Current applications of quantum cascade lasers in trace gas analysis and chemical sensing

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One of the principal applications of quantum cascade lasers (QCLs) is in chemical sensing, since these lasers can access directly the mid-infrared spectroscopic fingerprint region (~2-25 μm), where most gaseous chemical substances possess strong fundamental rotational-vibrational transitions [1-3]. To date we have detected 11 gases (CH_4, N_2O, CO_2, CO, NO, H_2O, NH_3, C_2H_4, COS , SO_2 and C_2H_5OH including isotopic signatures of carbon and oxygen at the ppm to the ppb level using QCLs. This talk will focus on the development of compact trace gas sensor platform technology based on QCLs and their application to sensitive, selective and quantitative trace gas detection. Current application topics include: atmospheric chemistry and environmental monitoring, urban and industrial emissions measurements, chemical analysis and industrial process control and medical applications

QCLs possess the key properties required for a mid-infrared spectroscopic source: (1) sufficient optical power to ensure high signal-to-noise ratios, (2) narrow linewidths and single frequency to obtain high selectivity (3) mid-infrared wavelength coverage with type I and II QCLs (4) continuous and broad wavelength tunability without mode hops, (5) quasi-room temperature operation (6) good beam quality and (7) high reliability and compactness. Until recently quasi-room temperature operation of QCLs was only possible for pulsed operation, but recently the first thermoelectrically-cooled, continuous wave (cw), mid-infrared, single frequency QCL was reported, which will greatly facilitate the use of QCLs in spectroscopic applications [4]

Current examples of QCL applications being investigated by us include trace gas sensing in NASA applications relevant to spacecraft environmental monitoring and advanced life support using quartz enhanced photoacoustic spectroscopy, high precision measurements of $^{13}CO_2/^{12}CO_2$ isotopic ratios at 4.3 μm and noninvasive medical diagnostics of various human diseases by means of breath analysis. One specific application is the measurement of NO in exhaled breath, since the presence of NO is an indicator of several physiological and biochemical processes taking place in the human body, in particular in assessing the severity of airway inflammation (i.e. asthma). A gas sensor based on a cw single frequency QCL operating at ~5.2 um (1900 cm-1) and off axis integrated cavity output spectroscopy is being developed to measure ppb levels of NO concentration in breath.

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A laboratory setup for QEPAS evaluation is schematically shown in Fig. 1. We used a wavelength modulation approach and detection at twice the modulation frequency, which eliminates photoacoustic signals from broadband absorbers such as dust particles or the TF itself. The TF resonant frequency f was determined prior to each set of measurements, and the laser modulation frequency was set to $f/2$. Data acquisition and analysis were performed by means of National Instruments (NI) DAQCard-6062E data acquisition card and a notebook computer with LabView based programs. Software modules from a NI Lock-in amplifier start-up kit (*NILockinStartupKit.llb*) available from the NI web site were included in the data acquisition and analysis programs to make the computer perform lock-in amplifier functions. A reference cell contained gas mixture with high concentration of the species to be detected. Photodiode signal demodulated at $3f/2$ frequency was used to lock the laser frequency to the center of absorption lines.

A target species for the first practical application of QEPAS sensor is ammonia (NH_3) to be detected via its absorption line at 6528.76 cm^{-1} [5]. However, the use of ammonia is not convenient at the sensor optimization stage because it is strongly adsorbed by stainless steel surfaces and is also toxic. Therefore, acetylene (C_2H_2) was used as NH_3 simulant. Its P(11) line of $\nu_1+\nu_3$ absorption band is positioned at 6529.16 cm^{-1}, thus closely matching the position of ammonia absorption line. An example of a QEPAS C_2H_2 spectrum is shown in Fig. 2. The Y component (Fig. 2b) can be used to estimate noise. Such an estimate resulted in the experimental value of a noise density at the transimpedance preamplifier output of $S=6.4\times10^{-6}$ V/√Hz.

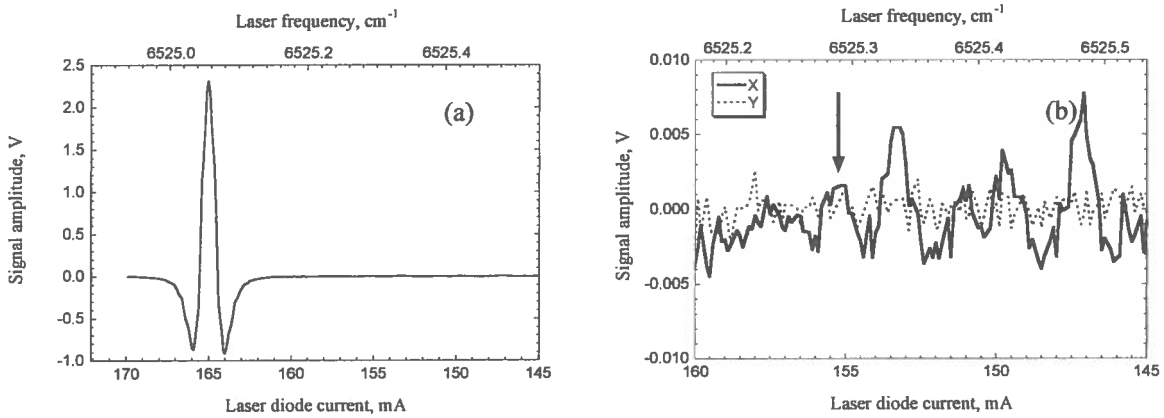

Fig. 2. QEPAS signal acquired for a 1.35% C_2H_2 in air mixture. Total pressure is 107 Torr, lock-in time constant is 0.3 s, laser power is 27 mW, and laser current modulation is 4 mA peak-to-peak. In-phase signal component is shown in (a). The strong peak corresponds to the P(11) line of C_2H_2 $\nu_1+\nu_3$ band. (b) depicts a part of the same data set. X and Y are respectively the in-phase and orthogonal components. Line marked by the arrow is 1225 times weaker than the P(11) line, according to direct absorption data.

Theoretical analysis of fundamental TF noise resulting from its thermal excitation was developed in [6]. Following the same approach we calculated the thermal noise density in each X and Y components at 108 Torr as $S_{th}=4.3\times10^{-6}$ V/√Hz. Hence, the measured noise is only 50% higher than the fundamental limit and is not related to the laser radiation. The excess noise is most probably due to imperfect grounding and related stray currents.

The QEPAS signal was measured as a function of total gas pressure and laser current modulation amplitude. The laser power and C_2H_2 concentration in the gas mixture remained constant. The results are shown in Fig. 3. The highest sensitivity, $k=2.3\times10^{-7}$ $cm^{-1}W/\sqrt{Hz}$ was observed at 265 Torr. This represents a 3.8 times improvement compared to the result reported by us in [4] for the same configuration. We believe this to be a consequence of the faster operational amplifier used in the transimpedance preamplifier circuit. The next step to obtain a higher sensitivity is to combine the TF with an acoustic microresonator. Such a combination was reported in [4] to provide 7.3 times better sensitivity. In that work two pieces of stainless steel capillary tube were used as such a resonator. Different materials and geometrical arrangements will be investigated for implementing an optimum design of a QEPAS gas sensor module.

Along with optimization of the QEPAS spectrophone, a compact dedicated electronics control unit, CU for a stand-alone automated QEPAS-based gas sensor was developed. This unit performs the following functions:

- Measures TF resonant frequency f
- Modulates laser current at $f/2$ (sine wave)

- Demodulates photodiode (PD) signal at $3f/2$ and uses it to lock the laser wavelength to an absorption line
- Converts TF current to voltage and amplifies it
- Demodulates TF signal at f, normalizes to PD signal and measures it on- and off- the absorption line to provide a number proportional to the species concentration
- Can operate autonomously or communicate with a PC via a RS232 port

The present version of the CU uses a 10-bit ADC, which is not sufficient to realize ultimate QEPAS sensitivity and dynamic range. A next version is presently under development, which will incorporate a 20-bit ADC, special low-$1/f$ noise chips at the front end and will perform some additional functions such as TF Q-factor measurements.

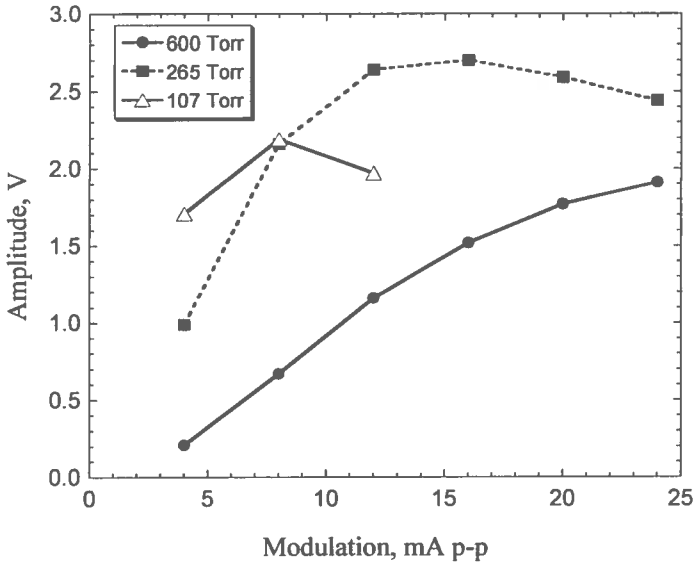

Fig. 3. QEPAS signal as a function of gas pressure and laser current modulation depth.

QEPAS has a potential to perform chemical analysis of gas samples with a volume ultimately limited by the gap size between the TF prongs, which is 0.15 mm^3 for the presently used TFs. Sensitivity of this method to date is about 10 times less than demonstrated for the state-of-the-art conventional PAS experiments, but we project the feasibility of further improvements of sensitivity levels. QEPAS is ideally suited for real-world applications because of its compactness and noise immunity.

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