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Spectroscopic Applications of QPM Devices

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Abstract: The development and application of a range of absorption spectrometers, which operate in the 3.2 – 4.6 μm spectral region, are presented. The sensors are based on difference frequency mixing two cw diode lasers in periodically poled $LiNbO_3$ to generate narrow linewidth light (<60 MHz). Ruggedness and increased power is achieved by the use of fiber optics for beam delivery and inline fiber amplifiers. Species detected in air include H_2CO, CO, CO_2, CH_4, H_2O, HCl with sensitivities down to the parts-per-billion level with direct absorption detection or < 100 ppt using 2-f modulation spectroscopy.

Summary: A significant issue in a range of air monitoring applications is the ability to measure particular trace and pollutant gases in real time with high sensitivity and specificity. The Rice University group has developed sensitive gas sensors operating in the mid-IR molecular fingerprint spectral region in recent years. Specific applications range from online monitoring of a closed human habitat for CO and H_2CO concentrations, detection of CO_2, CH_4 and H_2CO in ambient air, and monitoring of volcanic gas emissions. Sensors developed include a portable multi-species device based on difference frequency mixing a broadly tunable extended cavity diode laser and 1.1 μm diode laser to provide a tuning range of 3.2-4.6 μm [1]. Dedicated sensors where the frequency is set by the choice of diode laser wavelengths have been designed for sensitive and absolute detection of CO, CH_4 and H_2CO, with wavelengths at 4.6, 3.2 and 3.5 μm, respectively.

Our most recent development of sensitive difference frequency spectrometers has been targeted at detection of H_2CO, since this molecule is difficult to accurately monitor using traditional techniques such as wet chemistry or FTIR. H_2CO is produced by the photochemical breakdown of volatile organic carbon molecules and can also be a byproduct from incomplete combustion processes and is a pre-cursor to ground level ozone formation. In major urban environments, such as Los Angeles, New York and Houston, monitoring of H_2CO distribution and its daily concentration cycle is important in modeling complex ozone chemistry.

Sub-ppb detection of formaldehyde has been accomplished using cryogenically cooled Pb salt diode laser spectroscopy [2] at the fundamental ro-vibrational absorption near 2916 cm^{-1} (3.54 μm). To achieve the required sub-ppb sensitivity with DFG sensors for monitoring H_2CO in an urban environment (< 1ppb corresponding to ~2 x 10^{-5} @ 40 Torr), a range of improvements were implemented over our previously reported DFG sensors which generated < 10 μW and were limited to a detection of ~ 2 x 10^{-4} due to etalon interference in the spectroscopic path (coherent interference from optical elements). Hence, to increase the available difference frequency power we developed an architecture based on two frequency-stable

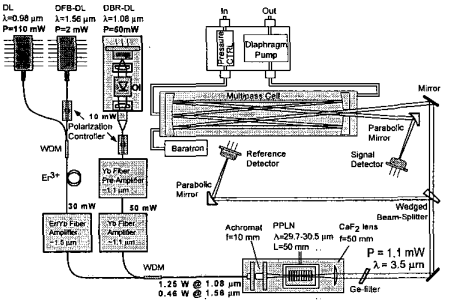

Fig. 1. Difference frequency based formaldehyde sensor using dual beam spectroscopy OI: optical isolator, WDM: wavelength division multiplexer.

diode lasers at 1.1 and 1.5 μm, which were amplified by high power Yb and Er/Yb fiber amplifiers, respectively. To date we have generated up to 1.1 mW of narrow-band (< 60 MHz) mid-infrared radiation. The higher power available allowed the use of an optical-noise-reducing dual-beam absorption configuration employing two DC-coupled Peltier-cooled HgCdTe detectors and an extended 100 m absorption pathlength that is achieved with a low-volume Herriot cell.

Fig. 1 is a schematic of the sensor configuration. The mixing lasers are a fiber pigtailed 2 mW 1561 nm DFB diode laser and a 50 mW 1083 nm DBR diode coupled into single mode fiber. An Er^{3+} doped

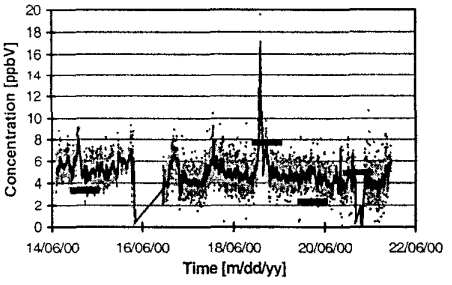

Fig. 2. Dual-beam DFG measurement of H_2CO in air over a 7 day period during a field campaign in Houston,TX. The bars are wet chemical measurements.

fiber pre-amplifier increases the 1561 nm seed power to 30 mW to saturate the gain in the 0.5 W Er/Yb fiber amplifier while the 1083 nm diode directly seeds the 1.5 W Yb amplifier. The two delivery fibers are combined into a single fiber by use of a wavelength division multiplexer with the resultant single fiber output imaged into a 50 mm PPLN crystal (M=11) by a f=1 cm lens. The primary beam is directed to a MCT detector after the multi-pass cell, and a reference beam incident on the second MCT is acquired from a ZnSe wedge placed in the beam before the multi-pass cell. This allows the etalons that arise from the lens and PPLN crystal in the difference frequency mixing stage to be eliminated by ratioing the two beams. The two channels are acquired simultaneously by the use of two A-D data acquisition cards. Spectral lineshapes are acquired by direct current modulation of the 1560 nm diode (triangular waveform at 0.1 to 1 kHz).

Fig. 2 depicts an intercomparison time study of formaldehyde concentrations measured over a 7-day

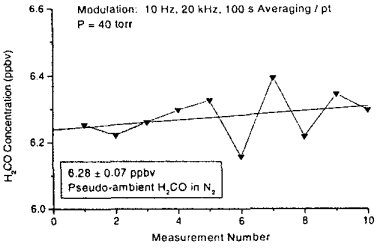

Fig. 3. Measurements of a flowing 6.3 ppb pseudo-ambient H_2CO in nitrogen, using 2-f modulation spectroscopy.

period in the Houston industrial area using the DFG sensor and a chemical derivative technique. Conditions for the DFG measurement include continuous online extractive sampling and each measurement is an average of 5000 spectra acquired over 20s.

To improve the formaldehyde sensitivity to sub-ppb levels, an alternative technique of dual beam 2-f wavelength modulation spectroscopy was implemented. Shown in Fig. 3 are 10 H_2CO measurements acquired from an online flowing pseudo-ambient 6.3 ppb H_2CO-N_2 gas mixture, acquired at a cell pressure of 40 torr, L=100 m and 100 s averaging time per point. To process these spectra a 2-f spectrum acquired from a 30 ppb calibration H_2CO mixture was superimposed on the 2-f lineshapes of the sample, yielding a H_2CO concentration of 6.28+-0.07 ppb.

These results demonstrate that DFG based spectroscopic sources are capable of high sensitivity and real-time trace gas sensing of multiple species at levels down to < 100 ppt.

References:

[1] Dirk Richter, David G. Lancaster, Frank K. Tittel, "Development of an automated diode laser based multi-component gas sensor," Appl. Opt. **39**, 4444-4450 (2000)

[2] A. Fried, B. Henry, B. Wert, S. Sewell, J. R. Drummond, "Laboratory, ground-based, and airborne tunable diode laser systems: performance characteristics and applications in atmospheric studies," Appl. Phys. B **67**, 317-330 (1998)

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