Sensitive Detection of Carbon Monoxide using a Compact High Power CW DFB-QCL based QEPAS Sensor  
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Abstract: Development of an ultra-sensitive, selective, and compact QEPAS-based CO sensor employing a high power CW DFB-QCL is reported. A minimum detectable concentration of 4ppbv was achieved for CO line (2169.2cm⁻¹) using a 5sec data acquisition time.  
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1. Introduction  
Carbon monoxide (CO) is considered to be one of the main global pollutants. Principal sources of CO production and emission to the atmosphere include various incomplete partial oxidations of carbon-containing compounds associated with automobiles combustion, fossil fuels burning by power plants, and petrochemical-related processes. Significant influence of CO upon atmospheric chemistry was recognized due to its close relation to the degradation of the ozonosphere and creation of acid rain, resulting from its reaction with hydroxyl (OH) and its indirect effect on the accumulation of greenhouse gases [1-3]. Even at low concentration levels CO may cause serious threat to human life since it is colorless, odorless and tasteless, and therefore hard to sense. Accurate and reliable real time monitoring of CO accumulation is important in medical diagnostics, since CO concentration levels of sub ppm can affect the human respiratory system [4].  
To perform quantitative and selective CO detection at low concentration levels a sensor platform based on quartz-enhanced photoacoustic spectroscopy (QEPAS) was developed. QEPAS, first reported in 2002 [5], is a sensitive technique that benefits from replacing a broadband and low Q-factor acoustic microphone of conventional PAS (CPAS) with a piezoelectric quartz tuning-fork (QTF) that has a sharp (Q factor of >80,000 in vacuum) acoustic resonance at ~32 kHz. In a QEPAS based sensor an acoustic wave that is generated when modulated optical radiation interacts with a trace gas is detected. This interaction leads to deformation of the QTF prongs that results in a separation of electrical charges on its electrodes. An enhancement of the QEPAS signal leading to the improvement of signal-to-noise ratio (SNR) is achieved when the QTF is positioned between two metallic tubes acting as a micro-resonator (mR). The reported high-power DFB-QCL based CO QEPAS system uses the length and inner dimensions of the mR tubes, which are 3.9 mm and 0.84 mm, respectively. Such a QEPAS sensor configuration is close to optimal in terms of SNR [6]. QEPAS based detection of CO uses a compact acoustic-detection module (ADM), with an ultra-small effective gas sample volume of ~4mm³. This architecture is especially applicable for applications requiring light weight and small dimensions of the sensor platform. Furthermore, QEPAS can be used for the detection of trace gas species in different spectral regions [7], with little or no modifications to the sensor design.  
2. CO QEPAS sensor architecture and performance  
A compact DFB-QCL based QEPAS sensor installed inside a 6”x14”x8” custom made housing is shown in Fig. 1.  
![Fig.1. Schematic (a) and (b) photo of completed design of compact high power, CW DFB-QCL based QEPAS sensor.](image-url)  
Aluminum breadboard base enables stable mechanical conditions for optical components, whereas a plexiglass enclosure provides a reliable sensor cover simultaneously suppressing the reflection of mid-IR radiation. A high power, CW, room temperature DFB-QCL laser from the Department of Electrical Engineering and Computer Science at Northwestern University (Evanston, Illinois) is employed as an excitation source to target the R(6) CO
line at 2169.2 cm\(^{-1}\) (4.61 μm). The DFB-QCL, operating at 15\(^{\circ}\)C, is capable of delivering ~280 mW of optical power at the frequency of the selected CO line. To remove the heat dissipated from the hot surfaces of the TEC module inside the ILX QCL mount (LDM-4872) an ultra-compact air-cooled liquid recirculation chiller (Oasis model from Solid State Cooling Systems) is used. The DFB-QCL beam is collimated using a black diamond antireflection coated (3-5 μm) aspheric lens with a 1.7 mm effective focal length (Lightpath model 390037-IR3). The collimated beam laser undergoes additional quality improvement process by employing a spatial filter consisting of 300 μm pinhole and two CaF\(_2\) plano-convex lenses (40 mm and 25 mm focal length, respectively). The purpose of the first lens is to focus the beam through the pinhole whereas the second one is used to direct the CW DFB-QCL beam through mR tubes and the gap of the QTF inside the ADM module.

To control the DFB-QCL temperature, set and perform modulation of the laser current, and acquire the QEPAS signal a 10” x10”x4” (LxWxH) custom made control electronics unit is used. The CO sensor is controlled by specifically designed LabVIEW based software, which is used for the acquisition and visual presentation of measured data on a laptop screen. For sensitive concentration measurements of atmospheric CO a 2f wavelength-modulation technique is employed when the laser current is scanned at 0.2 Hz. The total laser current tuning range necessary to scan across an atmospheric pressure broadened line of CO corresponds to ~70 mA (~0.4 cm\(^{-1}\)). For each acquired scan a laser current corresponding to a peak of the monitored CO line is recorded. This provides an opportunity to implement a control feedback loop that is responsible for eliminating any drift for the laser current. In this case a reference-cell and photodetector, which are essential when a gas sensor operates in a line-locking mode, become redundant. The CO concentration levels in outdoor air are monitored and determined by correlating the 2f WMS line shape profile for each acquired sample scan with the reference profile taken for a certified 5ppm CO:N\(_2\) mixture moisturized with 2.6% of water vapor (Fig. 2a). For this purpose a general least-square linear fitting algorithm, returning a fit coefficient as a result, is implemented. The addition of 2.6 % H\(_2\)O to the CO containing gas mixture helps to efficiently improve the energy transfer for the V-T states of a slowly relaxing CO molecules resulting in an ~8 times enhancement of the measured CO QEPAS signal when compared with the result obtained for a dry mixture. For the purpose of accurate measurements, software control of laser driving conditions is implemented to match current line profile to the reference, following its spectral displacement.

![Graph](image)

For a 5ppm CO:N\(_2\) calibrated mixture the calculated noise-equivalent (1σ) detection sensitivity is 4 ppbv at atmospheric pressure. An example of a continuous measurement of CO concentration levels in outdoor air for a 1 hour period is shown in Fig. 2b. Long term measurements for monitoring CO concentration levels in the atmosphere will be reported.

3. References