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TDLS 2003 Conference Schedule

Sunday July 13 2003

16:00 - 18:00 Registration

Monday July 14 2003

8:30 - Noon Registration
 8:45 - 12:30 Plenary Session
 8:45 - 9:00 Opening

Session Chair: *Claude Thibeaux*
 9:00 - 9:45 Invited Lecture 1 - A.R.W. McKellar
 9:45 - 10:30 Invited Lecture 2 - Nobukimi Ohashi
 10:30 - 11:00 Coffee Break

Session Chair: *Frank Tittel*
 11:00 - 11:45 Invited Lecture 3 - Ruedeger Koehler
 11:45 - 12:30 Invited Lecture 4 - Muriel Lepere

Lunch

14:00 - 16:00 Poster Session A
 16:00-16:30 Break

Session Chair: *Armin Lambrecht*
 16:30 - 17:15 Invited Lecture 5 - Stephane Schilt
 17:15-18:00 Invited Lecture 6- Daniel Hofstetter

18:00-19:00 Welcome Reception

Tuesday July 15 2003

Session Chair: *Peter Werle*
 9:00-10:30 Special Industrial Plenary Session I
 10:30-11:00 Coffee Break
 11:00-12:30 Special Industrial Plenary Session II

Lunch

Session Chair: *Peter Werle*
 14:00 - 15:00 Special Industrial Plenary Session III

Session Chair: *Alan Fried*
 15:00-17:00 Poster Session B
 17:00-17:45 Invited Lecture 7 - Yuri Ponomarev
 17:45-18:30 Invited Lecture 8 - Matthew Taubman

Wednesday July 16 2003

9:00 - 12:30 Plenary Session

Session Chair: *A.R.W. McKellar*
 9:00 - 9:45 Invited Lecture 9 - Georges Durry
 9:45 - 10:30 Invited Lecture 10 - Mark Zahniser
 10:30 - 11:00 Coffee Break

Session Chair: *Yuri Ponomarev*
 11:00 - 11:45 Invited Lecture 11 - Jürgen Röpcke
 11:45 - 12:30 Invited Lecture 12 - Daniel Hurtmans

Lunch

Session Chair: *Koichi Uehara*
 14:00 - 14:45 Invited Lecture 13 - Martin Fejer
 14:45 - 15:15 Break
 15:15 - 17:30 Poster Session C

19:00 Banquet

Thursday July 17 2003

9:00 - 12:30 Plenary Session

Session Chair: *Muriel Lepere*

9:00 - 9:45 Invited Lecture 14 – Bruno Gayral

9:45 - 10:30 Invited Lecture 15 - Bertrand Parvitte

10:30 - 11:00 Coffee Break

Session Chair: *Mark Zahniser*

11:00 - 11:45 Invited Lecture 16 - Dirk Richter

11:45 - 12:30 Invited Lecture 17 - Kay Niemax

Lunch

14:00 - 16:00 Poster Session D

Session Chair: *Daniel Hurtmans*

16:00 - 16:45 Invited Lecture 18 - Daniele Romanini

Friday July 18 2003

8:30-10:00 Poster Session E

10:00-10:30 Coffee Break

Session Chair: *Gisbert Winnewisser*

10:30-11:15 Invited Lecture 19 - Doug Baer

11:15-12:30 Invited Lecture 20 - Frank Tittel

12:30 Closing Remarks

Contents:

Part 1. Invited Lecture	7
Part 2. Industrial Session	29
Part 3. Poster Presentation	48
3.1. Poster Session A	48
3.2. Poster Session B	68
3.3. Poster Session C	88
3.4. Poster Session D	107
3.5. Poster Session E	127
Part 4. Author Index	147

Part 1. Invited Lecture.

Lecture 1. TDL SPECTROSCOPY OF SMALL HELIUM CLUSTERS

A.R.W. McKellar

Lecture 2. NEAR-INFRARED DIODE LASER SPECTROSCOPY ON FREE RADICALS

Nobukimi Ohashi

Lecture 3. TERAHERTZ QUANTUM CASCADE LASERS

Rüdeger Köhler, Alessandro Tredicucci, Fabio Beltram, Harvey E. Beere, Edmund H. Linfield, A. Giles Davies, David A. Ritchie

Lecture 4. LINE PROFILE STUDY WITH TUNABLE DIODE-LASER SPECTROMETERS

M. Lepère

Lecture 5. PHOTOACOUSTIC SPECTROSCOPY IN INDUSTRIAL APPLICATIONS

S. Schilt, L. Thévenaz, P. Robert

Lecture 6. LATEST PROGRESS ON INTERSUBBAND DEVICES: LASERS AND DETECTORS FROM THE NEAR-TO THE FAR-INFRARED

Daniel Hofstetter, Marcel Graf, Giacomo Scalari, Lassaad Ajili, Mattias Beck, David Ritchie, Edmund Linfield, Harvey Beere, Hong Wu, William J. Schaff, Lester F. Eastman, Jérôme Faist

Lecture 7. PHOTO-ACOUSTIC MEASUREMENTS OF GAS AND AEROSOL ABSORPTION WITH DIODE LASERS

Yu. N. Ponomarev

Lecture 8. QUANTUM CASCADE LASERS: STABILIZATION, INJECTION AND CONTROL.

Matthew Taubman, Tanya Myers, Bret Cannon, Richard M. Williams.

Lecture 9. IN-SITU SENSING OF THE MIDDLE ATMOSPHERE WITH BALLOONBORNE NEAR-INFRARED DIODE LASERS

G. Durry

Lecture 10. TRACE GAS MEASUREMENTS USING PULSED QUANTUM CASCADE LASERS - ATMOSPHERIC AND ENVIRONMENTAL MONITORING APPLICATIONS

Mark S. Zahniser

Lecture 11. RECENT PROGRESS IN DIAGNOSTICS OF MOLECULAR PLASMAS USING INFRARED DIODE LASERS

Jürgen Röpcke

Lecture 12. MOLECULAR LINE SHAPE ANALYSIS OF TDL SPECTRA BY MULTISPECTRUM FITS ACCOUNTING FOR FINE COLLISIONAL EFFECTS

Daniel Hurtmans

Lecture 13. MID-INFRARED COHERENT SOURCES BASED ON MICROSTRUCTURED NONLINEAR MATERIALS

Martin Fejer

Lecture 14. APPLICATION OF TLDAS TO GAS MIXTURE ANALYSIS – APPLICATION TO THE METHANE/ETHANE SYSTEM

Bruno Gayral and Stéphane Vannuffelen

Lecture 15. MID-INFRARED HETERODYNE DETECTION WITH TUNABLE LASERS

B. Parvitte

Lecture 16. ANALYTICAL PHOTONICS FOR HIGH PRECISION MID INFRARED TRACE GAS SENSING

Dirk Richter, Alan Fried, and James G. Walega

Lecture 17. ELEMENT SELECTIVE DETECTION OF MOLECULAR SPECIES USING CHROMATOGRAPHIC TECHNIQUES AND DIODE LASER ATOMIC ABSORPTION SPECTROMETRY

Kay Niemax

Lecture 18. CAVITY RING DOWN AND CAVITY ENHANCED ABSORPTION SPECTROSCOPY, AND TRACE DETECTION, WITH DIODE LASERS

Daniele Romanini

Lecture 19. BEYOND CAVITY RING DOWN: CAVITY ENHANCED SPECTROSCOPY TECHNIQUES USING TUNABLE DIODE LASERS

Doug Baer, Manish Gupta, Tom Owano, Anthony O'Keefe

Lecture 20. CHEMICAL SENSING WITH QUANTUM CASCADE LASERS

*F.K.Tittel, A.A.Kosterev, Y.Bakirkin, C.Roller,
D.Weidmann and R.F.Curl*

TDL SPECTROSCOPY OF SMALL HELIUM CLUSTERS***A.R.W. McKellar****Steacie Institute for Molecular Sciences
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Weakly bound molecular complexes and clusters are investigated using a tunable infrared diode laser spectrometer to probe a pulsed supersonic jet expansion. The laser operates in a rapid scan mode, repeatedly tuning over a fixed interval ($0.3 \sim 1.0 \text{ cm}^{-1}$) in a time of 1 msec while the pulsed jet nozzle is alternately open (for the signal) or shut (for the background). The resulting spectrum (signal minus background) is typically averaged for 100 to 500 pulses at a repetition rate of 1 to 5 Hz. The jet nozzle may be slit shaped, giving narrower line widths, or pinhole shaped, giving broader lines but lower rotational temperatures and more clustering. The laser beam is passed through the jet more than 100 times using a commercial toroidal mirror system mounted inside the vacuum chamber. The chamber is evacuated with a Varian VHS-10 diffusion pump backed by an Edwards EH500/E2M40 booster/mechanical pump combination.

By using moderately high backing pressures (< 40 atmospheres) and cooling the jet nozzle ($> 125 \text{ K}$), we have been able to observe high resolution spectra of clusters containing up to 20 He atoms and a single infrared chromophore molecule, OCS, N_2O , CO_2 , or CO. These are probably the largest van der Waals clusters which have so far been studied by high resolution spectroscopy.

In the case of OCS, the rotational assignments for clusters up to $\text{He}_8\text{-OCS}$ are confirmed by microwave observations of the analogous pure rotational transitions [see *Science* **297**, 2030 (2002)]. The results explore the formation of the first solvation layer, beginning with an equatorial ‘donut’ of five He atoms around the OCS molecule, and they are relevant for studies of the onset of superfluid effects in finite size systems. In the case of $\text{He}_N\text{-CO}$ clusters, two series of $R(0)$ transitions are observed, each correlating smoothly with the known a -type ($K = 0 \leftarrow 0$) and b -type ($K = 1 \leftarrow 0$) $R(0)$ lines of the binary complex, He-CO. Although the b -type series starts off about 7 times stronger for $N = 1$, it is observed to lose intensity to the a series with increasing N . The numbering of cluster size is reliably established up to $N = 14$ for the a -type and $N = 6$ for the b -type series. Two critical regions are observed in the cluster size evolution, at about $N = 7$ and 15. These may be related to the theoretically calculated maximum and minimum, respectively, in the incremental binding energy per helium atom.

NEAR-INFRARED DIODE LASER SPECTROSCOPY ON FREE RADICALS

Nobukimi Ohashi

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The near-infrared diode laser spectroscopy is one of powerful tools for studying spectra from molecular free radicals. The high-sensitivity, high resolution and tunability of the near-infrared diode laser system are of great advantage to investigation on energy levels of short-lived radicals which are complicated because of various intra-molecular interactions. In our laboratory, using 0.8 μm , 1.3 μm and 1.5 μm tunable diode lasers, absorption spectra of several radicals have been studied in their electronic transitions.

Results on HCSi, CCO (1) and FeC (2) obtained by studying in detail energy level structures with the use of 0.8- μm diode laser system will be reported mainly in the present time. Of these radicals, CCO was investigated mainly with the use of several sets of laser diodes oscillating with inconvenient mode gaps in the early stage of our near-infrared diode laser spectroscopic study on radicals, and, on the other hand, FeC and HCSi were studied using an external cavity diode laser.

For FeC, being an interesting radical composed of a 3d transition metal atom Fe, information on spin-orbit interaction between the triplet electronic ground state and a low-lying singlet electronic excited state will be reported somewhat in detail. For HCSi and CCO radicals, spectral varieties produced by Renner-Teller interaction, which is an interesting vibronic interaction, will be mentioned in a viewpoint of high-resolution spectroscopic interest. It can be said that details of spectral complication of these two radicals caused by combination of Renner-Teller effect and a spin-orbit interaction were made successfully clear of by using diode lasers which oscillate stably and are of high quality in tunability and resolution. Examples of solving the spectral complications will be shown.

- (1) M. Fujitake, R. Kiryu, and N. Ohashi, *J. Mol. Spectrosc.* **154**, 169(1992).
N. Ohashi, R. Kiryu, S. Okino, and M. Fujitake, *J. Mol. Spectrosc.* **157**, 50(1993).
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H. Abe, M. Mukai, M. Fujitake, and N. Ohashi, *J. Mol. Spectrosc.* **195**, 317(1999).
- (2) M. Fujitake, A. Toba, M. Mori, F. Miyazawa, N. Ohashi, K. Aiuchi, and K. Shibuya, *J. Mol. Spectrosc.* **208** 253(2001).

TERAHERTZ QUANTUM CASCADE LASERS

*Rüdeger Köhler,¹⁾ Alessandro Tredicucci,¹⁾ Fabio Beltram¹⁾
Harvey E. Beere,²⁾ Edmund H. Linfield,²⁾ A. Giles Davies,²⁾ David A. Ritchie²⁾*

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The use of terahertz radiation (1-10 THz) has proven to be a versatile tool in spectroscopy and sensing [1], in medical imaging and industrial process control, and in security screening. Yet, the exploitation and exploration of these fields has been hampered by the lack of appropriate, convenient sources. Common sources such as black body radiation, free-electron lasers, optically pumped gas lasers, the p-Ge semiconductor laser, photo-mixers, and Auston switches suffer from different shortcomings that prevent their use in real-world applications [2].

The quantum cascade laser demonstrated in 1994 by J. Faist *et al.* [3] at mid-infrared wavelengths has experienced a rapid development of its performance and eventually cw-operation at room-temperature was demonstrated. Since it is based on intersubband rather than interband transitions the wavelength can be tuned over very wide ranges by properly adjusting layer thickness and electric field using technologically mature materials like InGaAs/AlInAs/InP or AlGaAs/GaAs. We have demonstrated AlGaAs/GaAs quantum cascade lasers [4] that emit at 4.5 THz, at 3.5 THz [5], and very recently at 2.8 THz and that have the potential for device-like implementation. The active region consists of a hundred repetitions of a chirped superlattice, specially engineered to achieve population inversion at energies below the optical phonon resonance. This core is embedded into a novel type of partially metallic waveguide to confine the very long wavelength radiation without concomitant high optical losses. The concept is loosely based on the surface plasmon configuration but makes use of a thin, highly doped layer with appropriate dielectric constant between the low-doped active core and the semi-insulating substrate to guide THz radiation with low optical losses of ~ 5 -10 cm⁻¹. Our devices currently operate in continuous-wave mode with output powers of 4 mW and up to 45 K heat sink temperature. Under pulsed excitation, output powers of 4.5 mW at low temperatures and still 1 mW at 65 K are measured [6].

[1] D. Mittleman (Ed.), Sensing with Terahertz Radiation, Springer, Berlin, 2003.

[2] R. E. Miles, P. Harrison and D. Lippens (Eds.), Terahertz Sources and Systems, NATO Science Series II Vol. 27, Kluwer, Dordrecht, 2001.

[3] J. Faist *et al.*, Quantum Cascade Laser, Science 264, 553 (1994).

[4] R. Köhler *et al.*, Terahertz Semiconductor-Heterostructure Laser, Nature 417, 156 (2002).

[5] R. Köhler *et al.*, Low-threshold quantum cascade lasers at 3.5 THz ($\lambda = 85 \mu\text{m}$), Optics Letters, in press (2003).

[6] R. Köhler *et al.*, High-performance continuous-wave operation of superlattice terahertz quantum-cascade lasers, Appl. Phys. Lett. 82, 1518 (2003).

LINE PROFILE STUDY WITH TUNABLE DIODE-LASER SPECTROMETERS*M. Lepère**Postdoctoral Researcher with F.N.R.S., Belgium**Laboratoire de Spectroscopie Moléculaire, FUNDP,
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Diode-laser spectrometers are well adapted to the study of lineshapes for molecules in diluted phase. They permit to show the modifications induced by intermolecular forces on spectral line profile and give very precise line parameters for lineshape modelisation.

The different line profile models take into account several effects. The first effect results from random motion of the active molecules which leads to a broadening of the line described by a Doppler profile when the sample is at thermal equilibrium. This is valid only if there are no significant interactions between molecules (very low pressure). At pressures below 120 mbar, the Doppler and collisional broadenings are concurrent and the profile is usually described by a Voigt profile. However, the Doppler line is narrowed by the confinement of the active molecules in the buffer gas. This effect is generally referred to as Dicke narrowing (or confinement narrowing), then the line profile is well described by either the Rautian or Galatry models. As the pressure increases, the collisional broadening is progressively the main effect and depends on the relative speed of the collision partners for which it may be necessary to take into account the different classes of speed from the Maxwell-Boltzmann distribution for the absorber.

Precise determinations of spectroscopic line parameters such as collisional broadening and narrowing are very important for infrared remote sensing of the atmospheres. The temperature dependence of these parameters is also required for precise atmospheric sounding. For atmospheric temperatures (200-300K), it is important to determine precisely line broadenings and their temperature dependence. We will show examples of such studies (CH₄, CH₃D...) that we have realised using an absorption cell operating at selected temperatures (between room temperature and 77 K) with a temperature stabilization better than 0.5 K.

Preliminary calculations show that the intermolecular potential variations, that have no important effect at room temperature, can produce differences of several order of magnitude at very low temperature (below 20 K). Thus, it seems very interesting to make measurements up to these temperatures using collisional cooling technique. This technique allows to obtain a gas mixture in thermodynamic equilibrium, and thus to know the pressure and the temperature of the gas sample. It is an advantage for the study of line profile and parameters. In collaboration with Professor Mantz, we have realized first measurements of collisional broadenings of CH₄ diluted in He down to 15 K.

PHOTOACOUSTIC SPECTROSCOPY IN INDUSTRIAL APPLICATIONS

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Photoacoustic spectroscopy is an extremely sensitive technique for trace gas monitoring. In this method, the molecules of the species to be analyzed are selectively excited by a modulated laser beam of appropriate wavelength. The subsequent non-radiative relaxation of the excited molecules produces a periodic heating of the sample and hence, a pressure modulation. If the laser beam is modulated in the audio frequency range, an acoustic wave is thus generated at the same frequency. The amplitude of this sound wave is directly proportional to the amount of light absorbed in the sample (thus to the gas concentration) and can be easily detected using a simple and very sensitive microphone. In opposite to other traditional spectroscopic methods, in which the light transmitted through the sample is measured, photoacoustic spectroscopy allows the direct determination of the light *absorbed* in the sample. Therefore, it presents the advantage to be a zero-background technique, *i.e.* no signal is produced when no absorbing substance is present.

The sensitivity of the technique can be strongly improved using a resonant configuration, in which the measurement cell is carefully designed to be an acoustic resonator. When the laser modulation corresponds to an acoustic resonance of the cavity, an acoustic standing wave is built in the resonator. This standing wave can accumulate energy to an extent much larger than the energy input per cycle, leading to an increase of the wave amplitude in comparison to the non-resonant case. The acoustic signal is thus enhanced by the quality factor Q of the resonance, which can reach several hundreds for well-designed photoacoustic cells.

The basic principles of resonant photoacoustic spectroscopy will be described and the different types of resonances (longitudinal, radial, azimuthal) will be discussed. Then, an optimal design of a photoacoustic cell coupled to a CO₂-laser will be presented. This system has led to the realization of a commercial instrument for extremely low NH₃-concentrations measurement. Applications of this instrument to the control of the atmosphere in clean rooms in the semiconductor industry and to environmental monitoring will be demonstrated. Different experimental results obtained in these applications and showing a sub-ppb detection limit will be presented.

Finally, applications of photoacoustic spectroscopy using near-infrared semiconductor laser diodes will be presented. Different cell configurations will be discussed as a function of the laser specifications.

**LATEST PROGRESS ON INTERSUBBAND DEVICES: LASERS AND DETECTORS
FROM THE NEAR- TO THE FAR-INFRARED**

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*4th International Conference on Tunable Diode Laser Spectroscopy
Zermatt, Switzerland, July 14-18, 2003*

During the last ten years, opto-electronic devices based on intersubband transitions have seen a development at a very fast pace. As an example, quantum cascade lasers have become reliable sources for the various applications in the mid-infrared, and most recently also in the far-infrared. Likewise, quantum well infrared photodetectors are now important building blocks of thermal imaging systems in the mid-infrared. In the first half of this presentation, we report on room temperature continuous wave operation of an InP-based 9.1 μm quantum cascade laser, as well as on a 77 K operated continuous wave far-infrared quantum cascade laser built from GaAs/AlGaAs. The second part will be devoted to photodetectors. We recently demonstrated such devices in the far-infrared and in the near-infrared wavelength region. While the former device is contains a chirped AlGaAs/GaAs-superlattice, the latter is based on a regular GaN/AlN superlattice with a period of 40 Å.

PHOTO-ACOUSTIC MEASUREMENTS OF GAS AND AEROSOL ABSORPTION WITH DIODE LASERS

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Laser sensors and gas analyzers are now at the beginning of commercial applications in environmental monitoring of greenhouse gases and industrial pollutants.

TDLS techniques are available for measurements of nanoconcentrations of molecules in gases within IR spectral range. The most popular types of TDL instruments for spectroscopy or gas analysis are based on the usage of the different multipass absorption cells. The techniques provide the measurements of small values of the absorbing media optical depth up to 10^{-6} . That corresponds the limit concentration sensitivity at ppt–ppm level, depending on the value of the absorption cross section of the detected molecules. In another version of TDL spectrometers and gas analyzers the sensitive photo-acoustic detectors (PAD) of nonresonant or, previously, resonant type are used. The advantages of this kind of technique are:

- possibility to record PA spectra against zero background;
- linear dependence of the PAD signal amplitude on the concentration of the detected molecules;
- linearity of the PAD at variation of the concentration of the detected gas up to 6 orders of magnitude;
- usage of cheap transparent optical windows instead of high reflected multi-layer dielectric mirrors which are necessary for multipass cells.

In the paper the review of results of IAO SB RAS with collaborators on the creation and application of different types of PAD to high resolution and high sensitive spectroscopy of molecular gases and analysis of multi-component gas mixtures is presented.

The advantages of resonant PAD detectors for spectroscopy and gas analysis of gas flows, vibration kinetics of selectively excited molecules and high sensitive measurements of concentrations of molecules are discussed.

For the measurements of the non-resonant absorption of molecular gases a new type of PAD with a temporal and spatial resolution was tested. It provides the limit absorption sensitivity better than $10^{-10} \text{ cm}^{-1} \text{ J}$. The applicability of this PAD for measuring not only non-resonant absorption of gases but also weak absorption of submicron size aerosol particles is discussed.

The resonant differential PAD provides the possibilities of a new experiments, like recording of spectra of hot absorption bands of molecules excited preliminary by strong selective radiation of the IR laser or nonlinear absorption of gases are discussed in the paper.

QUANTUM CASCADE LASERS: STABILIZATION, INJECTION AND CONTROL.

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and Richard M. Williams.*

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Quantum Cascade Lasers (QCLs) are a relatively new type of semiconductor laser operating in the mid- to long-wave infrared. Being monopolar multilayered quantum well structures, they can be fabricated to operate anywhere in a 3 to 20 micron region. This makes them an ideal choice for infrared chemical sensing, a topic of great interest at present. Their utility is increased through stabilization, which both narrows the linewidth and locks the output frequency to a known standard, and through injection locking, which we have demonstrated to greatly reduce the amount of residual amplitude modulation (RAM) that results from current modulation of the devices. We present results of locking QCLs to both optical cavities and molecular absorption features in nitrous oxide achieving relative linewidths down to 5.6 Hz. We also present injection locking of two distributed feedback grating devices, demonstrating capture ranges of up to 500 MHz, and RAM suppression up to 56 dB.

**IN-SITU SENSING OF THE MIDDLE ATMOSPHERE WITH BALLOONBORNE NEAR-
INFRARED DIODE LASERS****G. Durry***Institut Pierre Simon Laplace (IPSL), Service d'aéronomie, UMR CNRS 7620,**B.P. 3, Verrières-le-Buisson, F-91371 Cédex, France**E-Mail : Georges.Durry@aerov.jussieu.fr*

Absorption spectroscopy with near-infrared telecommunication laser diodes is a very convenient technique to measure *in situ* water vapor, methane and carbon dioxide in both the upper troposphere (UT) and the lower stratosphere (LS) and thereby to address many topics in the science of the atmosphere. Indeed, the laser probing technique offers a high selectivity in the analyzed species, a precision error in the concentration retrieval of a few percents, a high temporal resolution that ranges from 10ms to 1s and a dynamical range of the measurements of four orders of magnitude that is necessary to monitor continuously H₂O in both the UT and the LS.

These capabilities combined with the instrumental conveniences obtained by working in the near-infrared, were a strong impetus for us to develop from year 1997, with the support of CNRS and CNES, the “Spectrometre a Diodes Laser Accordables (SDLA)”, a diode laser spectrometer devoted to the *in situ* measurement of H₂O, CH₄ and CO₂ in both the UT and the LS. The SDLA spectrometer is operated from stratospheric balloons. The SDLA was flown several times in years 1999 to 2002 at mid-and high latitudes, within the framework of the Third European Stratospheric Experiment on Ozone and with the purpose of validating satellite data (ODIN, ENVISAT). Furthermore, the development of the “micro-SDLA” sensor, a compact and fast-response version of the SDLA, is currently under way. The micro-SDLA should be capable of being operated from launching sites in Brazil to address water-vapor troposphere-stratosphere exchanges.

The instrumental set-ups of the SDLA and micro-SDLA are described and achieved atmospheric data are reported. In particular, recent H₂O measurements in the lower stratosphere are discussed. Future applications of the laser probing technique are also discussed, including the implementation of a laser hygrometer onboard the Russian stratospheric aircraft “Geophysika” and the realization of a laser sensor devoted to the *in situ* sensing of the Martian atmosphere.

**TRACE GAS MEASUREMENTS USING PULSED QUANTUM CASCADE LASERS -
ATMOSPHERIC AND ENVIRONMENTAL MONITORING APPLICATIONS**

Mark S. Zahniser

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Quantum cascade (QC) lasers have extended the possibilities for using tunable infrared laser differential absorption spectroscopy (TILDAS) to measure atmospheric and environmental trace gases in the mid-infrared spectral region where molecular absorptions are strongest. Their exceptional mode stability, high optical power, and near-room temperature operation, can substantially improve the ease of operation for instruments used in field measurements of atmospheric trace gases from ground-based and mobile measurement platforms. Both open-path-atmospheric-pressure, and closed-path-reduced-pressure configurations have been used to measure gases in the atmosphere including NH₃, C₂H₄, NO, NO₂, O₃, N₂O, CO, CH₄, and CO₂. The open path method with telescope and retroreflector is suitable for cross road measurements from moving vehicles at highway speeds. The closed path method using reduced pressure sampling into multiple pass absorption cells provides greater sensitivity and sub-part-per-billion detection limits with an absorbance precision of $2 \times 10^{-5} \text{ hz}^{-1/2}$. The advantages and disadvantages of pulsed-QC laser sources compared to conventional lead salt TDLs will be discussed. Examples from recent laboratory and field measurements will be presented, including high precision measurements of nitrous oxide and data from recent field campaigns characterizing urban emissions of ammonia and nitric oxide.

**RECENT PROGRESS IN DIAGNOSTICS OF MOLECULAR PLASMAS USING
INFRARED DIODE LASERS**

Jürgen Röpcke

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Low-pressure, non-equilibrium molecular plasmas are of increasing interest not only in fundamental research but also in plasma processing and technology. Molecular plasmas are used in a variety of applications such as thin film deposition, semiconductor processing, surface activation and cleaning, and in materials and waste treatment. The investigation of plasma physics and chemistry *in situ* requires detailed knowledge of plasma parameters, which can be obtained by appropriate diagnostic techniques. The need for a better scientific understanding of plasma physics and chemistry has stimulated the improvement of established diagnostic techniques and the introduction of new ones. Methods based on traditional spectroscopy have become amongst the most important. The increasing interest in processing plasmas containing molecular precursors, as e.g. hydrocarbons, fluorocarbons, organo-silicon or boron compounds, has led to further applications of infrared absorption spectroscopy techniques because most of these compounds and their decomposition products are infrared active.

The contribution will focus on recent progress in understanding of phenomena in several molecular plasmas containing hydrogen, hydrocarbons or boron. The key to an improved understanding of plasma chemistry and kinetics in non-equilibrium plasmas containing hydrocarbons or boron hydrides 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.

Transient molecular species, in particular radicals, influence the properties of nearly all molecular plasmas, both in the laboratory and in nature. They are of special importance for several areas of reaction kinetics and chemistry. The study of the behaviour of radicals together with their associated stable products provides a very effective approach to understanding phenomena in molecular plasmas. Radicals containing carbon or boron, on which this contribution will focus, are of special interest for basic studies and for application in plasma technology.

Further, mainly based on absorption spectroscopy using tunable infrared diode lasers molecular fragmentation processes and examples of the reaction kinetics of stable and transient species are going to be analysed in this paper. Thereby a link is provided with chemical modelling of the plasma.

A special account will be given to recent developments of multi-component acquisition systems based on infrared absorption spectroscopy for plasma diagnostics and control. These compact and transportable systems contain between two and four independent tunable diode lasers 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 10 microseconds to study chemical kinetic processes in plasmas.

MOLECULAR LINE SHAPE ANALYSIS OF TDL SPECTRA BY MULTISPECTRUM FITS ACCOUNTING FOR FINE COLLISIONAL EFFECTS

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The tunable diode laser spectrometer, located at LPMA in Paris, which is actively controlled by a Michelson interferometer, is characterized by a signal-to-noise ratio of about 2000 and a frequency stability better than $4 \times 10^{-5} \text{ cm}^{-1}(\text{I})$. It allows not only to record precisely spectral lines in order to determine their line shape parameters (intensities, broadening, shift...) but also to quantitatively record very weak absorption lines in the frame of atmospheric applications (concentration measurements). Achieving such high performances implies to model line shapes as well as instrumental effects to a comparable precision.

Recent theoretical developments (see e.g.: (2-4)) produced a rather extended variety of semi empirical line shapes models describing the collision (pressure) broadening, the molecular confinement (Dicke narrowing), the line mixing, and the speed dependence of the lines parameters not only in limit cases but also in intermediate regimes. Most of these effects produce usually rather fine deviations from the Voigt profile and are acting prominently in limited pressure ranges. To help to disentangle partly the contributions of each of these effects and to improve the precision on the determination of the line parameters, we have developed a multi spectrum fitting software that can handle simultaneously a large set of spectra recorded under different pressure conditions. Most of the recent models have been included in the code.

We will illustrate the technique on selected molecular mixtures samples recorded from room temperature down to 20K (using a collisional cooling cell(5)) with the LPMA spectrometer either in the mid infrared, using lead salt diodes, or in the near infrared, using distributed feed-back diodes. The ability of the models at describing the experimental spectra, the relevance of the line shape parameters and their relation to the knowledge of the instrumental contribution will be discussed.

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**MID-INFRARED COHERENT SOURCES BASED ON MICROSTRUCTURED
NONLINEAR MATERIALS**

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Rapid progress in the technology of semiconductor lasers over the past several years has enabled new generations of mid-IR sensors. Most work in this spectral range has focused on conventional and quantum cascade lasers emitting in the mid-IR, designed specifically for these applications. Despite the impressive results obtained with these mid-IR lasers, alternative sources based on nonlinear frequency conversion, that take advantage of the near-IR lasers whose development has been stimulated by the enormous recent investment in optical communications, offer some interesting opportunities. In this talk, progress on mid-IR sources based on microstructured nonlinear materials will be described.

Several types of nonlinear sources, including difference frequency generation (DFG), optical parametric amplifiers/generators, and optical parametric oscillators, can be applied to the generation of mid-IR generation. In all these sources, a near-IR pump (or two near-IR pumps) is converted to the mid-IR through a nonlinear interaction, in which the frequencies of the three interacting waves are related by $\omega_p = \omega_s + \omega_i$, where p, s, i represent pump, signal, and idler respectively. A key aspect of all such interactions is the requirement of phasematching, *i.e.* compensating for the normal material dispersion which normally violates the momentum conservation condition, $k_p = k_s + k_i$, where the k are the propagation constants of the interacting waves. In microstructured materials, with a nonlinear susceptibility that can be modulated in a periodic fashion, a “quasi-phasematching” (QPM) condition, $k_p = k_s + k_i + K_g$, where $K_g = 2\pi/\Lambda$ is the k-vector of the pattern imposed on the nonlinear coefficient, with a period Λ . Interactions in such quasi-phasematched offer notable advantages over those in conventional birefringently phasematched media, most notably the ability to “design” a material for essentially any operating wavelength through patterning of an appropriate QPM grating, and the use of the largest, often diagonal, nonlinear coefficient in the material. Two types of materials in which the sign of the nonlinear coefficient can be controlled have been exploited for QPM generation of mid-IR radiation, ferroelectric oxides in which the periodic reversal of domains of spontaneous electric polarization is obtained through application of electric fields on lithographically-patterned electrodes, and orientation-patterned GaAs grown on “template” substrates. Another important tool for increasing the efficiency of these interactions are dielectric waveguides, formed for example by indiffusion of a dopant into a QPM substrate, in which tight optical confinement can be obtained over long interaction lengths.

Examples of the types of sources possible in these media include milliwatt-level sources in the 2 – 4 μm spectral range by DFG in periodically-poled lithium niobate (PPLN) waveguides with spectral linewidths controlled by the near-IR pump lasers, and sources broadly tunable in the 8 – 10 μm range in orientation-patterned GaAs. Examples of such sources and their application in spectroscopic measurements will be presented.

APPLICATION OF TLDAS TO GAS MIXTURE ANALYSIS - APPLICATION TO THE METHANE/ETHANE SYSTEM

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The European project Gladis aims at building a natural gas composition analyzer based on tunable diode laser absorption spectroscopy. Indeed, depending on its geographical origin, the concentrations of the various alkanes varies in natural gas. A fair billing requires a measurement of the alkane composition so as to estimate the superior calorific value (SCV) of the natural gas.

Tunable diode laser absorption spectroscopy provides a good solution for a compact and precise alkane composition analyzer. Indeed, by measuring the absorbance spectrum of the unknown gas mixture, its composition can be measured by projecting this spectrum on the calibrated absorbance spectra of its individual components.

While the most common use for TDLAS is trace detection done by sweeping across a single absorption line, here multigas (>5 gases) mixture analysis requires scanning across several absorption lines of several gases. Moreover, while trace detection requires a high sensitivity and low relative precision, composition analysis requires a low sensitivity ($\alpha.L \sim 1$) and a high relative precision (precision on the SCV < 1%).

In order to assess the ability of the device to reach such metering performances, a noise chain analysis was performed. This analysis showed that the noise transfer from laser intensity measurement to superior calorific power measurement can be minimized at certain wavelengths. This lead to the choice of a particular central wavelength around 2.3 μm to perform the TDLAS analysis. As commercial tunable laser diodes are not available at this wavelength, one of the aims of the Gladis project is the development of laser prototypes emitting around 2.3 μm in the GaSb system, with a continuous single mode tuning range around 5 nm. Several technological routes are being explored: VCSELs and gain coupled DFB laser diodes fabricated by University of Montpellier, Nanoplus, Thalès Research and Technology and Prag University.

The other goal of the Gladis project is the practical implementation of the measurement set-up. In order to have reproducible measurements, the optical set-up needs to have optical elements that are as achromatic as possible over the tuning range of the laser diode.

First experimental results on the laser diode prototypes and on the reproducibility of the optical measurements after one year of Gladis project will be presented.

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Heterodyne receivers play a crucial role in the scientific exploration of the earth's atmosphere and in the investigation of astronomical objects. The high spectral resolution of heterodyne receivers is used from the microwave ($\lambda = 10$ mm) to the thermal infrared ($\lambda = 10$ μ m) to derive the volume mixing ratio profiles of stratospheric trace gases, to determine the absolute and relative abundance of chemical species in the interstellar medium, and to deduce the dynamical information from the fine structure of the spectra.

In this paper, only the infrared receiver technology and applications are discussed. In the optical domain, it was Forrester [1] who first suggested that a laser would be a suitable local oscillator, following upon his demonstration of heterodyne beats between incoherent sources. In the infrared, heterodyne detection has been associated to the development of the lasers, at first gas lasers like CO and CO₂ lasers and later on, tunable semiconductor lasers. Pb-salts diode lasers had long been the only kind of mid-infrared tunable laser sources available for heterodyne detection. Although promising results were obtained, some major drawbacks have restricted the opportunities for development of this technique. Actually, the most promising tunable mid infrared sources are quantum cascade (QC) lasers. QC lasers seems to have all the properties required for the realization of heterodyne receivers.

After an introduction about the theoretical aspects of heterodyne detection, we present an overview of technical aspects and applications of infrared heterodyne detection with both kinds of lasers.

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ANALYTICAL PHOTONICS FOR HIGH PRECISION MID INFRARED TRACE GAS SENSING

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Abstract: Quantitative high precision mid-infrared spectroscopic trace gas detection critically depends upon the laser source characteristics used in selectively probing transitions of the molecules of interest. The spectroscopic performance of a tunable mid-infrared laser system directly determines the measurement sensitivity, selectivity, and accuracy. The source also contributes significantly to the overall instrument size and robustness when operated in the field.

There has been significant progress in recent years utilizing new approaches (more optical power, pathlength scaling, modulation techniques) to achieve detection limits in the tens of parts-per-trillion by volume (pptv) range for a number of trace gases. However, none of the techniques have demonstrated such performance routinely in a completely hands-off autonomous instrument while in the field, and more specifically on airborne platforms.

In this talk, we will discuss the incremental progress of developing a highly sensitive, accurate and autonomous mid-IR laser based absorption spectrometer for airborne formaldehyde detection. Specifically, we will outline the limitations and issues such as beam quality, beam re-shaping requirements, and frequency stability we encountered using lead-salt diode and quantum cascade laser sources. To overcome these limitations, we are developing and validating the performance of a robust solid-state optical fiber pumped difference-frequency generation (DFG) based mid-IR tunable source. Such a source offers superior, near-gaussian beam quality ($> 90\%$), wide temperature ($>15\text{ cm}^{-1}$) and current ($>1\text{ cm}^{-1}$) tuning ranges, flexible center wavelength selection ($2.6 - 4.4\ \mu\text{m}$), narrow spectral linewidths ($< 1\text{ MHz}$), frequency stability and repeatability, single mode mid-IR optical powers in the mW range, and convenient room-temperature operation. The rigid opto-mechanical arrangement of a fiber pumped DFG laser source and close direct coupling to a multi-pass absorption cell, promises a better pressure and temperature controllability, which in turn reduces changes of the optical background during a measurement.

As will also be discussed, selected opto-electronic near-IR components can be integrated into the DFG based mid-IR source and enable control over the intensity, polarization, and frequency, independent from the pump/signal laser. This capability can be applied towards an advanced servo loop and may significantly reduce the technical noise that typically dominates in field-based measurements. Possible concepts will be presented towards a totally autonomous compact mid-IR DFG based gas absorption sensor employing opto-electronic technical noise-subtraction.

**ELEMENT SELECTIVE DETECTION OF MOLECULAR SPECIES USING
CHROMATOGRAPHIC TECHNIQUES AND DIODE LASER ATOMIC ABSORPTION
SPECTROMETRY**

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Atomic absorption lines can be measured very close to shot noise limit at relative high diode laser powers if two beam arrangements are used, the wavelength and the absorption is modulated by different frequencies in the kHz-range, and phase sensitive detection at the sum or difference of the modulation frequencies is applied [1,2]. This high detection sensitivity allows to measure element concentrations in the ppt or even ppq range by atomic absorption spectrometry if aqueous solutions are analysed in graphite furnace atomizers or analytical flames.

Atomic absorption spectrometry with tuneable diode lasers can also be used for the analysis of molecular species if the molecules are introduced and dissociated to its element components in appropriate atomizers such as analytical flames or plasmas. However, the analysis of a complex sample with different molecular species require separation techniques, such as chromatography or electrophoresis, before the analytes are introduced in the atomizer separated by time and then dissociated and measured by atomic absorption spectrometry.

Examples will be given where atomic absorption spectrometry with diode lasers is used in combination with gas and liquid chromatography and plasma and flame atomizer. A particular part of the contribution is devoted to the application of diode laser absorption spectrometry in miniaturized plasmas which can be integrated in chips with miniaturized separation systems ("lab-on-the-chip"). Such analytical systems are suitable for environmental and industrial process control.

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**CAVITY RING DOWN AND CAVITY ENHANCED ABSORPTION SPECTROSCOPY,
AND TRACE DETECTION, WITH DIODE LASERS**

Daniele Romanini

Cavity Ring Down Spectroscopy (CRDS) is a high sensitivity absorption method which has reached the threshold of 100 published papers published per year. It is a linear technique which allows precise and absolute absorbance measurements of molecular transition with an "effective pathlength" of tens of km. Light from a laser is first injected into a high finesse optical cavity, and then its exponential decay rate is measured. As this is repeated as a function of laser wavelength, variations in the decay rate allow detecting very weak absorption lines. In Cavity Enhanced Absorption (CEAS), which is also becoming popular for its simplicity, the intensity transmitted by the cavity is recorded as the laser tunes across cavity resonances. Absorption lines then appear enhanced by a factor proportional to the cavity finesse. However, a large noise level is present which demands long averaging times. We have developed CRDS and CEAS schemes functioning with telecom diode lasers (DFB type) and which take advantage of optical feedback (OF) from the cavity as a means of cavity injection. We will discuss OF-CRDS and OF-CEAS, and show their advantages with respect to their analogues working without optical feedback. We will present a device which can work both as a CRDS and as a CEAS spectrograph, able to monitor CO₂ in ambient air in real time with high sensitivity (ppm level).

**BEYOND CAVITY RING DOWN: CAVITY ENHANCED SPECTROSCOPY
TECHNIQUES USING TUNABLE DIODE LASERS**

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Cavity Enhanced Spectroscopy techniques (CES) based on the use of high-finesse optical cavities as absorption cells, which include cavity ringdown spectroscopy (CRDS), integrated cavity output spectroscopy (ICOS), and cavity enhanced absorption (CEA), offer the potential for very high sensitivity due to inherently long effective optical path lengths (typically thousands of meters). Practical implementation of these methods to real-world applications has been limited to date due to the relative complexity of these strategies compared with more traditional spectroscopic techniques.

In this work we review recent advances at Los Gatos Research in the development of novel instrumentation based a CES strategy called Off-Axis ICOS. In this strategy a laser beam is aligned off-axis with respect to a high-finesse optical cavity, as opposed to the conventional on-axis alignment used in CRDS, ICOS or CEA. The beam trajectory yields a significant decrease in the effective free spectral range of the cavity. The result is more continuous and efficient coupling through the cavity and improvement in measurement sensitivity compared with previous CRDS and ICOS results.

We will present recent Off-Axis ICOS measurements recorded using diode lasers for a variety of applications. The high measurement sensitivity (typically $\sim 3 \times 10^{-11} \text{ cm}^{-1}/\text{Hz}^{1/2}$) and low-cost components make this technique attractive for industrial process control, environmental and atmospheric monitoring and other applications that require real-time, accurate, gas concentration measurements.

CHEMICAL SENSING WITH QUANTUM CASCADE LASERS

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This talk will focus on the development of compact trace gas sensors based quantum cascade lasers for the detection, quantification, and monitoring of several key trace gas species in ambient air addressing important analytical instrumentation needs in atmospheric chemistry, industrial and medical applications. The use of quantum cascade lasers will permit to target strong fundamental rotational-vibrational transitions in the mid-infrared, which are one to two orders of magnitudes more intense than overtone or combination band transitions in the near infrared.

Novel quantum cascade distributed feedback (QC-DFB) lasers fabricated by band structure engineering and grown by molecular beam epitaxy offer an attractive new radiation source for mid-IR laser absorption spectroscopy in the 3.5 to 80 μm spectral range. The most technologically developed system to date is based on intersubband transitions (type-I QC) in InGaAs/InAlAs heterostructures [1].

The architecture and performance of several sensitive, selective and real-time gas sensors based on mid-infrared cw and pulsed QC-DFB lasers will be described. To date we have detected 11 gases (CH_4 , N_2O , CO_2 , CO , NO , H_2O , NH_3 , C_2H_4 , OCS , C_2H_6 and $\text{C}_2\text{H}_5\text{OH}$) including isotopic signatures of carbon and oxygen at the ppm to the ppt level [2-4]. This requires different sensitivity enhancement schemes such as multipass gas absorption cells, cavity ring down and photo-acoustic absorption spectroscopy which can realize minimum detectable absorbances in the range from 10^{-4} to 10^{-6} in several real world applications. Specific examples of sensors for detecting NH_3 , CO and NO will be reported.

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Part 2. Industrial Session.

IND-1 COMMERCIAL ASPECTS OF TDLAS

Johannes Kunsch

IND-2 DFB-LASER IN THE WAVELENGTH RANGE FROM 0.7 TO 2.5 μm FOR TDLS

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

IND-3 LONG-WAVELENGTH VERTICAL-CAVITY SURFACE-EMITTING LASERS FOR MOLECULAR ABSORPTION SPECTROSCOPY IN THE 1.5-1.8 μm RANGE

*M. Ortsiefer, R. Shau, M. Lackner, G. Totschnig, F. Winter,
J. Roskopf, C. Lauer, M.C. Amann*

IND-4 TUNABLE BLUE LASER-LIGHT FROM EXTERNAL CAVITY DIODE-LASERS

Lars Hildebrandt

IND-5 TUNABLE DIODE-LASERS FROM UV TO NIR WITH UP TO 1 Watt OUTPUT POWER

R. Böhm, A. Deninger and W. Kaenders

IND-6 LASER SOURCE MODULES AND SYSTEM COMPONENTS FOR MID-INFRARED TUNABLE DIODE-LASERS FROM 3 – 25 μm

Achim Högg

IND-7 APPLICATION OF TUNABLE DIODE-LASERS BETWEEN 3 AND 25 μm ($3300 - 400 \text{ cm}^{-1}$)

Lars Mechold

IND-8 PRECISION GAS MIXTURES AS RELIABLE CALIBRATION STANDARDS FOR TDLS

K. Brenner, B. Reimann

IND-9 TUNABLE DIODE-LASER ABSORPTION SPECTROSCOPY MEASUREMENT OF EXHALED BREATH

Patrick J. McCann

IND-10 A MOBILE METHANE PIPELINE INSPECTION SYSTEM

*Antonio Chiarugi, Francesco D'Amato,
Daniele Fogale, Gabriele Finardi*

IND-11 MEASURING MOISTURE OR OXYGEN IN BOTTLES
OR PROCESS GASES

Chris Hovde, Joel Silver and Mark Paige

IND-12 GAS ANALYZERS IN THE NEAR- AND MID-IR

Mark G. Allen

IND-13 HIGH POWER AND SINGLE FREQUENCY QUANTUM
CASCADE LASERS FOR GAS SENSING

*Stéphane Blaser, Lubos Hvozدارa, Yargo Bonetti, and Antoine Muller
Marcella Giovannini, Mattias Beck, and Jérôme Faist*

IND-14 ENVIRONMENTAL TRACE GAS INSTRUMENTATION USING
PULSED-QUANTUM CASCADE LASERS

*J. Barry McManus, David D. Nelson, Mark S. Zahniser
Yargo Bonetti, Lubos Hvozدارa and Antoine Muller*

IND-15 APPLICATION OF THE SICK|MAIHAK SENSOR
GM700-1C IN THE AUTOMOTIVE INDUSTRY

Kai-Uwe Pleban

IND-16 DEMANDING INDUSTRIAL APPLICATIONS
OF THE LDS 3000 DIODE-LASER SPECTROMETER

Michael W. Markus

COMMERCIAL ASPECTS OF TDLAS**Johannes Kunsch***Laser Components GmbH, Werner-von-Siemens-Str. 15,
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By means of Tunable Diode Laser Absorption Spectroscopy (TDLAS) superior detection limits can be achieved in analytics of many gases. [1,2]. However, application is still limited to laboratory applications or very small series production and the measurement technique is not yet broadly established (in comparison to methods like FTIR). A more widely acceptance can be expected if TDLAS can be better used in process control and monitoring. [3,4] The first part of the paper makes commercially successful identification of applications easier since TDLAS is a versatile and reliable but also relatively expensive tool.

In our experience it turns out that (beside the low detection limits and selectivity) the high measurement speed [4], the chance to run remote monitoring and the universal feature of the Lambert-Beer law are key advantages triggering broader need. The importance of the universal aspect may surprise at the first moment. However, oxygen is a good example here: At low target temperatures paramagnetic sensors are widely used, while at elevated temperatures ZrO sensors are most common. From an end-user point of view a standardized sensor for all temperature would be appreciated and the optical sensor based on TDLAS can do the job.[5]

Furthermore, the paper shortly reviews the product range of LASER COMPONENTS GmbH useful for TDLAS: We do offer single mode lasers in spectroscopic quality under the name "SPEC-DILAS". The IR series is based on IV-VI technology and covers the range from 3-10 μm . The range from 10-20 μm can also be covered by lasers based on iV-VI technology, but in multimode quality only. The V series (single mode VCSEL) is available at 760 nm (for oxygen detection), 850 nm and most recently also between 1.5 and 2 μm . The D-series (DFB) is available from 1.25 to 1.75 μm . Recently, the QUANTA diode laser assembled with peltier cooling having emission at 5.5 μm using pulsed conditions and the referring GENPULSE controller are launched into the market.

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DFB-LASER IN THE WAVELENGTH RANGE FROM 0.7 TO 2.5 μm FOR TDLS

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Stable single mode laser diodes are the essential key components for tunable diode-laser spectroscopy of various species to be monitored.

Nanoplus employs lateral metal gratings with precisely tunable grating periods (tunability in the sub-nanometer range) to achieve distributed feedback within the laser cavity. This approach allows for excellent emission wavelength control, mode hopping free operation and high side mode suppression ratios. Within the wavelength range from the visible (760 nm) up to the near infrared regime (2.5 μm) we offer customer specific devices based on different semiconductor compound systems such as GaAs, InP or GaSb. Hereby the desired wavelength may be specified with a high spectral accuracy. Typical side mode suppression ratios are below -35 dB for cw room temperature operation and ultra-narrow linewidths ensure high spectroscopic resolution.

LONG-WAVELENGTH VERTICAL-CAVITY SURFACE-EMITTING LASERS FOR MOLECULAR ABSORPTION SPECTROSCOPY IN THE 1.5-1.8 μm RANGE

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Electrically pumped vertical-cavity surface-emitting lasers (VCSELs) with emission wavelengths between 1.5 and 1.8 μm are presented for the first time in TDLAS experiments to probe rovibrational transitions of infrared active gases including methane (CH_4) at 1.685 μm (5935 cm^{-1}), ammonia (NH_3) at 1.537 μm (6506 cm^{-1}), hydrogen chloride (HCl) at 1.810 μm (5525 cm^{-1}) and water (H_2O) at 1.811 μm (5522 cm^{-1}). For all species, excellent agreement could be obtained between database-calculated and measured absorption spectra. The measurements were carried out using novel InP-based buried tunnel junction (BTJ)-VCSELs. This laser type is found to have excellent suitability for spectroscopy and to provide superior properties over conventional edge emitting lasers with respect to a large number of significant applications.

Up to now, BTJ-VCSELs could be realized with emission wavelengths from 1.3 to 2 μm , offering a convenient way to detect a large number of absorption lines in the near-infrared with easy to handle, room temperature operating laser diodes. The lasers emit in a single longitudinal and transverse mode with a small beam divergence around 15° . Typical threshold currents, threshold voltages and output powers at room temperature are below 1 mA, 1 V and 0.3-0.5 mW, respectively. This significantly reduced power consumption also supports long-time battery-operated applications. The maximum continuous-wave (cw) operating temperatures are well beyond room temperature with record values of 90°C @ 1.8 μm and 110°C @ 1.55 μm , respectively [1]. For the absorption measurements, a single-pass setup with a path length of 44 cm was chosen where the chips were directly contacted on the uncleaved wafer to demonstrate cost-effective “on-chip” testability as opposed to edge emitters. The measured current tuning rate of e.g. $+0.86\text{ nm/mA}$ ($-3.05\text{ cm}^{-1}/\text{mA}$) @ 1.68 μm is about an order of magnitude higher than for edge emitters whereas the temperature tuning rate of $+0.11\text{ nm/K}$ ($-0.40\text{ cm}^{-1}/\text{K}$) exhibits comparable values [2]. At this wavelength and at 15°C , the maximum continuous current tuning range was as high as 4.5 nm (16 cm^{-1}) which is very useful for measurements in linewidth broadening high-pressure environments. In contrast to edge emitters, the absolute output power variation associated with current tuning is much smaller. Besides the wide wavelength tuning, the capability for rapid tuning is also a significant advantage of VCSELs. By applying a triangular current ramp (0-4 mA) to a 1.68 μm BTJ-VCSEL, the tuning range decreases from 9.9 cm^{-1} at 25 kHz to 2.6 cm^{-1} at 1 MHz with a tuning rate as high as $5.2\text{ cm}^{-1}/\mu\text{s}$ at a frequency of 1 MHz. For pure methane at 397 mbar, the absorption spectrum was clearly resolved up to repetition rates of 5 MHz where the tuning range was about 0.21 nm (0.36 cm^{-1}).

In conclusion, TDLAS measurements with long-wavelength BTJ-VCSELs exhibit significant advantages for spectroscopy including wide ($> 3\text{ nm}$), fast (several MHz) and mode hop free wavelength tuning. With respect to their low-cost potential, long-wavelength VCSELs are expected to considerably expand the range of applications for gas detection systems.

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TUNABLE BLUE LASER-LIGHT FROM EXTERNAL CAVITY DIODE-LASERS

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Abstract not available

TUNABLE DIODE-LASERS FROM UV TO NIR WITH UP TO 1 Watt OUTPUT POWER

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TOPTICA Photonics (presently 60 employees) develops, produces and markets innovative diode laser systems. The product range includes laser and spectroscopy accessories for scientific, industrial and medical applications, as well as test systems for optical data storage systems. A universal tool for spectroscopic applications in physics, chemistry and life sciences is the grating stabilized external-cavity diode laser DL 100. The Littrow configuration offers high power levels (up to 150 mW), narrow linewidth (~ 1 MHz), high frequency stability and allows for a simple change of wavelength. Presently, diodes are available in the near-UV, violet and blue spectral range (375 – 450 nm), as well as in the red and NIR (625-1850 nm). TOPTICA Photonics also offers a modular set of control electronics, including scan generators, PID regulators, lock-in regulators, Pound-Drever detectors and computer interface boards. Still higher output power is available from tapered amplifiers TA 100. The flared structure of the semiconductor active region acts as a spatial mode filter while the cw output power is amplified up to 1 Watt. The TA 100 is thus a tunable single-mode laser with a near diffraction-limited beam, low optical noise and superior beam pointing properties. Wavelengths currently covered range from 730-1100 nm. Frequency doubling using TOPTICA's second harmonic generation laser systems SHG 100 fills the gaps in the blue and green wavelength range, previously inaccessible to semiconductor lasers. Non-linear crystals such as bulk KNbO_3 or periodically poled material generate tunable single-frequency laser light in the range of 430-540 nm at output powers up to 200 mW. UV wavelengths at the mW level have been realized by frequency quadruplication, serially combining two doubling stages. The compact set-up of the SHG 100 makes use of active resonator length stabilization by the polarization-sensitive Hänsch-Couillaud technique. As the "blue" (frequency-doubled) output power is proportional to the square of the fundamental power, tapered amplifier systems provide particularly suitable laser sources for frequency doubling.

In order to meet the need for a single-frequency, high-power laser system, TOPTICA Photonics developed the laser source XTRA. The laser provides single-mode cw output of more than 300 mW at 785 nm. The TEM_{00} beam can be focussed to a micrometer spot. In order to minimize the wavelength drift during operation, a new microprocessor-driven laser stabilization controller was developed: an active control loop prevents the occurrence of mode hops and mode instabilities, restraining the laser to longitudinal single-mode emission. Thus, a frequency drift of less than 3 GHz (0.1 cm^{-1}) over a 100 hour period is achieved. The XTRA is intended for applications in dispersive Raman spectroscopy and high-resolution Raman microscopy.

Apart from laser systems, TOPTICA Photonics offers a wide range of spectroscopy accessories. The FPI 100 is a high resolution confocal Fabry-Perot interferometer for measuring the spectral characteristics of cw lasers. Due to the confocal design, the instrument is readily adjusted. Different mirror sets are available for different wavelength regimes. Scanning and (optional) temperature stabilization are accomplished using TOPTICA's standard electronics modules. Two versions with different free spectral range (1 GHz and 4 GHz) are available.

A set of Fizeau interferometers can be utilized to measure the laser wavelength with great precision. This concept is realized in the Wavelength Meters, of which TOPTICA sells three different models. The most precise instrument, the Ångstrom-WS/8, achieves an accuracy ± 0.02 pm, making it the most accurate commercial wavelength meter to-date. The instrument can be used with both pulsed and cw lasers. A fiber coupler is provided for convenient operation of the device.

The Quadrature Interferometer is a novel instrument to control the frequency of a tunable laser system. It permits linear wavelength scanning, overcoming non-linearities of mechanics and actuators. In addition, the laser wavelength can be varied discontinuously ("stepped") in any desired manner. The instrument also allows for locking the laser wavelength to any value within the mode-hop free tuning range of the laser. (See separate abstract for poster presentation.)

The latest addition to our product portfolio is a multipass cell for absorption spectroscopy. The Herriott cell features two spherical mirrors, which reflect an incoming laser beam up to 74 times before it exits the cell again. Thus, a long interaction path of 30 m between the laser light and a gaseous sample is realized, maintaining a small volume of the cell (0.9 liter). The dimensions of mirrors and the spot sizes are chosen such as to avoid overlaps (and thus, interference) of the beam spots up to a laser wavelength of 3 μm . The setup is easy to align and tolerant of mechanical vibrations. The long optical path of the Herriott cell permits a fast classification of trace gases, e.g. by high resolution infrared laser spectroscopy. It is intended both for scientific research and for monitoring tasks in an industrial environment, e.g. to detect small concentrations of potentially dangerous gases in manufacturing units.

**LASER SOURCE MODULES AND SYSTEM COMPONENTS FOR MID-INFRARED
TUNABLE DIODE-LASERS FROM 3 – 25 μm**

Achim Högg

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Tunable mid infrared (MIR) lead salt lasers are available at any wavelength from 3 – 25 μm . This type of lasers consists of lead chalcogenides as PbS, PbSe and their mixture system and the basic emission range is determined by the material composition and is chosen by the ratio of Pb, S and Se. The emission range can be tuned continuously within certain limits. The bandgap depends on temperature, the refractive index depends on the injection current, so the tuning is achieved by varying the operating temperature and/or the injection current of the laser. The tuning range depends on each individual laser and a tuning of $\pm 25\text{cm}^{-1}$ will be guaranteed from the laser manufacturer, Laser Components. To cover the whole range from 3 – 25 μm there are generally two types of lasers available. These are the DH-type (double hetero structure) lasers with the approximately emission range from 3–10 μm and the H-type (homogenous structure) lasers with the emission range from 10 to 25 μm . Both types of lasers working at different basic operating temperatures and need different types of cooling device. While the H-type lasers need operating temperatures between 25K and 85K, are the DH-type lasers working between 85K and 120K. As a manufacturer of system components to operate Mid-infrared tunable diode lasers, Mütek Infrared Laser Systems can supply a few types of Laser Source Modules, based on different physical principles of cooling device, to allow a save operation of both laser types. For operating H-type lasers at temperatures between 25K and 85K (for laser wavelength 3-25 μm) the model TLS260 is available. This device is based on a closed cycle Gifford McMahon He- cooler consisting of a two stage cold head, a compressor and a set of flexlines. Because of power consumption, size and weight of the compressor, this type of cooling device is for lab use only. For the DH-type (for laser wavelength 3-10 μm) of lasers there are principle two types of laser source modules available. Type one of laser heads is based on a liquid nitrogen dewar vessel technique (TLS210 which is the spectrometer version and OLS150 which is the OEM version), type two of laser heads is based on closed cycle split stirling cooler technique (TLS265 and TLS265 OEM). All types of the above laser source modules working with the same model (TLS150) of temperature and current controller. The TLS150 is a combined temperature and current controller, where channel one of the controller supplies the injection current for the diode laser and channel two contains a high precision temperature regulator circuit to control the base temperature of the laser station. A high efficiency u-processor controlled Czerny-Turner type monochromator (TLS300) were developed to select modes or to suppress side modes of the diode laser and can be easily mounted to each TLS series laser source module to form the first part of a MIR diode laser spectrometer. Further spectrometer components as reference gas cells, multipass cells (pathlength up to 100m), different types of etalons,... are also available.

APPLICATION OF TUNABLE DIODE-LASERS BETWEEN 3 AND 25 μm (3300 - 400 cm^{-1})

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Trace gas analysis, process monitoring and controlling, as well as basic investigations of molecular structures are of increasing interest. With respect to daily discussions concerning global climate a need of measurements of atmospheric molecules can be expected. Also in medical applications it is now gaining more and more acceptance that several molecules in exhaled air are related to specific diseases. Since decades infrared tunable diode laser absorption spectroscopy (TDLAS) is a proven diagnostic method, well documented in a large number of scientific contributions. Lead-chalcogenide TDL's opened up the possibility to highly specific measurements of many molecules especially using their strongest rotational-vibrational absorption bands in the middle infrared (MIR). Based on fundamental bands the highest sensitivity of many molecules was found. Therefore single mode spectroscopic diode lasers, so-called Specdilars IR, are preferably used. They are produced as double-heterostructure diode lasers by means of molecular beam epitaxy based on the lead selenide material system. Specdilars IR usually emit radiation between 3300 and 1000 cm^{-1} depending on the material composition of the active zone. Homostructure diode lasers are mainly multi mode diode lasers available at MIR wavenumbers up to 400 cm^{-1} . The output power is in the range 0.1 mW to more than 1 mW. Also nowadays, these narrow-band radiation sources have the advantage of high absorbances of 10^{-4} , high spectral resolution of about 10^{-4} cm^{-1} and the capability of tuning the radiation over the absorption profile up to Doppler-broadened line profiles. For a large number of molecular species infrared TDLAS in the spectral region between 3 and 25 μm is a modern, promising technique. This contribution will underline the versatility and reliability of this diagnostic method based on the available variety of lead-chalcogenide diode lasers using several recent examples in plasma chemistry. TDLAS as a plasma diagnostic technique is mainly used for measuring number densities of stable molecules and especially their radical counterparts. Closer investigations were performed in microwave plasmas using $\text{CH}_4\text{-H}_2$ and $\text{CH}_3\text{OH-H}_2$ source gases [1,2]. Measurements focused on the CH_3 radical and related stable hydrocarbons. In case of additional oxygene admixture also formaldehyde, formic acid, carbon monoxide and carbon dioxide could be measured. With sufficient line strengths a sensitivity of 10^{10} molecules cm^{-3} can be reached for many molecules. The detection of neutral ground state molecules allows the direct monitoring of the major species in plasmas. Based on the high spectral resolution and the modal tuning range of usually 1 cm^{-1} more than one absorption line can be recorded simultaneously. Fortunately this can be used for calibration purposes, but also for measurements of more than one species in the same time. There can be different neutral molecules, different isotopes, or neutrals and charged molecules. Many example spectra show overlapping bands of different molecules which can be used for measurements provided the right spectral position was chosen. Spatial resolution can be achieved by reducing the cross section of the beam to several mm and by moving it with an optical system perpendicular to the line of sight. The time resolution of the absolute concentration measurement can basically be below the ms scale [3].

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PRECISION GAS MIXTURES AS RELIABLE CALIBRATION STANDARDS FOR TDLS

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As an internationally operating company, Messer Griesheim industrially manufactures and distributes pure gases, gas mixtures and various application technologies. Concerning composition and the range of components concentration, an enormous diversity characterises gas mixtures. Frequently strong effort has to be made to meet the customer requirements for a given application. As a consequence, such mixtures are often referred to as 'specialty gases'.

Gas mixtures with certified composition are frequently needed as quantitative reference for many different stand-alone analytical instruments, but also in measuring networks surveying e.g. the composition of exhaust gases or even the air quality in industrial, urban, and rural areas. With regard to other calibration techniques, the major advantages of calibration gas mixtures pressurised in pre-treated metal cylinders are the precisely estimated component concentrations, long time stability, high purity, simple availability, straightforward handling, storage and transport and low operating costs.

The production of reliable pressurised calibration gas mixtures with certification is processed on the basis of an interdependent system of traceability. Based on so-called primary standards, gas mixtures are produced at high expense entirely gravimetrically, i.e. only by weighing masses. However, commercial availability for calibration gas mixtures requires an economic manufacturing process often in large lot numbers. Thus, the gas mixtures produced must undergo afterward certification; it means the mixtures have to be referred by means of well defined comparison measurements to primary standards discussed above. In addition, long-time analytical measurements on gas mixtures controlling components concentration stability are also part of the certification procedure and further activities as comparison measurements with internationally accepted standard reference materials (SRM) or round robin experiments. By these steps, the dedicated gas mixture becomes a so-called secondary standard, being ready to be used externally in calibration measurements by customers, or serving as reference for creating at low expenses working and transfer standards by commonly acknowledged analytical comparison methods.

Two- and multi-components calibrating gas mixtures from pressurised gas cylinders, with well characterised properties as out-lined above, and certified often for a wide concentration range of components, may also be an interesting solution for calibration issues emerging in measuring systems based on the highly selective absorption of electromagnetic radiation from TDL. Small molecules as O₂, H₂O, CO, CO₂, NO_x, SO₂, HCl, HF of inorganic origin, but also organic compounds as CH₄, HCHO are favourite candidates for analytical determination in high-resolution TDLS gas phase measurements, as the same compounds often appear as components in gas standards produced industrially in pressure cylinders on a larger scale.

Finally, the gas industry has need for powerful, non-destructive analytical methods and instrumentation when for selected gaseous impurities or mixture components very low detection limits are required and when the product itself shows coincidentally as pure gas or balance (mixture main component) strong electromagnetic absorption in a wavelength range, where usually the analytical spectroscopic measurements are carried out. Such so-called matrix gases are typically 100% CO, CO₂, NO, N₂O, CH₄, F₂, Cl₂, HCl, HBr *etc.*

Both issues have been addressed at Messer Griesheim and preliminary work has already been done. In cooperation with external institutions, at the R&D department TDLS methods have been applied to determine e.g. NO₂ at sub-ppb level in low concentrated NO mixtures in N₂, and O₂ at ≥ 50 ppm in 100% fluorine, respectively.

**TUNABLE DIODE-LASER ABSORPTION SPECTROSCOPY MEASUREMENT
OF EXHALED BREATH**

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With their ability to measure low concentrations of specific gas phase molecules, tunable diode laser absorption spectrometers are often cited as having potential applications in medical diagnostics. This presentation will describe the development and operation of a TDLAS instrument designed for measurement of biomarker molecules in exhaled breath. This instrument has been successfully used in clinical settings to perform real-time simultaneous measurements of exhaled nitric oxide (eNO) and exhaled carbon dioxide (eCO₂) in the 5.2 micron spectral range. An internal calibration method using the absorption signal for CO₂ and its known concentration of about 4.5% at the end of a single exhalation (end tidal) was used to determine lower airway eNO concentrations. A minimum detection limit of about 0.5 ppb was obtained for a 2 second integration time. Measured eNO values have clinical utility in asthma diagnosis and anti-inflammatory therapy monitoring because high levels (greater than about 25 ppb) are associated with airway inflammation. Clinical research results show that the TDLAS instrument can accurately determine eNO concentrations and accurately identify steroid-naïve asthmatics in spite of variations in exhalation flow rates, exhalation time, and ambient NO levels. This is a very patient-friendly test that can be used by health care systems to assess airway inflammation, evaluate the effectiveness of anti-inflammatory therapy, and monitor treatment compliance. The simultaneous detection of eCO₂ and the internal calibration capabilities it provides for both the instrument and confirmation of proper breath donations will make this TDLAS technique well suited for diagnosing and monitoring asthmatic children.

A MOBILE METHANE PIPELINE INSPECTION SYSTEM

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We present our novel methane sensor, designed to operate on board of small vehicles, for the detection of leaks from distribution pipes under the roads. It is based on a room temperature, fiber coupled, distributed feedback diode laser emitting at the wavelength of 1.651 micron. The requests for such a detector are: Range: 1-10.000 parts per million; Resolution 1 part per million \div 10% according to the reading; Selectivity greater than 10.000 (this means that 10.000 parts per million of any other gas are read as less than 1 part per million of methane); Time resolution 1 second or better. The analyzer is based on the Beer-Lambert law for light absorption. As the absorbance varies in quite a wide range (0.0005-0.75) two detection techniques are adopted: two-tone frequency modulation spectroscopy for low concentrations [1], and direct absorption for high concentrations.

The whole instrument is hosted in a 3 units high container for a 19" rack. The interaction of the laser beam with air occurs inside a Herriott type multipass cell. This analyser is designed to be operated in parallel with other sensors mounted on board of the vehicle, and shares with them the air flux generated by a common pump. The optical pathlength of the multipass cell is properly dimensioned for the sensitivity and the overall noise, while its volume, coupled with the pump speed, provides the right air exchange rate. The electronics includes a computer which drives the instrument and provides the interface with the operator. No monitor or keyboard are necessary for the normal operation. Power consumption is less than 50 W @ 12 V. The instrument output is either 0 \div 10 V, or 4 \div 20 mA. A common data logger acquires the readings from all the instruments and visualizes them. The ethernet interface is used to drive the analyser by a remote computer. The van which hosts the instruments is equipped with carpets sliding on the asphalt. In these carpets the holes of the air intake system are drilled, in order to take only the air coming out directly from the ground, so minimizing the effects of wind, or turbulence due to other vehicles.

As for the selectivity, laboratory tests have proved, for instance, that a mixture of 1% propane in syntetic air gives the same instrumental response as syntetic air alone. It is possible to perform a standard calibration, by using syntetic air for the zero and known mixtures of methane in syntetic air for the different measurement ranges. There is also a self calibration procedure, which the instrument executes at the start-up, with the aid of a sealed off calibration cell which can be put across the laser beam. This procedure takes only one minute, and is a check of the stability of the device. Should the instrument fail to pass this check, a warning is issued.

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MEASURING MOISTURE OR OXYGEN IN BOTTLES OR PROCESS GASES

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Ensuring the purity of semiconductor process gases is a demanding application of analytical chemistry. Southwest Sciences recently demonstrated an online monitoring system for measuring water vapor in semiconductor gases at sub-part per billion levels. Our approach uses near-infrared diode lasers combined with wavelength modulation spectroscopy. Near infrared diode laser technology has been highly developed for fiber communications, resulting in reliable devices available with excellent spectroscopic properties. Wavelength modulation methods suppress noise, resulting in a wide dynamic range and sensitivity for water in nitrogen of better than 1 part per billion. Time response to upsets is a few seconds. This technology has been transferred to Delta F, a leading manufacturer of gas sensors for the semiconductor industry.

Another challenging application is the measurement of impurities inside sealed bottles. Pharmaceutical manufacturers must limit the amount of oxygen and water vapor in their products or the medicines may degrade over time. Existing approaches require that gas is extracted from the bottle into an analyzer, but sampling punctures the bottle's sterile seal and so is a destructive analysis. We have developed a non-intrusive monitor based on probing the head space of the bottle using laser spectroscopy. Oxygen or moisture content can be quantified in seconds, permitting measurements on the process line. A challenge of this approach is that the bottle is of modest optical quality.

GAS ANALYZERS IN THE NEAR- AND MID-IR

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Research and development programs at PSI have resulted in industrial and commercial prototype sensor technology based on tunable diode laser absorption spectroscopy in the wavelength range from 630 nm to 5.2 microns. This presentation will briefly describe the most mature near-IR sensor platforms and recently available, room-temperature mid-IR sensors using quantum cascade lasers.

Integrated Multi-Gas Analyzers. Many industrial process control systems require simultaneous, in-situ, and continuous measurements of multiple process parameters for proper optimization. Together with the AirLiquide Corporation, PSI has developed a multi-laser sensor for simultaneous measurements of the concentration of O₂ (763 nm), H₂O (1.57 microns), and CO (1.57 microns), as well as gas temperature, in materials processing furnaces. The temperature measurement is based on the absorption ratio of two water vapor transitions. The sensor features fiber transport and rugged industrial optical interfaces. Example results will be shown from pilot-furnace testing in oxy-fueled natural gas combustion and full-scale steel and aluminum heat treating furnaces.

Portable Gas Leak Detectors. Most TDL sensors measure absorption across a fixed pathlength using either separate launch and receive optical components or a distant retro-reflector. As near-IR diode lasers approach many 10's mW output power, the natural reflectivity of topographic targets (foliage, earth, buildings, etc.) can provide sufficient return signal for single-ended, portable survey tools. PSI, together with Heath Consultants and several US natural gas companies, has developed a portable natural gas leak detector using a 1.65 micron diode laser and a high-efficiency, compact optical telescope. It can operate over 8 hours on a single set of rechargeable batteries, with a detection limit on the order of a few ppm-m and at operating distances up to 30 m. Example data showing sensitivity and leak detection in typical residential services will be presented.

Room-Temperature Mid-IR Gas Analyzers. Gas sensors based on overtone transitions in the near-IR can generally achieve detection limits on the order of 1 ppm-m. In the mid-IR, strong fundamental transitions permit two orders of magnitude improvement in detection limit - important for potential applications in environmental monitoring, breath analysis, and industrial pollutant emission. Beginning in 1998, room-temperature quantum cascade lasers at wavelengths between about 4 and 12 microns became available. Working with Lucent Technologies and Alpes Lasers, PSI has developed prototype commercial gas analyzers for NO (5.2 microns) and CO (4.6 microns). The operation of the analyzers is substantially identical to industrial near-IR units, except that detection limits of a few 10 ppb-m are achieved. Applications will be shown for high-temperature pollutant emission monitoring, atmospheric trace gas monitoring, and breath analysis.

**HIGH POWER AND SINGLE FREQUENCY QUANTUM CASCADE
LASERS FOR GAS SENSING**

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Numerous applications, such as gas sensing, spectroscopy, pollution monitoring, atmospheric chemistry, detection of compounds, non-invasive medical diagnostics, optical wireless communications or lidar, require a powerful infrared light source with well defined properties. As the quantum cascade (QC) laser emit in the mid-infrared range between 3.5 and 25 μm , they represent very suitable semiconductor laser sources. The majority of such applications require a high average power and/or single-mode operation.

We present here a high-average power Fabry-Pérot (longitudinal multimode) QC laser and a distributed-feedback (DFB) QC laser operating near 8 μm .

A 3mm-long and 28 μm -wide Fabry-Pérot (FP) laser delivers a maximum average power of 0.8W at a temperature of 90K suitable for Stirling cooler. The laser is electrically pumped at a duty-cycle of 50% with 100ns-long pulses at a pulse repetition rate of 5 MHz. The threshold current density is around 0.7 kA/cm². At room-temperature, the maximum average power is still more than 150mW for a duty-cycle of 20% (100ns pulses at 2MHz), with a threshold current density of 1.5 kA/cm².

A similar QC structure processed as a DFB laser gives a maximum peak power of 1.7W and a maximum average power of 30mW at room-temperature. Single-mode operation was observed around 1196 cm⁻¹ (corresponding to 8.36 μm) with a sidemode suppression ratio > 20dB for the entire investigated temperature range (-30 to +40°C), with a tuning range as broad as 6cm⁻¹.

ENVIRONMENTAL TRACE GAS INSTRUMENTATION USING PULSED-QUANTUM CASCADE LASERS

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Quantum cascade (QC) lasers have provided new opportunities for instruments to measure atmospheric and environmental trace gases by tunable infrared laser differential absorption spectroscopy (TILDAS) in the mid-infrared spectral region where molecular absorptions are strongest. Exceptional mode stability, compact size, high optical power, and the elimination of cryogenic cooling has resulted in compact, robust, and automated instruments for field measurements and for laboratory applications.

Aerodyne Research, Inc. has developed optical designs and signal processing software for instruments to detect multiple trace gases using QC lasers from ALPESLASERS. As many as four lasers may be multiplexed using all-reflective optical elements with either open path absorption with retroreflector and telescope, or reduced pressure sampling using one or more multiple pass absorption cells. The open path system has been developed as an extension of our earlier instruments for automobile exhaust measurements¹ and is capable of simultaneous measurements of NO, NO₂, CO and CO₂ in cross road measurements from moving vehicles at highway speeds. The closed path configurations use our astigmatic multiple-pass absorption cells (AMACs) to obtain maximum path length in minimum volume.² QC-TILDAS systems using the AMAC-200 (200 m path, 5 liter volume) can detect trace gases such as ammonia, nitric oxide and ozone at sub-part-per-billion mixing ratios with sub-second response time.³ The smaller volume AMAC-76 (76 m, 0.5 l) provides rapid response (10 Hz) suitable for "greenhouse" gas flux measurements using eddy correlation techniques with relative precisions of 0.1% of ambient concentrations for methane, nitrous oxide and carbon dioxide. QC lasers in this application can be used to reduce the size, complexity, and operator attention compared to our earlier instruments using lead salt TDLs.⁴

The data acquisition and signal processing software product, TDLWINTTEL, which uses direct absorption with rapid sweep integration to retrieve absolute trace gas concentrations, has been extensively modified to accommodate pulsed QC lasers. The program can control up to four lasers and report simultaneous concentrations for eight gases using spectroscopic data from the HITRAN data base. Pulse normalization is used to reduce the effect of laser intensity variations inherent with pulsed QC lasers. Background subtraction, line locking to a reference cell, temperature feedback to the laser, and automated start-up routines are incorporated into the software package which can be used with either pulsed-QC or conventional cw TDL systems.

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**APPLICATION OF THE SICK|MAIHAK SENSOR GM700-1C IN THE AUTOMOTIVE
INDUSTRY*****Kai-Uwe Pleban****Sick AG Analyzers and Process Instrumentation,
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The GM700-1C sensor is a compact, industrial device for fast oxygen measurements which completes our automotive emission monitoring devices. The sensor is integrated into an adapted measurement system, that can be connected directly to the car exhaust to perform in-situ measurements in high gas flows.

A short overview of the architecture, the optical configuration, and the working principle will be given. The sensor consists of a VCSEL emitting near 760 nm, which allows the selective detection of oxygen. For the calculation of the gas concentration, a real-time fitting routine is combined with ab initio calculations. Thereby, costly calibrations of the sensors can be avoided.

Finally, some in-situ measurements of car exhaust gases on a road test simulator are presented.

DEMANDING INDUSTRIAL APPLICATIONS OF THE LDS 3000 DIODE-LASER SPECTROMETER

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Since more than a decade NIR diode lasers operating at room temperatures are commercially available. As the design wavelengths of these lasers originally developed for the telecom industry are by accident close to absorption bands of molecules of general interest like ammonia, hydrochloride, oxygen, carbon monoxide, ... diode laser spectrometers were designed for laboratory and industrial use, since then. For both ranges of application there is the need for a high stability, sensitivity and selectivity in the molecular detection. But where in the lab the properties of a spectroscopic set-up are mainly defined by the basic design of the spectrometer, itself, in industrial applications one has to consider multiple influences from the measurement environment. High particle loads, density fluctuations by turbulence, water vapour saturation, droplets, flames, ... are only a selection of process gas properties a laser spectrometer has to face in real life applications. Additionally, an industrial laser sensor must stand mechanical vibrations, wide ambient temperature fluctuations and strong electro-magnetic fields in its surroundings. As being designed from the very beginning for a high tolerance against strong and fast variations of the light transmission introduced while passing a process gas, and with its very robust sensor design the Siemens laser diode spectrometer LDS 3000 allows a wide range of demanding applications in various industrial environments.

Some of the most demanding applications can be found in the wide field of combustion related industries. As the basic process, the combustion itself, is highly dynamic a fast and close-to-the-process control established by the means of fast diode laser based in-situ gas analysers, is favourable to optimise the various process steps of modern combustion plants including the primary combustion and the several flue gas cleaning steps like DENOX, bag house filters, ECPs, ... etc. Taking a typical municipal waste incinerator as an example it could be shown that the Siemens LDS 3000 spectrometer can provide control signals directly from the flue gas which allow to increase the efficiency of each of these process steps, significantly.[1] The easy-to-install and easy-to-operate design of the laser spectrometer yield in a high acceptance for the "high-tech tool" diode laser in this fairly conservative branch of industry. For some individual applications like DENOX control the laser spectrometry is already considered as best-available technology well accepted in the market.[2]

Upstream the process the laser can provide information on primary process properties. The O₂ concentration and even the gas temperature can be derived from the combustion zone, where flames, dust, turbulence, complex gas mixtures and average temperature of 1000°C and above have to be expected. Measuring non-intrusively, very selective and along the line-of-sight the laser provides fast and characteristic signals well suited to feed forward to the process control loop of a combustion plant. As a consequence today concepts of modern combustion plants already consider openings for diode laser sensors all along the flue gas ducts to be able to get use of this state-of-the-art technology.

References:

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- [2] H. Zwahr, *Einsatz der NIR-Laserspektroskopie beim SNCR-Verfahren*, VDI-Berichte Nr. 1667, 9-14 (2002)

Part 3. Poster presentations.

Poster Session A.

A1. TUNABLE ANTIMONIDE-BASED QUANTUM WELL LASERS FOR TRACE GAS DETECTION IN ATMOSPHERIC WINDOWS.

A. Vicet, A. Ouvrard, L. Cerutti, A. Salhi, A. Garnache, F. Genty, Y. Rouillard, R. Teissier, A.N. Baranov and C. Alibert.

A2. TUNABLE SINGLE-FREQUENCY DIODE LASER AT WAVELENGTH $\lambda = 1.65 \mu\text{m}$ FOR METHANE CONCENTRATION MEASUREMENTS

A.V.Gladyshev, M.I.Belovolov, S.A.Vasiliev, E.M.Dianov, O.I.Medvedkov, V.P.Duraev, E.T.Nedelin, A.I.Nadezhdinskii, O.V.Ershov, A.G.Berezin

A3. MULTI GAS SENSING BASED ON PHOTOACOUSTIC SPECTROSCOPY BY USING TUNABLE DIODE LASERS

J-Ph. Besson, S. Schilt, L. Thévenaz, P. Robert

A4. COLLISIONAL BROADENING ANALYSIS BY DIODE-LASER SPECTROSCOPY: $\text{PH}_3 + \text{H}_2$.

Gh. Blanquet, J. Walrand, J. Salem, H Aroui, J.P. Bouanich

A5. LINE FREQUENCY SHIFT MEASUREMENTS BY DIODE-LASER SPECTROSCOPY FOR $\text{CH}_3\text{D-Xe}$

Ch. Lerot, Gh. Blanquet, J. Walrand, M. Lepère, J.P. Bouanich

A6. ABSOLUTE LINE INTENSITY MEASUREMENTS BY DIODE LASER SPECTROSCOPY: HOT BANDS OF OCS

J. Walrand, M. Lengelé, Gh. Blanquet

A7. CARBON AND OXYGEN ISOTOPE MEASUREMENTS OF CO_2 BASED ON OFF-AXIS INTEGRATED CAVITY OUTPUT SPECTROSCOPY

Hans-Jürg Jost, James R. Podolske, Todd R. Sauke, H. William Wilson.

A8. DETECTION OF HIGH TEMPERATURE WATER VAPOR WITH VCSEL NEAR 940 nm

H. Koivikko, T. Laurila and R. Hernberg

A9. TDL SPECTROSCOPY AND DEPLETION MODULATION: THE INFRARED SPECTRUM OF $\text{AR-H}_2\text{O}$

D. Verdes and H. Linnartz

A10. MULTIPLE SPECIES TUNABLE DIODE LASER
ABSORPTION SPECTROSCOPY: APPROACHES AND APPLICATIONS

Yvan Gérard, Robert Holdsworth, Philip Martin

A11. VAPOR MONITORING AND ANALYSIS OF RARE EARTH
ELEMENTS BY USING DIODE-LASER-BASED SPECTROSCOPY

*Hyunmin Park, Duck-hee Kwon, Kitae Lee,
Sungmo Nam and Yongjoo Rhee*

A12. DIODE LASER SPECTROSCOPY OF THE ν_8 BAND
OF THE SF₅CI MOLECULE

W. Raballand, N. Benoit, M. Rotger and V. Boudon

A13. X-RAY STUDIES AND TIME-RESOLVED
PHOTOLUMINESCENCE ON OPTICALLY PUMPED
ANTIMONIDE-BASED MIDINFRARED TYPE-II-LASER STRUCTURES

C. Schwender, J. O. Drumm, G. Hoffmann, B. Vogelgesang, H. Fouckhardt

A14. GAS TRANSPORT IN POROUS MATERIALS ASSESSED BY
DIODE LASER SPECTROSCOPY

*Gabriel Somesfalean, Mikael Sjöholm, Zhang Zhiguo, Janis Alnis,
Benjamin Anderson, and Sune Svanberg*

A15. CONCENTRATION MEASUREMENTS OF OZONE IN THE 1200
TO 300 PPBV RANGE: AN INTERCOMPARAISON BETWEEN THE
B. N. M. ULTRAVIOLET STANDARD AND INFRARED METHODS.

*Gaëlle Dufour, Annie Henry, Claude Camy-Peyret,
Alain Valentin, Daniel Hurtmans*

A16. IMAGING OF CARBON MONOXIDE IN COMBUSTIONS BY MID
INFRARED LASER SPECTROSCOPY

Alireza Khorsandi, Ulrike Willer, and Wolfgang Schade,

A17. MEASUREMENT OF HYDRAZINE RETENTION BY CELLULOSE
ACETATE FILTERS USING LEAD-SALT TUNABLE DIODE LASER
INFRARED SPECTROSCOPY

*Charles N. Harward, Milton E. Parrish, Susan E. Plunkett,
Joseph L. Banyasz, Kenneth H. Shafer*

A18. PRESSURE INDUCED SHIFT AND BROADENING
OF ACETYLENE LINES IN 6580-6600 cm⁻¹

A.I. Nadezhdinskii, Ya. Ya. Ponurovskii, M.V. Spiridonov

TUNABLE ANTIMONIDE-BASED QUANTUM WELL LASERS FOR TRACE GAS DETECTION IN ATMOSPHERIC WINDOWS.

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The 2-2.5 μm wavelength range is of particular interest for trace gas detection because of the very weak water vapour absorption. Sb-based Fabry-Perot laser diodes have already shown high performances in this transparency window [1] in tunable diode laser absorption spectroscopy (TDLAS) applications around 2.3 μm . The CEM2 is now extending its activity to longer wavelengths by developing multi-quantum well sources emitting up to 2.6 μm , as well as new kind of lasers for the 3-5 μm atmospheric transmission window.

Three emitting devices are reported. The two first are based on the same active zone made of type I compressively strained $\text{Ga}_{0.65}\text{In}_{0.35}\text{As}_{0.15}\text{Sb}_{0.85}$ quantum wells embeded between $\text{Ga}_{0.65}\text{Al}_{0.35}\text{As}_{0.03}\text{Sb}_{0.97}$ barriers. These structures can be electrically or optically pumped.

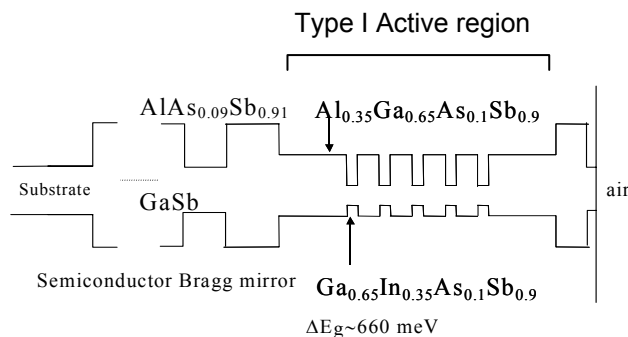


Fig 1 : Typical 1/2 VCSEL structure (Bragg + QW active region)

Edge emitting lasers emitting from 2.04 to 2.6 μm are reported. They operate up to 350K with a typical power up to 20mW and a 110K characteristic temperature. Narrow ridges (10 μm) are processed to force singlemode operation. These devices are well adapted for many gaseous species detection as HF, CH₄, CO₂, NH₃...

The second type of device is an optically pumped Vertical Cavity Surface Emitting Laser. The structure, designed to be pumped by a commercial diode laser emitting at 830nm, is composed of a bottom epitaxial Bragg mirror and a same type I active region on top (Fig. 1). From this design, two kind of devices can be made : a microcavity with an evaporated dielectric Bragg mirror or an extended cavity with a dielectric concave mirror. CW regime of operation has been achieved at 295K near 2.4 μm and low divergence ($\sim 6^\circ$ at $1/e^2$) [2]. We believe that tunable single frequency VCSELs are particularly well adapted for trace gas detection.

We finally present antimonide based AlSb/InAs/GaSb quantum cascade lasers that we are developing to cover the 3-5 μm atmospheric transmission window.

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[2] L CERUTTI, A. GARNACHE, F.GENTY, A.OUVRARD and C. ALIBERT, *IEE*, 39-3, pp. 291 (2003).

**TUNABLE SINGLE-FREQUENCY DIODE LASER AT WAVELENGTH
 $\lambda=1,65 \mu\text{m}$ FOR METHANE CONCENTRATION MEASUREMENTS**

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This report is devoted to the development of a tunable single-frequency laser with a fiber-optic output and meant for methane concentration measurements. The laser has a very simple design shown in fig.1. It consists of just two elements, namely a Fabry-Perot - type laser diode based on InGaAsP-heterostructure and a fiber Bragg grating (FBG) coupled to laser diode. Such a laser design is known to be promising for DWDM fiber-optic communication systems and for laser linewidth narrowing. However, to our knowledge, it has not been previously used for gas analysis. We show that properly constructed FBG-based external cavity diode lasers can be a very convenient, simple, and cheap solution for gas analysis.

To demonstrate the laser operation, the line R7 of methane absorption band $2\nu_3$ was chosen. This line is a doublet with a linewidth of $0,2 \text{ cm}^{-1}$. The laser module developed allowed us to achieve a mode-hop-free tuning range larger than 1 cm^{-1} ; therefore we were able to observe full line shape as shown in fig.2 for two cells with different methane concentration. The operating wavelength was tuned by injection current in the range 110-170 mA, and the time required for single line scanning was 2 ms. At the present stage of development, an optical power of $200 \mu\text{W}$ was obtained at the single-mode fiber output and can be enlarged in future by optimizing of the laser module design.

The approach we used to create a simple tunable laser for methane concentration measurements combines the advantages of tunable near-IR diode lasers and fiber optics. This approach could be easily applied to any gases having absorption lines in the optical fiber transparency window ($0,7 - 1,7 \mu\text{m}$). Only overtones and combination bands, which have much less absorption in comparison with fundamental bands in the mid-IR region are situated in this spectral range. Nevertheless near-IR-based gas analyzers allow one to achieve a very high sensitivity (~ 1 ppb for a multipass cell with an optical path length of 100 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.

MULTI GAS SENSING BASED ON PHOTOACOUSTIC SPECTROSCOPY BY USING TUNABLE DIODE LASERS

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Gas sensing using resonant photoacoustic spectroscopy has been proved to be a very good technique for low concentration measurements. In this work, we present a gas sensor capable to measure three substances simultaneously that are unwanted hydrogen precursors in fibre optics manufacturing. Water vapour (H₂O), methane (CH₄) and hydrogen chloride (HCl) at wavelength of 1368.6 nm, 1651.0 nm and 1742.4 nm respectively are measured with DFB tunable laser diodes. The coupling of the wavelengths is achieved by using optical fibres terminated with a collimator to launch the light directly into the photoacoustic cell.

The resonant photoacoustic cell is designed to operate on the first longitudinal acoustic mode. The optimisation of the cell constant to achieving the best acoustic signal is obtained by varying the geometric dimensions (radius and length) of the cell. Simulations show that the radius should be as small as possible and that the length should be as long as possible. In addition to those two parameters the resonant frequency and the volume must be reasonable (frequency must be greater than 1 KHz to avoid $1/f$ noise). A critical comparison between the simulations and the real cell will be presented.

First results show that a sensitivity of 0.3 ppm for water vapour, 0.4 ppm for hydrogen chloride and 1 ppm for methane can be obtained for such a cell.

**COLLISIONAL BROADENING ANALYSIS BY DIODE-LASER
SPECTROSCOPY: PH₃ + H₂.**

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Phosphine is a molecule of astrophysical interest since it has been observed in the atmosphere of Jupiter and Saturn which is mainly composed of hydrogen and helium. Therefore the determination of H₂-broadening coefficients of PH₃ may be useful in modeling planetary atmospheres.

H₂-broadening coefficients are measured for 41 lines of PH₃ in the ^QR branch of the ν₂ band and the ^PP, ^RP, and ^PQ branches of the ν₄ band, using a tunable diode-laser spectrometer. The recorded lines with *J* values ranging from 2 to 16 and *K* from 0 to 11 are located between 995 and 1106 cm⁻¹.

The collisional widths are determined by fitting each spectral line with a Voigt profile, a Rautian profile, and a speed-dependent Rautian profile. The latter model provides slightly larger broadening coefficients than the Voigt model.

These coefficients are also calculated on the basis of a semiclassical model of interacting linear molecules, using an atom-atom Lennard-Jones potential in addition to the weak electrostatic contributions.

The theoretical results are in satisfactory agreement with the experimental data, except for the ^QR(*J*,*K*) transitions with *K* = *J*, where they are notably underestimated.

**LINE FREQUENCY SHIFT MEASUREMENTS BY DIODE-LASER
SPECTROSCOPY FOR CH₃D-Xe**

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If numerous studies on the collisional line broadening have been realized by diode-laser spectroscopy only a few papers are devoted to the measurements of collisional shifts. Indeed, the frequency shift of lines also due to collisions between molecules is a much weaker effect than the collisional broadening and is difficult to measure accurately.

In the case of symmetric top molecules, the system of CH₃D in collision with Xe is well suited to the study of line shifts. First the perturber mass is greater than the absorber mass which leads to larger shifts. Moreover the lines of CH₃D are generally well isolated so that our measurements are not perturbed by the wings of neighbouring lines, even for high pressures of xenon. In this work, we have measured the shift coefficients for 5 lines [^QP(7,4), ^QR(6,4), ^QR(10,2), ^QR(10,7), ^QR(12,4)] belonging to the ν_3 band of ¹²CH₃D broadened by Xe at room temperature, using our tunable diode-laser spectrometer (1).

To measure the shift of one line, we recorded the transmitted signal passing successively through two cells: the first filled with a very low pressure of CH₃D and small absorption (our reference line) and the second containing the gas mixture, CH₃D diluted by Xenon at four pressures between 350 and 600 mbar. A small unshifted line is then superposed near the summit of the pressure-broadened line. The shift coefficient was determined by fitting simultaneously a Voigt profile for the reference line and a Voigt or a Rautian profile for the broadened line.

(1) M. Lepère, G. Blanquet, J. Walrand, and J.P. Bouanich, *J. Mol. Spectrosc.* 180, 218-226 (1996).

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**ABSOLUTE LINE INTENSITY MEASUREMENTS BY DIODE-LASER SPECTROSCOPY:
HOT BANDS OF OCS**

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High resolution spectroscopy allows detection of individual vibration rotation lines from absorbing molecules of terrestrial and planetary atmospheres. Thus, it is important to have a good knowledge of the frequencies, profiles, and intensities of spectral lines determined from laboratory data to analyze astrophysical observations including absorption bands of minor constituents. Infrared measurements on OCS are of particular interest to measure the concentration of this molecule in the atmosphere.

In last decades, some papers related to spectral intensities determined line by line have been published for transitions issued from the ground state levels (cold bands). For hot bands, only strengths of a few lines of the $11^10 \leftarrow 01^10$ transition (1) and of the $02^00 \leftarrow 01^10$ transition (2) were measured.

The aim of this work is to report extensive measurements of lines belonging to the first hot bands associated with the fundamental ν_1 band near 850 cm^{-1} . With a diode-laser spectrometer, we have recorded 58 lines for the e and f sub bands of the $\nu_1 + \nu_2^1 - \nu_2^1$ band and 36 lines for the $2\nu_1 - \nu_1$ band. The method of the equivalent width has been used to determine individual line strengths. Values for the band intensities and the transition dipole moments were deduced from the measured data.

**CARBON AND OXYGEN ISOTOPE MEASUREMENTS OF CO₂ BASED ON OFF-AXIS
INTEGRATED CAVITY OUTPUT SPECTROSCOPY**

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To reduce uncertainties in the quantification of the carbon cycling in the environment high temporal resolution isotope measurements of carbon dioxide play a central role. They will help in establishing the relative size of carbon sinks on land and in the oceans. The current state of the art method to measure carbon isotopes is the Isotope Ratio Mass Spectroscopy (IRMS). It is very accurate, but it also has limitations: real-time, *in-situ* measurements are not easily practicable due to the sample preparation and complex analysis instruments required. Therefore, the amount of available data is highly limited by these sampling requirements. Recent advances make laser spectroscopy a possible alternative to IRMS. The high temporal resolution and *in-situ* capabilities make it very attractive for airborne and ground based applications. We present results from a dual cavity system based on a laser operating at 1.63 μ m currently under construction. One cavity contains the sample gas, the other a standard. We configure the system for Off-axis Integrated Cavity Output Spectroscopy (OAICOS), which is a very robust setup and overcomes the difficulties of coupling laser and cavity in more traditional cavity ringdown setups.

DETECTION OF HIGH TEMPERATURE WATER VAPOR WITH VCSEL NEAR 940 nm***H. Koivikko, T. Laurila and R. Hernberg****Optics Laboratory, Tampere University of Technology,
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In this work, we report on our investigation of the potential of VCSELs for detecting high temperature water vapor. Detection of high temperature water vapor is an attractive tool for monitoring combustion processes, since water vapor yields information on process performance and gas dynamic parameters. In sensor applications tunable diode laser spectroscopy is an acknowledged and sensitive method to detect and monitor gas components.

Vertical cavity surface-emitting diode lasers (VCSELs) have many advantages over the traditional edge emitting diode lasers. VCSELs are easy to use, have good beam quality, large tuning range, narrow line width and they operate in a single mode. Despite these advantages, VCSELs have been rarely used for spectroscopic applications since they are available only in limited wavelength regions.

The absorption of the laser beam as it propagates through the medium is described by the Beer-Lambert law

$$\frac{I(\nu)}{I_0} = \exp[-S(T)\phi(\nu, T)PNL],$$

where S is the line strength, ϕ is the line profile, P is the partial gas pressure and N is the molecular number density of the gas. Accurate room temperature line strengths can be obtained from the HITRAN database [1]. However, the database predicts poorly the high temperature behavior of the line strengths. Therefore, in order to achieve accurate concentration measurements at high temperature, experimental data is needed.

We have determined high temperature line strengths for water vapor in combustion environment. VCSELs emitting near 940 nm were used as a light source. High temperature water vapor was produced in a hydrogen oxygen premixed flat flame. Temperature of the flame was changed by adjusting the fuel mixture. A dual-beam setup was used to account for the absorption due to the ambient air. The measurement setup was tested at room temperature and the obtained line strength values were in agreement with those from HITRAN. The obtained results for the high temperature line strengths agreed qualitatively well with the theoretical predictions.

[1] L. S. Rothman *et al.*, "The HITRAN molecular spectroscopic database and HAWKS (HITRAN ATMOSPHERIC WORKSTATION): 1996 edition", *J. Quant. Spectrosc. Radiat. Transfer* 60, 665-710 (1998).

**TDL SPECTROSCOPY AND DEPLETION MODULATION:
THE INFRARED SPECTRUM OF AR-H₂O**

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A sensitive detection technique for tunable diode laser spectroscopy is presented that is suited to study rotationally resolved spectra of weakly bound complexes. The method uses a low energetic plasma source to achieve an efficient concentration modulation in a supersonic planar jet expansion. The method is demonstrated with rotationally resolved spectra of the $\Pi(1_{10}) - \Sigma(1_{01})$ and $\Pi(2_{12}) - \Sigma(1_{01})$ internal rotation/vibration bands of ortho Ar-H₂O in the ν_2 bend region of H₂O. The latter transition has not been reported before and is recorded at 1658.0309(6) cm⁻¹.

The present technique might be more generally applicable and particularly interesting when etalon fringes cause S/N ratios to drop below the detection limit.

More information is available from Chem. Phys. Lett. 355 (2002) 538.

MULTIPLE SPECIES TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY: APPROACHES AND APPLICATIONS

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Tunable Diode Laser Absorption Spectroscopy (TDLAS) has been very successful over recent years in single gas species detection [1]. However there are many applications where multispecies detection is required and in keeping the advantages of TDLAS such as sensitivity, selectivity, rapid time response and fibre optic coupling. Alternative broadband techniques for multispecies detection such as FTIR are often unsuitable due to difficulty of spectral interpretation, the necessity for chemometrics as well as sensitivity and cost.

This work describes approaches to multiplexing in TDLAS for the monitoring of several gaseous species and discusses the advantages and disadvantages of each approach. The approaches investigated are as follows:

Time-Division Multiplexing (TDM) where each laser is sequentially operated;

Modulation Frequency Division Multiplexing (MFDM) where each laser is wavelength modulated at different frequencies and detected with a single detector;

Wavelength Division Multiplexing (WDM) where each laser wavelength is separated prior to detection.

Each approach has different complexities in terms of optical arrangement, detection and data acquisition. These will be considered in a generic manner and then applied to specific applications such as the remote sensing of vehicle emissions and combustion diagnostics. Different aspects of each technique such as noise due to detection of several diode laser beams on a single detector, in the case of MFDM, sensitivity or maximum scanning frequency have been studied in order to establish the most suitable method for each application.

[1] P.A. Martin, Chemical Society Reviews, 31, 201-210, 2002

**VAPOR MONITORING AND ANALYSIS OF RARE EARTH ELEMENTS BY USING
DIODE-LASER-BASED SPECTROSCOPY**

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Vapor monitoring is very important in many industrial processes such as atomic deposition and material coating. Up to now, a thickness monitoring equipment using a quartz oscillator has been used commercially to monitor vapor density or flow rate. The method is simple but it has some drawback in the identification of each element in vaporizing a mixture of several elements. Recently, Laser Absorption Spectroscopy (LAS) using a diode laser has revolutionized many industrial processes by permitting accurate, portable and nonintrusive real-time monitoring of specific vapors because the method is significantly less expensive and more reliable than prior devices. However, the vapor monitoring of rare earth elements has not widely investigated even though they are very useful in industrial and medical application. In this work, we developed the vapor monitoring process of Yb and Sm which are kinds of rare earth elements by using diode-laser-based LAS. Yb and Sm are expected to be very useful for Non-destructive Test (NDT) and medical application, respectively. For Yb vapor, we used the 398.8nm transition line to measure vapor density by using a UV tunable single-mode-diode laser. Likewise, for Sm, we used two transition lines, 650.944nm and 653.395nm using a NIR diode laser. Light from above mentioned diode laser was transmitted across an atomic vapor column generated by resistive heating while the frequency of it was scanned across the atomic transition line. By comparing the amount of incident light to the amount of light transmitted after the light passes through the vapor column, the vapor density was determined using some equations. Additionally, the results of vapor monitoring were compared with ones from a thickness monitoring device and also compared with ones from theoretical considerations

**DIODE LASER SPECTROSCOPY OF THE ν_8 BAND
OF THE SF₅Cl MOLECULE**

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The diode laser spectra of SF₅Cl has been recorded in the ν_8 band region at a temperature of *ca.* 240 K, a pressure of 0.15 mbar and an instrumental bandwidth of *ca.* 0.001 cm⁻¹. Mainly four regions have been performed: a first one in the *P*-region (906.849-907.687 cm⁻¹), a second one in the *Q*-region (910.407-910.944 cm⁻¹), and two other ones in the *R*-region (913.957-914.556 cm⁻¹ and 917.853-918.705 cm⁻¹).

Since the SF₅Cl molecule can be seen as a derivative species of the SF₆ spherical top, we have developed a tensorial model based on the $O(3) \supset O_h \supset C_{4v}$ group chain^{a,b}. So, in this context, the isolated $\nu_3(F_{1u})$ band of SF₆ splits into the $\nu_1(a_1)/\nu_8(e)$ dyad of SF₅Cl. This dyad has been previously recorded in the group of Pr. H. Bürger in Wuppertal by a Fourier transform infrared spectrometer^c. These data have been combined to our diode laser ones in the aim of re-analyzing the ν_1/ν_8 dyad of this molecule. The analysis has been done thanks to an effective Hamiltonian developed up to the fourth order and to the help of a set of programs called C4vTDS^d (available at the URL: <http://www.u-bourgogne.fr/LPUB/c4vTDS.html>); 1346 transitions for ν_1 , 405 (FTIR: 261, diode: 144) transitions for ν_8 , and 406 ground state combination differences have been assigned and fitted. A global fit has been obtained with a rms of 0.00081 cm⁻¹ for the $\nu_1(a_1)$ band, of 0.0012 cm⁻¹ for the FTIR data of the ν_8 (*e*) band, of 0.00055 cm⁻¹ for the diode laser data of this same band, and of 0.00064 cm⁻¹ for the ground state.

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X-RAY STUDIES AND TIME-RESOLVED PHOTOLUMINESCENCE ON OPTICALLY PUMPED ANTIMONIDE-BASED MIDINFRARED TYPE-II-LASER STRUCTURES

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We report on optically pumped antimonide-based midinfrared type-II-laser samples with different mixed anion interfaces and laser emission at a wavelength of 3.4 μm . The samples have been grown by molecular beam epitaxy. They consist of a 70-period InAs/GaSb/InAs/AlSb active W-region with 1.4 μm thick AlAsSb cladding layers differing in interface composition only. The crystal structure of the samples is analyzed by high-resolution X-ray diffraction (HR-XRD). With these results the unit cell shape of each layer is determined. The degree of relaxation and strain values are extracted. The electronic properties depending on structural parameters of the samples are investigated by measurement of the non-radiative recombination coefficients (Shockley-Read-Hall and Auger recombination) using a time-resolved photoluminescence setup. Furthermore, the devices are tested in cw and pulsed edge-emitting laser operation, respectively.

From HR-XRD data the average lattice constants of the active regions are determined to be 6.0959 \AA and 6.1061 \AA for the different samples.

The low values of Shockley-Read-Hall coefficients achieved, which are in the range $1.8 - 2.2 \cdot 10^8 \text{s}^{-1}$ are an indication of excellent growth quality and a low number of misfit dislocations.

From a convergence equation we obtain a small cubic Auger recombination coefficient C_3^0 of $1.2 \cdot 10^{-28} \text{cm}^6 \text{s}^{-1}$ for 50% InSb-like interfaces and for low carrier densities at 200 K.

In optically pumped cw edge emitting laser operation, one sample shows a characteristic temperature of $(54.2 \pm 2.3)\text{K}$ with a maximum operation temperature of 170 K which corresponds to the low Auger recombination coefficients and the very good growth quality. In pulsed laser operation mode (200 ns @ 80 K) the maximum operation temperature is 320 K.

The maximum output power obtained is 14 mW (cw) per facet. The differential quantum efficiency is 3.3 % at 80 K.

GAS TRANSPORT IN POROUS MATERIALS ASSESSED BY DIODE LASER SPECTROSCOPY

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The recently introduced **Gas in Scattering Media Absorption Spectroscopy (GASMAS)** technique provides new opportunities for non-destructive studies of gas in highly scattering natural and man-made porous materials [1,2]. The free gas molecules dispersed in porous materials have unique sharp absorptive signatures, typically ten thousand times narrower than the spectral features of the bulk material. The small absorption imprint in the emerging, multiply scattered, diffuse light can be detected sensitively by use of frequency modulation techniques, easily achievable using diode laser spectroscopy.

Here, the GASMAS technique was applied on wood samples using diode-laser-based spectroscopy on molecular oxygen [3]. The integrated oxygen absorption for wood of different densities was investigated, as well as the anisotropy related to the fibre structure. This kind of measurements can be of fundamental interest in the understanding of light transport in inhomogeneous porous materials. Studies of gas transport dynamics in different wood samples were also performed. One practical application is the assessment of the resistances to gas penetration of various protective covers, such as paint layers on wood.

The new technique can be applied to any gas having narrow absorption features that are in reach for tunable diode laser radiation. Both the penetration of atmospheric pollutants into porous stone materials, e.g. used in historical buildings, and their transport in porous catalysts, e.g. zeolites, are particularly interesting application areas. Initial measurements on nitrogen dioxide were performed using blue diode lasers. Further, we report on a novel scheme to produce UV light for sulphur dioxide detection at around 300 nm by employing the sum frequency generation technique mixing light from a blue and a NIR diode laser in a BBO crystal. Previously we have used this mixing technique to reach the 253.7 nm mercury line [4].

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

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**CONCENTRATION MEASUREMENTS OF OZONE IN THE 1200 TO 300 PPBV RANGE:
AN INTERCOMPARAISON BETWEEN THE B. N. M. ULTRAVIOLET STANDARD AND
INFRARED METHODS.**

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The LPMA tunable diode laser spectrometer (1), has been equipped with a four channel (one reference beam I_0 and three transmitted beams I_t) data acquisition device and a long path multi-reflection Herriott cell to perform accurate intensity measurements of weak lines. The new data acquisition device retains all the advantages of the stepping recording mode with the Michelson interferometer control of the emitted wavelength of the TDL and allows us to simultaneously record ratioed (I_t/I_0) spectra of a reference line and of the line being studied.

A low pressure pure ozone spectral line obtained with a short path cell is used as a reference line from which the line intensity and instrumental parameters are obtained. A mixture of ozone in air flows inside the Herriott cell at pressures between 10 and 20 mbar to obtain the infrared spectrum used to derive the ozone concentration. A mixture of ozone in standard air prepared by the 49PS Megatec ozone generator of the B.N.M. (with ozone concentration derived from UV absorption with the absorption parameter (2) as used on the N.I.S.T. Standard Reference Photometer) flows continuously through the Herriott cell. Ozone concentrations derived from infrared absorption measurements are compared to the ozone concentrations given by the B.N.M. ozone generator.

In order to improve the accuracy of the parameters derived from the experimental spectra a simultaneous analysis is performed in a multi spectral fitting program taking into account instrumental effects. The agreement between the two methods is well within the absolute uncertainty of each method, and confirms the absorption coefficient value reported by Hearn (2).

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IMAGING OF CARBON MONOXIDE IN COMBUSTIONS BY MID-INFRARED LASER SPECTROSCOPY

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Abstract. The P(26) rotational line of carbon monoxide is traced with absorption spectroscopy of mid-infrared laser light in a methane/air flame of a flat-flame burner and in industrial combustions such as glass furnaces or car engines. Difference-frequency generation of two diode lasers is used to generate narrow bandwidth tunable mid infrared laser light around 2032 cm^{-1} .

Summary. Carbon monoxide is an important combustion-generated species that can be used for optimizing the stoichiometry and hence for the reduction of costs and environmental pollutants and for process control. Since it has strong fundamental absorption lines in the mid-infrared spectral range, it can be traced by absorption spectroscopy using difference-frequency generation in AgGaS_2 as a narrow bandwidth laser source. Two continuous wave diode-lasers operating around the center wavelengths of 787 nm and 681 nm are applied to generate mid-infrared radiation by noncritical type I difference-frequency generation in AgGaS_2 . The mid-infrared wavelength is tunable from 4.9 to more than 5 μm by proper setting of the temperature and the current of the diode-lasers and the temperature of the nonlinear crystal [1]. A methane/air flame is prepared by a McKenna flat flame burner. Carbon monoxide is measured by recording the P(26) absorption line at 2032.352 cm^{-1} in the flame and in a 10 cm long absorption cell as a reference. The pump wavelength is fixed while the signal wavelength is scanned around its center wavelength using a voltage ramp of 1 V equal to 2.755 nm scanning width. The burner is operated at a methane flow rate of 1.2 l/min and a methane/air flow rate ratio of 0.75. The relative carbon monoxide concentrations are measured at different heights above the surface of the burner by fitting Voigt profiles to the measured data of the carbon monoxide absorption line detected in the flame. For each height, a two-dimensional tomographic profile is computerized by combining the data gained by absorption scans parallel to the surface of the burner and turning the burner with respect to the laser beam in steps of 10° between single measurements and perpendicular scanning of the flame in 5 mm steps [2]. Glass furnaces are often gas-fired and therefore the concentration of CO is a measure for the stoichiometry of the combustion. The laser beam is directed through the furnace rather than the exhaust gas to provide online informations of the gas concentrations during the combustion process. The strong thermal radiation of the furnace that is operated at temperatures above 1400°C is separated from the signal by use of a bandpass filter and lock-in technique. First results of measurements at Genthe-Glas in Goslar/Germany are presented. Financial support of the Arbeitsgemeinschaft industrieller Forschungsvereinigungen (AiF, Germany) and the Hüttentechnische Vereinigung der deutschen Glasindustrie (HVG, Germany) is gratefully acknowledged (AiF project no. 13006 N).

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**MEASUREMENT OF HYDRAZINE RETENTION BY CELLULOSE ACETATE FILTERS
USING LEAD-SALT TUNABLE DIODE LASER INFRARED SPECTROSCOPY**

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Cellulose acetate (CA) filters have been investigated to determine their hydrazine (N₂H₄) breakthrough characteristics using a system based on tunable diode laser absorption spectroscopy (TDLAS). The breakthrough mass loading sorption curves for hydrazine were dependent on both the flow rate and the concentration. In experiments using a 4.5 ppmv hydrazine standard, the amounts of hydrazine retained by the CA filter were 4.25 µg at a flow rate of 2.82 L/min and 65 µg at a flow rate of 0.28 L/min. These loadings are much greater than the 31.5 ng/cigarette of hydrazine reported in smoke for unfiltered cigarettes. Further, CA filters exposed to four and eight puffs of smoke actually made the filter more efficient in retaining hydrazine compared to CA filters that had not been exposed to smoke. Therefore, if hydrazine is present in smoke at the levels reported in unfiltered cigarettes, all of the hydrazine would be trapped by the CA filter, and would be unable to breakthrough during smoking. A unique feature of this analytical method is that the instrument does not require calibration after molecular parameters have been determined, in this case from previously acquired quantitative hydrazine FTIR reference spectra.

**PRESSURE INDUCED SHIFT AND BROADENING
OF ACETYLENE LINES IN 6580-6600 cm⁻¹**

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High precision measurements of pressure induced shift and broadening of acetylene lines in 6580-6600 cm⁻¹ by tunable diode laser spectroscopy were made. For these aim was used the three channel spectrometer with distributed-feedback diode laser, operated at wavelength $\lambda=1.53 \mu\text{m}$. Measurement of the spectral parameters of the acetylene lines in 1500-nm region are important to support wavelength-division-multiplexed optical fiber communication systems and gas analysis.

The laser generated pulses of 4-10 ms duration at the $\lambda=1.53 \mu\text{m}$ wavelength at a repetition frequency of 40 Hz. A temperature-stabilization system, using a thermoelectric Peltier cooling unit as the controlling component, ensured a temperature instability at the level of 10^{-4} K in the temperature range from -15 to +50 °C. There were three channels system of recording spectra, which ensured simultaneous data acquisition of absolute calibration frequency scale and sample gas absorption spectrum in real time. Accuracy of the frequency scale was better than 10^{-5} cm⁻¹ in all region of the DL frequency tuning. The 12-bit National Instruments data acquisition board PCI-MOI-16E-1 was used to record the signal and to control the DL. After accumulation the ADC ensured a signal/noise ratio better than $5 \cdot 10^4$.

We have measured the pressure induced shift and broadening for 6 lines in the $\nu_1+\nu_3$ rotational-vibrational band of acetylene ¹²C₂H₂. Self broadening and broadening in H₂, He₂,Xe, Ar was studied. The influence of the neighboring weak lines on determination of line center was taken into account. Dicke narrowing and asymmetry in the lineshapes was observed. Have been done the First attempt to describe the experimental absorption lineshapes by universal asymptotic contour of the Rautian have been done. The Rautian contour considers the Doppler effect of kinetic motion, collision broadening and change of particle speed in collision, wind-effect and collision time limit.

Poster Session B.

**B1. APPLICATION OF ANTIMONIDE DIODE LASERS
IN PHOTOACOUSTIC SPECTROSCOPY**

*S. Schilt, L. Thévenaz, A. Vicet, A. Perona,
P. Grech and A. N. Baranov.*

**B2. NEW DESIGN OF FIXED OPTICAL PATH CHERNIN
FOUR OBJECTIVES MATRIX MULTIPASS CELL**

*A.G.Berezin, G.A.Ermakov, O.V.Ershov, V.N.Kuryatov,
A.I.Nadezhdinskii, L.N.Razumov, E.N.Schukin*

**B3. COMPACT, ALL THERMOELECTRICALLY COOLED
QUANTUM CASCADE LASER SYSTEM**

*Th. Beyer, M. Braun, A. Peter, S. Hartwig,
Th. Pfaff und A. Lambrecht*

**B4. FIBER-COUPLED NEAR-INFRARED DIODE LASER BASED
IN SITU HYGROMETER FOR THE DETECTION OF WATER
TRACES IN CRYOGENIC AEROSOL CLOUDS**

C. Giesemann, H. Teichert, H. Saathoff, U. Schurath, V. Ebert

**B5. HIGHLY SENSITIVE AIRBORNE MEASUREMENTS
OF CH₂O DURING NASA'S 2001 TRACE-P CAMPAIGN:
MEASUREMENT BOX-MODEL COMPARISONS AND
THE EFFECTS OF CLOUDS ON THESE COMPARISONS**

*Alan Fried, James Walega, Bryan Wert, James Crawford, William Potter,
Ian Faloon, and Dirk Richter.*

**B6. QUANTIFICATION OF MINOR TRACE-GAS POLLUTANTS
IN AIR BY VARIABLE PRESSURE INFRARED
DIODE LASER SPECTROSCOPY**

S. Dusanter, B. Hanoune, B. Lemoine, P. Devolder

**B7. RECENT DEVELOPMENTS OF COMMERCIAL DIODE
LASER MONITORS AT NORSK ELEKTRO OPTIKK AS**

Peter Kaspersen, Ove Bjørøy, Ivar Linnerud and Viacheslav Avetisov

**B8. COMPARISON OF TRACE GAS MEASUREMENTS BETWEEN
A QUANTUM CASCADE AND A LEAD CHALCOGENIDE LASER**

R. Kormann, H. Fischer, C. Gurk, C. Mann, F. Fuchs.

**B9. ROTATIONALLY RESOLVED INFRARED SPECTRUM
OF THE CHARGE TRANSFER COMPLEX [Ar-N₂]⁺**

H. Linnartz, D. Verdes and J.P. Maier

B10. OPTIMIZATION OF TRACE MOLECULE DETECTION USING TUNABLE DIODE LASERS.

A.I.Nadezhdinskii

B11. QUAD QUANTUM CASCADE LASER WITH DUAL GAS CELLS FOR SIMULTANEOUS ANALYSIS OF MAINSTREAM AND SIDESTREAM CIGARETTE SMOKE

Randall E. Baren, Milton E. Parrish, Kenneth H. Shafer, Charles N. Harward

B12. ON QUANTITATIVE DETECTION OF METHYL RADICALS IN NON-EQUILIBRIUM PLASMAS

G. Lombardi, G. D. Stancu, F. Hempel, A. Gicquel, and J. Röpcke

B13. MULTI-COMPONENT TRACE GAS DETECTION WITH TDL AND RESONANT PHOTOACOUSTIC TECHNIQUE: APPLICATION TO THE METHANE, AMMONIA AND ETHYLENE SYSTEM AT 1.63 μm

M Scotoni, A. Rossi, L. Ricci, G. Demarchi, D. Bassi, S. Iannotta and A. Boschetti.

B14. INFRARED AND MILLIMETER-WAVE SPECTRA OF THE $^{13}\text{C}^{16}\text{O}$ DIMER: ASSIGNMENT AND PRECISE LOCATION OF ENERGY LEVELS

L.Surin, D.Fourzikov, B.Dumesh, G.Winnewisser, Jian Tang and A.R.W.McKellar

B15. MODE HOP RECOGNITION AND ON-LINE HIGH PRECISION OF LONG FREQUENCY SCANS WITH TUNABLE DIODE LASERS

Ondrej Votava

B16. TDL SPECTROSCOPY AND MONITORING VAPOR PHASE CONCENTRATIONS IN SUPERSONIC NOZZLES

Paolo Paci, Yury Zvinevich, Barbara Wyslouzil, Mark Zahniser, Joanne H. Shorter, David Nelson, Barry McManus

B17. REMOTE HELICOPTER-BORNE DETECTOR FOR SEARCHING OF METHANE LEAKS

A.G.Berezin, O.V.Ershov, A.I.Nadezhdinskii, S.G.Rudov, Y.P.Shapovalov, D.B. Stavrovskii, T.A.Shubenkina

B18. EXPLOSIVES DETECTION BY MEANS OF NITROGEN DIOXIDE TRACE CONCENTRATION MEASUREMENTS

A.I. Nadezhdinskii, Ya. Ya. Ponurovskii, M.V. Spiridonov E.A. Kudryashov

APPLICATION OF ANTIMONIDE DIODE LASERS IN PHOTOACOUSTIC SPECTROSCOPY

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Trace gas detection in the 2 – 2.5 μm window is of great interest for atmospheric and industrial applications because it contains strong absorption lines of many gaseous species such as CH_4 , CO , NH_3 , and HF while the water vapor absorption is weak. We report spectroscopic measurements made by photoacoustic spectroscopy at the EPFL using a GaInAsSb/GaAlAsSb based quantum well laser grown by molecular beam epitaxy at the CEM2.

The active zone of the device is made of three compressively strained $\text{Ga}_{0.65}\text{In}_{0.35}\text{As}_{0.08}\text{Sb}_{0.95}$ quantum wells between $\text{Ga}_{0.70}\text{Al}_{0.30}\text{As}_{0.03}\text{Sb}_{0.97}$ barriers. The optical confinement layers were made of $\text{Ga}_{0.10}\text{Al}_{0.90}\text{As}_{0.07}\text{Sb}_{0.93}$. The wafer was processed into 10- μm ridge waveguides providing single spatial mode emission. The devices were soldered epi-side down onto copper heat sinks and placed on a Peltier cooler into a housing filled with dry nitrogen.

The laser emitted near 2.25 μm in continuous wave (cw) regime at room temperature. Single frequency regime could be realized in a wide range of driving conditions, the side mode suppression ratio reaching 20 dB.

The laser was first characterised in order to determine its optimal working conditions for photoacoustic spectroscopy. Operating parameters were determined in order to obtain a single frequency emission from the diode.

The laser was then coupled to different types of photoacoustic cells for methane concentration measurements. First, the laser emission was injected into a photoacoustic cell resonating in its first radial acoustic mode at a frequency $f = 10.5$ kHz with a quality factor better than 650. In order to improve the sensitivity of the detection, other cell configurations were evaluated. Better performances can be reached by redesigning the cell in order to take into account the divergence of the beam. Divergence angles of 20° and 120° have been measured, resulting in a poor coupling of the laser power in a resonant photoacoustic cell.

For this reason, a Helmholtz resonance based configuration seemed better adapted to the laser characteristics and was designed.

The first experimental results of this new geometry will be presented.

NEW DESIGN OF FIXED OPTICAL PATH CHERNIN FOUR OBJECTIVES MATRIX MULTIPASS CELL

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Optical multipass cells are widely used in spectroscopy for increasing of optical path in absorbing medium and receiving better sensitivity in trace molecule detection. A new design of Chernin matrix optical multipass cell [1] with four objectives and two field mirrors was developed and manufactured. In contrast to previous design, the system was made with only few alignment units, which made this multipass cell almost insensitive to thermal changes and vibration.

A detailed analyses concerning a sensitivity of multipass cell operation to small changes of each mirror position and orientation has been performed. Specially written program calculated the whole optical path inside the multipass cell not only in ideal case, but in cases when one or several mirrors were shifted or disoriented. There was a possibility to calculate the optical path in the case of wrong focus distance between two sets of mirrors too. It was found that mutual position and orientation of four objective mirrors were most critical to correct alignment of multipass cell. As small desorientation of one of the objective mirrors with respect to others as 10 angle minutes was enough to have matrix of images distorted to a degree of losing of output beam. The system turned out to be much more tolerable (two orders of magnitude) to shifts and disorientations of field mirrors and focus distance.

In accordance with carried out analyses the objective mirrors were positioned on rigid plate and firmly fixed to it. A special technique of mirrors manufacturing and their positioning is under patenting now.

The multipass cell manufactured with new technology has 6 x 7 image matrix and correspondingly 156 passes. With 25 cm base length between two sets of mirrors whole optical path was 39 m. This value could not be changed, but instead the cell was very stable to vibration and thermal drifts. The results of tests in vibration chamber and climatic chamber are discussed.

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COMPACT, ALL THERMOELECTRICALLY COOLED QUANTUM CASCADE LASER SYSTEM

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Distributed-feedback(DFB) quantum cascade lasers (QCLs) find more and more use in gas spectroscopy. Many different detection methods like photoacoustical measurements, cavity ring down or the direct measurement of transmission are used. With DFB-QCLs an absorption line can be scanned within one single pulse as short as 35 to 100 ns and so this technique has a high capability for fast measurements, with measurement rates in the 100 kHz range and above.

We present a complete thermoelectrically cooled quantum cascade laser system with a modular design, so that it is possible to do extractive or open path measurements.

Measurement methods with high bandwidth detectors and fast A/D-conversion allow measurements of extinction down to $3 \cdot 10^{-4}$ with high integration times. Adapted methods with gated amplifiers give the possibility to measure with 10 kHz rates and more. With these methods, laboratory and field measurements with CO, CO₂ and NH₃ have been performed.

Additionally, data regarding linewidth and temperature of the waveguide of a QCL within one pulse will be presented, to explain the measured pulse form which is used for the spectroscopical measurements.

FIBER-COUPLED NEAR-INFRARED DIODE LASER BASED *IN SITU* HYGROMETER FOR THE DETECTION OF WATER TRACES IN CRYOGENIC AEROSOL CLOUDS

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Polar stratospheric clouds (PSCs) and the heterogeneous chemistry which takes place in them play key roles in the destruction of ozone over the arctic and Antarctica. Yet, the dynamic generation process of these clouds is only poorly understood. The formation and growth of the multi-component ice crystals is therefore currently under intense investigation in large, cryogenically cooled aerosol chambers with simulated stratospheric boundary conditions. One of very few research facilities able to perform such studies is the large (85m³) aerosol chamber AIDA located at and operated by the research center in Karlsruhe, Germany.

One of the most important parameters for the formation and growth of these ice crystals is the super saturation of the atmosphere with gaseous water. However this parameter is currently not available since all available measurements are based on extractive techniques yielding the total water content, i.e. the sum over all three phases. Hence there is an immediate need for a fast *in situ* technique that can selectively quantify gaseous water in the presence of liquid and solid water and which has enough sensitivity and dynamic range to precisely measure the trace concentrations (sub-ppm) that are present at cryogenic temperatures down to 190K as well as the high concentrations found at the higher operating temperatures up to 270 K.

For that purpose we developed a highly sensitive *in situ* H₂O spectrometer which uses the $\nu_1+\nu_3$ combination and $2\nu_1$ overtone-band at 1.37 μ m and an 82m White-cell directly attached onto the inside walls of the AIDA chamber. Also part of the instrument was a new fiber-coupled optical setup that was designed to withstand temperatures between 190K and 300K. This feature was essential to effectively avoid potentially large systematic errors caused by even very short high-humidity room-temperature sections of the absorption path. Applying PC-based direct absorption spectroscopy the sensor is completely calibration-free and showed at 1bar a 1- σ resolution of 15 ppb H₂O thanks to the effective suppression of room-temperature absorption. The absolute value of the water measurements were successfully verified under special operating conditions with an extractive reference humidity sensor. This spectrometer, successfully tested over a period of several weeks and the full temperature range (190-270K), allowed for the first time a direct, highly dynamic measurement of the water vapor super saturation during the formation processes of stratospheric ice particles. Additionally, combined with the extractive techniques for the determination of the total water content, this new technique constitutes for the first time the means to measure the dynamic partitioning between the water phases.

HIGHLY SENSITIVE AIRBORNE MEASUREMENTS OF CH₂O DURING NASA'S 2001 TRACE-P CAMPAIGN: MEASUREMENT BOX-MODEL COMPARISONS AND THE EFFECTS OF CLOUDS ON THESE COMPARISONS

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Formaldehyde (CH₂O) is a ubiquitous component of both the remote atmosphere as well as the more polluted urban environment. This gas, which is one of the most abundant gas phase carbonyl compounds found in the atmosphere, is formed by the oxidation of most anthropogenic and biogenic hydrocarbons initiated by reactions with the hydroxyl (OH) radical and ozone (O₃). Over the continents, oxidation of non-methane hydrocarbons dominates the production of CH₂O. In the remote atmosphere by contrast, methane oxidation becomes the dominant source of this gas. Through a number of decomposition pathways, CH₂O serves as an important source of the odd hydrogen radical hydroperoxy (HO₂) in the atmosphere. The hydroperoxy radical in conjunction with OH and H radicals are largely responsible for controlling the oxidation capacity of the atmosphere. Furthermore, as many hydrocarbon oxidation reactions proceed through CH₂O as an intermediate, CH₂O becomes critical in further testing our understanding of hydrocarbon reaction mechanisms. Comparisons of CH₂O measurements with photochemical box model results over a wide range of atmospheric conditions are particularly important in this regard. Thus, highly accurate measurements of CH₂O throughout the atmosphere, particularly on aircraft platforms, are essential.

Because of its broad range of sources, ambient CH₂O concentrations attain levels as high as several tens of parts-per-billion (ppbv) in urban areas to levels as low as tens of parts-per-trillion (pptv) in the remote background atmosphere. In the latter case, ambient measurements become quite challenging, particularly on airborne platforms where fast measurements (seconds to minutes) are required and severe vibrations and variable sampling conditions of temperature, pressure, and relative humidity are encountered. In the present poster we show results acquired with a highly sensitive airborne tunable diode laser absorption spectrometer, which has been developed and refined over the past decade to meet these demanding challenges. In addition to a brief presentation of the airborne spectrometer and its performance, the present poster will also give an overview of extensive measurement box model comparisons. We will give particular emphasis to comparisons carried out in and around marine clouds, where in a number of cases the results show direct evidence of gas-phase CH₂O uptake.

QUANTIFICATION OF MINOR TRACE-GAS POLLUTANTS IN AIR BY VARIABLE PRESSURE INFRARED DIODE LASER SPECTROSCOPY

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We recently developed a new protocol for the measurement of minor trace-gas pollutants in air : variable pressure infrared diode laser spectroscopy (Dusanter et al., Applied Optics, vol.41(24), pp. 5142-5147, 2002). Instead of scanning the laser emission around the feature of interest at a fixed pressure and adjusting the 2f absorption line to a calibrated spectrum, we stabilize the laser emission at the center of the line and measure the change in 2f intensity while the pressure increases inside the cell from 0 to about 20 Torr. The resulting curve of intensity versus pressure is in the low pressure range a straight line, with a slope proportional to the volume fraction of the absorbant. This procedure has been compared to the standard one, on the same instrument, and has been shown to lead to the same detection limit. However, it benefits from its ability to quantify heavier species with no isolated line, such as 1,3-butadiene, from its simplicity in the data analysis phase, and from its lower sensitivity to variations of the baseline. We will present in this poster our results on 1,3-butadiene, formaldehyde and acetaldehyde, as well as our ongoing work toward an automated field instrument.

RECENT DEVELOPMENTS OF COMMERCIAL DIODE LASER MONITORS AT NORSK ELEKTRO OPTIKK AS

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During the last years Norsk Elektro Optikk (NEO) AS has become one of the leading suppliers of commercial gas monitors based on near infrared diode lasers and single line spectroscopy. An extensive research program has made it possible for the company to provide a range of gas monitors for such gases as O₂, NH₃, HF, HCl, H₂O, CH₄, CO, CO₂, H₂S, HCN and others. More than 700 instruments have been installed worldwide and have proven successful operations in various environments and industrial processes.

Several versions of the monitors are available such as single path version with separate receiver and transmitter units, dual path and long path versions with a retro-reflector. The monitors are rugged, compact and require a minimum of maintenance. The wavelength modulation technique makes it possible to measure relative absorptions of less than 10⁻⁵, thus providing sub-ppm detection limits for many gases. The main challenge for sensitive measurements is, however, cross interference from water vapour absorption lines especially at higher temperatures of process gas. This requires careful selection of the absorption line for the gas of interest as well as implementation of advanced data processing techniques. The company has developed an ammonia monitor for selective catalytic NO_x reduction systems in coal fired power plants, which requires a measuring range of 0-10 ppm NH₃ at temperatures of 350-450°C with water content of 10-20 % and dust loads of more than 10 g/m³. Some performance data obtained during long-term operation of one of our monitors at Orlando Stanton Energy Center will be presented.

Recently NEO has introduced a new range of monitors that are capable of measuring several absorption lines using the same laser, making it possible to monitor several gases simultaneously as well as gas temperature. Among such commercially available instruments are now CO+CO₂, HF+H₂O and O₂+Temperature, and many other combinations are possible. Some industrial applications require measurements of molecular oxygen at temperatures above 1000°C. In this case the contribution of the ambient oxygen absorption is extremely difficult to subtract properly due to the temperature induced line-shift of the O₂ line. On the other hand, the use of nitrogen to purge the flanges continuously is often too expensive for many customers to support. To avoid the problem NEO has developed an oxygen monitor that uses two absorption lines. One line which originates from low energy level is used for line tracking, span check and calibration and the other line originating from high energy level is used to measure oxygen in high temperature process. In this case the flanges can be purged with cold air, which results in a negligible contribution from the flanges to the high-temperature absorption signal.

One of the most interesting projects which has been carried out at NEO in collaboration with Linde AG is the simultaneous in-situ monitoring of CO and O₂ in burner ports of Arc furnaces for steel production. Some performance data collected during one of several measurement campaigns at a steel production plant, which show very good agreement and correlation between measurements of CO, O₂, gas temperature and dust load, will be presented.

**COMPARISON OF TRACE GAS MEASUREMENTS BETWEEN A QUANTUM CASCADE
AND A LEAD CHALCOGENIDE LASER**

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We present comparative measurements of carbon monoxide by a quantum cascade as well as a lead chalcogenide laser in a two-laser spectrometer designed for trace gas measurements in the atmosphere. Both lasers measure the P(25) line of CO at 2037.025 cm^{-1} . At 298 K, this line has a strength of $5.13 \times 10^{-21}\text{ cm molecule}^{-1}$, which is about a factor of 100 smaller compared to the strongest lines in the fundamental CO absorption band. However, this allows a discussion of the small signal behavior of the lasers within the spectrometer in combination with the simple handling of diluted CO gas samples. Calibration gas as well as ambient air measurements are presented and discussed with respect to noise and signal stability. Sensitivity improvements of sub-ppbv trace gas detection through the use of quantum cascade lasers will be discussed.

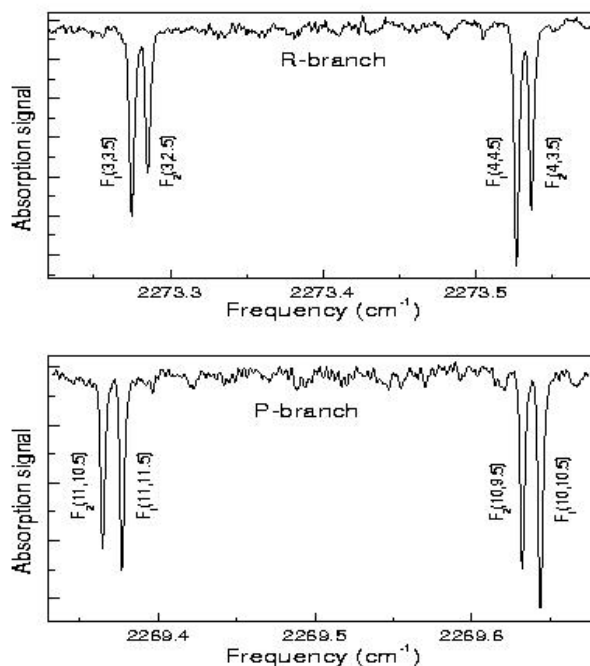
ROTATIONALLY RESOLVED INFRARED SPECTRUM OF THE CHARGE TRANSFER COMPLEX $[\text{Ar-N}_2]^+$

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Difficulties in preparing cluster ions for spectroscopic studies have limited our understanding of intermolecular forces in charged complexes that are typical of many reactive intermediates. In this contribution the infrared spectrum of the charge transfer complex $[\text{Ar-N}_2]^+$, recorded in a supersonic planar plasma with a tunable diode laser spectrometer, is presented. More than 70 adjacent rovibrational transitions were measured near 2272 cm^{-1} and assigned to the molecular nitrogen stretching fundamental in the $^2\Sigma^+$ ground state. An example is given in the figure. The accurate structural parameters that are determined confirm a linear structure and show that the major part of the charge is located at the argon atom. The latter result is surprising and implies a charge switch of the cationic center upon complexation.



A plasma modulated TDL spectrum of the charge transfer complex $[\text{Ar-N}_2]^+$.

More information is available from Science 297 (2002) 1166.

**OPTIMIZATION OF TRACE MOLECULE DETECTION USING
TUNABLE DIODE LASERS.***A.I.Nadezhdinskii**Natural Sciences Center of A.M.Prokhorov General Physics Institute of RAS
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Tunable Diode Laser Spectroscopy (TDLS) was demonstrated to be very efficient technique for trace molecule detection. New generation of Diode Lasers (DL) based systems promises mass application in environment protection, medicine, industry, critical situations control, etc. During last decade more than 30 different DL based systems were developed at NSC GPI for particular applications. System optimization approach will be considered taking into account physical properties of all system elements: DL, photo-detector, optical scheme, object of interest, etc.

Systems developed can be classified in several groups according to molecular object of interest, width of its spectral peculiarity, optical scheme in use, system operation mode, etc. Some representatives of instruments developed will be described. Optimization of these systems will be discussed taking into account spectral range in use, laser operation mode, signal acquisition strategy, physical origins of sensitivity limitations, etc.

B11.**QUAD QUANTUM CASCADE LASER WITH DUAL GAS CELLS FOR SIMULTANEOUS ANALYSIS OF MAINSTREAM AND SIDESTREAM CIGARETTE SMOKE*****Randall E. Baren, Milton E. Parrish, Kenneth H. Shafer****Philip Morris USA, Research Center, 4201 Commerce Road, Richmond, VA 23234 USA.****Charles N. Harward****Nottoway Scientific Consulting Corp., P.O. Box 125, Nottoway, VA 23955 USA.*

A compact, fast response, infrared spectrometer using four pulsed quantum cascade (QC) lasers has been applied to the analysis of gases in mainstream and sidestream cigarette smoke. QC lasers have many advantages over the traditional lead salt lasers, including near-room temperature operation with thermoelectric cooling and single mode operation with improved long-term stability. The new instrument uses two 36 m, 0.3 liter multiple pass absorption gas cells to obtain a time response of 0.1 seconds for the mainstream system and 0.4 seconds for the sidestream system. With this instrument we have measured simultaneously in mainstream and sidestream smoke the concentrations of ammonia, ethylene, nitric oxide, and carbon dioxide. A data rate of 20 Hz provides sufficient resolution to reveal the concentration profiles during each 2-s puff in the mainstream smoke. Different concentration profiles before, during and after the puffs have also been observed for these smoke constituents in the sidestream smoke. Also, simultaneous measurements of CO₂ from a non-dispersive infrared analyzer are used to obtain emission ratios of the smoke constituents relative to the amount of CO₂ produced during combustion for various types of cigarettes.

ON QUANTITATIVE DETECTION OF METHYL RADICALS IN NON-EQUILIBRIUM PLASMAS

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Carbon containing radicals are of special interest for basic studies and for application in plasma technology. Indeed, the decomposition of hydrocarbons in a variety of Plasma Enhanced Chemical Vapour Deposition (PECVD) processes is of interest because they are used to deposit thin carbon films. The methyl radical (CH₃), on which we are going to focus in this paper, is generally accepted to one of the most essential intermediates in hydrocarbon plasmas.

For the *in situ* detection of the CH₃ radical, only two approaches are suitable: mass spectroscopy and optical methods. In the first case threshold ionisation mass spectrometry (TIMS) or photo ionisation mass spectrometry (PIMS) are suitable for the detection of radicals. Non-invasive optical methods for detecting the methyl radical are based on absorption spectroscopy either with UV radiation at about 216 nm or in the mid IR near 3100 cm⁻¹ or 606 cm⁻¹.

Although in recent years several studies to quantify the methyl concentration in hydrocarbon plasmas have been performed in the ultraviolet and infrared spectral range, never have both spectroscopic approaches been compared directly to verify the applicability of the absorption cross sections or line strengths for the conditions under study. This comparison is of particular importance since the limitations of the validity of the line parameters are directly related to the accuracy of calculated methyl concentrations and in turn to the quality assessment of related plasma chemical modelling.

This contribution describes comparative quantitative studies of the methyl radical in non-equilibrium plasmas by absorption spectroscopic methods. Tunable infrared diode laser absorption spectroscopy (TDLAS) at 16.5 μm and broadband ultraviolet absorption spectroscopy at 216 nm have both been used to measure the ground state concentrations of the methyl radical in two different types of non-equilibrium microwave plasmas (f = 2.45 GHz), (i) in H₂-Ar plasmas of a planar reactor with small admixtures of methane or methanol, at a pressure of 1.5 mbar, and (ii) in H₂-CH₄ plasmas of a bell jar reactor, at pressures of 25 and 32 mbar under flowing conditions.

For the first time, two different optical techniques have been directly compared to verify the available data about absorption cross sections and line strengths of the methyl radical. It was found, that the application of the CH₃ absorption cross section of the B(²A₁') ← X(²A₂') transition at 216 nm, reported by Davidson et al. 1995 *J. Quant. Spectrosc. Radiat. Transfer* **53** 581, and of the line strength of the Q(8,8) line of the ν₂ fundamental band at 16.44 μm, given by Wormhoudt et al. 1989 *Chem. Phys. Lett.* **156** 47, leads to satisfactory agreement.

MULTI-COMPONENT TRACE GAS DETECTION WITH TDL AND RESONANT PHOTOACOUSTIC TECHNIQUE: APPLICATION TO THE METHANE, AMMONIA AND ETHYLENE SYSTEM AT 1.63 μm

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At present many chemical-physics processes, due to human activities, are subject to more and more accurate and sensitive controls for environmental quality, process quality or safety reason. Many of these processes can be monitored by non invasive detection of gaseous systems produced (atmospheric pollution, combustion, food preservation, agro-biological processes, breath analysis etc). Detailed understanding of such processes is more and more demanding in real time and high sensitivity detection of many molecular systems at the same time. Infrared radiation spectroscopy can be a valid multi-component detection method, complementary to other well-proven techniques like, for example, mass spectrometry and gas chromatography. A compact multi-component trace gas detector based on high resolution IR spectroscopy has been developed in our laboratory. The apparatus is composed by a 1.57-1.64 μm tunable diode laser coupled with a resonant photoacoustic cell. A region around 1.63 μm , where $2\nu_3$ (methane), $\nu_2+\nu_3+\nu_4$ (ammonia) and $\nu_5+\nu_9$ (ethylene) bands are present, has been investigated in order to find non overlapped spectral structures useful for selective detection in ambient air with ppm sensitivity. A resonant optical cavity is under test in order to obtain sub-ppm sensitivity.

**INFRARED AND MILLIMETER-WAVE SPECTRA OF THE $^{13}\text{C}^{16}\text{O}$ DIMER:
ASSIGNMENT AND PRECISE LOCATION OF ENERGY LEVELS**

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The infrared and millimeter-wave spectra of the fully substituted 13-C carbon monoxide dimer, ($^{13}\text{C}^{16}\text{O}$)₂, have been studied in order to compare the energy levels of this isotope with those of the normal isotope. Such comparison constitutes a subtle probe of the intermolecular potential, proving the reality of the two isomers discovered earlier for ($^{12}\text{C}^{16}\text{O}$)₂ and clarifying the nature of the tunneling motion.

Infrared spectrum has been observed with diode laser spectrometer in the region of the CO stretching vibration, around 2090 cm⁻¹. Over 120 lines have been assigned to transitions involving 49 rotational levels in the excited state and 24 levels in the ground state. The millimeter wave spectrum of ($^{13}\text{C}^{16}\text{O}$)₂, has been studied for the first time, confirming and extending the infrared study. Eighty-seven transitions in the 77 – 180 GHz region have been assigned and analyzed in terms of a model-independent term value scheme involving 57 rotational levels with $J = 0$ to 8. The levels can be classified into 7 “stacks” which have symmetry classifications of either A^-/B^+ or A^+/B^- , and K -values of either 0 or 1. The four A^+/B^- stacks have previously not been observed in the infrared study. The energetically lowest of the stacks fixes the tunneling splitting of ($^{13}\text{C}^{16}\text{O}$)₂ to be 3.769 cm⁻¹, slightly larger than the ($^{12}\text{C}^{16}\text{O}$)₂ value of 3.731 cm⁻¹. The energy splitting between the ground states of two isomers is 0.877 cm⁻¹ in ($^{12}\text{C}^{16}\text{O}$)₂, and 1.285 cm⁻¹ in ($^{13}\text{C}^{16}\text{O}$)₂.

MODE HOP RECOGNITION AND ON-LINE HIGH PRECISION OF LONG FREQUENCY SCANS WITH TUNABLE DIODE LASERS

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The lengths of continuous frequency scans with single mode lasers are often limited by laser mode hops. Single mode continuous scans of typical tunable diode lasers are usually less than 100GHz due to presence of mode hops. To cover longer spectral ranges individual single mode scans must be properly calibrated and concatenated. This is often slow and time consuming task that hinders effective collection and analysis of data of species with extended spectra and is a limiting factor for construction of automated, operator-free instrumentation.

We present a system with on-line calibration procedure that is capable to both recognize the mode hop free regions and perform precision frequency calibration in extended frequency scans. The procedure uses two-step nonlinear least square fit algorithm to calculate sequentially coarse and fine calibration based on information from traveling wavemeter and frequency stabilized confocal Fabry-Perot etalon respectively. The traveling Michelson wavemeter provides absolute frequency data points with accuracy exceeding 0.3GHz that are collected at regular intervals throughout the scan and provide information for recognition of the mode-hop free regions as well as the coarse frequency calibration of those regions. Transmission interference fringes from the Fabry-Perot interferometer (FSR = 0.375GHz) are used to refine the calibration yielding overall absolute calibration accuracy $\delta\nu < 3\text{MHz}$.

**TDL SPECTROSCOPY AND MONITORING VAPOR PHASE CONCENTRATIONS IN
SUPERSONIC NOZZLES**

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In our laboratory we study nucleation and nanodroplet growth in supersonic nozzles. Conventional pressure trace experiments characterize the condensing flow and small angle neutron scattering experiments (SANS) characterize the aerosol. The scattered neutron intensity depends both on the aerosol number density and the composition of the droplets. If all of the vapor entering the nozzle were to condense, then the overall composition of the aerosol would be well defined. Typically, only about 70% of the vapor condenses and, thus, the uncertainty in the composition of the droplets when multiple condensible species are present can be unacceptably large. To address this difficulty we have developed a Tunable Diode Laser Absorption Spectrometer (TDLAS) to measure the gas phase concentration of the condensible vapors - in particular H₂O, D₂O and ethanol. Preliminary experiments with unary condensation have shown that the mixing ratios measured by mass balance and the TDLAS are in agreement, and that we can detect the onset of condensation. In multicomponent nucleation, we can follow the concentration of at least one of the condensing species, and, by knowing the total heat released to the flow, we can determine the overall composition of the droplets. This talk will summarize our work to date.

REMOTE HELICOPTER-BORNE DETECTOR FOR SEARCHING OF METHANE LEAKS

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A portable remote high sensitive methane detector based on near infrared diode laser (DL) was developed and manufactured. Basic principals of operation are the following. DL radiation was collimated by objective and could be directed to any topographic object. Small portion of laser radiation scattered by the object was captured by the 28 cm diameter parabolic mirror and was focused on the photodetector. Assuming the distance from the device to the object of 50 m, object albedo of 1, DL radiation power of 5 mW, the power of laser radiation returned to photo-detector would be only ~ 10 nW. Low noise InGaAs photodiode and special preamplifier ensured noise equivalent power of 1 pW in the 10 kHz frequency range. Another problem is scattered sun radiation. For our optical system maximum scattered sun radiation hitting photodetector was 300 μ W for the whole spectral range. Special optical filter allowed decreasing of this value down to 5 μ W. Nevertheless the power of interfered sun radiation was 500 times higher than that of received laser radiation. For data processing we used 16-bit multifunction electronic board (National Instruments, Inc.), which ensured registration of 10^{-4} absorption for above conditions.

The program of the device controlling and data processing was written in LabVIEW-6. The laser was driven by trapezoid current pulses which ensured pulsed scan of DL radiation wavelength near R5 methane absorption line (1.651 μ m). The device incorporated reference optical channel with the methane filled cell. Averaged methane concentration along the optical path length from the device to topographic object and back was calculated as cross-correlation integral between registered analytical and reference signals. Such procedure ensured very high level of selectivity with respect to other gases. DL radiation pulse duration of 1 ms was minimum time required for one measurement. For increasing of accuracy the results might be averaged over a train of pulses. Special calculation procedure was used for decreasing the influence of relatively slow variation of sun illumination. The remote methane detector was equipped with GPS navigation system, which allowed getting distribution of methane concentration on the map along the route of flight. The device could function continuously without operator.

The remote methane detector is intended for detection of the natural gas leaks from pipes with a help of a helicopter. Measurement sensitivity depended on the distance to the object (Earth surface), albedo of the object, time of measurement and weather conditions (sun illumination, wind). In the laboratory test white paper with albedo ~ 1 was used as topographic object at the distance 50 m from the device. Standard deviation of the methane concentration noise was 100 ppb for measurement time 0.5 sec and 500 ppb for 20 ms. It is enough for detection of methane leaks at the level of trace concentration (1.7 ppm). The remote methane detector installed on helicopter was tested during number of flights with total duration 20 hours. The tests showed that the device allowed registration of natural gas leaks down to 5000 cm^3/s .

**EXPLOSIVES DETECTION BY MEANS OF NITROGEN DIOXIDE
TRACE CONCENTRATION MEASUREMENTS**

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Molecules of explosives are unstable by their nature. A rather noticeable decomposition of explosives is observed already at room temperature. The gaseous substances being yielded in this process are nitrogen oxides for the most part, particularly NO and NO₂ for industrial explosives such as trinitrotoluene, hexogen, octogen, tetranitropentaerithrite.

In order to be able to detect explosives the sensitivity required to measure NO₂ is about 10 ppb. This sensitivity may be acquired by using the diode lasers of visible spectral range and multipass optical system with an optical path over 100 m long.

The device developed is based on red (635-670) diode lasers and matrix Chernin multipass cells. The device employs two kinds of multipass systems, the prime difference between them consists of their dimensions and optical path lengths.

1. Base length of the system is 50 cm; number of passes – up to 300. The system may have the optical path length up to 150 meters. The system disadvantages include too big sizes and large gas volume (about 15 liters).

2. Base length of the system is 25 cm; number of passes – up to 160. The system may have an optical path length up to 40 meters. This system is advantageous in sufficiently small dimensions, about 2 liters volume, and good mechanical stability.

This work was supported by the International Scientific and Technology Center project #1945

Poster Session C.

C1. CO₂ DETECTION AROUND 2.05 μ m WITH A GASB-BASED QUANTUM WELL LASER

*V. Zeninari, B. Parvitte, A Vicet, A Perona, P Grech,
A. N. Baranov, G. Durry*

C2. MOBILE METHANE SENSOR BASED ON 1.65 μ m DIODE LASER: RESULTS OF FIELD TESTS

A.G.Berezin, O.V.Ershov, A.I.Nadezhdinskii, Yu.P.Shapovalov

C3. FAST AND PRECISE FREQUENCY TUNING OF DIODE LASERS USING A QUADRATURE INTERFEROMETER

Th. Müller-Wirts, K.-M. Knaak, A. Deninger and W. Kaenders

C4. COMPACT AND LIGHT-WEIGHT OPEN-PATH-HERRIOTT-CELL FOR SIMULTANEOUS IN-SITU-DETECTION OF H₂O AND CH₄ ONBOARD OF STRATOSPHERIC BALLOON PLATFORMS

C. Giesemann, T. Fernholz, H. Teichert, J. Wolfrum, V. Ebert

C5. PRESSURE BROADENING AND SHIFTS FROM WAVELENGTH MODULATED DIODE LASER SPECTROSCOPY

Jessica A. Eng, John L. Hardwick and Erich N. Wolf

C6. CAVITY ENHANCED ABSORPTION AND WAVELENGTH/FREQUENCY MODULATION DETECTION OF THE HYDROXYL RADICAL IN THE UV USING SUM-FREQUENCY GENERATION

G. Hancock, V.L. Kasyutich, R. Peverall, G.A.D. Ritchie

C7. MID-INFRARED WHISPERING GALLERY LASERS

A. Krier, D.A. Wright, V.V. Sherstnev & A. Monakhov

C8. CW CAVITY RING DOWN SPECTROSCOPY THROUGH A SUPERSONIC PLANAR PLASMA

*P. Birza, T. Motylewski, D. Khoroshev, A. Chirokolava,
H. Linnartz and J.P. Maier.*

C9. TDLWINTTEL: A COMPUTER PROGRAM FOR THE ACQUISITION AND ANALYSIS OF TDL AND QCL ABSORPTION SPECTRA

D. D. Nelson

C10. DETERMINATION OF MOLECULAR PARAMETERS FOR QUANTITATION OF NON-HITRAN MOLECULES USING LEAD-SALT TUNABLE DIODE LASER INFRARED SPECTROSCOPY

Charles N. Harward, Randall E. Baren, Milton E. Parrish

C11. DETERMINATION OF THE METHYL RADICAL LINE STRENGTH USING TIME-RESOLVED INFRARED ABSORPTION SPECTROSCOPY IN A PULSED PLASMA

G. D. Stancu, P. B. Davies, and J. Röpcke

C12. INFRARED DIODE LASER ABSORPTION SPECTROSCOPY OF REACTIVE SPECIES IN INDUCTIVELY AND CAPACITIVELY COUPLED RF DISCHARGES

A. Serdioutchenko, I. Möller, H. Soltwisch

C13. WAVELENGTH MODULATION SPECTROSCOPY FOR THE NON-INVASIVE, NON-DESTRUCTIVE MEASUREMENT OF TRACE GASES IN ACCELERATED MATERIALS AGEING TRIALS

Daniel W. Thomas

C14. THE EFFECTS OF TEMPERATURE AND PRESSURE INDUCED ABSORPTION LINE SHIFT ON LASER DIODE BASED SENSING OF H₂O AT 1.393 μ m

Richard Phelan, Michael Lynch, John Donegan and Vincent Weldon

C15. MEASUREMENTS OF TRACE WATER VAPOR IN A CARBON DIOXIDE REMOVAL ASSEMBLY PRODUCT STREAM USING A TUNABLE DIODE LASER SPECTROMETER

*J. Wormhoudt, J. H. Shorter, J. B. McManus,
D. D. Nelson and M. S. Zahniser*

C16. UF₆ ENRICHMENT MEASUREMENTS USING TDLS TECHNIQUES

*Nadezhdinskii, Ya. Ponurovskii, Yu. Selivanov, G. Grigorev,
Sh. Nabiev, N. Gorshunov, G. Bosler, R. Olsen, and V. Ryjikov.*

C17. MEASURING AIR CONTENT INSIDE INSULATING GLASS WINDOWS

A.I. Nadezhdinskii, Ya. Ya. Ponurovskii, M.V. Spiridonov

CO₂ DETECTION AROUND 2.05 μ m WITH A GASB-BASED QUANTUM WELL LASER

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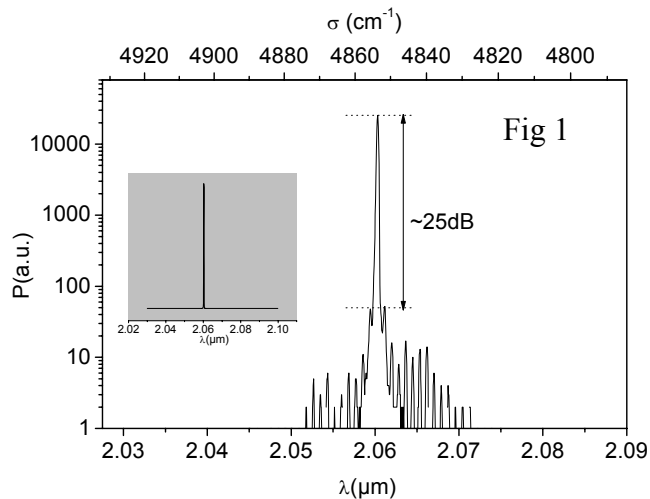
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Continuous wave (cw) quantum well lasers have been fabricated at the CEM2 (Montpellier, France). The devices are based on a type I GaInAsSb/GaAlAsSb/GaSb multiple quantum well structure grown on n-GaSb substrates by molecular beam epitaxy (MBE).

The active zone of the structure is made of three 10-nm-thick compressively strained GaInAsSb quantum wells between 30-nm-thick GaAlAsSb barriers. The 1.5- μ m-thick optical confinement layers are made of Ga_{0.1}Al_{0.9}AsSb lattice matched with GaSb. The wafer was processed



into 10 μ m ridge waveguides providing single spatial mode emission and cleaved to 750- μ m-long devices. The devices were then mounted on a Peltier cell for temperature stabilization and placed into a housing filled with dry nitrogen. The laser emission is centered near 2.05 μ m at room temperature. Single frequency regime (fig. 1) can be obtained for these Fabry-Perot devices in a wide range of driving currents and temperatures without a grating or additional technological process. The emission line can be tuned by current with a rate of about 1.25 GHz/mA.

The laser diode has been tested on a laboratory spectrometer (GSMA, Reims, France).

Some spectroscopic parameters (line strength and self-broadening coefficient) were determined for a line of the $(2\ 0^0\ 1) \leftarrow (0\ 0\ 0)$ band. These parameters have been compared with other experimental results and available databases.

This laser has also been tested on the laboratory version of the JETDLAG spectrometer developed by the Service d'Aéronomie of Verrières le Buisson (France).

We demonstrate with this laser line the possibility to detect CO₂ at ground level.

**MOBILE METHANE SENSOR BASED ON 1.65 μm DIODE LASER:
RESULTS OF FIELD TESTS**

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The car-borne automated high sensitive methane detector was developed on a base of laboratory prototype [1] for measurements of methane concentrations during car movement. The device was tested in laboratory and field conditions. The measurements were performed with non-cryogenic-cooled near-infrared tunable diode laser operating at 1.65 μm . The device incorporated multipass optical cell with optical path length 90 m at base length of 0.5 m. The main destination of the detector is the monitoring of methane content in the ambient air in order to find the gas leaks. Limit sensitivity (std) was found to be 0.1 ppm at 0.4 s. The detection technique based on registration of separate methane absorption line allowed reaching high selectivity of the detector with respect to other gases. The results of field tests on the streets and near gas-filling stations (methane) in Moscow are discussed. The detector could be rather easily adjusted for detection of other simple molecules such as CO, CO₂, HF, NO₂, H₂O and others by change of the diode laser and corrections in software.

[1] Nadezhdinskii A., Berezin A., Chernin S., Ershov O., Kutnyak V. *Spectrochimica Acta Part A*, 55, 2083 (1999).

FAST AND PRECISE FREQUENCY TUNING OF DIODE LASERS USING A QUADRATURE INTERFEROMETER

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Uniting frequency stabilization and fast detuning of external-cavity diode lasers is a challenging task. Limitations arise due to temperature induced drift, non-linearity and hysteresis of mechanical components and actuators. Frequency stabilization commonly relies either on an absolute frequency reference, such as an atomic transition, or a relative standard, e.g. a Fabry-Perot interferometer. However, since atomic resonances are only available at a few distinct frequencies, and high finesse interferometers only permit frequency stabilization to the regularly spaced transmission peaks, both methods do not lend themselves to stabilization of a laser to an arbitrary frequency with high precision.

We present a novel quadrature interferometer, designed as add-on for tunable lasers, which allows for performing fast and linear frequency scans. Any non-linearity of mechanics and piezo actuators is automatically compensated for. In addition, the interferometer provides a *continuous* relative frequency reference for an arbitrary tuning range. The concept is based on a measurement of the actual laser frequency using a temperature-controlled solid state etalon. Two probe beams strike the etalon under different angles, yielding interference signals with a relative phase of 90°. The signals are combined to provide a quadrature signal. The laser frequency corresponds to the phase of the quadrature signal, which can be precisely controlled.

The module is well suited to a wide wavelength range (380 nm to 1100 nm already in the standard version, can be extended into the UV or IR by adapting the utilized photodetectors). The digital control is based on a 32-bit microprocessor.

The thickness of the etalon determines resolution and final stability of the laser frequency, which is typically 400 times better than the selected Free Spectral Range (standard FSR is 17 GHz). Combining the quadrature interferometer and TOPTICA's diode laser DL 100, a frequency stability of $5 \cdot 10^{-8}$ (20 MHz @ 850 nm) has been achieved. The digital frequency control also permits rapid frequency stepping: The laser frequency can be shifted in any desired manner and by an arbitrary amount without sacrificing accuracy for tuning speed.

The quadrature interferometer is a versatile tool for applications involving laser monitoring, wavelength scanning or stepping, as well as wavelength locking. It provides a means to perform surveillance of wavelength drift, optimization of laser tuning parameters, monitoring of mode properties and stabilization ("locking") of a laser to an arbitrary frequency. In addition, the laser is rendered insensitive to mechanical vibrations. Applications include accurate and linear frequency scanning for spectroscopy, laser cooling, plasma monitoring, LIDAR seeding, laser on- and off-line monitoring and examination of optical components using phase-shifting interferometry.

**COMPACT AND LIGHT-WEIGHT OPEN-PATH-HERRIOTT-CELL FOR
SIMULTANEOUS IN-SITU-DETECTION OF H₂O AND CH₄ ONBOARD OF
STRATOSPHERIC BALLOON PLATFORMS**

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The depletion of stratospheric ozone is closely connected to the water vapor budget in the stratosphere, which is dominated by the entry of tropospheric water and the photolysis induced oxidation of CH₄ in the stratosphere. In order to make up the balance of the stratospheric water budget and to better understand the underlying transport processes, it is necessary to obtain frequent and simultaneous *in situ* determination of vertical concentration profiles of both contributing species, up to heights of 30 to 40 km. This task can only be solved by lightweight, compact and nevertheless highly sensitive CH₄-H₂O *in situ* sensors. Up to now the available techniques relied on retrieving gas samples for analysis, making them very susceptible to systematic errors caused by adsorption effects. These devices are also heavy and consequently require higher financial costs so that they are only used sparingly. To address improved CH₄-H₂O detection, one of the most compact and lightweight dual-species diode laser absorption spectrometers for use aboard stratospheric balloon platforms was developed in cooperation with the Institutes of Environmental Physics in Bremen and Heidelberg¹. This system is designed to simultaneously detect H₂O at the 2ν₁ and CH₄ at the 2ν₃ vibrational band. The core of this new instrument is a new compact, ultra-light-weight, multi-species open-path Herriott-cell, which allows the use of different path lengths for the two species (H₂O 36m, CH₄ 76m). A base length of 55cm and an extremely compact dual-species optical head, which allowed to confine the overall size of the complete optical setup to 75cm by 25cm. The use of specifically designed opto-mechanical components constricted the overall weight of the complete optics (including lasers, detectors, etc.) to 6.6kg and the total weight of the instrument to 20kg including batteries. The spectrometer operation was validated during two stratospheric flights with maximum heights of up to 35 km. Despite temperature variations of more than 100K and a high number of reflections (136 in case of the methane absorption path), the system showed excellent mechanical stability. This was in large part due to a new passive thermal compensation system that was used to compensate even the thermal expansion of the invar rods that separate the two main mirrors. The expansion movements of the invar rods were reduced by nearly an order of magnitude. The distance between the mirrors could be constrained to less than 20μm over the full temperature range. During the first two flights pressure dependent detectivities of 150-500ppb for H₂O and 50-600ppb for CH₄ were achieved. The low weight and compactness of this new instrument therefore constitutes a significant improvement over current instrumentation and should allow a much more frequent determination of the H₂O/CH₄ profiles by flying this instrument either alone on much smaller and therefore cheaper balloons or piggy-back on board larger instruments.

¹ W. Gurlit, C. Giesemann, R. Zimmermann, J. P. Burrows, U. Platt, J. Wolfrum, V. Ebert, „Lightweight diode laser spectrometer “CHILD” for balloon-borne measurements of water vapor and methane“, to be submitted to Applied Optics 2003

**PRESSURE BROADENING AND SHIFTS FROM WAVELENGTH MODULATED DIODE
LASER SPECTROSCOPY**

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Wavelength modulation spectroscopy using free-running visible and near-IR diode lasers provides a simple, inexpensive, and robust way of obtaining high resolution spectra of atomic and molecular systems. As an example, a temperature stabilized laser operating near 670 nm has been tuned using the injection current to produce high resolution spectra of the B-X transition of I₂. The resulting spectra exhibit characteristic unresolved quadrupole splittings that are easily modeled by fitting the line profile. Both pressure broadening and pressure shifts due to air have been identified and modeled. The method has also been applied to optogalvanic spectroscopy of Ar atoms, and the small pressure shift has been measured with reference to the accurately known cesium D₂ lines.

**CAVITY ENHANCED ABSORPTION AND WAVELENGTH/FREQUENCY
MODULATION DETECTION OF THE HYDROXYL RADICAL IN THE UV USING SUM-
FREQUENCY GENERATION**

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The hydroxyl radical (OH) is the most important oxidant in the atmosphere. It initiates the daytime oxidation of a large number of atmospheric pollutants, eventually leading to their conversion into species soluble in water. Its reactive nature, however, leads to low concentrations in the troposphere, with daytime maxima in the range $(1-10)\times 10^6$ molecule cm^{-3} (0.04 – 0.4 ppt). The most successful field methods for measuring OH concentrations have utilised the strong $A^2\Sigma^+ (\nu'=0) \leftarrow X^2\Pi (\nu''=0)$ transition at *ca.* 308 nm, either by long path absorption (1σ detection limit of 7.5×10^5 molecule cm^{-3} in 200 s [1]) or laser induced fluorescence (1σ detection limit of 5.2×10^5 molecule cm^{-3} in 150 s [2]). The bulky and heavy nature of the present instruments restricts their use to ground level experiments. By comparison cavity-enhanced absorption combined with wavelength/frequency modulation spectroscopy offers a competitive alternative for detection of OH as a function of altitude.

Initial investigations are described using an optical enhancement cavity in combination with cw radiation at 308nm. An IR tunable external cavity diode laser (835 nm) and an Ar⁺ laser (488 nm) were used to produce the tunable UV radiation with a power of a few μW by sum frequency generation in a beta-barium borate crystal. Preliminary experiments were carried out to detect OH radicals produced in a microwave discharge. Noise-equivalent absorbances of 8.7×10^{-4} , 4.4×10^{-5} and 3.4×10^{-5} were observed for direct, 1f and 2f harmonic detection, respectively, with a lock-in amplifier time constant of 0.3 s. A detection limit of 2.8×10^9 molecule cm^{-3} (for S/N = 1) was achieved over an optical path length of 46 cm for 2f-harmonic detection at a modulation frequency of 1 kHz. Experiments using cavity-enhanced techniques combined with wavelength/frequency modulation will be presented.

References:

- H.-P. Dorn, U. Brandenburger, T. Brauers, M. Hausmann, D.H. Ehhalt. In-situ detection of tropospheric OH radicals by folded long-path laser absorption. *Geophysical Research letters*: 23 (1996) 2537
- D.J. Creasy, D.E. Heard, J.D. Lee. OH and HO₂ measurements in a forest region of north-western Greece. *Atmospheric environment*: 35 (2001) 4713

MID-INFRARED WHISPERING GALLERY LASERS

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Semiconductor ring resonator lasers offer a range of advantages over other geometries that employ cleaved facets or gratings for optical feedback. These include ease of integration, a lack of spatial hole burning due to travelling wave operation and narrow linewidth single mode operation with high side-mode rejection. Until now ring lasers have been made predominantly at wavelengths $< 2\mu\text{m}$ and in GaAs/AlGaAs, using curved waveguides, as well as in InP/InGaAsP using large diameter rings or microdisks. In this paper we report the first mid-infrared ring laser diode based on InAs and grown by LPE. The diodes in this work were fabricated from III-V double heterostructures (DHs) grown using a conventional horizontal, multi-well LPE sliding boat onto n-type InAs (100) substrates. The resulting epitaxial structure comprised an unintentionally doped n-InAs active layer enclosed between P- and N- $\text{InAs}_{0.42}\text{Sb}_{0.18}\text{P}_{0.40}$ confinement layers. The P content in the confinement layers was 0.40 to create a high bandgap energy ($E_g = 640$ meV at 4 K) and large interface band offsets for good carrier confinement. Ring lasers were fabricated from the epitaxial wafers using conventional photolithography and reactive ion etching with $\text{CH}_4:\text{H}_2$ followed by passivation with Si_3N_4 to produce mesas $420\mu\text{m}$ in diameter. A $300\mu\text{m}$ diameter ohmic ring contact pad ($30\mu\text{m}$ width) was defined on the n- $\text{InAs}_{0.42}\text{Sb}_{0.18}\text{P}_{0.40}$ while the corresponding back contact was deposited over the entire rear surface of the chip. A microscope image of the resulting structure is shown in figure 1.

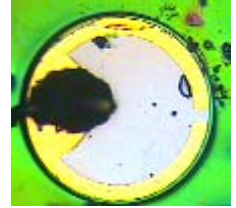


Fig.1.

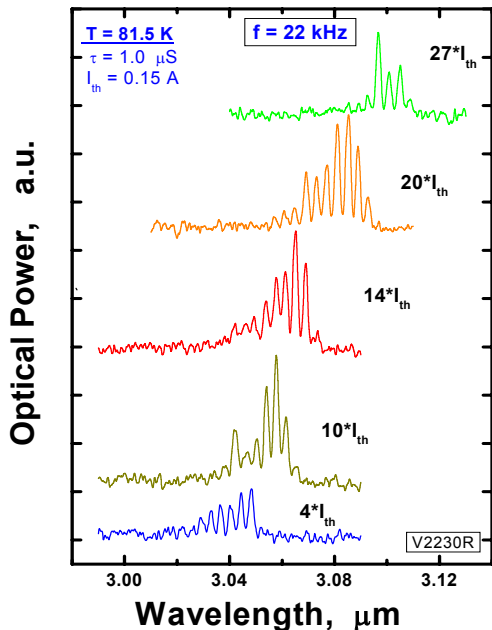


Fig. 2.

Coherent emission was obtained near $3.0\mu\text{m}$ at 80 K as shown in figure 2. This originates from in-plane propagation around the inside perimeter of the mesa due to a whispering gallery mode which is facilitated by total internal reflection with high Q. The mode spacing is calculated on a simple model and is given by $\Delta\lambda_{\text{WG}} = \lambda^2/2\pi Rn$. This enables us to estimate a whispering gallery mode spacing of 2.1 nm, which agrees reasonably with the value of 1.7 nm measured experimentally. The individual modes exhibited hardly any shift in wavelength with increasing injection current. We readily observed laser emission up to 27 times threshold. The peak output power was measured to be 5-10 mW. We obtained a characteristic temperature of $T_0 = 25$ K and a maximum operating temperature of 130 K in non-optimised structures having no output coupler. The ring lasers had significantly lower threshold current than equivalent Fabry-Perot lasers of the same epitaxial construction.

CW CAVITY RING DOWN SPECTROSCOPY THROUGH A SUPERSONIC PLANAR PLASMA

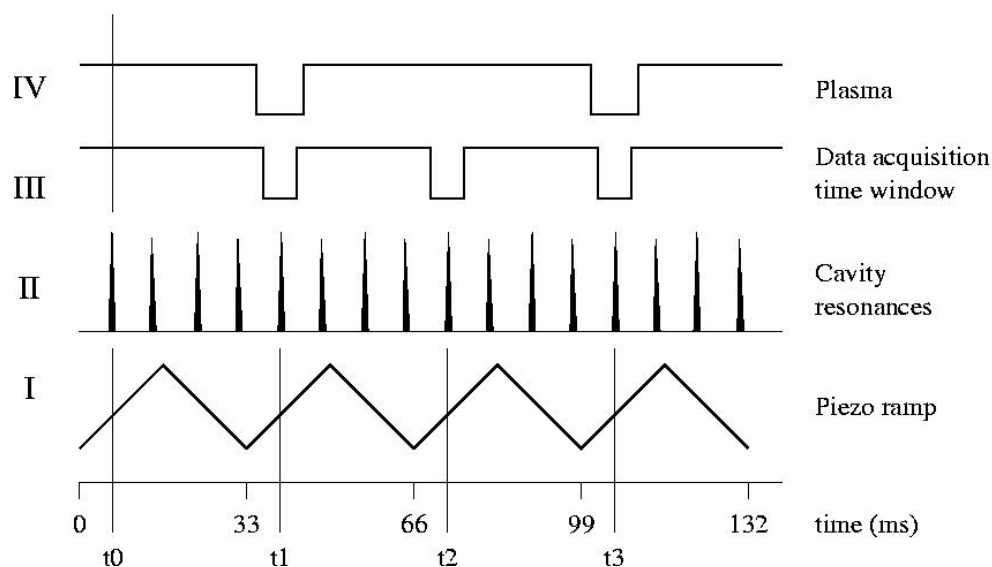
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A recently constructed high resolution setup for the detection of carbon chain radicals in the gas phase is presented. The setup consists of a tunable cw laser that is used to sample a supersonic planar plasma generated by discharging a high pressure gas pulse of acetylene in He in a multilayer slit nozzle geometry. Continuous wave cavity ring down spectroscopy is used as a sensitive detection scheme.

The method combines sensitivity with high spectral resolution. The poster describes in all details the difficulties that must be overcome when implementing a pulsed discharge in the cavity. The performance is demonstrated on the example of a completely rotationally resolved spectrum of the origin band of the $A^2\Pi_u - X^2\Pi_g$ electronic transition of the triacetylene cation, HC_6H^+ .



Part of the trigger scheme necessary to “chase” a resonance in a cw CRD experiment. A piezo voltage is used to scan the cavity length, inducing cavity resonances. The trigger scheme is made in such a way that plasma pulse and CRD event will overlap, even though the plasma causes a number of additional instabilities.

More information is available from Chem. Phys. 283 (2002) 119.

**TDLWINTEL: A COMPUTER PROGRAM FOR THE ACQUISITION AND ANALYSIS
OF TDL AND QCL ABSORPTION SPECTRA**

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A crucial aspect of any TDL or QCL spectrometer is the data acquisition and analysis software. The tasks performed by the software are complex but the user interface should be as simple as possible. For laboratory environments the software should maintain a high degree of flexibility. For commercial applications, flexibility is undesirable and extreme simplicity is the goal. We have developed a commercial software package called TDLWintel which has been used extensively in laboratory environments and is being extended for use in commercial turn-key systems. The program implements direct absorption spectroscopy which allows **absolute** concentration determination with no calibration.

TDLWintel is designed to frequency scan a tunable laser (pulsed or cw), acquire the resulting absorption spectrum, and analyze it by performing an advanced type of sweep integration. The laser frequency is swept across the spectral transition or group of transitions, then the absorbance of each line is derived using nonlinear least squares fitting to the known spectral line shapes and positions. Complete spectra can be obtained at rates up to 20 kHz. The sweep rate is fast enough to suppress the effects of 1/f noise thus removing the requirement for frequency modulation (FM) detection. The spectra are averaged for .01-1s in a background process, maintaining a full duty cycle, then fit using the Levenberg- Marquardt approach to a set of baseline and Voigt line shape functions (determined by pressure and temperature). The laser power spectrum is represented as a slowly varying polynomial of adjustable order, typically quadratic or cubic. The program has several frequency locking options and methods for suppressing background interference, and allows scheduling of automatic background corrections and calibrations. There is also a triggered data acquisition mode which allows concentration measurements with the time resolution of a single spectral sweep which can be as fast as 15 μ s.

We will focus on recent extensions to TDLWintel which support the use of multiple pulsed QC lasers. These extensions include 1) TTL gate and trigger signals which allow the acquisition of fast (~50 ns) signal and reference detector signals, 2) "pulse normalization" which reduces the effects of pulse to pulse amplitude noise, 3) multiplexed laser operation of up to four lasers on a single detector with frequency locking, 4) improved laser line shape modeling for spectral analysis in the presence of significant laser frequency chirp and 5) automatic program startup or turn-key operation. Examples from several recent applications will be presented.

DETERMINATION OF MOLECULAR PARAMETERS FOR QUANTITATION OF NON-HITRAN MOLECULES USING LEAD-SALT TUNABLE DIODE LASER INFRARED SPECTROSCOPY

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A technique has been developed for the determination of a set of molecular parameters (line positions, line strengths, and air broadening coefficient) for the quantitation of non-HITRAN molecules using a dual channel lead-salt Tunable Diode Laser Absorption Spectroscopy (TDLAS) system that was developed for the quantitation of gaseous constituents in cigarette smoke. Several molecules of particular interest have populations of highly overlapping absorption lines in their spectra. The developed technique provides a way of estimating these molecular parameters for these overlapping absorption lines from quantitative reference spectra taken with the TDLAS at different pressures and concentrations. This poster will describe the technique and some of the factors influencing the accuracy of the quantitation of 1,3-Butadiene.

DETERMINATION OF THE METHYL RADICAL LINE STRENGTH USING TIME-RESOLVED INFRARED ABSORPTION SPECTROSCOPY IN A PULSED PLASMA

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The methyl radical is generally accepted to be one of the most essential intermediates in hydrocarbon plasmas. For an improved understanding of the chemistry in carbon-containing plasmas, the measurement of the absolute ground state concentration of methyl radical is of great importance. For the purpose of quantifying of the methyl concentration in the infrared spectral range, the line strength of only one line Q(8,8) of methyl has ever been measured with an uncertainty of 30 % [1] and the dipole momentum of the CH₃ $\nu_2=1\leftarrow 0$ band has been calculated [2]. This contribution will describe spectroscopic studies of pulsed H₂-Ar microwave plasmas ($f=2.45$ GHz) containing hydrocarbon precursors, as e.g. CH₄ or C₂H₂. Different absorption lines of CH₃ have been used in order to calculate the integral value of the absorption coefficient and absolute concentrations.

By combining a planar microwave reactor with an optical multi pass cell the detection sensitivity for transient plasma species by infrared tunable diode laser absorption spectroscopy (TDLAS) has been considerably improved over earlier measurements. Based on time resolved TDLAS measurements the concentration and CH₃ has been measured directly leading to accurately determined line strengths of several absorption lines of CH₃ around 16 μm . Preliminary results of line strengths determination are presented and discussed.

[1] J. Wormhoudt and K. E. McCurdy; Chem. Phys. Lett.; 156, 47 (1989)

[2] C. Yamada and E. Hirota; J. Chem. Phys.; 78, 669 (1983)

INFRARED DIODE LASER ABSORPTION SPECTROSCOPY OF REACTIVE SPECIES IN INDUCTIVELY AND CAPACITIVELY COUPLED RF DISCHARGES

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Radio-frequency plasmas of reactive gases are used for the deposition of hydrogenated carbon films. These films have found a great number of industrial and technical applications due to the unique combination of their properties, defined by deposition parameters such as the gas composition and its time development. Presently the understanding of chemistry and kinetics of complex plasmas is far from being complete. For both applied and fundamental research, a basic study of the gas densities in RF-discharge is necessary.

Nowadays the tunable diode laser absorption spectroscopy allows to detect a wide range of molecules with a high sensitivity, the possibility of time resolution and sub-Doppler spectral resolution. Therefore, it is a perfect diagnostic for the analysis of densities and temperatures of molecules and radicals.

In the present work two diode laser spectrometers have been installed with diode lasers operating on 6075 cm^{-1} for detection of CH_4 molecules and 800 cm^{-1} for C_2H_2 and C_2H_6 . Multipass cells of the Herriott type, providing 40 passes, have been set up for increasing the sensitivity. Measurements were performed at two different plasma chambers under a set of conditions typical for film deposition, revealing dependencies of the species densities on the external parameters (as the applied power, the flow rate and the pressure) and their time behaviour. First comparison of the experimental results with data from a plasma chemistry model shows good agreement.

WAVELENGTH MODULATION SPECTROSCOPY FOR THE NON-INVASIVE, NON-DESTRUCTIVE MEASUREMENT OF TRACE GASES IN ACCELERATED MATERIALS AGEING TRIALS

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Materials are contained under reduced pressure inside stainless steel vessels that have optical windows to facilitate transmission spectroscopy. The system operates with very limited optical path lengths totalling <50cm. The aim of the project is to monitor changes in the composition of the atmosphere inside these vessels over periods of months or years and at a range of temperatures from ambient to 75°C, in order to understand long-term compatibility and ageing issues. Light is coupled into fiber optic cables and can be sent to and collected from remote/hazardous areas to provide non-invasive and non-destructive analysis. Transmission, 1st and 2nd harmonic spectra of CO₂ and H₂O have been measured in the NIR using external cavity diode lasers. A piezoelectric device which is part of the cavity tuning element imposes wavelength modulation at 1kHz, and the signal is demodulated using a lock-in amplifier. As the pressure inside the vessels is typically ca.200mbar, it is possible to discriminate between pressure broadened background features and the narrower signals arising from inside the vessel. The discrimination is shown to improve in the following order: zero'th, first and second harmonics of the transmission spectrum. Maintaining the spectral discrimination, by keeping the amplitude of wavelength modulation small, is deemed preferable to increasing the modulation amplitude to 2.2 times the linewidth, otherwise the discrimination is rapidly lost. Detection limits of 200ppm.m and 300ppb.m are reported for CO₂ and H₂O respectively, in a 1Hz bandwidth.

**THE EFFECTS OF TEMPERATURE AND PRESSURE INDUCED ABSORPTION LINE
SHIFT ON LASER DIODE BASED SENSING OF H₂O AT 1.393 μ m**

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Typically, in atmospheric open path trace gas measurements, there is little deviation in gas pressure and temperature from standard values (≈ 1000 mbar, 293K). However in various industrial contexts (e.g. gas emanating from a stack) large variations in operating conditions, may result in for example, a gas temperature in the range 300K–1100K, its value dependent on the industrial process. Hence in sensing using laser diode based spectroscopy, the use of a reference cell to lock the emission wavelength of the laser diode to a target absorption line may be impaired by a modification of spectral characteristics of the sample gas as a function of temperature and pressure. Therefore, knowledge of absorption line characteristics as a function of temperature and pressure is necessary for the application of a spectroscopic based sensor in industrial environments.

We targeted the water vapour vibrational combination band $\nu_1+\nu_3$ centred at 1.38 μ m, where ν_1 denoted the symmetric OH stretch and ν_3 the asymmetric OH stretch. Specifically, the water vapour rotational absorption line at 1.3928 μ m, which has a linestrength of 2.52×10^{-22} cm.molecule⁻¹ was targeted and spectral shifts as a function of pressure and temperature in the range 0 - 1000mbar and 293K – 1100K respectively were measured. These are critical characteristics for laser diode based gas sensing where the temperature and pressure of the sample gas may differ significantly from that of the gas in a reference cell which is used to implement line locking.

**MEASUREMENTS OF TRACE WATER VAPOR IN A CARBON DIOXIDE REMOVAL
ASSEMBLY PRODUCT STREAM USING A TUNABLE DIODE LASER
SPECTROMETER**

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

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A tunable diode laser spectrometer configured for the measurement of trace concentrations of water vapor was used in diagnostic tests of a Space Station Carbon Dioxide Removal Assembly (CDRA) in a simulation facility at the NASA Marshall Space Flight Center. A primary issue in further CDRA development, involving addition of a compression stage to its exhaust, is the possibility that condensation of liquid water may damage the compressor. In five days of round-the-clock data acquisition, the water content of the exhaust was characterized, and enough evidence was accumulated that the source of high water concentrations was found.

A key feature of the apparatus was a sampling system that allowed response times short compared to the time scales of changing water vapor concentrations. One important component of this system was a small-volume (0.3 liters), long-path (36 m) multipass absorption cell, of the astigmatic Herriott cell design developed at Aerodyne. Other important components included a valving system that allowed automated switching between sample and reference flows and allowed sample gas to flow through the sampling line at all times, and a cell pressure regulator that minimized the effect of this switching on the absorption spectrum. The spectrometer used a lead-salt laser to measure absorption at one of the strongest of all water lines, at 1616.712 cm^{-1} . Aerodyne's TDLWintel laser control, data acquisition and analysis software wrote a continuous record of concentrations, saved files of spectra and instrument parameters such as multipass cell pressures, and kept the laser locked to a low pressure water absorption line in a reference cell.

The tunable diode laser spectrometer met or exceeded all the specifications for the test, including sensitivity, time response, and time of operation. Detection levels of well under the specified 50 ppbv were achieved, while the high water levels of greatest interest turned out to be about 400 ppmv. Its good sensitivity, good time resolution, high dynamic range (measured concentrations varied over four orders of magnitude), its first-principles calibration, its excellent stability, and its ability to display and analyze data in real time, were all critical to the success of the test.

UF₆ ENRICHMENT MEASUREMENTS USING TDLS TECHNIQUES***A. Nadezhdinskii and Ya. Ponurovskii****NSC of A.M.Prokhorov General Physics Institute**Vavilov str. 38, 119991 Moscow, Russia****Yu. Selivanov****P.N. Lebedev Physical Institute**Leninski 53, 119991 Moscow, Russia****G. Grigorev, Sh. Nabiev, and N. Gorshunov****Institute of Molecular Physics of RRC "Kurchatov Institute"**Kurchatov sqv.1, 123182 Moscow, Russia****G. Bosler, R. Olsen, and V. Ryjikov****International Atomic Energy Agency**Wagramer Str. 5, P.O. Box 100, A-1400 Vienna, Austria*

The first use of Tunable Diode Laser Spectroscopy (TDLS) in a number of countries was related to examining one molecule. This was the uranium hexafluoride molecule (UF₆) as used with laser uranium isotopic enrichment experiments. The dramatic progress in TDLS techniques achieved during last decades and the success of detection of trace complex molecules having unresolved spectra brought our attention to examining the UF₆ molecule in addressing IAEA safeguards requirements. The goal of present work has been to develop an instrument and associated algorithms for relatively quick field measurements of UF₆ isotope enrichment with high accuracy (better than 0.6%).

Spectra of UF₆ gas mixtures have been investigated using Fourier Transform Spectrometers Vector 22 and Bruker 66v. The observed spectral features were identified, and model spectra of different gas mixture components have been developed. An optimal spectral range for measurements is determined near the maximum UF₆ combination band $\nu_1+\nu_3$. UF₆ is an example of a molecule with a broadband absorption structure with many unresolved spectral lines. The absorption spectrum of the gas sample under investigation is the sum of two main molecular isotopic spectra (²³⁸UF₆ and ²³⁵UF₆). At the present stage of TDLS development, the technique is able to distinguish these spectra and to determine the enrichment of a gas sample under investigation.

A laboratory multi-channel prototype instrument using a tunable diode laser has been built, and algorithms of its operation have been developed to measure the isotopic ratios of gaseous UF₆. The diode laser operates at a wavelength of $\lambda=7.68 \mu\text{m}$ and is cooled by liquid nitrogen. Three instrument channels are used for laser frequency calibration and spectra recording.

The instrument has been successfully tested using a UF₆ gas mixture. The observed accuracy has been analyzed, and error sources have been identified. A random measurement error of isotope ²³⁵U is characterized by a root-mean-square spread of about 0.27% for short measurement times and 1% for long measurement times of more than an hour. Overcoming present known experimental problems should improve the error by at least an order of magnitude. Finally the prototype instrument has been tested at the IAEA UF₆ test loop located in Seibersdorf, Austria.

MEASURING AIR CONTENT INSIDE INSULATING GLASS WINDOWS

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Filling the space between insulating glass (IG) windows by noble gas (Ar, Kr, Xe) allows to reduce heat conductance of windows. The technique in commercial window manufacturing is to inject argon between layers of IG. The standard argon content after refilling is about 90%. Insufficient argon concentrations result in lower energy efficiency, and increased heating and cooling costs; and wasted money replacing windows that don't need it. However, there is no method to quickly and accurately measure the amount of argon between the window panes when they are manufactured or determine if argon has depleted in windows that are already installed in buildings. Existing methods of measuring argon content in windows are not sufficiently precise, reliable, or timely. Costly and time consuming laboratory techniques are required to make an accurate measurement.

Argon content cannot be measured directly by diode laser spectroscopy technique, but, when windows are injected with argon, the space between contains a mixture of argon and air, and air contains about 20% oxygen. This means that if one can measure level of oxygen inside IG, then the argon level can be easily calculated.

A portable device to measure oxygen concentration between IG was constructed. This device is based on commercial 760 nm Fabri-Perot diode laser. A detection limit of oxygen is about 0.1% at the optical pathlength 3 cm, and this makes it possible to measure argon content between IG with accuracy better than 0.5%.

The device is compact, battery powered and can be used for field measurements.

Poster Session D.

D1. HIGH-SENSITIVITY MEASUREMENTS OF HYDROCARBON SPECIES USING INTERBAND CASCADE LASERS OPERATING NEAR 3.3 MICRONS

Mark G. Allen, David M. Sonnenfroh, and Seonkyung Lee

D2. HIGH SENSITIVE 1.31 μm DIODE LASER HYDROGEN FLUORIDE SENSOR WITH DETECTION LIMIT 1 ppb

A.G.Berezin, O.V.Ershov, A.I.Nadezhdinskii, Ya.Ya.Ponurovskii

D3. RAPID PASSAGE AND POWER SATURATION EFFECTS IN PULSED QUANTUM CASCADE LASER SPECTROMETERS

M.T. McCulloch, G. Duxbury and N.Langford

D4. PROCESS GAS ANALYSIS BY INFRARED SPECTROSCOPY IN THE SEMICONDUCTOR INDUSTRY

L. Emmenegger, J. Mohn

D5. MEASUREMENTS OF RELATIVE INTENSITY NOISE OF QUANTUM CASCADE LASERS

T. Gensty, W. Elsäßer

D6. DIODE LASER TWO-LINE ATOMIC FLUORESCENCE THERMOMETRY IN FLAMES

J. Hult, I. Burns and C.F. Kaminski

D7. A DUAL-WAVELENGTH DIODE LASER SPECTROMETER FOR WATER ISOTOPE RATIO ANALYSIS

L. Gianfrani, G. Gagliardi, M. van Burgel, and E. R. Th. Kerstel

D8. RAPID ABSORPTION SPECTROSCOPY FOR *IN-SITU* OXYGEN MEASUREMENTS IN HOSTILE ENVIRONMENTS (MULTI-PHASE AND FLAMES) USING A 761 NM VERTICAL-CAVITY SURFACE-EMITTING LASER (VCSEL)

Maximilian Lackner, Gerhard Totschnig, Franz Winter

D9. DIODE LASER SPECTROSCOPY OF AMMONIA AND ETHYLENE OVERTONES

A. Lucchesini, S. Gozzini

D10. AN AXIAL MOLECULAR BEAM MID-INFRARED TUNABLE DIODE LASER SPECTROMETER

H. D. Osthoff, J. Walls, W. A. van Wijngaarden, and W. Jäger

D11. NEAR-INFRARED DIODE LASER SPECTROSCOPY OF CO₂ AND ATMOSPHERIC APPLICATIONS

B. Parvitte, V. Zeninari, L. Joly, I. Pouchet, and G. Durry

D12. CO₂ DECOMPOSITION IN A NON-SELF-SUSTAINED DISCHARGE WITH A CONTROLLED ELECTRONIC COMPONENT OF PLASMA.

S.N. Andreev, V.V. Zakharov, V.N. Ochkin, S.Yu.Savinov

D13. HIGH RESOLUTION TUNABLE DIODE LASER SPECTRUM OF OH GROUP SECOND OVERTONE IN ETHANOL

S.Shaji, Shibu M Eapen, T.M.A.Rasheed and K.P.R.Nair

D14. OPTIMAL PARAMETER FIT FOR BORN-OPPENHEIMER BREAKDOWN OF CaH IN X²Σ⁺ STATE

Hiromichi Uehara

D15. A MID-INFRARED LASER SPECTROMETER FOR THE *IN-SITU* MEASUREMENT OF STRATOSPHERIC NITROUS OXIDE

F. D'Amato, M. De Rosa, P. Mazzinghi, M. Pantani, P. Poggi, P. W. Werle, F. Castagnoli

D16. NEW IMPROVEMENTS IN PHOTOACOUSTIC DETECTION OF METHANE

V. Zeninari, B. Parvitte, D. Courtois, V. A. Kapitanov, and Yu. N. Ponomarev

D17. STAND-OFF ETHANOL SENSOR

A.G.Berezin, O.V.Ershov, A.I.Nadezhdinskii, Y.P.Shapovalov, D.B.Stavrovskii.

D18. ANALYSIS OF TUNABLE DIODE LASER SPECTRA OF R_Q(J,0) LINES IN CH₃F NEAR 1475 CM⁻¹ USING A MULTI-SPECTRUM FITTING TECHNIQUE

Muriel Lepere, R. Gobeille, N. Kolodziejski, V. malathy Devi, D. Chris Benner, M. A. H. Smith, W. McMichael, B. Aoaeh, K. Wilkinson and A. W. Mantz

**HIGH-SENSITIVITY MEASUREMENTS OF HYDROCARBON SPECIES USING
INTERBAND CASCADE LASERS OPERATING NEAR 3.3 MICRONS**

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Progress in Type-II, Interband Cascade Laser (ICL) technology has resulted in room-temperature semiconductor lasers operating at wavelengths near 3.3 microns. This wavelength region is technologically significant for high-sensitivity detection of a variety of hydrocarbon species such as methane, ethylene, and mixed vapors from gasoline.

This poster will present initial results using a single-mode Distributed FeedBack (DFB) ICL device to measure methane. The present DFB device is operated cw at liquid nitrogen temperatures, although room-temperature devices are expected later in 2003. The poster will describe the overall sensor configuration and discuss laser operating parameters such as threshold current, operating power, tuning range, and linewidth.

HIGH SENSITIVE 1.31 μm DIODE LASER HYDROGEN FLUORIDE SENSOR WITH DETECTION LIMIT 1 ppb

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The automated high sensitive laboratory prototype of hydrogen fluoride sensor was developed on a base of 1.31 μm diode laser spectrometer operating in pulsed regime [1]. In the region 1.26 - 1.33 μm hydrogen fluoride has rather strong absorption band (first overtone of the single fundamental band). There are plenty of commercially available diode lasers at wavelength 1.31 μm that could reach several absorption lines of HF (P4 – 1.32125 μm , P3 – 1.31259 μm , P2 – 1.30453 μm), which could be used for detection. However, choice of diode lasers used for detection was rather difficult. Most convenient single-mode single-frequency distributed feedback (DFB) diode lasers should be carefully tested before applying to measurements, otherwise HF absorption line frequency may get into the dead intervals of their operation (intervals of mode hopping). Taking into account large distance between HF lines, which could be compared with diode laser tuning range, many of tested DFB lasers were useless for detection in spite of their single frequency (within one mode) operation. An employment of Fabry-Perout lasers instead of DFB lasers leads to another problem. These lasers have several modes with broader tuning range involving water lines. In this case it was difficult to distinguish between HF absorption line in main mode and additional absorption of water in satellite generation modes. Finally Fabry-Perout diode laser was chosen for detection of P2 line and water absorption was subtracted by data processing.

The device incorporated Chernin four-objective multipass optical cell with optical path length 39 m at base length of 25 cm. Electronics controlling the device along with single-mode-fiber-coupled diode laser and reference cell were mounted in separate box, connected to multipass cell via optical fiber and to computer via electric cable. The device was run by computer program written in LabVIEW-6. The device was rechargeable battery powered; the energy supply was enough for 8 hrs of continuous operation. The main destination of the sensor was the monitoring of HF content in the ambient air. Std limit for 0.4 s averaging was found to be less than 1 ppb, which is quite acceptable for a number of applications.

[1] Nadezhdinskii A., Berezin A., Chernin S., Ershov O., Kutnyak V. *Spectrochimica Acta Part A*, 55, 2083 (1999).

**RAPID PASSAGE AND POWER SATURATION EFFECTS IN PULSED QUANTUM
CASCADE LASER SPECTROMETERS**

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Recently there has been considerable interest in adiabatic passage effects in atomic and molecular gases subject to short laser pulses. In the infrared region the relaxation times of low pressure molecular gases are on the microsecond time scale. In our experiment the time of passage of the chirped QCL pulse through a Doppler broadened line is sub-ns, very much faster than in earlier experiments, greatly enhancing the chance of seeing rapid passage effects. Since the intensity of the pulse is about, 10^4 W m^{-2} , the combination of high intensity and a short interaction time, which is much faster than the relaxation processes, leads to the observation of strong adiabatic rapid passage signals and power dependent bleaching. We have observed these effects in several gases, in particular ethylene, methyl chloride and ammonia.

Examples are given of the effects of the short interaction time and power bleaching on the observed spectral profiles of lines, even when pressure broadened with up to 100 Torr of nitrogen. Although only three molecular examples are considered in detail, we will show that these effects are present when any short, intense QCL pulse is used to probe the spectrum of specific molecules such as ethylene, irrespective of the mode of operation of the spectrometer.

**PROCESS GAS ANALYSIS BY INFRARED SPECTROSCOPY IN THE
SEMICONDUCTOR INDUSTRY**

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A wide range of speciality gases are used in the production of microelectronic devices, such as CMOS, LEDs and TFTs. These gases include mainly (per)fluorocompounds (e.g. CF₄, WF₆, NF₃), silanes (SiH₄, [(C₂H₅O)₄Si]), and dopants (AsH₃, PH₃). The use and abatement of these gases must be optimised because of their high costs, aggressive properties and strong global warming potential. The present study includes chemical vapour deposition (CVD) of tungsten and silicon dioxide, with special focus on the gaseous reactions and mass balances during cleaning steps.

Extractive on-line FTIR was used for qualitative and quantitative analysis of the main gaseous products. Materials and analytical parameters were optimized to achieve rapid instrumental response at high spectral resolution. Quantification was done by classical least-square algorithms. The measurement of adequate reference spectra was one main challenge because of the reactive and uncommon gases studied.

The results indicate large optimization potential for some process steps. The quantitative results and spectral information will be valuable for the development of enhanced process control and adequate analytical methods. FTIR has proven to be a powerful tool for overall studies. The results obtained will promote future, more specific developments of analytical systems - including TDLS - for process gas analysis in the semiconductor industry.

MEASUREMENTS OF RELATIVE INTENSITY NOISE OF QUANTUM CASCADE LASERS

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We present measurements of the relative intensity noise (RIN) of quantum cascade (QC) lasers. The RIN is analyzed for free-running QC lasers and for QC lasers under optical feedback. Since their first realization in 1994 [1], QC lasers have made tremendous progress. Recently, continuous wave (cw) operation has been reported at room-temperature [2]. Because of the high operation temperatures and the high output power in the mid-infrared spectral region, QC lasers have already become suitable light sources for trace gas sensing and for optical free-space communication. So far, only little attention has been paid to the intensity noise properties of these novel devices.

Here, we present investigations of the RIN of Fabry-Perot QCLs [3] and DFB QC lasers. Figure 1 depicts the RIN^* (measured under quasi-cw operation) of three different QC lasers.

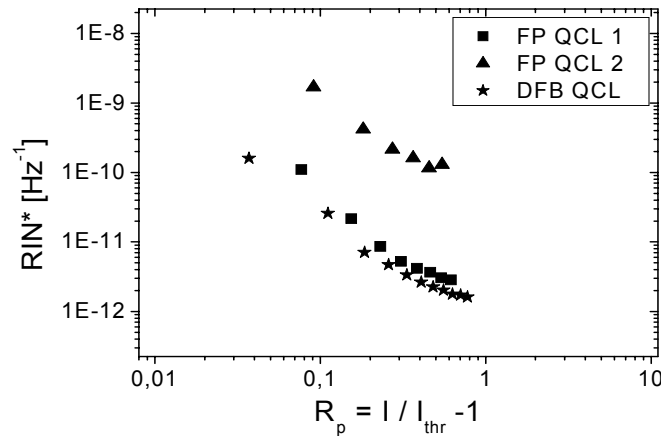


Figure 1 RIN^* measured at 9.5 MHz for Fabry-Perot (FP) QC lasers and for a DFB QC laser. The lasers have been operated under quasi-cw conditions (100 ns pulse width, 1 kHz repetition rate).

These results are analyzed with a single mode rate equation noise approach taking into account the different device parameters, possible multi-mode contributions and the particular difference between QC lasers and edge emitting lasers and vertical-cavity surface-emitting lasers [4]. Finally, we introduce controlled optical feedback and compare the RIN results with those of the free-running case. Possible consequences for measurement system applications will be discussed.

[1] J. Faist et al., Science 264, 553 (1994).

[2] M. Beck et al., Science 295, 301 (2002).

[3] Q. K. Yang et al., Appl. Phys. Lett. 80, 2048 (2002).

[4] D. M. Kuchta et al., Appl. Phys. Lett. 62, 1194 (1993).

DIODE LASER TWO-LINE ATOMIC FLUORESCENCE THERMOMETRY IN FLAMES***J. Hult, I. Burns and C.F. Kaminski****Department of Chemical Engineering, University of Cambridge, New Museums Site,
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This poster will describe the development of a technique to measure flame temperatures with high spatial resolution using diode lasers. It is based on two-line atomic fluorescence (TLAF) of indium atoms seeded to flames. Flame temperature is one of the most important parameters characterising a combustion system. Several laser techniques for temperature measurements in flames exist, however these are not easily applied in sooting flames, owing to the strong absorption, particulate scattering, and non-specific molecular fluorescence that occur in such environments. However, TLAF of indium, which is seeded at trace concentrations (ppb) to the flame, can provide accurate temperature information even in highly sooting flames.

In LIF thermometry, one probes a number of temperature sensitive electronic states, whose relative population is governed by the local gas temperature. In indium the 5P level is the atomic ground state, and is split into the 5P_{1/2} and 5P_{3/2} sub levels (separation: ~2300 cm⁻¹). In thermal equilibrium these levels are populated according to a Boltzmann distribution. For TLAF the 5P_{1/2}→6S transition is excited using a laser at λ₂₀=410 nm and then observing a LIF signal F₂₁ at 451 nm from the 6S→5P_{3/2} transition. The corresponding signal is proportional to the population in the ground state 5P_{1/2}. Similarly, one probes the population in the 5P_{3/2} level using a second laser at λ₂₁=451 nm, exciting the 5P_{3/2}→6S transition and observing a fluorescence signal F₂₀ at 410 nm (corresponding to 6S→5P_{1/2}). The ratio of the two signals can be shown to be related to the temperature T via:

$$T = \frac{\varepsilon / k_B}{4 \ln \frac{\lambda_{21}}{\lambda_{20}} + \ln \frac{I_{12}}{I_{02}} + \ln \frac{F_{21}}{F_{20}} + C}$$

Where ε is the splitting between the 5P_{1/2} and 5P_{3/2} levels, k_B is the Boltzmann's constant, I₀₂ and I₁₂ are the laser excitation intensities, and C is a system dependent calibration constant obtained by a reference measurement at a known temperature. The sensitivity of the indium transitions being probed spans the entire temperature range of interest in technical combustion.

Two GaN laser diodes (410 nm and 451 nm) from Nichia are used for the fluorescence excitation, the two beams being combined and focused to a point in the flame. Photomultipliers are used to detect the two fluorescence signals, which are separated using interference filters.

TLAF has hitherto required expensive pulsed lasers and detectors, however the present system, which is based on blue diode lasers is cheaper and more compact. The strong oscillator strength of atomic species allows diode lasers to be used for fluorescence excitation in flames, which leads to a good spatial resolution compared to conventional path averaged absorption techniques. The technique holds great promise as a thermometry tool for sooting flames for which there are no other reliable temperature diagnostics available. The poster will present the development of the diode laser TLAF technique and preliminary results from flame studies.

A DUAL-WAVELENGTH DIODE LASER SPECTROMETER FOR WATER ISOTOPE RATIO ANALYSIS

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We report on the recent results obtained with a novel diode laser spectrometer developed at the Groningen Center for Isotope Research, enabling the accurate determination of isotope abundance ratios in water. Particularly, we have implemented a dual-wavelength approach, ensuring ideal conditions for high-precision and simultaneous measurements of $^2\text{H}/^1\text{H}$, $^{17}\text{O}/^{16}\text{O}$, and $^{18}\text{O}/^{16}\text{O}$ ratios in water. The system is based on the use of a pair of 1.4- μm diode lasers, which provide the opportunity to select the most advantageous line pairs, in terms of line intensity and temperature dependency. One laser was tuned in coincidence with H^{16}OH , H^{17}OH , and H^{18}OH ro-vibrational lines around 7183 cm^{-1} , while a second laser probed a $\text{H}^{16}\text{OH} / \text{HO}^2\text{H}$ line pair near 7198 cm^{-1} . Using frequency modulation multiplexing, we demonstrated the possibility to measure all three isotope ratios with $1\text{-}\sigma$ standard deviations (precision) of 0.2 ‰ for $\delta^{18}\text{O}$, and 0.5 ‰ for $\delta^2\text{H}$ and $\delta^{17}\text{O}$. The results of a first test of the spectrometer on a real (natural) water samples are also discussed.

**RAPID ABSORPTION SPECTROSCOPY FOR *IN-SITU* OXYGEN
MEASUREMENTS IN HOSTILE ENVIRONMENTS
(MULTI-PHASE AND FLAMES) USING A 761 NM
VERTICAL-CAVITY SURFACE-EMITTING LASER (VCSEL)**

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In tuneable diode laser absorption spectroscopy (TDLAS), the laser frequency is swept over the absorption line of interest in order to simultaneously determine the extent of resonant absorption by the target species in the center and the amount of non-specific beam attenuation such as introduced by beam steering or scattering in the wings of the absorption feature. A prerequisite of this approach is that the time scale on which the disturbing effects occur be smaller than the time necessary to tune the laser over the absorption feature. A vertical-cavity surface-emitting laser (VCSEL) is used to probe rovibrational transitions at 761 nm in the oxygen A band. The laser is sent through flames (gaseous and liquid fuels with the flame being up to 1 m in length) and particle laden gaseous media (silica sand with 80-100 and 400-500 μm size, respectively). The time scales of the major sources of experimental noise (i. e beam steering, emissions from premixed and non-premixed flames, partial blocking of the beam by soot and sand particles) are investigated. The fastest fluctuations were found to occur on a 100 μs time scale. The tuning properties by injection current of the VCSEL were investigated using an air-spaced (293 mm) etalon composed of ZnSe windows (free spectral range $0.17 \text{ cm}^{-1} = 0.01 \text{ nm}$). In order not to be limited by the bandwidth of available commercial laser diode drivers, a 0-10.8 V triangular voltage ramp (corresponding to 0-7.4 mA) was applied to the laser in series with a 1 kOhm resistance. The continuous current tuning range was found to be as high as 32 cm^{-1} (1.85 nm) at 20 kHz, 20.5 cm^{-1} at 100 kHz, 4.3 cm^{-1} at 1 MHz and still 0.85 cm^{-1} (0.05 nm) at 5 MHz. The current tuning coefficient was found to be $\Delta\lambda/\Delta I = -5.0 \text{ cm}^{-1}/\text{mA}$ (0.29 nm/mA), the temperature tuning coefficient $\Delta\lambda/\Delta T = -0.86 \text{ cm}^{-1}/\text{K}$ (0.05 nm/K). The threshold current of the VCSEL at 25°C was 2.3 mA. Values for a comparable 760 nm DFB laser taken from the literature are $\Delta\lambda/\Delta I = -0.081 \text{ cm}^{-1}/\text{mA}$ (0.0047 nm/mA), $\Delta\lambda/\Delta T = -1.03 \text{ nm}/\text{K}$ (0.0597 nm/K) and a threshold current of $\sim 30 \text{ mA}$ (25°C).

It is concluded that due to the fast wavelength tuning ability of VCSELs, which is tenfold the value of DFB or Fabry Perot type diode lasers, these lasers are particularly suited for the investigation of transient phenomena.

DIODE LASER SPECTROSCOPY OF AMMONIA AND ETHYLENE OVERTONES

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Some overtone absorption lines of ammonia and ethylene have been examined by using a diode laser (DL) spectrometer [1] in the region around 12650 and 11800 cm^{-1} respectively.

The spectrometer sources are commercially available double heterostructure InGaAlAs and AlGaAs DLs. Even if operating in "free-running" mode, the high resolving power ($\sim 10^7$) of the spectrometer permitted the detection and the study of the absorption features of such molecules with a precision of less than 0.01 cm^{-1} .

In order to maximize the signal to noise ratio (S/N) and to extract the necessary informations either on the line width and on the line position for the detected molecular resonances, the wavelength modulation spectroscopy (WMS) along with the 2nd harmonic detection techniques have been applied. For this purpose the fit procedure took into account the instrumental effects and the amplitude modulation (AM) always associated to the frequency modulation (FM) of these type of sources [2]. This technique permitted also the measurement of the collisional broadening and shifting coefficients by different buffer gases at room temperature.

1. A. Lucchesini, S. Gozzini, Eur. Phys. J. **D 22**, 209-215 (2003)
2. M. De Rosa, A. Ciucci, D. Pelliccia, C. Gabbanini, S. Gozzini, and A. Lucchesini, Opt. Commun., **147**, 55-60 (1997)

AN AXIAL MOLECULAR BEAM MID-INFRARED TUNABLE DIODE LASER SPECTROMETER

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A novel molecular beam spectrometer for the purpose of trace gas sensing is described. Sensitivity is greatly enhanced and absorption interference by atmospheric H₂O and CO₂ is greatly reduced by using a molecular expansion of helium gas seeded with the analyte gas. The adiabatic expansion results in rotational cooling and population enhancement of low-lying energy levels. The instrument employs a tunable lead salt diode, which is operated in single mode near the R(0) transition of the asymmetric stretch of CO₂. We have constructed a specially adapted 60 m Herriott multipass cell. The sample gas is injected axially through a coupling hole in one of the spherical mirrors, resulting in the observation of a Doppler pair. Axial injection increases the residence time of the molecular beam in the sampling region. Pulsed operation of the nozzle allows background subtracted spectra to be acquired. The laser is either rapidly scanned over the absorption feature of interest, or locked to the centre frequency and modulated at a frequency of 50 kHz. 2f demodulation and careful tuning of the modulation amplitude allow the simultaneous sampling of both Doppler components.

Sample spectra of CO₂ and of several CO₂ containing van der Waals complexes are presented. The instrument's stability was assessed in long-term environmental monitoring trials. Key problem areas are pulse-to-pulse reproducibility, diode laser stabilization and gas sampling issues. In addition, several post-data acquisition digital filtering techniques, including Wiener and Kalman filters, were evaluated.

NEAR-INFRARED DIODE LASER SPECTROSCOPY OF CO₂ AND ATMOSPHERIC APPLICATIONS

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A diode laser spectrometer was used in the laboratory to study CO₂ line intensities and pressure broadening coefficients near 1.6 μm. The spectral region ranging from 6230 to 6250 cm⁻¹ which is suitable for the in-situ sensing of carbon dioxide in the lower stratosphere was studied using a commercial telecommunication-type diode laser (Distributed Feed-Back type purchased from Anritsu).

Thirteen lines of the (30⁰1)_{III}←(000) band of CO₂ have been studied. The results of intensity measurements are compared to previous determinations and available databases. Furthermore the broadening coefficients by N₂ and O₂ are also reported and analyzed.

Finally preliminary measurements of stratospheric CO₂ achieved in 2002 with the "Spectromètre à Diodes Laser Accordables" (SDLA) of the Service d'Aéronomie (a balloon TDL spectrometer) are discussed.

CO₂ DECOMPOSITION IN A NON-SELF-SUSTAINED DISCHARGE WITH A CONTROLLED ELECTRONIC COMPONENT OF PLASMA.

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The energy efficiency of nonequilibrium plasmachemical process depends on which set of channels it flows, i.e., on the mechanism of the process. On the other hand, the mechanism is defined, mainly, by the parameters of gas discharge. The reduced electric field strength E/N (E is the

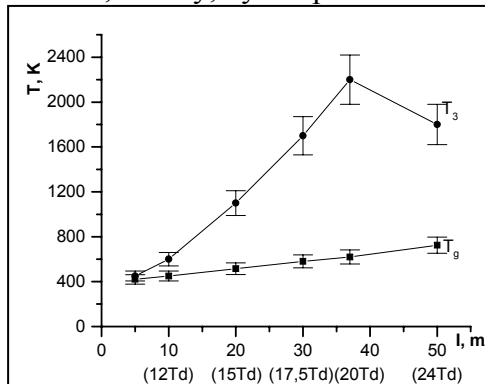


Fig. 1. Dependences of gas T_g and vibrational temperature of asymmetric mode T_3 on discharge current. Non-self-sustained discharge, CO₂ pressure $p=11.6$ Torr, gas flow rate at normal condition $V=1.5\text{cm}^3/\text{s}$ and external ionization power $W_{\text{ion}}=8$ W.

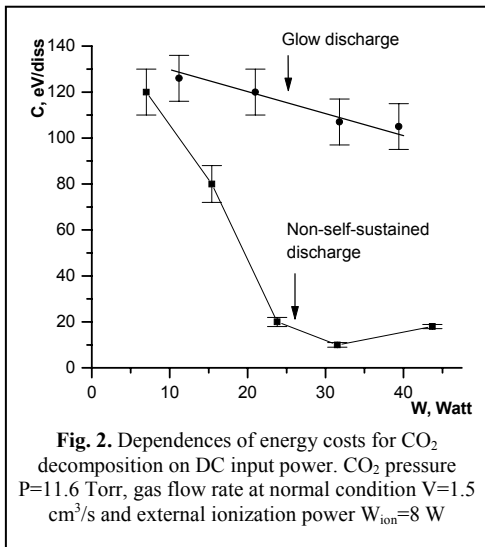


Fig. 2. Dependences of energy costs for CO₂ decomposition on DC input power. CO₂ pressure $P=11.6$ Torr, gas flow rate at normal condition $V=1.5$ cm³/s and external ionization power $W_{\text{ion}}=8$ W

longitudinal electrical field strength and N is the density of neutral plasma gas particles) is one of major parameters. This parameter determines mean energy of electrons in plasma and, accordingly, the energy balance of different degrees of freedom of the atomic and the molecular components in plasma. In turn, E/N depends on the type of a discharge and the kind of plasma gas. For self-sustained discharges, its magnitude is determined by a balance of formation and losses of charged particles in plasma and cannot be changed by external effect.

We provide a system on the basis of a non-self-sustained discharge with controlled parameters of electronic component of plasma for optimization of selective plasmachemical processes. Carbon dioxide decomposition in a non-self-sustained discharge was studied by the methods of diode laser spectroscopy and mass-spectrometry. Fig.1 shows the results of measurements by the methods of diode laser spectroscopy of gas and vibrational temperature T_3 in a non-self-sustained discharge at CO₂. In brackets the corresponding parameters E/N are indicated. In Fig.2 the dependences of the CO₂ dissociation cost from a DC input power for self-sustained and non-self-sustained discharges are represented. One can see that energy consumption on a dissociation of molecules CO₂ in a non-self-sustained discharge it is much less practically in all cases in conditions under investigation. It was shown that the effective control of the mechanism of a plasmachemical reaction is possible by varying the parameter E/N . This allowed us to reduce the energy cost of dissociation CO₂ by more than on an order of magnitude as compared to the dissociation process in a self-

sustained glow discharge.

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HIGH RESOLUTION TUNABLE DIODE LASER SPECTRUM OF OH GROUP SECOND OVERTONE IN ETHANOL

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We report here the high-resolution spectrum of OH second overtone ($\Delta V_{OH} = 3$) in ethanol using a tunable diode laser, a long path multipass cell with a maximum pathlength of 36 m and a solid state photodetector. The tunable diode laser absorption spectrometer set up is interfaced to a computer using labVIEW 6.0 for laser control, data acquisition and analysis. Tunable diode lasers with narrow radiation line allows realization of ultimate spectral resolution of linear spectroscopy. The use of multipass optical systems as sample holders provides longer pathlength and facilitates operation at low pressure and thus avoids broadening of spectral lines with better absorption. The spectrometer using a tunable diode laser in the range 936-976 nm with 0.01 nm tunability is advantageous to study the high resolution spectrum of the OH group absorption frequencies in all OH containing molecules in the transition in $\Delta V=3$ region [1]. The OH overtones of ethanol in this region was reported earlier by Fang et. al. [2] using intra cavity photoacoustic spectroscopy. They could obtain the OH overtones composed of two bands corresponds to the transitions of two conformers of the OH bond in the *trans* or *gauche* position with respect to the methyl group. The studies of integrated intensities of OH vibrational overtones in alcohols by Phillips et. al. [3] also reported the presence of these two conformers in ethanol. We could obtain the highly resolved spectra with P, Q and R branches of these two bands corresponding to *trans* and *gauche* conformers.

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**OPTIMAL PARAMETER FIT FOR BORN-OPPENHEIMER BREAKDOWN
OF CaH IN X²Σ⁺ STATE**

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A Dunham-like treatment of an effective Hamiltonian for diatomic molecules in ²Σ states that includes contributions of Born-Oppenheimer breakdown has yielded an expression for vibrational-rotational energy by an expansion in power series of $(v+1/2)^i [N(N+1)]^{j-k} (N'/2)^k$ (1), where N' denotes N or $-(N+1)$ for $J=N+1/2$ or $N-1/2$ spindoublet state, respectively, and $k = 0, 1, \dots, j$. The expansion coefficients Y_{ij0}^{*vJ} for $k=0$ terms are exactly the same as Y_{ij}^{*vN} coefficients given for ¹Σ states, the Dunham coefficients Y_{ij} modified by the contributions of Born-Oppenheimer breakdown. Therefore, applying the same treatment given in Ref (2), the coefficient Y_{ij0}^{*vJ} results in Y_{ij0}^* that is expressed with optimal parameters. Optimal parameters are determinable clusters of expansion coefficients of $Q_{a,b}(\xi)$, $R_{a,b}(\xi)$, and $S_{a,b}(\xi)$, *i.e.*, corrections of nonadiabatic vibrational, nonadiabatic rotational, and adiabatic effects of Born-Oppenheimer breakdown, respectively. These three effects are separately determined using functions for dipole moment and g value after Ogilvie (3).

Spin-rotation energy is given by the terms with coefficients Y_{ijk}^{*vJ} ($k \geq 1$) (1). There are no Y_{ijk}^{*vJ} ($k \geq 2$) terms in the previously known methods of analysis for ²Σ molecules. Corrections of Born-Oppenheimer breakdown for spin-rotation terms are also expressed in a formulation of Y_{ijk}^* ($k \geq 1$) terms with optimal parameters.

Infrared diode laser spectrum of $v=1-0$ band ⁴⁴CaH in natural abundance was observed using a spectrometer, Spectra Physics (Laser Analytics) SP5000, equipped with a nitrogencooled laser source L5736 and HgCdTe detectors L5913. ⁴⁴CaH was generated in discharged CaH₂ vapor at 1070 K. Combining spectral data reported for ⁴⁰CaH and ⁴⁰CaD, all spectral lines of three isotopomers were simultaneously analyzed with present method of analysis well within experimental errors.

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A MID-INFRARED LASER SPECTROMETER FOR THE *IN-SITU* MEASUREMENT OF STRATOSPHERIC NITROUS OXIDE

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The composition of the Earth's atmosphere is changing rapidly due to industrial and agricultural emissions. Nitrous oxide is a trace gas component of the atmosphere with a 120-year atmospheric residence time. It is an important atmospheric constituent with regard to atmospheric chemistry, because in the troposphere, N₂O acts as a greenhouse gas, with a radiative impact about 200-300 times that of CO₂ on a molecular basis, while in the stratosphere N₂O oxidation is the major source of NO_x radicals that play an important role in stratospheric ozone chemistry. The increasing abundance of nitrous oxide is therefore a long-term concern for the climate and, therefore, it becomes important to develop in-situ methods to understand its contribution to global budget. In order to characterise the spatial and temporal variations of N₂O in the upper troposphere and stratosphere we investigate vertical profiles from measurements of N₂O during aircraft flights. The system described here was designed as a subsystem of a composite airborne instruments package, devoted to the chemical and microphysical diagnostics of stratospheric aerosols and developed in the frame of the Airborne Platform for Earth-observation programme (APE). This Geophysica platform is the conversion of the former Russian high altitude reconnaissance aircraft Myasishchev M55 to the scientific investigation of the atmosphere at an altitude up to about 22 km. This payload is designed specifically to be installed in the unpressurised front bay of the Geophysica and N₂O profiles are measured during flights in the stratosphere performed in a mid-latitude and in a polar campaigns.

The spectrometer is based on a liquid nitrogen cooled lead-salt diode-laser, emitting at 2190 cm⁻¹. The detection technique is fast scan direct absorption. The instrument is divided into several pressurized compartments containing the optics, the computer for data processing and also the electronics. This is a prerequisite for a proper operation of the electronics, and on the other side to keep the liquid nitrogen boiling temperature constant. The laser beam from the dewar is spatially filtered by a field stop of 6 mm of diameter that rejects the high divergence part of the laser beam, and reduces the divergence and the beam is then refocused at a distance of 360 mm by a 18 mm focal length A/R coated ZnSe lens. The laser beam is splitted into two optical lines, where a fraction of the beam is used for frequency reference and calibration. The beam passes across a germanium etalon and a reference cell filled with a few mBar of N₂O, and then hits a Peltier cooled InSb detector. The position of the absorption line and the etalon fringes from a ZnSe etalon provide the necessary frequency calibration function. The main laser beam goes through a multipass cell and impinges on a HgCdTe detector located in the laser Dewar. The multipass cell is a commercial astigmatic Herriott cell, modified to improve mechanical stability, which provides an absorption path of 36 m with 182 passes between a pair of quasiconfocal, toroidal mirrors set at a distance of 20 cm. The air flux through the multipass cell is maintained by a pump. Under normal flight conditions the flow was more than 5 l/min, giving a sample clearance time of about 7 s. The detection scheme is based on a rapid sweep integration over the pressure broadened absorption line. This is achieved by scanning the laser diode emission wavelength and synchronously measuring the transmitted power. At a scan repetition frequency of 2 kHz the software averages 5000 scans and stores the averaged waveform in the computer memory. The transient digitiser input is multiplexed to three channels: one for the measurement signal, with a DC coupling and a gain level set to match the full dynamic range of the whole signal amplitude; the second again for the measurement channel but with an AC coupling and a higher gain to acquire spectral features with high resolution; the third channel is connected to the reference detector. The wavelength calibration curve is obtained from the reference spectrum considering the ZnSe etalon signal and the line absorption position. All signals are normalised with respect to the impinging power and a fit of the absorption features is made to determine the integral absorption. The concentration of the absorbing species is finally calculated for the recorded pressure and temperature of the sample. With this setup ambient stratospheric concentrations of around 100 ppbv can be well resolved with a time resolution of about 2.5 s. The system operates unattended for several hours experiencing strong mechanical vibrations under changing ambient conditions: during flight, the pressure is ranging from 1000 down to 30 mbar, temperature ranges from +70°C to -90°C. Typical flight measurements are performed at an altitude between 10 and 22 km and a cruising speed of 160–190 m/s.

NEW IMPROVEMENTS IN PHOTOACOUSTIC DETECTION OF METHANE

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The Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA, Reims, France) in collaboration with the Institute of Atmospheric Optics (IAO, Tomsk, Russia) has developed since 1997 a photoacoustic cell based on differential Helmholtz resonance for infrared gas detection [1,2]. 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 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 in [1,3] and the system has been improved significantly so as to increase sufficiently the sensitivity for sub-ppm methane detection. We will present here the major improvements and the most recent results obtained with a non-mechanical chopper.

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STAND-OFF ETHANOL SENSOR

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Alcohol detector was intended for remote detection of ethanol vapor inside the moving vehicles. The detector was based on tunable near infrared Diode Laser (DL) operating at room temperature and radiating at wavelength 1.392 μm near maximum of ethanol absorption band. Base scheme of measurements is following. Main part of the device including DL, optomechanics and photodetectors was installed on the one side of the road at the level of car windows. Radiation of DL passed through the side windows of a moving car, was reflected from the cube reflector, installed on the opposite side of the road, passed once more through the car enclosure and hit photodetector. Photodetector signal was processed in computer and special calculation procedure allowed determination of ethanol vapor content inside moving car. The ethanol detector was controlled by multifunctional 16-bit board (National Instruments, Inc), which was inserted into the PCI bus of computer. The program of the device controlling and data processing was written in LabVIEW-6.

Low-noise registration system and special techniques of laser driving and signal processing allowed achieving the minimum detectable absorbance of 10^{-5} of the incident laser power. Achieved sensitivity of remote detection of ethanol vapor inside a car was found to be 0.6 Pa*m for one measurement (2.6 ms). Thus the device allowed registration of ethanol vapor concentration of standard legal limit for car drivers (20 Pa partial pressure of ethanol, that is equivalent to 0.8 mg of alcohol in 1 ml of human blood). 20 - 100 readings could be made while car passed by the laser beam (depending on the car speed), and the results might be accumulated. Selectivity of ethanol measurements with respect to water was 50 to 1. It was sufficient for measurements of ethanol concentrations up to 5 Pa, while humidity changed at 20%. Selectivity of alcohol measurements with respect to such substances as CO, CO₂, acetone and gasoline was at least 10^4 to 1, because these substances have a rather weak absorption in the used wavelength range. Special techniques were used in the alcohol detector to make measurements insensitive to curvature and dirt on the surfaces of car windows, to variations of sunlight illumination and to device optomechanics vibrations. Field tests of the remote alcohol detector show its reliability for practical application. The measurements are fully automated and the Alcohol detector may function without an operator.

Some techniques (such as the way of the laser controlling and signal processing, the mode of the laser temperature stabilization with accuracy $2 \cdot 10^{-4}$ K), elaborated in the device may be useful for application in other spectroscopic devices based on diode lasers. Besides, absorption spectrum of ethanol consists of unresolved lines similar to spectra of complex organic molecules, so elaborated technique may be used for detection of substances with characteristic spectral features $\sim 5 \text{ cm}^{-1}$.

ANALYSIS OF TUNABLE DIODE LASER SPECTRA OF $^RQ(J,0)$ LINES IN CH_3F NEAR 1475 cm^{-1} USING A MULTI-SPECTRUM FITTING TECHNIQUE

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We have analyzed the methyl fluoride $^RQ(J,0)$ Q branch lines located near 1475 cm^{-1} using a simultaneous multi-spectrum fitting technique. In this analysis we have used previously recorded diode laser data in which we collected many data points covering only one or two Q branch lines in a particular run. The analysis consists of simultaneously fitting 57 spectra collected with numerous pressure and path length conditions for all absorption lines. The data are concatenated to create one continuous spectrum of the Q branch. We have determined the intensity and self-broadened widths at 294 K for 23 $^RQ(J,0)$ lines.

PosterSession E.

E1. NEAR-INFRARED WATER VAPOUR SENSOR USING AN EXTERNAL CAVITY DIODE LASER

H.J. Altmeyer, A. Abou-Zeid

E2. RAMAN FIBER AMPLIFIER AT 1.65 μm FOR REMOTE SENSING APPLICATION

*A.G.Berezin, O.N.Egorova, O.V.Ershov, A.S.Kurkov,
A.I.Nadezhdinskii, V.M.Paramonov*

E3. ADIABATIC RAPID PASSAGE AND OTHER NONLINEAR SPECTROSCOPIC EFFECTS IN THE SPECTRA OF NITRIC OXIDE AND METHANE AT 5 μm

G. Duxbury, James F. Kelly, Thomas A. Blake

E4. A COMPACT FIBER-OPTIC CO AND CO₂ SPECTROMETER: ANALYSIS OF NOISE, SENSITIVITY AND LINESHAPES

R. Engelbrecht, F. Kuntz, J. Euring, M. Krause, S. Neumann, L.-P. Schmidt.

E5. A PORTABLE DIODE LASER SPECTROMETER FOR ISOTOPE ANALYSIS IN CO₂

A. Castrillo, R.Q. Iannone, G. Casa, G. Gagliardi and L. Gianfrani

E6. FIRST RESULTS OF QUANTUM CASCADE LASER SPECTROSCOPY IN REIMS

*L. Joly, B. Parvitte, V. Zeninari, D. Weildmann, D. Courtois,
Y. Bonetti, T. Aellen, M. Beck, J. Faist, D. Hofstetter.*

E7. ESTIMATION OF FLUX ERRORS FOR H₂O&H₂¹⁸O OPEN PATH TDLAS ANALYZERS USING A SYNTHETIC REFERENCE

Gary Kidd

E8. FREQUENCY-DOUBLED EXTERNAL-CAVITY DIODE LASER FOR HIGH-RESOLUTION ULTRAVIOLET ABSORPTION SPECTROSCOPY

Toni Laurila and Rolf Hernberg

E9. ASSYST - ADVANCED LASER SENSOR SYSTEMS FOR LEADING EDGE MANUFACTURING

*V.Hopfe, P.A. Martin, R.J.Holdsworth, D.W.Sheel, P.Kaspersen,
P.K.de Bokx, P.Mackrodt, M.E.Pemble, A.Linton, F.Petzold*

E10. DIODE-LASER-BASED DOPPLER-FREE SPECTROSCOPY OF RARE EARTH ATOMS IN NIR AND NUV REGION

Hyunmin Park, Duck-hee Kwon, Yongho Cha, Jaemin Han and Yongjoo Rhee

E11. CAVITY ENHANCED AND POLARISATION STUDIES USING TUNABLE DIODE LASERS

G. Hancock, A. Hutchinson, R. Peverall, G. Ritchie

E12. INFLUENCE OF TEMPERATURE ON THE COLLISION BROADENING OF IR SPECTRAL LINES OF CO₂ MOLECULES

S.N. Andreev, V.N. Ochkin, S.Yu. Savinov

E13. A LABVIEW BASED AUTOMATED NEAR INFRARED TUNABLE DIODE LASER HIGH RESOLUTION SPECTROMETER FOR -OH SECOND OVERTONE DETECTION

S.Shaji, Shibu M Eapen, T.M.A.Rasheed and K.P.R.Nair

E14. DEVELOPMENT OF A STABILIZED LOW TEMPERATURE INFRARED ABSORPTION CELL FOR USE IN STANDARD LOW TEMPERATURE AND COLLISIONAL COOLING EXPERIMENTS.

Alain Valentin, Annie Henry, Christophe Claveau, Daniel Hurtmans, Arlan W. Mantz

E15. MEASUREMENT OF CH₄ CONCENTRATION IN THE STRATOSPHERE BY MEANS OF AN AIRBORNE NEAR-INFRARED DIODE LASER ANALYZER

F. D'Amato, M. De Rosa, P. Mazzinghi, M. Pantani, P.W. Werle

E16. OPTICALLY PUMPED LEAD-CHALCOGENIDE MID-INFRARED LASERS ON SI-SUBSTRATES

Klaus Kellermann, Karim Alchalabi, Dmitri Zimin, Hans Zogg

E17. SWITCHING MODE OF DIODE LASER OPERATION FOR TRACE MOLECULES ABSORPTION DETECTION

A.G.Berezin, O.V.Ershov, A.I.Nadezhdinskii.

E18. WAVELENGTH MODULATION AND DOUBLE MODULATION DIODE LASER ABSORPTION SPECTROMETRY – FOURIER SERIES DESCRIPTION AND APPLICATION TO TRACE ELEMENT ANALYSIS

Florian M. Schmidt, Regina Larsson, Jörgen Gustafsson, Pawel Kluczynski, Rui Guerra, and Ove Axner

NEAR-INFRARED WATER VAPOUR SENSOR USING AN EXTERNAL CAVITY DIODE LASER

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Tunable diode laser absorption spectroscopy (TDLAS) is a general-purpose technique for measuring concentrations of atmospheric trace gas species. In this work we use an external-cavity diode laser (ECDL) system in Littman-configuration to measure the water vapour abundance with the direct absorption method.

The ECDL operate in the near infrared spectral region between 1,3 μm and 1,4 μm and have a mode-hop-free tuning range of about 100 GHz. In the above-mentioned spectral window there exist several strong overtone water absorption lines (H_2^{16}O), which have no absorption interference due to other air constituents. The sensor employs an open two fold absorption path of 100 cm and the data acquisition of line shape were performed by scanning the laser over the water absorption line. To determine the moisture from the integral absorption, a least-square fit to Voigt-profile was applied, by using the line parameters from the updated HITRAN database, edition 2000. The room-temperature absorption measurements, which were conducted under normal laboratory environmental conditions, yields the partial water vapour pressure and the estimated relative measurement uncertainty is $\pm 0.5 \%$ with a scan rate of 50 Hz.

We have developed a near infrared diode laser hygrometer for in-situ measurements of water vapour. The measurements demonstrate the capability of ECDL system to provide fast and precise quantitative detection of water vapour. The first results will be presented and perspectives of this method will be discussed.

Preferred type of presentation: poster

Keywords: diode laser, absorption spectroscopy, water vapour

RAMAN FIBER AMPLIFIER AT 1.65 μm FOR REMOTE SENSING APPLICATION***A.G.Berezin, O.N.Egorova*, O.V.Ershov, A.S.Kurkov*, A.I.Nadezhdinskii, V.M.Paramonov*****Natural Sciences Center of A.M.Prokhorov General Physics Institute of Russian Academy of Sciences 119991 GSP-1 Vavilova st. 38, Moscow, Russia*** Fiber Optics Research Center of A.M.Prokhorov General Physics Institute of Russian Academy of Sciences 119991 GSP-1 Vavilova st. 38, Moscow, Russia*

Remote sensing of gas leaks from pipes with a help of helicopter-borne sensor using topographical target as a reflecting surface requires rather powerful laser radiation to have the returned laser pulse well above a detector noise. Normally spectroscopic diode lasers used for detection of trace molecule concentration have a power no more than few mW, which could be insufficient for detection from distances more than 50 m. In this paper an optical amplifier for 1.65 μm diode laser for methane detection is discussed.

It is well known that rare-earth doped fiber amplifiers do not cover the required spectral range. The widely used Er-and Er:Yb-doped lasers only operate in a range of 1.53-1.6 μm whereas Tm-doped lasers operate in the 1.8-2 μm interval. Therefore, Raman fiber amplifier seems to be a reasonable solution to develop an amplification for the 1.6-1.75 μm spectral interval.

Typically Ge-doped fibers are used as an active medium for Raman fiber amplifiers. Taking into account that a value of the Raman shift in such glass is of approximately 450 cm^{-1} , it is necessary to use a high power pump source emitting at 1.53 μm . One of the ways to construct such source consists in the application of the Raman conversion of a high power fiber laser. As for an initial pump source we used a semiconductor device providing a maximum power of 8.0 W at 978 nm from the fiber pigtail with a diameter of 100 μm . This source was used to pump the Yb-doped double-clad laser based on the polymer coated active fiber and two Bragg gratings centered at 1089 nm. A maximum power of 5.1 W at 1089 nm has been achieved. As for a medium of the Raman fiber converter we used a P-doped fiber with 250 m length. A P-doped fiber has a Stokes shift of 1330 cm^{-1} that is possible to simplify the converter scheme due to the reduction of cascade number. It is also possible to convert the radiation wavelength of an Yb-doped fiber laser to the output within a range of 1.47-1.6 μm using two stages of conversion. In contrast an applications of Ge-doped fibers requires 5-6 stages of the conversion. An application of this converter scheme allowed us to achieve an output power as high as 2.1 W at 1533 nm. That corresponds to a conversion efficiency of 40%.

Raman amplifier used a fiber with a high content of GeO_2 providing a gain of 10 dB/W·km. Pump power from the Raman converter and signal from the semiconductor source were coupled into amplifier using WDM. Maximum pump power coupled to the active medium was of 900 mW. Losses of the pump power are explained by a mismatch of the fiber mode field diameters. A maximum gain of 25 dB and an output power of 70 mW were measured.

Thus we have demonstrated the Raman amplifier at 1.65 μm with a gain of 25 dB. This value can be increased through an optimization of the Raman fiber parameters. It should be noted that this approach could be applied for any wavelength within a range 1.1 – 1.7 μm .

**ADIABATIC RAPID PASSAGE AND OTHER NONLINEAR SPECTROSCOPIC
EFFECTS IN THE SPECTRA OF NITRIC OXIDE AND METHANE AT 5 μm**

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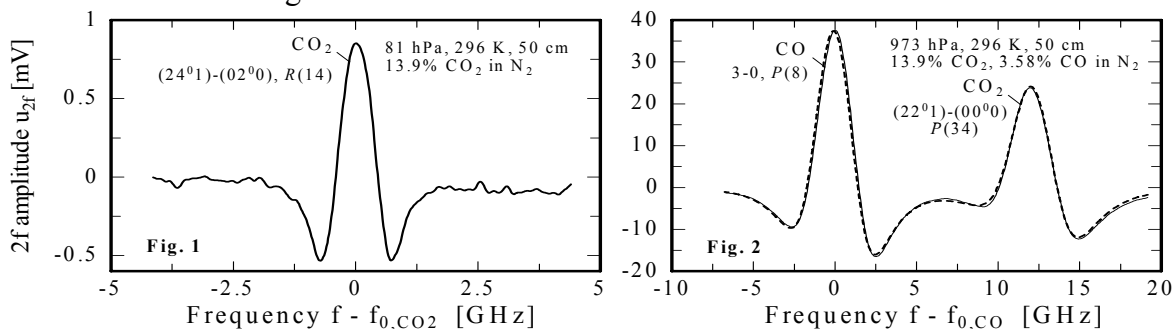
Following rapid passage experiments by McCulloch, Duxbury and Langford using a pulsed down-chirp quantum cascade laser spectrometer, we have extended the method by utilizing a novel system in which short red or blue frequency chirped pulses can be applied to specific molecular velocity classes across a Doppler broadened molecular absorption line.

The output from the QCL passes through either an astigmatic Herriott cell with an effective path length of approximately 100 m, and in parallel through a short reference cell. The molecules studied in this way have been nitric oxide and methane. We will describe a variety of nonlinear optical phenomena which can be explored in this way, including adiabatic following, electromagnetically induced absorption, Stark induced rapid adiabatic passage, and the Autler-Townes effect. The relationship between this selective probing of specific velocity groups of the Doppler broadened lines and the adiabatic passage experiments involving all velocity components will be described.

A COMPACT FIBER-OPTIC CO AND CO₂ SPECTROMETER: ANALYSIS OF NOISE, SENSITIVITY AND LINESHAPES

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We present a compact fiber-optic spectrometer for fast and quasi-simultaneous measurements of CO and CO₂ gas concentrations. A DFB diode laser at 1582 nm is used. At reduced pressures a pair of closely adjacent CO/CO₂ lines at 1581.95 nm with a line separation of 3.65 GHz is measured. A second line pair at 1583.05 nm with 12.24 GHz spacing is used at atmospheric pressures [1]. The laser frequency is swept periodically over one CO/CO₂ line pair at a maximum rate of 50 Hz by a current ramp. A $2f$ WMS modulation and lock-in detection scheme is superimposed. A modified balanced-receiver setup based on [2] is applied to suppress the intensity noise of the diode. All electronic and fiber-optic components are integrated alignment-free into a portable 19-inch modular housing. PM fibers guide the light to the measurement location and enable a remote operation of the spectrometer. Measured spectral noise power densities at the output of the balanced-receiver are only 6.7 dB above the calculated shot noise resulting from 4.3 mW of laser power both on the signal and on the reference photo diode. The practical sensitivity is mainly limited by residual etalons. A weak CO₂ line with a calculated absorption in the line center of $4 \cdot 10^{-5}$ was used to test the sensitivity (Fig.1). SNR is 21.6 with an effective system noise bandwidth of 8.3 Hz. Thus a detection limit of $6.4 \cdot 10^{-7}$ with an SNR of 1 at 1 Hz BW was derived. With the used lines, this equals a sensitivity limit of 5.1 ppm CO and 9.1 ppm CO₂ with 1 m absorption path at 80 hPa in air. At ambient pressure the sensitivity is worse roughly by a factor of seven. For calibration and interpretation of the $2f$ line shapes the static and dynamic laser intensity (IM) and frequency (FM) responses by current modulation were measured. With this results and HITRAN line data, a rigorous analytical model of the diode laser and all components was implemented for real-time line fitting on a PC. The phase shift of 21° between the sinusoidal IM and FM modulation responses has effects on the line shapes, especially on measurements at ambient pressure where larger modulation strengths are necessary. The excellent agreement of calculated (dashed) and measured (solid) line shapes (Fig.2) allows a stable and reliable concentration evaluation without recalibration when gas pressure or temperature changes. Our applications are development of high-power CO₂ gas lasers and environmental sensing.



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A PORTABLE DIODE LASER SPECTROMETER FOR ISOTOPE ANALYSIS IN CO₂

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Analysis of stable isotope abundance ratios represents a powerful tool in modern science as it provides important information, which are not accessible by measurements of gas concentrations or effluxes alone. Measurements of the $^{13}\text{CO}_2/^{12}\text{CO}_2$ ratio are of primary importance in ecology, to constrain the global atmospheric CO₂ budget, in biology, to study the metabolism in living systems, but also find relevant applications in atmospheric chemistry, medicine, geochemistry and volcanology. Particularly, in the last research field, the $^{13}\text{CO}_2/^{12}\text{CO}_2$ ratio gives indication on the sources from which volcanic gases are generated and its temporal variation may arise from changes in the status of a volcano.

Here, we report on our recent efforts, in the framework of an INGV (National Institute for Geophysics and Volcanology) project, aimed to develop a portable diode laser spectrometer for the accurate determination of the $^{13}\text{C}/^{12}\text{C}$ isotope ratio in volcanic CO₂ emissions. The spectrometer is based on the use of a DFB diode laser at a wavelength of 2.008 μm . In this spectral region, several line pairs can be found, some of them exhibiting ideal spectral features for this kind of application. Wavelength modulation spectroscopy, with 1st harmonic detection, is performed in order to detect absorption signals with high sensitivity in a pair of gas cells, simultaneously. The results of a wide variety of laboratory tests are illustrated, performed in CO₂ samples as well as in certified air mixtures, with different CO₂ mixing ratios. Precision levels between 0.1 and 1 ‰, in the $\delta^{13}\text{C}$ determination, are demonstrated, depending on the line pair and on the gas mixture.

FIRST RESULTS OF QUANTUM CASCADE LASER SPECTROSCOPY IN REIMS

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We report the first results obtained in Reims with a Distributed FeedBack Quantum Cascade Laser (DFB QCL) from Neuchâtel. This laser emits in 9.1 μm region.

First we report spectral linewidth measurements. The free running QCL beam was mixed with a waveguide isotopic C^{18}O_2 laser onto a high speed HgCdTe photomixer and beat notes were recorded from a radiofrequency spectral analyser. Beating was performed at two operating conditions, first near the QCL laser threshold (beating with the C^{18}O_2 R10 line), and second at a high injection current (beating with the C^{18}O_2 R8 line). Overall, beat note widths between 1.3 MHz and 6.5 MHz were observed. This proves a free running QCL short term spectral width near 1 MHz.

In a second part we report infrared spectra of sulfur dioxide recorded with this laser. The spectral region ranging from 1088 to 1091 cm^{-1} was studied. The SO_2 pressure varies from 1 to 10 Torr in a 20 cm long cell. A confocal Fabry Péroet interferometer is used for frequency calibration (free spectral range 0.01 cm^{-1}). To retrieve the absolute intensity of the line we apply a nonlinear least-squares fit to the molecular transmission using a Voigt-profile for the modeling of the line shape. The results of intensity measurements are compared to previous determinations and available databases.

ESTIMATION OF FLUX ERRORS FOR H₂O&H₂¹⁸O OPEN PATH TDLAS ANALYZERS USING A SYNTHETIC REFERENCE

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Mole fraction estimates from gas analyzers can be strong functions of temperature, pressure, extra gas mole fraction, and broadband noise processes, which cause variations in the mole fraction signal and limit the accuracy and resolution in gas flux estimates. For the eddy correlation technique, these variations lead to flux estimate errors when the vertical velocity and the mole fraction processes are correlated or uncorrelated. Theory and digital techniques used to minimize mole fraction variation and correlation with the mentioned error processes are presented along with simulation results. Mole fraction and error processes are correlated over a typical run time period to estimate correlation coefficients and flux errors. For open path gas analyzers, H₂O and H₂¹⁸O show strong lines in the 1.3 μm, 1.8 μm, 2.7 μm and 6.2 μm bands, however useful HITRAN lines for H₂¹⁸O are only defined for the 1.8 μm, 2.7 μm and 6.2 μm bands. A major drawback to open path analyzers has been line overlap from collision broadening and a higher density of interference lines in the 1.8 μm, 2.7 μm and 6.2 μm bands. This can be overcome for certain lines by interference line absorbance function synthesis and subtraction within the digital analysis methods. Useful HITRAN lines for H₂O have been identified in the 1.3 μm, 1.8 μm, 2.7 μm and 6.2 μm bands but the 1.3 μm band is preferred due to low cost detectors and telecom lasers and optics. For H₂¹⁸O, the 1.3 μm band is also preferred. The optimum HITRAN line for H₂O in the 1.3 μm band requires minimal interference correction while the optimum line for H₂¹⁸O requires strong interference line rejection. For completeness of error estimation, interfering lines were synthesized, added to the sample absorbance function and rejected as functions of temperature, pressure, extra gas and noise in a separate set of simulations and results are discussed. Results show minimal effect on mole fraction estimates by interference lines. For the temperature, pressure and extra gas and noise simulations, typically broadband noise dominates and the resulting power spectra are flat and the processes are uncorrelated. Mole fraction accuracy is linearly related to only pressure sensor accuracy. Typical resolution errors for H₂¹⁸O are 0.2 ‰ over a period of 100 seconds and flux ratio error of 3‰ in a half hour run. Mole fraction and flux accuracy and resolution errors are compared to those of other instruments and techniques.

FREQUENCY-DOUBLED EXTERNAL-CAVITY DIODE LASER FOR HIGH-RESOLUTION ULTRAVIOLET ABSORPTION SPECTROSCOPY

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Ultraviolet (UV) is an important region of the electromagnetic spectrum for atomic and molecular physics, because the resonance lines of most of the elements and several molecules lie in this region. In molecular spectroscopy ro-vibrational transitions lying in the infrared are usually used for quantitative analysis. However, in the UV electronic transitions are notably stronger. Light sources available for high-resolution spectroscopy in the UV are currently limited to element-specific discharge lamps and conventional solid-state, dye and gas lasers. Therefore, there is a growing need for compact, easily operable, tunable high-resolution UV light sources. As the shortest diode laser wavelength today is 370-375 nm, non-linear frequency conversion is still in many cases the only way by which the absorption wavelength range of interesting species can be reached using a diode laser. High sensitivity can be obtained due to diode lasers' capability for various modulation schemes.

In this work we present a frequency-doubled diode laser that has been developed for high-resolution absorption spectroscopy in the range 320-327 nm. The external cavity diode laser based on a transmission diffraction grating [1] provides the fundamental frequency at 650 nm. The line width of the fundamental beam is 4 MHz. The fundamental truly single-mode beam is frequency-doubled in a lithium iodate crystal. 60 nW cw output power in the UV has been obtained in a single-pass configuration. The UV beam can be tuned continuously over 40 GHz without mode hopping. The performance of the light source was demonstrated by measuring the absorption spectrum of the $4^2S_{1/2} - 4^2P_{3/2}$ transition of atomic copper at 325 nm. The tuning range was large enough to cover the 324.75 nm copper transition at atmospheric pressure with a single continuous scan. The copper spectrum was measured in various sources: a hollow cathode lamp, a flame and a direct current plasma of an on-line heavy metal analyser [2]. Contribution of different line broadening mechanisms to the copper line width was determined in each case.

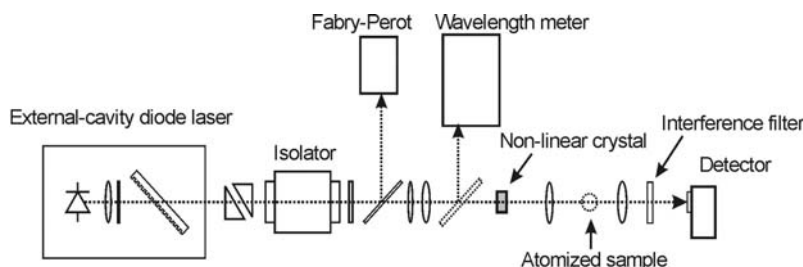


Fig. 1. Experimental setup

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**ASSYST - ADVANCED LASER SENSOR SYSTEMS FOR LEADING EDGE
MANUFACTURING**

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ASSYST is an EU Framework 5 project which targets the development of novel sensors to achieve next generation product quality and process control levels. Optical sensors based on tunable diode lasers in the near-infrared have clear advantages in many applications where, for instance, non-invasive, in-situ technique is required. It can also be the only industrial choice where reactive or corrosive gases are involved. Recent rapid developments in technologies critical to NIR-Diode Laser spectroscopy, mainly in the telecoms industry, and the emergence of potential new application areas have catalysed this project and hold out the potential for a step-change in spectroscopic monitoring. Five promising applications have been first selected. The partnership is well-balanced between equipment and technology developers and end users many having a large share in the market they operate in. 4 countries (including less favoured) and 5 innovative expanding SMEs are included. Details of the project will be presented.

**DIODE-LASER-BASED DOPPLER-FREE SPECTROSCOPY OF RARE EARTH ATOMS
IN NIR AND NUV REGION**

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For the last few decades, the atomic spectroscopic data on rare earth elements has been widely investigated experimentally and theoretically because they are very important in industrial and medical applications and they provide valuable information regarding the fundamental properties of the nucleus and the atom. However, in the NUV and NIR region, only a limited number of results have been reported due to the lack of tunable laser sources in the regions. Recently, the tunable diode lasers have been widely used in high resolution spectroscopy in NUV and NIR range because of their narrow linewidth, wide tunability and compactness. In this work, we conducted a high-resolution spectroscopy of rare-earth elements such as La, Sm, Yb, Er, and Dy in the 397-400nm and 635-690nm region by using a single-mode tunable diode laser. The oscillators of the diode laser are Littrow-type (UV region) and Littman-type(IR region) which enable the lasers to be operated in a single longitudinal mode and to be continuously tunable with minimum mode hops. The power of the diode laser was normally about 5mW and especially it was amplified to more than 500mW by using master-oscillator power-amplifier(MOPA) configurations in the wavelength region of 670-690nm. For atomic sources of rare earth elements, a hollow-cathode-lamp(HCL) was used for elements(La, Er, Dy) with a high melting point and a long vapor cell for elements(Yb, Sm) with a low melting point, respectively.

To obtain the Doppler-free spectra on the transition lines of above mentioned elements, we used a saturation absorption spectroscopy. Moreover, we adopted a polarization intermodulated excitation method (POLINEX) in order to decrease the velocity-changing-collision(VCC) effects which produce a Gaussian pedestal on the Lorentzian shape of a narrow spectral line. As experimental results, isotope shifts and hyperfine structures of many transition lines of rare earth elements were newly measured with a good resolution and were analyzed by using several methods. We expect that our results will be helpful for a theoretical consideration, such as multi-configuration Dirac-Fork calculation of the large mass atoms.

**CAVITY ENHANCED AND POLARISATION STUDIES USING
TUNABLE DIODE LASERS**

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A simple fibre based cavity enhanced diode laser spectrometer is described for the accurate measurement of isotope ratios in carbon dioxide. Radiation from a fibre pigtailed distributed feedback diode laser is coupled into a vacuum vessel containing a high finesse optical cavity. The cavity provides an effective optical pathlength of several km. The technique of cavity enhanced absorption spectroscopy is used to record the spectrum of a few Torr of CO₂ around 1.6 μm where there are adjacent ¹³CO₂ and ¹²CO₂ lines of similar strength for the naturally occurring ¹²C/¹³C ratio. The sensitivity of the technique allows the ratio to be measured with a precision that approaches that of the mass spectrometric gold standard, within a relatively short time.

Tunable diode laser systems have also been developed for the non-invasive interrogation of technical plasmas. In particular, Doppler free polarisation spectroscopy is demonstrated in a neon plasma, using single mode Fabry-Perot devices between 635 nm and 660 nm to probe excited states of neon. Spectral line widths as low as 50 MHz are observed for those transitions from metastable states (i.e. those transitions involving states with a long lifetime). The suitability of this technique for the elucidation of magnetic and electric fields within the plasma is investigated.

INFLUENCE OF TEMPERATURE ON THE COLLISION BROADENING OF IR SPECTRAL LINES OF CO₂ MOLECULES

S.N. Andreev, V.N. Ochkin, S.Yu. Savinov

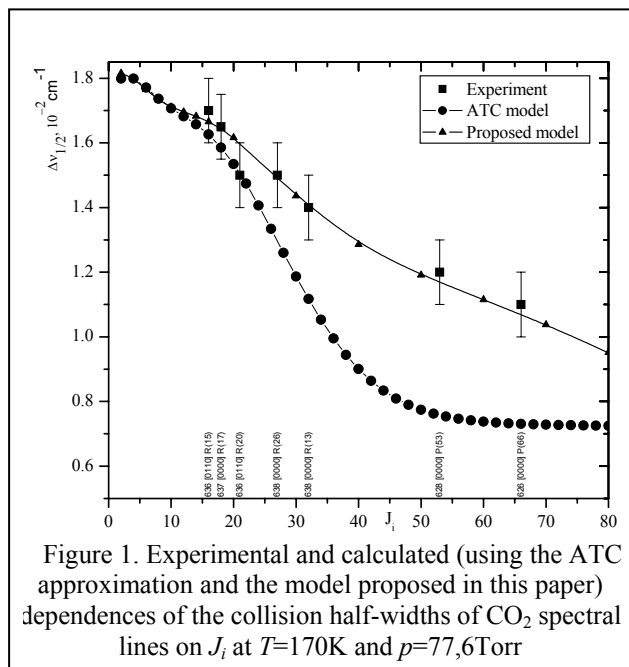
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CO₂ gas transmission at 4.5μ band (vibrational-rotational radiating transitions $V_1V_2^lV_3 \rightarrow V_1V_2^l(V_3 + 1)$) have been measured by means of tunable diode laser spectroscopy technique. On this base the IR linewidths of CO₂ molecules were obtained in wide field of a gas temperature (T) and rotational quantum numbers (J). It has been found that there are no existing semiclassical models of pressure broadened linewidths to describe satisfactorily our and other published experimental results.

A new cutoff-free semiclassical model of pressure broadening of rotation-vibration spectra in gases was provided. It corresponds to all experimental results quite well. The model takes into account:

1. trajectory bend of moving particles by intermolecular forces,
2. increasing of optical cross section for molecules with low relative energy of translation motion due to orbiting collisions.

It takes not so much computing time to calculate the impact broadened linewidths (only slightly more time than calculations by Anderson-Tsao-Curnutte theory). It enables us to compute the shape of IR spectral lines with correct averaging over a distribution of relative velocities. The



important role of particles collisions with low relative energy of translation motion E_μ ($E_\mu/\varepsilon < 0.8$, where ε is constant of Lennard-Jones intermolecular potential) even under room temperature has been shown. This role is increased essentially at lower temperature. In Figure 1 experimental dependence of the collision half-widths of CO₂ spectral lines on J_i at $T=170\text{K}$ and $p=77,6\text{Torr}$ is represented. The calculated results also displayed. One can see that discussed above model quite sufficiently fits experimental data. It has been found that commonly applied calculation scheme of average linewidths over a Maxwell-Boltzmann distribution of relative velocities can lead to systematic errors. The above features make our results attractive for its usage for determinations of exact linewidths in molecular infrared spectra.

The work was partially supported by Federal programs “Integration” (project A0133), “Optics, laser physics”, Sc.Progr. of RAS “Optical spectroscopy”, grant of the RFBR 02-02-81008, NATO research grant JSTC.CLG.978204.

A LABVIEW BASED AUTOMATED NEAR INFRARED TUNABLE DIODE LASER HIGH RESOLUTION SPECTROMETER FOR -OH SECOND OVERTONE DETECTION

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A tunable diode laser absorption spectrometer for high resolution –OH second overtone spectra is described in this paper. A Tunable diode laser operating between 936 nm – 976 nm with 0.01 nm tunability is used as the source, a multipass cell with an optimum pathlength of 36 m which can be used at low pressure and a high sensitivity solid state photodetector. Tunable diode lasers with narrow radiation line allows realization of ultimate spectral resolution of linear spectroscopy. In laser absorption spectroscopy, the absorption signal strength is proportional to the product of oscillator strength of the absorption transition and the number of molecules in the path of the laser beam. The use of multipass optical systems as sample holders provides longer path length and facilitates operation at low pressure and thus avoids broadening of spectral lines with better absorption. The control of the laser and data acquisition is done by interfacing the setup to a PC using Labview 6.0 software and the necessary hardware. The setup is calibrated using the absorption lines of water vapor from HITRAN 96 database [1, 2] and OH second overtone in methanol [3]. The spectrometer using a tunable diode laser with tunability range 936-976 nm is advantageous to study the spectrum of the OH group absorption frequencies in all OH containing molecules in the transition region $\Delta V = 3$. By using a detector with log output, the chopper and lock-in-amplifier can be avoided.

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DEVELOPMENT OF A STABILIZED LOW TEMPERATURE INFRARED ABSORPTION CELL FOR USE IN STANDARD LOW TEMPERATURE AND COLLISIONAL COOLING EXPERIMENTS.

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The feasibility of adapting the collisional cooling technique, originally described by De Lucia and co workers, see for example (1), using microwave transitions, to the study of infrared transitions utilizing tunable diode lasers was first demonstrated several years ago by Mantz and co workers (2). In an effort to improve the accuracy in the determination of spectral line parameters at temperatures as low as 7 K, we have constructed and tested a low temperature cell using the open cycle liquid helium technique. The cell has an absorption path of 16.8 cm. The temperature range over which this cell is actively temperature controlled is 200 K to 7 K. This is illustrated by spectra of carbon monoxide perturbed by argon or helium using the collisional cooling technique for the lowest temperatures. The temperature stability of the cell is better than 0.1 K. With this approach the temperature dependence of spectral line parameters can be accurately determined.

In these experiments we use an interferometer controlled multi beam tunable diode laser spectrometer developed at LPMA and recently modified to permit the simultaneous recording of analytical and reference spectra. The simultaneous recording of a reference spectrum with the analytical spectrum overcomes systematic effects coming from the instrument itself and gives the possibility to accurately measure the pressure shift and its temperature dependence. The line and instrumental parameters are determined by a multi-spectra fitting software which incorporates most of the recent line shape models. Results of simultaneous analyses are discussed by D. Hurtmans in an invited paper in which this multi spectral technique is thoroughly described.

In this poster we will provide a complete description of the cell and some line parameters determined for sample temperatures down to 7 K.

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MEASUREMENT OF CH₄ CONCENTRATION IN THE STRATOSPHERE BY MEANS OF AN AIRBORNE NEAR-INFRARED DIODE LASER ANALYZER

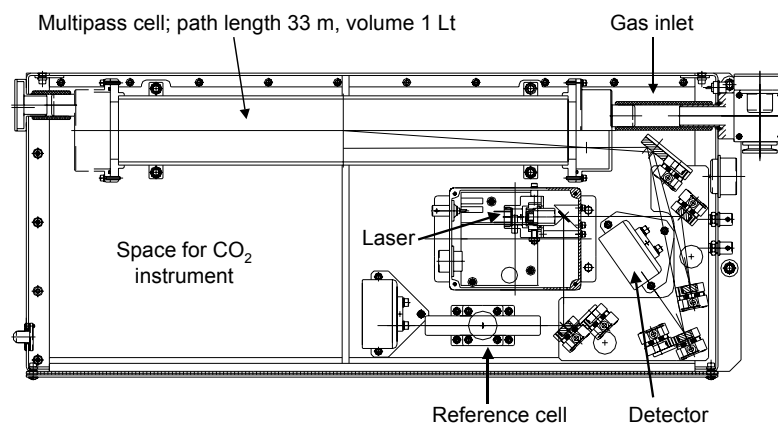
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We present the results of the measurements of CH₄ concentration performed in a mid-latitude and in a polar campaign on board of "Geophysica" stratospheric aircraft. The analyzer is based on a room temperature, distributed feedback laser emitting at the wavelength of 1.651 μm . The instrument is located in the bay in front of the rear left wheel of the aircraft. The air is sampled by a pipe pointing in the aircraft forward direction and is heated before entering the instrument. A computer driven valve closes the cell at altitudes lower than 5000 m. The instrument is divided into two parts, one containing the computer and the electronics, and the second containing the optics. The optical scheme is shown in the figure below. The laser beam is divided into two beams. One of them is sent across a reference cell, filled with pure methane, onto a reference germanium detector, used only for the active laser wavelength stabilization. The second beam interacts with air inside a Herriott-type multipass cell (SIT Mod. Aero-33) and is focalized onto a measurement detector (InGaAs-PIN). The detection technique is the two-tone frequency modulation spectroscopy. The temperature at the entrance and exit of the multipass cell is monitored by two sensors, as the reading is a function of temperature. The available space in the lower left corner will be used for an additional CO₂ measurement channel. In this case the multipass cell will be smaller and the reference arm will be missing. The laser frequency is scanned across the methane absorbing multiplet 20 times per second. Each acquired waveform is processed separately, and the final value is averaged in an on-line rolling average. The time resolution is 1 second. Every second the computer stores the instrument reading and the main operating parameters (laser current and temperature, air temperature and pressure etc.). The calibration of the analyzer with respect to pressure will be discussed as pressure effects the number of absorbing molecules and on the shape of the absorption curve. With our detection scheme, this latter feature has a significant influence on the reading.



OPTICALLY PUMPED LEAD-CHALCOGENIDE MID-INFRARED LASERS ON SI-SUBSTRATES

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PbSe double hetero (DH) and quantum well (QW) structures embedded in $\text{Pb}_{1-x}\text{Eu}_x\text{Se}$ and EuSe cladding layers are grown on Si(111)-substrates with the aid of CaF_2 buffer layers. They are employed for two types of optically pumped infrared emitters with wavelengths in the 3-6 μm range. As pump sources, low cost III-V laser-diodes with up to 7 W_p power and emitting between 800 and 1550 nm are employed.

a) PbSe/PbEuSe edge emitting DH and QW lasers:

Since the laser edge-mirrors can not be cleaved, dry processing techniques are used to etch grooves forming $\lambda/4$ Bragg mirrors. Reflectivities are up to 98%. With the limited pump power, we presently observe laser emission in the 3-5 μm range up to 250K. Output power is up to 150 mW_p , quantum efficiencies up to 10%, and characteristic temperatures T_0 up to >200K (at 870 nm pump wavelength). Note that the temperature tuning is as large as $3 \cdot 10^{-4}/\text{K}$ for IV-VI based emitters. In addition, if inhomogenous slightly wedge-shaped layers are grown, the emission wavelength may be tuned mechanically over a large range by just shifting the laser bar with respect to the pump source. Lenses may be used to focus the pump beam onto the IV-VI laser bar; or, even more simple, the emission face of the pump diode may just be arranged a few μm apart from the IV-VI laser bar without any lenses.

b) "Wavelength transformer" structure:

It consists of a VCSEL operated in sub-threshold and is used to down-convert the incoming light from the pump diode to e.g. 4.2 μm wavelength. The structure consists of an active $\lambda/2$ cavity layer containing PbSe QWs which emit according to the luminescence of the QWs and the cavity length. The cavity is embedded in a top and bottom Bragg mirror consisting of alternating $\lambda/4$ layers with high and low refraction index. Due to the high index contrast, only a few pairs are needed to obtain narrow line widths. The device operates at RT with a conversion efficiency of presently about 10^{-4} . The emission wavelength is determined by the length of the resonator, and the line width (10-250 nm) by the Q-factor of the cavity. Both can be tuned by design to fit, e.g., the absorption bands of important gases like CO, CO₂, CH₄ or H₂O for spectroscopic applications.

SWITCHING MODE OF DIODE LASER OPERATION FOR TRACE MOLECULES ABSORPTION DETECTION

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In gas analyzers developed in our Center, standard driving and data acquisition device was used. This device included one of standard multifunction electronic boards (National Instruments, Inc.) and three analogous electronic units: diode laser (DL) current supply, Thermister signal transformer and Peltier supply. First unit transmitted the board output voltage to the laser current. The multifunction board was installed into PCI bus of computer and was controlled by means of LabVIEW program.

There are various diode laser operation modes used for gas detection. To our opinion, optimum strategy is to perform single measurement as soon as possible (to get rid of flicker noise) and then to average signal readings. According to this strategy, short repetitive current pulses were used for DL operation. Waveform of each photo-detector signal pulse was separately recorded and processed and only then averaged over train of pulses. Computer program could generate any waveform of DL excitation current for each pulse in train.

Let us consider optimum time parameters for the DL pulse. Thermal processes in laser active area determine DL radiation properties. There are two characteristic times t_1 and t_2 . For $t < t_1 \approx 10 \mu\text{s}$ excess noise and instability of radiation will occur due to inhomogeneous temperature distribution in laser active area (random distribution of excitation current density together with inhomogeneous current carriers mobility). For $t > t_2 \approx 3 \text{ ms}$, long-term changes of laser contacts properties influence temperature distribution in laser active area that provide additional radiation instability. Hence, optimal time scale of DL waveform is between $10 \mu\text{s}$ and 1 ms . With this respect, for trace absorption detection we used data sampling time $5\text{-}15 \mu\text{s}$ and pulse duration $0.2\text{-}1.5 \text{ ms}$.

The waveform used for trace molecule detection is following. Excitation current consists of trapezium pulse and modulation part. Modulation period was equal to 2 data sampling times ($5 - 10 \mu\text{s}$). Recorded signal looked like two different data sets of odd and even signal points. This waveform looked like laser radiated "simultaneously" at two frequencies and these frequencies were tuned during laser pulse and corresponded to two data sets. Data processing of photo-detector signal included calculation of ratio logarithm of each two adjacent odd and even signal values that was proportional to difference of absorptions for two wavelengths. This way of data processing made final result insensitive to several disturbance factors of absorption detection: to background radiation variations, to optomechanics vibrations, to DL intensity variations being slow with respect to modulation period.

Development of described techniques is switching of the DL radiation between two laser modes with usual wavenumber shift $3 - 5 \text{ cm}^{-1}$. In this case modulation amplitude may be 2 - 4 times higher than DL threshold current. This DL operation mode is especially useful for detection of complex organic molecules with unresolved absorption spectrum. Described technique was successively applied for detection of ethanol vapors with $1.392 \mu\text{m}$ DL (Sensors Unlimited, Inc., USA) and for trace methane detection with $1.647 \mu\text{m}$ DL (Nolatech, Russia).

**WAVELENGTH MODULATION AND DOUBLE MODULATION DIODE LASER
ABSORPTION SPECTROMETRY – FOURIER SERIES DESCRIPTION AND
APPLICATION TO TRACE ELEMENT ANALYSIS**

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A powerful theoretical description of Wavelength Modulation Absorption Spectrometry (WMAS) and Double Modulation Absorption Spectrometry (DMAS) for detection of species in trace amounts/concentrations is given. The formalism is capable of giving a clear and comprehensible description of the contributions to the analytical and background signals for the two techniques. The description is given in terms of Fourier series, which implies that the measured harmonic components are expressed in terms of Fourier coefficients of wavelength modulated lineshape functions, intensity modulations, and the transmission in the optical system. It is shown how background signals can appear as a result of combinations of a laser intensity modulation and etalon effects. It is also shown why WMAS with frequency doubled light gives rise to significantly higher background signals than does ordinary WMAS.

An effective means to reduce background signals is to utilize double-modulation. A new DMAS technique that makes use of a simultaneous optically induced population modulation and ordinary wavelength modulation in order to reduce background signals from etalons is presented. The simultaneous population- and wavelength-modulation is achieved by splitting the light from a wavelength modulated diode laser into two beams; a strong pump beam and a weak probe beam, that subsequently are overlapped in the sample compartment. The pump beam, which is chopped, periodically transfers population from the state with which the weak probe beam interacts. The signal is measured at a frequency that is a combination of various harmonics of the wavelength modulation and chopping frequencies. The purely optical population modulation makes the new technique more generally applicable than other DMAS techniques.

Experiments were carried out on the 780 nm transition in Rb in a window-equipped graphite furnace (GF) used as an atomizer for aqueous solutions of Rb in ppt concentrations. The limit of detection obtained for the WMAS technique has previously been shown to be around 15 fg for an open GF and around a few hundred fg for a window-equipped GF. With the new DMAS technique applied to a window-equipped GF was more than an order of magnitude better than for the ordinary WMAS technique applied to the same type of window-equipped GF, i.e. 10 fg.

Part 4. Author Index

1	Abou-Zeid A.	129
2	Aellen T.	134
3	Ajili Lassaad	14
4	Alchalabi Karim	144
5	Alibert C.	50
6	Allen Mark G.	42, 109
7	Alnis Janis	63
8	Altmeyer H.J.	129
9	Amann M.C.	33
10	Anderson Benjamin	63
11	Andreev S.N.	120, 140
12	Aoaeh B.	126
13	Aroui H.	53
14	Avetisov Viacheslav	76
15	Axner Ove	146
16	Baer Doug	27
17	Bakhirkin Y.	28
18	Banyasz Joseph L.	66
19	Baranov A.N.	50, 70, 90
20	Baren Randall E.	80, 99
21	Bassi D.	82
22	Beck Mattias	14, 43, 134
23	Beere Harvey E.	11, 14
24	Belovolov M.I.	51
25	Beltram Fabio	11
26	Benner D. Chris	126
27	Benoit N.	61
28	Beresin A.G.	51, 71, 86, 91, 110, 125, 130, 145
29	Besson J-Ph.	52
30	Beyer Th.	72
31	Birza P.	97
32	Bjorøy Ove	76
33	Blake Thomas A.	131
34	Blanquet Gh.	53, 54, 55
35	Blaser Stéphane	43
36	Böhm R.	35
37	Bonetti Yargo	43, 44, 134
38	Boschetti A.	82
39	Bosler G.	105
40	Bouanich J.P.	53, 54
41	Boudon V.	61
42	Braun M.	72

43	Brenner K.	38
44	Burns I.	114
45	Camy-Peyret Claude	64
46	Cannon Bret	16
47	Casa G.	133
48	Castagnoli F.	123
49	Castrillo A.	133
50	Cerutti L.	50
51	Cha Yongho	138
52	Chiarugi Antonio	40
53	Chirokolava A.	97
54	Claveau Christophe	142
55	Courtois D.	124, 134
57	Crawford James	74
58	Curl R.F.	28
59	D'Amato Francesco	40, 123, 143
60	Davies Giles	11
61	Davies P.B.	100
62	De Bokx P.K.	137
63	De Rosa M.	123, 143
64	Demarchi G.	82
65	Deninger A.	35, 92
66	Devi V. malathy	126
67	Devolder P.	75
68	Dianov E.M.	51
69	Donegan John	103
70	Drumm J.O.	62
71	Dufour Gaëlle	64
72	Dumesh B.	83
73	Duraev V.P.	51
74	Durry G.	17, 90, 119
75	Dusanter S.	75
76	Duxbury G.	111, 131
77	Eapen Shibu M	121, 141
78	Eastman Lester F.	14
79	Ebert V.	73, 93
80	Egorova O.N.	130
81	Elsäßer W.	113
82	Emmenegger L.	112
83	Eng Jessica A.	94
84	Engelbrecht R.	132
85	Ermakov G.A.	71
86	Ershov O.V.	51,71,86, 91,110,125,130, 145
87	Euring J.	132
88	Faist Jérôme	14, 43, 134
89	Faloona Ian	74
90	Fejer Martin	21
91	Fernholz T.	93

92	Finardi Gabriele	40
93	Fischer H.	77
94	Fischer M.	32
95	Fogale Daniele	40
96	Fouckhardt H.	62
97	Fourzikov D.	83
98	Fried Alan	24, 74
99	Fuchs F.	77
100	Gagliardi G.	115, 133
101	Garnache A.	50
102	Gayral Bruno	22
103	Gensty T.	113
104	Genty F.	50
105	Gérard Yvan	59
106	Gianfrani L.	115, 133
107	Gicquel A.	81
108	Giesemann C.	73, 93
109	Giovannini Marcella	43
110	Gladyshev A.V.	51
111	Gobeille R.	126
112	Gorshunov N.	105
113	Gozzini S.	117
114	Graf Marcel	14
115	Grech P.	70, 90
116	Grigorev G.	105
117	Guerra Rui	146
118	Gupta Manish	27
119	Gurk C.	77
120	Gustafsson Jörgen	146
121	Han Jaemin	138
122	Hancock G.	95, 139
123	Hanoune B.	75
124	Hardwick John L.	94
125	Hartwig S.	72
126	Harward Charles N.	66, 80, 99
127	Hempel F.	81
128	Henry Annie	64, 142
129	Hernberg Rolf	57, 136
130	Hildebrandt Lars	34
131	Hoffmann G.	62
132	Hofstetter Daniel	14, 134
133	Högg Achim	36
134	Holdsworth Robert	59, 137
135	Hopfe V.	137
136	Hovde Chris	41
137	Hult J.	114
138	Hurtmans Daniel	20, 64, 142
139	Hutchinson A.	139

140	Hvozdar Lubos	43, 44
141	Iannone R.Q.	133
142	Iannotta S.	82
143	Jäger W.	118
144	Joly L.	119, 134
145	Jost Hans-Jürg	56
146	Kaenders W.	35, 92
147	Kaminski C.F.	114
148	Kapitanov V.A.	124
149	Kaspersen Peter	76, 137
150	Kasyutich V.L.	95
151	Kellermann Klaus	144
152	Kelly James F.	131
153	Kerstel E. R. Th.	115
154	Khoroshev D.	97
155	Khorsandi Alireza	65
156	Kidd Gary	135
157	Kluczynski Pawel	146
158	Knaak K.-M.	92
159	Koeth J.	32
160	Köhler Rüdiger	11
161	Koivikko H.	57
162	Kolodziejski N.	126
163	Kormann R.	77
164	Kosterev A.A.	28
165	Krause M.	132
166	Krier A.	96
167	Kudryashov E.A.	87
168	Kunsch Johannes	31
169	Kuntz F.	132
170	Kurkov A.S.	130
171	Kuryatov V.N.	71
172	Kwon Duck-hee	60, 138
173	Lackner Maximilian	33, 116
174	Lambrecht A.	72
175	Langford N.	111
176	Larsson Regina	146
177	Lauer C.	33
178	Laurila Toni	57, 136
179	Lee Kitae	60
180	Lee Seonkyung	109
181	Legge M.	32
182	Lemoine B.	75
183	Lengelé M.	55
184	Lepere Muriel	12, 54, 126
185	Lerot Ch.	54
186	Linfield Edmund H.	11, 14
187	Linnartz H.	58, 78, 97

188	Linnerud Ivar	76
189	Linton A.	137
190	Lombardi G.	81
191	Lucchesini A.	117
192	Lynch Michael	103
193	Blank space	
194	Mackrodt P.	137
195	Maier J.P.	78, 97
196	Mann C.	77
197	Mantz Arlan W.	126, 142
198	Markus Michael W.	47
199	Martin Philip	59, 137
200	Mazzinghi P.	123, 143
201	McCann Patrick J.	39
202	McCulloch M.T.	111
203	McKellar A.R. W.	9, 83
204	McManus J. Barry	44, 85, 104
205	McMichael W.	126
206	Mechold Lars	37
207	Medvedkov O.I.	51
208	Mohn J.	112
209	Möller I.	101
210	Monakhov A.	96
211	Motylewski T.	97
212	Muller Antoine	43, 44
213	Müller-Wirts Th.	92
214	Myers Tanya	16
215	Nabiev Sh.	105
216	Nadezhdinskii A.I.	51, 67, 71, 79, 86, 87, 91, 105, 106, 110, 125, 130, 145
217	Nair K.P.R.	121, 141
218	Nam Sungmo	60
219	Nedelin E.T.	51
220	Nelson David D.	44, 85, 98, 104
221	Neumann S.	132
222	Niemax Kay	25
223	Nikles M.	13
224	O'Keefe Anthony	27
225	Ochkin V.N.	120, 140
226	Ohashi Nobukimi	10
227	Olsen R.	105
228	Ortsiefer M.	33
229	Osthoff H.D.	118
230	Ouvrard A.	50
231	Owano Tom	27
232	Paci Paolo	85
233	Paige Mark	41
234	Pantani M.	123, 143

235	Paramonov V.M.	130
236	Park Hyunmin	60, 138
237	Parrish Milton E.	66, 80, 99
238	Parvitte B.	23, 90, 119, 124, 134
239	Pemble M.E.	137
240	Perona A.	70, 90
241	Peter A.	72
242	Petzold F.	137
243	Peverall R.	95, 139
244	Pfaff Th.	72
245	Phelan Richard	103
246	Pleban Kai-Uwe	46
247	Plunkett Susan E.	66
248	Podolske James R.	56
249	Poggi P.	123
250	Ponomarev Yu. N.	15, 124
251	Ponurovskii Ya.Ya.	67, 87, 105, 106, 110
252	Potter William	74
253	Pouchet I.	119
254	Raballand W.	61
255	Rasheed T.M.A.	121, 141
256	Razumov L.N.	71
257	Reimann B.	38
258	Rhee Yongjoo	60, 138
259	Ricci L.	82
260	Richter Dirk	24, 74
261	Ritchie David A.	11, 14
262	Ritchie G.A.D.	95, 139
263	Robert P.	13, 52
264	Roller C.	28
265	Romanini Daniele	26
266	Röpcke Jürgen	19, 81, 100
267	Rossi A.	82
268	Roskopf J.	33
269	Rotger M.	61
270	Rouillard Y.	50
271	Rudov S.G.	86
272	Ryjikov V.	105
273	Saathoff H.	73
274	Salem J.	53
275	Salhi A.	50
276	Sauke Todd R.	56
277	Savinov S.Yu.	120, 140
278	Scalari Giacomo	14
279	Schade Wolfgang	65
280	Schaff William J.	14
281	Blank space	
282	Schilt S.	13, 52, 70

283	Schmidt Florian M.	146
284	Schmidt L.-P.	132
285	Schukin E.N.	71
286	Schurath U.	73
287	Schwender C.	62
288	Scotoni M.	82
289	Selivanov Yu.	105
290	Serdioutchenko A.	101
291	Seufert J.	32
292	Shafer Kenneth H.	66, 80
293	Shaji S.	121, 141
294	Shapovalov Yu.P.	86, 91, 125
295	Shau R.	33
296	Sheel D.W.	137
297	Sherstnev V.V.	96
298	Shorter Joanne H.	85, 104
299	Shubenkina T.A.	86
300	Silver Joel	41
301	Sjöholm Mikael	63
302	Smith M. A. H.	126
303	Soltwisch H.	101
304	Somesfalean Gabriel	63
305	Sonnenfroh David M.	109
306	Spiridonov M.V.	67, 87, 106
307	Stancu G.D.	81, 100
308	Stavrovskii D.B.	86, 125
309	Surin L.	83
310	Svanberg Sune	63
311	Tang Jian	83
312	Taubman, Matthew	16
313	Teichert H.	73, 93
314	Teissier R.	50
315	Thévenaz L.	13, 52, 70
316	Thomas Daniel W.	102
317	Tittel F.K.	28
318	Totschnig Gerhard	33, 116
319	Tredicucci Alessandro	11
320	Uehara Hiromichi	122
321	Valentin Alain	64, 142
322	Van Burgel M.	115
323	Van Wijngaarden W.A.	118
324	Vannuffelen Stéphane	22
325	Vasiliev S.A.	51
326	Verdes D.	58, 78
327	Vicet A.	50, 70, 90
328	Vogelgesang B.	62
329	Votava Ondrej	84
330	Walega James G.	24, 74

331	Walls J.	118
332	Walrand J.	53, 54, 55
333	Weidmann D.	28
334	Weildmann D.	134
335	Weldon Vincent	103
336	Werle P.W.	123, 143
337	Werner R.	32
338	Wert Bryan	74
339	Wilkinson K.	126
340	Willer Ulrike	65
341	Williams Richard M.	16
342	Wilson H. William	56
343	Winnewisser G.	83
344	Winter Franz	33, 116
345	Wolf Erich N.	94
346	Wolfrum J.	93
347	Wormhoudt J.	104
348	Wright D.A.	96
349	Wu Hong	14
350	Wyslouzil Barbara	85
351	Zahniser Mark S.	18, 44, 85, 104
352	Zakharov V.V.	120
353	Zeninari V.	90, 119, 124, 134
354	Zhiguo Zhang	63
355	Zimin Dmitri	144
356	Zogg Hans	144
357	Zvinevich Yury	85