

Novel Trace Gas Detection Techniques With Quantum-Cascade Lasers

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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 17 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 as spectroscopic sources, to determine the modes of operation best suited for gas detection and to demonstrate prototype gas sensors capable of ppb-level detection of a number of trace gas species.

Continuous wave QC-DFB laser based detection of simple molecules (CH_4 , N_2O , H_2O isotopic species)

The highest spectral resolution can be achieved with a CW QC-DFB laser.^{2,3} The CW operation mode of QC-DFB lasers currently requires cryogenic cooling. In our prototype sensor (Fig.1) the laser emitting near $\lambda = 7.9 \mu\text{m}$ was mounted in a liquid nitrogen optical cryostat. Type-I quantum cascade lasers (presently the only kind of QC lasers capable of single-frequency mid-IR operation) dissipate as much as 10 W in CW operation. The power consumption causes fast boil off of liquid nitrogen and frequency drift, which restricts data acquisition times. We have found that a convenient way to avoid these effects is to operate the laser in a

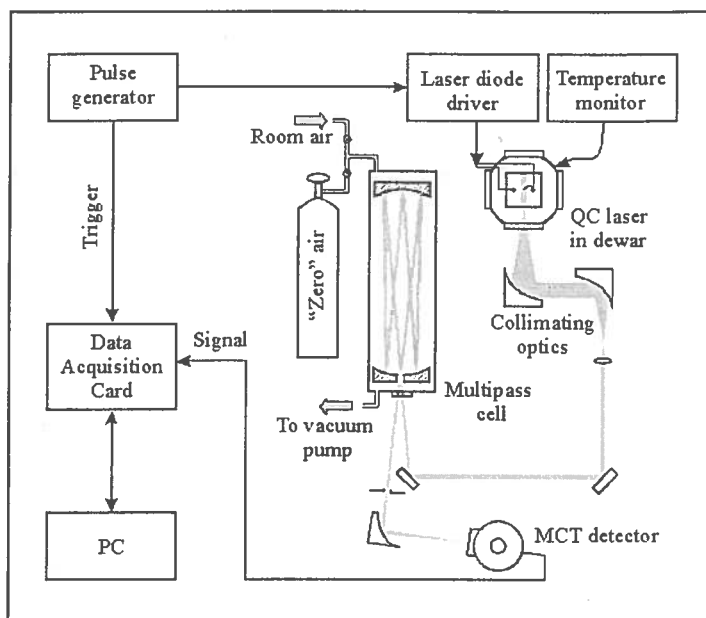


Figure 1. Schematic of the QC-DFB based gas sensor

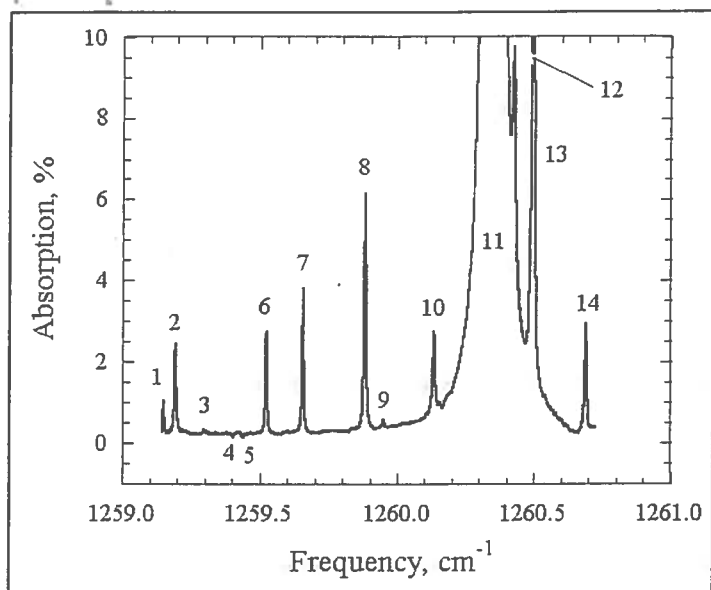


Figure 2. An example of an absorption spectrum of room air obtained with a 100 m pathlength multipass cell and a zero-air background subtraction technique. The assignment of the strong spectral lines is shown: $H_2^{16}O$ -1, 11, 13; N_2O -2, 3, 10; CH_4 -6, 7, 8, 14; $H_2^{18}O$ -9; HDO -12; and CO_2 in the reference zero-air that appears as a negative absorption-4, 5.

quasi-CW mode supplying current in pulses of 120 to 235 μs duration at a 800 to 1000 Hz repetition rate. This somewhat reduces the duty cycle, but does not adversely affect the frequency resolution. From each pulse a frequency scan of up to 2 cm^{-1} is produced and a number of such scans are averaged to obtain a good signal-to-noise (S/N) ratio.

In Fig. 2, an example of the ambient air absorption spectrum acquired in a 100 m pathlength multipass cell is shown. The absorption lines of CH_4 and N_2O were detected with a high S/N ratio. The lines of several isotopic components of water vapor were observed. Concentrations of CH_4 , N_2O and H_2O in air were measured by fitting absorption lines with a Voigt function and comparing the results to the HITRAN spectroscopic database. The sensitivity of detection was estimated to be 2.5 ppb for CH_4 , 1.0 ppb for N_2O and 60 ppb for H_2O . The relatively low sensitivity for water vapor is due to the choice of laser wavelength in a region where only the weaker H_2O absorption lines are present, which helps to avoid potential interference of water vapor absorption in trace gas measurements.

CW QC-DFB laser based detection of complex molecules (C_2H_5OH)

Along with gases composed of simple molecules, it is also important to detect volatile organic compounds (VOCs), and ethanol (C_2H_5OH) is one of the important species to be monitored. For a number of VOCs detection in the region of lower-frequency vibration modes ($>7 \mu m$) presents the advantage of resolved spectral structure compared to C-H stretch region ($\sim 3 \mu m$). This is important for detection with QC lasers, which have a very limited (~ 1 -3 cm^{-1}) tuning range. An absorption spectrum of ethanol vapor in a 43 cm long cell acquired with the CW QC-DFB laser



TEAM DIRECTOR—Dr. Thomas L. Harman has organized engineering and computer researchers from the University of Houston—Clear Lake and Rice University in league with Lucent Technologies.

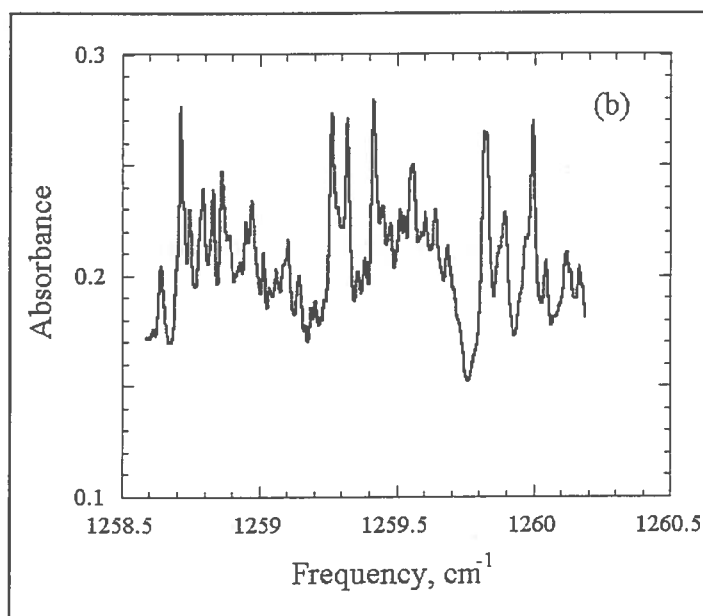


Figure 3. Ethanol vapor absorption spectrum obtained in a 0.43 m long gas cell: 1 Torr partial pressure, room air added to a total pressure of 36.6 Torr.

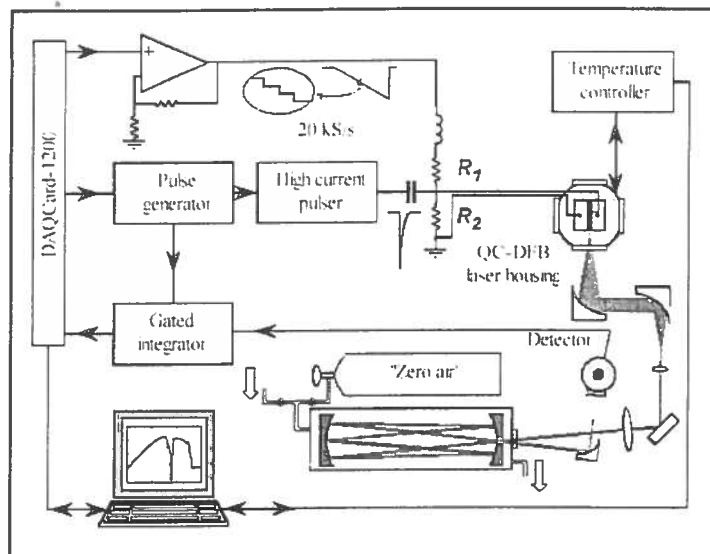


Figure 4. Experimental arrangement for absorption spectroscopy with a pulsed QC-DFB laser. The laser is mounted on a thermoelectric cooler in an evacuated housing.

near $7.9 \mu\text{m}$ is shown in Fig. 3. The partially resolved spectrum allows the identification of ethanol. However, the high density of the pressure-broadened spectral lines makes the technique of individual line fitting with a Voigt profile inapplicable. Therefore, another approach was used to find the ethanol concentration in air. It is principally based on finding the correlation between a previously acquired reference spectrum with the known ethanol vapor concentration and a spectrum of the sample under investigation (which we shall call a "test spectrum") under the same line-broadening conditions (i.e., same air pressure and temperature). The procedural steps are as follows:

- 1) Generate two arrays of data $T(i)$ and $R(i)$ representing test and reference absorption sampled at the same frequencies ν_i (ν_i are supposed to be equally spaced);
- 2) Numerically derivate the spectra: $dT(i) = T(i) - T(i + n)$ and $dR(i) = R(i) - R(i + n)$, where n is a fixed number;
- 3) Perform a linear regression analysis to find the best fit of $dT(i) = k(dR(i))$. The coefficient k yields the concentration of ethanol in the test sample.

The described procedure enabled us to measure ethanol concentrations with a detection limit of 125 ppb. This result can be improved if a laser frequency is selected to match a stronger absorption band.

Pulsed QC-DFB laser based trace gas detection

Pulsed operation of QC-DFB lasers gives a unique opportunity to design a liquid nitrogen-free mid-IR spectroscopic sensor. However, specific problems are associated with this mode of operation.^{4,5} The peak power in pulsed mode is essentially the same as for CW operation, but the duty cycle has to be less than 0.1 percent to avoid an overheating of the device. Therefore, the average power is less than the power generated by the CW operation. This difference requires either more sensitive detection of average power or gated detection of peak power.

Another problem is laser frequency chirping during the current

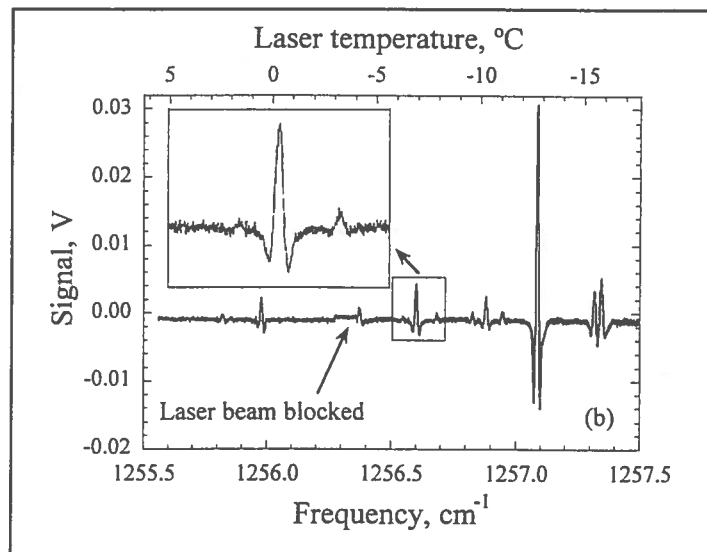


Figure 5. Second-derivative absorption spectrum of ambient air. Inset shows (left to right) weak H_2O , CH_4 and HDO absorption lines. Two lines to right on the main plot correspond to N_2O and HDO absorptions. The second-derivative signal is not normalized for changing laser power. The data are acquired at 50 Torr of air in the multipass cell.

pulse. This effect causes broadening of laser linewidth, limiting the spectral resolution and complicating data processing. These features associated with pulsed operation should be considered in the design of a trace gas sensor.

We performed a set of feasibility experiments to determine optimum parameters for pulsed excitation, as well as the optimum way to couple a source of excitation pulses to the QC-DFB laser. The narrowest (close to Fourier-transform limited) linewidth can be achieved with ~ 5 ns duration pulses. The current pulses were supplied through a high-frequency stripline with a carefully chosen coupling resistor.

A schematic of the pulsed QC-DFB laser based gas sensor is shown in Fig. 4. The optical arrangement of this sensor is the same as the optical arrangement for the CW QC-laser. The laser frequency can be changed both by varying the laser temperature and by applying an offset of slow-changing (~ 40 Hz in our case) sub-threshold current.⁴ The offset current was computer-controlled by means of a National Instruments DAQcard-1200 multi-function data acquisition card.

The detection of trace gases in ambient air was performed in two different ways:

- 1) The laser temperature was set to make the laser emit at slightly higher frequency than a selected absorption line; then the line was detected by fast-scanning of the laser frequency by changing the sub-threshold current. Fast scanning was possible for 0.25 cm^{-1} only, because the laser behaved unstably at higher offset currents.
- 2) The laser temperature was varied slowly, which allowed the laser frequency to be tuned $\sim 3 \text{ cm}^{-1}$ when the temperature changed from -30°C to $+5^\circ\text{C}$ ($-0.084 \text{ cm}^{-1}/^\circ\text{C}$). In this mode of operation, it was important to suppress the noise caused by acoustic vibrations that otherwise limits the sensitivity. We



AIR QUALITY—Dr. Frank Tittel (*l.*), Rice University, consults with Dr. Anatoliy A. Kosterev (*r.*), Post-Doctoral Aerospace Fellow of the University of Houston—Clear Lake. They are concerned with developing methods for testing air quality on spacecraft during flight patterns to protect astronauts and work crews.

suppressed the noise by applying a modulated sub-threshold current, which allowed the acquisition of a second-derivative (2d) spectrum free of low-frequency noise (Fig. 5).

The sensitivity limit with both fast scanning and slow 2d data acquisition techniques is, we found, the same when normalized to the number of laser pulses involved in measuring an absorption line. This limit is defined by detector noise. The sensitivity of the pulsed QC-DFB laser based prototype gas sensor is 1.7×10^{-4} absorption, which corresponds to 6 ppb of CH_4 or 2.5 ppb of N_2O in air.

Cavity enhanced/cavity ring-down detection using CW QC-DFB lasers

A promising method of obtaining a long efficient absorption path-length without an optical multipass cell consists of using a high-finesse optical cavity. At present, a number of techniques involving an optical cavity have been developed (see, for example, reference 6-9). The simplest way is to measure the transmission of the gas-filled unstabilized cavity in exactly the same manner as it is made with an optical multipass cell.⁶ We have tested this method for the detection and quantification of *NO* at the ppb level. It was found that although the effective pathlength is indeed ~1000 m, the noise related to fluctuations of the cavity mode structure prevents achieving a high sensitivity. Therefore, our efforts are presently focused on developing a sensor based on measurements of the cavity ring-down time (cavity ring-down

spectroscopy).⁷⁻⁹ We expect to create a simple technique that does not require locking the laser to the cavity, extreme stabilization of the cavity modes, or electro- (acousto-) optic modulators. Such a gas sensor requires a CW QC-DFB laser. Presently, this mode of operation is possible only at cryogenic temperatures, but thermoelectrically cooled CW QC-DFB lasers are expected to be developed in the near future. Then cavity ring-down spectroscopy can become the basis for compact, inexpensive trace gas sensors.

Future developments

We plan to make the QC-DFB laser based gas sensors more compact, rugged and automated in order to make them suitable for a number of field applications. As a first step in this direction, we are currently redesigning the pulsed laser housing to incorporate a single short-focus collimating lens ($f = 3$ mm) which will replace three optical elements (two $\varnothing 3$ inch parabolic mirrors and a BaF_2 lens; see Fig. 4). We also plan to replace commercial stand-alone devices (temperature controller, gated integrator, pulse generator etc.) with small computer-controlled boards. We already do not use a stand-alone function generator in the pulsed sensor configuration but synthesize the necessary subthreshold current waveform with a computer, which adds to the flexibility of this device. As QC-DFB lasers at other mid-IR wavelengths become available from both Lucent and a recently-formed Houston company, Applied Optoelectronics, Inc., we plan to extend the monitoring of spacecraft air to other gas species, in particular H_2CO , NH_3 and VOCs.

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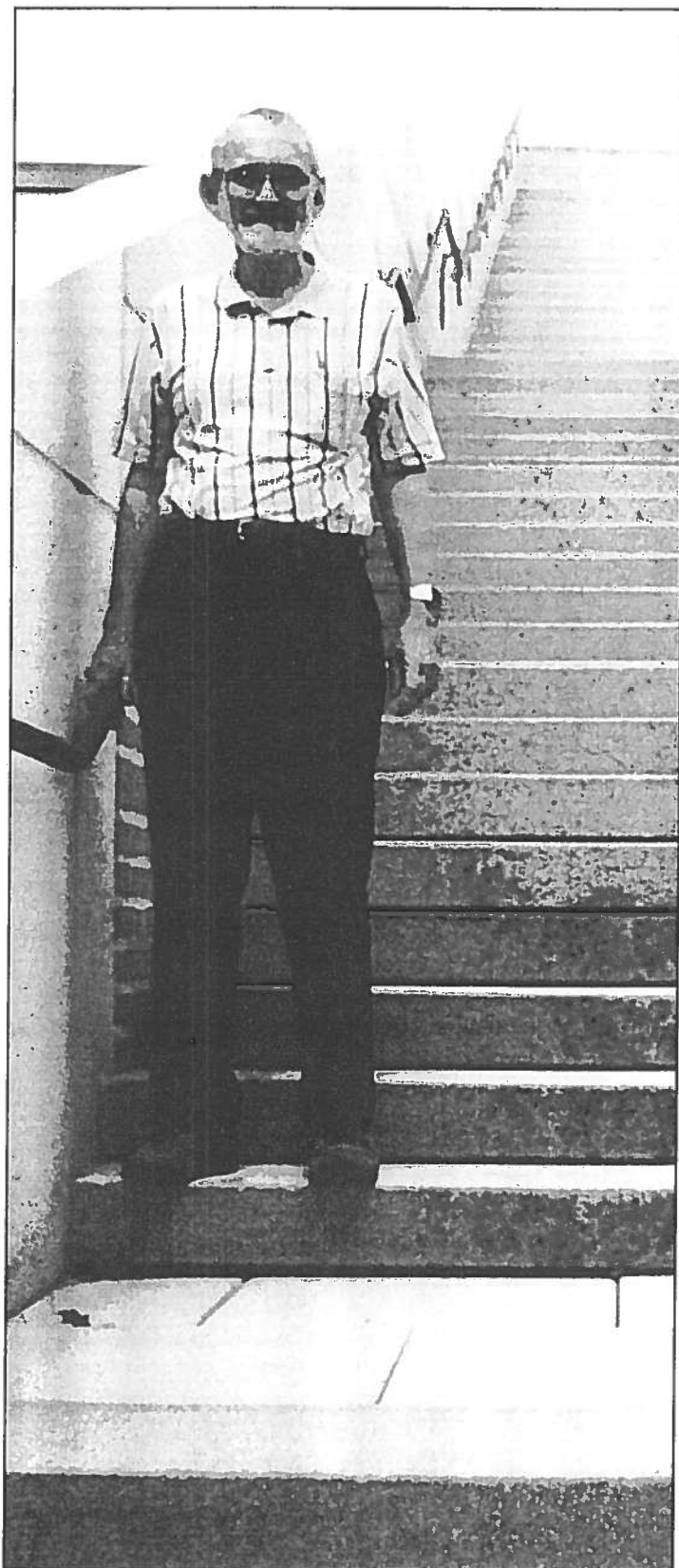
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NOBEL LAUREATE—Dr. Robert F. Curl, Harry C. and Olga G. Weiss Professor of Natural Sciences, Rice University, Houston, Texas; Winner of the Nobel Prize in Chemistry, 1996. Dr. Curl provides fundamental knowledge of spectroscopy using quantum-cascade lasers.

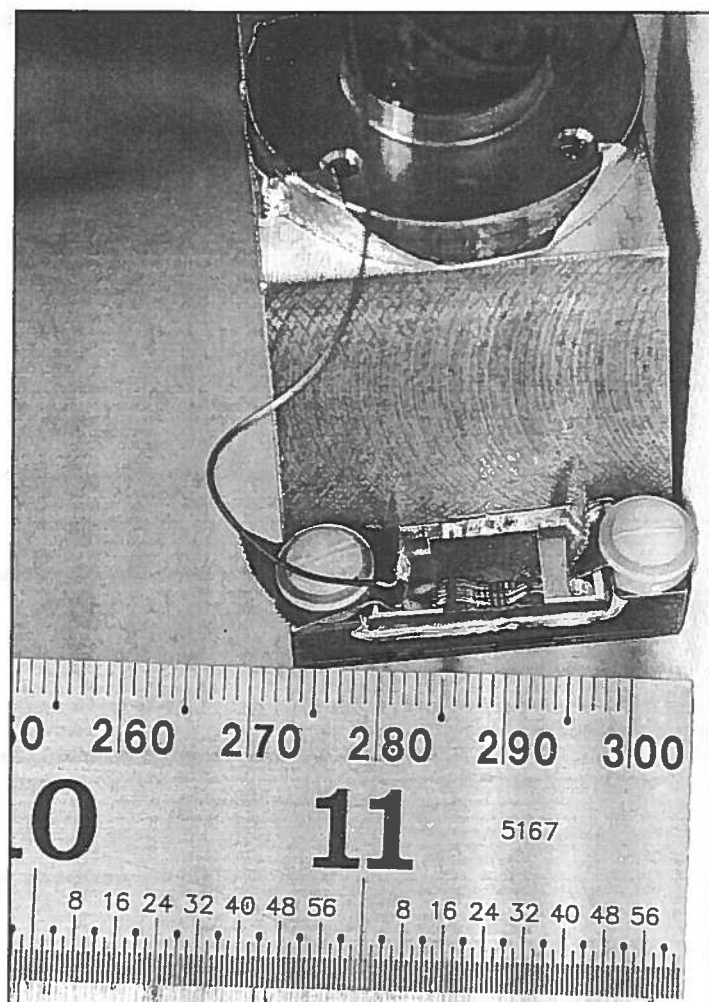
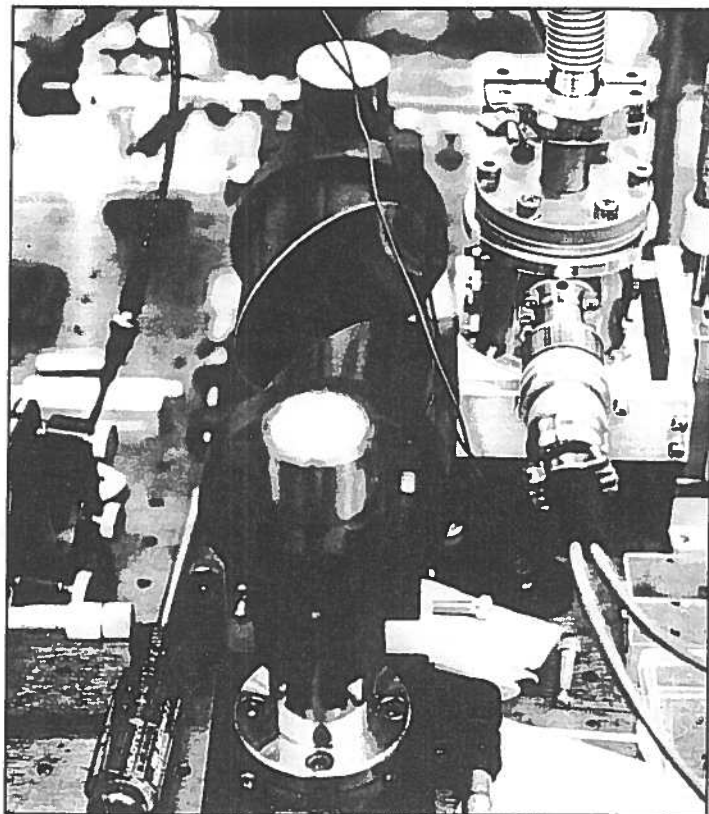
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Funding

"Environmental and Industrial Monitoring of Trace Gases with Novel Quantum Cascade Lasers." Principal Investigator: F. K. Tittel; Texas Advanced Technology Program, Jan. 1, 2000-Aug. 31, 2002; \$236,265.

"Diode Laser-Based Trace Gas Monitors for Semiconductor Manufacturing Process Control." NSF-Eng-ES Division, Aug. 2000, 3 years; \$435,000 (*submitted*).



ROOM TEMPERATURE OPERATION—Pulsed QC lasers are the only compact lasers able to emit mid-IR radiation at room temperature. A housing of the pulsed $\lambda = 8 \mu\text{m}$ laser is shown above. The diverging laser radiation is collected and collimated with two $\varnothing 3''$ off-axis parabolic mirrors. The technology allows the realization of compact, tunable, selective gas sensors based on molecular absorption detection in the mid-infrared. **Right:** An array of six QC-DFB lasers mounted on a cold finger of the cryostat.