



ABSTRACTS OF PAPERS

**3rd International Conference on
Tunable Diode Laser Spectroscopy**

July 8 - 12 2001

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Zermatt, Switzerland

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Conference Schedule

Sunday, July 8 2001

17:00 - 19:00 Registration

21:00 - 23:00 Registration

Monday, July 9 2001

08:00 - 13:00 Registration

09:00 - 12:15 Plenary session.

09:00 - 09:30 Opening

09:30 - 10:15 Invited lecture (Ronald Hanson)

10:15 - 11:00 Invited lecture (Claire Gmachl)

11:00 - 11:30 Coffee break

11:30 - 12:15 Invited lecture (Jan Peter Toennies)

Lunch

14:00 - 15:30 Plenary session.

14:00 - 14:45 Invited lecture (Maxim Spiridonov)

14:45 - 15:30 Invited lecture (Jerome Faist)

15:30 - 16:00 Coffee break

16:00 - 18:00 Poster session A

18:00 Welcoming reception

Tuesday, July 10 2001

9:00 - 11:45 Plenary session.

9:00 - 9:45 Invited lecture (Andrei Berezin)

9:45 - 10:30 Invited lecture (Thomas Giesen)

10:30 - 11:00 Coffee break

11:00 - 11:45 Invited lecture (Claude Alibert)

Lunch

Tour of the Goernergrat Observatory

17:00 - 19:00 Poster session B

20:00 - Conference banquet

Wednesday, July 11 2001

9:00 - 11:45 Plenary session.

9:00 - 9:45 Invited lecture (Carlo Sirtori)

9:45 - 10:30 Invited lecture (Harold Linnartz)

10:30 - 11:00 Coffee break

11:00 - 11:45 Invited lecture (Haruo Nagai)

Lunch

13:30 - 15:30 Poster session C

15:30 - 16:00 Coffee break

16:00 - 18:00 Poster session D

Thursday, July 12 2001

9:00 - 11:45 Plenary session.

9:00 - 9:45 Invited lecture (Yuri Selivanov)

9:45 - 10:30 Invited lecture (Trevor Sears)

10:30 - 11:00 Coffee break

11:00 - 11:45 Closing remarks

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Part I
Invited Lectures

DIODE LASERS FOR COMBUSTION SENSING AND CONTROL

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Continued improvements in availability and reliability of tunable near-IR lasers, particularly room temperature, cw semiconductor diode lasers, have revolutionized capabilities for *in situ* measurements of critical engineering quantities in hostile environments such as combustion and propulsion systems. Quantities of primary interest include species concentrations, gas temperature, pressure and velocity, all of which can be measured by line-of-sight spectrally resolved absorption using rapid-scanning diode laser sources. Diagnostics providing such measurement capability have high value in both research and development of advanced combustion systems, and also as fast-response sensors in a new generation of combustion control strategies. In the present paper, we provide representative results from three recent applications of diode laser absorption to combustion sensing and control: high-sensitivity (sub-ppm) monitoring of CO (a regulated pollutant) at a combustor exhaust, using FM detection of 2.3-micron diode laser light; development of a wavelength-multiplexed (up to five wavelengths) diode laser sensor for continuous measurements of temperature and water vapor concentration in an advanced propulsion system known as a pulse detonation engine (PDE), typically using diode lasers at wavelengths of 1.3-1.4, 1.5-1.6 and 1.65 microns; and application of a fast diode laser sensor (for temperature, water concentration and pollutant emissions such as CO, methane and ethylene) for near-real-time control of a compact forced-combustion incinerator with low exhaust emissions.

RECENT ADVANCES IN InP-BASED QUANTUM CASCADE LASERS AND APPLICATIONS

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Quantum cascade (QC) lasers have reached very high levels of performance, such as emission wavelengths ranging from 3 to 24 μm , very high peak output power levels in the Watt range, and above room temperature operation. As a result, new interest is directed towards the investigation and optimization of more complex device properties such as the lasers' high-speed properties and more sophisticated designs fulfilling more complex tasks, such as selective multiple-wavelength operation.

Here we focus first on improved QC lasers fabricated with chalcogenide lateral waveguide claddings. Several-micrometer thick $\text{Ge}_{0.25}\text{Se}_{0.75}$ glass has been deposited by pulsed laser ablation onto the side walls of narrow, deep etched laser ridges. The intrinsically low mid-infrared attenuation of the chalcogenide material helped reduce the waveguide loss of the lasers significantly, by up to $\sim 50\%$, when compared to conventional ridge waveguides. This resulted in an improved overall laser performance, such as a reduction of the threshold current density, an increase in slope efficiency, and an improved temperature performance. The thick chalcogenide cladding and burying layer also significantly reduced stray capacitance of the devices and improved their high-speed modulation properties.

Second, we present a QC-laser with a heterogeneous cascade containing two QC-laser sub-stacks previously optimized to emit at 5.2 μm and 8.0 μm wavelength, respectively. Devices with a heterogeneous cascade are the most recent example for QC-lasers designed to perform specialized tasks, such as multiple wavelength operation. The low-temperature performance of the two-wavelength laser is comparable to the respective homogeneous stack lasers, indicating no penalty from the heterogeneity of the cascade. The structure is furthermore "self-aligning" under an applied bias; i.e. each sub-stack is apportioned the optimum fraction of the applied bias. This demonstrates the general applicability of the new scheme. In addition, an etch-stop layer inserted between the two sub-stacks allowed fabrication of a "tap" into the cascade. The latter was used to selectively manipulate the laser threshold of one sub-stack, turning the 8.0 μm laser on and off while the conjoined 5.2 μm QC-laser was operating undisturbed.

The lasers' high-speed capabilities have been exploited for their active and passive mode-locking. In both cases, pulses as short as a few (3-5) picoseconds with a repetition rate around 12 GHz, the round-trip frequency of the lasers have been measured. These lasers may find use in time-resolved spectroscopy in the mid-infrared wavelength range and free-space optical wireless applications.

Finally, we will shortly discuss the characterization and stabilization of ultra-narrow linewidth QC-lasers, an ongoing collaboration with R. Williams et al. from Pacific Northwest National Labs.

HIGH RESOLUTION SPECTROSCOPY OF MOLECULES AND CLUSTERS IN SUPERFLUID HELIUM-FOUR DROPLETS

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Helium clusters are the only clusters which are definitely liquid and, since they are superfluid, exhibit unusual properties. Large droplets with $10^3 - 10^4$ atoms are readily produced in nozzle beam expansions of the cold gas. Their mean sizes, size distributions and densities have all been measured. On passing through a gas filled pick-up cell they readily absorb one or several molecules or mixtures of atoms and molecules. Heliophobic species such as the open shell alkali atoms and the alkaline earth atoms remain at the surface, whereas closed shell atoms and molecules, which are heliophilic, reside in the interior of the droplets where they may agglomerate to form complexes. A large number of embedded heliophilic molecules and van der Waals complexes have now been probed in the infra-red (IR), visible and UV by observing either laser induced fluorescence or the depletion in droplet size resulting from the evaporation following photon absorption. In most cases sharp spectral features with line widths of ≈ 100 MHz have been observed [1].

In the vibronic spectra of organic molecules the phonon wing is separated by a gap from the sharp zero phonon lines thereby providing direct evidence that the droplets are superfluid [1]. The well resolved IR rotational lines indicate, moreover, that the molecules rotate virtually without friction while retaining the same symmetry as the free molecules. The rotational line intensities indicate droplet temperatures of 0.37 K for pure ^4He droplets and 0.15 K for pure ^3He droplets as well as for mixed $^4\text{He}/^3\text{He}$ droplets with an inner ^4He cluster core. The free rotations of the embedded molecules have been shown to be a new manifestation of superfluidity [2]. These experiments demonstrate that He provides the coldest and gentlest spectroscopic matrix.

With this technique the spectra of over 30 different molecules ranging from small molecules such as OCS to large molecules such as C_{60} , and the amino acids tryptophan and tyrosine have been studied either in the visible or in the infra-red [1]. It has even been possible to observe an exothermic chemiluminescent reaction between Ba and N_2O via sharp emission lines of BaO molecules in the interior of the droplets [3]. Large Ag clusters with up to about 100 atoms have been formed. HCN and HCCCN clusters exhibit unexpected linear structures with up to about 10 molecules in a line not seen in the gas phase [4]. Recently taylor made clusters have been used to search for superfluidity in para-hydrogen (pH_2). OCS- $(\text{pH}_2)_N$ clusters with $N = 1-17$ were created by adding successively increasing numbers of molecules and from the resolved IR spectra the rotational constants for each N could be determined. For $N \geq 11$ the spectra change on cooling from 0,37 K (pure ^4He droplets) to 0,15 K (mixed droplets) in a manner consistent with the transition to a superfluid state of the pH_2 molecules [5].

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PRECISION LINESHAPE MEASUREMENTS USING NEAR-IR DIODE LASERS

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Spectrometers based on tunable diode lasers are the most precise devices to study the shapes of absorption lines. At the present time the absorption line shape can be recorded with 0.5 - 1% accuracy using diode laser spectrometers.

On the other hand, various fine effects of intermolecular interactions have influence on the line shape at the level of less than 1%, thus experimental studies of these effects require the accuracy of line shape measurements as good as 0.1 - 0.2%.

We can outline several factors having essential influence on the accuracy of spectral line shape registration:

- measurement of optical zero level;
- measurement of total transmission level (baseline);
- calibration and linearization of the diode laser tuning frequency scale;
- frequency and intensity fluctuations of a diode laser radiation.

We will consider in details influence of these factors on the accuracy of spectral line shape measurements. Besides, we will demonstrate that taking into account these factors and the diode laser instrumental function can improve significantly the accuracy of spectral line shape registration.

BOUND-TO-CONTINUUM QUANTUM CASCADE LASERS FOR CHEMICAL SENSING

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University of Neuchâtel

The quantum cascade laser [1] is now maturing as a technological device for both physics and applications. This semiconductor laser does not rely on transitions between conduction band electron and valence band holes, but is based on inter-subband transition in quantum wells. For this reason, it allows design of lasers of widely different wavelengths from the same heterostructure material. So far, lasers between 3.4 and 19 μm wavelengths have been realized in the InGaAs/AlInAs heterostructure material grown on InP.

The atomic-like nature of the intersubband transition and the inherent flexibility that modern growth techniques such as molecular beam epitaxy offers enables the fabrication of electronic potentials with an almost arbitrary shape. This, in turn, has spurred the development of a whole zoology of quantum cascade laser designs: from structures based on a single quantum well to ones based on finite superlattices incorporating six or more wells, these structures have in common the advantages inherent to design based on a cascade of intersubband transition that are high optical output power and room temperature operation. Because of these excellent performance levels, these devices have attracted great interest from the sensor community for their application in high sensitivity, low cost portable chemical sensors based on optical techniques.

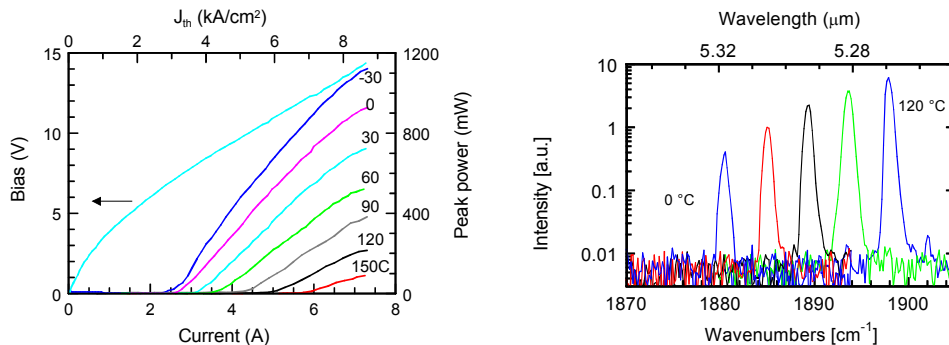


Fig.1 a) High temperature light versus current characteristics of a bound-to-continuum QC laser. b) Tunable emission from a single-mode DFB QC laser

We will discuss here the recent developments in this research area, including the work accomplished in the University of Neuchâtel. The latter includes the development of designs based on bound-to-continuum and resonant two phonon emissions. Using such approaches, record performances were achieved, such as operation with 100mW peak power up to a temperature of 150C, 0.8W single mode peak output power at room temperature and a wavelength of 5.3 μm . Finally, the reduction of threshold current density allowed us to operate for the first time a QC laser device in continuous wave on a Peltier element at -30C.

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TRACE GAS DETECTION WITH NEAR INFRARED DIODE LASERS

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The report is a review of recent results obtained at Diode Laser Department of Natural Sciences Center of GPI, aimed at reaching high sensitivity in trace molecular detection by means of near infrared diode lasers (NIR DL) spectroscopy.

Although strong fundamental absorption lines of most gases are located in mid infrared region (3 – 40 μm), this region is still inconvenient for routine devices. Commercially available mid IR DL and detectors require deep cooling and that is a serious drawback for a potential user. NIR DL (0,7 – 2,0 μm) can operate at room temperatures, but this region covers only overtones and combination bands, which are sometimes several orders of magnitude less absorbing. To reach high sensitivity with NIR DL one has to use longer optical path (for example, multipass cell) and has to learn to detect very weak absorption lines. The last approach seems more attractive than to use deep cooling and the report is dedicated to analysis of restriction for obtaining better sensitivity, having technical and physical origin.

The approach for detection of weak absorption lines depends on the relationship between the spectral width of the absorption line (or some spectral peculiarity, in more general case), chosen for the detection, and the diode laser tuning range. Typical value for most convenient current tuning of solitary DL is few cm^{-1} .

In the case of simple molecules, having spectra resolved into narrow separate lines with FWHM of 0.1 cm^{-1} , and even less at lowered pressure, the main restrictions are laser noise and etalon fringes. Among technical restrictions the noise caused by the limited bit value of analogue-to-digital converter used for data acquisition and even digital-to-analogue converter used for DL control may be significant. The strategy for sensitive detection of narrow lines is in the choice of optimum frequency modulation (or scan rate in case of pulsed technique) and bandwidth of detector signal amplification. Realization of the above approach resulted in the development of mobile Fabry-Perot DL spectrometer with short-term sensitivity for methane 10 ppb in open atmosphere (corresponding to $3 \cdot 10^{-5}$ line absorption).

Detection of complex molecules with unresolved spectra by means of DL spectroscopy is also possible, but more difficult. In this case the tuning range of DL is compared or even less than the peculiarity in the molecular spectra. Main restrictions, apart from mentioned above, are: changes in laser diagram direction during frequency during laser scan, long term instability of laser parameters, interference from overlapping absorption lines of other gases. Various techniques to overcome these difficulties, such as mode hopping for increasing tuning range, high frequency modulation and others are discussed. It has been shown that complex molecules, with change in intensity as small as 10^{-4} within laser scan, could be detected. The technique was applied to the detection of Ethanol in the air, and sensitivity 5 Pa at the optical path of 3 m was achieved.

HIGH RESOLUTION IR-SPECTROSCOPY OF SMALL CARBON CLUSTERS

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The molecular structure of carbon clusters and their formation processes are of increasing interest ever since the discovery of the magic number cluster C_{60} in 1985 by Kroto *et al.* This continued attention to research on carbon clusters stems from the fact that answers to some fundamental and long standing problems in astrophysics and other fields of molecular physics can be found, once the detailed spectroscopic properties are understood. Remarkable progress has been made in recent years in both theoretical interpretation and experimental techniques in producing and sensitively measuring the different carbon clusters. For cluster sizes up to 20 carbon atoms *ab initio* calculations predict two structures to be most stable, a linear form for small clusters and a cyclic form for the larger ones.

Spectroscopic studies with the aim of deriving the structures of carbon clusters have been commenced (for a review see Weltner *et al.* 1989 and Van Orden *et al.* 1998). Due to the zero permanent dipole moment of pure carbon clusters, no pure rotational spectra can be observed. They can, however, be studied by rotationally resolved IR tunable diode laser spectroscopy which in some cases even allows a detailed analysis of the molecular fine structure.

We present our ongoing efforts concerning the production, measurement, and assignment of small carbon clusters by using a IR tunable diode laser spectrometer combined with an intense supersonic jet of cold carbon clusters.

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GAS ANALYSIS USING ROOM TEMPERATURE DIODE LASERS IN THE 2-2.5 MICRON RANGE

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The wavelength range between 2.2 and 2.4 μm is of great interest for molecular spectroscopy and environmental monitoring. In this spectral region the water vapor absorption is very weak while absorption lines of some atmospheric pollutants are very strong. One of the most sensitive techniques for selective gas analysis is Tunable Diode Laser Absorption Spectroscopy (TDLAS). To reduce the cost and dimensions of the equipment single frequency diode lasers operating in continuous wave (cw) regime at room temperature or above are required.

In this contribution we summarize the results obtained at the University of Montpellier in collaboration with Thales LCR in the development of GaSb-based quantum well (QW) diode lasers and their applications for trace gas detection.

The laser structures were grown by molecular beam epitaxy on GaSb substrates. The active zone of the lasers consists of several GaInSbAs quantum wells containing 10-20% of arsenic and 20-40% of indium. The composition of barrier layers varied between GaSb and $\text{Ga}_{0.2}\text{Al}_{0.8}\text{SbAs}$ resulting in a type-II band alignment with the QW in the first case and type-I QW structures when the Al concentration in the barriers exceeds 20%. The type-II structures are easier to grow, they can provide, in principle, longer wavelengths emission but it is (was) not evident to obtain lasing with such kind of the band alignment because of small efficiency of radiative recombination. The type-I structures exhibit very efficient radiative recombination, excellent carrier confinement can be achieved in the GaInSbAs QW with GaAlSbAs barriers, which is promising to obtain high temperature operation of lasers.

The type-I and type-II laser structures were grown and processed to narrow ridge index guided Fabry-Perot lasers that were investigated from the point of view of their use for gas detection. Both kinds of devices operated in continuous wave regime at RT emitting up to 50 mW of optical power per facet, the threshold current being as low as 20 mA for 400-500- μm -long lasers. The internal quantum efficiency was found to be very high, near 90% for best wafers of both types. The type-II lasers were able to work in cw regime up to 50°C, while for the type-II devices the maximum cw operation temperature reached 140°C and 180°C for pulsed regime. The type-II lasers exhibited single frequency operation in a large range of driving conditions with the side mode suppression reaching 30 dB. For the type-I lasers the single frequency operation was observed, as a rule at low currents, with the side mode suppression of 10-20 dB.

The current and temperature tunability of the lasers have been studied and analyzed. To estimate spectral purity of the laser emission mode mapping of the lasers has been performed using a Fabry-Perot interferometer or directly absorption lines of gases of interest. We present also some results on TDLAS of methane, carbon monoxide, carbon dioxide, and HF in trace concentrations, obtained with the diode lasers used in cw regime at temperatures up to 80°C.

ROOM TEMPERATURE OPERATION OF GaAs QUANTUM CASCADE LASERS

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GaAs/AlGaAs, is an attractive technologically proven optoelectronic material system that, through quantum design, can now be exploited for laser emission in the mid-infrared (9-11 μ m) using the quantum cascade (QC) laser concepts [1]. Over recent years significant advances have been demonstrated in GaAs based QC laser technology, [2]. However, the utility of these devices has been limited by the need to operate at cryogenic temperatures in order to increase their efficiency and manage the large quantity of heat dissipated during operation. Room temperature operation of a GaAs QC laser has now been achieved at $\lambda \approx 9.5\mu\text{m}$, [3]. These devices show 500 mW peak power at 250 K, a temperature readily accessible using electrocooled elements. Moreover, by fabricating DFB lasers we obtained single mode emission up to 335 K, with very high spectral quality and side mode extinction ratio.

The new structures operating room temperature are grown using AlGaAs (Al = 45%) as a barrier material, the limit of the mutual degeneracy of the Γ , X and L valleys. We estimate that this gives the maximum band offset without inducing the presence of indirect barrier states. An in depth study on the best Al content to use in GaAs based devices is under investigation.

These devices are conceived within an Al free waveguide which has very good intrinsic thermal properties. The latter have been already characterised using $\lambda \approx 11.5\mu\text{m}$ lasers where we used a planarised processing for an epi-side down mounting to improve the thermal dissipation in the device. The measured value of the thermal resistance, $R_{\text{therm}} = 6.7\text{K/W}$, is in good agreement with the predictions and demonstrates the importance of our whole GaAs-based waveguides for good thermal conductivity. Operating on a Peltier element, these devices were able to yield average optical powers of 2.2mW at 240K with duty cycles of 2.5%, a current record for GaAs based QC lasers.

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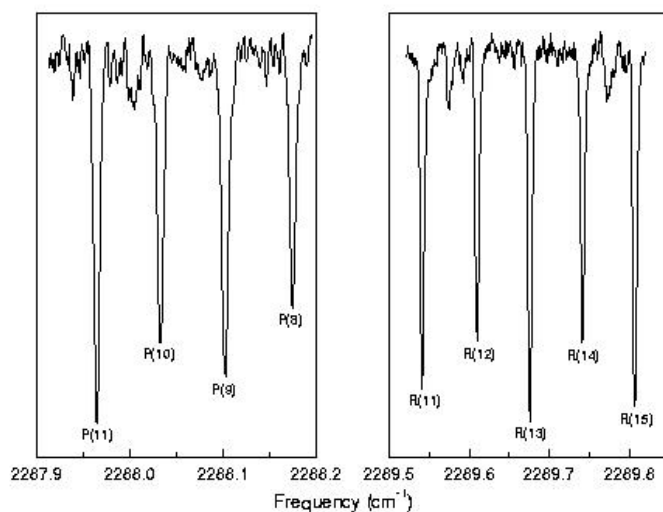
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TUNABLE DIODE LASER SPECTROSCOPY OF MOLECULAR IONS AND IONIC COMPLEXES

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Molecular ions and ionic complexes are considered to be important intermediates in processes that are relevant to atmospheric and interstellar chemistry. In this contribution a technique will be presented that allows high resolution *direct absorption* spectroscopy of such species in the infrared. A supersonic planar plasma, generated by electron impact ionization of gas expanded through a long and narrow slit, is used in combination with a tunable infrared diode laser spectrometer. This method combines high molecular densities and a relatively large absorption pathlength with an effective adiabatic cooling. Applications are shown towards high resolution rovibrational spectra of molecules, such as the linear and centrosymmetric N_4^+ and $\text{N}_2\text{-Ar}^+\text{-N}_2$ (see figure) or the proton bound complexes Ar-HN_2^+ and $\text{N}_2\text{-H}^+\text{-N}_2$. It will be shown that plasma modulation offers an effective alternative to frequency modulation. The results are compared with the outcome of recent *ab initio* calculations.



Rotationally resolved transitions in the P- and R-branch of $\text{N}_2\text{-Ar}^+\text{-N}_2$ upon excitation of the anti-symmetric stretching vibration. A clear spin statistical alternation is observed.

For further reading: J. Chem. Phys. 113 (2000) 895; J. Chem. Phys. 111 (1999) 8400; J. Chem. Phys. 113 (2000) 2736 and Rev. Sci. Instrum. 71 (1999) 1811.

DEVELOPMENT ON GAS DETECTION SYSTEMS USING BY InGaAsP/InP LASER DIODES IN 1.6-2 μm WAVELENGTH REGION

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This talk outlines our recent activities of gas monitoring by TDLAS using an InGaAsP/InP DFB LDs as a light source. The performance and applications are reviewed along with recent progress in fabricating InGaAsP/InP DFB LDs in the 1.7-2 μm wavelength region. Laser oscillation up to 2 μm has been achieved by using strained quantum wells as the active layer and gain coupled DFB structure without degradation of threshold current, quantum efficiency and power output(1). Here, portable remote methane sensor, light-scattering optical cell methane sensor mounted on a bicycle and diagnostic for combustion system are introduced as the examples. Harmonic detection is used as the gas detection principle for these applications.

Portable remote methane sensor: Methane is a main constituent of city gas and leak detection is important. However, no conventional gas sensor is capable of remote sensing. The spectroscopic method is the only way to provide such sensing. A portable remote methane sensor has been developed(2) using a 1.65 μm InGaAsP/InP DFB LD. The sensor is designed as a portable lidar with a range of up to about 10 m. An operator can easily search for gas leaks by scanning the laser light. **(Fig.1)**

Light-scattering optical cell methane sensor: Surveying buried gas lines is a tedious work, usually involving crews on foot with utility vehicles crawling along the curb at walking speeds. TDLAS could improve the efficiency of this work, and we have developed a methane sensor mounted on a bicycle using a 1.65 μm DFB LD. A unique light-scattering optical cell was developed and used for this purpose. This cell is not delicate in optical alignment and is expected to construct an inexpensive and tough measurement system. (Fig.2)

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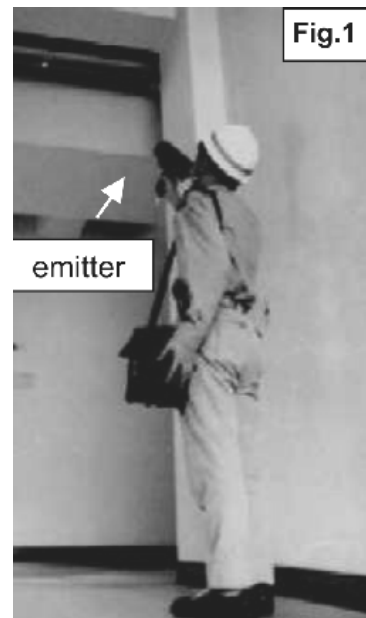


Fig.1

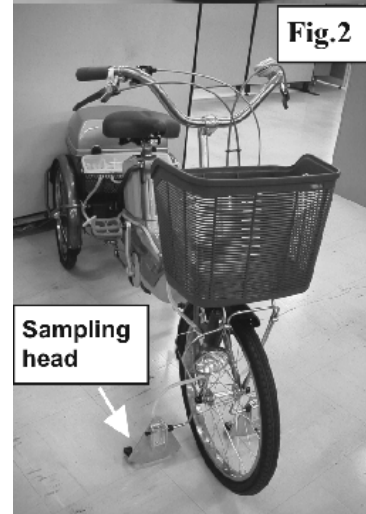


Fig.2

RECENT DEVELOPMENTS IN LEAD SALT BASED NANOSTRUCTURES FOR INFRARED LASERS

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Traditionally lead salt diode lasers are used for high resolution spectroscopy and gas analysis. Today IV-VI based lasers face a great challenge from the novel type II and quantum cascade III-V family lasers. The need to increase CW operating temperatures for mid-IR sources is driven by the prospects for compact and inexpensive portable gas analysis systems. Theoretical consideration and recent results on pulsed above room temperature operation of PbSe/PbSrSe double heterostructure¹ (DHL) and vertical-cavity surface-emitting lasers² clearly indicate that IV-VIs still hold there positions and are quite competitive compared to a complex novel approaches.

This talk will present recent results on high temperature CW operation of PbSnSe/PbSrSe separate confinement multiple quantum well (MQW) diode lasers. The laser structures have been grown by molecular beam epitaxy on (100) PbSe substrates. MQW active area contained seven PbSnSe quantum wells with a typical thickness of 400 Å embedded between 200 Å PbSrSe barriers. The Sn mole fraction varied between 0.003 and 0.01, the Sr barrier composition was $x=0.03$. Electronic confinement 500 Å PbSrSe layers with $x=0.03$ were enclosed in PbSrSe ($x=0.045$) optical confinement layers doped by Bi₂Te₃ or Tl₂Te for n- and p-type respectively.

After the 12 µm stripe contacts were applied on the epi-side the laser structure substrate was thinned by chemo-mechanical polishing down to 180 µm or 15 µm, followed by the second broad area contact deposition. Fabry-Perot resonators were cleaved and mounted between two cooper heat sinks. Maximum CW operating temperatures T_{\max} for the lasers made from the 180 µm thick wafer were consecutively 30 to 70 K lower than T_{\max} for the 15 µm thick lasers. The reason is a minimum of thermally resistive PbSe material left with 15 µm wafer. For the best laser made from 180 µm wafer T_{\max} was 168 K, while the best 15 µm wafer diode reached 240 K. This is the highest CW temperature for the lead salt lasers. At 220 K the laser threshold current, wavelength and total power output were 950 mA, 5.09 µm and 150 µW, respectively. The difference of 70 K between the two highest T_{\max} is due to the better heat dissipation for 15 µm wafer and correlates with a model calculation.

Experimental data for MBE growth as well as for DH and MQW lasers will be presented and will include information on compensation as derived from Hall effect measurements, SIMS depth impurity profiling, CW and pulsed threshold data, power output and spectral measurements. Recent results show that substrate removal technique is very promising for reliable thermoelectrically cooled CW operation.

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DIODE LASER SPECTROSCOPY OF MOLECULAR FREE RADICALS

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This presentation will concentrate on transient infrared diode laser absorption spectroscopy of small organic free radicals produced by *u.v.* laser flash photolysis. High resolution spectra of numerous radicals have now been detected in this way, many for the first time. Hirota[1] has published a useful bibliography that includes references to work in this, and related fields, up to the end of 1999. I will concentrate on recent spectroscopic measurements on ethyl, C₂H₅, hydroxyformyl, HOCO, and mono-bromomethylene, HCB_r. C₂H₅ is the smallest alkyl radical that exhibits internal rotation as well as a low frequency out-of-plane vibrational motion at the –CH₂ radical center. The internal rotation, or torsion, mode is of very low frequency in C₂H₅ and dramatically complicates the spectroscopy of the radical at ambient temperature due to the large population in excited torsional levels. However, careful analysis of the observed IR spectrum combined with *ab initio* calculation permits a detailed understanding of the potential energy surface governing the motion.

HOCO is the intermediate in the reaction OH + CO → H + CO₂ which is extremely important in combustion and atmospheric chemistry. Some time ago [2], we obtained the first high resolution spectra of this species and showed that the ground state has a *trans*-configuration. Recently, calculations have suggested that the *cis*- isomer should also be detectable under ambient temperature conditions and we have spent some time searching for its spectrum in the C=O stretching region. Progress in these experiments will be reported.

Finally, HCB_r is related to CH₂, the prototype for all divalent carbon species. In common with all simple species of this type, HCB_r has three low-lying electronic states, two of singlet character connected by an allowed electronic transition, and one triplet. In contrast to CH₂, HCB_r has a singlet ground state, but both theory and experiment suggest the triplet is extremely low-lying. The availability of tunable, extended cavity diode lasers in the near-IR has opened up the possibility for studying the spectrum of this and the many other radical species that possess excited states at energies corresponding to near-IR photons. We have recorded the high-resolution electronic spectrum of HCB_r through this wavelength region with the aim of locating the position of the triplet state via perturbations in the measured singlet state spectrum. Present evidence suggests the zero point level of the triplet lies just below the energy of the doubly excited bending vibrational level of the ground singlet.

Acknowledgement

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Part II

Poster Presentations

TRACE GAS DETECTION WITH DISTRIBUTED FEEDBACK QUANTUM CASCADE LASERS

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Quantum cascade lasers with distributed feedback (QC-DFB) are single-frequency semiconductor mid-IR light sources capable of delivering >100 mW of continuous wave power with an intrinsic linewidth of ~ 1 MHz. In pulsed mode, QC lasers can be operated at a near room temperature. These unique features make QC-DFB lasers convenient new sources for spectroscopic trace gas detection in the 4 to 19 micron region. Gas sensors based on cw (cryogenic temperature) and pulsed (near room temperature) operated QC-DFB lasers will be described [1-3]. Recent advances in photonic technologies and spectroscopic detection schemes have been employed in various sensor platforms to achieve minimum detectable absorption coefficients of 10^{-9} cm^{-1} in real world applications.

For sensitivity enhancement different techniques have been investigated that include a multipass cell, balanced detection, cavity enhanced spectroscopy (CES), and cw cavity ringdown spectroscopy (CRS). The gas sensor architecture depends on the concentration levels of a desired trace gas species. A number of gases such as CH_4 , N_2O , NO , CO , NH_3 , $\text{C}_2\text{H}_5\text{OH}$, and H_2O have been detected and quantified to date in ambient air and other gas mixtures with sensitivity of several parts per billion by volume. Detection of biomedically produced nitric oxide (NO) is of particular importance because of its critical role in human physiology. NO in human breath samples was detected by its fundamental absorption at $5.2 \mu\text{m}$ (1921.6 cm^{-1}) with a CES technique. Application of CRS yielded a single ringdown event sensitivity to absorption of $2 \cdot 10^{-8} \text{ cm}^{-1}$. Recently also ammonia detection at $10.04 \mu\text{m}$ (997 cm^{-1}) was carried out at the NASA Johnson Space Center, Houston, on a bioreactor being developed for water reprocessing in future spacecraft habitats.

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SELF-CALIBRATING NEAR INFRARED TDL SPECTROMETER FOR BALLOONBORNE TRACE-GAS DETECTION

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The instrument described here is planned to form part of the TRIPLE-balloon payload for the validation of the atmospheric chemistry instrument SCIAMACHY on ENVISAT within the framework of the ESABC (Envisat Stratospheric Aircraft and Balloon Campaign). The in-situ TDL spectrometer for the measurement of stratospheric CH₄ and H₂O profiles has low mass (<25 Kg) and low power consumption (<50 W). The compact design makes the instrument an ideal candidate for piggy-back operation on existing payloads. Measurement takes place in the free air using an open-path Herriott-cell, thus avoiding sampling and the associated inlet problems like deposition effects and pressure errors known from the more conventional TDL designs using a pressurised absorption cell. Fully automated measurements are possible over extended periods of time.

Long-term stability is assured by a number of novel technical features. The instrument automatically detects contamination and drift of optical parts as well as ageing of the diode laser. Changes of light intensity caused by these effects are then electronically compensated in realtime. The most important sources of measurement artifacts are thus cancelled out. A novel strategy of signal processing combines baseband- and modulation technique. This results in a low MDA (minimum detectable absorbance) and a high absolute accuracy at the same time. Development of the instrument is to the greatest part concluded on a laboratory level, but the final flight package still needs to be assembled. Development and making of the original instrument take place within the framework of a joint project of the Universities of Bremen and Heidelberg. Our presentation will focus on instrumental aspects, laboratory results and present planning of the balloonborne activities.

IN SITU MONITORING OF TRACE-GAS IN THE STRATOSPHERE WITH NEAR-INFRARED LASER DIODES

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For issues in climatology, chemistry or dynamics of the atmosphere, laser diode absorption spectroscopy can be of high interest as it provides precise *in situ* trace-gas measurements at high temporal resolution and with a large dynamic range of the measurements. Particularly, InGaAsP laser diodes emitting in the 1-to-2 μ m spectral range are convenient spectroscopic tools as a reliable single mode emission with no mode-hops over the tunability range is obtained at room-temperature. In addition, functional highly-linear detectors are available to detect the laser beams in that spectral range and optical fibers can be used to ensure light connections with the purpose of designing compact sensors.

These monitoring capabilities were a strong impetus for us to start from year 1997 the development of the « Spectromètre à Diodes Laser Accordables » (SDLA), a laser diode sensor operated from a stratospheric balloon and devoted to the *in situ* monitoring of CH₄ and H₂O in the troposphere and the lower stratosphere. The sensor is based on an multipass cell open to the atmosphere that provides a 56m-path-length. Two DFB InGaAsP laser diodes emitting in the 1.65- μ m and 1.39- μ m spectral regions to monitor CH₄ and H₂O are coupled with the cell by means of optical fibers. A dual-beam detector made of two InGaAs photodiodes is used in conjunction with the multipass cell to reach a detection limit of 10⁻⁵ absorption units. The absorption spectra for both species are obtained simultaneously at 1s-intervals. The mixing ratio retrieval is based on a nonlinear least-squares fit to the full molecular line shape in conjunction with *in situ* pressure and temperature measurements.

The SDLA was flown successfully several times in years 1998 to 2000 from stratospheric balloons operated by the CNES, the French space agency. For each flight, approximately ~10000 concentration measurements were obtained for both species at ascent and descent of the gondola, with a precision error within a few percents in compliance with the science objectives. Currently, the development of a compact CH₄-H₂O laser sensor capable of flying from various platforms, small balloon, stratospheric and pilotless aircraft is underway supported by the CNES and the CNRS. That new sensor will be used to better understand the evolution of H₂O in the lower stratosphere and to study atmospheric turbulence and mixing in conjunction with wind-speed measurements obtained by means of an ionic anemometer. Furthermore, we are thinking of developing in the coming year a light-weight diode laser sensor to measure *in situ* water vapor isotopes in the Martian atmosphere within the framework of the space experiments scheduled in year 2007.

TUNABLE DIODE LASER SPECTROSCOPY FOR AUTOMOBILE EXHAUST GAS ANALYSIS AT HIGH TEMPORAL RESOLUTION

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This paper reports on the development of tunable diode laser spectrometers which will be installed at the Volkswagen company, Wolfsburg, as a diagnostic tool for automobile exhaust gas. The measurement data provided by the three instruments ordered so far will serve to optimize both the motor management and catalyst processes to comply with future US and European automobile emission standards. Owing to the fast time response of down to 5 ms even events with single motor cycle duration can be resolved by the measurements thus offering the perspective to study emission reduction processes through the catalyst chain under highly dynamic conditions.

The spectrometers each use three individual lead salt diode lasers to monitor the absorption of carbon monoxide, nitric oxide and nitrogen dioxide simultaneously in the mid-infrared spectral range. The combined beam of the three diode lasers is split into one reference and four measurement channels for the simultaneous measurement from up to four sampling ports in the catalyst chain. The gas sampled is equilibrated in temperature by a counter flow arrangement to approximately 100 °C before the injection into the optical measurement cells which are maintained at the same temperature in order to avoid condensation of water vapor.

The gas pressure in the measurement cells is regulated to 50 mbar. The time response is limited to 5 ms by the gas exchange time of the measurement cells, whereas the turbulent flow through the sampling line imposes a time delay of approximately 20 ms, but no further bandwidth reduction. To analyze the spectral signature recorded during a laser scan, we use a sweep integration scheme implemented in programmable logic devices.

In addition to the technical description of the instruments currently developed this paper presents measurement results of an existing prototype which was used to measure nitric oxide and carbon monoxide from two sampling ports at the Volkswagen company last year.

GaN BLUE DIODE LASERS IN SPECTROSCOPIC APPLICATIONS

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With the introduction of GaN violet and blue continuous-wave diode lasers [1] through the work of Nakamura et al. at the Nichia Corporation, the spectroscopic applicability of diode lasers was much augmented. By special agreement with the manufacturer, our group was able to perform very early experiments with two units: one operating close to 404 nm and another one close to 397 nm. In this contribution we report on our experience with these new spectroscopic sources [2-4]. The spectroscopic applications of the blue diode lasers have also been investigated in [5,6].

The output power of the blue/violet lasers used is about 5 mW, although at present 30 mW diode lasers are also available. The lasers need an external tunable cavity to operate in a single longitudinal cavity mode, and the power is then reduced to about 1 mW. Our first experiments [2] concerned the second resonance lines of potassium at 404.5 and 404.8 nm. Absorption, fluorescence and opto-galvanic spectroscopy were demonstrated. Ultra-sensitive atomic detection employing two-tone frequency modulation spectroscopy was demonstrated on potassium and on the lead 405.8 nm line originating from a weakly populated metastable level [3]. $^{40}\text{Ca}^+$ excitation in an ion storage ring using a Littrow-type external-cavity stabilised blue diode laser was performed in collaboration with the Manne Siegbahn Institute in Stockholm for lifetime determination of metastable states.

Initial investigations using a simple photometer setup and frequency modulation spectroscopy for high sensitivity detection of nitrogen dioxide NO_2 in air were performed.

We also demonstrated sum-frequency generation to the 253.7 nm mercury line [4]. Here the light from the 404 nm and a 688 nm diode laser was mixed in a BBO crystal. In low pressure samples the well-resolved spectral structures of mercury isotopes could be seen. This type of mixing to the ultra-violet region is quite useful in generating new frequencies as is the difference-frequency generation to the mid-infrared region (see, e.g., [7]).

A further use of violet diode lasers is as excitation sources for laser-induced fluorescence. We have built a very compact fibre-optic fluorosensor combining a violet diode laser with an integrated spectrometer [8]. The unit has been used, e.g. for early cancer detection.

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DIODE LASER SPECTROSCOPY ON GAS DISPERSED IN SCATTERING MEDIA

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A novel field of diode laser spectroscopy is demonstrated, that can be used for the study of free gas dispersed in scattering materials [1]. The technique, referred to as GASMAS (Gas in Scattering Media Absorption Spectroscopy), opens up new possibilities for characterization and diagnostics of scattering solids and turbid liquids. The GASMAS project emerged from the interaction of diode-laser gas spectroscopy [2, 3] with optical mammography [4] and differential absorption lidar [5], which all contain elements of the new technique.

Many substances, of both organic and synthetic origin, are porous and contain free gas distributed throughout the material. For instance, wood, fruits, sintered powders, isolating materials, and foams can be considered. Generally, gas can be analyzed *in situ* employing absorption spectroscopy by the use of a sufficiently narrow-banded light source in combination with the Beer-Lambertian law. However, the straightforward application of this method fails for turbid media, since the radiation is heavily scattered and light emerges diffusely.

Gas detection is made possible by the contrast of the narrow absorptive features of the free gas molecules with the slow wavelength dependence of the absorption and scattering cross-sections in solids and liquids. A single-mode probing diode laser is used for the GASMAS measurements, detecting molecular oxygen by wavelength modulation spectroscopy at wavelengths close to 760 nm. Spurious signals from the ambient air can be avoided by placing the laser in a nitrogen-flushed chamber and by guiding the radiation to the sample using a fiber. Temporally resolved measurements employing a picosecond-pulsed diode laser establish the photon history inside the scattering sample, and were consequently used to deduce the imbedded gas concentration [6]. Internal gas pressure can also be measured.

The new possibility to observe free gas in scattering media does not only allow static gas assessment, but also the study of dynamic processes, i.e. how imbedded gas is exchanged with the environment. Feasibility studies were performed on polystyrene foam, where the oxygen penetration into a sample originally subjected to a nitrogen atmosphere was observed to occur with a time constant ($1/e$) of 44 min. In very small enclosures or bubbles of free gas, additional pressure-induced broadening and shifts of diagnostic value can be expected.

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DEVELOPMENT OF A CO₂ GAS TEMPERATURE AND CONCENTRATION SENSOR USING 2.0 μ m DFB DIODE LASER

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A Diode Laser Absorption Spectroscopic technique has been applied for the precise measurement of concentration of H₂O, CH₄, NO, CO, CO₂. With this technique, simultaneous measurement of concentration and temperature using wavelength intensity ratios is feasible. In this work, the diode laser wavelength is 0.7 μ m to 1.7 μ m, since it was developed for telecommunication purposes. The advantages of using this type of laser are that the supply is plentiful, it is relatively cheap, and peripheral devices are available. The main disadvantage is that the line strength of absorption is relatively weak. Hence, a longer wavelength diode laser is preferred.

This research is focused on establishing the feasibility of a diode laser absorption sensor system for non-intrusive concentration and temperature measurement. Two DFB diode lasers operating near 2.0 μ m (1.996 μ m and 2.049 μ m) were used to scan over CO₂ bands at a high tuning repetition rate. The 2.049 μ m wavelength is almost the longest InGaAsP, room-temperature, DFB diode laser operating wavelengths. Concurrently, we developed a compact package for the instrument. The box includes the lasers, detectors, and all optics for convenient transport and setup at the measurement site. The motivation to develop this sensor is to fill a demand for real-time monitoring, such as for automotive engine analysis. A current area of active engine research is the cold start emissions problem, that is, high levels of UHC and other undesirable pollutants are exhausted during the cold start period, because the catalyst is not at operating temperature.

Two sets of experiments were carried out: the first was performed using a static heated cell, the second with a premixed laminar flame. A slight discrepancy in CO₂ temperature was noted at the elevated temperatures, compared to the HITEMP database. A premixed laminar flame was also used for actual temperature measurements. The measurement position was set very close to the flame front. A thermocouple was used for temperature comparison. The repetition rate was varied within the range of 100Hz, 1KHz and 10KHz. The error was estimated to be approximately 14% in each case. The errors resulted from various sources, including optical alignment, instrumental noise, etalon effect, beam steering, and baseline matching. Based on the system evaluation and actual combustion measurements demonstrated in this presentation, one can conclude that this Diode Laser Absorption Spectroscopic technique opens the possibility to perform *in-situ* combustion measurements and diagnostics.

TUNABLE FREQUENCY-DOUBLED DIODE LASER FOR ATOMIC ABSORPTION SPECTROSCOPY OF COPPER

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There is a growing interest in the development of measurement instruments based on the diode laser technology. More strict demands on the control of combustion processes are being placed, and diode laser based instruments provide many advantages in meeting these demands [1].

A heavy metal monitoring instrument based on plasma excited atomic absorption spectroscopy has been developed in the Optics laboratory for combustion environments [2]. However, traditional hollow cathode lamps provide modest light powers for absorption spectroscopy. In this work a light source based on a frequency-doubled diode laser is under development for atomic absorption spectroscopy of copper.

An external-cavity diode laser (ECDL) is constructed at 650 nm. The ECDL is based on a transmission grating that is manufactured by electron beam lithography technique [3]. The tunable light from the ECDL will be frequency doubled in an external enhancement cavity. The enhancement cavity is a ring resonator in bow-tie configuration.

Copper has two possible transitions at 325 nm region ($^2P_{1/2} \rightarrow ^2S_{1/2}$ 327.5 nm, $^2P_{3/2} \rightarrow ^2S_{1/2}$ 324.8 nm) that can be observed by the instrument under construction.

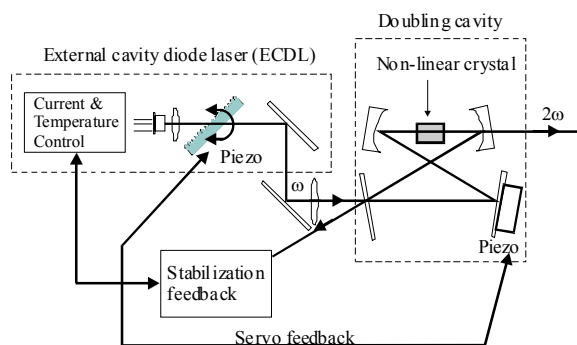


Figure 1. Schematic representation of the light source for copper line absorption

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IN-SITU-DETECTION OF POTASSIUM ATOMS IN HIGH-TEMPERATURE COAL-COMBUSTION SYSTEMS USING NIR-DIODE LASERS

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Since the combustion of fossil fuels -especially coal- will remain an important energy source over the next decades, it becomes an urgent task to minimize CO₂-emission by maximizing the total efficiency of the power plant. For this purpose high-temperature combined-cycle combustion processes are investigated and developed. But the high process temperatures lead to an increased release of alkali and heavy metal compounds incorporated in the coal. These compounds are likely to enhance the corrosion problems in the hot gas turbines, so that many turbine producers impose strict limits for these species at the turbine entrance and innovative high temperature filters as well as detailed knowledge of the high temperature chemistry of the alkali compounds is needed. The usefulness of conventional probe sampling techniques to probe these high temperature processes and to monitor these highly reactive species is in doubt due to the reactivity of the flue gas constituents.

For the purpose of quantitative *in-situ* species detection within the flue gas duct, and in order to allow on-line monitoring of the function of the high temperature filters, that are needed to protect the turbines, we started to develop a compact laser-based absorption spectrometer for the sensitive detection of atomic or molecular species and temperature. Disturbing effects caused by fluctuations of the transmission of the measurement path, thermal background radiation or refractive index gradients are effectively compensated. By using direct absorption signals an absolute concentration value can be determined without any calibration processes. The necessary sensitivity is achieved by scan integration techniques. In a first test we used this device to monitor potassium produced by thermal dissociation of KCl in a high-temperature oven at up to 1000°C. With an absorption length of 60 mm inside the furnace we demonstrated a sensitivity of $7,5 \cdot 10^6$ atoms/cm³. We also determined pressure induced broadening and shift of the absorption line by various collision partners. In the meantime *in-situ* measurements were realized under industrial conditions, detecting for the first time potassium behind the high temperature filters of atmospheric and high-pressure coal-combustors at up to 12 bar pressure. Using absorption paths between 140 and 300 mm we achieved a detection limit of 10 ng/Nm³ at a temporal resolution of 1 sec. Different laser types were used including standard Fabry-Perot-type lasers and Vertical-Cavity-Surface-Emitting-Lasers, VCSEL. Due to its very high current tuning coefficient the VCSEL - despite the low output power of 200µW- proved to be most important to recover the severely broadened potassium lines under high pressure conditions. With these results we could show that fast, compact and inexpensive *in-situ* sensors for the surveillance of high-temperature flue gas filters are feasible.

TUNABLE DIODE LASER MEASUREMENTS OF NITROUS OXIDE AND CARBON DIOXIDE AT 1.5 μm

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Near-Infrared Tunable Diode Laser Absorption Spectroscopy (TDLAS) was applied to the measurement of nitrous oxide (N_2O) and carbon dioxide (CO_2) at a wavelength of 1.5 μm . These two linear tri-atomic molecules are important as greenhouse gases.

Near-infrared absorption spectra of N_2O was investigated using a high-resolution Fourier-transform infrared spectrometer (FTIR), and a measurement wavelength of N_2O was selected from among the many absorption lines observed in the wavelength region between 1.282 and 1.792 μm . The TDLAS spectra of N_2O were observed using an InGaAs-DFB diode laser, which is a new custom device available through Anritsu Corp. and is superior because it is specifically designed to access the near-infrared bands of NO_x . In laboratory studies of TDLAS, a sample gas was held in an absorption cell with an effective path length of 150mm. Commercial premixed and calibrated gases were used as samples. The detection limit of N_2O was estimated to be 2.8 ppm-m/ $\text{Hz}^{1/2}$ at 1.517121 μm using the dual modulation technique.

The measurement wavelength of CO_2 was selected from among the many absorption lines reported in the HITRAN database in order to avoid interference from coexisting gases in the atmosphere. In laboratory studies, the detection limit of CO_2 was estimated to be 3.3 ppm-m/ $\text{Hz}^{1/2}$ at 1.572335 μm .

In field experiments, we succeeded in measuring the concentration of CO_2 gas in automobile exhaust gases using TDLAS. Rapid changes of the concentration of CO_2 gas accompanied by changes in engine load were observed. We also detected CO_2 gas in exhaust gases from automobiles passing by.

Research is underway to further improve detection limits and to apply the TDLAS technique to combustion diagnostics and controls, as well as environmental monitoring.

EXTENSION OF THE DYNAMIC RANGE OF WAVELENGTH MODULATED DIODE LASER ABSORPTION SPECTROMETRY

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The sensitivity of Diode Laser Absorption Spectrometry (DLAS) may be significantly improved by the use of Wavelength-Modulation (WM) techniques. WM gives a good suppression of constant or linearly wavelength dependent background absorption, reduces noise by shifting the detection to higher frequencies, and suppresses the noise outside the detection bandwidth.

The WM-DLAS technique produces a signal that is directly proportional to the density of absorbers (or the sample optical thickness, SOT) when small amounts of analyte are detected. For large SOTs, however, the signal is no longer linear with the SOT. One application of the WM-DLAS techniques is sensitive trace element detection with a graphite furnace (GF) as atomizer. The fast heating rate of GFs, often around 1000 K/s, and the relative slow diffusion of the atoms, can often give rise to temporarily high analyte concentrations (even if the total amount of the analyte is low). This implies that SOT values above those for which the technique produces a linear response occasionally can appear.

A methodology for analyzing WM-DLAS signals from situations under which large SOTs temporarily appear has therefore been developed [1]. The same methodology also serves the purpose of extending the dynamic range of the WM-DLAS technique [1]. It is based upon the fact that the SOT is a calculable multi-valued function of the WM-DLAS signal [2] and is accomplished with the technique optimized for detection of small sample amounts. A parameterisation of a calibration curve (WM-DLAS signal strength as a function of SOT [2, 3] and temperature [4]) constitutes a means for extraction of SOT vs. time curves from experimental WM-DLAS signal vs. time curves. The pilot transition in the methodology development was the 780 nm transition in Rb and so-called $2f$ -detection was used.

The methodology has extended the range of the $2f$ -WM-DLAS technique to approximately 20 integrated absorbance units (s), implying a capability of detecting Rb atoms in a GF from a few femtograms to several nanograms with no need for any changes of the laser settings.

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A SECOND HARMONIC TDL INSTRUMENT TO MEASURE CH₄ AND N₂O UP TO 30 KM.

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The Argus instrument, a dual channel CH₄ and N₂O tracer instrument is a small (40 cm x 30 cm x 35 cm), lightweight (24.5 kg), versatile instrument that has been successfully flown on balloon payloads and on the NASA ER-2. It runs completely unattended for up to 9 hours. The Argus instrument has a high accuracy because it has a closed *and* temperature controlled sampling cell. This allows *in situ* calibrations of Argus and also minimizes the corrections to the Argus data required by the strong temperature dependence of the molecular (CH₄ and N₂O) spectral line parameters. On the ER-2 precision is 3 ppb and 18 ppb for N₂O and CH₄, respectively.

The diode laser infrared beam exiting the custom liquid nitrogen dewar is shaped by 2 antireflection coated lenses into an f/40 beam focused at the entrance aperture of the Herriott cell. The Herriott cell is common to both optical channels and is a modified commercial astigmatic cell. The cell is set up for a 182 pass state (for a total path of 36 m). Instrument calibration is always carried out using calibrated gas standards with the Herriott cell operating at its infrared design wavelengths, 3.3 and 4.5 micrometers respectively for CH₄ and N₂O detection.

The electronic processing of the second harmonic spectra is done by standard phase sensitive amplifier techniques with demodulation occurring at twice the laser modulation frequency of 40 kHz. To optimize signal retrieval in the changing pressure environment the laser modulation amplitude is updated every 10 seconds to its optimal theoretical value based upon the measured pressure in the Herriott cell.

Data reduction uses a non-linear, least squares Marquardt-Levenberg fitting procedure; the theoretical fitting function is the second Fourier component of the modulated Voigt line shape with 5 free fitting parameters.

Argus is regularly calibrated in the laboratory against a CMDL (Climate Monitoring and Diagnostics Lab) whole air standard for CH₄ and N₂O. Flow-mixing of this standard with a zero gas (boil-off from liquid nitrogen) provides us with absolute calibration and linearity data as inputs to the *in situ* flight record analysis.

Argus has acquired high quality data on 5 OMS (Observation of the Middle Stratosphere) balloon launches to date (1996-1998) and on 16 flights during the NASA SAGE III Ozone Loss and Validation Campaign (SOLVE) mission (1999-2000).

INVESTIGATION OF HYDROCARBONS IN HEXAMETHYLDISILOXANE PLASMAS OF RF DISCHARGE

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Hexamethyldisiloxane (HMDSO), $(\text{CH}_3)_3\text{Si-O-Si}(\text{CH}_3)_3$, is widely used in plasma assisted deposition applications [1]. Together with a film characterization the study of gas-phase processes lets find the optimal process parameters for the aimed deposition of the films of a required quality. The investigation of low-molecular species is performed with the aim of enhancing the understanding of the plasma phase reactions which take place in rf discharge.

The HMDSO plasma was produced in a cylindrical stainless steel vacuum chamber with the volume of 20 l. The capacitively coupled discharge was maintained by an rf (13.56MHz) generator between the powered electrode and the grounded wall of the vacuum chamber. The plasma process parameters were varied in the following ranges: discharge power from 20 to 200 W, total gas pressure 0.08 – 0.6 mbar, gas flow rates 1 – 5 sccm. Gas phase was analysed by IR tuneable diode laser spectroscopy (CH_3 , CH_4 , C_2H_2 , and C_2H_6) and mass spectrometry (stable neutral species).

Spectroscopic measurements were performed using He-cooled infrared (IR) tuneable diode laser operating system. Selected mode of the laser beam entered and left the plasma chamber through KBr windows. The laser beam passed the reactor at a distance of about 5mm above the powered electrode and was focused on a mercury cadmium telluride (MCT) detector. Direct and second harmonic absorption techniques were used.

The important process in the HMDSO is the cleavage of CH_3 radical from the monomer molecule as result of dissociation and dissociative ionization. Molecular hydrogen and ethane, formed from methyl radicals, are the dominant stable species in the HMDSO plasmas. The enhancing discharge power leads to the higher concentrations of the analysed hydrocarbons due to the intensified fragmentation of the monomer. The rates of the HMDSO conversion into the stable hydrocarbons decrease with pressure and increase with gas flow.

The extension of the present study includes TDLAS measurements of HMDSO itselfs and Si-containing radicals like Si-O, Si-H etc. The study of such neutral species and charged particles let carry out the comprehensive description of the plasma chemistry and the reaction kinetics in the HMDSO plasma of low pressure rf discharge.

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NEAR-INFRARED DIODE LASER SPECTROSCOPY IN PROCESS AND ENVIRONMENTAL MONITORING

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Open-path near-infrared diode laser open path sensors have been developed for a wide range of applications from industrial process control to environmental monitoring. These sensors are ideal for rapid, *in situ* measurements in hostile environments.

As an example of process control near-infrared diode laser absorption spectroscopy (NIRDLAS) has been used to monitor the atmospheric pressure chemical vapour deposition of tin oxide on a glass substrate at 650°C [1]. By detecting methane as a product of the reaction it has been shown that this correlates with the thickness of the tin oxide thin film and so can be used for controlling the deposition process. By using a quartz reactor the NIR beam can be passed directly through the reactor walls negating the requirement for optical windows. External cavity diode lasers having a tuning range of 100 nm have also been used for searching for reaction intermediates in the same systems.

For combustion control DFB lasers have been used for simultaneous concentration and temperature determination. Flame temperatures are determined by measuring ratios of carbon monoxide absorptions which derive from different vibrational states.

A low-cost sensor has also been developed for remote vehicle emission monitoring [2]. By passing the near-infrared diode laser beam through the exhaust of a moving vehicle it is possible to detect various pollutants and thus identify vehicles which are known as 'gross polluters'. Near-infrared laser spectroscopy is currently much more practical than mid-infrared diode laser spectroscopy for this type of field application.

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RECENT RESULTS IN TDLAS-DIAGNOSTICS OF HYDROCARBON CONTAINING PLASMAS

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Plasmas containing hydrocarbons are used in a variety of Plasma Enhanced Chemical Vapour Deposition (PECVD) processes to deposit thin carbon films. Another important use of plasma technology is the efficient conversion of natural gas, which contains methane as its main component, to higher hydrocarbons. In either case, the monitoring of transient or stable plasma reaction products, in particular the measurement of their ground state concentrations, is the key to an improved understanding of plasma chemistry and kinetics in molecular non-equilibrium plasmas. Many other applications of plasma processing also require data on ground state concentrations. Among the non-invasive diagnostic methods used for chemically active plasmas infrared Tunable Diode Laser Absorption Spectroscopy (TDLAS) between 3 and 20 μm is a modern, promising technique for measuring number densities of stable molecules and radicals.

This contribution describes our recent results of spectroscopic diagnostics and plasma chemical modeling of low-pressure plasmas containing hydrocarbons. TDLAS has been used to detect the methyl radical and 12 stable molecules in $\text{H}_2\text{-Ar-O}_2$ and $\text{H}_2\text{-Ar-N}_2$ planar geometry microwave plasmas containing small percentages of methane or methanol [1,2]. The molecular concentrations in the plasma and the degree of dissociation of the precursor molecules were monitored over a wide range of gas mixtures to elucidate the nature of the plasma chemical processes. The conversion of methane into higher hydrocarbons has been studied in hydrogen surface wave discharges from the perspective of energy conversion [3]. In this study a new experimental technique using time-resolved species detection and on-line determination has been developed [4].

The experimental studies are complemented by model calculations. In the framework of the model an extensive set of rate equations for the various species has been solved to determine theoretical concentrations of measured species. The experimental and theoretical results are compared and a detailed analysis of the main reaction pathways has led to improved knowledge about basic plasma chemical phenomena.

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SULFUR DIOXIDE DETECTION IN A COMBUSTION PROCESS

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In this paper, pollutants concentrations and temperature measurements, in a flame environment are presented. Such an environment in a combustion process is often incompatible for any measuring probe. Tunable diode laser is an appropriate check instrument for non-intrusive measurement methods.

We describe here a mid infrared tunable diode laser spectrometer for probing the burnt gases region of a methane/air flame. For this purpose, we designed and built in the laboratory a specific burner. Its working pressure is between the atmospheric pressure and 70 torr. The flame can be doped by a small amount of another gas. We choose sulfur dioxide, as it is a major pollutant involved in combustion process.

The diode laser frequency tuning is made by applying a fine temperature ramp. We recorded two kinds of spectra: on the one hand high temperature water absorption spectra, which permit us to determine the post-flame region temperature via the two lines method. In this case, the results were checked by intrusive measurements (thermocouples). On the other hand, absorption spectra were recorded with an SO₂-doped flame. A fitting algorithm was used to retrieve the pollutant concentration.

Such a flame may be also considered as a radiative source. Then the SO₂ emission can also be detected with the diode laser used as the local oscillator in a heterodyne system.

SOFTWARE ANALYSIS OF IV-VI DIODE LASER EMISSIONS FOR BROAD BAND ABSORPTION SPECTROSCOPY

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Typical applications for IV-VI diode lasers involve measuring ro-vibrational molecular spectral lines with continuous single frequency wavelength scans spanning less than 3 cm^{-1} . Recent experiments have demonstrated that measurement of broad absorption bands of large molecules is possible by using discontinuous single and multi-frequency scans covering spectral ranges up to 200 cm^{-1} . The technique, which involves modulating the diode temperature at a fixed injection current, increases the total number of molecules a single device can measure while utilizing the optical power the laser has available for high sensitivity measurements. This paper outlines a software controlled tunable diode laser spectrometer testing method for simultaneous modulation of the injection current and heat sink temperature of a IV-VI diode laser to measure both large (> 10 atoms) and small molecules in a single testing procedure.

Diode emissions as a function of injection current and heat sink temperature, for over four thousand distinct operational points ranging between ~ 200 - 1000 mA and 70 - 120 K , respectively, are measured using a Fourier transform infrared (FTIR) spectrometer. Emission stability and monochromatic data are shown in a three-dimensional format instead of traditional 2D dot plots to facilitate user interpretation of wavelength, power, and single mode continuous tuning widths. An automated algorithm is proposed to extract tuning information across the entire operational range of the device to maximize the percentage of a temperature tuned wavelength scan that is single frequency emission and minimize scanning times. Extracted data have been used to generate broad band absorption spectra for various molecules including CS_2 , C_6H_6 , and C_7H_8 . Issues such as background subtraction, temperature tuning linearity, sampling resolution, and co-adding of multiple spectra will be addressed.

METHANE ANALYZER BASED ON TDL'S FOR MEASUREMENTS IN THE LOWER STRATOSPHERE: PRELIMINARY RESULTS

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Methane (CH₄) is the second molecule, after CO₂, responsible for greenhouse effect, contributing for 26%. It is released in the atmosphere either during digging and distribution of hydrocarbons, or from fermentation of organic waste. In the lower stratosphere water vapour is also mainly determined by the oxidation of methane. CH₄ is also a sensible tracer for the determination of the air mass transport, because of its relatively short residence time (~ 10 years) in the stratosphere. High resolution concentration profiles of CH₄ in the upper troposphere - lower stratosphere are then needed in the modelling of the homogeneous and heterogeneous atmospheric chemical processes, including the removal of nitrogen and chlorine species through hydrolysis reactions or the formation of polar stratospheric clouds involved in the polar ozone depletion.

This kind of measurement requires a very high sensitivity (≤ 30 ppb) with a high time resolution (≤ 1 s), only available from optical instruments. In this work we present a recently developed methane analyser, based on a distributed feed-back diode laser at 1.65 μm . The detection technique is the two-tone frequency modulation spectroscopy. The absorption path is in a dedicated Herriott-type multipass cell, suitable for aircraft applications (it resists to 12 g accelerations) with effective length is 33 m, the volume 1.09 l, the air flows through two holes, in the centers of the mirrors. The analyser is formed by two parts: electronics (31x13x35 cm³) and optomechanics (60x24x15 cm³), both suitable for aircraft applications, according to the RTCA DO-160 C specifications (up to 12 g accelerations).

We will discuss the main features of this device, the calibration procedure and the first tests, comparing the results with the expected performances. The first measurements are planned during winter 2001-2002, in an international campaign with the instrument on board of the stratospheric aircraft M55 Geophysica [1].

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

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Pressure induced shift of acetylene (¹²C₂H₂) rovibrational lines of ν₁+ν₃ band R-branch in 1.52 μm spectral region was measured. Interest to the precise measurements of acetylene pressure induced shifts is produced by metrology needs, because acetylene is used as a secondary frequency standard in the mid-infrared region.

Distributed feedback A₃B₅ diode laser operating in λ = 1.52 μm region was used. Frequency calibration was performed by a confocal interferometer with D* = 0.008487 cm⁻¹ and a Fabry-Perot interferometer with D* = 0.049272 cm⁻¹. Dynamic range (signal-to-noise ratio) of the spectrometer was better than 10⁴.

Accuracy of pressure induced shift measurements was as high as 3·10⁻⁵ cm⁻¹. Certain deviations from linear dependencies of shift vs pressure was disclosed. These deviations can be explained by three-particles collisions of acetylene molecules.

Pressure induced shift coefficients were measured for R(10) - R(16) lines of ν₁+ν₃ band of ¹²C₂H₂.

NOISE IN DIODE LASER SPECTROSCOPY OF THE SPECTRAL LINE PROFILE

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Intensity and frequency noises of a diode laser exert significant influence to the quality of a recorded absorption spectra. Distortions of a spectral line shape caused by diode laser radiation noises can be as high as 1%, which is comparable with the distortions related to fine effects of intermolecular interactions (asymmetry of a spectral line shape, Dicke narrowing, etc.) Thus, knowledge of diode laser generation spectrum conditioned by various sources of noise is very important.

In this paper the instrumental function of a diode laser spectrometer was investigated in details using A_3B_5 DFB laser diode ($\lambda=1.53 \mu\text{m}$) and absorption lines of $\nu_1+\nu_3$ band of acetylene (C_2H_2).

Analytical expression of the diode laser emission spectrum determined by frequency fluctuations was derived:

$$S(\nu) = \frac{g_0}{\pi(\nu^2 + g_0^2)} \frac{\Omega^4}{(\Omega^2 - \nu^2)^2 + \nu^2 \Gamma^2}.$$

Parameters of the diode laser field spectral density g_0 , Ω and Γ determine central part and wing of the diode laser emission line. Mean values of these parameters were found to be 0.0026 cm^{-1} , 0.12 cm^{-1} , and 0.13 cm^{-1} respectively. These parameters were obtained using two independent techniques: by fitting of a Doppler broadened C_2H_2 absorption line at low pressure, and from residual transmittance ΔI and width $\Delta\omega$ of a spectral line with saturated absorption.

COMPACT SYSTEM FOR GAS-MEASUREMENTS WITH QUANTUM-CASCADE-LASERS

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The use of quantum-cascade-lasers in laser spectrometers becomes more and more interesting, but still the advantage of near-room-temperature operation is slightly compensated by short pulse operation and liquid nitrogen cooled HgCdTe-detectors for the desired bandwidth.

We demonstrate a compact, completely thermoelectrically cooled quantum-cascade-laser-spectrometer to measure NH_3 at 972 cm^{-1} .

The measurements will be compared to measurements with leadsalt-lasers at cryogenic temperatures.

DIODE LASER SPECTROSCOPY OF THE BORON MONOXIDE FREE RADICAL

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The spectroscopy of the boron monoxide (BO) free radical extends back to the early years of molecular spectroscopy and its interplay with the development of quantum mechanics[1]. The A - X electronic transition of BO in emission has been particularly well studied, culminating in the high resolution investigation of Coxon and co-workers [2]. The more recent investigations of the electronic spectrum of BO has been stimulated by the possibility of a BO chemical laser based on the A - X system [3]. The microwave spectrum of BO has been studied by Tanimoto *et al* [4]. This provided highly accurate fine and hyperfine constants for the $v = 0$ level of both ^{11}BO and ^{10}BO .

In the present study diode laser spectroscopy has been used to detect the fundamental bands of both ^{11}BO and ^{10}BO in the $^2\Sigma^+$ ground state. The radical was generated in a discharge-flow system, which was part of a multiple reflection (White-type) absorption cell, by reacting oxygen atoms with boron trichloride vapour. In order to form BO rather than BO_2 the oxygen atoms were generated by the $\text{N} + \text{NO}$ reaction. By suitable choice of flow conditions it was possible to fill a 1 m long cell with the blue chemiluminescence characteristic of the A - X emission of BO. Fifteen lines of ^{11}BO and three from ^{10}BO have been measured. They were easily identified using the optical and microwave results to predict line positions. The ^{10}BO lines show a resolved doublet splitting which is currently under investigation.

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PERFORMANCE AND DESIGN OF WIDELY TUNABLE QW LASERS WITH FLAT GAIN SPECTRA

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Laser diodes with a wide range tuned spectrum are successfully applied in spectroscopy and environment monitoring instead of other more complicated and expensive sources. Use of asymmetric multiple-quantum-well (QW) heterostructures gives additional possibilities to stipulate required laser regimes. In the work, spectral characteristics and output features of the asymmetric multiple-QW lasers are studied theoretically. For novel laser diodes, various ways of selection of the emitted spectra are analyzed and optimal schemes of the band gap diagrams are proposed. The tuning parameters of the lasers in an external cavity are determined and control of their radiation polarization and gain spectra is described.

Two problems concerning the tunability are considered, i.e., the widening of the gain spectrum and tuning curves and the attaining of the narrow-linewidth continuous tuning with no mode hops at enough high output powers. The control of the performance characteristics by widths, compositions, arrangement, and order of the QWs, cladding and barrier layer profile and by using the composite barriers and suitable their doping is studied to determine optimal structures of the multi-wavelength and widely tunable lasers. As shown, it is possible to obtain practically a flat modal gain spectrum in a wide spectral range. It occurs since the differ QWs give certain contributions to the total gain in different intervals of the spectrum in the conditions of non-uniform excitation of the active region. The required conditions are provided for a suitable mole composition and thickness of the doped barrier layers. Some different designs are possible for the tunable asymmetric multiple-QW lasers [1]. The active region can contain QWs of varied widths and the same composition [2]. Extended tunable gain spectra is also realized where the active region includes QWs of different compositions or QWs of varied widths and component compositions as well.

As an example, the modified Littman and Metcalf configuration of a selective external cavity is considered. Dispersion and feedback parameters of the diffraction grating and tuning mirror are optimized to enhance the laser power and to obtain stable output at the tuning. For the wavelengths near 820 nm, the GaAs–AlGaAs system is preferred. In this case, the width of the gain band reaches 50 nm and the tuning curve is practically flat at the output power of 10 mW. Using the other semiconductor materials in the laser active region allows to shift tuning curves to a required spectral range. For multi-component semiconductors, e.g., InGaAsP, the lasing wavelength can be displaced at 1.5 μm and the tuning range with a fixed output power of radiation reaches up 200 nm.

At a special design of the asymmetric multiple-QW heterostructures, gain spectra can be light polarization insensitive due to a superposition of optical transitions via heavy and light holes subbands in different QWs. The proposed tunable QW laser diodes are attractive as effective sources for a wide variety of applications, such as spectroscopy, chemical analysis, environment monitoring, metrology, and WDM optical networks.

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**RESULTS OF A SIMULTANEOUS ANALYSIS OF AN RQ (J, 0) Q BRANCH
IN METHYL FLUORIDE AT 1475 cm⁻¹**

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We have re-analyzed the Methyl Fluoride RQ (J,0) Q branch at 1475 wavenumbers using the simultaneous fit program previously described by Benner. The data we used is previously recorded diode laser data in which we measured only one or two lines in a particular run. The data are pieced together to create one continuous spectrum of the Q branch which we have measured under numerous conditions, all at room temperature.

We will describe the results of our analysis.

**STUDY OF THE SENSITIVITY OF A RESONANT PHOTOACOUSTIC CELL
WITH DIFFERENT COMMERCIAL MICROPHONES
FOR DIODE-LASER SPECTROMETERS**

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The theoretical and experimental study of the Differential Helmholtz resonant (DHR) cell sensitivity under varying of the gas pressure was made for the series of the commercial microphones (Knowles, Sennheiser, Bruel&Kjaer).

The infrared lasers (CO₂ lasers and room-temperature diode laser) were applied to measure the response of DHR cell vs. pressure of the absorbing gas and frequency of the laser radiation intensity modulation. The several molecular absorbers like CO₂, CH₄, C₂H₄ mixed with atomic or molecular buffer gases were used to investigate the behavior of the photoacoustic signal characteristics with a closed and open DHR cell. The experimental data are compared with the results of computer simulation.

The minimal detectable concentrations of CO₂, CH₄, C₂H₄ and other gases were determined for the DHR cell for every commercial microphones above mentioned.

RESONANCE PHOTOACOUSTIC SPECTROSCOPY AND GAS-ANALYSIS OF GASEOUS FLOW AT REDUCED PRESSURE.

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The results of theoretical and experimental studies of sensitivity of the resonant photo-acoustic Helmholtz resonator detector at gas flowing through a photo-acoustic cell under reduce pressure presented in this paper. The measurements of the sensitivity and ultimate sensitivity of the differential photo-acoustic cell were performed with – the near IR room-temperature diode laser using the well-known H₂O absorption line (12496,1056 cm⁻¹) as a reference one. The measured value of the ultimate sensitivity $(3 \div 5) \cdot 10^{-7} \text{ W} \cdot \text{m}^{-1} \cdot \text{Hz}^{-1/2}$ is in satisfactory agreement with calculated one which equals to $(15 \div 5) \cdot 10^{-7} \text{ W} \cdot \text{m}^{-1} \cdot \text{Hz}^{-1/2}$. The obtained value of the ultimate sensitivity provides the measurements of the concentration of molecules on ppb – ppm level.

HIGH RESOLUTION TDL SPECTROSCOPY OF RARE GAS-METHANE COMPLEXES

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The spectra of the weakly bound complex molecules Ne-CH₄, Ar-CH₄, and Kr-CH₄ in the 7 μm region were discovered and analysed. Measurements were made by probing a supersonic gas expansion with a tunable diode laser (TDL).

The spectra were measured in the region of the ν_4 fundamental band of the methane monomer. Located near the $R(0)$ transition of CH₄ at 1311.43 cm^{-1} , a conspicuous absorption feature of P , Q , and R branches was observed, respectively for Kr-CH₄, Ar-CH₄, and even for the very weakly bound Ne-CH₄. These transitions correspond to $j=1\leftarrow 0$, where j denotes the angular momentum of the methane unit inside the complex. Among a multitude of further Ar-CH₄ and Kr-CH₄ transitions (which are located in a spectral region from 1295 to 1330 cm^{-1}) a similar but weaker absorption pattern was detected near methane $P(1)$ at 1300.28 cm^{-1} corresponding to $j=0\leftarrow 1$. Assignment and analysis of both the $j=1\leftarrow 0$ and $j=0\leftarrow 1$ transitions were carried out using a Hamiltonian model, which incorporates the Coriolis coupling between the total angular momentum of the complex and the angular momentum of the methane unit. The model describes the splitting of the $j=1$ levels due to the Coriolis interaction and the potential effect to the almost free rotation of the methane monomer inside the complex.

The Ar-CH₄ data were compared with abinitio calculations.

**THIS – INFRARED REMOTE SENSING
WITH A TUNEABLE AND TRANSPORTABLE HETERODYNE SPECTROMETER**

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A new infrared heterodyne instrument has been developed which allows the use of both tuneable diode laser (TDL) and quantum cascade laser (QCL) as local oscillators (LO). The continuous tuning range of our system presently extends from 900 to 1100 cm^{-1} while the IF-bandwidth is 1.4 GHz using an acousto-optical spectrometer (AOS). The frequency resolution and stability of the system is approximately $3 \cdot 10^7$. Depending on availability of suitable mixers and lasers the operating range may extend from 3 to 30 μm and the IF-bandwidth can be extended to about 3 GHz. The instrument is fully transportable and can be attached to any infrared telescope.

The semiconductor laser is stabilized to a Fabry-Perot ring-resonator, which is also used as an efficient diplexer to superimpose the LO and the signal radiation. The laser linewidth and phase noise is greatly improved by controlled feedback due to the cavity established by the reflection from the HgCdTe-photomixer and the laser, whereby it is filtered through the narrow resonance of the diplexer.

As a first step measurements of trace gases in Earth's atmosphere were carried out and observations in planetary atmospheres are in progress. Astronomical observations from ground-based infrared telescopes and the air-borne observatory SOFIA are planned for the future. Particularly observations of the rotational lines of interstellar molecular Hydrogen at 17 or 28 μm are of interest.

EVANESCENT-FIELD FIBER SENSORS

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Laser absorption spectroscopy is a very suitable technique for measuring gaseous environmental pollutants because of its high sensitivity and selectivity and the capabilities for online and in-situ applications. In this context the mid-infrared (MIR) spectral region is of special interest because nearly all molecules have characteristic absorption bands within this “fingerprint” region. Recent developments in compact MIR laser sources make this spectral region even more interesting for analytical applications as there are DFB-diode lasers, difference-frequency generation (DFG) with “off-the-shelf” diode lasers and very recently quantum cascade lasers.

In general laser absorption spectroscopy requires an open optical path or a one- or multi-pass absorption cell that contains the gas under investigation. Laser and detector are located at opposite places of the probe. This technique requires optical thin media, scattering processes have to be negligible, and only optical accessible paths or locations can be used for diagnostics. This limits the possibilities of the method for several in-situ applications. However, evanescent-field laser spectroscopy in the MIR provides a technique that allows to apply absorption spectroscopy for diagnostics even in optical thick media, in media with strong optical scattering and at places that are not easy to access.

In the present paper evanescent-field laser spectroscopy is applied to measure H₂S concentrations online and in-situ in volcano gases (Solfatara, Italy) by tuning a single frequency DFB-diode laser around 1.57 μm . As a sensor material fused silica fibers are used. Typical gas flow streams out of the volcano fumerols are 10 ms^{-1} and the temperature is about 150 °C. Because of the extreme toxic environment the evanescent-field fiber sensor consists of the core material of the fiber only, no additional polymer layer is used for a selective adsorption of single molecules (in this case H₂S).

**A FAST CHEMICAL SENSOR
FOR EDDY CORRELATION MEASUREMENTS
OF METHANE EMISSIONS FROM RICE PADDY FIELDS**

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A high frequency modulation spectrometer /1/ with a lead-salt diode-laser operating in the ν_4 -band of CH_4 at $7.8 \mu\text{m}$ has been used as a fast chemical sensor to measure ambient methane concentrations of 2 ppmv with a time resolution of 10 Hz for micrometeorological flux measurement /2/. To assess the quality of data on methane emissions from rice paddy fields a comparison with simultaneously recorded data from the 'state-of-the-art' closed chamber technique showed that closed chamber measurements reported about 60-90% higher emissions than eddy correlation measurements during the campaign. This demonstrates that diode laser spectroscopy is a valuable tool for quality assurance /3/.

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A HIGH PERFORMANCE TUNABLE DIODE LASER ABSORPTION SYSTEM FOR AIRBORNE MEASUREMENTS OF FORMALDEHYDE I

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Formaldehyde (CH₂O) is a ubiquitous component of both the remote atmosphere and polluted urban atmospheres. This important gas-phase intermediate is a primary emission product from hydrocarbon combustion sources as well as from oxidation of natural hydrocarbons emitted by plants and trees. In the remote atmosphere, far removed from local sources, methane oxidation becomes the dominant source of CH₂O. Through its subsequent decomposition by photolysis and reaction with the hydroxyl (OH) radical, CH₂O serves as a source of the hydroperoxy radical (HO₂) and carbon monoxide (CO). In producing HO₂, CH₂O affects the partitioning among odd hydrogen radicals (HO_x = [H] + [OH] + [HO₂]), which through their rapid reactions with hydrocarbons control the oxidation capacity of the atmosphere. Radical production from CH₂O becomes particularly relevant at high solar zenith angles (sun near the horizon) and in the mid to upper troposphere, where other sources of odd hydrogen radicals become less important. Formaldehyde decomposition also produces carbon monoxide (CO), and in air masses not influenced by local pollution, CH₂O decomposition becomes a major source of CO to the global atmosphere. Finally, as many hydrocarbon oxidation reactions proceed through CH₂O as an intermediate, CH₂O becomes important in further testing our understanding of hydrocarbon reaction mechanisms. Highly accurate measurements of CH₂O throughout the mid to upper troposphere are thus important for improving our understanding of tropospheric photochemistry.

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. The present paper discusses an airborne tunable diode laser absorption spectrometer, which has been developed and refined over the past 5 years, to meet these demanding challenges. Numerous features and procedures, which have been adopted for high sensitivity, fast response times, and high accuracy, will be discussed. The present system achieves a 1-second CH₂O measurement precision (1σ level) of 100 to 150 pptv during airborne operation. One minute of averaging improves the precision to 15 to 30 pptv.

A HIGH PERFORMANCE TUNABLE DIODE LASER ABSORPTION SYSTEM FOR AIRBORNE MEASUREMENTS OF FORMALDEHYDE II: MEASUREMENTS DURING RECENT AIRBORNE CAMPAIGNS AND ATMOSPHERIC INFERENCES

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The importance of highly accurate, sensitive, and fast airborne measurements of CH₂O has been discussed in the previous abstract along with a high performance tunable diode laser absorption system (TDLAS) to carry out such measurements. In the present paper, we will discuss airborne CH₂O measurements carried out with such a system during a number of recent airborne campaigns. These include: (1) measurements carried out over the North Atlantic Ocean during the 1997 North Atlantic Regional Experiment (NARE-97); measurements carried out in the Arctic during the 2000 Tropospheric Ozone Production about the Spring Equinox (TOPSE) Study; and measurements during the 2000 Texas Air Quality Study (TexAQS 2000).

The present paper will discuss a number of specific aspects for some of the studies above. During the NARE-97 study, a comprehensive airborne comparison between the TDLAS measurements of CH₂O with those acquired by a coil/2,4-dinitrophenylhydrazine (CDNPH) technique operating onboard the same aircraft platform will be presented. This represents the first comprehensive airborne CH₂O comparison study in which two instruments based upon different measurement principles have been compared on a continuous basis throughout an entire airborne campaign. Six hundred and sixty five overlapping data points spanning ambient CH₂O levels ranging from 2 parts-per-billion (ppbv) down to background levels less than 50 parts-per-trillion (pptv) have been compared. The combined data set thus derived is then used to explore CH₂O measurement-model relationships in the clean background atmosphere. Measurement-model relationships in the clean background atmosphere (i.e., where methane oxidation is the primary source of CH₂O) in a number of previous studies have exhibited both positive and negative deviations. This divergence has raised numerous questions regarding both atmospheric models and the assumptions therein (including CH₂O sinks, photolysis frequencies, OH concentrations employed, and model CH₂O yields from CH₄ oxidation) as well as the veracity of the CH₂O measurements. Fast airborne CH₂O measurements carried out over Houston, Texas during the TexAQS 2000 study will also be discussed briefly.

TRACE GAS DETECTION WITH ANTIMONIDE-BASED QUANTUM-WELL DEVICES.

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Widely tunable GaInAsSb/GaAlAsSb quantum well lasers have been grown by molecular beam epitaxy on GaSb substrates. Narrow ridge (5 μ m) lasers have been fabricated from the grown wafers to provide single mode operation. These lasers were able to operate in continuous wave (cw) regime up to 140°C, which provides wide tunability between 2 and 2.4 μ m above RT and makes them suitable for detection of many gases. The single frequency behaviour required for spectroscopy applications could be obtained under certain driving conditions. It is very important for gas detection to know exactly the driving current and temperature providing the single mode emission at wavelengths corresponding to absorption lines of gases to be studied.

Two type of maps have been developed to characterise quickly spectral quality of the laser emission and gas detection conditions. The spectral quality is estimated by using a Fabry-Perot interferometer. The laser emission is tuned by a current ramp and the light beam is collimated through the interferometer. The acquired signals show oscillations which give information about the spectral quality of the emission. Many acquisitions were carried out to build the maps and zones of currents and temperatures with single frequency emission have been found after numerical treatment of the data.

It is quite attractive to know the spectral purity of the laser, but it is more important to know if the device is suitable to detect desired gas species. Wavelength modulation spectroscopy is known to be a sensitive gas detection technique often used in tunable laser diode spectroscopy to achieve traces detection. It can be used to build an absorption map, to show if the device is adapted to a given gas specie.

Many gases can be detected with these laser diodes thanks to their extremely large tuning range. A working open path demonstrator has been developed to perform gas detection in the ambient air at atmospheric pressure. The setup using a 13m long absorption path allows to detect the ambient methane with a sensitivity of 5 ppm.m. CO, CO₂, H₂O, HF and NH₃ have also been detected.

TUNABLE DIODE LASERS WITH WAVELENGTH 1250-1650nm

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In this report we present the results of diode lasers with wavelength 1250-1650nm characteristics. The single mode and single frequency lasers were constructed using methods of liquid phase epitaxy (LPE) and metalorganic chemical vapor deposition (MOCVD) growth technique. The active regions of the lasers are multi-quantum-well (MGW)

The investigation of the laser diode was made using a thermocooler. The laser diode spectrum was analyzed in a diffraction monochromator. The intervals of wavelength tuning were 20nm.

Laser diodes with 1250-1650nm wavelength were used for high-resolution spectroscopy.

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MOBILE METHANE DETECTOR BASED ON NEAR-IR DIODE LASER

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Portable automated high sensitive methane detector was developed and constructed for measurements of the trace gas concentration in the atmosphere. The device includes "Chernin" optical matrix multipass cell (50 cm base and up to 100 m optical path length). The main advantages of this cell are: suitability of changing optical pass length and vibrostability. Used in the detector near InfraRed (IR) tunable Diode Laser (DL) operating at wavelength 1.65 μm at room temperatures allowed avoiding coolants. The device is controlled by electronic multifunctional board (produced by National Instruments, Inc), which is inserted into the PCI bus of computer. The mode of the device controlling and data processing are produced in the program, created in LabView. The methane detector is fully automatized and can function continuously without operator; checked duration of the device continuous operating was 1 month.

Low-noise registration system and special techniques of DL controlling and signal processing allow to achieve the minimum detectable absorbance of $3 \cdot 10^{-6}$ of the incident laser power for atmosphere broadened spectral lines. Short-term sensitivity of methane detection in the open atmosphere was found to be 10 ppb, long-term stability (1000 hours) - 100 ppb, which is enough for methane concentration monitoring in the open atmosphere. Sensitivity of the methane detector is limited mainly by the optical interference changing and DL radiation flicker noise. Minimum time duration of one measurement without accumulation was 1 msec. Special techniques of signal processing also allow us to detect methane with very high selectivity with respect to other gases. Selectivity of the device with respect to propane and butane is more than 10^4 , to water vapor - more than $5 \cdot 10^5$, to CO_2 – more than $2 \cdot 10^5$.

The methane detector is rather compact and can be installed on a car or a helicopter for mobile real time measurements. We have produced such measurements in the streets of Moscow. We have measured methane concentration in car exhausts, near refill gas stations (leakages), near thermal power station, in the waster field. On the base of our measurements we found maps of methane distribution. Test measurements of methane leakages from gas-pipes were produced with the device, which was installed on helicopter.

REMOTE ALCOHOL DETECTOR

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Alcohol detector is intended for remote detection of ethanol vapour inside moving cars. The detector is based on tunable near infrared Diode Laser (DL) operating at room temperature and radiating at wavelength $1.392\ \mu\text{m}$ near maximum of ethanol absorption band. Base scheme of measurements is following. Ground part of the device including DL, optomechanics and photodetectors is installed on the one side of the road at the level of a car window. Radiation of DL passes through the side windows of moving car, is reflected from the cube reflector, installed on the opposite side of the road, passes once more through the car and hits photodetector. Photodetector signal is processed in computer and special calculation procedure allows determining of ethanol vapour content differences before, inside and after moving car.

The device is controlled by electronic multifunctional board (produced by National Instruments, Inc), which is inserted into the PCI bus of computer. The mode of the device controlling and data processing are produced in the program, created in LabView. The measurements are fully automatized and the Alcohol detector may function without an operator.

Low-noise registration system and special techniques of signal processing allow achieving the minimum detectable absorbance of 10^{-5} of the incident laser power in the alcohol detector. Achieved sensitivity of remote detection of ethanol vapour inside a car equals $1000\ \text{Pa}\cdot\text{cm}$ for one measurement (3.6 ms). Thus the device allows registering ethanol vapour concentration of standard legal limit for car drivers (20 Pa). From 10 to 100 readings can be made inside moving car (depending on the car speed), and the results may be accumulated. Selectivity of ethanol measurements with respect to water equals 100 : 1 in the Alcohol detector. It is sufficient for measurements of ethanol concentrations up to 5 Pa, while humidity is changed at 20%. Selectivity of alcohol measurements with respect to such substances as CO, CO₂, acetone and gasoline is at least $10^4 : 1$, 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.

CO₂ SENSOR BASED ON NIR DIODE LASER

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A prototype of diode laser (DL) based sensor for monitoring the content of CO₂ in patient breath has been developed and tested at one of the Moscow clinics (Botkinskaya). The sensor consist of Fabry-Perot DL (wavelength 1570 nm), two pass optical cell with inlet and outlet for patient breathing, reference cell with pure CO₂, computer with National Instrument Inc electronic board PCI-MIO-16E-4 installed for DL control and data acquisition, two Ge-photodetectors for each channel. The DL, operating in pulsed mode, was scanned across one of the CO₂ absorption lines. The signals in reference channel and in analytical channel were compared, and correlation function, proportional to the CO₂ concentration, was calculated. Two pass cell was manufactured from stainless steel tube 40 mm diameter and 500 mm length thus making the minimum necessary volume for measurements slightly more than 300 ml. While operation the glass windows of the cell were heated to 40° by wire spirals wound around the windows sides and held at voltage 5 V. Otherwise, the condensation of water from very humid air of patient breath covered the surfaces of windows with dew, dispersing laser beam. Inlet and outlet of the cell were connected to the standard 20 mm diameter flexible hoses, connected in series to outlet of artificial breath ventilator.

The accuracy of CO₂ concentration measurements was found to be 0.1 % volume within the range 0.1 – 10 % at the sampling rate 0.1 sec. The sensor could operate in real time, as well as measure the averaged CO₂ concentration during the chosen period. When the averaged CO₂ concentration falls down below the given level, alarm sounds to attract attention of medical personal.

The test carried out during two months at Botkinskaya clinics in Moscow under auspices of Prof. V.I. Molchanov with number of patients shown the perspective of the sensor application to the monitoring CO₂ in human breath. Among main advantages of the sensor there should be mentioned: first of all, high selectivity, specially to water vapor; high accuracy; fast response time (if necessary); variety of options. Among the drawbacks – large volume required for measurements and somewhat higher price compared to LED infrared sensor.

ABSOLUTE LINE INTENSITIES DETERMINATION IN THE ν_7 BAND OF C_2H_4 .

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In this work, we intend to test methods to determine with accuracy the absolute line intensities. These measurements concern 31 lines of the ν_7 band of ethylene C_2H_4 in the region of 1000 cm^{-1} . The lines with $5 \leq J'' \leq 21$, $1 \leq K_a'' \leq 3$, $2 \leq K_c'' \leq 20$ are located in the spectral range $915 - 970\text{ cm}^{-1}$.

For the intensity measurements, we have used two methods: the equivalent width method and the fitting profile method. In each case, for a given transition under study, four records have been made at different pressures, from which we have deduced an averaged value of the line intensity.

For the equivalent width method, the lines are recorded at very low pressure (between 0.12 and 0.5 mbar) to be in the Doppler regime and with a pathlength of 11 cm. For the line fitting method, the records are made at higher pressure in the range of 2.7 - 11 mbar and with an absorption path of 2.4 to 15.0 cm. For the modeling of the line, we have considered Voigt, Rautian and Galatry profiles.

The results from the different methods are discussed and the comparison with previous measurements are presented when it is possible. ^(1,2)

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**CYANOGEN CHLORIDE: SELF-BROADENING AND INTENSITIES
IN THE REGION OF 13 μm .**

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Recently, the cyanogen chloride has been the subject of several studies at high resolution. Global analysis of vibration-rotation spectra have been realized by Fayt et al. ⁽¹⁾ (see this paper for the references). In particular, the line positions of the ν_1 and $2\nu_2$ bands have been measured using a diode-laser spectrometer ⁽²⁾ and a Fourier transform spectrometer ⁽³⁾. But as far as we know, there is no study dedicated to the lines intensities for this molecule.

In the present work, we have recorded, in the case of the $2\nu_2$ band, 63 absorption lines (35 for the $^{35}\text{ClCN}$ isotopomer near 780 cm^{-1} and 28 for the $^{37}\text{ClCN}$ form) and, in the case of the ν_1 band, 78 absorption lines (42 for $^{35}\text{ClCN}$ and 36 for $^{37}\text{ClCN}$) in the vicinity of 710 cm^{-1} . Moreover, we have recorded 29 lines for the determination of self-broadening coefficients in the fundamental ν_1 band but only for the $^{35}\text{Cl}^{12}\text{C}^{14}\text{N}$.

From the analysis of the line intensities, we determine the absolute band strengths and the Herman-Wallis factors. As the ν_1 and $2\nu_2$ bands are perturbed by a strong Fermi resonance, there is a large transfer of the band intensity and we have analyzed this influence of the perturbation.

A semi-classical calculation of the self-broadening coefficients, performed by considering the main electrostatic interactions only, was compared with the experimental data.

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**PRESSURE BROADENING STUDY OF CARBON DISULFIDE
FOR ATMOSPHERIC DETECTION**

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Carbon disulfide was reported as a trace gas in the atmosphere and has been shown to be present in many samples of clean and polluted air collected at ground level ⁽¹⁾. It produces both OCS and SO₂ on oxidation and may provide an important source of sulfur dioxide ⁽²⁾.

N₂ and O₂ broadening coefficients have been measured for lines in the ν_3 fundamental band and in the $\nu_3-\nu_1$ band. These lines with J values ranging from 0 to 78 in the ν_3 band and from 4 to 70 in the $\nu_3-\nu_1$ band are located in the spectral ranges 1514-1548 cm⁻¹ and 853-858 cm⁻¹ respectively. The collisional widths are obtained by fitting the spectral lines with a Voigt and a Rautian profile.

Semi-classical calculations of these broadening coefficients have been performed by considering, in addition to electrostatic interactions, successively the atom-atom Lennard-Jones model and a simple formulation for the anisotropic dispersion forces leading to more satisfactory results.

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APPLICATION OF TRISTAR, A THREE-LASER TDLAS, DURING MINATROC

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We describe the application of the three laser **TR**acer **In-Situ** Tdlas for Atmospheric Research (TRISTAR), measuring nitrogen dioxide, formaldehyde and hydrogen peroxide, during a measurement campaign on Mt. Cimone (44°11'N, 10°42'E, 2165m asl, Northern Appenines, Italy) in June 2000 as part of the EU-project MINATROC, "MINeral dust And TROpospheric Chemistry". The TRISTAR instrument formed the main component of a measurement package, provided by the Max-Planck-Institut für Chemie, to investigate gas phase chemistry of the troposphere in the Appenines. Here we discuss the optical, electronic, gas flow and calibration set-up of the TDLAS used during the campaign. We extensively characterize the instrument's performance during a preparation phase in the laboratory, which is compared to the in-field results. Consistency checks with additional measurements obtained during the campaign create high confidence in the measured concentrations. Correlations between different gas species, along with other evaluation tools, allow full chemical characterization of airmasses to meet the goals of the campaign.

OPTICAL FREQUENCY MEASUREMENT WITH FABRY-PEROT INTERFEROMETER STABILIZED BY TWO PHOTON SPECTRUM OF Rb.

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Although many tunable laser diode systems of wide tuning range in the near infrared region have been available, progress of laser frequency measurement techniques which can be applied to a wide frequency range and in an accuracy of 10^{-9} has not been so made. We have usually measured laser frequency using the following techniques. (1) By tracing atomic or molecular spectra authorized as frequency standards with fringe marker signals generated by a Fabry-Perot interferometer (FPI) simultaneously. (2) By counting the fringe signals of an observed laser beam and those of a reference beam by driving one of the optical mirrors of a Michelson interferometer. (3) By using a heterodyne optical frequency measuring system.

In this work, we propose an absolute frequency measuring system that uses a FPI whose mirror gap is absolutely locked to the two photon signals of Rb. A block diagram is shown in Fig.1. The frequency of laser 1 was stabilized at the fringe signal of the FPI. This beam was introduced to the block shown as "Locking Loop 1" from which a frequency discriminator was generated by the two photon signal of Rb to fix the position of the mirror M_1 . The mirror M_2 of the FPI was locked by another "Locking Loop 2". The cavity length of the FPI was tuned to satisfy the operational condition of $\Delta n(c/2d) = \nu_2 - \nu_1$ (Δn : integer, c : light velocity, d : effective cavity length). The frequencies of the two fringe signals were locked at the frequencies ν_1 and ν_2 , respectively as shown in Fig.2. If the frequency of the 3rd laser is swept, the frequencies of the fringe signal generated by the FPI are given by

$$\nu_n = \nu_1 + \frac{c}{2d} \times n = \nu_1 + \frac{\nu_2 - \nu_1}{\Delta n} \times n. \quad (1)$$

The FPI was locked at the condition of fringe signals of $n=28$ between ν_1 (^{85}Rb , $5S_{1/2} \leftarrow 5D_{3/2}$, $F=2-4$) and ν_2 (^{85}Rb , $5S_{1/2} \leftarrow 5D_{5/2}$, $F=3-5$). Its FSR was 1464.68649(4) MHz and the accuracy of the system was estimated to be 10^{-9} using the Cs D_1 line frequencies.

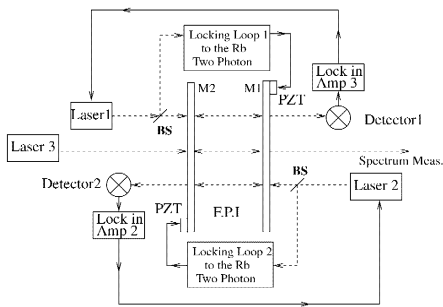


Fig. 1 Stabilized system of cavity length

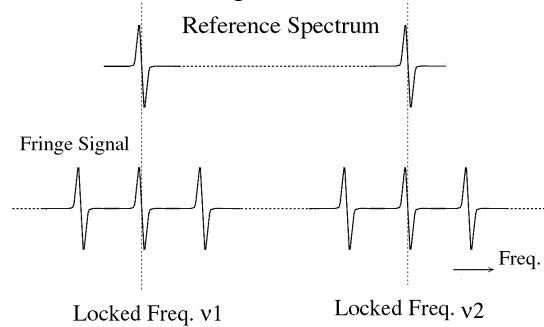


Fig. 2 Model of stabilized method

SATURATED ABSORPTION SPECTROSCOPY OF Xe USING A GaAs SEMICONDUCTOR LASER

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The high resolution spectroscopy of the electronic transitions from the $5P^56S$ states of Xe has lately been studied using atomic beam methods and the hyperfine structures have been reported¹⁻²⁾. Although the saturated absorption spectroscopy is much simpler than that of the atomic beam, it has been difficult to resolve the isotope shifts of even mass Xe³⁾. We report the isotope shifts of $^{136-128}\text{Xe}$ of natural abundance measured by a doubly modulated GaAs semiconductor laser beam. The diode laser (EOSI and New Focus) was frequency modulated by a 300 Hz sine wave and was introduced into the laser galvatron (Hamamatsu Photonics) counter-directionally against the pump beam. The gas pressure and the discharge current were adjusted to give a proper absorption condition at several tens of Pa and of 0.3 to 0.7 mA, respectively. The pump beam was chopped at 33 Hz by a conventional chopper. The saturated absorption signals were detected using two phase sensitive amplifiers connected in series. The first one was tuned at 600 Hz and the second derivative of the intensity-modulated dip signal was lock-in detected using a time constant of 1 to 10 ms. The output signal was then fed to the second one tuned to the chopping frequency and processed with a longer time constant of 300 ms. The powers of the pumping and probe beams were several mW and several tens of μW , respectively. The 5 transitions from the $5P^56S$ $J=2$ and 0 to the $6P[5/2]2$, $6P[5/2]3$, $6P[3/2]1$, $6P[3/2]2$, and $6P'[3/2]1$ states and the 4 transitions from $J=1$ to the $6P'[1/2]1$, $6P'[3/2]2$, $6P[3/2]2$ and $6P[1/2]0$ were measured from 0.81 to $0.91\mu\text{m}$ region. The recorder trace of the $6P[5/2]2 \leftarrow 6S[3/2]2$ transition is shown below. The splittings between $^{134-132}\text{Xe}$ and $^{132-130-128}\text{Xe}$ in the $J=1$ lines were hidden in the stronger component of ^{132}Xe . Using the King's plot⁴⁾ these shifts were estimated to be smaller than 40 MHz and the lines are overlapped by the broader width of 50~60 MHz caused by the short life time at the $J=1$ state. The electronic factors for the specific mass shifts and the field shifts will be presented.

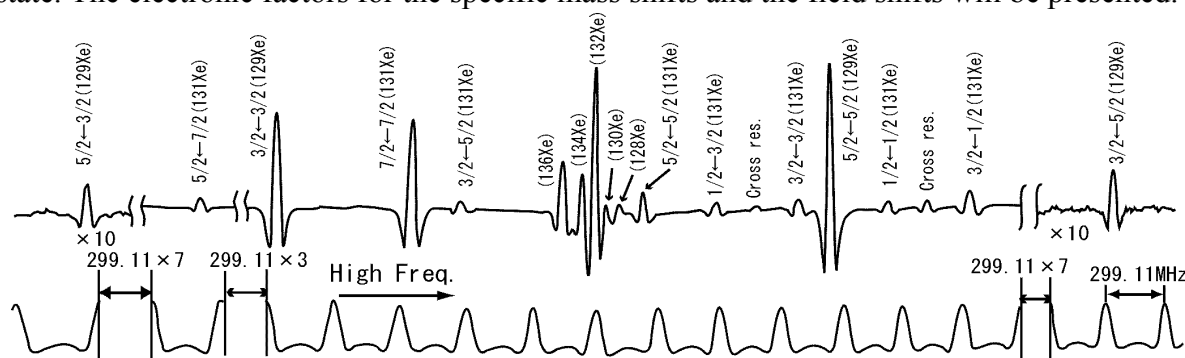


Fig. 1 $6P[5/2]2 \leftarrow 6S[3/2]2$ Transition of Xe(904.5 nm)

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INVESTIGATION OF INDUCTIVELY COUPLED LOW-DENSITY CH₄/O₂ PLASMAS BY MEANS OF TUNABLE DIODE LASER SPECTROSCOPY

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High-frequency discharge plasmas of methane and oxygen are used in technical applications for the deposition of hydrogenated carbon films. Admixtures of oxygen are employed to influence the properties of the deposited films but the understanding of the complex plasma chemistry and kinetics are far from being complete due to the large number of molecular species.

Absorption spectroscopy with tunable diode lasers can provide direct information on the molecular densities. A spectrometer with 5 different diode lasers has been set up to measure the densities of the following species: the source gases (CH₄ and O₂), some intermediate species (CH₃, C₂H₆) and some stable products (CO₂, CO and H₂O). To increase the sensitivity, a multipass cell (Herriott type) is installed, which provides 40 passes through the reactor chamber. A further increase of the detection limit is achieved by using the frequency modulation technique. Due to the sub-Doppler resolution the determination of translational temperatures of the molecular species is possible.

This work presents measurements in an inductively coupled GEC reference cell (13.56 MHz) with methane and oxygen as feed gases. The dependences of molecular densities on external parameters as the applied power, the flow rate and the gas composition are shown, and the behaviour of the detected species is discussed for different discharge modes (E-mode and H- mode).

THE COLOGNE CARBON CLUSTER EXPERIMENT

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The Cologne Carbon Cluster experiment combines a high resolution infrared diode laser spectrometer with a UV-laser ablation source for carbon clusters production.

We present the first measurements on linear C₈ in the gasphase and the analysis of the data.

The signal-to-noise ratio was usually in the order of 5:1 or less. It is thus obvious that for weaker infrared bands, e.g. the asymmetric stretching modes of cyclic clusters or the less populated overtone bands of linear carbon chains, the sensitivity has to be increased at least by one or two orders of magnitude.

This can be achieved by using an external cavity as an absorption cell to increase the effective absorption path length. Moreover it is well known that an external cavity can serve as an optical feedback element to lock a semiconductor laser to the resonance frequency of the cavity [1]. Optical feedback also leads to a reduction of the laser linewidth, which results in an improved spectral resolution.

To test and to characterize such a system we have used a 5 μm lead-salt diode laser and a high reflective confocal cavity. The cavity is built by two dielectric spherical planconcave mirrors with a reflectivity of 98 % at 5 $\mu\text{m} \pm 160$ nm and a free spectral range of 500 MHz. One of the mirrors is mounted on a piezo element to tune the resonance frequency of the cavity.

First measurements and the setup will be presented.

[1] see talk: THIS – Infrared Remote Sensing with a Tuneable and Transportable Heterodyne Spectrometer by G. Sonnabend, D. Wirtz and R. Schieder

ACCURATE DETERMINATION OF THE $^2\text{H}/^1\text{H}$, $^{17}\text{O}/^{16}\text{O}$, AND $^{18}\text{O}/^{16}\text{O}$ ISOTOPE RATIOS IN WATER BY MEANS OF TDLS AT 1.39 μm .

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The accurate measurement of isotope abundance ratios is an extremely important and, in fact, often indispensable research tool in a wide variety of natural sciences, such as bio-medicine, hydrology, paleo-climatology and atmospheric physics. At the Groningen Center for Isotope Research we have developed a relatively new, laser based, spectroscopic technique for the determination of such abundance ratios for environmentally relevant molecules, and water in particular. This technique has some major advantages over the traditional isotope-ratio mass spectrometer (IRMS) method: smaller sample sizes and direct measurement of isotope ratios in the water vapor, avoiding time consuming and inaccurate sample preparations that are otherwise required. Moreover, with the spectroscopic method it is possible to measure the $^{17}\text{O}/^{16}\text{O}$ ratio in water (in addition to the $^{18}\text{O}/^{16}\text{O}$ and $[\text{D}]/[\text{H}]$ ratios), as well as site-selective isotope ratios in more complex molecules. Both of these are not possible with the conventional mass-spectrometer, and provide ample opportunities for completely new research. This we will demonstrate by discussing applications in the fields of bio-medicine (the so-called “doubly-labeled-water” method to quantify the metabolism of free-roaming animals in their natural habitat) and paleo-climatology (ice-cores as archives of Earth’s past climate).

The original apparatus is based on direct absorption, gas phase spectroscopy using a color center laser at 2.73 μm , exciting ro-vibrational transitions belonging to the ν_1 or ν_3 OH-stretching fundamental. Signal detection is done by phase-sensitive detection at the frequency of amplitude modulation of the laser. In this paper we demonstrate that we can obtain a similar accuracy for the isotope ratios when using instead a frequency modulated, DFB, single-mode diode laser operating near 1.393 μm , despite the more than one order of magnitude lower transition strength in the overtone region. This enables the construction of a much more compact and cheaper apparatus, that may in principal be used on-site (or airborne).

**SELF-INDUCED PRESSURE-BROADENING MEASUREMENTS
OF OXYGEN TRANSITIONS IN THE A-BAND
WITH VERTICAL-CAVITY SURFACE-EMITTING LASERS**

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A very important factor when optimizing a combustion process is the O₂ content. To achieve accurate measurements of O₂ concentration, molecular parameters such as the pressure broadening coefficients have to be known.

An investigation of self-induced pressure broadening coefficients of the electronic transition $^1\Sigma_g^+ \leftrightarrow ^3\Sigma_g^-$ in the O₂ molecule has been performed. This transition is responsible for the weak absorption band around 13160 cm⁻¹, often called the red band or the A-band

In this work a single mode vertical-cavity surface-emitting laser (VCSEL) was used for the high-resolution measurements. Low-frequency wavelength-modulation spectroscopic (WMS) technique with second harmonic (2f) detection was employed when recording the spectra.

The experimental investigation was performed at 296 K and in a pressure range of 0.1-10 bar.

A synthetic 2f spectrum based on a Voigt profile was fitted to the measured data using a non-linear least square fit.

The result of this work demonstrates the importance of automatic line shape analysis for *in situ* O₂ measurements using tunable diode laser systems in gas monitoring and process control.

**ON-LINE AND IN-SITU MONITORING OF OXYGEN CONCENTRATION
AND GAS TEMPERATURE IN A REHEATING FURNACE
UTILIZING TUNABLE DIODE-LASER SPECTROSCOPY**

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Increased demands on energy savings and quality control in metallurgical processes have created incentives for new methods to monitor and control the process. In this paper we will present a field trial that shows the potential of tunable diode-laser spectroscopy (TDLS) for simultaneous measuring and monitoring of the oxygen concentration as well as the gas temperature in a reheating furnace during production.

The field trials were carried out at an oil-fueled reheating furnace during seven weeks of production. The tunable diode-laser spectrometer was measuring *on-line* and *in-situ* across the preheating zone and the soaking zone in the furnace. During the campaign the oxygen concentration and the gas temperature in the furnace environment were simultaneously monitored and instantaneous variations in these parameters could easily be recorded and subsequently correlated to actual changes in the process. Furthermore, the much shorter response-time of the TDLS technique compared to conventional measurement methods such as thermocouples and extractive gas analyzers was also demonstrated during the trials.

The results show the potential for the TDLS technique to be used for energy savings as well as product quality improvements by controlling the burners in the reheating furnace.

In its extension, the results indicate that the TDLS technique would be applicable to other metallurgical processes where the dust load isn't critical, e.g. in the blast furnace.

HIGH POWER InGaAsSb(Gd)/InAsSbP DIODE LASERS ($\lambda=3.3 \mu\text{m}$)

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Many researchers are now concentrating their efforts on studying the capabilities of III-V mid-infrared ($3\div 6 \mu\text{m}$) LEDs and diode lasers for environmental monitoring materials since these possess high thermal conductivity and metallurgical stability compared with II-VI and IV-VI systems.

We propose to use Gd doping in InGaAsSb(Gd)/InAsSbP Diode Lasers emitting at $\lambda=3.3 \mu\text{m}$. The rare earth (Gd) impact is a significant decrease of free electron concentration down to $8 \cdot 10^{15} \text{ cm}^{-3}$ and 10-fold increase of luminescence intensity due to Auger rate decrease.

Narrow stripe ($W=20 \mu\text{m}$) and broad contact ($W=200 \mu\text{m}$) lasers were fabricated from the wafer consisting of a wide-gap $n\text{-InAs}_{1-x-y}\text{Sb}_x\text{P}_y$ ($0.05 \leq x \leq$

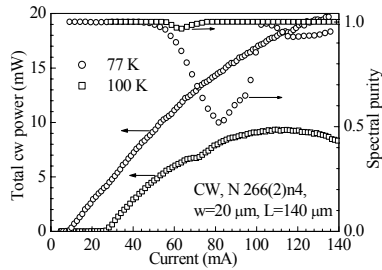


Fig.2 Total CW power – current dependence (left axis) and spectral purity (right axis) for narrow stripe lasers.

as high as 1.56 W is achieved at $I=9.5 \text{ A}$ in pulsed operation and 160 mW at $I=1 \text{ A}$ in CW regime at 77 K.

Strong current tuning in combination with narrow laser linewidth ($5\div 7 \text{ MHz}$) and high single mode power of $20 \mu\text{m}$ wide stripe lasers (19 mW, CW, 77K) (Fig.2) allows us to use them for gas analysis using wavelength modulation spectroscopy. Fig. 3 presents mode chat of a single-mode laser with $L=120 \mu\text{m}$ and $d\bar{\nu}/dI=70 \text{ cm}^{-1}/\text{A}$ (a), oscillograms of a sawtooth pump diode current pulse (b, left axis), and signals from a photodetector measuring the radiation transmitted through a Fabry-Perot etalon and 10 cm long gas cell filled with a 1% CH_4+N_2 mixture at atmospheric pressure (right axis).

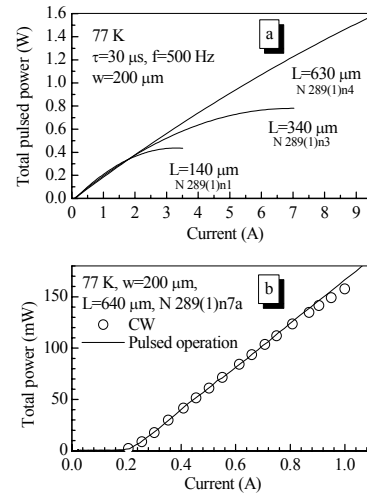


Fig.1 Total power – current dependence in pulse mode (a) and in CW (b) for broad contact lasers.

$0.09, 0.09 \leq y \leq 0.18$) confining layer, an $n\text{-In}_{1-v}\text{Ga}_v\text{As}_{1-w}\text{Sb}_w$ ($v \leq 0.07, w \leq 0.07$) active region and a wide-gap $p(\text{Zn})\text{-InAs}_{1-x-y}\text{Sb}_x\text{P}_y$ ($0.05 \leq x \leq 0.09, 0.09 \leq y \leq 0.18$) emitter. Fig.1 presents total (from two facets) power-current dependence in pulse (a) and in CW (b) regimes of a $200 \mu\text{m}$ wide laser emitting at multi modes centered at $3.3 \mu\text{m}$ at 77 K with threshold current density of $j_{\text{th}}=130 \text{ A/cm}^2$ ($I_{\text{th}}=164 \text{ mA}$, $L=630 \mu\text{m}$) and differential quantum efficiency as high as 54 %. As seen from Fig.1 output power

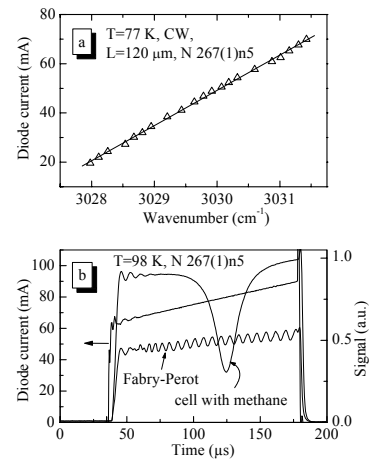


Fig.3 Tunability characterization of the single mode laser

DIODE LASER EMISSION LINEWIDTH DETERMINATION: APPLICATION TO H₂O LINE PROFILE STUDIES IN THE 5 AND 1.4 μ m REGIONS.

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The importance of H₂O in atmospheric sounding justifies the need for a precise determination of spectroscopic parameters describing the exact line profile of the absorption features used for such measurements.

Our H₂O line profile studies are covering two infrared regions with different tunable diode lasers (TDL): the R-branch of the ν_2 band (5 μ m) studied with lead salt diode lasers cooled in a liquid nitrogen dewar or in a helium closed cycle cryostat and the near infrared region (1.4 μ m) where the DFB diode laser operates at room temperature.

The absorption line profile measurements require a precise knowledge of the diode laser emission line shape. Using our TDL spectrometer with the diode laser wavelength accurately controlled by a Michelson interferometer, we have determined the emission line shape of the different diode lasers by analysing an absorption line observed at very low pressure.

Broadening and narrowing parameters were determined for H₂O lines taking into account the TDL emission line shape and using the soft or hard collision models to describe the H₂O line profiles. The absorber speed dependent effect has to be also taken into account for the widest lines. The consistency of measurements obtained in a large range of pressures from 10 Torr to several hundreds Torr is an additional check of our good knowledge of the TDL emission line shape.

**STABILIZED TUNABLE DIODE LASER MEASUREMENTS
OF THE R(0) AND P(2) LINES IN THE ^{13}CO FUNDAMENTAL BAND
BROADENED BY HELIUM FROM ROOM TEMPERATURE DOWN TO 12 K.**

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The active control of the diode laser emission by a Michelson interferometer developed at LPMA allows accurate line profile studies. This is the case even when line widths become comparable to the width of the Tunable Diode Laser (TDL) emission, a situation appearing for the lowest temperatures reached with the collisional cooling cells built at Connecticut College.

Below approximately 30 K, a regime where the collisional cooling technique is used, the maximum total pressure reaches only a few Torr and precise values of collisional broadening may be determined only if the shape of the diode laser emission is accurately known.

We have determined He broadening parameters for the R(0) and P(2) lines in the fundamental band of ^{13}CO from room temperature down to 12 K and the collision broadening cross sections have been deduced. Our results agree well with microwave measurements on pure rotational transitions of ^{12}CO previously reported by Beaky et al ⁽¹⁾.

Moreover from room temperature down to 50 K and for pressures between 10 and about one hundred Torr, it was necessary to describe the line profile by accounting for confinement narrowing (Dicke effect). The narrowing parameter has been determined by using the soft collision model of Galatry and evidence for its temperature dependence has been obtained.

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PRESSURE BROADENING STUDY AT LOW TEMPERATURE: APPLICATION TO METHANE

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Precise determinations of spectroscopic line parameters such as collisional broadening and narrowing are very important for atmospheric applications. In particular, the temperature dependence of these parameters are required for precise atmospheric sounding. This work is devoted to absorption lines of methane and we have started our study with the R(0) line of the ν_4 band of CH₄ located at 1311.43 cm⁻¹.

The spectra were recorded at high resolution with a tunable diode-laser spectrometer operating with a PbSnTe diode. The emission of the diode laser is stabilized with the help of a Michelson interferometer ^(1,2). The residual wavenumber fluctuations are smaller than 4 x 10⁻⁵ cm⁻¹.

In the first part of this study, we used an absorption cell with a path length of 40 cm operating at low temperature (between room temperature and 77K) with a temperature stabilization better than 0.5K ⁽³⁾. We have recorded spectra of the R(0) line at three temperatures: 153 K, 188 K and 223 K with N₂ and O₂ as perturbers and in a total pressure range of 15 mbar to 110 mbar.

In the second part of the present study, we used an absorption cell with a 4.2 cm path length. This cell is mounted directly on the second stage of a CTI-Cryogenics cooler, which permits a lowest temperature of approximately 12 K ⁽³⁾. In this case, we have recorded the R(0) line of CH₄ with He as perturber gas.

The line profiles have been fitted with a Voigt profile and with more elaborate profiles as the Galatry and Rautian –Sobel'man models. Preliminary results of this study are presented.

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**CHARACTERIZATION OF InAlAs/InGaAs/InP MID-INFRARED
QUANTUM CASCADE LASERS GROWN BY GAS SOURCE MBE ***

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Strong interest has been shown in the use of mid-infrared quantum cascade lasers based on intersubband transitions for trace gas sensing. For this type of lasers, quite large pulse current driving is often used. Because of the large amount of heat dissipated in the device, extraordinary short pulse duration as well as lower duty cycle are often needed. Further more, the room temperature background radiation also located in the mid-infrared band. For the characterization of this type of lasers, special considerations should be needed.

The InAlAs/InGaAs/InP quantum cascade lasers have been grown by gas source MBE. For the characterization of fabricated lasers, a GPIB programmable I-P and I-V measurement system based on direct waveform measurement with extraordinary wide pulse duration and duty cycle tuning ability has been developed. Double modulation technique has been introduced into a Fourier transform infrared spectroscopy system to measure the spectral characteristics of the lasers.

Based on above measurement system, the I-P, I-V and spectral characteristics of the InAsAs/InGaAs/InP quantum cascade lasers at different driving conditions as well as different temperatures have been measured, the results have been discussed.

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TRACE GAS DETECTION WITH MQW-DFB DIODE LASERS AND CAVITY RING-DOWN SPECTROSCOPY.

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It has been demonstrated that Cavity Ring Down Spectroscopy (CRDS) is well adapted to trace gas detection and measurement. We have already presented a scheme which allows CRDS in a CW or quasi CW mode. Here we will present and discuss, with details, our injection scheme based on optical feedback from a V-shaped cavity toward a telecom MQW-DFB diode laser.

We built trace-gas detectors for CH₄ and HF, characterized by a low cost, simplicity, compactness and sensitivity. Operating wavelength are 1.312 μm for HF and 1.65 μm for methane. The optical setup includes a multi-quantum wells (MQW) distributed feed-back (DFB) diode laser, temperature stabilized by a Peltier, a collimating lens, 2 steering mirrors, a V shaped optical resonator and InGaAs photodiode. The V-cavity is made of three low-cost super mirrors ($R \sim 99.998\%$) and contains the air sample to be analyzed ($\sim 20\text{cm}^3$). In standard atmospheric conditions the detection limits for 1 second integration time are of 50 ppb for HF and 200 ppb for methane corresponding to a sensitivity of $8 \cdot 10^{-10}/\text{cm}/\sqrt{\text{Hz}}$. We present fig 1, a schematic drawing of our apparatus.

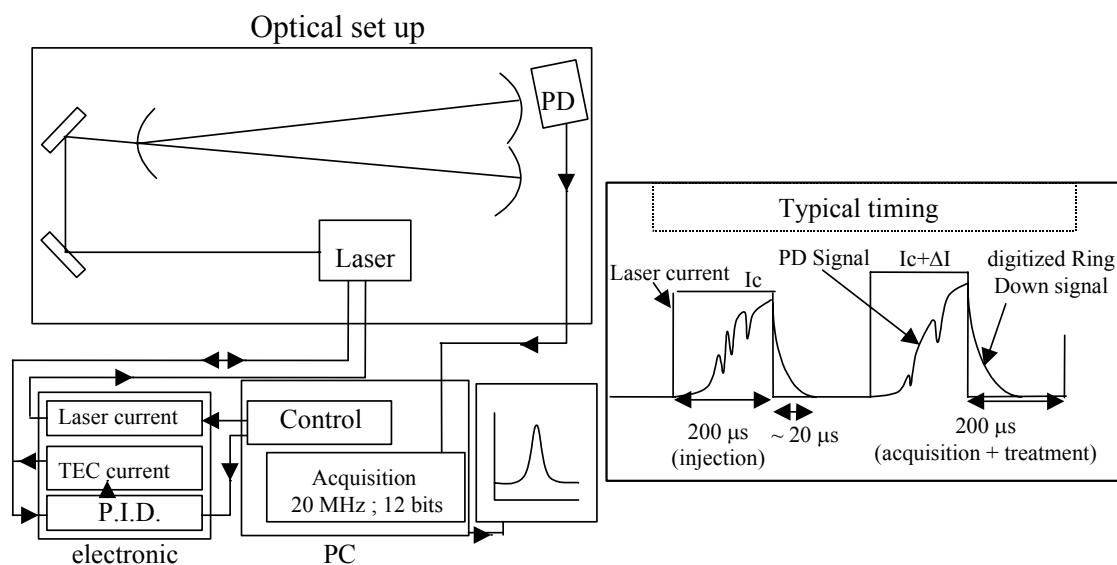


Fig 1

The optical feedback has been carefully studied and the roles of main parameters as optical path between laser and cavity, speed of wavelength scanning related to current pulse length, were understood and determined. A modelisation of injection efficiency vs scanning speed will be presented. The influence of all these parameters on the performances of the apparatus in term of sensitivity, measurement time and dynamic range, was also given. Experimental solutions for the precise control of that parameters are proposed and discussed.

**METHOD TO SYNTHESIZE POLYNOMIAL CURRENT WAVEFORMS
AND INTENSITY COMPENSATION FUNCTIONS FOR DFB LASERS
IN DIGITAL SWEEP INTEGRATION GAS ANALYZERS**

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With direct detection sweep integration analysis methods using linear current ramps, the resultant non-linear laser intensity and wavenumber functions can produce offsets and gain errors in concentration estimates in open path gas analyzers. The voltage/current, intensity, temperature and wavenumber relationships of the laser are embedded in a method to digitally synthesize polynomial current waveforms and intensity compensation functions to produce linear wavenumber functions and to minimize offset and gain errors. The method is applied in real time to manage the wavenumber modulation on a DFB laser with tuning widths in the range of 0.9 to 1.3 cm^{-1} suitable for H_2O at atmospheric pressure. To evaluate the method, quantitative results are presented comparing concentration values with and without the polynomial current waveform. Digital simulation of etalon fringes and non-linear wavenumber and intensity functions are also presented to allow visual identification of these errors through the Fourier (discrete cosine) transform harmonics and their ratios of the sample and reference absorbance functions.

**AN OPEN PATH H₂O/CO₂ GAS ANALYZER
FOR EDDY CORRELATION SYSTEMS: THEORY AND DESIGN**

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A fast response, open path TDLAS H₂O/CO₂ gas analyzer suitable for eddy covariance concentration measurements in near surface turbulent environments is presented. The turbulent temperature characteristics, analysis theory, analysis methods, design structure and specifications of this dual laser analyzer are detailed. A fiber connected optical head with folded optical path is used to extend the resolution to ppb levels for H₂O at 1.393 μm and CO₂ at 2.014 μm . The Fourier (discrete cosine) transform absorbance ratio analysis methods are outlined along with the modifications for temperature and pressure measurements in turbulent fields. Synthesis of the reference absorbance function using measured temperature, pressure and the Hitran parameters is extended with incorporation of the Hitran parameters n , gamma temperature exponent and E'' , lower state energy. Additionally, the mole fraction equation developed for this Hitran model is presented. Simulation results on mole fraction estimations and errors are presented for synthetic temperature and laser noise processes and are used to justify the specifications.

A FOURIER ANALYSIS APPROACH TO WAVELENGTH MODULATION DIODE LASER ABSORPTION SPECTROMETRY

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Wavelength-modulation diode laser absorption spectrometry (WM-DLAS) is a powerful tool for sensitive and selective detection of atoms and molecules. An major advantage of using modulation techniques is a significant reduction of noise and thus improvement of the detectability by a few orders of magnitude. The wavelength of diode lasers can be easily modulated which makes them extremely suitable for this purpose. The interaction of the spectrally modulated light with various species leads to the generation of absorption signals at various harmonics (nf) of the modulation frequency (f) which can then be easily extracted with phase sensitive electronics (lock-in amplifier).

A number of theoretical descriptions of the WM-technique have appeared in the literature throughout the years. However, none of these descriptions has been able to give a proper and general description of WM-DLAS signals. The present work presents a new comprehensive theoretical formalism based on Fourier analysis that is capable of handling both analytical and background harmonic signals under a variety of experimental situations [1]. As a part of this work, a new general non-complex formula for an arbitrary Fourier component of a modulation broadened Lorentzian absorption line shape function has been derived [2].

With the use of the formalism it was possible to perform a detailed study of various types of background signals which often limit the detectability of the WM-techniques like etalon effects [3] and background signals originating from frequency doubling processes [4]. The results were directly confirmed by experiments and have yielded good agreement with theory [3,5]. An extensive paper revisiting most of the features of the WM-DLAS is presented in [6].

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**RECENT LASER SPECTROSCOPIC SYSTEMS DEVELOPMENTS
AT AERODYNE RESEARCH, INC.**

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This paper describes several laser spectroscopic systems recently developed at Aerodyne Research, Inc. First, we describe two systems using lead-salt tunable diode lasers operating in liquid nitrogen cryostats. One system has been constructed for making carbon isotope measurements which employs a novel two-pathlength astigmatic Herriott absorption cell. The ratio of pathlengths of approximately 100:1 nearly matches the relative isotopic abundances, so that absorption lines of nearly equal strength can be used. Absorption transitions with nearly matched ground state energies gives reduced temperature sensitivity in these high precision measurements. The second TDL system we will describe employs a long open path (~1 km) for monitoring of ambient pollutants. Finally, we will describe a QCL based system used to measure ammonia at a sensitivity level of 50 parts-per-trillion rms in 1 second.

ETHYLENE SPECTROSCOPY USING A QUASI-ROOM-TEMPERATURE QUANTUM CASCADE LASER

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Mid-infrared (3-20 μm) is an important spectral range for gas spectroscopy, as most of the atmospheric constituents and pollutants present strong rotational-vibrational absorption bands in this region. The novel semiconductor quantum cascade (QC) lasers have shown very promising properties for infrared gas spectroscopy and are probably the future sources for this kind of application. Based on a fundamentally new principle (intersubband transition), their wavelength can be tailored using the same material over a broad band in the mid-infrared. These unipolar devices present several advantages in comparison with conventional lead-salt lasers previously used in the mid-infrared: their optical power is much higher and single-mode emission is possible in a distributed feedback (DFB) structure.

We report spectroscopic measurements on ethylene (C_2H_4) using a quasi-room-temperature DFB-QC laser emitting in the 10.3 μm range. Two different methods were experimented: (1) transmission spectroscopy with direct detection using a MCT detector for spectra analysis and (2) photoacoustic spectroscopy for low concentrations measurements. In our experimental set-up, the laser was mounted in a hermetic home-made housing and was cooled with a 2-stage Peltier element. It was operated in pulsed mode, with a pulse duration varying between 20 ns and 50 ns.

Wavelength tuning of the laser was achieved by scanning the laser holder temperature. A tuning range over more than 4.5 cm^{-1} and centered at 969.5 cm^{-1} was achieved by changing the laser temperature over 50°C . This corresponds to a tuning coefficient of $-0.095\text{ cm}^{-1}/^\circ\text{C}$. In this spectral range, several absorption lines of C_2H_4 and NH_3 were observed, showing an excellent agreement with the HITRAN database.

The effect of the pulse duration on the laser linewidth was analysed using direct detection of a strong C_2H_4 line at 969.96 cm^{-1} . The apparent width of this absorption line gets broader for increasing laser pulse duration, showing a broadening of the laser emission line. The laser linewidth enhancement as a function of the pulse duration was estimated from the apparent profile of the absorption line. A broadening coefficient of $9\cdot 10^{-4}\text{ cm}^{-1}/\text{ns}$ was obtained. This effect is expected to be produced by thermal heating of the laser during the pulse, shifting the laser line to longer wavelengths.

Photoacoustic (PA) spectroscopy was also investigated using this QC laser. For this purpose, the laser beam was coupled into a PA cell resonating in the first radial acoustic mode at a frequency $f \cong 10.5\text{ kHz}$ with a quality factor better than 600. The strongly diverging emission of the QC lasers results in large losses in the collimating optics and consequently poor light coupling into the cell, so that a limited sensitivity of 60 ppm was achieved. Better performances are expected by optimising the light injection and redesigning the cell to take into account the diverging characteristics of QC lasers emission.

Post-deadline papers

1. Simultaneous Detection of N₂O and H₂O Using a DFG Spectrometer at 3μm
A. Bruno, G. Pesce, G. Rusciano, A. Sasso
2. High Resolution Infrared Spectroscopy of Ar-HN₂⁺, N₂-H⁺-N₂, and N₂-Ar⁺-N₂
D. Verdes, H. Linnartz, J.P. Maier
3. A Novel Single Frequency Stabilized Fabry-Perot Laser Diode at 1590 nm for H₂S Gaz Sensing
Vincent Weldon, Karl Boylan, Brian Corbett, David McDonald, James O'Gorman
4. Analysis of Cigarette Combustion Gases Using High Resolution Infrared Laser Spectroscopy
Susan Plunkett, Milton Parrish, Zhiyuan Min, Ken Shafer, David Nelson, Mark Zahniser
5. FIR Generation and Mid-IR Spectroscopy Using an 8-μm CW Quantum Cascade Laser
G. Gagliardi, P. De Natale, S. Viciani, M. Inguscio, C. Gmachl, F. Capasso, D. L. Sivco, J. N. Baillargeon, A. L. Hutchinson, A. Y. Cho

