Photoacoustic investigation of QCL modulation techniques

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Abstract. High detection sensitivity and spectral selectivity is important for gas analysers to identify the measured compound and to detect low concentrations. We investigated three different modulation methods – pulse gate modulation, pulse frequency modulation and chopper modulation – for a new pulsed quantum cascade laser based photoacoustic sensor. The spectral selectivity and the detection limit for the three modulation methods are compared by measuring nitric oxide absorption lines and different concentrations. The highest detection sensitivity of 70 ppb was achieved with pulse gate modulation but at the lowest spectral resolution. The highest spectral resolution was achieved with chopper modulation but at the lowest detection sensitivity. It is demonstrated that for the three modulation methods a compromise has to be made between selectivity and sensitivity for each measuring task.

1. Introduction
Photoacoustics (PA), as many other spectroscopic methods, requires a modulated operation of the radiation source. The most common method to modulate a radiation source is a rotating chopper wheel. This method is preferred for broadband sources and gas lasers, but can be applied with any radiation source. Continuous wave semiconductor lasers can usually be modulated by modulating the injection current. For pulsed semiconductor lasers the pulses can be gated or the pulse frequency can be changed periodically.

The modulation method, however, has a considerable influence on detection selectivity and sensitivity of the spectroscopic system and the influence is varying for different radiation sources. The radiation source used in this study is a quantum cascade laser (QCL). This semiconductor laser covers the wavelengths range from 3 to 300 µm. This range is of great interest for spectroscopic gas detection because it covers the strong fundamental rotational-vibrational absorption lines of most relevant gases. The two lasers used in this study are pulsed single mode distributed feedback QCLs. With their wavelengths of 5.27 µm and 5.23 µm they cover the strong absorption lines of nitric oxide (NO). NO is an important environmental gas. It is generated as product of incomplete combustion and is involved in ozone generation. In the field of medical diagnosis NO is an important biomarker. It can serve as diagnostic tool because of its elevated concentration in breath samples of asthma patients.

In this article we compare three modulation methods – a rotating chopper wheel and two electronic modulation techniques – according to the achieved spectral selectivity and detection limit for our QCL based photoacoustic system. The aim is to reach the highest detection limit with an appropriate selectivity.
2. Photoacoustic detector

Like all spectroscopic systems, photoacoustic spectroscopy uses a radiation source to transfer molecules into a higher energetic level by absorbing electromagnetic energy. Most of this excitation energy will be transferred into kinetic energy of the surrounding molecules via inelastic collisions. This causes a local pressure increase in the absorbing gas. If the radiation source is modulated a sound wave with the frequency of the modulation is generated. This sound wave can be detected with a microphone and measured phase-sensitively with a lock-in amplifier. The sensitivity of the PA system can be considerably improved by taking advantage of acoustical resonances of the sample cell. Modulating the radiation source equivalent to an acoustical eigenfrequency of the cell enables an enormous enhancement of the signal.

2.1. Experimental setup and modulation methods

The experimental setup depicted in Figure 1a shows the photoacoustic cell with a 60mm cylindrical resonance tube and buffer volumes at both ends. This so called H-cell has the first longitudinal mode at about 2.8 kHz [1]. An electret microphone detects the photoacoustic signal which is amplified and then phase sensitively measured with a lock-in amplifier. The PC is used to control the temperature of the QCL and for data acquisition.

The different methods of modulating the pulsed laser are demonstrated in Figure 1b. The two electronical methods use the lock-in oscillator as modulator and as frequency reference. For pulse gate modulation, the high-frequency pulses are generated only during the positive half wave. For pulse frequency modulation the repetition frequency increases during the increasing period and decreases during the decreasing period of the lock-in signal. For chopper modulation the pulses are generated continuously and are blocked through the rotating chopper wheel. The frequency of the chopper is measured with a photo detector and is used as reference frequency for the lock-in amplifier.

![Figure 1](image)

**Figure 1.** (a) Experimental setup and measured response around the first longitudinal mode of the photoacoustic cell. (b) Modulation techniques for the pulsed QCL.

2.2. QCLs

The lasers used in this study are pulsed DFB-QCLs operating at or near room temperature. The wavelength of their single-mode emission can continuously be tuned via their operational temperature with a tuning rate of (0.40±0.05) nm/°C. With their wavelengths of 5.27 µm and 5.23 µm they cover the strong fundamental absorption lines of NO. The QCL specifications can be found in Table1.
DFB Single-Mode SMSR > 30 db
Spectral Tuning 0.4 nm/°C
Pulse Length < 100 ns (duty cycle 2% max.)
Wavelength Range 5.267 µm to 5.275 µm 5.225 µm to 5.233 µm
Output Power (peak) 10 mW @ -10°C 12 mW @ 30°C
Temperature -30°C to -10°C 15°C to 35°C

Table 1. QCL Specifications

3. Results

3.1. Spectral selectivity
To determine the spectral selectivity for the three different modulation techniques a calibrated gas mixture of 100 ppm NO in nitrogen was used. For pulse gate and chopper modulation the lasers were operated with a constant duty cycle of 1.5%. For pulse frequency modulation the duty cycle reaches 1.5% at the highest repetition frequency. The spectra of the calibrated NO mixture were recorded by sweeping the wavelength of the lasers with their operating temperature. The measurements are performed with different pulse lengths for the QCLs and Figure 2a depicts exemplary some measured NO spectra recorded with laser 1 and pulse gate modulation. Figure 2a also shows the calculated HITRAN absorption spectrum of 100 ppm NO in N₂ at 293 K and 1013 hPa [2]. The linewidth of the laser was calculated by using the HITRAN spectrum and the measured NO spectra [3]. Figure 2b demonstrates the calculated spectral laser linewidth as function of the pulse length for the three different modulation methods. The narrowest linewidth has been achieved with chopper modulation. For pulse frequency modulation the linewidth is slightly larger and for pulse gate modulation the linewidth is the largest. This is reasonable, because for pulse gate and pulse frequency modulation the changing repetition frequency and the gate switching of the laser pulses, respectively, cause an additional shift of the laser temperature. This results in an additional broadening of the laser linewidth [3].

Figure 2. (a) Exemplary PA spectra for different pulse lengths recorded with pulse gate modulation. (b) Calculated laser linewidth as function of pulse length for three different modulation techniques.

3.2. Detection sensitivity
To determine the detection sensitivity for the three modulation methods the wavelengths of the lasers were tuned to the stronger NO absorption peak and then held constant. The wavelength of the stronger absorption peak is 5.2715 µm for laser 1 shown in Figure 2a and 5.2299 µm for laser 2. Concentrations of NO between 1 ppm and 20 ppm were prepared by using the 100 ppm calibrated...
mixture and a gas blending system. The measurements were performed with the gas flowing through the cell to avoid wall adsorption of the polar NO molecules. The flow rate was set to 100 ml/min to avoid turbulent noise. Figure 3 shows the dependency of the PA signal on the NO concentration for all three methods.

![Figure 3](image)

**Figure 3.** Dilution series for the three modulation methods and calculated detection limit for both lasers. (a) pulse gate modulation (b) pulse frequency modulation (c) chopper modulation

The sensitivity for all methods is calculated with a signal to noise ratio of 1 after subtracting the offset measured with nitrogen. The offset was subtracted from the 1 ppm signal for pulse gate and pulse frequency modulation and from the 5 ppm signal for chopper modulation, respectively. The highest sensitivity was achieved with pulse gate modulation. This is reasonable because the duty cycle for pulse gate modulation is constant at 1.5% for the whole positive period of the lock-in oscillator. For pulse frequency modulation the duty cycle of 1.5% is available only for a short time at the highest repetition frequency. Thus, the average power for pulse gate modulation is higher than for frequency modulation. Chopper modulation is not usable for our setup because the rotating wheel produces a lot of coherent noise at a chopping frequency of 2.8 kHz.

4. Conclusion

We investigated three different modulation methods for a pulsed QCL based photoacoustic detector and compared them according to spectral selectivity and detection limit. It has been shown that the highest spectral resolution is achieved with chopper modulation but also that the detection limit is very low because of coherent noise of the rotating chopper wheel. The spectral resolution for frequency modulation is slightly lower and the detection limit was calculated as 105 ppb (laser 1). The highest detection limit of 70 ppb (laser 1) was achieved with pulse gate modulation but at the lowest spectral resolution. If high detection sensitivity is needed and the spectral resolution with pulse gate modulation is sufficient for the measuring task, this will be the best modulation technique.

References

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