Wavelength Modulated Photoacoustic Spectroscopy using Quantum Cascade Lasers

Mark E. Paige, Steven M. Massick, and David Bomse
Southwest Sciences, Inc., Santa Fe, NM 87505
dbomse@swsciences.com
and
Anatoliy A. Kosterev and Frank K. Tittel
Rice Quantum Institute, Rice University, Houston, TX 77251-1892
akoster@rice.edu

1. INTRODUCTION

The combination of quantum cascade (QC) laser excitation with photoacoustic detection offers the possibility of exceptional gas detection sensitivities. Some potential advantages of this approach include:

High sensitivity. Wavelength modulated photoacoustic spectroscopy reduces noise due to absorption by cell windows or by the wings of absorption lines due to background species. Previous work using cw, near-infrared diode lasers achieved absorbance sensitivities (1 Hz bandwidth) as small as 4×10^{-11} cm^{-1} W [1] and predict single digit part per billion detection limits for gases with moderately strong mid-infrared absorption cross sections ($\sim 5 \times 10^{-20}$ cm^2) using QC lasers with an average power of only 10 mW. Detection limits improve linearly with increasing laser power.

High Selectivity. Wavelength modulation helps discriminate weak absorptions due to target species in the presence of large absorbances due to cell windows or to the tails of absorption lines due to dominant species. This advantage occurs because wavelength modulation provides a differential signal between peak and baseline.

Impervious to etalons. Unwanted optical interference fringes (etalons) are usually limit the detection sensitivity for trace gas detection using diode laser spectroscopy. Typical detection limits ($\sim 10^{-5}$ fractional absorbance) are two to three orders of magnitude worse than the fundamental limits imposed by laser shot noise and/or detector thermal noise. Photoacoustic detection is not impaired by these etalons, however, because the fringes do not introduce a background photoacoustic signal.

Impervious to laser excess noise. Most high sensitivity spectroscopic techniques (such as wavelength modulation and noise canceller approaches) using diode lasers provide a method for rejecting excess laser noise (1/f noise). This can be a significant problem with QC lasers operated near room temperature because the lasers must be pulsed, and shot-to-shot variations in laser output add noise. When photoacoustic detection is used, however, the laser variations become small errors on the photoacoustic signal, and are not excess signals that can overwhelm the target absorbances.

Small volume. The sample region within the photoacoustic cell used for these experiments is only 3 in diameter × 100 mm long, or 0.7 cm^3.

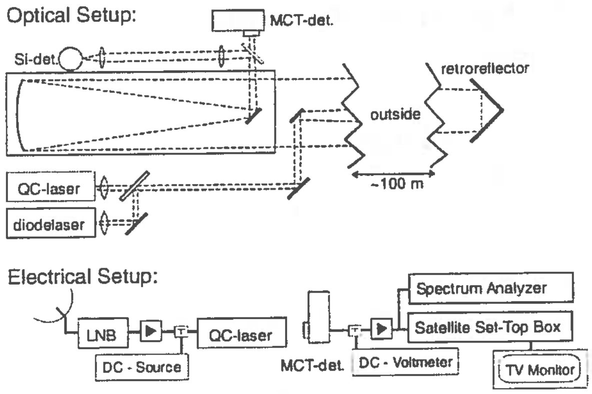

Figure 2: Optical and electrical setup of the transmission link.

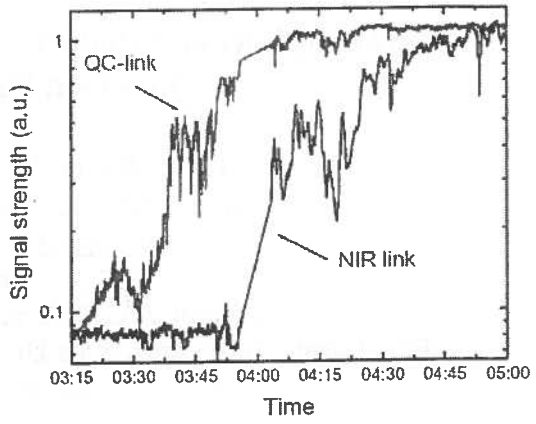

Figure 3: Comparison of the received intensities of the mid-IR and near-IR link.

link, a near infrared (0.85 µm) beam was included in the path. The dc-biased QC-Laser was modulated by the digitally encoded data stream (750 MHz – 1.45 GHz) taken directly from a satellite receiver system (LNB). The dc component of the detected signal was used to monitor the received laser intensity, whereas the high frequency part was fed parallel into a spectrum analyzer and into a standard satellite set-top-box connected to a TV monitor.

Under typical QC laser operating conditions (500mA dc current at a temperature of 25K) the link could be run continuously and stably for at least 5 hours. The link power margin was measured to be 7 dB. To show the advantage of the longer wavelength relative to the collinearly propagating near-infrared beam (0.85 µm) both intensities were monitored in parallel. Under good weather conditions about 10% of the emitted intensity was detected for both wavelengths, where the losses are attributed to beam spreading and losses in the optical elements. This remained unchanged for strong rain and thunderstorm. Nevertheless, during a dense fog situation a strong difference in transmission was seen. Figure 2 shows the temporal evolution of the detected dc intensities for both laser links starting under conditions of very dense fog. As the fog lifted, the QC-laser link regained transmission much quicker than the near-IR link, reaching nearly 70% of its optimal value when the intensity of the near-IR link was still below the detection limit.

The work performed at Bell Laboratories, Lucent Technologies was partly supported by Darpa/US Army Research Office under contract DAAD19-00-C-0096. Stevens Institute of Technology acknowledges support from the US Department of Energy under Contract DE-FG08-99NV13656 and the US Army CECOM under Contract DAAB07-98-D-A759.

1. MARTINI, R., GMACHL, C., FALCIGLIA, J., CURTI, F.G., BETHEA C.G., CAPASSO, F., WHITTAKER, E.A., PAIELLA, R., TREDICUCCI, A., SIVCO, D.L., and CHO, A.Y.: 'High-speed modulation and free-space optical audio/video transmission using quantum cascade lasers', Electron. Lett., 2001, 37, pp. 111-112.
2. BLASER, S., HOFSTETTER, D., BECK, M., and FAIST, J.: 'Free-space optical data link using Peltier-cooled quantum cascade laser', Electron. Lett., 2001, 37, pp. 778-780.
3. CAPASSO, F., GMACHL, C., PAIELLA, R., TREDICUCCI, A., HUTCHINSON, A.L., SIVCO, D.L., BAILLARGEON, J.N., CHO, A.Y., and LIU, H.C.: 'New Frontiers in Quantum Cascade Lasers and Applications', IEEE J. of Sel. Top. Quant. Electron., 2000, 6, pp. 931 - 947, and references therein.
4. PAIELLA, R., CAPASSO, F., GMACHL, C., BETHEA, C.G., SIVCO, D.L., BAILLARGEON, J.N., HUTCHINSON, A.L., CHO, A.Y., and LIU, H.C.: 'Generation and Detection of High-Speed Pulses of Mid-Infrared Radiation with Intersubband Semiconductor Lasers and Detectors', IEEE Photonics Technol. Lett., 2000, 12, pp. 780 – 782
5. LIU, H.C., LIN, J., BUCHANAN, M., and WASILEWSKI, Z.R.: 'High-Frequency Quantum-Well Infrared Photodetectors Measured by Microwave-Rectification Technique', IEEE J. Quantum Electron., 1996, 32, pp. 1024 - 1028

2. RESULTS and DISCUSSION

Experiments were performed at Rice using a 10.1 μm QC laser (Lucent) operated at 350 kHz with 20 nsec pulses. The average laser power, only 40 μW, is smaller than is typical for pulsed QC lasers near room temperature and is indicative of the low duty factors needed for operation near room temperature. The laser wavelength was scanned across the spectral features by changing the temperature between -30 and 0 °C. Wavelength modulation was effected by changing the pulse repetition rate [2]. The photoacoustic experiments used a modified square wave modulation. This modulation form is a three level function with a timing sequence of center, high, center, low. Photoacoustic signals were processed by connecting the microphone output to a lock-in amplifier set to twice the modulation frequency.

Fig. 1 compares wavelength modulated *absorption* spectrum of 100 ppm ammonia in nitrogen with the wavelength modulated *photoacoustic* detection. At 80 Hz pulse frequency modulation, the absorption spectrum is dominated by excess laser noise and sensitivity is not much improvement over the unmodulated spectrum earlier acquired by the Tittel group; that sensitivity was ~100 ppm-cm-Hz implying a minimum detectable absorbance of 3.4×10^{-3}. The photoacoustic spectrum is dominated by ambient background noise; detection sensitivity is ~130 ppm-$Hz^{½}$. If the laser power were 10 mW instead of 40 μW, the sensitivity would be 0.5 ppm-$Hz^{½}$. Based on previous photoacoustic results obtained with a cw near-infrared diode laser, we expected ammonia detection sensitivities of 0.8 ppm-$Hz^{½}$ with a 40 μW laser. This nearly 200-fold difference in performance is likely due to the relatively broad linewidth of the QC laser. Further improvements in QC laser technology, including the recently reported cw operation at room temperature, imply that significant improvements in gas detection sensitivity are possible using photoacoustic detection.

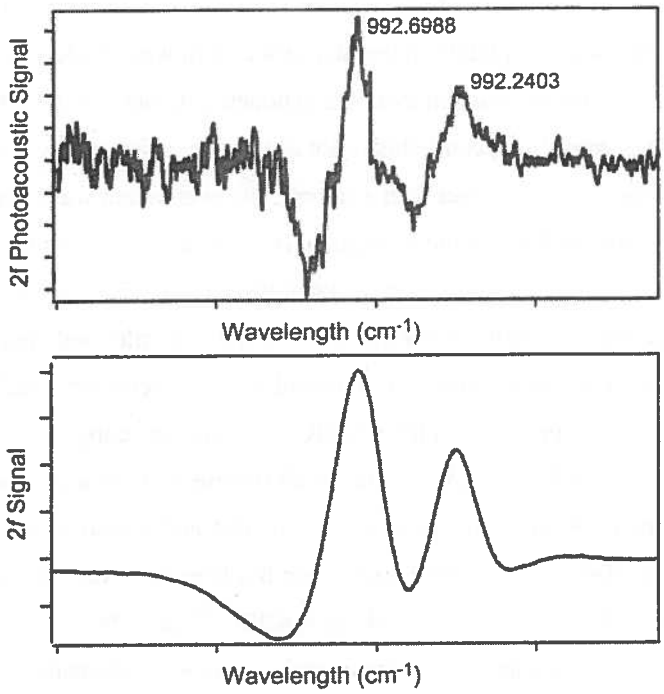

Figure 1 - Wavelength modulated photoacoustic (top) and absorption (bottom) spectra of 100 ppm ammonia

3. ACKNOWLEDGMENTS

Southwest Sciences researchers were supported by NASA contract NAS5-01216 and NSF grant DMI-9983349.

4. REFERENCES

1. M. Feher, Y. Jiang, J. P. Maier, and A. Miklos, Appl. Opt. **33**, 1655 (1994).
2. A. A. Kosterev, R. F. Curl, F. K. Tittel, M. Rochat, M. Beck and J. Faist, "Chemical sensing with pulsed QC-DFB lasers operating at ~15.6 μm," submitted to Applied Phys. B, (May, 2002).