

Detection of nitric oxide in air with a 5.2 μm distributed-feedback quantum cascade laser using quartz-enhanced photoacoustic spectroscopy

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Abstract: We demonstrate the detection of nitric oxide in both air and nitrogen atmospheres with a 5.2 μm distributed-feedback quantum cascade laser in a quartz-enhanced photoacoustic spectroscopy system. The photoacoustic signal generated by nitric oxide is shown to be several times larger in air than in nitrogen due to the faster vibrational-translational energy relaxation process induced by the presence of oxygen. A sensitivity of 2.5 parts-per-million by volume is achieved in air at atmospheric pressure.

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References and Links

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1. Introduction

High output power quantum cascade lasers (QCL) operating in the mid-infrared wavelength range are ideal sources for performing spectroscopy and sensing of trace gases. QCLs have been demonstrated across a wide wavelength range covering $\sim 3.7\text{--}20\ \mu\text{m}$ and coinciding with the absorption bands of many molecular species. Additionally, the development of quartz-enhanced photoacoustic spectroscopy (QEPAS) [1], allows the detection of trace gases with part-per-million concentration levels in sample volumes of the order of 1mm^3 . In a QEPAS system the photoacoustic signal is generated by the absorption of infra-red energy in the vibrational bands of a molecule followed by subsequent relaxation to translational energy of the host gas molecules through molecular collisions. The translational energy is then used to drive a low cost, high-Q quartz tuning fork resonator such as those typically used in electronic timing devices. The speed of this energy relaxation process, and hence the strength of the photoacoustic signal, is strongly dependent on the energy levels of the host gas in which the molecule of interest is dissolved. To date, the QEPAS technique has been demonstrated for several molecular species including ammonia, water vapor, carbon monoxide, carbon dioxide

and nitrous oxide (N_2O) [1]. QEPAS sensing of N_2O in air was significantly enhanced by the addition of 5% of SF_6 to promote the vibrational-translation (V-T) energy relaxation process [2] and allowed sensitivities of several parts-per-billion to be achieved.

The detection of nitric oxide (NO) is important in many applications such as atmospheric sensing and breath analysis for disease diagnosis. Detection of NO using QCLs with 500 ppb sensitivity has been reported in conventional photoacoustic spectroscopy systems using much larger sensing volumes than are used in QEPAS [3]. Recently, the detection of NO in a QEPAS system was demonstrated using an external-cavity QCL with a detection sensitivity of 15 parts-per-billion by volume [4]. This high sensitivity was achieved by a combination of several factors including operating at a low pressure of 250 Torr to enhance the Q-factor of the quartz tuning fork, by using a relatively long integrating time of 5 seconds and also detecting the NO in a hydrated nitrogen atmosphere. The presence of water vapor was used to enhance the V-T relaxation process and increase the photoacoustic signal compared to only a pure nitrogen atmosphere. For real world sensing applications such as detecting the presence of NO in air at atmospheric pressure, the role of other molecules, particularly oxygen, on the V-T relaxation process must also be considered. In this paper we describe the use of a $5.2\ \mu\text{m}$ distributed-feedback QCL in a QEPAS system to detect nitric oxide (NO) in both nitrogen and air hosts. The sensitivity of NO detection in air is approximately four times better than in pure nitrogen because of a faster V-T relaxation of the NO molecule in the presence of oxygen.

2. Experiment

The configuration of the QEPAS experiment is depicted in Fig. 1 and is similar to that described in [1]. The output of a single-transverse mode distributed-feedback QCL, similar to that described in [5], is collimated and then focused between the prongs of a quartz tuning fork with a nominal resonant frequency of $f_0 = 32.768\ \text{KHz}$. The exact resonance parameters of the tuning fork vary slightly with the temperature and pressure of the surrounding gas but for the experiments performed in this work at 1 atmosphere pressure and a temperature of 20°C the Q-factor of the tuning fork is typically ~ 2500 .

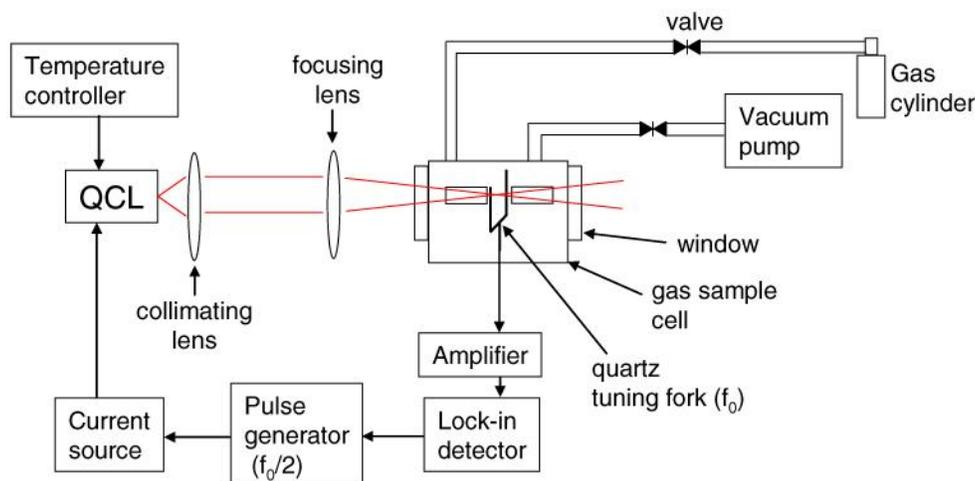


Fig. 1. Layout of QEPAS system.

The tuning fork is enclosed inside a gas cell with calcium fluoride windows to allow the mid-infra-red light to be coupled in and out. The gas cell is connected on one side to a vacuum pump and on the other side to a cylinder containing the gas mixture to be tested. The QCL is operated in a pulsed mode at a repetition rate of $f_0/2$ with an above threshold DC bias current of 300 mA, a peak current of 350 mA and a pulsewidth of 1 μsec . A lock-in amplifier is used to detect the in-phase and quadrature components of the tuning fork response at f_0

with an averaging time of 1 second. The temperature of the QCL is controlled by a thermo-electric cooler (TEC). The operating wavelength of the QCL is tuned through the absorption lines of the NO molecule by adjusting the temperature with a tuning rate of $-0.135 \text{ cm}^{-1}/\text{K}$. In each experiment the temperature of the QCL was varied between 20 and 35°C corresponding to a tuning range of approximately 1913.40 cm^{-1} to 1911.34 cm^{-1} . Over this temperature range the output power of the QCL varies from 32 mW down to 20 mW

3. Results

Figure 2 plots the amplitude and phase of the tuning fork oscillation as a function of the QCL temperature with various gas mixtures present in the cell. With only air present in the cell at atmospheric pressure, no significant features are observed in the amplitude and phase response of the tuning fork. Next, a mixture comprising 100 ppm NO in a nitrogen atmosphere was introduced to the gas cell and the experiment repeated. Two peaks due to NO appear at QCL temperatures of 26.6 and 31.9°C corresponding to NO($v = 0-1$) absorption features at 1912.79 cm^{-1} and 1912.07 cm^{-1} respectively [6].

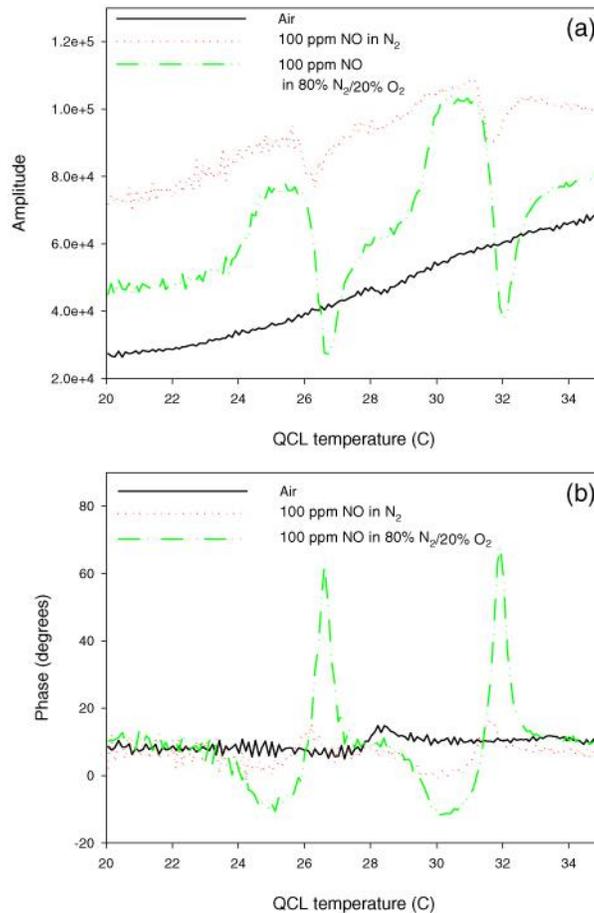


Fig. 2. (a) Amplitude and (b) Phase of tuning fork response to photoacoustic signal.

The relative magnitudes of the photoacoustic signal and noise level suggest a sensitivity for NO detection of approximately 10 ppm. A further experiment was performed with 100 ppm NO in a host mixture of 80% N_2 and 20% O_2 to simulate NO sensing in air. In this case the same two NO lines are observed but the QEPAS sensor showed a response almost four times larger than for the case of only an N_2 host thus increasing the sensitivity to

approximately 2.5 ppm. In spite of the decrease in QCL output power as the temperature increases, a larger photoacoustic response is observed for the 1912.07 cm⁻¹ absorption line because it has almost twice the absorption of the 1912.79 cm⁻¹ line [6]. It should be noted that in Fig. 2a there is a difference in the non-resonant background level of the tuning fork response away from the absorption lines. The traces in Fig. 2a were recorded several days apart and it is thought that the changes in non-resonant background are due to slight differences in experimental conditions such as temperature or relative humidity, especially since there is a strong OH absorption line close by at 1910 cm⁻¹. No attempt was made to subtract this background signal from the experimentally recorded data as it does not affect the basic conclusion of this paper in anyway.

The explanation for the observed results appears to be the rate at which the vibrational energy excited in the NO molecules is quenched by the N₂ and O₂ molecules in the surrounding gas. It has been shown that the quenching rate of NO (v = 1) to N₂ is 1.7x10⁻¹⁶ cm³s⁻¹ while for NO(v = 1) to O₂ it is 2.4x10⁻¹⁴ cm³s⁻¹ [7]. The total decay rate for vibrational energy of NO(v = 1) in a mixture of nitrogen and oxygen is therefore given by

$$k(x) = n[1.7 \times 10^{-16}(1-x) + 2.4 \times 10^{-14}x] \quad (1)$$

where n is the molecular density (n = 2.5x10¹⁹ cm⁻³ at atmospheric pressure) and x is the fractional concentration of oxygen (0 ≤ x ≤ 1). For NO in a pure N₂ host Eq. (1) gives a quenching lifetime, τ(x) = 1/k(x), of 240 μsec which is significantly longer than the 30.5 μsec resonant period of the quartz tuning fork used in these experiments. Therefore only a small fraction of the vibrational energy is quenched in one oscillation period of the tuning fork and only a weak photoacoustic signal is generated. For NO in air (80% N₂/20% O₂) the quenching lifetime is reduced to only 8.5 μsec which is sufficient to allow almost complete quenching of the NO vibrational energy and generate a much stronger QEPAS signal.

We can model the decay of the vibrational energy in the NO molecules between successive optical pulses with the following exponential function:

$$f(t, x) = Ae^{-k(x)t}, 0 \leq t \leq \frac{2}{f_0}, f(t + \frac{2N}{f_0}, x) = f(t, x) \quad (2)$$

where N is an integer and A an arbitrary constant. The relative magnitude of the QEPAS signal as the O₂ concentration is changed can be estimated by taking the Fourier transform of f(t,x) in Eq. (2) and finding the amplitude of the component driving the tuning fork at frequency f₀ = 32.768 KHz. The calculated amplitude at f₀ as a function of oxygen concentration is plotted in Fig. 3 normalized to the value with no O₂ present.

The value of the amplitude for an 80% N₂/20% O₂ mixture is 3.75 times higher than that calculated for NO in a nitrogen only atmosphere. This is in excellent agreement with the observed increase in signal amplitude presented in Fig. 2a. The phase of the Fourier component at f₀ is also calculated to shift by 30 degrees for the 80%N₂/20%O₂ mixture relative to the nitrogen only host. This is in qualitative agreement with Fig. 2b where the phase of the tuning fork response shows a significant change with the addition of oxygen. Figure 3 also demonstrates that there is an optimum value for the oxygen concentration, equal to 0.10, which maximizes the photoacoustic signal for the particular resonant frequency of the tuning fork used in these experiments. As the oxygen concentration is increased beyond this point the faster decay of the vibrational energy reduces the amplitude of the Fourier component of f₀.

From this analysis it is clear that QEPAS based sensing of NO can be optimized by appropriately choosing the resonant frequency of the tuning fork to match the decay rate of the NO molecules if the host gas mixture is known. For example, if air is the host medium a resonant frequency close to 65 KHz would be optimum. Alternatively, if NO is being sensed in a low O₂ atmosphere then the QEPAS response could be enhanced by the addition of an appropriate amount of oxygen gas to the gas cell.

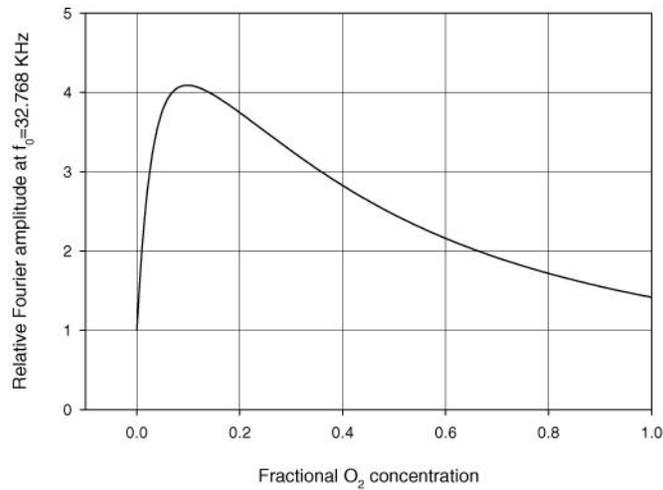


Fig. 3. Fourier amplitude of f_0 component of NO relaxation as a function of oxygen concentration

4. Conclusion

In conclusion, we have demonstrated the use of quartz enhanced photoacoustic spectroscopy for the detection of nitric oxide molecules in both air and nitrogen atmospheres. The sensitivity in air is approximately four times better than in pure nitrogen because of the faster rate of vibrational-translational energy relaxation of NO in the presence of oxygen. The NO detection sensitivity is approximately 2.5 parts-per-million by volume.

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