QC-DFB—Dr. Thomas L. Harman, Professor and Chair of the Computer Engineering Department (UHCL) develops chemical sensors designed to measure air quality in the habitats of space. His findings and designs also have applications in environmental science and in medical diagnostics. New techniques and technology provide for fast, sensitive, and selective gas detection based on laser spectroscopy. He and his researchers use QC-DFB lasers to meet specifications for more accurate gas concentration measurements based on novel pulsed and cw quantum cascade lasers.

Novel Trace Gas Detection Techniques with Quantum-Cascade Lasers

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Abstract

There is an increasing need in many chemical sensing applications ranging from air quality in spacecraft habitats to environmental science and medical diagnostics for fast, sensitive, and selective gas detection based on laser spectroscopy. The recent availability of novel pulsed and cw quantum cascade distributed feedback (QC-DFB) lasers as mid-infrared spectroscopic sources address this need. A number of spectroscopic techniques based on QC-DFB lasers have been employed by ISSO investigators to demonstrate the monitoring and quantification of trace gases and isotopic species in ambient air at ppmv and ppbv levels by means of direct absorption, wavelength modulation, cavity enhanced, and cavity ring-down spectroscopy.

SENSITIVE, COMPACT DEVICES FOR THE QUANTIFICATION OF trace gases are required for a number of applications that include air quality in spacecraft habitats, in environmental monitoring, and in non-invasive medical diagnostics. A well-established technique for detecting molecular species in the gas phase is high-resolution infrared absorption spectroscopy. Until recently, real-world applications of this method were limited because of the absence of convenient tunable coherent light sources in the mid-IR region (3 to 20 μm) where the fundamental absorption bands of most molecules are located. This situation is changing with the development of quantum cascade (QC),[1,2] especially single-frequency devices with an imbedded distributed feedback structure (QC-DFB).

QC-DFB lasers are capable of delivering tens, and for certain devices, even hundreds of milliwatts of narrow-linewidth mid-IR radiation. QC lasers can be operated in pulsed mode up to and above room temperature, which is of particular interest for real-world gas-sensing applications because it eliminates the bulkiness and cost of an optical cryostat and cryogenic consumables (liquid N_2). The first laboratory demonstration of the sensitive absorption spectroscopy with a pulsed QC-DFB laser was reported in Namjou et al.[3] where wavelength modulation was used to improve signal-to-noise ratio (SNR). The application of the direct absorption technique with a pulsed QC-DFB laser for trace gas detection in ambient air was first described in Kosterev et al.[4] In this report, we present details of the design and performance of a robust, portable ammonia sensor based on a pulsed QC-DFB laser operating at ~10 μm. This sensor has been successfully applied to dynamic ammonia concentration monitoring of bioreactor vent gases in the NASA-Johnson Space Center (JSC), Houston, TX.

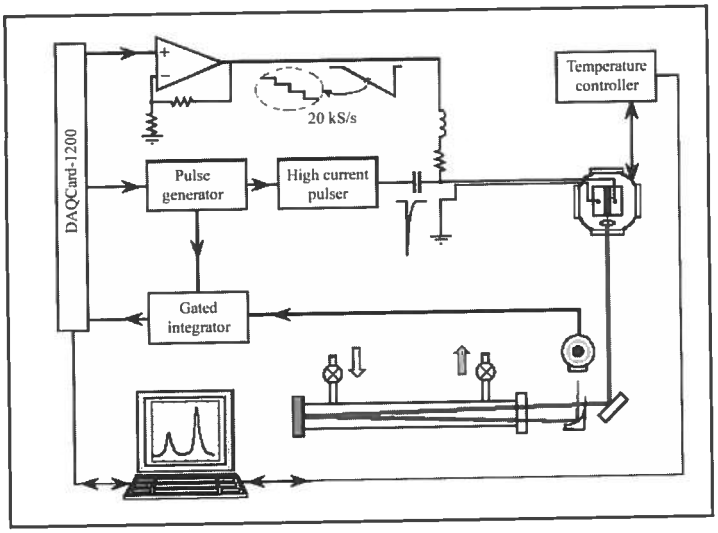


Figure 1. Schematic of QC-DFB Laser Based Ammonia Sensor

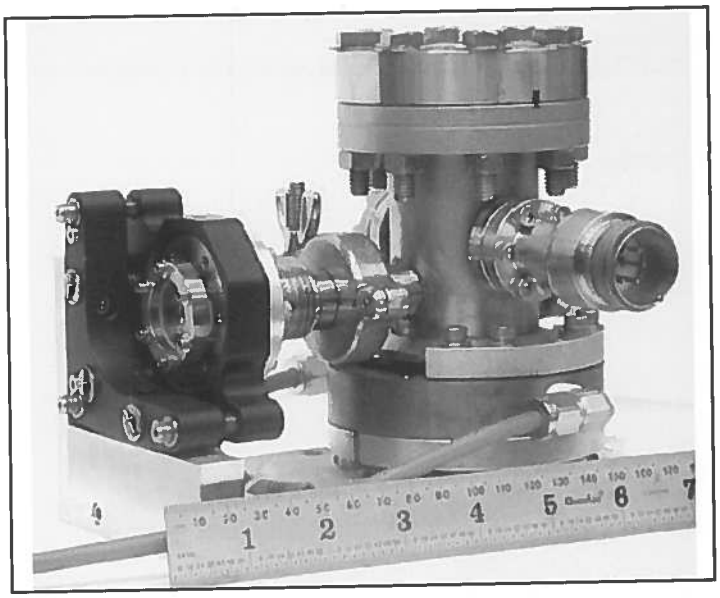


Figure 2. Photograph of the vacuum-tight pulsed QC-DFB laser housing. The QC laser is mounted on a three-stage thermoelectric (TE) element inside housing. Windows on top and opposite to the beam output facilitate alignment of the collimating lens (f = 3 mm, Ø6 mm). The bottom of the housing is made of copper for better thermal conductivity. It is soldered to the TE element and if necessary can be water-cooled.

Technical Plan and Equipment

To detect NH_3, the absorption lines ${}^aR_1(2)$ at 992.4503 cm^{-1} and ${}^aR_0(2)$ at 992.6988 cm^{-1} (~10.1 μm) in the ν_2 fundamental absorption band were selected. These lines are strong, well resolved at pressures below 200 Torr, and free from interference by water absorption and absorption by other air components. The pulsed QC-DFB laser available for this work accessed this wavenumber region when operated at a temperature of -11.7°C.

Ultrasensitive ammonia detection in this spectral region with pulsed QC-DFB laser has been reported before in Kosterev et al.[4] In this work, a multipass cell with a 209 m effective path-length and two IR detectors were used to achieve improved sensitivity in detection. The emphasis in the present work was to achieve moderate (sub-ppm) sensitivity levels with a simple and cost-effective sensor platform (i.e., a single detector and no multipass gas cell).

The NH_3 sensor design is shown schematically in Fig. 1. The QC-DFB laser was mounted on top of a three-stage thermo-electrical unit inside a vacuum-tight housing with overall dimensions of 100×160×180 mm^3 (Fig. 2) assembled from commercially available vacuum and opto-mechanical components. To remove the heat generated by the operation of the Peltier cooler, the bottom of the thermo-electrical unit was soldered to a water-cooled housing base. A temperature controller (Wavelength Electronics LFI-3751 TE) was used to set and monitor the laser temperature. With this arrangement, the operating QC-DFB laser could be cooled to -55°C.

The laser emission was collimated using an aspheric AR coated *ZnSe* lens with a focal length of 3 mm and a diameter of 6 mm mounted inside the housing. The lens position could be adjusted externally. The collimated laser light emerged from the housing through a 30 ft. wedged AR coated *ZnSe* window and was directed into a 0.5 m-long optical gas cell. This cell consisted of a glass tube fitted with Teflon valves and stainless steel window holders based on commercial 1-1/3 in. vacuum flanges. One end of the cell was equipped with a 30 ft. wedged AR coated *ZnSe* window and the other one with a *SiO* protected flat *Al* mirror (both Ø25.4 mm). This resulted in a two-pass configuration with a total optical path-length of 1 m. The exiting beam was focused onto a liquid nitrogen cooled *HgCdTe* detector with a built-in preamplifier (Kolmar KMPV10-1-J1/DC, 20 MHz bandwidth) by means of a 25.4 mm diameter off-axis parabolic mirror.

The utilization of a cryogenic detector does not imply strong limitations on the sensor performance because it uses only a small amount of liquid nitrogen and has a holding time of ~ 15 hours. In the future, researchers envision the use of a thermoelectrically cooled detector. The air to be analyzed flowed continuously through the absorption cell at a low controlled flow rate. The relatively slow flow was necessary because the bioreactor vent system permitted gas sampling only at a rate of 10 sccm or lower. A pressure controller was used to maintain the pressure inside the cell at 95 Torr. The laser housing, optical gas cell, gas flow meter, pressure controller, IR detector, visible diode laser for alignment, and optical components were mounted on a 30.5 cm × 61 cm aluminum breadboard.

Experimental Activity

The laser current was supplied in 5 ns long, ~4A peak current pulses at a 20 kHz repetition rate, as described in previous publication.[4] A compact driver (Directed Energy PCO-7110 model 40-4) was used for the QC-DFB laser excitation and a computer-controlled sub-threshold current pedestal was added to each pulse for setting the optical pulse frequency. By appropriate ramping of the sub-threshold current, 512 laser pulses at a 20 kHz repetition rate scanned the desired spectral range. The tuning voltage that defines the sub-threshold current was applied in the shape of a linear ramp with an offset to compensate for the initial bias of the QC laser. A DAQ-1200 data acquisition card and LabView software (National Instruments) was used to trigger the laser pulser, set the sub-threshold current, and acquire spectral data. The num-

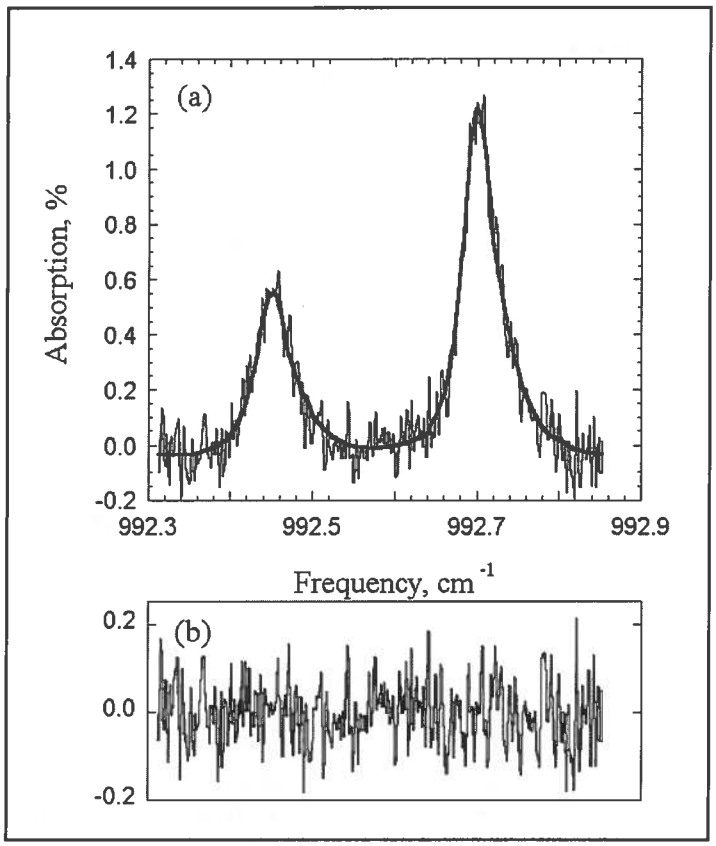


Figure 3. (a) Example of an acquired data set after automated baseline correction and fitting with the previously tabulated function (See section on "Experimental Activity"). The fitting yielded a 6.7 ppm NH_3 concentration in the sample. The fit residual is shown in (b).

ber of pulses in a scan was limited by the capabilities of this card. The repetition rate was limited by the gated integrator (Stanford Research Systems, model SR250) used as an interface between the fast IR detector and data acquisition card. The scans followed each other with ~50% duty cycle because of computer software/hardware limitations. In most sensor runs, data were analyzed to determine the NH_3 concentration after acquiring and averaging 400 scans. The measurement sequence was repeated every four minutes.

The position of NH_3 absorption lines provided an absolute frequency reference for frequency calibration. The frequency scale was linearized by means of interference fringes from two air-separated uncoated *ZnSe* surfaces. The scan length was set to 0.75 cm^{-1} in order to observe simultaneously the 992.4503 and 992.6988 cm^{-1} lines. By using data acquired at relatively high NH_3 concentration, researchers determined that the QC laser possessed a linewidth of ~0.02 cm^{-1} with an asymmetric shape. This broad, asymmetric laser line shape makes traditional analysis of spectra by fitting the lines with either Lorentz or Voigt functions inapplicable. Instead, the following procedure was used:

1. A reference spectrum in terms of base e absorbance was acquired using a N_2:NH_3 mixture containing ~100 ppm of NH_3. The actual concentration of NH_3 in this reference sample was determined by comparing the area of the absorption lines ($\alpha\delta\nu$, where α [cm^{-1}] is the absorption coefficient) to the area predicted by the HITRAN database for the same temperature. The spectrum was then stored in the computer memory as a function $y_i = f(i)$, where i is a data point number (i.e., a number of the corresponding laser pulse in the frequency scan). This function results from the convolution of the real absorption spectrum and the laser line-shape.
2. A spectrum of the gas sample containing an unknown concentration of NH_3 was acquired at the same pressure and temperature.
3. Using a high concentration reference spectrum, three (almost) absorption-free parts of the spectral scan were defined (i.e., between and to both sides from the two NH_3 absorption lines). The baseline of the low concentration, unknown gas sample spectrum was determined by fitting a sixth order polynomial to the corresponding segments of its spectrum. The fractional absorption, y_i, of the unknown sample was computed extending the baseline under the two absorption lines. Because the absorbance was small for the unknown spectrum, conversion to base e absorbance was not needed.
4. The best fit of the sample fractional absorption by the function
$$y_i = Bf(i-x) + b \quad (1)$$
was found. The parameter x is introduced to compensate for slow drift of the line positions on the scan because of slight variations of the laser temperature. The b parameter helps to partially correct for an error in the baseline interpolation. Usually the fit resulted in $b \approx 0$. The parameter B yields the concentration in the test gas sample relative to the reference gas sample.

In order to perform the fitting in step 4, we modified a LabView procedure "*Nonlinear Lev-Mar Fit.vi*" so that it can use a tabulated function instead of an analytic expression. An example of the fitted data is presented in Fig. 3. This spectrum corresponds to 6.7 ppm of NH_3 and was acquired with 400 frequency scans. The standard single-point deviation of the fit is $\sigma = 7.14\times10^{-4}$ fractional absorbance (with a l0 s data acquisition time).

The 1 Mhz-equivalent sensitivity was 3.2×10^{-4} $Hz^{-1/2}$ after applying normalization to the repetition frequency (i.e., the square root of the frequency ratio). The primary source of noise in our measurements is attributed to fluctuations of the laser pulses energy. Two-channel detection can be used if improved sensitivity is required for a specific application. In a separate experiment, we could obtain at least one order of improved sensitivity by normalization to a reference channel.

Real-time determination of the actual trace gas concentration in a system such as the atmosphere or bioreactor, as reported in this work, can be made more accurate by taking into account intrinsic system properties. In our case, the short time fluctuations in the measured concentration reflect the sensor properties and not the behavior of the gas concentration in the system. For this system, the actual NH_3 concentration is not expected to exhibit stochastic fluctuations every four minutes as measurements are performed. Changes in the bioreactor occur on a time scale of hours. Ammonia absorption and desorption from the walls of the tubing connecting the sensor to the system add further inertia to the measurements. Therefore, mathematical filtering that removes part of the high-frequency variations from one measurement to the next should improve the measurement accuracy.

To discern slow trends in concentration in real time, a Kalman filtering technique[5] can be applied to trace gas measurements for

various slow-changing systems. With an appropriate choice of filter parameters, such filtering has been shown to reduce the scatter greatly.[6,7] An important advantage of the Kalman filter over more common averaging techniques is that it keeps track of the whole measurement history without retaining all the previous data in memory and acts in real time, thereby providing a corrected concentration value after each measurement. It is especially useful if the measured concentration is used to control the system via a feedback loop.

The QC-DFB laser based NH_3 sensor described here was used to continuously monitor NH_3 concentration levels in bioreactor vent gases for more than 72 hours at NASA-JSC. The detected NH_3 concentration never exceeded a 0.5 ppm level, which was considered satisfactory in terms of bioreactor performance.

Conclusions

We have designed a compact portable ammonio sensor based on a thermoelectrically cooled pulsed QC-DFB laser operating at ~10 μm. This device was applied to NH_3 concentration measurements. Furthermore, the configuration of this sensor will serve as the basis for the design of future portable QC-DFB laser based gas sensors for single or multiple trace gas quantification. The present sensitivity can be considerably improved by adding a second infrared detector. Such a two-beam configuration will cancel the noise caused by laser shot-to-shot energy fluctuations.

Acknowledgments

We acknowledge the assistance of Dr. Darrin Leleux in providing the Kalman filtering program. Financial support of the work performed by the Rice group was provided by the Institute for Space Systems Operations (ISSO), the National Aeronautics and Space Administration (NASA), the Texas Advanced Technology Program, the National Science Foundation, and the Welch Foundation.

Special Note

After serving several years as a post-doctoral fellow on the trace gas detection project supported by ISSO, Dr. Anatoliy Kosterev joined the Rice Quantum Institute as a full-time employee. Dr. Kosterev will be a research scientist at Rice University and he will continue to contribute to the advancement of technology in Houston.

References

[1]F. Capasso, C. Gmachl, R. Paiella, A. Tredicucci, A. L. Hutchinson, D. L. Sivco, J. N. Baillargeon, A. Y. Cho, and H. C. Liu. "New Frontiers in Quantum Cascade Lasers and Applications," IEEE *J. on Selected Topics in Quantum Electronics* 6 (2000): 931-46.

[2]C. Gmachl, F. Capasso, R. Köhler, A. Tredicucci, A. L. Hutchinson, D. L. Sivco, J. N. Baillargeon, and A. Y. Cho. "The Sense-Ability of Semiconductor Lasers," *Circuits & Devices* (May 2000): 10-18.

[3]K. Namjou, S. Cai, E. A. Whittaker, J. Faist, C. Gmachl, F. Capasso, D. L. Sivco, and A. Y. Cho. "Sensitive Absorption Spectroscopy with a Room-Temperature Distributed-Feedback Quantum-Cascade Laser," *Opt. Lett.* 23 (1997): 219-21.

[4]A. A. Kosterev, F. K. Tittel, C. Gmachl, F. Capasso, D. L. Sivco, J. N. Baillargeon, A. L. Hutchinson, and A. Y. Cho. "Trace-Gas Detection in Ambient Air with a Thermoelectrically Cooled, Pulsed Quantum-Cascade Distributed Feedback Laser," *Appl. Opt.* 39 (2000) 6866-72.

[5]R. E. Kalman. "A New Approach to Linear Filtering and Prediction Problems," *J. Basic Eng.* 82 (1960): 35-42.

[6]H. Riris, C. B. Carlisle, and R. E. Warren. "Kalman Filtering of Tunable Diode Laser Spectrometer Absorbance Measurements," *Appl. Opt.* 33 (1994): 5506-08.

[7]D. P. Leleux, R. Claps, W. Chen, F. K. Tittel, and T. L. Harman. "Adaptive Filtering Applications to Realtime Simultaneous CO_2 and NH_3 Measurements," *Appl. Phys. B* (June 2001).

Publications

Kosterev, A. A., F. K. Tittel, W. Durante, M. Allen, R. Köhler, C. Gmachl, F. Capasso, D. L. Sivco, and A. Y. Cho. "Detection of Biogenic *CO* Production above Cell Cultures Using a Near-Room Temperature QC-DFB laser," *Appl. Phys. B* 74 (2002): 95-99.

Kosterev, A. A., R. F. Curl, F. K. Tittel, R. Köhler, C. Gmachl, F. Capasso, D. L. Sivco, and A. Y. Cho. "Transportable Automated Ammonia Sensor Based on a Pulsed Thermoelectrically Cooled QC-DFB Laser," *Applied Optics* 41 (2002): 573-78.

Kosterev, A. A., R. F. Curl, F. K. Tittel, R. Kochler, C. Gmachl, F. Capasso, D. L. Sivco, A. Y. Cho, S. Wehe, and M. Allen. "Room Temperature Quantum Cascade Laser Based Gas Sensor for Continuous Monitoring of Atmospheric *CO*," *Applied Optics* 41 (2002): 1169-73.

Kosterev, A. A. and F. K. Tittel. "Chemical Sensors Based on Quantum Cascade Lasers," IEEE *JQE Special Issue on QC Lasers* 38 (2002): 582-91.

Kosterev, A. A., F. K. Tittel, R. F. Curl, M. Rochat, and J. Faist. "Chemical Sensing Applications with Long Wavelength Mid-infrared QC-Lasers," *Applied Physics B* 75 (2002): 351-57.

Kosterev, A. A., Y. A. Bakhirkin, R. F. Curl, and F. K. Tittel. "Quartz-Enhanced Photoacoustic Spectroscopy," *Optics Letters* 27 (2002): 1902-04.

Presentations

Allan, M., F. K. Tittel, and T. O'Keefe. "Photonic Techniques for Early Detection of Human Disease," Joint NASA-NCI BPC Meeting, Monterey, CA, July 30-Aug. 1, 2002.

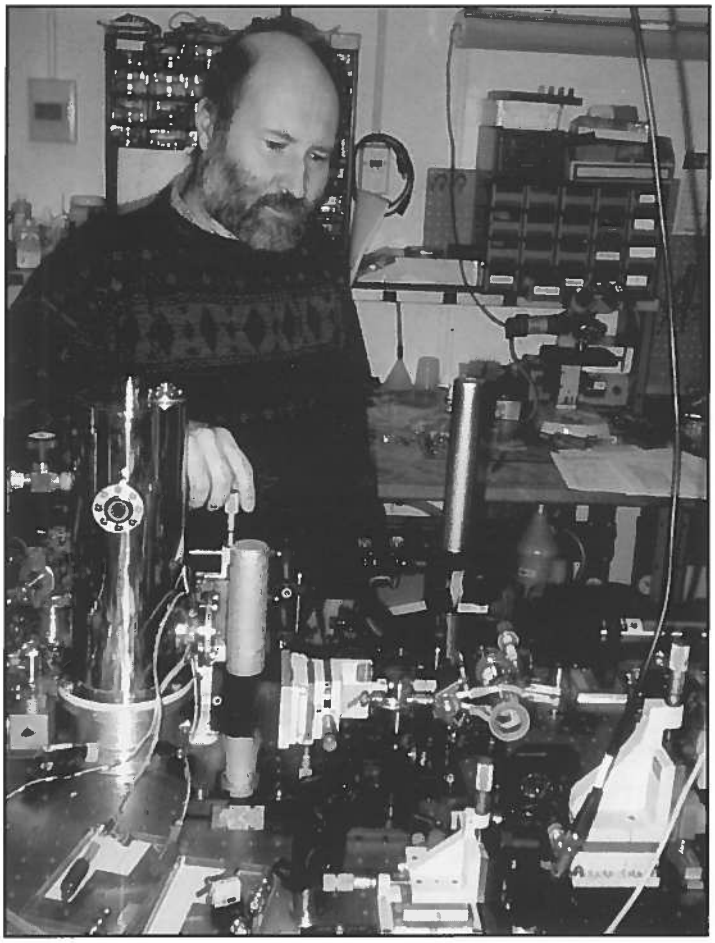
Kosterev, A. A. and F. K. Tittel. "Trace Gas Sensing Applications of Quantum Cascade Lasers," invited, OSA Annual Meeting, Orlando, FL, Oct. 14-18, 2002.

Kosterev, A. A., F. K. Tittel, C. Gmachl, and F. Capasso. "Trace Gas Concentration Measurements Using Quantum Cascade Lasers," IQEC/LAT, Moscow, Russia, June 22-28, 2002.

Kosterev, A. A., Y. Bakhirkin, F. K. Tittel, and R. F. Curl. "Photoacoustic Spectroscopy in Gases with High-Finesse Solid-State Resonators," OSA Annual Meeting, Orlando, FL, Oct. 14-18, 2002.

Kosterev, A. A., F. K. Tittel, M. Rochat, M. Beck, and J. Faist. "Chemical Sensing with a Pulsed 16 Microns QC-DFB Laser," Conference on Lasers and Electro-Optics (CLEO), Long Beach, CA, May 19-24, 2002.

Kosterev, A. A., F. K. Tittel, S. Wehe, D. M. Sonnenfroh, M. G.



SENSORS—Dr. Anatoliy A. Kosterev, Department of Computer Engineering at UHCL, conducts research into compact gas sensors for industrial applications, utilizing wavelength modulated photoacoustic spectroscopy. He engages in research in laboratories at both Rice University and UHCL.

Allen, R. Köhler, C. Gmachl, F. Capasso, D. L. Sivco, and A. Y. Cho. "Spectroscopic Trace Gas Detection with Pulsed Quantum Cascade Lasers," Laser Applications to Chemical and Environmental Analysis (LACEA), Boulder, CO, Feb. 7-10, 2002.

Paige, M. E., S. M. Massick, D. Bomse, A. A. Kosterev, and F. K. Tittel. "Wavelength Modulated Photoacoustic Spectroscopy Using Quantum Cascade Lasers," MIOMD-V, Annapolis 2002, Annapolis, MD, Sept. 8-11, 2002.

Tittel, F. K. "Chemical Sensing Applications of Laser Based Spectroscopic Sources," Physics Department Colloquium, Jena University, Germany, June 24, 2002.

Tittel, F. K. "Chemical Sensors Using Quantum Cascade Lasers," 3rd Quantum Cascade Laser Workshop, Fraunhofer Institute, Freiburg, Germany, Sept. 19-20, 2002.

Tittel, F. K. and A.A. Kosterev. "Trace Gas Detection using Laser Spectroscopy, Air Quality Measurements in Spacecraft Habitats," Environmental Sentinels 2002, NASA-Johnson Space Center, Houston, TX, Sept. 17-18, 2002.

Tittel, F. K., A. A. Kosterev, C. Gmachl, and F. Capasso. "Compact Gas Sensors Based on Pulsed Quantum Cascade Lasers for Industrial Applications," International Symposium on Gas Flow and Chemical Lasers and High Power Laser Conference, Wroclaw, Poland, Aug. 26-30, 2002.

Tittel, F. K., A. A. Kosterev, M. Rochat, M. Beck, and J. Faist. "Chemical Sensors Based on Quantum Cascade Lasers," 2002 SPIE International Symposium on Optical Science and Technology, *Diode Lasers and Applications*, Seattle, WA, July 7-11, 2002.

Funding and proposals

"Diode-Based Trace Gas Monitors for Semiconductor Manufacturing Process Control." ATP, 2001, Rice University, $99,260, UHCL, $131,850 (*not funded*).

"Diode-Based Trace Gas Monitors for Semiconductor Manufacturing Process Control." NSF, 2001, Rice U, $143,393, UHCL, $558,422, three years (*not funded*).

"Early Detection of Human Diseases Based on Breath Analysis Using Photonic Technologies." ATP, June, 2003, Rice University, $94,880, UHCL, $94,880 (*pending*).

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