The 4th International Conference on Tunable Diode Laser Spectroscopy

(July 14–18, 2003, Zermatt, Switzerland)

The International Conference on Tunable Diode Laser Spectroscopy (TDLS) is held every two years. This conference attracts an increasing attention of scientists and specialists in designing diode lasers for fundamental and applied investigations and analytical instrumentation on their basis including devices for remote measurements. The 4th International Conference TDLS-2003 gathered 180 participants from 20 countries. Professors A.W. Mantz (USA) and A.I. Nadezhdinskii (Russia), the chairs of the Conference, devoted considerable efforts to organize the Conference and select the invited reports.

The program of the Conference included 45-minute invited lectures, a poster section, and a special session for representatives of industrial companies producing diode lasers and instrumentation on their basis. In parallel with the poster section, there worked an exhibition of scientific equipment fabricated by the companies.

Reports on the following problems were included in the program of invited lectures:

– diode laser high-resolution spectroscopy of molecules, radicals, ions, and clusters;

– diode laser spectroscopy of spectral line shapes;

– applications of diode laser spectroscopy to industry and atmosphere investigations;

– design of frequency tunable diode lasers and photodetectors for diode laser spectroscopy, improvement of experimental methods and apparatus.

The posters presented a series of results on creation of analytical measurers for measurement of gas trace concentrations in air and control for technologic processes.

A feature of the TDLS-2003 was a special industrial session, where the representatives of industrial companies, producing diode lasers and devices on their basis for physical and analytical investigations, delivered their 20-minute lectures.

Make a concise review of the invited reports and most interesting reports of the industrial and poster sections.

A.R.W. McKellar (Steacie Institute for Molecular Sciences, Ottawa, Canada) presented results of investigation of weakly bound molecular complexes and clusters with a tunable infrared diode laser spectrometer to probe a pulsed supersonic jet expansion. He studied high-resolution spectra of clusters containing up to 20 He atoms and a single infrared chromophore molecule, OCS, N_2O, CO_2, or CO. These are the largest van der Waals clusters, which have been studied by high-resolution spectroscopy methods. Two critical regions were observed in size evolution of clusters of CO–He_N type, at about $N = 7$ and 15.

Investigations of molecular free radical spectra (HCSi, CCO, FeC) with the use of the near-infrared (0.8, 1.3, and 1.5 μm) diode laser systems were reported by N. Ohashi (Kanazawa University, Japan). Manifestations of spin-orbit interaction and Renner–Teller effect were found in a thin structure of HCSi radicals.

The report by M. Lepère (Laboratoire de Spectroscopie Moléculaire, FUNDP, Namur, Belgium) and D. Hurtmans (Université Libre de Bruxelles, Belgium) discussed the results of studying spectral line shapes of molecular gases measured with high-resolution diode laser spectrometers. Based on a series of experimental results, different models of line shapes accounting for Dicke effect, speed distribution of molecules, and effect of temperature variations have been tested. Pioneer measurements of collisional broadenings of CH_4 diluted in He down to 15 K, conducted in collaboration with A.W. Mantz, were presented.

An improvement of cavity ring down spectroscopy (CRDS) and cavity enhanced spectroscopy (CES) techniques was a topic of two invited reports presented by D. Romanini, as well as D. Baer, M. Gupta, T. Owano, and A. O'Keefe (Los Gatos Research, Mountain View, USA). The first report presented results of real time monitoring of the atmospheric CO_2 with CRDS and CES spectrometers having a sensitivity at the ppm level.

The latter report informed on recent advances in the development of novel instrumentation based on a CES strategy called Off-Axis ICOS (integrated cavity output spectroscopy). In this strategy, the beam trajectory yields a significant decrease in the effective free spectral range of the cavity. Recent Off-Axis ICOS modification with diode lasers of a threshold sensitivity of $\sim 3 \cdot 10^{-11}$ $cm^{-1}/Hz^{1/2}$ and low-cost components was proposed.

High-sensitive instruments for photoacoustic detection and diode lasers with amplitude or frequency modulation of radiation allow designing a many-purpose instrumentation for molecular spectroscopy and gas-analysis of industrial gas mixtures and atmospheric air. Capabilities of different modifications of photoacoustic detection were discussed in reports submitted by S. Schilt, L. Thévenaz, P. Robert (Swiss Federal Institute of Technology, Lausanne, Switzerland) and M. Niklès (Omnisens SA, Lausanne, Switzerland), Yu.N. Ponomarev (Institute of Atmospheric Optics,

0235-6880/03/11 955-04 $02.00

Tomsk, Russia), and F.K. Tittel, A.A. Kosterev, Y. Bakhirkin, C. Roller, D. Weidmann and R.F. Curl (Rice Quantum Institute, Houston, USA).

The first report presented the investigation results on characteristics of photoacoustic detectors of different types for measuring trace gas components with CO_2 and diode lasers. Using CO_2 lasers, the authors have realized measurements of extremely low NH_3 concentrations.

The second report was devoted to design and application of differential photoacoustic detector (Helmholtz resonator) for the room temperature investigation of absorption spectra and spectral line shapes of H_2O and CH_4 molecules, using near-infrared diode lasers. The differential Helmholtz resonator provides for limit absorption sensitivity better than 10^{-10} cm^{-1} J. The measurements of nonselective molecular and aerosol absorption coefficients were demonstrated, which were obtained with the help of photoacoustic cell with acoustic concentrator and temporal resolution of signals.

In the lecture delivered by F.K. Tittel et al. the architecture and performance of several sensitive selective and real-time gas sensors based on mid-infrared cw and pulsed quantum cascade distributed feedback (QC-DFB) lasers were described. To date they have detected 11 gases (CH_4, N_2O, CO_2, CO, NO, H_2O, NH_3, C_2H_4, OCS, C_2H_4 and C_2H_5OH) including isotopic signatures of carbon and oxygen at the ppm to the ppt level. In design of the sensors, the authors used multipass gas absorption cells, photoacoustic detectors based on quartz cavities and cavity ring down, as well as absorption spectroscopy methods. Minimal detectable absorbances from 10^{-4} to 10^{-6} were achieved.

In the program of invited reports, investigations on gas analysis and detection of molecules and atoms were presented most widely. G. Durry (Institut Pierre Simon Laplace, Verrières-le-Buisson, France) reported about a diode laser spectrometer for measuring atmospheric concentrations of H_2O, CO_2, and CH_4 from stratospheric balloons in the upper troposphere and the lower stratosphere. This spectrometer was successfully used in 1999–2002 for measuring concentrations of these gases at mid- and high altitudes.

M.S. Zahniser (Aerodyne Research, Inc, Billerica, MA, USA) reported about creation of open-path-atmospheric-pressure (with telescope and retroreflector) and closed-path-reduced-pressure configurations of gas analyzers based on quantum-cascade lasers.

These were used to measure atmospheric gases including NH_3, C_2H_4, NO, NO_2, O_3, N_2O, CO, CH_4, and CO_2. The open path method is suitable for measurements from moving vehicles under field conditions. The closed path method using reduced pressure sampling into multiple pass absorption cells provides a greater sensitivity and sub-ppb detection limits with an absorption precision of $2{\cdot}10^{-5}$ Hz$^{-1/2}$. Examples from recent laboratory and field measurements were demonstrated.

Bruno Gayral and Stéphane Vannuffelen (SCHLUMBERGER EPS-SRPS, Clamart, France) reported on development of a meter of methane and ethane concentrations in the natural gas based on diode laser operating in 2300 ± 2.5 nm range. Measurement results were presented aimed at working out a monitoring system for estimation of the superior calorific value (SCV) of the natural gas. The results were obtained in the framework of the European project Gladis.

Problems of heterodyne measurements in the Infrared spectral range with tunable lasers for detection concentration profiles of molecular components of the atmosphere were discussed in the report presented by B. Parvitte (Faculté des Sciences, Reims, France) including first results on creation of a heterodyne system based on quantum cascade diode lasers.

The progress in the high-sensitive, accurate, and autonomous mid-IR instrumentation and diode laser gas analysis was a topic of the report presented by D. Richter, A. Fried, and J.G. Walega (National Center for Atmospheric Research, Boulder, USA). The authors developed and validated the performance of a robust solid-state optical fiber pumped difference-frequency generator with very high operation characteristics: near-Gaussian beam quality (> 90%), wide temperature (> 15 cm^{-1}) and current (> 1 cm^{-1}) frequency tuning range, flexible center wavelength selection (2.6–4.4 μm), narrow spectral line width (< 1 MHz), and single mode optical powers in the mW range. They developed the concepts towards totally autonomous compact mid-IR difference-frequency generators based on a gas absorption sensor employing opto-electronic technical noise-subtraction, that makes them highly applicable to measurements of atmospheric trace gases in the field and from airborne platforms.

Application of diode lasers to diagnostics of low-pressure, non-equilibrium molecular plasma was treated in the lecture delivered by J. Röpcke (Institut für Niedertemperatur-Plasmaphysik Greifswald, Greifswald, Germany). The absorption spectroscopy methods using diode IR lasers were applied to study molecular fragmentation processes and the reaction kinetics of stable and transient plasma species. The reported multicomponent acquisition systems contain between two and four independent tunable diode lasers, which can be directed through a plasma or into a multi-path cell for exhaust gas detection.

K. Niemax (Institute of Spectrochemistry and Applied Spectroscopy, Dortmund, Germany) presented examples where diode laser atomic absorption spectrometry was used in combination with gas and liquid chromatography, as well as the plasma and flame atomizer intended to analyze the atom formation in the process of molecular dissociation. The reported analytical systems are suitable for control for environmental and industrial processes.

Several invited reports presented results of working out diode lasers for laser spectroscopy and gas analysis, as well as laser systems on their basis.

A series of research groups, R. Köhler, A. Tredicucci, F. Beltram (NEST-INFM and Scuola Normale Superiore, Pisa, Italy), H.E. Beere, E.H. Linfield, A.G. Davies, and D.A. Ritchie (University of Cambridge, UK) have designed quantum-cascade cw lasers of terahertz range (2.8, 3.5, and 4.5 THz) with output powers of 4 mW and up to 45 K temperature. Under pulsed excitation, output powers of 4.5 mW at low temperatures and still 1 mW at 65 K were achieved.

The problems of frequency stabilization and narrowing line width of quantum-cascade laser generation were observed in the report given by M. Taubman, T. Myers, B. Cannon, and R.M. Williams (Pacific Northwest National Laboratory, Richland, WA, USA).

Recent achievements in designing diode lasers and semiconductor detectors for mid- and far IR spectral ranges were demonstrated in the report by D. Hofsteller, M. Graf, G. Scalari, L. Ajili, M. Beck, J. Faist (University of Neuchâtel, Institute of Physics, Neuchâtel, Switzerland), D. Ritchie, E. Linfield, H. Beere (University of Cambridge, UK), and H. Wu, W.J. Schaff, L.F. Eastman (Cornell University, Ithaca, NY, USA). The authors reported on room temperature cw operation of an InP-based 9.1 μm quantum cascade laser, as well as on a 77 K operated cw far-infrared GaAs/AlGaAs lasers and novel photodetectors.

M. Fejer (E.L. Ginzton Laboratory, Stanford University, Stanford, CA, USA) presented results of investigation of mid-infrared coherent sources based on microstructured nonlinear materials including difference frequency generators, as well as optical parametric amplifiers and generators. In all these sources, a near-IR pump (or two near-IR pumps) is converted to the mid-IR through a nonlinear interaction of optical waves. Examples of different sources including mW-level sources in 2–4 and 8–10 μm spectral ranges were used in spectroscopic measurements.

The industrial session included the reports presented by industrial companies, producing diode lasers and analytical systems based on diode lasers, such as Laser Components GmbH (Germany), Nanoplus Nanosystems and Technologies GmbH (Germany), VERTILAS GmbH (Germany), ProcessEng Engineering GmbH (Austria), Sacher-Lasertechnik Group, TOPTICA Photonics AG (Germany), Ekips Technologies, Inc. (USA), SIT.r.l. and Huberg S.a.s. (Italy), Southwest Sciences, Inc. (USA), Physical Sciences, Inc. (USA), Alpes Lasers SA (Switzerland), Aerodyne Research, Inc. (USA).

A series of reports presented by representatives of the industrial companies informed on new devices elaborated in cooperation with scientific groups of university researches and brought up to commercial production.

The Alpes Lasers SA company, for example, informed the auditory on quantum-cascade single-mode Fabry–Perot laser and a distributed-feedback QC laser operating near 8 μm. At room temperature, the maximum average power of the Fabry–Perot laser is more than 150 mW, and the second laser gives a maximum peak power of 1.7 W and a maximum average power of 30 mW, operating around to 8.36 μm and a tuning range of 6 cm^{-1}.

In cooperation with the Aerodyne Research, Inc., the Alpes Lasers SA designs sensors for diagnostics of atmospheric and polluting gases under field and laboratory conditions.

The open path gas analyzers for automobile exhaust measurements were presented capable of simultaneous measurements of NO, NO_2, CO, and CO_2 from moving vehicles at highway speeds.

The closed path configuration uses astigmatic multi-pass absorption cell allowing one to obtain up to 200 m path length and detect trace gases such as NH_3, NO, and O_3 at sub ppb level of concentrations.

M.G. Allen (Physical Sciences, Inc., USA) has demonstrated specifications of a series of analytical instruments based on near-IR and mid-IR diode lasers:

– *Integrated Multi-Gas Analyzer* (developed together with the AirLiquide Corporation) for simultaneous measurements of O_2, H_2O, and CO concentrations, as well as gas temperature based on the absorption ratio of two water vapor transitions;

– *Portable Gas Leak Detector* using a 1.65 μm diode laser for natural methane leakage measurements;

– *Room-Temperature Mid-IR Gas Analyzer* for NO (5.2 μm) and CO (4.6 μm) with 10 ppb sensitivity based on diode lasers produced by Lucent Technologies and Alpes Lasers SA companies.

The Italian companies SIT.r.l. and Huberg S.a.s. have presented a new methane sensor based on a diode laser operating at 1.65 μm wavelength and designed to operate on board of small vehicles. It operates within a concentration measurement range 1–10000 ppm at 1 ppm sensitivity.

It should be noted that the sensitivity of this sensor is an order of magnitude lower than of a similar system devised by A.I. Nadezhdinskii group (General Physics Institute of the Russian Academy of Sciences, Moscow, Russia) for vehicle- and aircraft-board operation. Their results were also presented at TDLS-2003 as a poster.

One of the main problems in development of analytical instruments based on diode lasers and intended for measuring the composition of atmospheric and technical gases at ppm-ppb and ppt levels is a manufacturing of calibration gas standards of the same accuracy class.

Specialists from the Messer Griesheim GmbH company K. Brenner and B. Reimann have discussed the problem of manufacturing two- and many-component calibrating gas mixtures, as well as the necessity of using highly precise methods of gas analysis in the manufacturing.

Laser modules and components for manufacturing frequency tunable mid-IR (3–25 μm) diode lasers were presented by the Mütek Infrared

Laser Systems. They proposed two types of lasers for this spectral range: double hetero structure lasers (3–10 μm) and homogeneous structure lasers (10–25 μm). Lasers of the former type operate at 85–120 K, the latter ones – at 25–85 K. The company offered a series of laser systems.

Most high-power laser systems were presented by two industrial companies: TOPTIKA Photonics AG (up to 1 W in 375–450 μm range) and Sacher-Lasertechnik Group (in the near-IR, 625–1850 μm). Laser emitters of the Tiger series produced by the latter company are oriented to the program of laser cooling of alkali metal atoms.

A series of diode lasers with emission wavelength between 1.5 and 1.8 μm for molecular spectroscopy were presented by the VERTILAS GmbH, ProcessEng Engineering GmbH companies, and two Institutes: Institut für Verfahrenstechnik, TU-Wien, and Walter Schottky Institut, Technische Universität München.

This cooperation is working out the vertical-cavity surface-emitting lasers (VCSEL), whose radiation is absorbed by CH_4, NH_3, HCl, and H_2O. The lasers with output powers ≤ 1 mW operate in the single mode at the room temperature.

Stable single-mode lasers with distributed feedback for spectroscopic investigations in the range 0.7–2.5 μm were offered by the Nanoplus Nanosystems and Technologies GmbH company as well.

Commercial aspects of TDLAS were a topic of the report made by J. Kunsch (Laser Components GmbH, Germany). The speaker noted that the region of applicability in spectroscopic measurements of the TDLAS is still in disadvantage in relation to FTIR methods, but TDLAS can be successfully used in the control and monitoring systems.

The papers presented at the TDLS-2003 poster section well complemented the topics of the invited reports. Dwell on those, which demonstrated new results of fundamental and applied character.

Fiber-coupled near-infrared diode laser based *in situ* hygrometer was developed for detection of water traces in cryogenic aerosol clouds by C. Giesemann, H. Teichert, and V. Ebert (Physikalisch-Chemisches Institut, University Heidelberg, Germany), H. Saathoff and U. Schurath (Institut für Meteorologie und Klimaforschung, Karlsruhe, Germany). The hygrometer, based on a diode laser (1.37 μm) and multi-pass 82 m White-cell, provides for measurements of H_2O concentration at 15 ppb level.

A series of optimization methods for trace molecule detection with tunable diode lasers, their classification and principle limitations were discussed in the paper by A.I. Nadezhdinskii (Natural Science Center of A.M. Prokhorov General Physics Institute, RAS, Moscow, Russia).

Infrared and millimeter-wave spectra of the $^{13}C^{16}O$ dimer, studied in order to assign and precisely locate energy levels, were reported in the paper by L. Surin, D. Fourzikov, G. Winnewisser (Physikalisches Institut, Universität zu Köln, Germany), B. Dumesh (Institute of Spectroscopy, RAS, Troitsk, Russia), and J. Tang and A.R.W. McKellar (Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Canada).

Application of diode lasers to detection of traces of explosive matters (from the presence of a specific tracer, NO_2) and UF_6 was a topic of the poster presented by A.I. Nadezhdinskii, Ya.Ya. Ponurovskii, M.V. Spiridonov, E.A. Kudryashov, Yu. Selivanov, G. Grigorev, Sh. Nabiev, N. Gorshunov, G. Bosler, R. Olsen, and V. Ryjikov. The investigations were performed in cooperation of NSC of A.M. Prokhorov General Physics Institute with P.N. Lebedev Physical Institute, Institute of Molecular Physics of RRC "Kurchatov Institute" (Moscow, Russia), and International Atomic Energy Agency (Vienna, Austria).

A dual-wavelength diode laser spectrometer devised by L. Gianfrani, G. Gagliardi (Dipartimento di Scienze Ambientali, Seconda Universita di Napoli and INFM-Gruppo Coordinato Napoli 2, Caserta, Italy), and M. van Burgel and E.R.Th. Kerstel (Center for Isotope Research, University of Groningen, The Netherlands) was applied to measuring the isotope composition of water.

Significant progress in power enhancement of diode laser systems for their use in laser sensing of the environment can be reached due to application of Raman fiber amplifiers. This direction was elucidated in the poster by A.G. Berezin, O.N. Egorova, O.V. Ershov, A.S. Kurkov, A.I. Nadezhdinskii, and V.M. Paramonov (Natural Science Center and Fiber Optics Research Center of A.M. Prokhorov General Physics Institute of RAS, Moscow, Russia). The amplifiers provide for output powers up to several watts (instead of initial several mW) in the range 1.1–1.7 μm.

Results of development of a stabilized low temperature infrared absorption cell for determination of spectral line parameters at temperatures as low as 7 K were presented by A. Valentin, A. Henry, C. Claveau (Université Pierre et Marie Curie, Paris, France), D. Hurtmans (Université Libre de Bruxelles, Bruxelles, Belgium), and A.W. Mantz (Connecticut College, Connecticut, USA). Data on the shape of absorption line collisional contour at low temperatures, obtained using the tunable diode laser based spectrometer, were applied to an analysis of the accuracy of theoretical models.

As a whole, the TDLS-2003 Conference has demonstrated a noticeable progress in diode laser spectroscopy technique and, particularly, its analytical applications. The result of the highly efficient cooperation of scientific organizations and industrial companies is the rapid commercialization of a diversity of scientific designs.

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