Cw-OPO based photoacoustic spectrometer for highly sensitive detection of ethane and other volatile organic compounds

Frank Müller*[ab], Alexander Popp[ac], Stephan Schiller[b], Frank Kühnemann[ad]
[a]Institut für Angewandte Physik, Universität Bonn, Wegelerstr. 8, D-53115 Bonn, Germany;
[b]Institut für Experimentalphysik, Universität Düsseldorf, Universitätsstr. 1, D-40225 Düsseldorf, Germany;
[c]Medizinische Fakultät, TU Dresden, Fetscherstr. 74, D-01307 Dresden, Germany;
[d]Max Planck Institut für Chemische Ökologie, Hans Knöll Str. 8, D-07745 Jena, Germany

Abstract

We present an all-solid-state, transportable photoacoustic spectrometer operated with a continuous-wave optical parametric oscillator. The PPLN-based OPO has a dual cavity configuration (pump-resonant singly-resonant) in order to combine low threshold with good tuning characteristics. A complete spectral coverage between 3.1 and 3.9 µm with a single-frequency output power of 2 x 100 mW is achieved. At 30 seconds lock-in time constant the noise level of the background corresponds to a minimum absorption coefficient of 7.2×10^{-10} cm^{-1} , yielding an ethane detection limit of 25 ppt. The OPO based photoacoustic spectrometer including the wavemeter is installed on a 120 cm x 75 cm breadboard. The ethane concentration of ambient air is determined by a multigas analysis. Additionally an online-measurement of biogenic ethane emissions by a freeze-stressed lima bean leaf is presented. The results indicate a high potential of this transportable spectrometer for biological and medical applications.

Keywords: optical parametric oscillator, photoacoustics, mid infrared spectroscopy, trace gas analysis

1. Introduction

Trace gas detection plays an important role in biology, atmospheric chemistry and medicine. Hydrocarbons, aldehydes and alcohols show strong absorption spectra in the 3 µm wavelength region. Ethane (C_2H_6) is one very prominent example. It is produced by plants, animals and humans in the process of lipid peroxidation and thus an indicator for cell damages [1]. This fact is known as oxidative stress. The influence of point freezing on the ethane synthesis of sugar beet leaf discs has been described by Elstner and Konze in 1976 [2]. In medicine ethane is of special importance because it can be studied noninvasively via breath analysis. One approach is to collect the breath air in a sample bag and to analyze it off-line using gas chromatography - mass spectrometry (GC-MS) after a preconcentration with a trapping technique [3]. The goal of our work is to develop a transportable spectrometer for a sensitive and selective online detection of ethane and other volatile organic compounds, without using methods for preconcentration. Mid infrared photoacoustic spectroscopy (PAS) has proven its usefulness for biological and medical applications [4,5]. Sensitivity and selectivity of this technique are determined by the power and frequency tunability of available laser sources. High power CO overtone gas lasers are limited by the tunability from line to line. In contrast, difference-frequency generation (DFG) offers good frequency tunability, but poor output power. Continuous-wave optical parametric oscillators (OPOs) combine frequency agility with high output power and have therefor lately been established as laser sources for PAS [6]. An ethane detection limit of 10 parts per trillion at 40 seconds scan time has been reported with PAS based on a singly resonant OPO (SRO) [7]. This SRO was pumped by a 10 Watt Nd:YAG pump laser. Our goal was to set up a transportable spectrometer using a pump laser of moderate power. By resonating the pump beam, OPO threshold can be lowered externally. Our solution is a dual cavity pump-resonant SRO, combining frequency agility and output power with a compact design [8,9]. In this manuscript we demonstrate, that this transportable OPO based photoacoustic spectrometer allows highly sensitive and selective multigas analysis and online detection of ethane.

* f.mueller@iap.uni-bonn.de; phone +49 (0)228 733453; fax +49 (0)228 733474

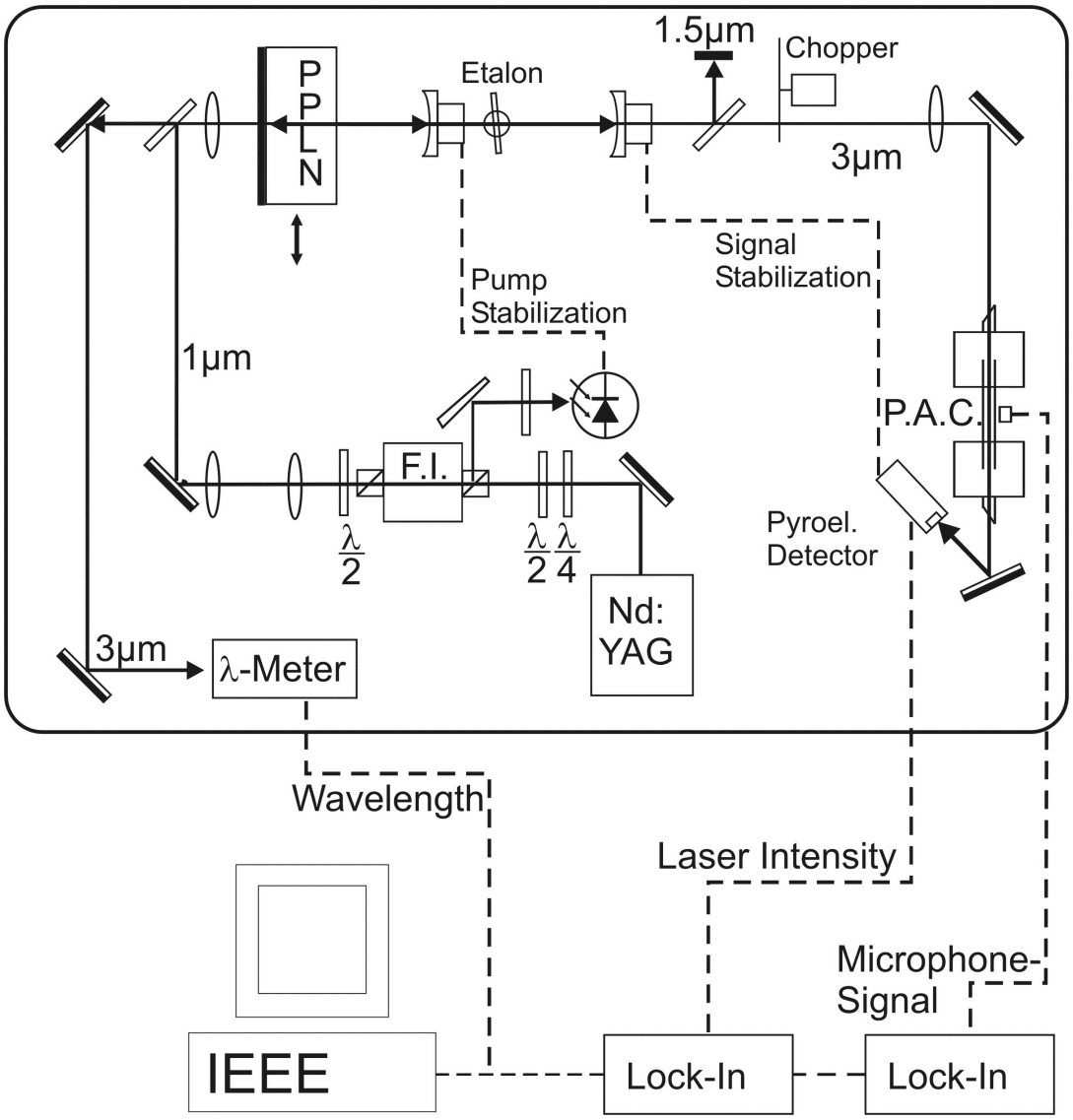

Fig. 1. Schematic of the OPO based photoacoustic spectrometer.

2. Experimental setup

The spectrometer has been described in detail in a separate paper [9]. It consists of the OPO, chopper, photoacoustic cell (PAC), pyroelectric detector and the wavemeter (Burleigh WA 1500) and is mounted on a 120 cm x 75 cm breadboard (Fig. 1).

2.1 Optical parametric oscillator

With 2 W cw incident pump power at 1064 nm the periodically poled lithium niobate (PPLN, crystal: Length=19mm, Width=50mm, Thickness=0.5mm) [10] based OPO delivers 2 x 100 mW of idler output power at each end of the OPO with a full spectral idler wavelength coverage between 3.1 – 3.9 µm. The signal can be tuned between 1.46 – 1.62 µm. One crystal surface serves as mirror for pump (94.3 %) and signal (99.9 %) waves. The pump cavity is closed by a meniscus mirror (99.9 % for pump, < 2 % for signal and < 5 % for idler) and signal cavity by a concave mirror (99.9 % for signal and <5 % for idler). The length of both cavities can be controlled by using piezoelectric transducers (PZT). By pump resonance (short cavity) the threshold of about 5 W is lowered externally down to 380 mW. Signal resonance

inside an independent (long) cavity (FSR=450 MHz) in combination with a turnable signal etalon ensures frequency agility. Frequency tuning is performed in 5 steps :

1. Coarse tuning between 3.1-3.9 µm by selecting one of the 19 crystal gratings using a motorized translation stage.
2. Temperature tuning of the PPLN inside the self designed oven between 150 and 200°C.
3. 450 MHz steps modehop tuning (52 GHz working range) by turning the etalon via a galvanometer.
4. Continuous tuning over 450 MHz by changing signal cavity length via the PZT.
5. Continuous tuning by tuning the pump laser (Mephisto, Innolight). 40 GHz in total and up to 3 GHz mode hop free is reached.

For PAS at atmospheric pressure the etalon mode hop tuning is sufficient, because typical width are between 3 (single pressure broadened lines) and 50 GHz (broad structures consisting of many overlapping lines). The Pound-Drever-Hall [11] method is used for the stabilization of the pump cavity to the laser. The signal cavity can be frequency stabilized on a maximum of idler output power.

The frequency tunability of the dual-cavity cw pump-resonant, singly-resonant OPO allows to scan molecular absorption structures at atmospheric pressure. Its frequency stability, which is better than the ± 30 MHz wavemeter accuracy, allows time-resolved gas absorption measurements at any preset frequency [9].

2.2 Photoacoustic spectroscopy

The idler output beam of the OPO is modulated in amplitude by a mechanical chopper and coupled into the PAC via a lens. The amount of radiation absorbed by the molecules inside the PAC is measured by its conversion into heat. If the modulation frequency is equal to the resonance frequency of the PAC, a standing sound wave is generated and its amplitude is amplified by the Q-factor (Quality-factor),

$$Q = \frac{\nu_{res}}{\Delta\nu} \tag{1}$$

where ν_{res} is the mid-frequency and $\Delta\nu$ the width of the PAC resonance. The sound amplitude is measured with a microphone (Knowles EK3024) and the laser intensity with a pyroelectric detector. Both signals are processed with lock-in amplifiers (SR 830). The normalized photoacoustic signal (NPAS) is the ratio of the microphone signal U_{mic} and laser intensity I_{las}. The PAC consists of the acoustical resonator (length 7cm, diameter 6 mm) with the microphone, buffer volumina and brewster-angled windows. The gas is directly inserted into the resonator, which allows a fast gas exchange, and it leaves the cell at both buffer volumina (positioned at both ends of the open resonator). Two further gas inlets can be used for washing out the brewster window areas. The whole PAC is coated (Restek Silcosteel®) against gas adsorptions. The Q-factor is 17.4 (Fig. 2).

The OPO frequency tuning (PPLN crystal temperature, crystal grating period, etalon angle, signal cavity length and pump laser frequency) and the data acquisition (wavelength, microphone signal and laser intensity) is completely controlled by a Labview® computer program.

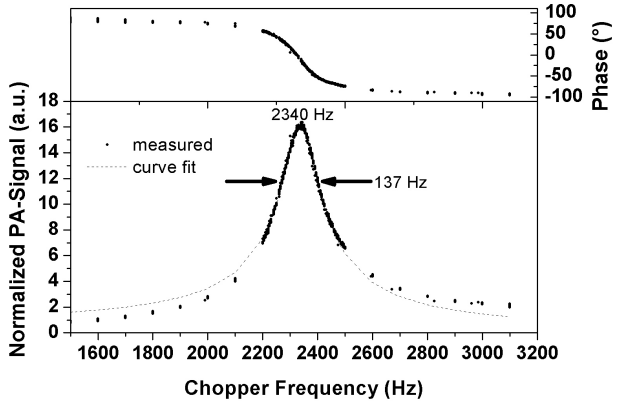

Fig. 2. Measurement of the Q-factor with ethane inside the PAC.

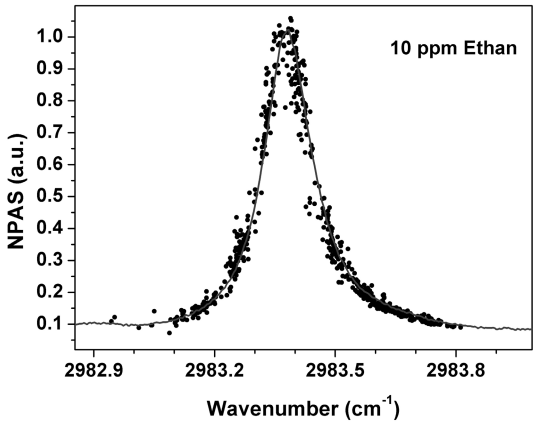

Fig. 3. Scan over an ethane absorption peak (atmospheric pressure).

3. Measurements

3.1 Calibration and performance of the OPO photoacoustic spectrometer

Before performing a measurement, the photoacoustic spectrometer has to be calibrated for concentration measurements with a certified gas mixture.

$$U_{mic} = \mu \cdot \kappa \cdot c_{gas} \cdot F \cdot I_{las} \tag{2}$$

(microphone sensitivity μ , absorption coefficient κ ,concentration c_{gas} of the absorbing gas, PAC constant F). We used a certified gas mixture of 10 ppm ethane in hydrocarbon-free air for the calibration. First, a scan over the $^{P}Q_1$ sub-branch of ethane at atmospheric pressure was performed (Fig. 3). Lock-in time constant was 100 ms and the flow rate through the PAC was 1 litre per hour. This scan was compared to an appropriately scaled FTIR spectrum [12], showing good agreement. For the evaluation of the detection limit the same certified gas mixture was diluted with pure hydrocarbon-free air using two flow-controllers (MKS) (Fig. 4). The flow rate through the PAC was 1 litre per hour. At 30 seconds lock-in time constant the noise level of the background corresponds to a minimum absorption coefficient of 7.2 x 10^{-10} cm^{-1} , yielding an ethane detection limit of 25 ppt. This is a further improvement compared to previous results [9].

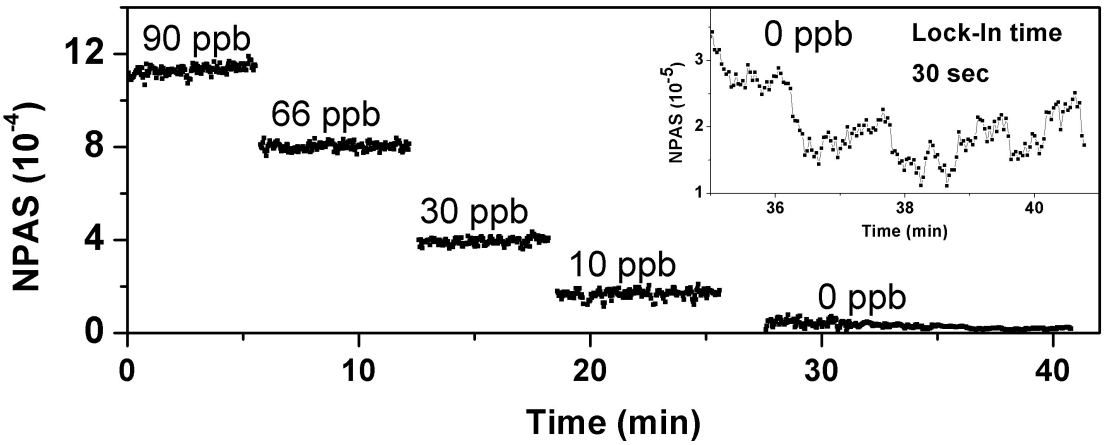

Fig. 4. Normalized PA-Signal (NPAS) at different preset ethane concentrations as a function of time including the background signal. The insert shows the background at 30 sec time constant.

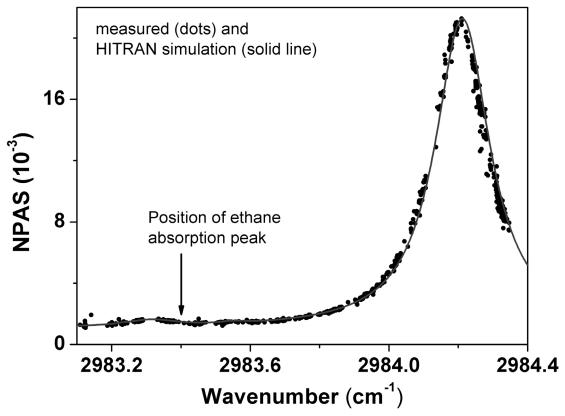

Fig. 5. Scan over ambient air at atmospheric pressure without using a liquid nitrogen cooling trap compared to a HITRAN simulation of pure water.

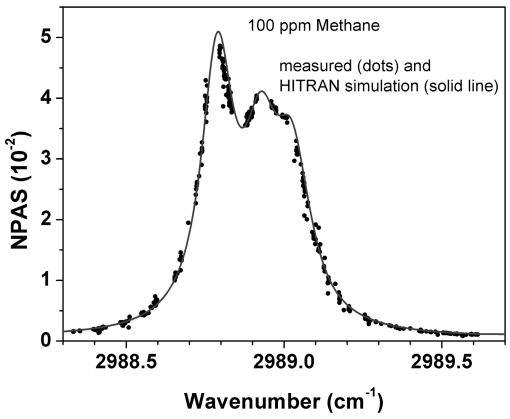

Fig. 6. Scan over a methane absorption structure at atmospheric pressure using a certified mixture of 100 ppm methane in nitrogen.

3.2 Multigas analysis

Besides the scanning of absorption peaks of one single absorbing gas, the performance of the spectrometer allows also a multigas analysis of ambient or breath air. Selectivity can be improved by reducing the pressure of the gas. This kind of measurement has recently been demonstrated by us by means of an OPO based cavity leak-out spectrometer at 100 mbar gas pressure without a liquid nitrogen cooling trap [13]. At atmospheric pressure, the disturbing water absorption is dominating. Figure 5 shows a scan of ambient air at atmospheric pressure with the photoacoustic spectrometer compared to the HITRAN [14] simulation of water. This measurement demonstrates the impossibility to evaluate the ethane concentration using the peak position shown in figure 3. Another method for increasing the selectivity is to freeze out most of the disturbing gases using a liquid nitrogen cooling trap at 115 K. The freezing temperature of ethane and methane is lower, and so these gases pass the trap. For a calibration of the methane content in ambient air, a scan over an absorption structure was performed (Fig. 6), using a certified gas mixture of 100 ppm of methane in nitrogen. Lock-in time was 3 seconds and the gas flow rate 1 litre per hour. The comparison of the shape with the HITRAN simulation shows a very good agreement. These calibration measurements show us, that HITRAN database is correct for the scanned molecules at the used wavelengths regions and it can though be used for fitting.

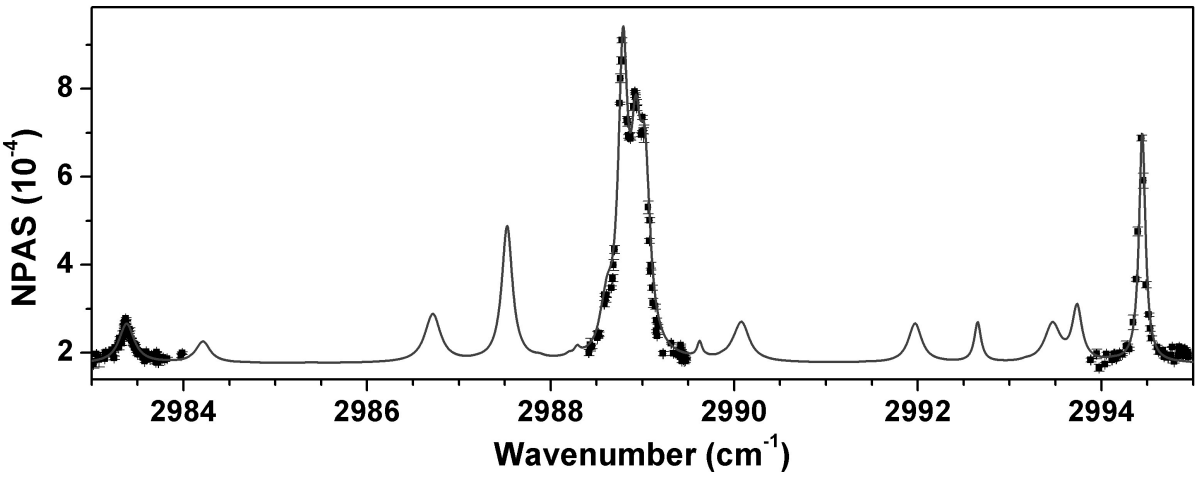

Fig. 7. Scan over the significant absorption structures of the ambient air in our laboratory (fit: HITRAN, solid line). The dots are averaged at each measured wavenumber position.

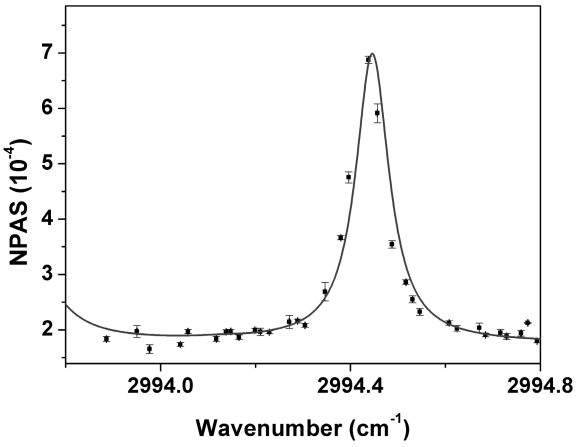

Fig. 8. Zoom of the water absorption structure of the ambient air sample.

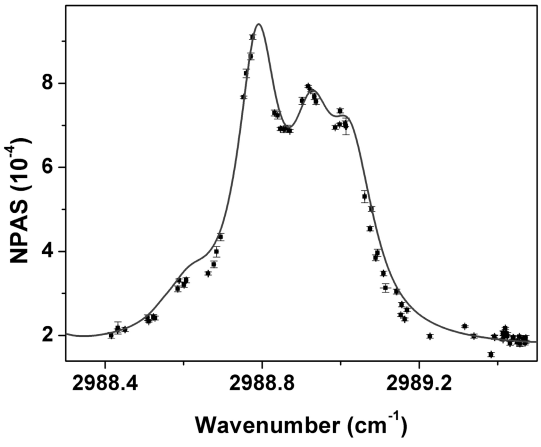

Fig. 9. Zoom of the methane absorption structure of the ambient air sample.

For the demonstration of a multigas analysis, which is similar to a breath measurement, the PAC is filled with ambient air, using a cooling trap. Positions of significant absorption peaks of ethane (C_2H_6), methane (CH_4) and remaining water (H_2O) are scanned (Fig. 7). The background offset is due to rests of gases, like acetone or isoprene, whose absorptions are spectrally flat in the scanned region, and especially to the remaining water. The lock-in time constant of this measurement was 1 second. The scanned absorption peaks are compared to the HITRAN simulation of an appropiately scaled gas mixture of water, methane and ethane. The figures 8, 9 and 10 show a zoom on the significant water, methane and ethane absorption structures. The ethane concentration can then easily be evaluated from the measerement shown in figure 10. We find an ethane concentration of (4.5 $\pm$ 0.5) ppb. The methane concentration of (1.7 $\pm$ 0.5) ppm is in good agreement with [13]. For a breath analysis one will have to compare the (ethane) concentrations of the exhaled gas components with those of the inhaled ambient air, since breath ethane concentrations are expected to be at the same level or below. Basic research on breath analysis using mid infrared laser spectroscopy utilizing a stationary spectrometer is currently in progress [16].

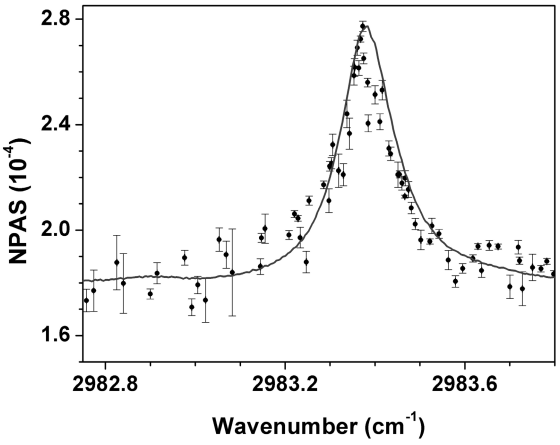

Fig. 10. Zoom of the ethane absorption structure of the ambient air sample.

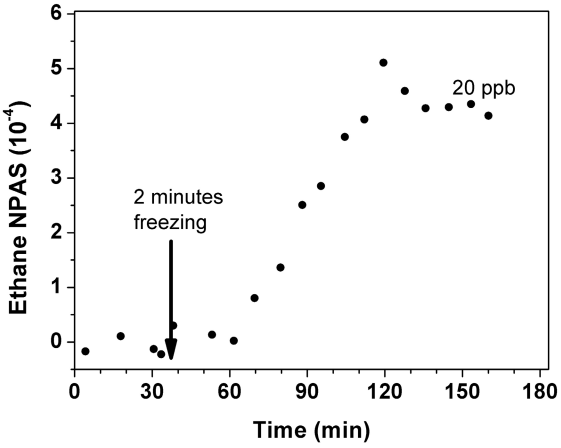

Fig. 11. Online ethane emission measurement of a lima bean leaf after 2 minutes of freezing.

3.3 Online trace gas analysis

In order to demonstrate the feasibility for online trace gas analysis we performed a measurement on a biological sample. The aim was to observe ethane emission from a single lima bean leaf (*phaseolus lunatus*) subjected to freezing stress. A leaf was placed at the bottom inside a cuvette. The cuvette is flushed with hydrocarbon-free air. The flow rate through the PAC was 2 litres per hour. The plants emissions were scanned and analyzed analogously to the ambient air scan described before (each dot for the ethane NPAS is a result of a multigas measurement and analysis analog to figures 7-10). After 38 minutes the bottom of the cuvette was dipped into liquid nitrogen for 2 minutes. The measurement is shown in figure 11. About 20 minutes after freezing the leaf started to emitt ethane as a result of lipid peroxidation, which indicates cell damages. The measured ethane concentration was about 20 ppb, demonstrating the high sensitivity of online multigas measurements. Ethane emissions of freeze-stressed leafs have also been observed by A.A.E. Martis et al. [15], who used a CO-overtone laser based photoacoustic spectrometer. For lower emission rates, the flow rate through the PAC can be lowered. Online measurements can also be performed on animals or human beings [16].

4. Summary

We set up a transportable OPO based photoacoustic spectrometer. The output power and tuning qualities of this OPO allow a reliable scan over absorption structures in the 3µm wavelength region. At atmospheric pressure the background corresponds to a minimum absorption coefficient of 7.2 x 10^{-10} cm^{-1} , yielding an ethane detection limit of 25 ppt. A multigas analysis was performed by using a cooling trap at 115 K. We have detected ethane, methane and water simultaneously. The method could easily be extended to other volatiles (ethanol, acetaldehyde, acetone...) using an appropriately selected cooling trap temperature. We have furthermore shown that an online analysis of gases in mixtures can be performed. The results are important steps towards a fully automated highly sensitive and selective

multicomponent gas sensor. The spectrometer has a very good perspective for applications in biology, atmospheric chemistry and medicine.

Acknowledgments

We are grateful to the Deutsche Forschungsgemeinschaft (DFG) for funding, to A. Peters (Humboldt Universität Berlin) for providing OPO optics, and to K. Buse (Universität Bonn) for lending us a wavemeter.

References

1. R. M. Harber and L. H. Fuchigami, "The relationship of ethylene and ethane production to tissue damage in frozen rhododendron leaf discs", *J. Amer. Soc. Hort. Sciences*, **11**, (434-436), 1986.
2. E. F. Elstner and J. R. Konze, "Effects of point freezing on ethylene and ethane production by sugar beet leaf disks," *Nature*, **263**, (351-352), 1976.
3. M. D. Knutson, G. J. Handelman, and F. E. Viteri, "Methods for measuring ethane and pentane in expired air from rats and humans," *Free Radical Biology & Medicine*, **28**, (514-519), 2000.
4. F. Kühnemann, *Laser in environmental and life science*, Chapter 16, Springer, Heidelberg-Berlin, 2003.
5. F. J. M. Harren, R. Berkelmans, K. Kuiper, S. te Lintel Hekkert, P. Scheepers, R. Dekhuijzen, P. Hollander, and D. H. Parker, "On-line laser photoacoustic detection of ethene in exhaled air as biomarker of ultraviolet radiation damage of the human skin", *Appl. Phys. Lett.*, **74**, (1761-1763), 1999.
6. F. Kühnemann, K. Schneider, A. Hecker, A. A. E. Martis, W. Urban, S. Schiller, and J. Mlynek, "Photoacoustic trace-gas detection using a cw single-frequency parametric oscillator", *Appl. Phys. B*, **66**, (741-745), 1998.
7. M. M. J. W. van Herpen, S. Li, S. E. Bisson, and F. J. M. Harren, "Photoacoustic trace gas detection of ethane using a continuously tunable, continuous-wave optical parametric oscillator based on periodically poled lithium niobate", *Appl. Phys. Lett.*, **81**, (1157-1159), 2002
8. G. A. Turnbull, D. McGloin, I. D. Lindsay, M. Ebrahimzadeh, and M. H. Dunn, "Extended mode-hop-free tuning by use of a dual-cavity, pump-enhanced optical parametric oscillator," *Opt. Lett.*, **25**, (341-343), 2000.
9. F. Müller, A. Popp, F. Kühnemann, and S. Schiller, "Transportable, highly sensitive photoacoustic spectrometer based on a continuous-wave dual-cavity optical parametric oscillator", *Optics Express*, **11**, (2820-2825), 2003.
10. L. E. Myers, R. C. Eckardt, M. M. Fejer, R. L. Byer, W. R. Bosenberg, and J. W. Pierce, "Multigrating quasi-phase-matched optical parametric oscillator in periodically poled $LiNbO_3$," *Opt. Lett.*, **21**, (591-593), 1996.
11. R. W. P. Drever, J. L. Hall, F.V. Kowalski, J. Hough, G.M. Ford, A. J. Munley, and H. Ward, "Laser phase and frequency stabilization using an optical resonator," *Appl. Phys. B*, **31,** (97–105), 1983.
12. A. Popp, H. Dahnke, F. Kühnemann, J. Orphal, G. v. Basum, and J. Burrows, FTIR, unpublished work report, 1999.
13. G. von Basum, D. Halmer, P. Hering, M. Mürtz, S. Schiller, F. Müller, A. Popp, and F. Kühnemann, "Parts per trillion sensitivity for ethane in air with an OPO cavity leak-out spectrometer", *Opt. Lett.*, (accepted for publication).
14. HITRAN data base, URL:http://cfa-www.harvard.edu/HITRAN/.
15. A.A.E. Martis, S. Büscher, F. Kühnemann, and W. Urban, "Simultaneous ethane and ethylene detection using a CO-overtone laser photoacoustic spectrometer: A new tool for stress/damage studies in plant physiology", *Instr. Science & Technology*, **26**, (177-187), 1998.
16. G. von Basum, H. Dahnke, D. Halmer, P. Hering, and M. Mürtz, "Online recording of ethane traces in human breath via infrared laser spectroscopy", *J. Appl. Physiol.*, **95**, (2583), 2003.