Sensitive absorption spectroscopy with a room-temperature distributed-feedback quantum-cascade laser

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We report what we believe are the first spectroscopic measurements to be made with a room-temperature quantum-cascade distributed-feedback laser. Using wavelength modulation spectroscopy, we detected N₂O and CH₄ in the chemical fingerprint wavelength range near 8 μm. The noise equivalent absorbance for our measurement was 5 parts in 10⁵, limited by excess amplitude modulation on the laser output, which corresponds to a 1-Hz bandwidth detection limit of 250 parts N₂O in 10⁴ parts N₂ in a 1-m path length. © 1998 Optical Society of America

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There is a wide range of measurement and control applications that require, in situ, chemically selective detection of molecular species in the gas phase. Laser absorption spectroscopy is ideally suited for this purpose, and low detection limits have been reported.¹⁻³ Because the strongest line strengths for molecules occur in the middle-infrared portion of the spectrum, the lead salt family of tunable semiconductor diode lasers has been the standard choice for use in this spectral region. Effective methods for detecting weak absorbances have been developed.³,⁴ However, as a source in a practical sensing instrument these devices have two limitations: Lead salt lasers must always be operated cryogenically, and they are available commercially only as Fabry–Perot cavity oscillators and hence are subject to cavity mode hopping and tuning gaps.

The quantum-cascade (QC) laser⁵⁻⁸ overcomes these two drawbacks, and we report here what is to our knowledge the first application of the QC laser to the detection of dilute samples of molecules through their absorption spectrum. The QC laser derives its gain from the transition of electrons between two excited states in the conduction band of a coupled quantum-well structure. Inversion is obtained by careful engineering of the carrier lifetimes, determined by longitudinal phonon scattering. The active region and a matching electron injector are cascaded many times to increase output power. The lasing wavelength is determined by the thickness of the active region’s quantum-well layer, essentially independently of the semiconductor bandgap. Devices with wavelengths ranging from 4 to 11 μm have been fabricated with an AlInAs/InGaAs lattice matched to InP.⁷ This spectral range overlaps the most important part of the molecular fingerprint region and includes a substantial fraction of the lead salt lasing range. However, unlike the lead salt laser, the QC laser is capable of operating at room temperature and above.⁹ Furthermore, room-temperature QC lasers with a distributed-feedback (DFB) architecture have also been demonstrated to have continuous, single-mode tuning of >20 cm⁻¹.¹⁰

Figure 1 diagrams a sensitive detection measurement that we implemented by using such a QC DFB laser. The laser, designed to emit near 8 μm,¹⁰ is mounted in a temperature controlled, evacuated chamber. The laser is driven by a 2.6-A amplitude, 1-MHz train of 11-ns-wide current pulses (~1% duty factor), resulting in 10-μW collected average laser output power. The thermoelectric cooler temperature is set to 4 °C. This setup tunes the laser resonance close to the N₂O absorption line of interest. We fine tune the laser by superimposing upon the pulsed waveform a 4-Hz current ramp, which alone would be insufficient in amplitude to bring the laser above threshold but which causes a temperature modulation on the laser sufficient to sweep the lasing frequency by approximately one wave number. Finally, we combine the ramp with a 1.8-kHz sinusoidal dither, which adds a second, higher-frequency temperature modulation, resulting in a concomitant wavelength modulation (WM).¹¹
The modulated laser beam is collimated and then directed through a 10-cm-long gas cell equipped with wedged CaF$_2$ windows. The transmitted light is focused onto a HgCdTe photoconductive detector, cooled to 77 K. The detector is coupled to a matched preamplifier whose output is detected by a lock-in amplifier. The wavelength-modulation dither serves as the lock-in reference, and the lock-in output is recorded with a 14-bit digital signal-processor-equipped computer. The computer records individual ramp scans and can be set to average these scans. The data reported here were recorded mostly by use of 16-scan averaging with a lock-in bandwidth of 250 Hz, resulting in a net detection bandwidth of 16 Hz. Because the dither frequency is much lower than the underlying pulse repetition frequency, this arrangement results in WM absorption spectroscopy.

The gas cell was filled with commercially premixed volumes of diluted gas, which were further diluted with high-purity dry N$_2$. For most of the measurements reported here we used samples of 10%, 1%, and 0.1% N$_2$O in N$_2$ diluted in steps of five as many as three times with total pressures from 1 to 20 Torr.

By fixing the temperature of the thermoelectrically cooled laser head, we obtained sets of scans by using the 4-Hz current ramp, whose center frequency could be estimated from the wavelength calibration of the QC DFB laser obtained independently with a Fourier-transform infrared spectrometer. Figure 2 shows several such scans overlaid to provide a continuous temperature scan from $\sim$17 °C to 6 °C, corresponding to a 2.5-cm$^{-1}$ laser frequency scan starting at 1280 cm$^{-1}$. The spectral data show the characteristic derivative line shape of WM spectroscopy obtained from a 10% N$_2$O/90% N$_2$ premixed sample with a total pressure of 1 Torr. We checked the frequency calibration by comparing the data with the known frequencies and line strengths of the N$_2$O 10$^{00}0$–00$^00$ band obtained from the HITRAN database. These are shown on the bottom of the figure. As an additional check on frequency calibration we include a scan obtained from a 10% CH$_4$/90% N$_2$ sample at 10-Torr total pressure.

By switching the laser modulation from frequency dither to mechanical chopping we were able to measure direct absorption and thus calibrate the WM signal to absolute absorbance. Figure 3(a) shows the resultant spectral scans obtained with 40 Torr of the 10,000-parts-in-10$^6$ (ppm; 1%) N$_2$O-in-N$_2$ sample. The solid curve shows the absorption dip associated with one of the strong N$_2$O lines from Fig. 2. The dotted curve shows a background trace with the gas cell evacuated, and the dashed–dotted curve shows the trace with the beam blocked. We obtained the dashed trace by passing the beam through a 1.44-GHz free-spectral-range solid germanium etalon.

Figure 3(b) shows the fractional attenuation of the laser beam on line center as a function of N$_2$O concentration inferred from the magnitude of the absorption dip for the 10,000-ppm sample and two 5× dilution steps (circles) and the undiluted 1000-ppm sample (square). The straight line is a least-squares fit to the data including the point (0 absorbance, 0 ppm). The slight deviation at low concentration is due to accumulated error in dilution and the low signal-to-noise ratio at low absorbance.

WM affords a substantial improvement over the direct measurement in sensitivity to absorbance. Using the two premixed samples of N$_2$O and the dilution procedure outlined above, we measured the WM signal amplitude for one of the strongest N$_2$O lines as a function of N$_2$O concentration. We calibrated the WM signal for absorbance by matching the WM signal to the directly measured absorbance at the highest concentrations. The result is plotted in Fig. 4. The solid line is a linear least-squares fit from the data from dilutions of both premixed samples, where we forced the

![Infrared Frequency in cm$^{-1}$](image1)

**Fig. 2.** WM signal versus laser frequency for 10% diluted samples of N$_2$O and CH$_4$ with corresponding HITRAN data plotted below.

![Transmitted Intensity vs. Relative Laser Frequency](image2)

**Fig. 3.** (a) Transmitted laser power versus frequency with the N$_2$O sample (solid curve), a calibration etalon (dashed curve), or an opaque block (dotted–dashed line) in the beam. (b) Absorbance versus concentration, obtained by dilution of the samples as discussed in the text.
Fig. 4. Plot of WM signal amplitude versus N\textsubscript{2}O concentration for 20-Torr total pressure samples. The error bars represent the amplitude of the background signal fluctuations depicted in Fig. 5.

Fig. 5. (a) WM signal that is due to a 1000-ppm N\textsubscript{2}O sample at 10-Torr total pressure. (b) Background trace for an evacuated sample cell. (c) Background trace with the laser beam blocked.

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