Quartz-enhanced photoacoustic spectroscopy with semiconductor lasers: the road to ultracompact trace gas sensors

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Quantification of trace chemical components in gases is required in such diverse applications, such as industrial process control, automotive exhaust analysis, environmental monitoring and medical diagnostics. Ultrasensitive chemical analysis of compounds in the gas phase based on molecular absorption in the mid-IR region is a well-established approach. A number of techniques have been developed to measure absorption coefficients as low as $\alpha=10^{-9}$ cm^{-1} or less, allowing in some cases quantification of chemical species at 10^{-12} by volume (pptv) concentration levels. However, most methods demonstrated in the laboratory are unsuitable for field deployment because of the sensor size comprising optical elements such as a laser source and multipass cell as well as high sensitivity to vibrations and temperature variations.

Recent developments in semiconductor quantum electronics resulted in a new generation of compact mid-IR laser sources such as quantum cascade lasers (QCLs) and interband cascade lasers (ICLs). They are capable of generating tens to hundreds of mWs of optical radiation in the molecular fingerprint region and do not require cryogenic cooling. In order to take a full advantage of these devices for chemical sensing applications, an equally compact absorption detection module is required. Direct absorption detection can not satisfy this requirement because of the long optical pathlength needed for high sensitivity. A characteristic size for a multipass gas cell volume is 1000 cm^3. Photoacoustic spectroscopy (PAS) based on the detection of sound generated in the media upon absorption of modulated optical radiation allows comparable detection limits to be reached with a much smaller sample cell volume, typically starting from ~10 cm^3. However, PAS performance can be strongly degraded by ambient acoustic noise which prevents its widespread use in the design of portable gas sensors.

We report a novel approach to PAS called quartz-enhanced PAS, or QEPAS [1]. This technique is based on a quartz tuning fork (TF) used as a resonant acoustic transducer. The TFs are designed to be normally used as frequency standards in electronic clocks, resonating at f~32 768 (2^{15}) Hz. Clock TFs are mass-produced elements and therefore very inexpensive (<$0.5/piece). QEPAS makes use of the extremely high Q-factor of these quartz vibrators, which allows the signal build-up during $(1\text{-}3)\times10^4$ modulation periods. The largest dimension of a TF is typically <5mm, thus matching the size of a semiconductor laser source. QEPAS proved to be highly immune to ambient acoustic noise. The sensitivity limiting factor of QEPAS is the fundamental thermal noise

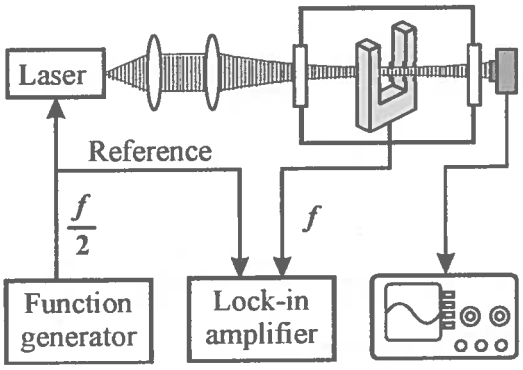

Fig. 1. Basic QEPAS sensor configuration.

of the TF [2]. A gas cell is optional and may be needed only to isolate the gas sample from the ambient atmosphere. Its volume can be as small as a few cubic millimeters.

A schematic of the basic QEPAS arrangement is shown in Fig. 1. All the experiments to date were performed in a wavelength modulation mode. The laser current is modulated at a *f/2* frequency, causing the laser wavelength to be modulated at the same frequency and resulting in photoacoustic signal at *f* if an absorption line is present. Such a mode of operation eliminates signals that could appear due to nonselective absorption of the laser radiation by the TF itself.

An ammonia gas sensor based on QEPAS in combination with a fiber-coupled commercial near-IR DFB laser (NTT Electronics Corporation model NLK1C5J1AA) with a noise-equivalent sensitivity of 0.65 ppmv with a 1s time constant was demonstrated [3]. Based on these results, a normalized sensor detection limit (k) is calculated to be $k=7.2\times10^{-9}$ $cm^{-1}W/Hz^{1/2}$. This number is in the same range as the best reported results for conventional PAS.

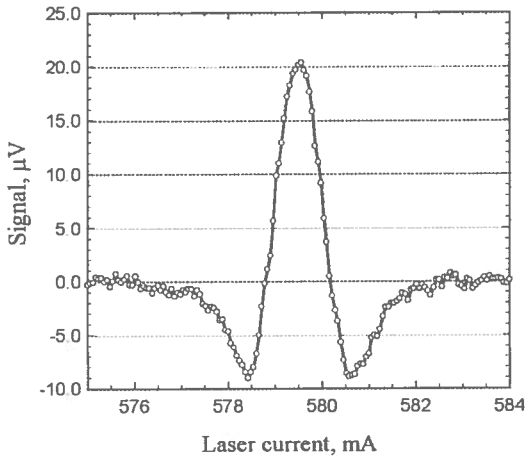

Fig. 2. QEPAS spectrum of air in the vicinity of P(30) line of the N_2O ν_3 mode.

Absorption cross-sections of molecular transitions in the near-IR (overtone) region are typically 100 or more times lower than cross-sections of fundamental transitions. Therefore much lower detection limits can be expected if mid-IR spectroscopic sources are utilized. We investigated the detection of N_2O in ambient air using QCL to access the P(30) line of the ν_3 mode at 2195.633 cm^{-1}. The air was doped with 5% SF_6 to promote V-T relaxation of the vibrationally excited molecules. The N_2O spectrum obtained using QEPAS is shown in Fig. 2. These data yield a single-point SNR=50. Since the atmospheric N_2O concentration is known to be stable at 320 ppbv, the observed noise-equivalent detection limit corresponds to 6.5 ppbv for the QEPAS-QCL based gas sensor.

References

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