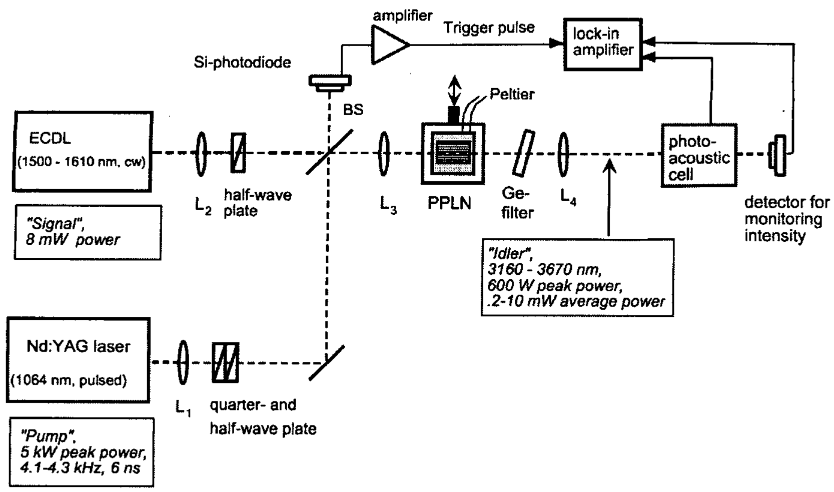

CThT4 Fig. 1. The set-up used for the photo-acoustic measurements.

tuations are preferable. To enable PA measurements even at the low average power available from our DFG source, we developed a resonant PA cell whose first longitudinal resonance corresponds to the pulse repetition rate of the Nd:YAG pump laser around 4.2 kHz. This results in a cell length of 32 mm.

Our first PA measurements concentrated on the detection of methane (CH_4). In Fig. 2, the normalised PA signal (PA amplitude on laser power) is plotted as a function of the wavelength for a mixture of 100 ppm CH_4 buffered in synthetic air at atmospheric pressure and room temperature. Good agreement is found with HITRAN data (solid line). The background signal recorded in nonabsorbing synthetic air is shown for comparison. From these results, a detection limit of 30 ppm for a SNR = 3 is derived. This demonstrates that PA measurements are feasible even at average powers below 1 mW and large pulse-to-pulse fluctuations which also explain the low signal points occasionally present in the spectrum of Fig. 2.

Current studies focus on the design of a new PA cell with a radial resonance frequency around 8 kHz equipped with several microphones. The operation of the Nd:YAG laser at 8 kHz yields an average DFG power of several mW which is expected to result in a CH_4 detection limit in the sub-ppm concentration range, i.e. suitable for ambient CH_4 monitoring. This renders the PA method competitive with other schemes like cavity ring-down, but at much lower complexity and costs.

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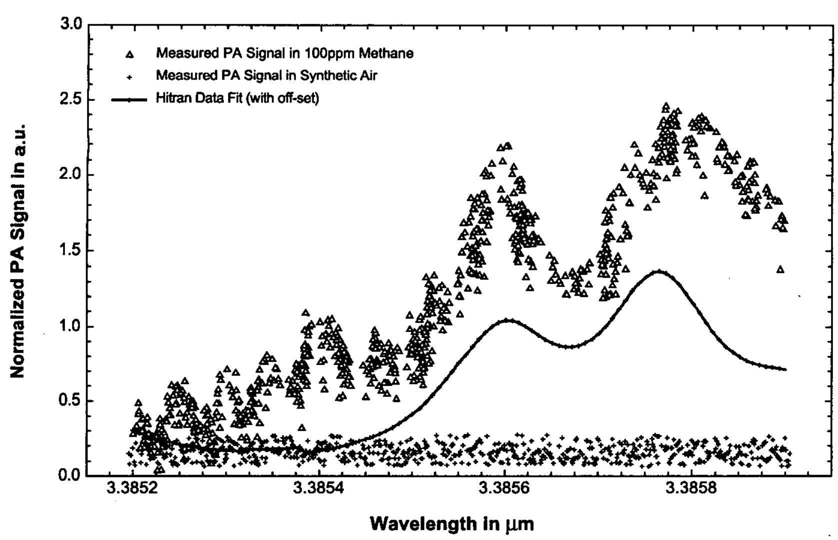

CThT4 Fig. 2. The measured photo-acoustic signal of 100 ppm methane in synthetic air as a function of the wavelength. Clearly two peaks (at 3.3856 µm and 3.3858 µm) are visible. The solid line shows the theoretical curve from the Hitran database.

CThT5 **5:45 pm**

Environmental and chemical sensing applications of diode and quantum cascade laser based gas sensors

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In recent years, laser-based techniques for the real time detection of trace gases with ultra high sensitivity and excellent selectivity have been developed. The principal optical gas sensor technologies are based on absorption spectroscopy of fundamental bands in the 3 to 25 µm spectral region and near-infrared vibrational overtone and combination bands from 1 to 3 µm. In this talk we report the development of portable, automated gas sensors based on three different types of device architectures. If the anticipated concentration levels are sufficiently large of a desired trace gas and if this species exhibits near IR resolved rotational-vibrational transitions that are free of interfering species (such as CO_2 and H_2O), then a sensor based on distributed feedback (DFB) diode lasers are ideally suited. If, however, trace gas detection at ppb and ppt levels is required for a specific application, it is convenient to select a sensor architecture suitable for the mid-IR based on difference-frequency generation (DFG) of two diode lasers in a nonlinear optical material such as periodically poled lithium niobate[1] or quantum cascade-DFB lasers[2] in the 3 to 5 µm and 4 to 17 µm spectral region, respectively. Each of these three sensor designs can be used with different detection schemes that are selected to achieve minimum detectable absorbances ranging from 10^{-9} to 10^{-6} cm^{-1}, depending on the applications driven sensing scenario. Balanced detection, wavelength modulation, and cavity enhanced spectroscopy and combinations thereof were used to realize enhanced trace gas detection sensitivities at the sub-ppb level. In the case of the two types of diode laser DFG based gas sensors, we have used robust fiber pigtailed telecommunications DFB diode lasers and, when appropriate, Yb and Er/Yb optical fiber amplifiers to boost their power and fibered beam delivery. The QC-DFB based gas sensors have so far been operated either cw or pulsed, cooled to liquid nitrogen and room temperatures, respectively. Details of the spectroscopic parameters for the three spectroscopic devices will be reported, specifically their available power, linewidth, and wavelength tunability.

All three gas sensors have been applied to NH_3 detection, which is of interest in various applications such as in combustion, in chemical analysis, and in environmental trace gas monitoring. NH_3 concentration measurements using vibrational overtone spectroscopy at 1.53 (6528.8 cm^{-1}), fundamental to vibrational spectroscopy at 3.035 µm (3295.4 cm^{-1}) and at 10.04 µm (997 cm^{-1}), respectively, have been performed both in the laboratory and at the NASA Johnson Space Center on a bioreactor developed for water reprocessing.

In addition, a 1 mW cw mid-infrared DFG

source based on frequency mixing two fiber amplified diode laser pump sources at 1.08 and 1.56 μm in periodically poled $LiNbO_3$ (PPLN) shown in Fig. 1 has been used to quantify atmospheric formaldehyde (H_2CO). Figure 2 depicts continuous time resolved H_2CO concentration measurements at ppb levels with a precision of 0.6 ppbV at 3.53 μm (2831 cm^{-1}) performed over a five-day period at an environmental monitoring site in the Houston area. Other chemical sensing applications that were investigated recently included isotopic measurements of CH_4w ith a 8 μm QC laser and volcanic emissions monitoring at the Masaya volcano in Nicaragua with a multi-species DFG based gas sensor.

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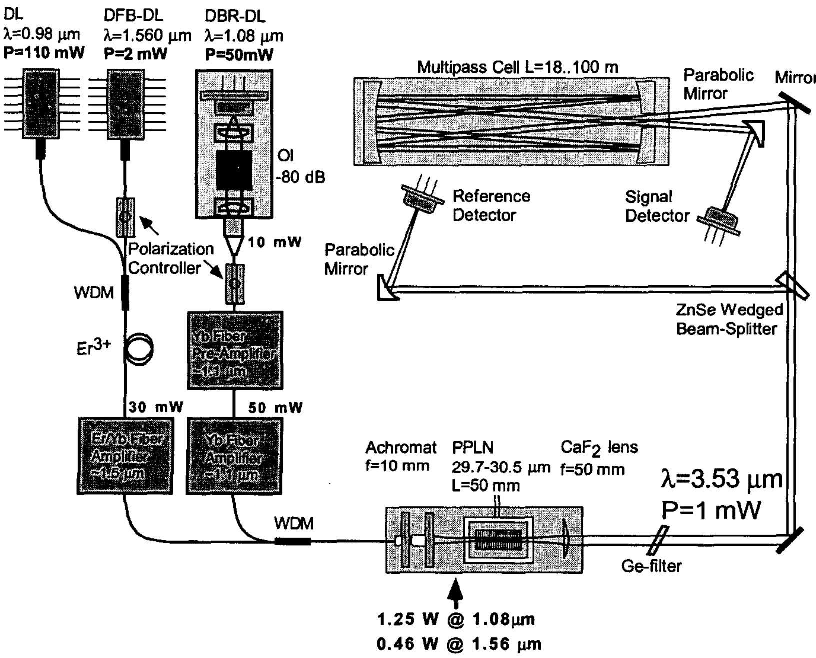
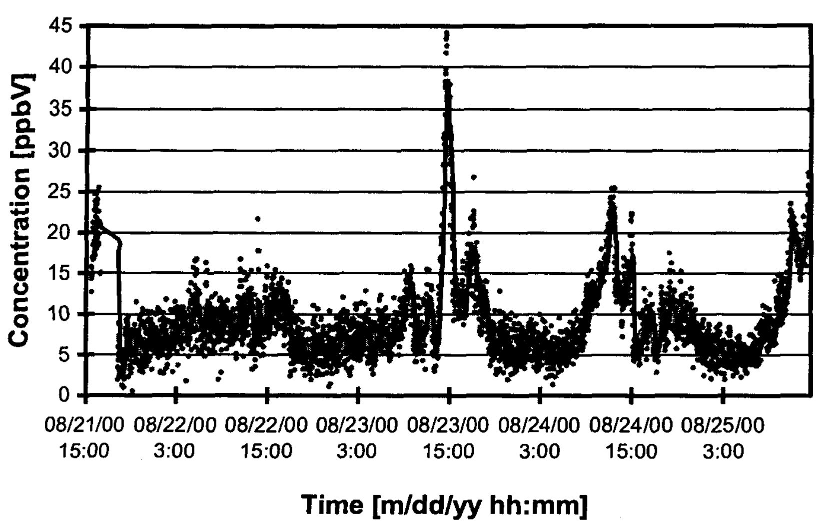


CThT5 Fig. 1. Tunable 1 mW narrow-linewidth mid-infrared DFG based trace gas sensor.



CThT5 Fig. 2. Five days of H_2CO data obtained at Channelview, TX using the DFG based gas sensor depicted in Fig. 1.

CThT6 **6:15 pm**

Mobile photoacoustic trace-gas monitoring using high power quantum-cascade lasers as pump sources operated near room temperature

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Photoacoustic detection offers the advantage of wavelength-independent and simple operation and low cost. However, since the measurable photoacoustic signal is proportional to the laser power absorbed by the gas inside the detection cell, high power lasers are normally used as pump sources with typical output powers in the Watt regime, e.g. line-tunable CO_2 lasers. The highly sensitive multipass resonant photoacoustic cell[1] employed in our set-up is in the first place optimized to be operated with continuous-wave CO_2 lasers as pump sources but also well suited for other laser sources such as quantum-cascade lasers (QCLs) as is demonstrated here.

QCLs offer some distinct advantages: In principle, they can be produced with emission wavelengths between 3.5 and 19.2 microns and therefore they can be adapted to the strongest absorption lines of the trace gases to be monitored. (Hitherto, QCLs with emission wavelengths around 4.6 μm, 5.3 μm, 7.8μm, 8.5μm, 9.4μm, 10.3μm, and 19.2μm are available.) Furthermore, they offer the possibility to measure absorption lines of gases in wavelength regions which are not accessible with other laser sources. As a result of their continuous wavelength tunability (few wavenumbers) theses sources reduce absorption interferences in multicomponent mixtures that sometimes limit the detection selectivity achievable with discretely tunable laser systems. On the other hand, however, owing to the small tuning range, one can cover only a few absorption lines which limits the multicomponent capability. Finally the dimensions and costs of such a system can be reduced substantially.

The operation temperature of the pulsed quantum-cascade laser[2] used in our mobile system is between –40°C to +60°C achievable with a simple Peltier- and water-cooling system. The coefficient for the wavelength tuning is –0.06 cm^{-1}/K. At –40°C the maximum peak power is 250 mW corresponding to an average power of 8 mW with a duty cycle of 3% and 30 ns pulses. This quasi-cw radiation is modulated with a mechanical chopper at the first longitudinal resonance frequency of our multipass photoacoustic cell at 1240 Hz. Figure 1 shows measured photoacoustic spectra of 10 ppmV ammonia (NH_3) buffered in synthetic air (80% N_2 and 20% O_2). The spectra have been recorded at room temperature and at different total pressures. Taking the laser line width of 0.3 cm^{-1} into account the comparison with HITRAN data (solid line) yields excellent agreement. From these data a detection limit for ammonia of 0.3 ppmV for a signal-to-noise ratio of 3 is derived. In addition to trace gas monitoring future studies include relaxation rate measurements of excited molecules.