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Low power quantum-cascade laser photoacoustic spectrometer for trace-gas monitoring

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The development of a novel type of highly sensitive multipass resonant PA cell for trace-gas detection enables the use of new compact low-power laser sources such as quantum-cascade lasers (QCLs) because the effective power present in the cell is increased by a factor of ~ 20 compared to a one-pass arrangement. Based on an existent mobile CO_2-laser photoacoustic (PA) spectrometer we implemented additionally a pulsed QCL with a tunable emission wavelength between 981.5 cm^{-1} and 983.5 cm^{-1} working near room temperature as pump source. Its average power is ≤ 1.7 mW and the laser-line width is < 0.2 cm^{-1}. With reference to HITRAN data a minimum measurable absorption coefficient $\alpha_{min} = 2.2\times10^{-5}cm^{-1}$ corresponding to a minimum measurable line intensity $S_{min} = 2.5\times10^{-25}$ $cm^{-1}/(molecule\cdot cm^{-2})$ is achieved even at the low QCL power. First measurements are presented to characterize the performance of our QCL based system.

Experimental

In previous work we reported on the implementation of a mobile CO_2-laser based photoacoustic (PA) spectrometer and its successful application for *in-situ* multicomponent monitoring of trace gases in different environments [1]. Recently we have developed a novel type of multipass resonant PA cell to further increase the detection sensitivity of the system [2]. This highly sensitive PA sensor is particularly attractive in combination with new compact low-power lasers such as quantum-cascade lasers (QCLs) [3-5] as pump sources.

Figure 1 shows a schematic diagram of the mobile experimental set-up. As light source we use either a line-tuneable sealed-off $^{12}C^{16}O_2$- or $^{13}C^{16}O_2$-laser with an active power stabilisation based on a Piezo-driven outcoupling mirror or, alternatively, a QCL.

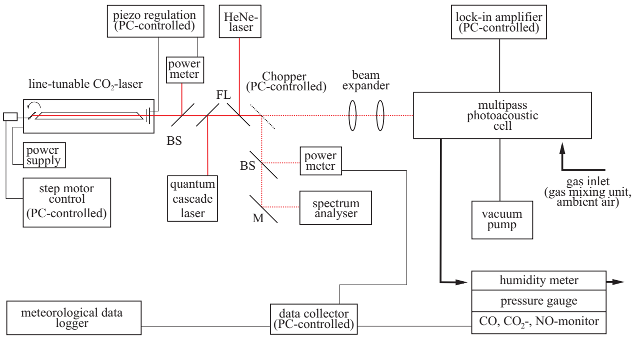
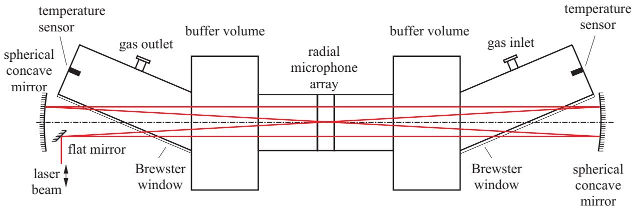


Fig. 1: Experimental set-up of the laser photoacoustic spectrometer (BS – beam splitter, FL – flipper mirror, M – mirror)

The pulsed QCL used in our study is operated near room temperature. The emission wavelength is varied by changing the temperature (controlled by a Peltier cooler). The coefficient for the laser wavelength tuning is -0.06 cm^{-1}/K in the temperature region between -5 and -40°C (resulting in a tuning range of ≈ 3 cm^{-1}). The average power coupled into the cell is ≤ 1.7 mW and the laser-line width is < 0.2 cm^{-1}. The QCL operates at a duty cycle of < 4% with a pulse duration around 30 ns.

The optical adjustment of the system and particularly of the PA cell can be checked with the visible beam of a HeNe-laser coupled into the optical path via a flipper mirror. The wavelength of the different CO_2-laser emission lines can be checked by a spectrometer. After expanding the laser beam by a telescope it is coupled into the photoacoustic (PA) cell. Additionally to the PA amplitude and phase we measure further data (such as CO-, NO-, CO_2-concentration, humidity, wind velocity, wind direction, solar radiation, different system temperatures ...) as depicted in Fig. 1. Measurements are done without any pre-concentration or pre-treatment of the gas.

Figure 2 illustrates the set-up of the resonant multipass PA cell, basically consisting of two parts: A resonant PA cell [6,7] is integrated into a Herriott-multipass arrangement [8,9] with 36 passes (extendable to up to 78 passes) resulting in an optical path length of 24 m. In the centre of the cell a microphone array (with 16 microphones) is implemented for detection of the first longitudinal resonant acoustic mode at 1250 Hz. The cell with a volume of 2.3 l is designed for stop-flow and flow-mode operation (up to 2 litres/min). To reduce acoustic noise, caused by the gas flow and window heating signals from the ZnSe-Brewster windows, two buffer volumes adjacent to the resonator are attached.



dimensions:

	length:	diameter:
cell overall	700 mm	140 mm
PA resonator	120 mm	50 mm
buffer volume	60 mm	120 mm
total optical path length	23680 mm	
path length within the PA part	15100 mm	

number of microphones:	16
number of beam passes:	36
curvature radius of the mirrors:	1000 mm

Fig. 2: Multipass photoacoustic cell with Herriott cell, photoacoustic resonator and cylindrical microphone array.

Optical multipass arrangement of the PA cell

As a result of the optical multipass arrangement a η-times higher laser power is available inside the cell for the generation of the PA signal than in a usual one-pass arrangement. Figure 3 shows the calculated power enhancement factor η versus the number of beam passes taking into account transmission and reflection losses.

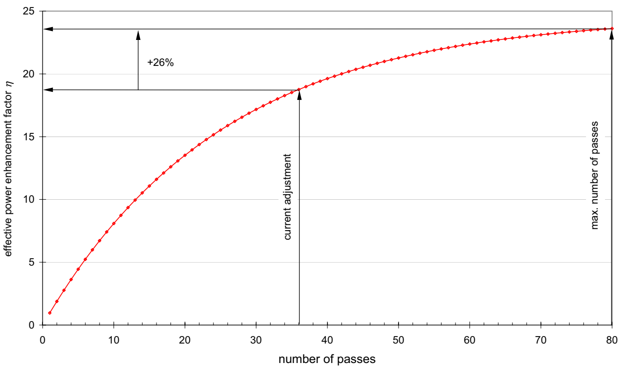


Fig. 3: Calculated effective power enhancement factor η in dependence of the number of beam passes in the Herriott cell

In general the PA signal is proportional to the absorbed laser power, i.e. to both the incident power and the absorption coefficient $\alpha(\tilde{\nu})$ of the absorbing gas. This is one important fact that enables the use of new low-power lasers as pump sources.

Non-linear dependence of the PA signal on gas concentration

At high trace-gas concentrations the radiation absorption by the gas is not neglectable any more for the calculation of the power enhancement factor η introduced above. The consequence is a non-linear dependence of the PA signal on the gas absorption coefficient $\alpha(\tilde{\nu})$ as depicted in Figure 4. Using low-power pump sources like QCLs implies small PA signals. Hence, only higher gas concentrations (assuming a comparable PA signal amplitude and identical absorption coefficient) are measurable in comparison to the CO_2-laser based system.

However, the manufacturing process of the QCls permits the tailoring of the emission wavelength which can thus be adapted to the maximum absorption of the gas.

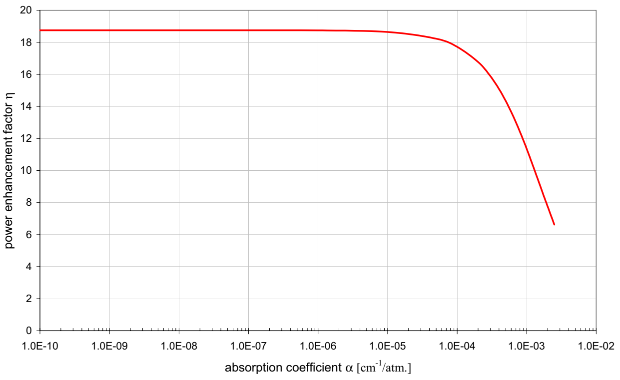


Fig. 4: Calculated effective power enhancement factor versus the gas absorption coefficient $\alpha(\tilde{\nu})$

Measurements and results

The spectral tuning range of our system with a QCL as pump source is demonstrated by a photoacoustic spectrum taken of pure CO_2 at atmospheric pressure and room temperature in the wavelength region around 982 cm^{-1}. The 10R(30) and 10R(32) absorption lines of CO_2 are clearly resolved as illustrated in Figure 5. The rather small PA signal is due to the non-linear dependence at high gas concentrations as discussed above.

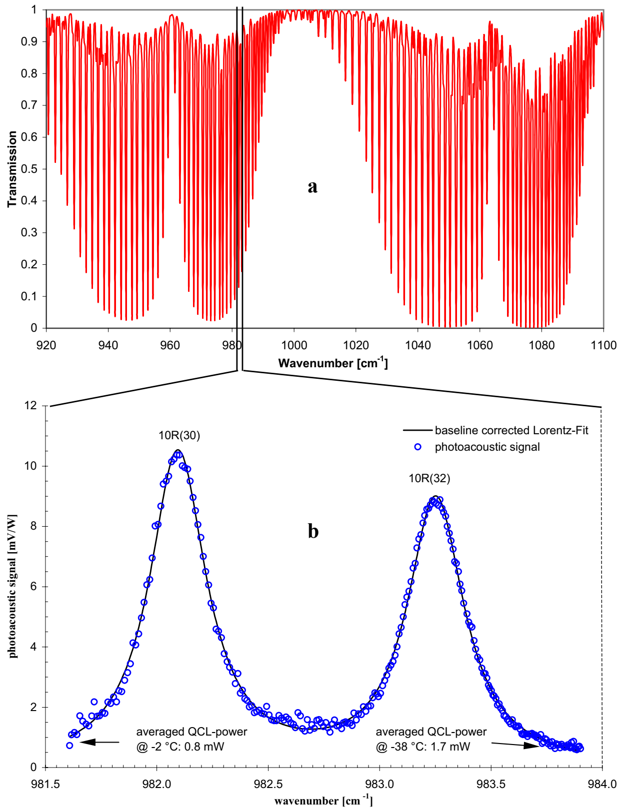


Fig. 5 **a:** Calculated CO_2 transmission spectrum (15 m path length = optical path length within the PA part of our cell, 1 bar, room temperature, HITRAN database [10])

b: Photoacoustic spectrum near 982 cm^{-1} of two CO_2-absorption lines, recorded with a quantum cascade laser as pump source.

Figure 6 shows measurements on methanol vapor (CH_3OH) buffered in synthetic air (80% N_2, 20% O_2) at 1 bar and room temperature. The FTIR spectrum of 500 ppmV CH_3OH between 980 and 1080 cm^{-1} is plotted as overview (Fig. 6a) whereas Fig. 6b shows a detailed view with a spectral resolution of 0.2 cm^{-1} between 981 and 983.5 cm^{-1}. This spectrum can be compared with the QCL-PA spectrum of 100 ppmV CH_3OH vapor (Fig. 6c). As depicted in part a, the emission wavelength of the QCL isn't adapted to the maximum absorption of methanol which occurs at 1033 cm^{-1}. However, it can be measured with a signal-to-noise ratio (*SNR*) ≈ 5 at 983.5 cm^{-1}. The noise decrease with increasing wavenumber is explained by the increasing laser power.

These measurements imply a detection limit (with SNR=3) for methanol of 60 ppmV at this spectral position. (Using a QCL with an emission wavelength around 1033 cm^{-1} and similar power we estimate a detection limit of 5ppmV.)

The detection limit and the minimum measurable absorption coefficient α_{min} of the QCL-PA system can be determined either from the CO_2 - or the methanol measurement:

With reference to HITRAN CO_2 data, $\alpha_{min} = 2.2\times10^{-5}cm^{-1}$, corresponding to a minimum measurable line intensity $S_{min}=2.5\times10^{-25}cm^{-1}/(molecule\cdot cm^{-2})$, is achieved even at the low QCL average power of ≤1.7 mW.

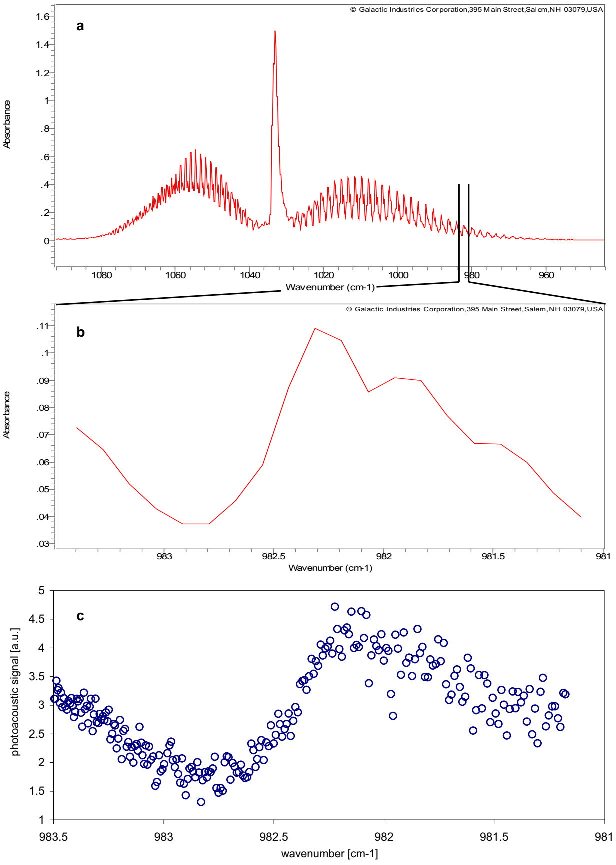


Fig. 6 **a:** FTIR spectrum of 500 ppmV methanol (CH_3OH) buffered in synthetic air at 1 bar and 300 K (path length 3 m) [11]

b: enlarged part of a: in the wavenumber region 981 – 983.5 cm^{-1}

c: PA spectrum of 100 ppmV methanol buffered in synt. air at 1 bar and 300 K measured with our QCL-PA system in the wavenumber region 981 – 983.5 cm^{-1}

Comparison between the CO_2 - and the quantum-cascade-laser as pump source

The deployment of the described pulsed QCL as pump source results in a minimum measurable absorption coefficient

$$\alpha_{min\,(QCL)} = 2.2\times10^{-5}cm^{-1}\ (SNR=3).$$

With a line-tunable continuous wave CO_2-laser as pump source sub-ppbV (< 10^{-9} per volume)-concentrations can be measured with laser powers of a few Watts [2], corresponding to

$$\alpha_{min(CO_2)} = 2\times10^{-9}cm^{-1}\ (SNR=3).$$

In comparison to discretely tunable CO_2 lasers QCLs offer some advantages: Ideally, the wavelength of QCLs can be tuned to individual molecular absorption lines thereby reducing absorption interferences in multicomponent mixtures that sometimes limit the detection selectivity of the system when operated with a discretely tunable laser. Furthermore, absorption lines of other gases can be recorded in wavelength regions not accessible with CO_2 -laser lines. And finally, the dimensions and costs of the system can be reduced substantially. The present limitations of QCLs in laser spectrometers are the rather broad line width, the low power and the limited wavelength availability.

By using a QCL with similar output power but other emission wavelength (within the atmospheric windows around 4 and 10 µm where the CO_2 - and H_2O absorption is negligible) other gases such as CO, NO, N_2O, CH_4 or NH_3 could be monitored with our current system. Up to now, different QCLs with wavelengths around 4.6 µm, 5.2 µm, 7.9 µm, 9.4 µm and 10.2 µm are available [3-5], but most of them operate at temperatures below 80 K which aren't reachable with a simple Peltier-cooling system as used in our mobile spectrometer.

Since our system is optimized for continuous wave lasers as pump sources the acoustic resonance frequency of the cell isn't adapted to the pulse repetition frequency of the QCL. This results in a correspondingly lower PA signal. Our first QCL-PA measurements could thus not take full advantage of the acoustic resonance enhancement.

Acknowledgement

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