

humidifier. A commercial gas dilution system (EnviroNics, series 4040) and a certified mixture of 10 ppm NO in N₂ were used to produce the various NO concentrations levels. The NO dilution results acquired with a 1-s averaging time (0.785 Hz bandwidth) and 66 mW EC-QCL excitation power are plotted in Fig. 6(a) and Fig. 6(b). The phase of the detected signal was found to be independent of the NO concentration. The scatter of consecutive measurements at certain concentration levels also did not depend on the concentration and was in agreement with Eq. (1). Based on the data in Fig. 6(a) and (b), the NO concentration that results in a noise-equivalent (1 σ) concentration with a 1s averaging time is 4.9 ppbv. The corresponding absorption coefficient normalized to the detection bandwidth and optical power is $5.6 \times 10^{-9} \text{ cm}^{-1}\text{W}/\text{Hz}^{1/2}$. This minimum detection limit for NO is achieved as the result of the optimal mR design and the faster V-T relaxation rate induced by the presence of 2.5% water vapor. This result is only slightly higher than the value $3.3 \times 10^{-9} \text{ cm}^{-1}\text{W}/\text{Hz}^{1/2}$ measured for C₂H₂ detection using the NIR optimal mR tube size [6].

In order to verify the linearity for NO concentration measurement, all the readings of each concentration step are averaged and plotted in Fig. 6(c). This plot confirms the linearity of the system response to concentration. The dynamic range of the NO QEPAS sensor covers at least four orders of magnitude.

6. Conclusions

In summary, it was demonstrated that the QEPAS sensor design based on two acoustic mR tubes with wider internal diameters and shorter lengths as compared to optimum design for NIR lasers is optimal for MIR trace-gas detection using QCLs. Unlike the previous mR performance of a MIR QEPAS gas sensor reported in Ref [9], the 3.9 mm long mR tubes with an internal diameter of 0.84 mm eliminate the interference pattern superimposed on the QEPAS signal, resulting in a background-free thermal-noise-limited QEPAS $2f$ signal. Thus, background subtraction based on the averaging of spectral multi-scans can be avoided. Instead, the laser wavelength can be locked to the target absorption line center to monitor the trace gas concentration, which facilitates data processing as well improves the detection sensitivity. The NO detection limit of 4.9 ppbv with 1-s averaging time achieved so far is ~10 times better than the result reported in Ref [9] if the same laser power and averaging time are employed. The present minimum detection limit can be further improved if higher power CW, single frequency QCL devices become available or if the sensor application permits the use of longer signal averaging times. Furthermore, the use of CW distributed feedback (DFB) QCL sources will allow larger wavelength modulation ranges as compared to an EC-QCL, which can be beneficial at operating pressure of >160 Torr in the ADM. The presence of water vapor in the analyzed mixture can efficiently promote the NO V-T relaxation rate resulting in a stronger QEPAS signal. However, different water vapor concentrations lead to different sensitivities. Hence it is necessary to control and monitor the water concentration that is present in a NO QEPAS based sensor. The QEPAS sensor architecture when compared to other laser spectroscopic techniques potentially allows the conversion of a laboratory setup into a compact, portable device suitable for applications in environmental monitoring and medical diagnostics of human diseases based on exhaled breath analysis as well as in industrial processing.

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