentration with minimum detectable concentration at ppt level

A. Berezin, S. Chernin, A. Makkaveiskii, S. Malyugin, T. Moskalev, A. Nadezhdinskii, D. Namestnikov, Ya. Ponurovskii, Yu. Shapovalov, D. Stavrovskii

NSC of A. M. Prokhorov General Physics Institute

NAD@nsc.gpi.ru

Detection of trace NO_x concentration is important for variety of applications. NO_2 molecule has intensive vibronic transition in near UV, visible, and near IR. In [1] near IR DL was used for its sensitive detection, ultrasensitive detection with visible DL was achieved in [2]. Research in this direction started in GPI several years ago and its preliminary results were presented in [3].

The instrument developed contains visible diode laser and two channels: analytical and reference ones. Analytical cannel includes Chernin multipass optical cell (0.5 m, 300 passes). The molecule under detection concentration was determined using signals in analytical and reference channels and cross-correlation algorithm [4, 5] proposed for complex spectra with overlapping lines. This algorithm provides optimal signal filtering and gives additional sensitivity improvement proportional to N (N is the number of spectral peculiarities in recorded spectrum).

Approaches developed recently (see separate posters) were incorporated in present instrument operation. Noise equivalent absorption achieved for this particular case was limited by diode laser intensity quantum noise and was equal to 10^{-7} for 1 sec averaging time.

Taking into account above mentioned parameters of experimental setup, instrument operation mode, and calibration procedure discussed minimum detectable absorption was found to be 2.7 ppt (atmosphere pressure — atmosphere broadened spectrum) and 0.75 ppt (for reduced pressure when broadening is close to Doppler one).

References

[1] W. Lenth, M. Gehrtz, Appl. Phys. Lett., 1263–1265 (1985)

[2] D. Sonnenfroh, M. Allen, Appl. Opt., 35, #21, 4053–4058 (1996)

[3] A. Nadezhdinskii, Ya. Ponurovskii, M. Spiridonov, E. Kudryashov, in TDLS 2003, Abstracts of papers, Zermatt, 2003, p.87

[4] I. Zasavitskii, Yu. Kosichkin, A. Nadezhdinskii, E. Stepanov, A. Tishenko, A. Shotov, Kratkie soobsheniya po fizike, _9, 13–17 (1983) (in Russian)

[5] A. Nadezhdinskii, I. Zasavitskii, in “Monitoring of gaseous pollutants by tunable diode lasers”, R.Grisar, H. Preier, G. Schmidtke, G. Restelli (Ed.), Proc. Int. Symposium, Freiburg, FRG 1986, D. Reidel Publ. Com., Dordrecht, 1987, p.95–106

D-11

Statistical analysis of data series in TDLS

A. Nadezhdinskii

NSC of A. M. Prokhorov General Physics Institute

38 Vavilov str., 119991 Moscow, Russia

NAD@nsc.gpi.ru

Allan plots were proposed initially to analyze long-term laser frequency stability [1]. In TDLS it was used for the first time for concentration measurements in [2]. Allan approach in addition to FFT is efficient for analysis of any data series. In the paper we'll present experimental investigation and model calculations of Allan plots for main noises models: white noise, white noise after different filters, flicker noise, drift. Several examples of software developed for real time calculation of FFT and Allan plots will be presented. Some applications in TDLS of software developed will be considered.

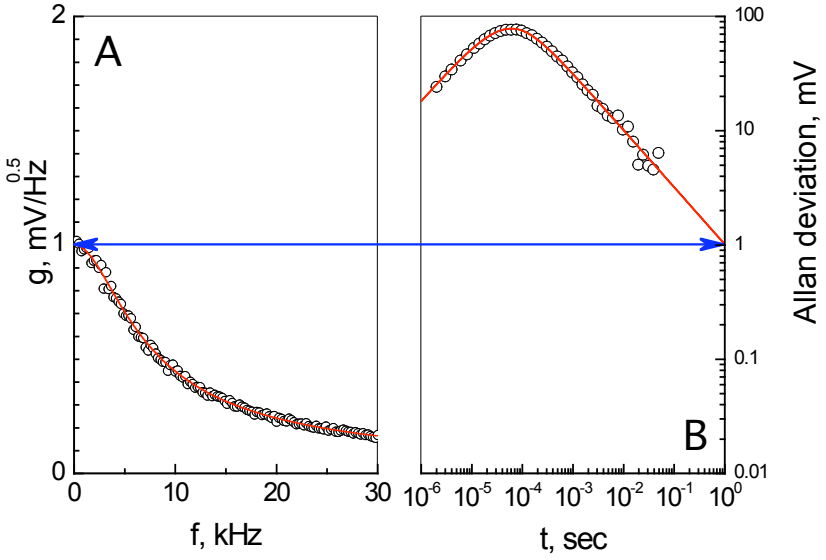


Fig.1 Noise spectral density (left) and Allan plot (right) for white noise after first order filter.

Fig.1 shows example of this investigation. In this particular case, white noise after first order filter was investigated. Important result of this investigation: values of noise spectral density at f = 0 and Allan deviation at t = 1 sec have to be the same. This result does not depend on filter type. Hence, it is good check of experimental accuracy. Moreover, either spectral density or parameters of Allan plot can be determined from independent measurements. **It necessary to mention, that many references failed with this fundamental check.**

References

[1] D. W. Allan, Proc. IEEE 54, 221-230 (1966).

[2] P. Werle, R. Mucke, F. Slemr, Appl. Phys. B 57, 131-139 (1993).

D-12

Tunable single-frequency diode laser at wavelength _ = 1.52 _m for ammonia concentration measurements

A. V. Gladyshev, M. I. Belovolov, S. A. Vasiliev, O. I. Medvedkov

Fiber Optics Research Center at A.M. Prokhorov General Physics Institute of the Russian Academy of Sciences, 38 Vavilov Str., 119991, Moscow, Russia

V. P. Duraev, E. T. Nedelin

NOLATECH Joint Stock Company, 3 Vvedensky Str., 117342, Moscow, Russia

A. I. Nadezhdinskii, Ya. Ya. Ponurovskii

A. M. Prokhorov General Physics Institute of the Russian Academy of Sciences, 38 Vavilov Str., 119991 Moscow, Russia

We present a novel tunable single-frequency diode laser on an InGaAsP/InP heterostructure for ammonia concentration measurements. The laser has a hybrid cavity based on a fiber Bragg grating (FBG) and the rear facet of the laser diode. To our knowledge, so-designed lasers have not been previously used for gas analysis. In our previous paper [1] we showed that, if constructed properly, FBG-based external cavity diode lasers can be very a convenient, simple, and cheap solution for the gas-analysis applications.

In this work, a mode-hop-free tuning range of hybrid lasers as wide as □_=40 GHz (1.33 cm^{-1}) has been achieved for the first time. Single-frequency operation with a linewidth of less than 15 MHz has been obtained, the SMRS being larger than 20 dB and the output power larger than 5 mW. These parameters enabled us to detect a multiplet structure of the ammonia absorption near _=1.5225 _m (Fig.1). The operating wavelength was tuned by the injection current.

The approach we used could be easily applied to any gases with absorption lines in the optical fiber transparency window (0.7–1.7 _m). The presence of a fiber-optic output is an additional advantage of the laser design developed, because it makes it possible to carry out remote gas analysis.

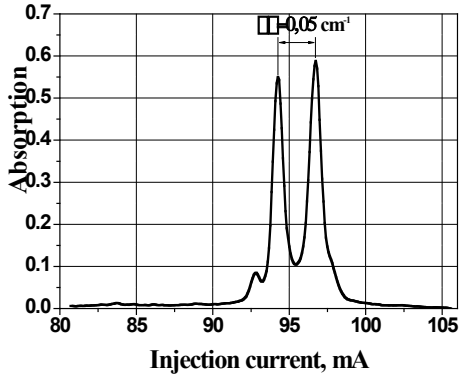


Fig.1. Experimentally observed ammonia absorption multiplet near _=1.5225 _m at a pressure P=12 Torr and temperature T=300 K. The cell length was 40 cm.

[1] A. V. Gladyshev, M. I. Belovolov, S. A. Vasiliev, E. M. Dianov, O. I. Medvedkov, A. I. Nadezhdinskii, O. V. Ershov, A. G. Beresin, V. P. Duraev, E. T. Nedelin, “Tunable single-frequency diode laser at wavelength

λ = 1.65 μm for methane concentration measurements", *Spectrochimica Acta Part A*, **60**, 14, p.3337–3340, 2004.

D-13

Optimal spectral range and operation mode for trace molecule detection with diode lasers

A. Nadezhdinskii

NSC of A.M.Prokhorov General Physics Institute

38 Vavilov str., 119991 Moscow, Russia

NAD@nsc.gpi.ru

Optimization of Tunable Diode Laser based systems for trace molecule detection is of great importance for different applications. System optimization approach was considered briefly in [1] taking into account physical properties of all system elements: DL, photo-detector, optical scheme, object of interest, etc. In present paper we'll pay more attention to three main components of the system: molecule, photo-diode, and diode laser. Fig.1 presents comparison between molecular absorption and photo-diode NEP.

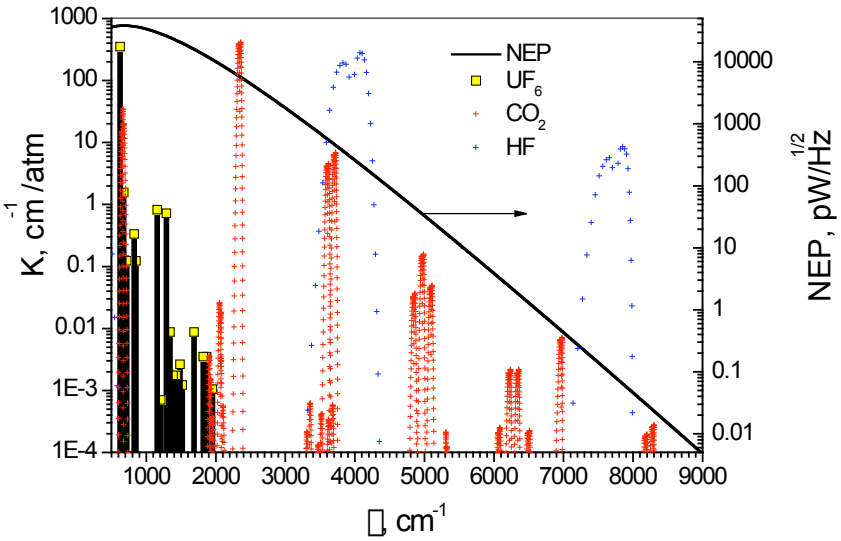


Fig.1 Comparison between absorption spectra of three molecular groups representatives and photo-diode NEP (Noise Equivalent Power).

Molecules can be classified into 3 main groups with respect to their Born-Oppenhimer parameter (ratio of electron mass to effective mass of normal vibration). For many molecules S/N ratio is higher in near IR spectral range where overtones and combination bands are located in comparison with fundamentals in mid IR. Comparison of quantum and thermal detectors will be given. History of diode laser operation modes will be considered and their new generation with respect to technique progress and diode laser physical properties understanding will be presented.

References

[1] A. Nadezhdinskii, Optimization of trace molecule detection using tunable diode lasers, in TDLS 2003, Abstracts of papers, Zermatt, 2003, p.79.

D-14

Measurement of water isotopomers via TDLS in the vicinity of 1.392 _

T. Kumanskaya, A. Nadezhdinskii, Ya. Ponurovskii, Yu. Shapovalov, D. Stavrovskii, I. Vyazov

Natural Sciences Center of the A. M. Prokhorov General Physics Institute RAS
38 Vavilov str., 119991 Moscow, Russia. E-mail: stavr@nsc.gpi.ru

A. Babichev, G. Grigoriev, S. Malyugin, Sh. Nabiev, A. Ustinov

Russian Research Centre "Kurchatov Institute", 1 Kurchatov sq, 123182 Moscow, Russia

Production of oxygen isotopes with vacuum water rectification is an important sector of stable isotopes industry. The ^{18}_ isotope (oxygen-18) is widely applicable in medicine, most of all, in positron-emission tomography (PET scanners) diagnostics and researches of various metabolism processes in live tissues. Mass-spectrometer measurements of water isotopomer composition are rather expensive and time-consuming; densitometry is a cheap and rapid method, but lacking the necessary accuracy. TDLS is a good alternative method [1]. This report suggests a prototype of the device intended for rapid analysis of water isotopomer composition with the use of near-infrared diode laser.

Distributed feedback (DFB) diode laser (DL) from Laser Components GmbH was used. The wavelength of lasing was in the vicinity of 1.392 _m. The DL was pumped with trapezoidal pulses of 0.5–1 ms duration and 1–2 kHz repetition rate. Frequency tuning of the DL radiation was produced in the frequency interval 7183.2–7185.0 cm^{-1} This interval was chosen to ensure simultaneous detection of 5 water isotopomers ($H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$, $HD^{16}O$, $D_2{}^{16}O$) [1,2].

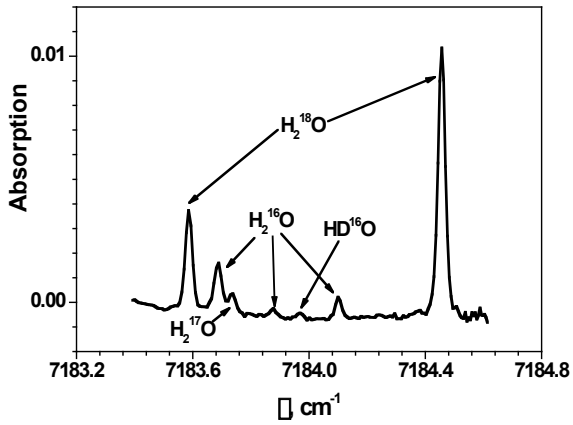


Fig. 1 Example of water isotopomers spectrum.

Samples of water vapor with various isotope contents were placed under pressure from 3 to 10 Torr in one of two cells with optical paths of 80 and 10 cm, depending on the task ("enrichment" or "depletion"). The 80-cm cell is intended for measuring the water isotope composition at low ^{18}_ isotope content (from 0.01 to 1%). The other cell is used for measuring high ^{18}_ isotope contents (0.5–100%). Absorption spectra of water vapor were detected with a NI DAQ I/O board. Software developed was based on LabVIEW. Isotopic ratio factors were calculated by use of integral cross section data of HITRAN-2004 [3]. The time interval of single measurement was ~ 0.2 s. The time of single probe development was much greater (up to 10 minutes). It depends mainly on pumping and filling process to reduce memory influence of previous sample. Fig. 1 presents example of experimental spectrum for one of the water samples.

The results obtained in the interval of 0.5–98% ^{18}O concentration were compared with the results of mass spectrometry measurements. A good agreement was observed. The apparatus and procedures developed are used for routine measurements to control water isotopomers separation process at Kurchatov Institute.

[1] E. R. T. Kerstel et al. *Spectrochimica Acta Part A 58* (2002) 2389-2396.

[2] R. A. Toth, *Appl. Opt. 33* (1994) 4851–4867; *Appl. Opt. 33* (1994) 4868–4879; *J. Mol. Spectrosc. 186* (1997) 66–89.

[3] L. S. Rothman et al, The HITRAN molecular spectroscopic database, *JQSRT*, vol. **82**, numbers 1–4, 15 November–15 December (2003). http://cfa-www.harvard.edu/hitran/

D-15

A novel technique for rapid wavelength scanning of extended cavity diode lasers

J. Hult, I. S. Burns, C. F. Kaminski

Department of Chemical Engineering, University of Cambridge,

Pembroke Street, Cambridge CB2 3RA, UK

E-mail: clemens_kaminski@cheng.cam.ac.uk

Extended cavity diode lasers have been used extensively in high resolution spectroscopy and gas sensing due to their wide tunablity and high spectral purity. The multi-mode Fabry-Pérot diode laser is forced to emit on a single longitudinal mode by narrow-band optical feedback that is typically provided by a reflection grating mounted in the Littrow geometry. In order to achieve mode-hop free scanning over a broad spectral range, it is necessary to rotate the grating while simultaneously tuning the lengths of the extended cavity and of the internal FP cavity. This can be done for example by tuning the diode laser injection current while simultaneously modulating the voltages applied to multiple piezo-electric transducers within the grating mount [1].

As the rate at which such mode-hop free tuning is performed rises, the bandwidth of the scan reduces, and it is difficult to achieve useful tuning ranges at scanning rates of above about 1 kHz. This limitation results from non-linearities and hysteresis in the response of the piezo elements, and mechanical resonances in the system.

An innovative approach has been developed in which the need to match carefully the grating and current tuning is obviated. Instead the grating position is kept fixed throughout the scan and only the current is tuned. This causes a series of mode-hops, but useful data can nonetheless be extracted. This scanning method has been tested by performing laser induced fluorescence of indium atoms. It has been observed that during the current scan, there are regularly spaced regions in which the laser is single-mode and on resonance with an electronic transition of atomic indium. These regions are separated by a frequency corresponding to the free-spectral range of the diode FP cavity. Between such regions, where a fluorescence signal is detected, the laser is emitting on another diode mode that does not overlap with the indium transition. This is because the width of the indium transition being probed is less than the diode FP mode-spacing. Wavelength scanning by this method has been performed at rates of up to 20 kHz and the indium spectra thus acquired show good agreement with a fitted theoretical spectra.

Full details of the advantages and limitations of this wavelength tuning technique, and an outline of the types of situations to which it is applicable, will be given in our poster presentation.

[1] J. Hult, I. S. Burns, C. F. Kaminski, “Wide bandwidth mode-hop free tuning of extended cavity GaN diode lasers” Applied Optics, 2005, *in press*

D-16

Tunable diode laser spectroscopy of the $[Ar\text{-}N_2]^+$ complex: new experimental/theoretical results

H. Verbraak [a], J. Bouwman [a], D. Verdes, H. Linnartz [a]

J. van Stralen [b] and F. M. Bickelhaupt [b]

[a] *Laser Centre and Department of Physical Chemistry, Vrije Universiteit Amsterdam*

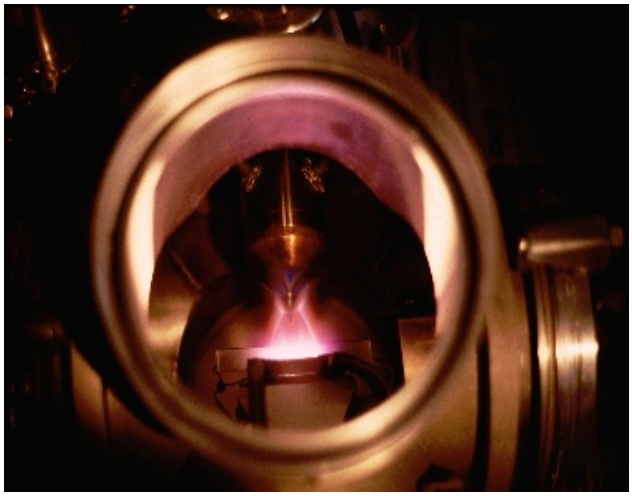
[b] *Department of Theoretical Chemistry, Vrije Universiteit Amsterdam*

De Boelelaan 1083, NL 1081 HV Amsterdam, the Netherlands

There exists much interest in high resolution infrared spectroscopy on molecular cluster ions. These complexes are benchmark systems to study the nature of intermolecular forces in charged environments, and in addition, cluster ions are present in the Earth's upper atmosphere where they play a role as a starting point in aerosol formation. A particularly interesting complex is the $[Ar\text{-}N_2]^+$ charge-transfer complex. The ionization energies of Ar and N_2 are approximately the same (15.760 and 15.581 eV, respectively). This means that an intermolecular quasi-covalent bond can be formed through the interaction of the $3p_z$ atomic orbital of Ar and the $3\sigma_g$ molecular orbital of N_2, resulting in a $^2\Sigma^+$ ground state with a relatively large binding energy (~1.2 eV). It is interesting to study what happens during the complexation as another well known feature shows that upon photodissociation the complex prefers the Ar^+/N_2-channel even though the Ar/N_2^+-channel is energetically more favorable.

In our present setup it is possible to produce large abundances of $[Ar\text{-}N_2]^+$ in mass spectrometrically controlled supersonic planar plasma, which is generated through electron impact ionization of a gas mixture (400 mbar Ar / 200 mbar N_2) that expands supersonically through a long and narrow slit (Fig. 1). A tunable diode laser spectrometer is used to record the signals in direct absorption. High detection sensitivity is obtained by applying production modulation and using lock-in amplifiers.

The present work is an extension of previous work [1]. The number of observed transitions has been extended to more than 100 and a detailed theoretical study allows conclusions beyond the experimental work. The geometry of $[Ar\text{-}N_2]^+$ has been optimized with the help of CCSD(T) using a cc-pVQZ basis set. Density functional theory has been applied to calculate the dipole moment, all vibrational frequencies, hyperfine interactions and charge distribution. Conclusions regarding the charge transfer can be made now.



References

[1] H. Linnartz, D. Verdes, J.P. Maier, Science **297** (2002) 1166.

[2] H. Verbraak, J. Bouwman, D. Verdes, H. Linnartz, J. van Stralen, F. M. Bickelhaupt, in preparation.

D-17

Trace gas detection of CO using a pulsed quantum cascade laser

B. W. M. Moeskops, S. M. Cristescu, F. J. M. Harren

Molecular and Laser Physic, Institute for Molecules and Materials,

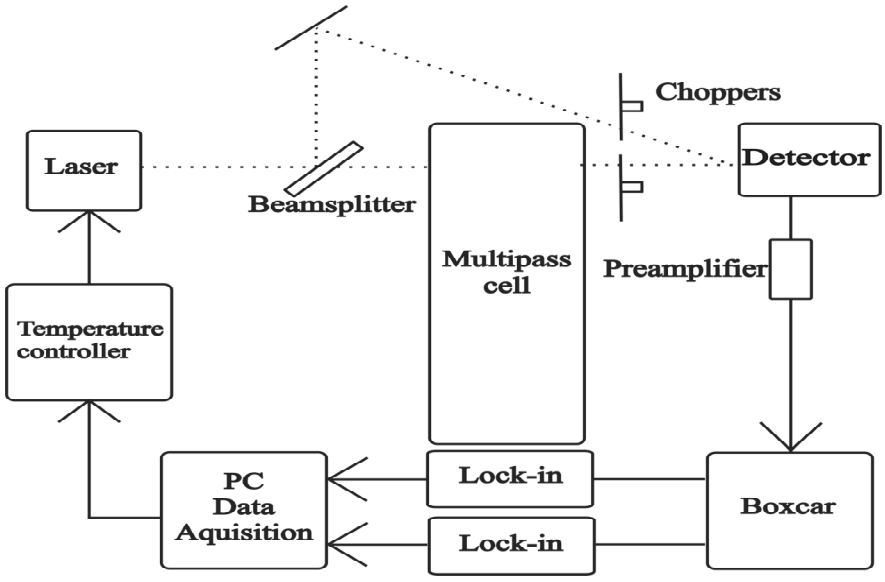
Radboud University Nijmegen

NL-6500 GL Nijmegen, The Netherlands

E-mail:B.Moeskops@science.ru.nl

A pulsed quantum cascade laser is used for the detection of carbon monoxide (CO) at ppbv levels. For medical applications CO is an interesting molecule because it is derived in the body not only from exogenous sources, but also from endogenous ones. Normally, the main part of the endogenously formed CO comes from the degradation of erythrocytic and hemoprotein heme [1]; the remainder is suspected to be derived from non-heme involving processes, such as lipid peroxidation. Breath measurements have shown increased levels of CO for both these types of conditions. Our QC-laser operates between 2176 cm and 2183 cm and has a average output power of 0.2 mW with a repetition rate of 20kHz and a pulse length of 20 nsec. The laser is passed through a 20 m absorption cell and in parallel through a reference cell and then detected on a single, fast infrared detector. The difference in arrival time (70 nsec) makes it possible to distinguish both signals. A single boxcar gate over these two pulses is used to improve the duty cycle and amplify the signal. Two choppers and lock-ins are then used to separate both signals further.

CO is detected at the strong R(9) ro-vibrational transition at 2180 cm^{-1} with a detection limit of 30 ppbv which give an equivalent sensitivity of the sensor of 2 x 10^{-7} cm^{-1} $\sqrt{Hz}$.



References

[1] S. A. Kharitonov and P. J. Barnes, Am J Respir Crit Care Med Vol 163. pp 1693–1722, 2001

D-18

650-kHz wide Lamb dip of the 3.3 micron band of methane with difference frequency generation and enhanced cavity

K. Anzai, H. Sasada, N. Yoshida [1]

Department of Physics, Faculty of Science and Technology

Keio University

3-14-1, Hiyoshi, Kohoku-ku, Yokohama, 223-8522, Japan

[1] *Department of Environmental Science and Technology*

Interdisciplinary Graduate School of Science and Engineering

Tokyo Institute of Technology

4259, Nagatsuta-cho, Midori-ku, Yokohama, 226-8502, Japan

We have observed a narrow saturated absorption line of the ν_3 band transitions of methane. The 3.4-μm radiation is provided by difference frequency generation using a periodically poled lithium niobate (PPLN), in which a 1.064-μm YAG laser beam is overlapped with the 1.55-μm light beam from a widely tunable external-cavity diode laser followed by a fiber amplifier. The spectral linewidth of the mid-infrared radiation is less than 0.1 MHz with the output power of a few μW. To enhance the optical field strengths for nonlinear spectroscopy, we have employed a Fabry-Perot cavity absorption cell. [1]. The frequency of the mid-infrared radiation is servo-locked to one of the cavity resonances, which is swept for recording the spectrum.

Figure 1 shows the observed spectrum of the P(7) E transition of $^{12}CH_4$. The 650-kHz wide (FWHM) Lamb dip is observed at the peak of the 270-MHz wide Doppler broadened absorption line. The sample pressure is 2 mTorr, and the contrast is about 1.2 %. The linewidth is probably determined by the transit-time across the 0.8-mm wide cavity mode.

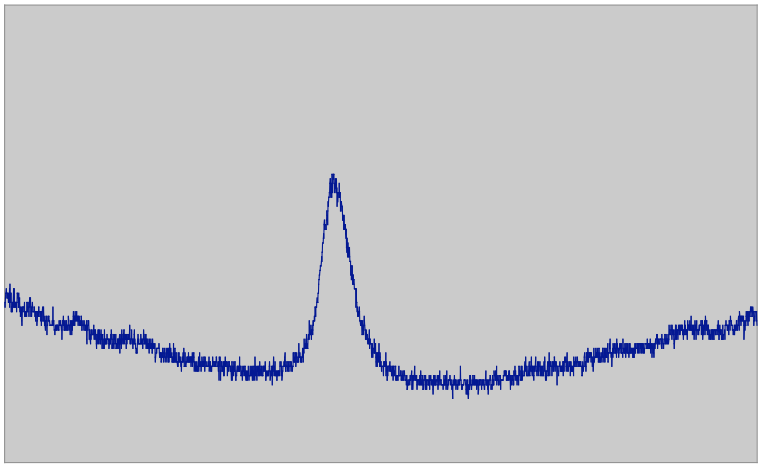


Fig. 1 The observed Lamb dip of the ν_3 band transitions of methane.

References

[1] M. de Labacherelie, K. Nakagawa, and M. Ohtsu, *Opt. Lett.,* **19**, 840-842 (1994)

D-19

2.3 µm single-frequency tunable VCSEL for gas detection

A. Ouvrard [a], A. Garnache [a], L. Cerutti [a], F. Genty [a] and D. Romanini [b]

[a] *Centre d'Électronique et de Micro-optoélectronique de Montpellier, CNRS-UMR5507 Université Montpellier II, France*

[b] *Laboratoire de Spectrométrie Physique, CNRS-UMR5588 Université Joseph Fourier de Grenoble, France*

We present a study of single-frequency Sb-based semiconductor VCSEL's operating at 2.3µm in CW at room-temperature. Two kinds of VCSEL are presented ; a micro-cavity VCSEL (µC-VCSEL) and an external-cavity VCSEL (VECSEL). These lasers are studied in terms of output beam quality, polarization stability and spectral behavior for spectroscopy applications in the 2-2.5µm atmospheric transparency window (CH4, NH3, CO2...). The GaSb -_-VCSEL structure, is composed of a Bragg mirror (>99.8% of reflectivity) and quantum well based active layer [1]. The VECSEL is formed by the _-VCSEL, a 15mm air gap, and a concave dielectric mirror (99.4% of reflectivity). The µC-VCSEL is formed by a dielectric mirror (99% of reflectivity) [2] evaporated on the _-VCSEL. Optical pumping is achieved using a single transverse mode low power 830nm laser diode.

CW operation was obtained for the VECSEL (µC-VCSEL) near 2.3µm (2.34µm), up to 350K (320K). The VECSEL reaches 5mW at 288K with a threshold power density of 600W/cm2, as low as GaAs-based VECSEL. VECSELs exhibit a circular low divergent TEM00 beam with a M2<1.1 (M2=2.3 for the µC-VCSEL), that allows long collimation (200m). VECSEL emission is single-frequency up to 5mW with a laser linewidth < 22kHz, limited by the apparatus function. We measured a side-mode suppression-ratio >30dB and a polarization extinction ratio of 45dB. The µC-VCSEL reaches 3mW at 283K with a threshold one order of magnitude higher. It shows single-frequency emission (SMSR=20dB) with 5MHz of linewidth and a polarization extinction ratio of 32dB.

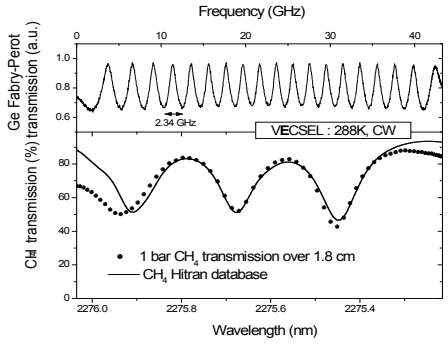


Figure 2

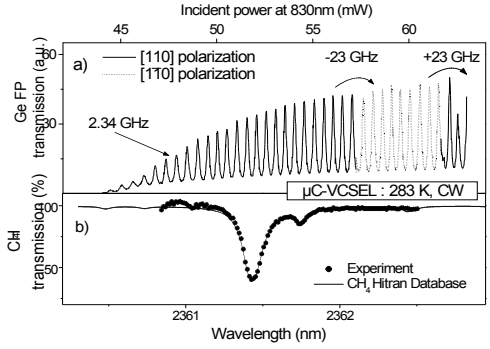


Figure 3

For the VECSEL, frequency tuning is obtained by modulating the cavity length thanks. For the µC-VCSEL, it is achieved by modulating the incident power. The VECSEL reaches a continuous tuning of 50GHz (Fig.2-Top). The µC-VCSEL shows 45GHz of continuous tuning (Fig.3-Top). A change of the heatsink temperature and the incident pump power on the VECSEL allow up to ~1.46THz (24nm) of total frequency emission range. Finally we probed methane absorption lines by laser absorption spectroscopy using a 1.8cm cell containing 1bar of methane for both devices (Fig.2-Bottom, Fig.3-Bottom).

This work was supported in part by the European Project GLADIS IST program, by the Languedoc Roussillon region and by OLDHAM Group.

[1] L. Cerutti, A. Garnache, A. Ouvrard, and F. Genty, J. Cryst. Growth, vol. 268, pp. 128–134, 2004

[2] L. Cerutti, A. Garnache, A. Ouvrard, M. Garcia, E. Cerda and F. Genty, Electron. Lett., vol. 40, pp. 869–871, July 2004

D-20

Vibrational-rotational spectroscopy of AlF: an analysis based on the non-Born-Oppenheimer effective hamiltonian

Hiromichi Uehara and Koui Horiai

Department of chemistry, Josai University

Keyakidai, Sakado, Saitama 350-0295, Japan

In analyses of high-resolution vibrational-rotational and rotational spectra of diatomic molecules, one must include adiabatic and non-adiabatic corrections for the breakdown of the Born-Oppenheimer approximation. However, the main stream [1] of the approach that includes non-Born-Oppenheimer fitting parameters, in place of the conventionally used empirical parameter Δ_{ij}, proposes the individual expansion coefficients of the correction functions as the fitting parameters as though they were determinable from experiment. Moreover in a numerical approach [2], it is not clear how to find the fitting parameters for the molecules that include atoms of a single nuclide.

We have presented an effective non-Born-Oppenheimer rovibrational Hamiltonian [3],

$$H = -B_e(1+\Delta_{B})\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} + \frac{B_e(1+\Delta_{B})}{(1+\rho)^2}\left(1+\sum_{i=1}\rho_{iq}\rho^i\right)J(J+1)$$

$$+\frac{[\rho_e(1+\Delta_{\rho})]^2}{4B_e(1+\Delta_{B})}\rho^2\left(1+\sum_{i=1}a_i(1+\Delta_{aiq})\rho^i\right) \qquad (1)$$

Since, clearly from Eq. (1), the non-Born-Oppenheimer parameters, Δ_{B}, Δ_{ρ}, Δ_{aiq}, and ρ_{iq} (i = 1, 2, …) (optimal parameters) have different v, J dependences, these parameters are experimentally determinable [4]. The optimal parameters are the clusters of the expansion coefficients. Even for a molecule AB that contains only a single isotopic species, non-Born-Oppenheimer parameters ρ_{iq} (i = 1, 2, …) should be included in the fit as the fitting parameters [3, 5], which has not been noticed before.

In the present study, we measured vibrational-rotational spectrum of AlF to determine physically meaningful parameters with full internal consistency by accumulating many spectral lines in highly vibrationally excited states. AlF has only one isotopomer in natural abundance. A diode-laser spectrometer, Spectra Physics (Laser Analytics) SP5000 and an FTIR spectrometer Bruker IFS125HR have been used. The new 876 spectral lines for Δv = 1 transitions up to v = 11-10 and 613 lines for the new Δv = 2 transitions up to v = 6-4 were observed in this study. These transitions, combined with the vibrational-rotational and rotational lines reported in the literature were analyzed with the fitting parameters $U_B(1+\Delta_{B})$, $U_{\rho}(1+\Delta_{\rho})$, $a_i(1+\Delta_{aiq})$, and ρ_{iq} in which i = 1, 2, ... Details will be presented.

[1] J. A. Coxon and M. Molski, J. Mol. Spectrosc., 223, 51-66 (2004).

[2] J. K. G. Watson, J. Mol. Spectrosc., 223, 39-50 (2004).

[3] H. Uehara, Bull. Chem. Soc. Jpn., 77, 2189-2191 (2004).

[4] H. Uehara and J. F. Ogilvie, J. Mol. Spectrosc., 207, 143-152 (2001).

[5] H. Uehara, K. Horiai, and S. Umeda, Chem. Phys. Lett., 404, 116-120 (2005).

D-21

Q-MACS — a compact quantum cascade laser absorption spectroscopy system for process monitoring

***J. Röpcke*, S. Glitsch, F. Hempel, S. Saß, K.-D. Schulz*, K.-D. Weltmann, H. Zimmermann**

INP-Greifswald, Friedrich-Ludwig-Jahn-Str. 19, 17489 Greifswald, Germany

**) Schulz & Walter Elektronik GmbH, 17509 Kemnitz, Germany*

Plasmas containing molecular precursors are used in a variety of plasma enhanced chemical vapour deposition and etching systems to deposit or remove thin films. For reasons of enhanced efficiency, increased stability and product quality the direct control of such plasma applications is a challenging subject for plasma technology. The key to an improved understanding and control of chemical active discharges is the analysis of the fragmentation of the precursor and the monitoring of transient or stable plasma reaction products, in particular the measurement of their ground state concentrations. Therefore appropriate diagnostic tools are necessary allowing an on-line process monitoring in such applications.

The recent development and commercial availability of quantum cascade lasers with distributed feedback (DFB-QCL) offers an attractive new option for infrared absorption spectroscopy. Pulsed DFB-QCL are able to emit mid-IR radiation near to room temperature. Compared to lead salt lasers, QCLs allow the realization of very compact mid-infrared sources characterized by narrow line width combining single-frequency operation and considerably higher power values of tens of mW. The output power is sufficient to combine them with thermoelectrically cooled infrared detectors, which permits a decrease of the apparatus size and gives a unique opportunity to design compact liquid nitrogen-free mid-IR spectroscopic systems. Such a quantum cascade laser absorption spectroscopic (QCLAS) system of decreased instrument size and weight would lead to a reduced transport logistics. “Turn-Key” operation and unattended remote monitoring and control at an improved safety level and at a low level of maintenance could be ensured. These positive features of QCLAS systems can open up new fields of application in research and industry, including studies of gases in atmospheric, environmental and plasma chemistry but also for in-situ control of industrial plasma processes.

This contribution describes a compact quantum cascade laser measurement and control system (Q-MACS) which has been developed for time-resolved plasma diagnostics, process control and trace gas monitoring [1]. The Q-MAC system contains a tuneable quantum cascade laser which can be directed through a plasma or into a multi-pass cell for exhaust gas detection. Rapid scan software with real-time line shape fitting provides a time resolution up to 1 μs to study kinetic processes of infrared active compounds in plasmas or gases [2]. With examples of trace gas detection and of phenomena in plasmas the capabilities of the Q-MAC system is demonstrated.

References

[1] http://www.q-macs.de

[2] D. D. Nelson, J. H. Shorter,. J. B. McManus, and M. S Zahniser, *Appl. Phys. B,* 75, 343, 2002.

This work was partly supported by the Deutsche Forschungsgemeinschaft, Transferbereich 36, and by the Bundesministerium für Bildung und Forschung, FKZ 13N7451/8.

D-22

Biological and medical applications of gas in scattering media absorption spectroscopy using tunable diode lasers

Mikael Sjöholm, Linda Persson, Mats Andersson, Gao Hong*, and Sune Svanberg

Atomic Physics Division, Lund Institute of Technology,
P.O. Box 118, SE-221 00 Lund, Sweden

** Department of Applied Physics, Harbin Institute of Technology,*
P.O. Box 406, Harbin 150001, P. R. China

In this contribution we report on some recent progress concerning biological and medical applications within the field of gas in scattering media absorption spectroscopy (GASMAS) [1]. GASMAS deals with non-destructive, *in-situ* measurements of gas inside porous materials such as polymers, ceramics, wood, and fruits using narrow-banded radiation from tunable diode lasers. The possibility to measure the gas contained in such materials relies on the fact that the gas absorption lines are extremely sharp compared to the absorption and scattering structures of the porous matrix. Due to scattering there is no well-defined path length for the light that passes through the material, and the mean path lengths traversed are frequently orders of magnitude longer than the geometrical dimensions of the sample. The first recordings of this type were reported in Ref. 1 and combined with time-resolved measurements the gas concentrations could be assessed [2]. Further studies on wood were reported in Ref. 3, where the influence of density and anisotropy of the samples were illustrated.

In the present work the GASMAS technique was applied to biological and medical issues, in particular studies of molecular oxygen which is one of the key components in the respiration process of living organisms. Since tissue contains a substantial fraction of water there is an upper limit for the wavelengths that can be used to probe the tissue due to the heavy absorption of water above approximately 1.4 μm, which limits the use of for instance quantum cascade lasers. Therefore, the oxygen was studied using diode-laser-based wavelength modulation spectroscopy at around 760 nm. The tissue was sampled both in a simple transmission geometry and in a more practical reflection geometry while studying gas exchange processes [4, 5]. Furthermore, the possibility to use the technique for postharvest monitoring in the fruit industry [5, 6] and some preliminary aspects concerning medical applications are reported in this communication.

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

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

[3] J. Alnis, B. Anderson, M. Sjöholm, G. Somesfalean, and S. Svanberg, *Appl. Phys. B*. **77**, 691 (2003).

[4] M. Sjöholm et al., "Gas diffusion measurements in porous media by the use of a laser spectroscopic technique", *to appear*.

[5] L. Persson, H. Gao, M. Sjöholm and S. Svanberg, "Diode laser absorption spectroscopy for studies of gas exchange in fruits", *Accepted for publication in Optics and Lasers in Engineering* (2005).

[6] L. Persson, B. Anderson, M. Andersson, M. Sjöholm and S. Svanberg, *Proc. Frutic05, Montpellier* (2005).

D-23

Widely tunable narrrow linewidth diode laser system for coherent spectroscopy

P. Huke [1], R.-H. Rinkleff [1], S. Chepurov [2], A. Wicht [2], K. Danzmann [1,3]

[1] *Institut für Atom- und Molekülphysik, Universität Hannover, D-30167 Hannover*

[2] *Institut für Experimentalphysik, Heinrich-Heine-Universität Düsseldorf, D-40225 Düsseldorf*

_*Max-Planck-Institut für Gravitationsphysik, D-30167 Hannover*

Quantum coherence between different atomic or molecular states plays a key role for experimental fields like investigations of electromagnetically induced transparency or absorption (EIT or EIA, respectively), slowing or stopping of light, atom interferometry or preparation of rotational and vibrational molecular coherence. These experioments require widely tunable narrow linewidth laser systems which can easily be phase locked to an optical reference. We present a laser system which combines existing designs, i.e. the diode laser with resonant optical feedback (ECDL) and the grating diode laser. A laser system operating at a center wavelength of 850 nm can be contineously tuned by 50 GHz and the overall tunability is more then 46 nm. The short term linewidth is determined to be less than 35 kHz.

Our system applies optical feedback from an external cavity which is coupled to an AR-coated laser diode through the first order diffraction of a volume-holographic transmission grating. The key point of our concept is the design of the external cavity which has to ensure that the spectral selevtivity of the grating is maintained.

We present for the first time, to our knowledge, the application of the Hänsch-Couillaud locking scheme to an optical feedback cavity in order to stabilize the phase of the optical feedback. Locking of the feedback phase is mandatory to achieve the large continous tuning ranges given above. Further, we develop a phase-frequency detector to frequency-lock our laser system to another standard ECDL in order to supress low frequency (<400 Hz) jitter for beat note measurements.

We report on the status of the development of a similar laser system for coherent spectroscopy of molecules at 1400 nm. We plan to lock two identical laser systems to a fs-optical frequency comb at an ultra-stable difference frequency of 4 THz.

References

[1] Flemming, M. W. Mooradian, A. IEEE Quant. Elect. 17, 44 (1981).

[2] Dahmani, L., Hollberg, L., Drullinger, R. Opt. Lett. 12, 876 (1987).

[3] Belenov, E. M. et al Sov. J. Quant. Elect. 13, 792 (1983).

[4] Wicht, A., Rudolf, M., Huke, P., Rinkleff, R.-H., Danzmann, K., Appl.Phys. B 78, 137 (2004);

[5] Hänsch, T. W. and Couillaud, B, Opt. Comm. 35, 3 (1980).

D-24

Electric field induced alignment – orientation conversion in Cs atoms at diode laser excitation

M. Auzinsh, K. Blushs, R. Ferber, F. Gahbauer, A. Jarmola, and M. Tamanis

Department of Physics and Institute of Atomic Physics and Spectroscopy, University of Latvia, 19 Rainis Blvd., LV-1586 Riga, Latvia

ferber@latnet.lv

We present an application of tunable diode lasers to the observation of the alignment-orientation conversion (AOC) phenomenon produced by the Stark effect in a homogeneous external electric field $\mathbf{E}_{el}$ [1]. Atomic cesium was studied, since it is a challenging object for frontier research in a number of fields, including parity non-conservation, laser cooling and BEC, the search for a permanent electric dipole moment of the electron and the testing of Zeeman coherence manifestation. Additional motivation is connected with the possibility of using Cs vapor for optical imaging of an external electric field distribution [2], with the advantage of exploiting the all-diode-laser technique. Alignment of the $7^2D_{3/2}$ level was achieved in stepwise $6^2S_{1/2}$ → $6^2P_{3/2}$ → $7^2D_{3/2}$ excitation by two linearly polarized tunable diode lasers, $\mathbf{e}_1$ and $\mathbf{e}_2$, sent contra-propagating perpendicularly to $\mathbf{E}_{el}$. The first laser with a LD-0850-100sm diode causing the $6^2S_{1/2}$ → $6^2P_{3/2}$ transition was polarized as $\mathbf{e}_1 \parallel \mathbf{E}_{el}$, while the $\mathbf{e}_2$ - vector of the second HL6738MG laser causing the $6^2P_{3/2}$ → $7^2D_{3/2}$ transition was directed at angle $\pi/4$ to $\mathbf{E}_{el}$. Electric fields up to 2.5 kV/cm were produced by planar transparent indium-tin oxide (ITO) electrodes on a glass background with 2.5 mm spacing. The creation of Cs ($7^2D_{3/2}$) state orientation was certified by measuring the appearance of circular polarization of the $7^2D_{3/2}$ → $6^2P_{1/2}$ laser induced fluorescence (LIF) which has been observed in the direction along the laser beams. The normalized quantity, namely the degree of circularity $C = (I_1-I_2)/(I_1+I_2)$ was detected, I_1 and I_2 being right-handed and left-handed circularly polarized LIF intensities measured using an achromatic quarter-wave plate. Rather large circularity values reaching ca. 10% at E_{el} about 1.0 kV/cm have been obtained. The AOC signals from the Cs ($7^2D_{3/2}$) atomic ensemble in the present excitation-observation scheme were calculated using the Zeeman coherence rate equations [3] for the interaction of atoms with radiation in the presence of an external electric field; the calculated signals are in agreement with the experimental results.

We gratefully acknowledge financial support from NATO through the Science for Peace Grant SfP-978029 "Optical Field Mapping", from the EC 5th Frame Growth Grant G1MA-CT-2002-04063, from the Latvian Ministry of Education and Science (Grants TOP-04-44 and ES-03-40) and Latvian Science Council (Grants 04.1308, 05.1865), as well as from the European Science Foundation.

References

[1] Marcis P. Auzinsh and Ruvin S. Ferber, *Phys. Rev. Lett*. **69**, 3463 (1992)

[2] M. Auzinsh, L. Jayasinghe, L. Oelke, R. Ferber, and N. Shafer-Ray, *J. Physics* **34 D**, 1 (2001)

[3] Blush Kaspars, Auzinsh Marcis, *Phys. Rev.* A **69**, 063806 (2004)

D-25

Airborne measurement of CH_4 profiles during the TROCCINOX-2 campaign with the near infrared TDL instrument "ALTO"

F. D'Amato, P. Mazzinghi, S. Viciani, P. W. Werle,

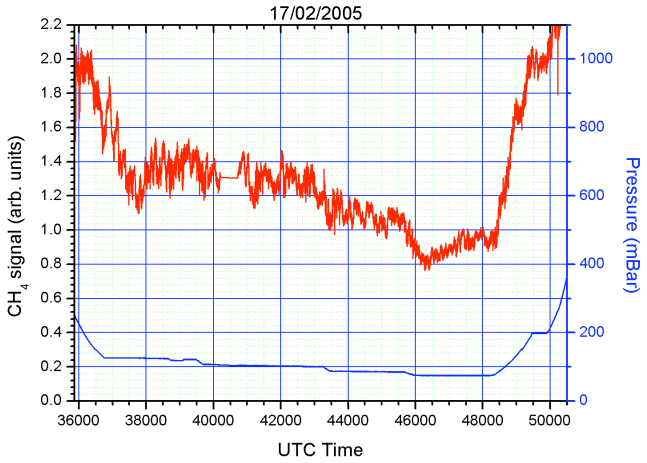
F. Castagnoli [1], M. De Pas [2], M. Giuntini [2]

INOA, Largo E. Fermi 6, 50125 Firenze, Italia, damato@inoa.it

[1] IFAC-CNR, V. Panciatichi 64, 50127 Firenze, Italia

[2] LENS, Università di Firenze, V. N. Carrara 1, 50019 Sesto Fiorentino (FI), Italia

The contribution of tropical thunderstorms to the production of NOx is one of the main goals of the European Project TROCCINOX (TROpical Convection, Cirrus, and Nitrogen OXides Experiment) [1]. The TROCCINOX-2 field campaign started from the DLR in Oberpfaffenhofen (Germany) on Jan. 18, 2005 with the transfer flights of the russian M55 Geophysica and DLR´s Falcon to Araçatuba near Sao Paulo (Brazil). A set of airborne atmospheric research instruments (including LIDAR, Gaschromatograph and other chemical and meteorological sensors) provided *in-situ* atmospheric data during a 4 weeks airborne measurement campaign over Brazil. We have measured the CH_4 concentration during 15 flights with the near infrared spectrophotometer ALTO, which has been designed for unattended airborne operation [2,3]. A preliminary analysis of a methane flight profile is shown below. The flight profiles and the data quality will be discussed.



Typical recording of the CH_4 absorption signal strenght and outer pressure vs. time.

This activity has been sponsored by EC through contracts EVK2-CT-2001-00122 and EVR1-2001-00020, and by ESA in the frame of the ENVISAT validation programme.

References

[1] See: http://www.pa.op.dlr.de/troccinox

[2] F. D'Amato, P. Mazzinghi, and F. Castagnoli, *Appl. Phys*. **B75**, 195-202 (2002).

[3] M. Pantani, F. Castangnoli, F. D´Amato, M. De Rosa, P. Mazzinghi, P. W. Werle, Inf. Phys. & Technology **46**, 109-113 (2004).

Part 5. Author Index