

sensitive detection techniques. Typical near-IR transition line strengths of 10^{-22} to 10^{-23} cm^{-1} have been measured. The BRD enables this high sensitivity without the need for high-frequency modulation approaches, yet maintaining sensitivities equivalent to those obtained with FM techniques.^{2,3} The operational, electronic, and mechanical simplifications afforded by room-temperature, near-IR lasers (versus cryogenic mid-IR lasers) in combination with the BRD circuit will allow detection limits of a few ppm/meter in standard atmospheric pressure, room temperature air. Higher sensitivity will be achieved by use of compact multi-pass cells.

The initial investigations of the application of near-IR diode laser absorption spectroscopy to the detection of VOCs have concentrated on the recording of Fourier transform infrared (FTIR) spectra of the species of interest. Because the near-IR transitions are typically orders of magnitude weaker than the mid-IR transitions, there are few references available in the spectroscopic literature. Figure 1 is an example FTIR spectrum of methanol in the 1.34 to 1.44 micron region. This spectrum was recorded at a neat methanol pressure of 5.2 torr, with an absorption pathlength of 5 meters achieved by use of a white cell. Similar spectra of additional VOCs have been recorded to quantify the wavelengths and strengths of the absorption transitions. These spectra are used as guides for the application of diode laser absorption spectroscopy. During this talk we will also present preliminary diode laser absorption spectra of VOCs. These spectra are recorded with use of DFB and external-cavity diode laser systems. We will report on absorption strengths and potential interferences for the identification of optimum spectral regions for the development of compact, electro-optic, VOC sensors.

1. P. C. D. Hobbs, *SPIE Laser Noise* 1376, 216-221 (1990).
2. M. G. Allen, K. L. Carleton, S. J. Davis, W. J. Kessler, K. R. McManus, presented at the 25th Plasmadynamics and Laser Conference, AIAA paper 94-2433 (1994).
3. M. G. Allen, K. L. Carleton, S. J. Davis, W. J. Kessler, C. E. Otis, D. A. Palombo, D. M. Sonnenfroh, *Appl. Opt.* 34, No. 18, 3240-3249 (1995).

CFN3 (Invited)

1:30 pm

Tunable diode laser absorption spectroscopy for measuring atmospheric molecular species

Alan Fried, *The National Center for Atmospheric Research, Atmospheric Chemistry Division, PO Box 3000, Boulder, Colorado 80307; E-mail: fried@acd.ucar.edu*

The technique of tunable diode laser absorption spectroscopy (TDLAS) has been widely employed for well over 10 years for measuring atmospheric chemical constituents and studying atmospheric processes. The high sensitivity, selectivity, versatility, and fast time response of the technique are important attributes in this regard. Because of these features, TDLAS has been used in a wide variety of

atmospheric studies and settings. This technique, for example, has been successfully employed in laboratory spectroscopy and kinetic studies, in ground-based measurements at remote locations utilizing trailers and vans, in measurements on conventional as well as high flying aircraft, and on balloon-borne payloads. The present talk will give a brief overview of the technique principles and capabilities, detailing some of the atmospheric molecular species studied, the sensitivities achieved, and the current limitations of the technique. This will be followed by a presentation of two recent applications of the technique carried out in our laboratory at the National Center for Atmospheric Research (NCAR): laboratory kinetic studies between stratospheric gases and aqueous sulfuric acid (H_2SO_4) aerosols that are involved in stratospheric ozone (O_3) depletion; and recent ambient measurements of formaldehyde (HCHO) carried out on ground-based and aircraft platforms.

Formaldehyde is an important trace atmospheric constituent formed in the oxidation of most natural and anthropogenic hydrocarbons. As with many such trace gases, ambient measurements of HCHO requires extremely high sensitivity; measurement precision below 0.1 parts-per-billion by volume (ppbv) is typically required to further our understanding of atmospheric processes. Aircraft measurements provide extended spatial and vertical coverage of HCHO as well as many other constituents not possible in ground-based studies. However, such measurements demand high sensitivity along with fast response times of several minutes or less. A new field TDLAS system was developed at NCAR to achieve these stringent requirements on an aircraft platform. Numerous hardware and software features were incorporated in this system for this purpose. These new features include a high pathlength small volume astigmatic Herriott cell; rapid background subtraction; digital signal processing lockin demodulation; Fourier filtering; demeaning and wavelength shifting on a scan-by-scan basis; on-line spectral fitting; and full computerized automation by use of the Lab View Graphical System.

Many of these features will be discussed in the present talk. However, rapid background subtraction and the resulting significant performance improvement (factor of 4 to 5) will be given specific emphasis. In this technique, made possible by the small volume sampling cell, sample and background spectra were acquired in a time period fast (≈ 20 to 30 seconds) compared with changes in background structure. Subtraction of the averaged-background (immediately before and after the sample) very effectively removed performance-degrading optical noise. Based on replicate measurements of HCHO gas standards employing 5-minute integration periods, routine detection sensitivities of 0.04 ppbv have been achieved over many hours with use of this technique in an actual field setting. The relationship between replicate and fit precision, a precision estimator obtained with every fit, will be given in this discussion. Employing Fourier filtering and scan-by-scan demeaning, improved the HCHO detection sensitivity even further to 0.02 ppbv in four minutes of integration, one of the lowest HCHO detection

limits reported by an actual field TDLAS system. This corresponds to a minimum detectable absorbance ($S/N = 1$) of 6×10^{-7} . Recent ground-based and aircraft measurement programs employing this system will be discussed.

CFN4

2:00 pm

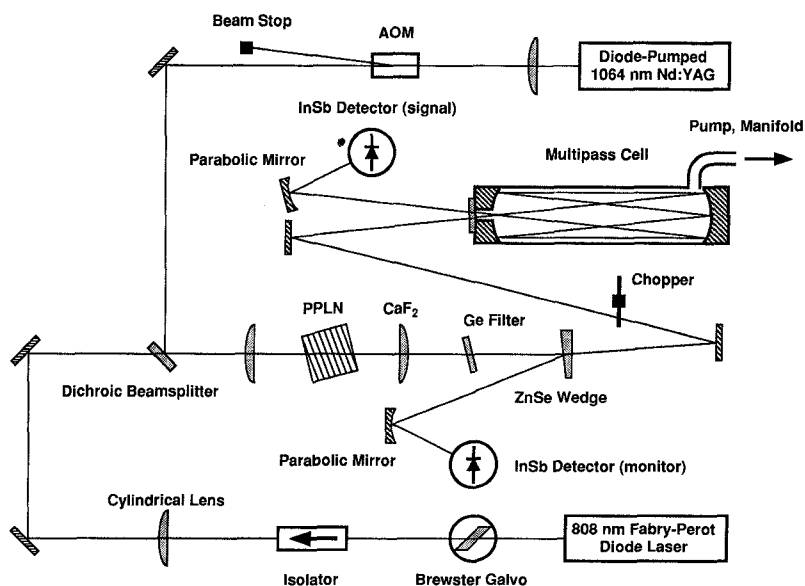
High-precision mid-infrared spectrometer using diode-pumped difference-frequency generation in PPLN

K. P. Petrov, F. K. Tittel, S. Waltman,* L. W. Hollberg,* E. J. Dlugokencky,** M. A. Arbore,† M. M. Fejer,† *Rice Quantum Institute, Rice University, 6100 Main Street, Houston, Texas 77005-1892*

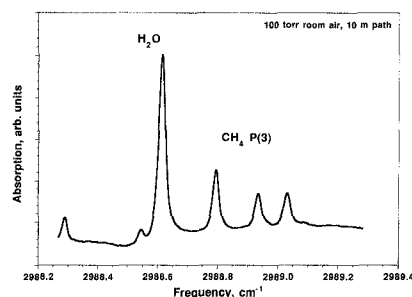
Precise measurements of the global distribution of trace greenhouse gases such as CH_4 , CO_2 , and N_2O provide some of the best known constraints on their global budgets, i.e., sources to, and removal from, the atmosphere. The NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) operates a globally distributed network of surface air sampling sites from which more than 7,000 air samples are analyzed for CH_4 each year.¹ The current measurement technique, gas chromatography, is robust and precise (with relative precision of $\sim 0.1\%$), but it is slow, requiring approximately 15 minutes for each sample measurement.

Infrared laser spectroscopy is a uniquely effective method for the measurement of trace gas concentrations in that it combines high precision, remote sensing capabilities, and fast response. Here we report operation of a compact 3.4 μm difference-frequency spectrometer (Fig. 1) using bulk periodically poled lithium niobate (PPLN). The 1-cm-long, 0.5-mm-thick PPLN crystal was pumped by a 100 mW solitary diode laser at 808 nm and a 500 mW diode-pumped monolithic ring Nd:YAG laser at 1064 nm. Quasi-phase-matched generation at 3.35- μm (idler) was achieved with an effective grating period of 22.2 μm . With 70 mW diode power and 500 mW Nd:YAG power incident on the crystal, a maximum of 3.4 μW idler power was measured. Approximately 40% of the IR output was sampled for power stabilization. A compact multi-pass absorption cell with 18 m effective path length was used for absorption measurements. Fine wavelength tuning and scans were performed by modulation of the diode laser drive current. The maximum available fine tuning range of 35 GHz without mode-hops was sufficient for simultaneous observation of several strong molecular transitions of methane and water (Fig. 2). For absorption measurements, a tuning range of 7 GHz was adequate to capture a single methane peak. The peak amplitude was extracted from the trace using nonlinear least squares fitting. Parameters of fitting included peak position, pressure- and Doppler-broadened linewidths, and a linear fit to the baseline. Voigt line shape was assumed.

The performance of the DFG spectrometer was tested with use of four high-pressure aluminum cylinders filled with dry air that were supplied by NOAA CMDL. All four cylinders had been calibrated for methane at CMDL by gas chromatography with an accuracy of better



CFN4 Fig. 1 Schematic diagram of a compact 3.4 μm spectrometer based on bulk PPLN pumped by two solid-state lasers.



CFN4 Fig. 2 Absorption spectrum of room air near 3.35 μm at 100 torr in a 10-m multi-pass cell. The observed transitions belong to water (2988.6 cm^{-1} and lower) and the P(3) group of methane (2988.8 cm^{-1} and higher). The trace shown is a 1024-sweep average with baseline subtracted. The sweep rate was 100 Hz.

than 1 ppb, and methane mole fractions were assigned relative to the CMDL methane scale. Testing was performed in two parts. In the first part, two cylinders (identification numbers

30516 and 37057) were supplied with their methane mole fractions. The second part was a blind test; the two authors performing the spectroscopic measurements (KPP and SW) were not told the methane mole fractions in two other cylinders (64040 and 30482). A summary of data obtained for all samples analyzed in the experiment is given in Table 1. The combined uncertainty of the spectroscopic measurements over 1 minute was less than 1 ppb for a typical ambient methane mixing ratio of 1700–1900 ppb. The uncertainty was limited by residual interference fringes in the multi-pass cell. Without reference gas, the uncertainty of 20 ppb was limited by the long-term stability and reproducibility of the spectroscopic baseline.

We have demonstrated a precise spectroscopic application of diode-pumped difference-frequency generation. Diode-pumped DFG in PPLN^{2,3} can effectively replace lead-salt diode lasers^{4,5} and gas lasers in spectroscopic and trace gas monitoring applications requiring low-noise, single-frequency sources, continuously tunable

in the 3–5 μm region, and eliminate the need for cryogenic cooling.

*Time and Frequency Division, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80303

**Climate Monitoring and Diagnostics Laboratory, National Oceanic and Atmospheric Administration, 325 Broadway, Boulder, Colorado 80303

†Edward L. Ginzton Laboratory, Stanford University, Stanford, California 94305-4085

1. E. J. Dlugokencky, L. P. Steele, P. M. Lang, K. A. Masarie, J. Geophys. Res. **99**, 17021 (1994).
2. A. Balakrishnan, S. Sanders, S. DeMars, J. Webjörn, D. W. Nam, R. J. Lang, D. G. Mehuys, R. G. Waarts, D. F. Welch, Opt. Lett. **21**, 952 (1996).
3. K. P. Petrov, L. Goldberg, W. K. Burns, R. F. Curl, F. K. Tittel, Opt. Lett. **21**, 86 (1996).
4. C. R. Webster, R. D. May, C. A. Trimble, R. G. Chave, J. Kendall, Appl. Opt. **33**, 454 (1994).
5. M. S. Zahniser, D. D. Nelson, J. B. McManus, P. L. Keabian, Phil. Trans. R. Soc. Lond. A **351**, 4371 (1995).

CFN5

2:15 pm

Tunable mid-infrared source pumped by fiber-coupled communications lasers

K. P. Petrov, R. F. Curl, F. K. Tittel, L. Goldberg,* Rice Quantum Institute, Rice University, 6100 Main Street, Houston, Texas 77005-1892; E-mail: fkt@rice.edu

The use of diode lasers operating at wavelengths of 1.3 μm and 1.5 μm as pump sources for difference-frequency generation (DFG) in AgGaSe₂ was proposed by Simon *et al.* in 1993.¹ The advantage of this scheme is the possibility of convenient generation of cw tunable narrowband light in the spectroscopic "fingerprint" region between 8 μm and 12 μm using readily available communications diode lasers. The recent development of Er/Yb co-doped fiber amplifiers² near 1.5 μm , and Pr³⁺-doped fluoride fiber amplifiers³ near 1.3 μm has made single-frequency output power in excess of 100 mW available. Such sources can be utilized for nonlinear optical conversion techniques, specifically for cw tunable low-noise DFG at the power level of a few microwatts. This radiation can be used for high-resolution mid-infrared molecular spectroscopy and, potentially, for spectroscopic detection and measurement of trace air contaminants such as ammonia, ethylene, sulfur dioxide, methane, nitrous oxide, and phosphine.

We report the operation of a compact all-solid-state room-temperature DFG source (Fig. 1) that employed a high-power Er/Yb co-doped fiber amplifier at 1.554 μm ("signal") and a 35 mW fiber-coupled diode-pumped monolithic ring Nd:YAG laser at 1.319 μm ("pump"). The amplifier was injection-seeded by an optically isolated 2 mW pigtailed distributed-feedback diode laser and operated near saturation, producing up to 0.5 W single-frequency power. The amplifier was

CFN4 Table 1 Summary of methane mixing ratios measured using the 3.4 μm DFG spectrometer. Four samples were available in the experiment, and one of them (30516) was used as a reference in all measurements. The methane mixing ratio in this sample was assumed to be known exactly. Standard deviation shown for the DFG data therefore only includes errors of measurement of absorption, temperature, and pressure. Sample 37057 was measured without cancellation of interference in the multi-pass cell, hence the large error bar

CYLINDER IDENTIFICATION NUMBER	CMDL CH ₄ ASSIGNMENT (ppb)	STANDARD DEVIATION (ppb)	3.4- μm DFG MEASUREMENT (ppb)	STANDARD DEVIATION (ppb)
64040	1753.8	0.2	1754.3	0.8
30516	1775.3	0.1	used as a reference	n/a
30482	1781.9	0.9	1781.1	0.8
37057	1896.7	1.3	1896.2	3.0