Recent advances and applications of mid-infrared semiconductor based trace gas sensor technologies

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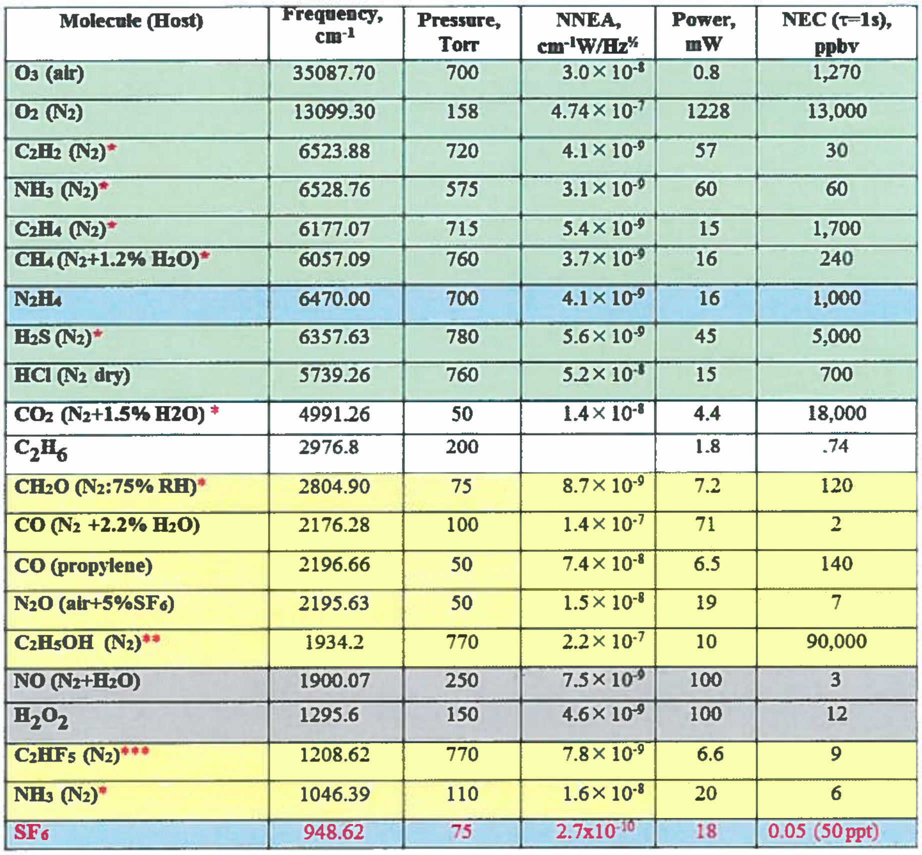
Recent advances of sensor systems, based on mid-infrared interband cascade lasers (ICLs) and quantum cascade lasers (QCLs) for the detection of trace gas species and their applications in environmental monitoring, atmospheric chemistry, life sciences, and the petrochemical industry, will be reported. The development of compact ICL and QCL based trace gas sensors will permit the targeting of strong fundamental rotational-vibrational transitions in the mid-infrared, which are one to two orders of magnitude more intense than transitions involving overtone and combination bands in the near-infrared. One of most robust detection technique is based on the PhotoAcoustic Spectroscopy (PAS). It takes advantage of the thermal expansion of the target gas when it absorbs radiation from the excitation laser. These molecules, once excited by the absorbed optical radiation, subsequently relax to their ground state via non-radiative processes which produce localized heating within the sample and, hence, a localized pressure wave. In the standard PAS, the pressure wave is detected by a microphone. Quartz-enhanced PhotoAcoustic Spectroscopy (QEPAS) is an alternative approach to PAS detection of trace gases, utilizing a quartz tuning fork (QTF) as an ultra-compact resonant acoustic transducer with a high quality factor to detect photoacoustic excitations. . In QEPAS, quartz crystals with a resonant frequency of 32,768 Hz (2^{15}) are used due to their low cost, since they are used in timing applications such as watches, clocks and cell phones. Furthermore, a frequency of 32.768 kHz is slow enough for relaxation processes within the target gas of interest not to reduce the acquired QEPAS signal and fast enough that the signal build up time is <1 s . An acoustic micro-resonator (mR) tube for sound wave enhancement is an important component that is acoustically coupled with the QTF to strongly enhance the acoustic wave field. In a standard QEPAS configuration, a stainless steel tube is cut into two pieces and the QTF is inserted between them.

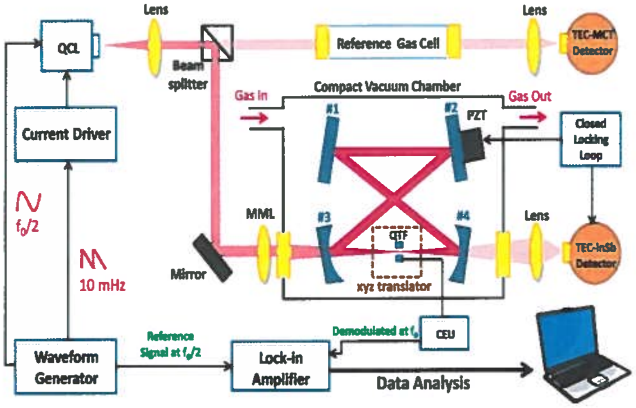
In Table 1 the results obtained so far by us for QEPAS based gas sensors are listed. For each target gas, we report the operating spectral region and the optimum gas pressure, the available continuous wave (CW) laser power and the sensor performance in terms of Noise Equivalent Concentration (NEC) and Normalized Noise Equivalent Absorption (NNEA) coefficient [1]. NNEAs measured to date using QEPAS are significantly larger than the best conventional PAS results. In the mid-IR a record NNEA of $2.7 \cdot 10^{-10}$ $\mathrm{cm^{-1}W/Hz^{1/2}}$ is obtained for SF_6 detection at a gas pressure of 75 Torr, employing an external cavity QCL fiber coupled to the QEPAS spectrophone. The sensitivity of the sensor is a result also of exceptionally large SF_6 absorption cross-sections and its fast vibrational-translational relaxation rate.



Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{1/2}$	Power, mW	NEC (τ=1s), ppbv
O_3 (air)	35087.70	700	3.0×10^{-8}	0.8	1,270
O_2 (N_2)	13099.30	158	4.74×10^{-7}	1228	13,000
C_2H_2 (N_2)*	6523.88	720	4.1×10^{-9}	57	30
NH_3 (N_2)*	6528.76	575	3.1×10^{-9}	60	60
C_2H_4 (N_2)*	6177.07	715	5.4×10^{-9}	15	1,700
CH_4 (N_2+1.2% H_2O)*	6057.09	760	3.7×10^{-9}	16	240
N_2H_4	6470.00	700	4.1×10^{-9}	16	1,000
H_2S (N_2)*	6357.63	780	5.6×10^{-9}	45	5,000
HCl (N_2 dry)	5739.26	760	5.2×10^{-8}	15	700
CO_2 (N_2+1.5% H2O) *	4991.26	50	1.4×10^{-8}	4.4	18,000
C_2H_6	2976.8	200		1.8	.74
CH_2O (N_2:75% RH)*	2804.90	75	8.7×10^{-9}	7.2	120
CO (N_2 +2.2% H_2O)	2176.28	100	1.4×10^{-7}	71	2
CO (propylene)	2196.66	50	7.4×10^{-8}	6.5	140
N_2O (air+5%SF_6)	2195.63	50	1.5×10^{-8}	19	7
C_2H_5OH (N_2)**	1934.2	770	2.2×10^{-7}	10	90,000
NO (N_2+H_2O)	1900.07	250	7.5×10^{-9}	100	3
H_2O_2	1295.6	150	4.6×10^{-9}	100	12
C_2HF_5 (N_2)***	1208.62	770	7.8×10^{-9}	6.6	9
NH_3 (N_2)*	1046.39	110	1.6×10^{-8}	20	6
SF_6	948.62	75	$2.7\text{x}10^{-10}$	18	0.05 (50 ppt)

Table 1. QEPAS detection of trace gases.

Future work will include the detection of other important target analytes. For example, H_2S detection has been realized with a THz QEPAS sensor system using a custom quartz tuning fork (QTF) with a new geometry and a QCL emitting at 2.913 THz [2]. A minimum detection limit (MDL) of 30 ppm with a 3 seconds integration time was achieved with an optical power of 1.1 mW. A CW quantum cascade laser (QCL) based absorption sensor system was demonstrated and developed for simultaneous detection of atmospheric nitrous oxide (N_2O), methane (CH_4), and water vapor (H_2O) in the mid-IR spectral range [3]. This single QCL based multi-gas detection system possesses applications in environmental monitoring, atmospheric chemistry and breath



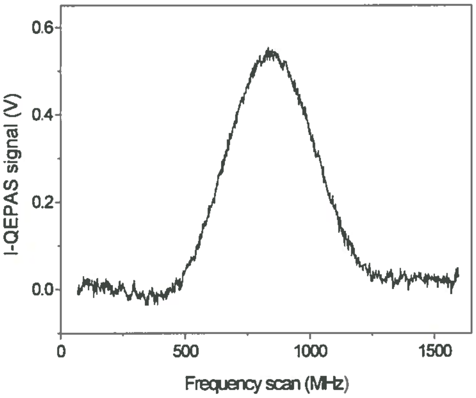


Fig. 1 Development of an intracavity optical build-up QEPAS sensor design. The bow-tie cavity is composed by 4 mirrors with a reflectivity of R=99.9%. The electronic control loop and the piezo driver lock the cavity resonant frequency to the QCL frequency.

Fig. 2 Intra-cavity QEPAS performance in locked mode. NEC = 300 ppt @ 4 sec integration time based on Allan-Werle deviation analysis. NNEA = $3.2\text{x}10^{-10}$ cm^{-1} $W(Hz)^{-1/2}$. Power enhancement factor is ~ 250.

analysis. Furthermore, two new approaches aimed to achieve enhanced detection sensitivities with QEPAS based sensing can be realized. The first approach make use of an optical power buildup cavity, which leads to significantly lower minimum detectable gas concentration levels of < 10 ppt. In Fig. 1 we depict the experimental setup of an intracavity optical build-up QEPAS sensor. This method was used to detect CO_2, reaching a sensitivity of 300 ppt with a 4 s averaging time and a corresponding NNEA of $3.2 \cdot 10^{-10}$ $Wcm^{-1}/Hz^{1/2}$. In Fig. 2 a representative spectral scan obtained with a CO_2 concentration of 200 ppb in pure $N_2$is shown. The second approach will use custom fabricated QTFs capable of improved detection sensitivity. The resonance frequency of the fundamental mode was reduced to a few kHz, in order to appproximate the typical energy relaxation time of targeted gases, while maintaining a high resonator quality factor [4]. A lowering of the fundamental resonance frequency also reduces the overtone frequencies, which lead to their investigation and use in QEPAS based gas sensor systems. QTF overtone modes having the highest quality factor exhibit the largest QEPAS signal, demonstrating that by optimizing the QTF prongs sizes, the overtone modes can provide a higher QEPAS sensor performance with respect to using the fundamental mode [5,6].

[1] P. Patimisco, G. Scamarcio, F.K. Tittel, and V. Spagnolo, "Quartz-enhanced photoacoustic spectroscopy: a review" *Sensor: Special Issue "Gas Sensors-2013"* 14, 6166206, 2014.
[2] V. Spagnolo, P. Patimisco, R. Pennetta, A. Sampaolo, M. Vitiello, and F.K. Tittel, *Opt. Exp.* 23, 7574-7582, 2015
[3] M. Jahjah, W. Kiang, N.P. Sanchez, W. Ren, P. Patimisco, V. Spagnolo, S.C. Herndon, R.J. Griffin, F.K. Tittel, "Atmospheric CH_4 and N_2O measurements near Greater Houston area landfills using QCL-based QEPAS sensor system during DISCOVERY-AQ 2013", *Optics Letters* 39, 957 (2014).
[4] P. Patimisco, A. Sampaolo, L. Dong, M. Giglio, G. Scamarcio, F. K. Tittel, V. Spagnolo, "Analysis of the electro-elastic properties of custom quartz tuning forks for optoacoustic gas sensing", *Sensors and Actuators: B Chemical* 227, 539-546, 2016.
[5] F. K. Tittel, A. Sampaolo, P. Patimisco, L. Dong, A. Geras, T. Starecki, V. Spagnolo, "Analysis of overtone flexural modes operation in quartz –enhanced photoacoustic spectroscopy." *Opt. Exp.* 24, A682-A692, 2016
[6] A. Sampaolo, P. Patimisco, L. Dong, A. Geras, G. Scamarcio, T. Starecki, F. K. Tittel, V. Spagnolo; "Quartz-Enhanced Photoacoustic Spectroscopy exploiting tuning fork overtone modes", *Appl. Phys Lett.* 107, 231102, 2015

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