NO DETECTION—Dr. Thomas Harman, chair of the Computer Engineering Department at the University of Houston-Clear Lake (*l.*), and Dr. Frank Tittel, professor of the Department of Electrical and Computer Engineering at Rice University (*r.*), are developing a spectroscopic gas sensor for the detection of NO, the major oxide of nitrogen formed during high-temperature combustion. Their research will improve air quality for human life support systems in space.

Novel Trace Gas Detection Techniques With Quantum-Cascade Lasers

Abstract—

A spectroscopic gas sensor for the detection of *NO* at the parts per billion (ppb) concentration level based on cavity ringdown spectroscopy (CDRS) has been designed, built and evaluated. *NO* is both the major oxide of nitrogen formed during high-temperature combustion and an important nitrogen containing species in the atmosphere. In addition *NO* is also involved in a number of vital physiological processes, and its detection in human breath has potential applications in noninvasive medical diagnostics. A cryogenically cooled cw mid-infrared DFB-QC laser operating at 5.2 mm (1903.1 cm^{-1}) was used as a tunable, single frequency spectroscopic source for interference-free *NO* detection. The sensor architecture was designed to perform cw CRDS detection by using a high-finesse optical cavity. Researchers achieved a single ringdown event sensitivity to absorption of 2.2×10^{-8} cm^{-1}. This sensitivity resulted in a minimum detectable *NO* concentration of 0.7 ppbv for an 8 s data acquisition time compared to 3 ppbv with a multi-pass cell or 16 ppbv when using cavity enhanced spectroscopy the previous year. Experiments performed to date showed that it is possible to detect *NO* in exhaled breath. With the expected development of near-room temperature thermoelectrically cooled cw QC lasers and progress in low-loss mid-infrared mirror technology, CRDS offers potential for developing compact ultra-sensitive gas sensors to target multiple trace gas species.

LONG-DURATION SPACE MISSIONS REQUIRE PRECISE AND online assessment of spacecraft air quality important to human life support systems. Infrared laser absorption spectroscopy is an extremely effective tool for detecting trace gases at the parts per billion (ppb) level. Presently, the usefulness of the laser spectroscopy approach is limited by the availability of convenient tunable sources in the spectroscopically important "fingerprint" region from 3 to 20 μm. The recent development of quantum cascade lasers with distributed feedback (QC-DFB) fabricated by band structure engineering offers an attractive option for IR absorption spectroscopy.[1] QC-DFB lasers allow the realization of compact, tunable, narrow-linewidth mid-IR sources combining single-frequency operation and high powers (tens of mW) at mid-IR wavelengths (3.5 to 24 μm). Pulsed QC-DFB lasers are the only semiconductor lasers able to emit mid-IR radiation at room temperature.

The main objectives of this project are to characterize continuous wave (CW) and pulsed QC-DFB lasers made available to us by Lucent Technologies, Alpes Lasers and Applied Optoelectronics, Inc., as spectroscopic sources, to determine the modes of operation best suited for sensitive gas detection and to demonstrate prototype gas sensors capable of long term monitoring and

quantification of a number of trace gas species.

Technical Plan and Equipment

Sensitive laser absorption spectroscopy often requires a long effective pathlength of the probing laser beam in media being analyzed. Traditionally, this requirement is satisfied using an optical multipass cell. Such an approach has a number of shortcomings, especially for compact gas sensors. Multipass cells tend to be bulky. For example, a commercial 100 m pathlength cell has a volume of 3.5 L. Such gas absorption cells also require costly large-aperture mirrors sometimes with aspheric surfaces. Light scattering or beam clipping on input apertures create interference fringes that limit sensitivity.

An alternative way to obtain a long optical path is to make the light bounce along the same path between two parallel ultralow-loss dielectric mirrors. In this case, the effective optical pathlength L is given by the expression $L = l / 1 - R$, where l is the mirror spacing and R is the reflection coefficient of each mirror. An effective optical pathlength of several kilometers can be obtained in a very small volume $V = Sl$, where S is the laser beam cross section area. Light leaking out of such an optical cavity can be used to characterize the absorption of the intracavity medium. Presently a variety of techniques exists to perform high-sensitivity absorption spectroscopy in a high finesse optical cavity (see, for example, Berden et al[2]). In year two of our ISSO grant, we have investigated one of these methods in detail.

Cavity ringdown spectroscopy (CRDS) was first introduced in Berden et al.[2] This work was carried out with a high-power pulsed laser. A short light pulse injected into a high finesse optical cavity produces a sequence of pulses leaking out through one of the mirrors (cavity ringdown) due to consecutive reflections. The intensity of pulses in such a pulse train decays exponentially with a time constant

$$\tau = \frac{l}{c} \cdot \frac{1}{\alpha l - \ln R} \quad , \qquad (1)$$

where α is the absorption coefficient of the intracavity medium. This technique is simple and immune to laser power fluctuations. Unfortunately, it cannot be directly utilized with pulsed QC lasers. The energy of the first pulse in the ringdown sequence is $(1-R)^2$ times less then the exciting laser pulse. Mirrors for CRDS experiments typically have a $R > 99.95$ percent. This makes the measurements with ~ 1 nJ IR pulses (available energy E~100 mW×10 ns) practically impossible.

The cavity throughput can be made much higher if the laser linewidth $\Delta\nu_L \ll \Omega$. This condition can be satisfied if a narrow-line cw laser is used. When the laser frequency coincides with one of the cavity modes, the cavity throughput is approximately $T = \Delta\nu_C / \Delta\nu_L$, where $\Delta\nu_C$ is the spectral width of the cavity mode and $\Delta\nu_L$ is the laser linewidth. After the cavity is filled with radiation, the laser emission can be interrupted and the ringdown decay measured in the same manner as it is done with a pulsed laser.

The first work on CRDS measurements with a QC-DFB laser used a cw laser generating 16 mW at λ =8.5 μm.[3] The measured ringdown time of the empty three-mirror cavity was 0.93 μs. An acousto-optic modulator was used to interrupt the cavity injection for ringdown time measurements. The system was tested on diluted ammonia mixtures, and a noise-equivalent sensitivity of 0.25 ppbv achieved. An estimated 1.0×10^{-9} cm^{-1} detectable absorbance

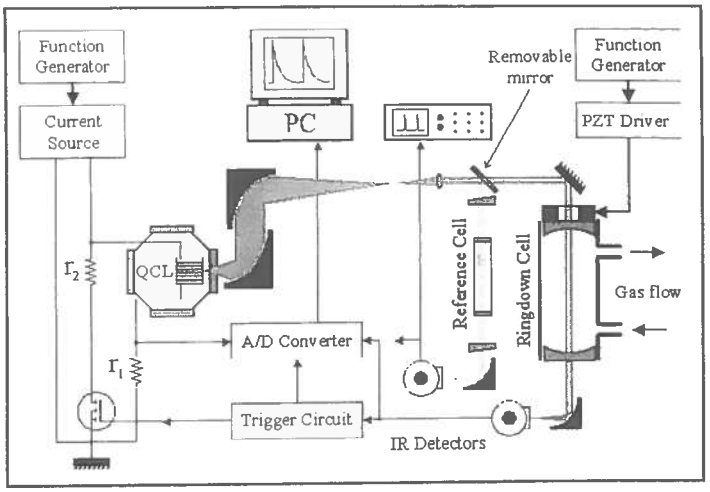

Figure 1. Schematic of a CRDS based gas sensor schematic.[4] r_1 - current monitor resistor; r_2 -current-limiting resistor. Two wedged *ZnSe* windows shown near the reference cell were used to form an etalon for fine frequency calibration.

limit was reported. In our work a cw QC-DFB laser operating at 5.2 μm was used as a tunable single-frequency light source.[4] The CRDS technique consists of the following features:

1) The laser frequency is slowly scanned across the absorption line of interest;
2) One of the cavity mirrors is dithered back and forth to ensure periodic, random coincidences of the laser frequency with a cavity mode;
3) Once such a resonance occurs and the cavity is filled, the laser beam entering the cavity is abruptly interrupted or set off-resonance, and the decay rate of the exiting light is measured.

From Eq. (1), the absorption coefficient can be determined as

$$\alpha = \frac{1}{c}\left(\frac{1}{t} - \frac{1}{t_{empty}}\right) \qquad (2)$$

where τ_{empty} is the decay constant of the cavity when evacuated.

The sensor schematic is shown in Fig. 1. Both frequency tuning and the laser emission interruption were realized by manipulation of the QC laser pump current. No active temperature control was applied to the QC-DFB laser located in a liquid nitrogen optical cryostat. The laser current was supplied by a low-noise home-built current source and monitored using the 0.5 Ω resistor denoted by r_1 in Fig. 1. The laser frequency was tunable from 1922.9 to 1920.8 cm^{-1} when the pump current changed from 300 mA (lasing threshold) to 660 mA. At higher current levels the laser emission was multimode.

Experimental Activity

The tuning range of our CDRS based sensor permitted *NO* detection by accessing absorption lines at 1921.599 cm^{-1} and 1921.601 cm^{-1} (R(13.5) components of the fundamental absorption band). Absorption lines of water vapor and CO_2 were also observed. The l = 37 cm long, linear high-finesse optical cavity was formed by two concave mirrors with a 6 m radius of curvature. Radiation exiting the CDRS cell was focused on a liquid nitrogen cooled photovoltaic *HgCdTe* detector (1 mm^2 area) with a

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built-in 10^4 V/A transimpedance preamplifier, DC to 20 MHz bandwidth. The preamplifier output never exceeded 0.5 V, which is well below its saturation level of 6 V. Therefore, the detector/preamplifier response was assumed to be linear. Additionally, the signal was amplified 5 to 20 times with an external amplifier. The measured decay time of the amplified simulated ringdown signal proved only ~40 ns longer than that of the unamplified signal in the decay time range of 1.3 μs to 10 μs, although the specified external amplifier bandwidth is 1 MHz. This small systematic error does not noticeably influence the experimental results.

The measured ringdown time of the evacuated cavity was $\tau \approx 3.5$ μs, corresponding to $\Delta\nu_C \approx 45$ kHz. The laser linewidth was estimated to be $\Delta\nu_L = 3$ MHz. When a certain level of the detector signal was reached signaling that a TEM_{00} cavity mode is coupled to the laser, a triggering circuit (TC) opens a metal-oxide semiconductor field-effect transistor (MOSFET) to shunt the laser current, thereby reducing it to a sub-threshold value. At the same time, the TC triggered an analog-digital converter, and the detector signal showing the cavity ringdown is digitized for ~30 μs and stored in computer memory. The MOSFET is kept open for 35 μs, so that the laser radiation does not interfere with measurements of the cavity decay constant. This triggering-and-acquisition process is repeated and consecutive ringdown transients are stacked in the A/D memory until a desired number of transients is acquired. (See Fig. 2.)

Discussion and Results

The results were post-processed to fit each transient with an exponential decay function yielding a ringdown time τ. An inverse ringdown time plotted as a function of the laser current provides the absorption spectrum. An example of the *NO* absorption in a mixture with pure N_2 is presented in Fig. 3. The noise-equivalent sensitivity was estimated to be 0.7 ppbv for an 8 s data acquisition time. It was not possible to use this sensor directly for measurements of *NO* concentration in exhaled air (~10 ppbv) because of a strong CO_2 interference, which however can be avoided if the appropriate *NO* absorption line is chosen (e.g. the R(7.5) components at 1903.123 and 1903.134 cm^{-1}).

Conclusions

We have demonstrated that the CRDS technique using current control of a cw QC-DFB laser can be applied to sensitive absorption spectroscopy in the mid-IR. The demonstrated sensitivity can be considerably improved by implementing the following measures:

1) Ensuring less ripple and drift for the QC-DFB laser current.
2) Improving design of the PZT mirror mounts to eliminate the decay time dependence on the mirror positions.
3) Utilizing an improved QC laser cryostat design to avoid drift of the laser beam during liquid nitrogen boil-off.
4) Utilizing a QC laser capable of targeting the *NO* line pair at 1903.123/1903.134 cm^{-1}. [R(7.5)] is desirable in order to detect *NO* in exhaled air. These lines are free of CO_2 and H_2O interference and also more than three times stronger than the pair at 1921. 60 cm^{-1} used in this work.

At this time, we obtain a sensitivity of 0.7 ppb *NO* in pure N_2 with 4000 ringdown events. However, with the proposed improvements implemented, it is estimated that it will be possible to detect *NO* in exhaled air down to sub-ppb levels with the acquisition of 1,000 ringdown events. At a laser shutdown rate of ~500

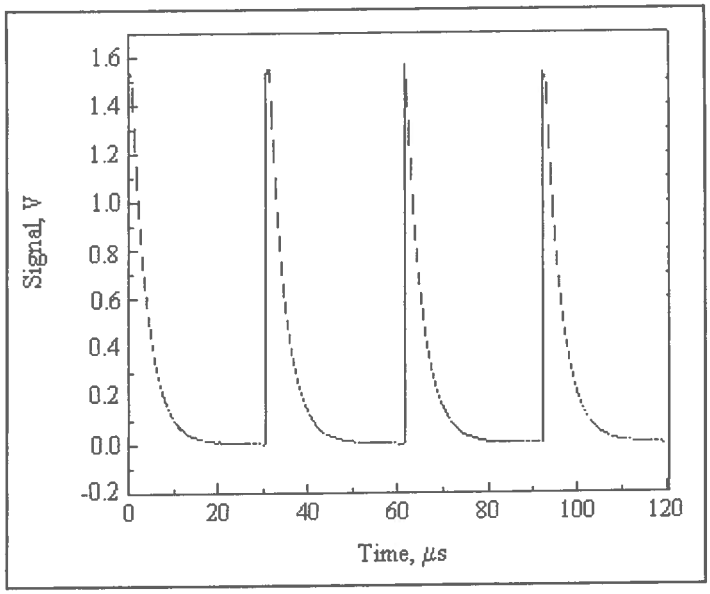

Figure 2. A sample of experimental data showing repetitive ringdown events.

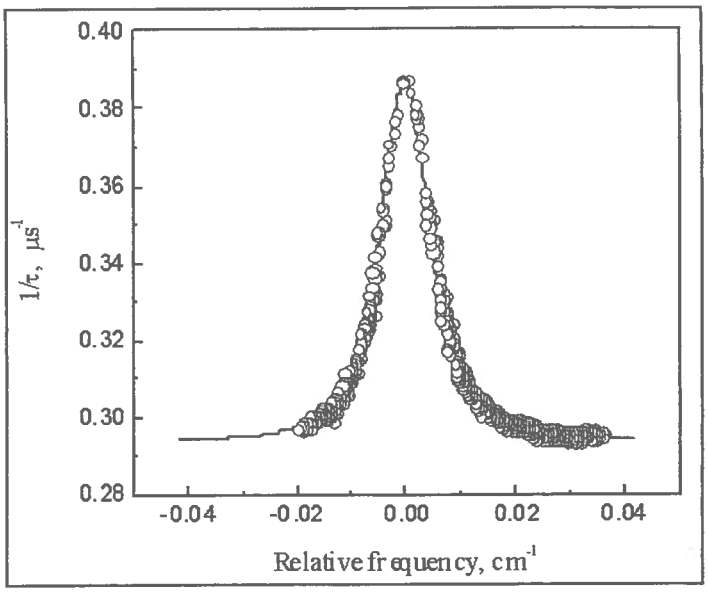

Figure 3. CRDS spectrum of *NO* in N_2, unresolved lines at 1921.599 cm^{-1} and 1921.601 cm^{-1}. The solid line shows a Voigt fit, which resulted in *NO* concentration of 622 ppbv.

Hz this requires only 2 s of time, plus mathematical post-processing which can be very fast with optimum software. With the expected development of near-room temperature CW QC lasers and further progress in low loss mid-IR mirror technology CRDS offers the potential for the design of compact ultra-sensitive gas sensors.

Acknowledgements

The investigators thank Dr. Robert F. Curl of Rice University for useful discussions and Drs. Federico Capasso and Claire Gmachl of the Bell Laboratories, Lucent Technologies for making the QC-DFB laser available to us. Financial support of the work performed by the Rice group was provided by the National Aeronautics and Space Administration (NASA), Institute for Space Systems Operations (ISSO), the Texas Advanced Technology Program, the National Science Foundation, and the Welch Foundation. The work performed at Bell Laboratories was partially supported by DARPA/US Army Research Office under grant No. DAA G 55-98-C-0050.

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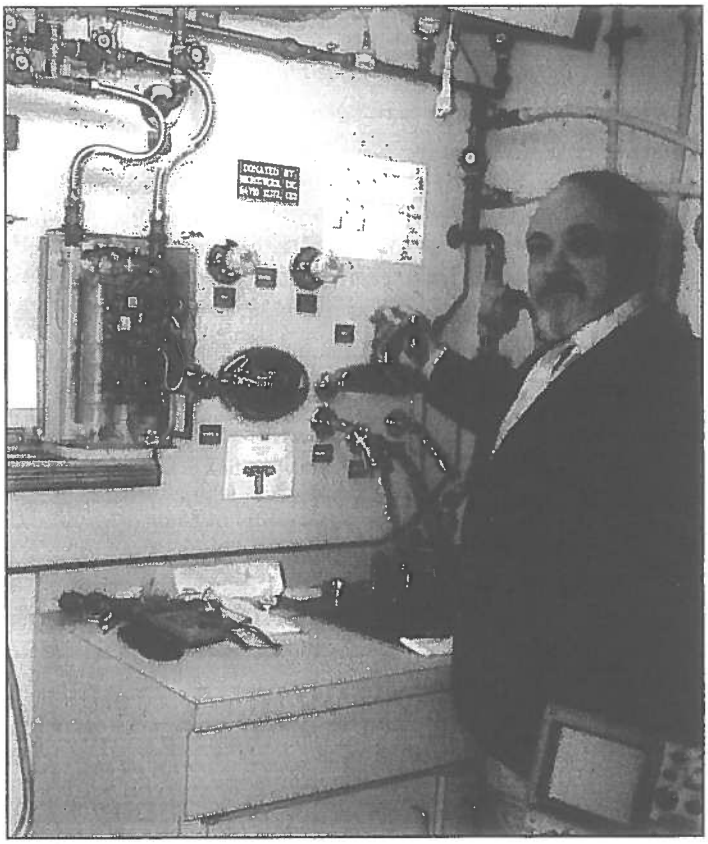


WATER HEATER—Dr. Thomas L. Harman, Director of the Robotics and Computer Control Systems Laboratory at the University of Houston-Clear Lake, has developed software for modeling an instantaneous water heater mounted on a wall, a replacement for the 60-gallon water tanks normally used to heat water in homes. The goal is minimization of equipment.

Funding and proposals

"Quantum Cascade Laser Based Sensors for Chemical and Environmental Analysis," Texas Advanced Technology Program, Rice University PI., Jan. 1, 2002-Mar. 31, 2005, $115,000.

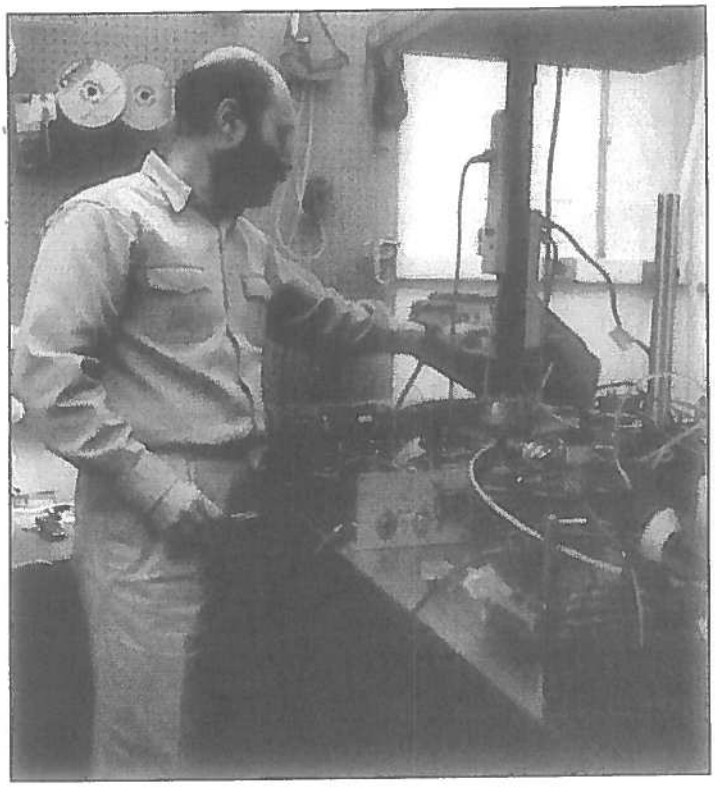
"Laser Based Absorption Sensor for Trace Gas Monitoring in a Spacecraft Environment," National Aeronautics & Space Administration (NASA), Rice University PI, Aug. 6, 1999-Aug. 5, 2002, $419,720.

"Development and Application of Real Time Optical Sensors of Atmospheric Formaldehyde," Environmental Protection Agency (EPA), Rice University PI, Sep. 1, 1999-Aug. 31, 2002, $138,128.

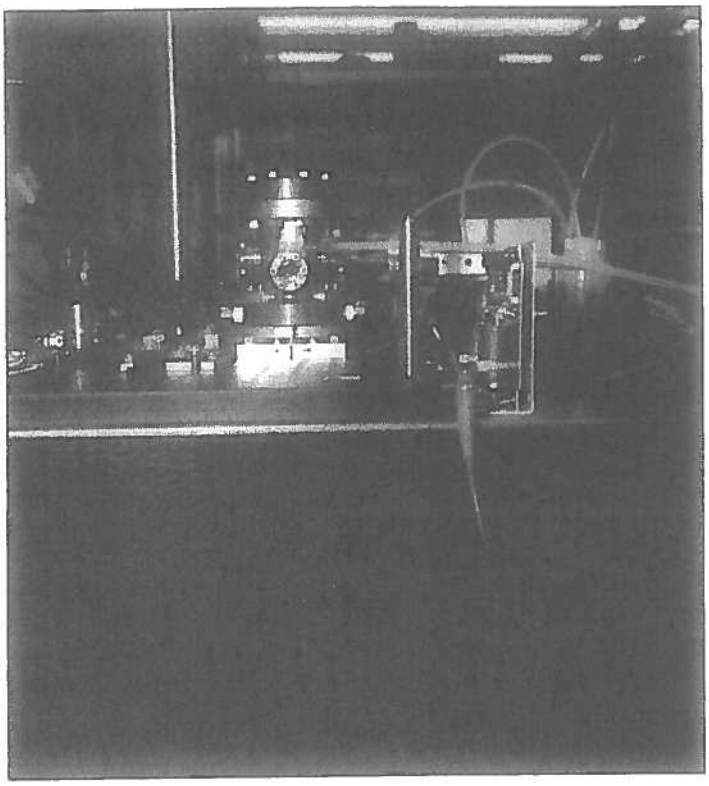
"High Resolution Spectroscopy with Lasers," Welch Foundation, Rice University PI, June 1, 2000-May 31, 2004, $135,000.

"Photonic Technologies for Early Detection of Human Disease," NASA-National Cancer Institute, Rice University PI, Apr. 1, 2002-Mar. 31, 2005, $377,000.

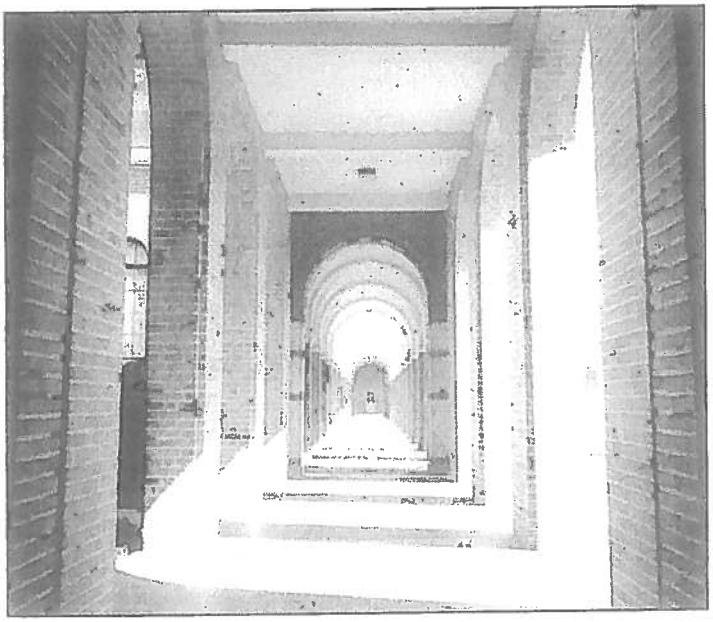
"High-Precision 13CO2/12CO2 Ratio Measurements Using an Optically Fiber Based Difference Frequency Generation Laser Source," NSF, Rice University PI, July 1, 2002-June 30, 2004; *submitted*.



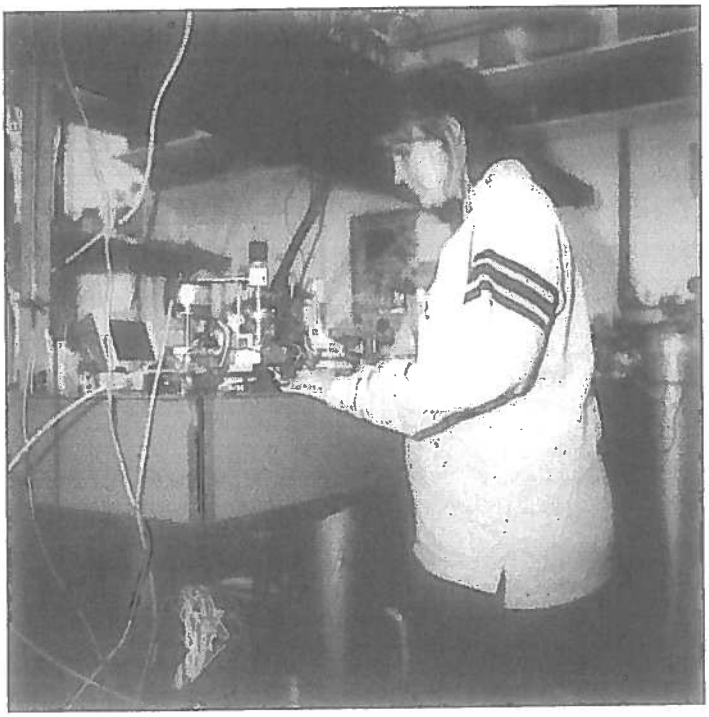
INDUSTRIAL COOPERATION—Dr. Anatoliy A. Kosterev, Rice University Computer Engineering Department, is fine-tuning infrared laser absorption spectroscopy equipment for detecting trace gases at the parts per billion (ppb) level. The project is afforded the opportunity to test lasers made available to Rice, UH, and NASA researchers by Lucent Technologies, Alpes Lasers, and Applied Optoelectronics, Inc.



CRDS—The CRDS technique (Cavity ringdown spectroscopy), utilizing current control of a cw QC-DFB laser, can be applied to sensitive absorption spectroscopy in the mid-IR, and its sensitivity improved by a set of optimized measures.



BYZANTINE ARCH—The Neo-Byzantine architecture of neighboring Rice University provides an arched pathway to the Space Science Building where Dr. Thomas Harman joins Dr. Frank Tittel in research on infrared laser absorption spectroscopy for detecting trace gases at the parts per billion level.



DOW CHEMICAL—Dr. Wendy Flory, a chemist for the Dow Chemical Company, has a short-term research assignment to participate in the *NO* research project being conducted jointly by a NASA-UH-Rice University research team to develop innovative spectroscopic gas sensors.