PHOTOACOUSTIC GAS SPECTROSCOPY USING TUNABLE LIGHT GENERATORS

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The performance of phototoacoustic gas registration using a broad-band optical parametric oscillator (OPO) was tested. The OPO was capable of generating tunable pulses of about 7 ns duration and about 5 cm^{-1} spectral bandwidth in the 0.72–1.9 μm range (idler), thus covering overtones of stretching vibrations and combination vibrations of the hydrogen atom of the analyte molecules. A nonresonant one microphone acoustic registration scheme was employed. The measured phototoacoustic spectra of water vapour and methane conform with absorption spectra calculated with the aid of HITRAN database. For the 1.361 μm absorption line, the 4.3 ppmv detection threshold was evaluated for ambient water vapour (ppmv is 1 part in 10^6 by volume).

Keywords: photoacoustic gas spectroscopy, pulsed near-infrared optical parametric oscillator, HITRAN data base

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1. Introduction

Control of gas species is of environmental, industrial, and safety importance. Besides the nondispersive infrared technique, correlation spectrometers, and dispersive systems for spectral gas analysis, laser-based analysis techniques find their gas analysis niche. Due to the recent improvements in all-solid-state tunable lasers, quantum cascade lasers, and optical parametric oscillators (OPOs) various laser systems are at the threshold of routine applications in environmental monitoring and industrial process gas analysis. As the number of substances to be measured increases continuously, multicomponent laser analysers allowing the simultaneous measurement of different gases or pollutants are required because such systems will be more cost effective and flexible than systems based on individual analysers.

The optical techniques widely used in gas detection are absorption spectroscopy [1, 2], cavity ring down spectroscopy [3], and photoacoustic spectroscopy [4–6]. The lasers are usually operated in the continuous-wave single-frequency mode. The advantages of using these high-resolution continuous-wave lasers are their selectivity and high sensitivity. However, under typical atmospheric conditions the pressure-broadened linewidth of detected gases is in the range of a few tenths of cm^{-1}. Under atmospheric conditions the pressure-broadened linewidth of gases reduces the significance of the narrow line width of single-mode lasers. Instead, an optical parametric oscillator capable of producing several millijoules of infrared pulse energy is more suitable for excitation of ambient gas species. For the high volume laser gas sensing business it is necessary to test the sensing performance with simple laser schemes producing spectrally broader pulses than the width of gas absorption lines. Characteristics of photoacoustic gas detection using the broad-band pulsed near-infrared OPO were tested in this work.

2. Experimental set-up

A scheme of the experimental set-up is shown in Fig. 1. Our tunable laser source was an optical parametric oscillator PG122 (EKSPLA) pumped by the third harmonic of the Nd:YAG laser. The OPO generates pulses at the 10 Hz repetition rate at almost any frequency in the 0.42–0.71 μm spectral range (signal) and 0.72–1.9 μm (idler) with pulse energies at the 2 mJ level in the idler branch. The spectral bandwidth of the source and duration are about 5 cm^{-1} and about 7 ns, respectively.

The photoacoustic cell is of nonresonant type made of a massive aluminum body. An acoustic working
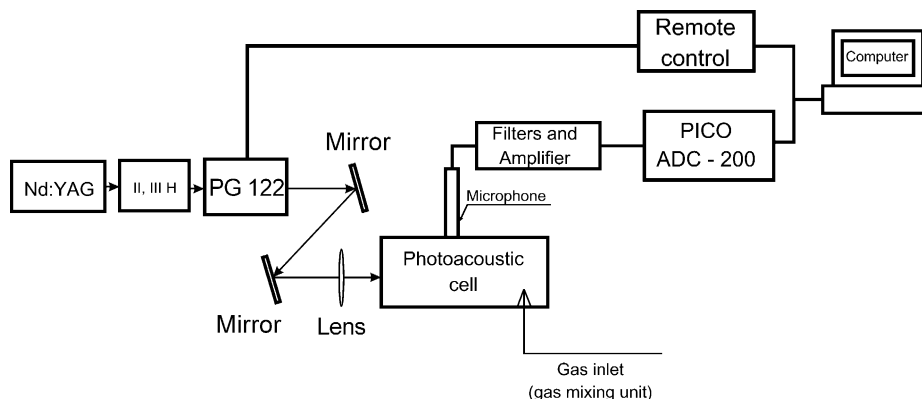
Fig. 1. The block scheme of the experimental set-up.

chamber has a length of 45 mm and an inner diameter of 3 mm with two larger buffer volumes with the 15 mm diameter and the 30 mm length. Buffer volumes are arranged coaxially with the working chamber at its end. A capacitor type microphone (Bruel & Kjear 4176) is mounted flush into the chamber side wall. The laser beam enters and leaves the cell through glass windows mounted at the Brewster angle to avoid back-reflections into the cell. The laser beam is focused into the photoacoustic cell by using a glass lens with the $f = 20$ cm focal length.

The frequency-filtered (the lower cut-off frequency is 100 Hz) and amplified photoacoustic signal was measured with the aid of an ADC-200 oscilloscope (PicoTechnologies) and stored in a PC. Laser driving and data acquisition were realized by the LabView programming language (National Instruments).

3. Gas photoacoustic spectra and analyte detection thresholds

The photoacoustic effect is based on the detection of acoustic waves arising from the absorption of laser pulse energy by the analyte molecules. Part of the absorbed energy turns into translational energy (heat) by the collisional exchange with unexcited molecules. A quick local temperature increase causes a subsequent quick pressure increase in the acoustic chamber. The pressure increase discharges itself into buffer chambers by acoustic waves which are registered as a microphone signal like that shown in Fig. 2. To avoid the large acoustic signal of the laser lamp discharge and improve the signal-to-noise ratio the delayed and gated acoustic signal registration was employed. The first positive acoustic oscillation lobe was stored and averaged. The temporal position of the registration gates is shown in Fig. 2 by vertical dotted lines.
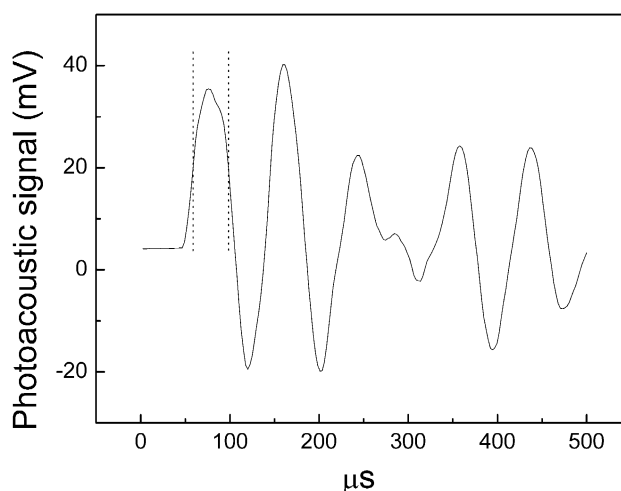

Fig. 2. Joint gas cell and microphone temporal response to absorption of the 7 ns duration pulse. Vertical dotted lines mark the position of the registration gates.

One cubic centimetre of natural gas containing about 80% of methane was injected into the cell for the primary test. Before analyte injection, the cell was flushed down with dry nitrogen to remove residuals of the former analyte molecules and molecules of ambient air (carbon dioxide and water vapour are infrared active ambient molecules). OPO was scanned in the 1620–1720 nm range in 0.5 nm steps thus covering the methane stretch overtone band centred at 1666 nm. The signal was averaged over 10 laser shots at every scan step. The narrow unresolved rotational Q branch as well as resolved rotational structure of the P and R branches of methane can be seen in Fig. 3.

The measured photoacoutic spectrum was compared to the simulated methane 1620–1720 nm range absorption spectrum recovered from the HITRAN database [7]. The calculated absorption spectrum consists of a huge number of narrow spectral lines. On the other hand, measured peaks have the spectral width of about
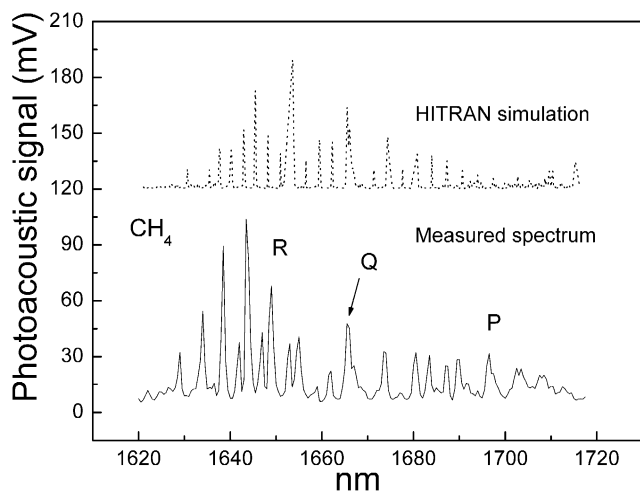
Fig. 3. The measured photoacoustic spectrum and the simulated absorption spectrum of methane. The simulated spectrum is rescaled and offset for clarity.
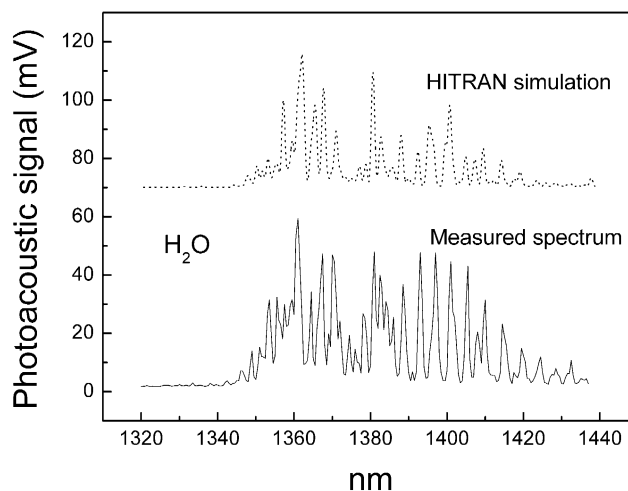

Fig. 4. Measured photoacoustic and simulated absorption spectra of the ambient air water vapour. Room temperature is 15 °C and the relative humidity is 50%. Rescale and offset of the simulated spectrum are done as in Fig. 3.

1.5 nm because of a wide OPO band. For compatibility of the calculated and measured spectrum, the theoretical spectrum was integrated with the 3 nm base triangle convolution function, which approximately represents the 1.5 nm half-width of the exciting pulse. The convoluted theoretical spectrum shown in Fig. 3 by dotted line qualitatively conforms to the measured spectrum. The peak positions coincide, more or less, whereas peak heights of some peaks differ significantly. The discrepancy of spectra may be caused by luminescence of laser-excited molecules. The luminescence is the energy relaxation channel which contributes to gas heating indirectly and with low efficiency, therefore, from the point of view of the photoacoustic effect luminescence is wasted energy. As a rule, the luminescence efficiency is not proportional to the absorption line strength (or to the peak height of simulated spectra in Fig. 3), therefore, heights of simulated absorption and measured photoacoustic peaks differ.

The cell content tends to equilibrium with ambient air due to the molecular diffusion through the open gas inlet and outlet tubing. The photoacoustic ambient air spectrum one hour after the dry nitrogen flush is shown in Fig. 4. The spectrum is recorded over the 1320–1440 nm spectral range in 0.5 nm steps by averaging over 10 laser shots at each step. Water vapour molecules are the main analyte responsible for absorption. The absorption spectrum of H_2O molecules recovered from the HITRAN database is shown by dotted line in the same figure. As for the CH_4 spectrum, the theoretical spectrum of water molecules was integrated with the 3 nm base triangle function. The peak positions of the calculated absorption spectrum coin-

cide with the spectral position of photoacoustic peaks, whereas measured and calculated peak heights differ as in the case with methane.

When the laser beam was blocked, a 0.52 ± 0.03 mV electric signal was measured. 0.52 mV is the value of the electric and acoustic signal related to the pump laser lamp discharge. Only the tail of a discharge pulse contributes to the gated registration signal. This signal is reproducible and stable over a few-hour duration of the experiment. $N = 0.03$ mV is the real registration noise value which characterizes the equivalent lowest possible acoustic signal which can be detected by the present experimental scheme. The photoacoustic signal S is a linear function of analyte concentration, therefore, the ratio of signals is equal to the ratio of concentrations:

$$\frac{S}{N} = \frac{C_0}{C_{th}}. \tag{1}$$

Here C_0 is the analyte reference concentration for which the photoacoustic signal is registered and C_{th} is the threshold concentration of the same analyte. The formula for the threshold concentration follows from Eq. (1):

$$C_{th} = \frac{C_0 N}{S}. \tag{2}$$

For the proper detection threshold determination the concentration and signal values should exceed those of the threshold by a few orders of magnitude at least.

The water vapour detection threshold can be obtained for the 1361 nm line which has the largest ab-

sorption and photoacoustic signal over the scanned overtone band. The analyte reference concentration C_0 is water vapour partial pressure. At the $15\,^{\circ}$C room temperature and 50% relative humidity the concentration amounts to 8300 ppmv (ppmv is 1 part in 10^6 by volume). The signal S at the 1361 nm peak is 59 mV, thus a 4.3 ppmv detection threshold calculated by the above formula is achieved.

The acoustic signal can be amplified by tuning the modulation frequency to the acoustic resonance of the cell. In this case the cell acts as an acoustic amplifier, and the acoustic signal is amplified by the factor from ten to thousand. Additional advance in the detection threshold reduction can be gained employing the two-microphone differential acoustic signal registration. The difference acoustic scheme effectively eliminates the background noise. Thus in the near infrared range, a 0.2 ppmv detection threshold of ammonia is attained by using a differential acoustic resonator [8]. Bearing in mind these possible acoustic registration improvements, the 4.3 ppmv detection threshold obtained by pulsed OPO excitation with the nonresonant one-microphone registration scheme is sufficiently low. Future work will be directed to improvement of the acoustic registration scheme and gas excitation by the OPO operating in the range of fundamental vibration frequencies of molecules. This changing of the excitation range will additionally lower the gas detection threshold more than by an order.

4. Summary

The photoacoustic gas spectroscopy method is tested using the high volume broad-band OPO excitation. Spectra of methane and water molecules available in the ambient air were registered. Measurements have been carried out in the 1.32–1.72 μm range which covers the second overtone band of methane and water vapour. Photoacoustic spectra of these species were obtained with 1.5 nm spectral resolution. The measured spectra qualitatively conform to those calculated from the HITRAN database. The 4.3 ppmv detection thresh-

old of water vapour was obtained for the acoustic signal averaging over the 10 laser shots.

Acknowledgements

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FOTOAKUSTINĖ DUJŲ SPEKTROSKOPIJA PANAUDOJANT DERINAMO BANGOS ILGIO ŠVIESOS GENERATORIUS

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Santrauka

Tikrinamas fotoakustinės dujų registracijos našumas panaudojant plačios spektrinės juostos optinio parametrinio osciliatoriaus (OPO) šaltinį. 0,72–1,9 μm ruože OPO generavo derinamo bangos ilgio maždaug 7 ns trukmės ir apie 5 cm^{-1} spektrinės juostos impulsus. Šis spektro ruožas perkloja analizuojamosios medžiagos molekulių vandenilio atomų fundamentinių virpesių kombinacinius ir obertonų dažnius. Naudojama nerezonansinė vieno mikrofono akustinių virpesių registravimo schema. Pamatuotieji vandens garų ir metano optoakustiniai spektrai kokybiškai sutampa su šių medžiagų sugerties spektrais, apskaičiuotais panaudojant HITRAN duomenų bazę. Registruojant ties 1,361 μm sugerties linija aplinkos oro vandens garams įvertintas 4,3 ppmv dydžio aptikimo slenkstis (ppmv yra viena milijoninė tūrinė dalis).