Detection of ammonia by photoacoustic spectroscopy with semiconductor lasers

Andreas Schmohl, András Miklós, and Peter Hess

Sensitive photoacoustic detection of ammonia with near-infrared diode lasers (1.53 μm) and a novel differential acoustic resonator is described; a sensitivity of 0.2 parts per million volume (signal-to-noise ratio = 1) is attained. To eliminate adsorption–desorption processes of the polar NH_3 molecules, a relatively high gas flow of 300 SCCM was used for the ammonia–nitrogen mixture. The results are compared with recent ammonia measurements with a NIR diode and absorption spectroscopy used for detection and photoacoustic experiments performed with an infrared quantum-cascade laser. The performance of the much simpler and more compact setup introduced here was comparable with these previous state-of-the-art measurements. © 2002 Optical Society of America

OCIS codes: 300.6260, 300.6340, 140.2020, 300.1030.

1. Introduction

Because of the increasing importance of environmental problems, the development of molecule-specific spectroscopic detection methods for real-time monitoring of pollutants in biology, medicine, and the environment (e.g., atmosphere, traffic, industrial flues) is currently important. To achieve the necessary sensitivity and selectivity, the use of high-resolution laser techniques in the infrared (IR) and the near-infrared (NIR) fingerprint regions is of special interest. In fact, the availability of tunable laser sources with suitable linewidths is essential for the further development of optical diagnostic techniques already well established in trace-gas analysis. For practical applications, the main requirements for those light sources are small size, low weight and cost, narrow linewidth, large tuning range, and no cooling requirements.

In this respect, single-mode distributed-feedback (DFB) AlGaAs diode lasers with their high spectral resolution are ideally suited for detecting chemical bonds such as N–H, O–H, and C–H. These versatile NIR lasers function near room temperature and allow simple, robust, low-cost, and portable detection of trace gases. Currently available DFB quantum-cascade (QC) lasers make the IR accessible, where the absorption coefficients are 1–2 orders of magnitude higher. These lasers can be operated in pulsed mode near room temperature or in continuous-wave (cw) mode at cryogenic temperatures and reach power levels comparable with those of DFB diode lasers (1–50 mW).

The present work concentrates on the detection of NH_3 with semiconductor lasers. Versatile cw diode lasers have been applied to monitor molecules of interest with high spectral resolution.[1,2] Specifically, NIR diode lasers, which excite overtone and combination vibrations, have been applied in connection with absorption spectroscopy[3–9] or photoacoustic (PA) detection schemes.[10,11] In addition, PA NH_3 measurements have been performed with a QC laser, which radiates in the spectral range of fundamental vibrations.[12]

Sensitive monitoring is of great interest in checking NH_3 emission from animal production facilities and traffic, to name two main sources of NH_3. In addition, NH_3 is widely used in power plants and incinerators to reduce NO_x emissions. In medicine, for example, the detection of small amounts of respiratory NH_3 in real time is of great interest.

The detection of small concentrations of strongly polar molecules such as NH_3, H_2O, and NO_2 is extremely difficult because they tend to adsorb at the inner surfaces of the detector, gas mixing, and tubing system. Therefore it is practically impossible to monitor small concentrations in a closed detection

A. Schmohl, A. Miklos, and P. Hess (peter.hess@urz.uni-heidelberg.de) are with the Institute of Physical Chemistry, University of Heidelberg, Im Neuenheimer Feld 253, D-69120 Heidelberg, Germany.

Received 21 May 2001; revised manuscript received 8 October 2001.

0003-6935/02/091815-09$15.00/0

© 2002 Optical Society of America

system accurately. Sensitive PA measurements of NH_3 have been reported,[13,14] and a strongly nonlinear concentration dependence of the PA signal was observed.[10] It has been clearly demonstrated that adsorption and desorption of NH_3 from the cell and tube walls contributed to the detected signal at low NH_3 concentrations.[11]

The adsorption problem can be solved if continuous gas flow through the detector is used. Because adsorption and desorption processes are relatively slow, the error caused by adsorption can be reduced substantially by an increase in the flux of molecules. However, detection at high flow rates may cause other problems. For example, the strongly nonlinear increase of the flow noise with the flow velocity may reduce the detection limit in PA trace-gas detection considerably. In this paper accurate experimental results are presented that were obtained with an optimized differential PA detector that was designed for continuous-flow operation at relatively high flow rates. A review of the application of acoustic resonators in gas detection, giving more details of the differential detector used, has been published recently.[15]

The performance of PA detection with a cw DFB diode laser radiating in the NIR spectral range is compared with that of using a cw DFB QC laser operating in the IR. In addition, a detailed discussion of the characteristics of different NH_3 detection schemes with NIR diode lasers is provided by comparing state-of-the-art NH_3 detection by means of absorption spectroscopy and PA spectroscopy.

2. Experiments

PA measurements of NH_3–N_2 mixtures were performed with the setup shown schematically in Fig. 1. As light sources, two different NIR diode lasers were tested, namely a 5-mW Mitsubishi DFB diode laser and a 42-mW GEC-Marconi DFB diode laser, both radiating at 1.53 μm. Light absorption was monitored by a differential PA detector, which is described elsewhere.[10,15] This detector (see Fig. 2) was specifically designed for fast time response, low acoustic and electric noise characteristics, and high sensitivity. To reduce the flow noise and external electromagnetic disturbances, a fully symmetrical design of the two resonator tubes was chosen. Thus all noise components that are coherent in the two resonators of the detector (acoustic resonance frequency, ~4 kHz) are suppressed effectively.

The detection system was designed for continuous-flow operation with a nominal flow rate of 300 SCCM (SCCM denotes cubic centimeters per minute at STP). When the volume of the acoustic filter between the gas inlet and resonator tubes of ~17 cm^3 and that of the resonator tubes of ~2 cm^3 were taken into account, a time delay of 3.4 s and a rise time of 0.4 s were derived for the PA signal from the nominal gas flow rate. Thus a response time of ~4 s could be expected for sudden concentration changes occurring at the input of the PA detector.

In addition, a second differential PA detector with a similar design was tested. The material of this detector was selected to reduce adsorption effects at the inner surfaces. This cell was made of polypropylene (PP) instead of brass and could be heated up to 40–50 °C. Moreover, antireflection-coated wedge-shaped windows were used to reduce the background signal caused by light that was reflected back from the windows and absorbed at the detector walls. More information on the PP detector can be found elsewhere.[11]

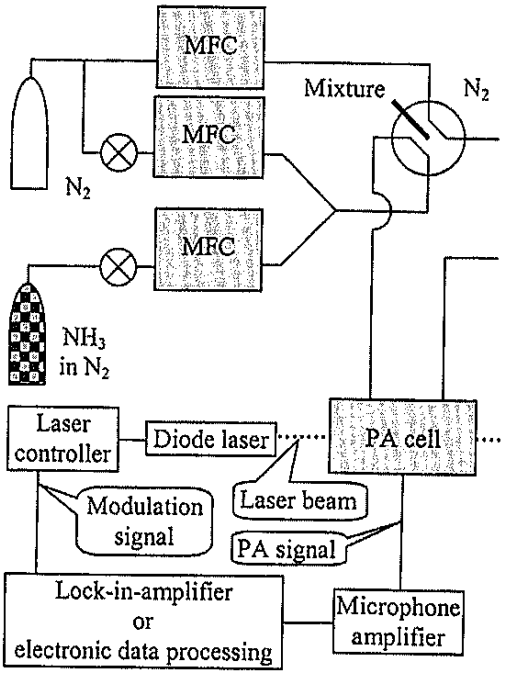

Fig. 1. Block diagram of the setup used for the PA detection of NH_3 including the gas-mixing system (MFC, mass flow controller).

To generate a PA signal, we modulated the laser radiation by switching the diode laser current between two preset values using the internal reference signal of a lock-in amplifier (Stanford SR 830). The frequency of this reference signal was tuned to an acoustic resonance of the PA detector. The Q factor

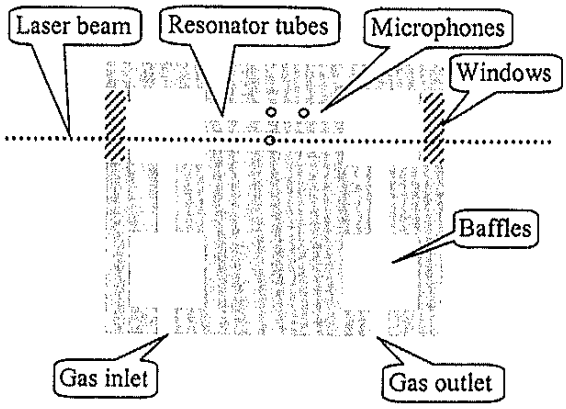

Fig. 2. Schematic drawing of the differential metal cell.

Kopie bereitgestellt durch Universitaetsbibliothek der Universitaet der Bundeswehr Hamburg

of the resonator was $Q = 17$, which corresponds to a full width at half-maximum (FWHM) of ~240 Hz for N_2 at room temperature. Because the temperature dependence of the resonance frequency[11] was ~7.2 Hz/°C, no temperature stabilization of the PA cell was necessary. The microphone signal was amplified by a low-noise differential amplifier and was measured with the two-phase lock-in. Both outputs were continuously recorded on a personal computer. This method was applied in all PA measurements performed with the Mitsubishi diode laser. The experiments with the GEC-Marconi laser diode were carried out with a simulated lock-in technique. Here the preamplified PA signal was digitized with a multifunction input–output card and evaluated by a specially written software, which simulated a lock-in amplifier. The sampling rate of the analog-to-digital (AD) conversion was synchronized to the modulation frequency.

In most cases the concentration measurements of NH_3 were carried out at a flow rate of 300 SCCM. Certified mixtures of 1000-, 96.7-, 50.1-, and 5.38-ppmV NH_3 in N_2 (where ppmV is parts per million volume) (Messer-Griesheim, accuracy of concentration, ±3%) were diluted by N_2 by use of mass flow controllers (Tylan, FC-260). The measurements were performed at the peak wavelength of the pressure-broadened NH_3 absorption line at 1531.7 nm. The absorption peak was located by a temperature scan of the diode laser. The line profile recorded was similar to the shape measured by Fourier transform IR (FTIR) spectroscopy.[10] The peak absorption coefficient was found to be 9.1×10^{-5} cm^{-1} for 550-ppmV NH_3 diluted in N_2. We calculated the integrated line strength S by assuming a Lorentzian line shape and taking $\Delta\nu = 0.11$ cm^{-1} for the half-width at half-maximum (HWHM) from Fig. 3 of Ref. 10. The calculated value of $S = 2.3 \times 10^{-21}$ cm/molecule agrees well with the value given in Table 1 of Ref. 7 for line A. The peak absorption coefficient for pure NH_3 can be calculated as 0.17 cm^{-1}. This value has been used for the estimation of the sensitivity of the PA detector.

The temperature of the DFB diode laser was kept constant to within 0.04 °C near 28.6 °C. Because the temperature dependence of the laser wavelength was approximately 0.1 nm/°C ≅ 0.43 cm^{-1}/°C, the corresponding wave-number fluctuations were smaller than ±0.02 cm^{-1}. This value is substantially smaller than the FWHM of the absorption peak (~0.22 cm^{-1}). Thus the fluctuations of the PA signal that were due to wavelength fluctuations of the diode were small. The fluctuations were measured by use of a closed reference cell filled with a mixture of 1% NH_3 in N_2. The standard deviation of long-term PA measurements with the lock-in (300-ms time constant) was 0.25% and therefore much smaller than the fluctuations of the PA signal measured in the flow-through mode. For this reason, the PA measurements were not normalized by the laser power.

3. Results

A. Measurements with the 5-mW Mitsubishi Distributed-Feedback Laser

In a series of measurements the NH_3 concentration was reduced in 21 steps from 340 to 5 ppmV. The background signal was measured during irradiation in a pure N_2 flow, and the flow and electromagnetic noise were determined by blocking of the laser beam. First the noise performance was checked without any gas flow. The intrinsic noise of the miniature electret microphones was very large; a value of 15.7 μV was measured for the broadband noise. With a microphone sensitivity of 102 mV/Pa, this signal corresponds to a sound pressure of 154 μPa. Fortunately this large noise contribution was completely uncorrelated.

The noise measured by the lock-in (time constant, 10 s) was only 38 nV when the laser beam was blocked. The noise increased slightly (~20%) at 1000-SCCM flow rate. The background signal measured for pure N_2 was roughly four times larger (175 nV). Because the background is usually coherent with the laser radiation, i.e., it has quite a stable phase lag of θ_{BG} to the lock-in reference and the PA signal has another constant phase θ_{PA}, the measured signal U_{PA} can be regarded as a vectorial sum of a constant background B, a signal S, and an incoherent noise N in the form of

$$U_{PA} = [S^2 + 2SB\cos(\theta_{PA} - \theta_{BG}) + B^2 + N^2]^{1/2}. \quad (1)$$

Taking into account that the PA signal S is strictly linear with the concentration x, the following functional dependence can be used to fit the measured data:

$$U_{PA} = [(ax)^2 + bx + c^2]^{1/2}, \quad (2)$$

where U_{PA} and x are the measured PA signal in microvolts and the concentration in parts per million volume, respectively. The fit parameter a is the sensitivity of the ammonia detector given in microvolts per parts per million volume. By comparing Eqs. (1) and (2) we obtain for the other fit parameters $b = 2aB\cos(\theta_{PA} - \theta_{BG})$ and $c = (B^2 + N^2)^{1/2}$.

The experimental data and the corresponding fit curve are shown in Fig. 3. The low-concentration part of this curve can be seen in the inset. Note that linear units were used for the axes of the inset, and therefore the measured background at zero concentration can also be seen. This point is missing in the logarithmic plot of Fig. 3. It is important to note that the fit is excellent down to the background. The parameter values of this fit are $a = 0.0831 \pm 0.0015$ μV/ppmV, $b = 0.00436 \pm 0.0031$ $(\mu V)^2$/ppmV, and $c = 0.138 \pm 0.054$ μV.

The standard deviation of the detector sensitivity a is smaller than 2%. The parameter c gives the sum of the uncorrelated acoustic and electronic noise N and the background B generated by light absorbed by the windows and cell walls. The value of c should be close to the background measured in N_2. The mea-

Kopie bereitgestellt durch Universitaetsbibliothek der Universitaet der Bundeswehr Hamburg

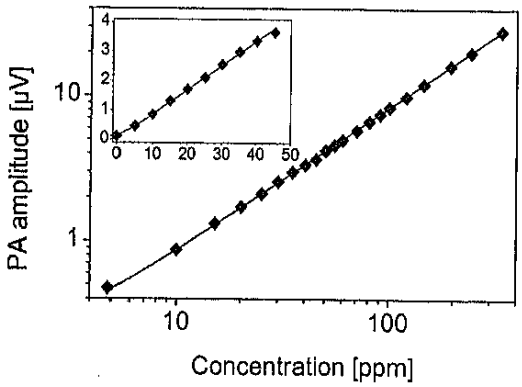

Fig. 3. Logarithmic plot of the PA signal versus NH_3 concentration measured with the 5-mW Mitsubishi DFB diode. Diamonds, measured PA signal; solid line, vectorial fit. The inset is a linear plot of the PA signal versus concentration (lower part of the curve) showing also the background at 0 ppm.

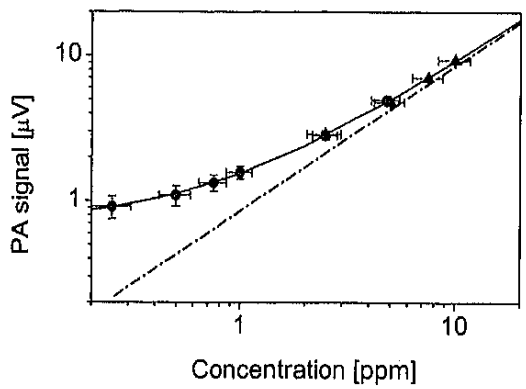

Fig. 4. Logarithmic plot of PA signal versus NH_3 concentration measured with the 42-mW GEC-Marconi diode. Triangles, low-power PA measurement; circles, high-power PA measurement; solid curve, vectorial fit. Standard deviations of signal and concentration are shown as error bars. Dashed–dotted line: straight line with slope obtained from vector fit.

sured background value was 0.125 μV, slightly lower than $c = 0.138$ μV. The background measured in a separate experiment was 0.157 μV, so the fitted value turned out to be approximately halfway between the measured ones.

The residuals of the fit, expressed in concentrations, were smaller than ±1.5 ppmV. The standard deviation of the 21 residual values was 0.65 ppmV. If the residuals are regarded as a Student distribution with a degree of freedom of 20, the deviation of a measured concentration from the true value can be expected to be smaller than 1.4 ppmV with a probability of 95%. That is, the precision of the PA measurements can be regarded as ±1.4 ppmV in the entire range of 5–340 ppmV. This value corresponds to ~30% precision at 5 ppmV. The precision at 340 ppmV was better than 2%.

B. Measurements with the 42-mW GEC-Marconi Diode Laser

The sensitivity of PA gas detection can be increased by application of a higher laser power. Therefore a DFB diode laser with a nominal power of 60 mW was purchased and built into our laser head (Melles-Griot). Because of the low beam quality, only approximately two thirds of the emitted light power was collected by the collimating lens built into the laser head (numerical aperture, 0.5). The power of the collimated laser beam was measured by a pyrodetector to be 42 mW.

We performed NH_3 concentration measurements by diluting a certified NH_3–N_2 mixture (50.1 ppmV, ±3%) with pure N_2 by using mass flow controllers. These measurements were performed by the simulated lock-in technique. The preamplified PA signal was first digitized by a multifunction input–output card and then evaluated by a specially written software that simulates a lock-in amplifier. The sampling rate of AD conversion was synchronized to the modulation frequency.

The PA signal was determined by repeated sampling and evaluation of the preamplified microphone signal. For a single measurement, 64-kbyte samples were collected and the signal amplitude and phase were extracted by the software. The time needed for a single measurement was slightly less than 2 s. Two series of experiments were carried out in the low-concentration range. The PA signal was measured continuously, and the concentration was reduced stepwise by a change in the ratio of the flow of the NH_3 mixture and pure N_2. The total flow rate was kept constant at 300 SCCM. Because a stabilization time of a few minutes was needed after a new concentration was set, the duration of a concentration measurement was ~10 min. When the measurements were finished, ~60 data points were selected for each step and the mean values and standard deviations of the measured PA amplitudes were determined.

The results of the two measurements and a vectorial fit of the data points can be seen in Fig. 4. Because the PA signal is relatively small for the low concentrations, it is not surprising that the curve deviates considerably from linearity. However, the function corresponding to the vectorial sum of the signal, background, and noise fits the measured data almost perfectly with the fit parameters $a = 0.853 \pm 0.016$ μV/ppmV, $b = 1.162 \pm 0.183$ (μV)^2/ppmV, and $c = 0.697 \pm 0.078$ μV. The background and noise were obtained in separate measurements. The background value measured in pure N_2 was $c = 0.62 \pm 0.15$ μV and the noise with the blocked laser beam was $N = 0.21 \pm 0.11$ μV.

The noise and the background values are higher than the corresponding values measured with the low-power diode and lock-in amplifier because the dynamic range of the 12-bit AD converter was not sufficient for highly sensitive measurements. Using the maximum amplification of the preamplifier 1 bit corresponded to ~0.3 μV; thus the noise and the

Kopie bereitgestellt durch Universitaetsbibliothek der Universitaet der Bundeswehr Hamburg

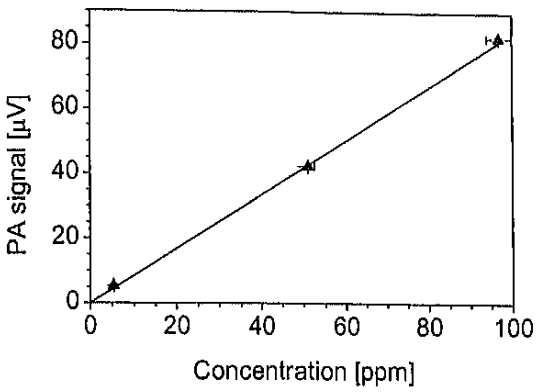

Fig. 5. Calibration measurements for NH_3. Solid line: straight line drawn through the origin with the slope obtained from the fit of Fig. 4; triangles, PA signals of three certified gas mixtures with 5.38-, 50.1-, and 96.7-ppmV NH_3.

background were significantly influenced by the error of the AD conversion process.

Because the PA signal is a linear function of the concentration, the sensitivity given by the fitting parameter a should also be valid for higher concentrations. Therefore three calibration points were determined by the measurements of the PA signals of certified gas mixtures. These three calibration points are presented in Fig. 5 with error bars. The straight line with slope a agrees almost perfectly with these calibration points. This means that the true PA signal can be regarded as linear from the highest concentration of 340 ppmV down to 250 ppbV (ppbV is parts per billion volume).

The large linear range of the PA signal is limited by the absorption of light in the acoustic resonator. The PA signal depends linearly on concentration as long as the absorbed light power is proportional to the absorption coefficient. The light power absorbed in the resonator is given by

$$P_{abs} = P_{inc}[1 - \exp(-\alpha l)], \tag{3}$$

where P_{abs}, P_{inc}, α, and l are the absorbed and the incident laser power, the absorption coefficient, and the length of the resonator tube, respectively. The quantity $\alpha l = \log(P_{inc}/P_{tr})$, where P_{tr} denotes the transmitted light power, is known as the optical density of the gas in the resonator tube (this quantity is also called absorbance). For small αl values, $1 - \exp(\alpha l) \cong \alpha l$, and therefore the PA signal depends linearly on the absorption coefficient and its dependence on the concentration is also linear. At $\alpha l = 0.06$, a deviation of ~3% is expected from linear behavior. An optical density of 0.06 may thus be regarded as the upper limit of the extensive linear range of a PA detector.

Because the length of the acoustic resonator tubes was 4 cm, the value of the limiting absorption coefficient was $\alpha_{max} = 0.015\ cm^{-1}$. The absorption coefficient of NH_3 was $0.17\ cm^{-1}$, as extracted from previous FTIR measurements. Therefore the linear range of the detector extends up to an NH_3 concentration of 90,000 ppmV (~9%). Consequently the PA signal can be modeled as a linear function of concentration in the full range from 0.25- to 90,000-ppmV ammonia. This range extends over 5 orders of magnitude, as expected for PA detection!

The linear dependence of the PA signal on concentration and the known behavior of the background and noise facilitate the calibration of the PA detector. In principle, it is sufficient to determine the sensitivity by measuring the PA signal (amplitude U_{PA} and phase θ_{PA}) of one certified gas mixture at a sufficiently high partial pressure (for $x \gg x_{min}$: $S \gg B$, N and $U_{PA} \approx S$) and to fit a straight line through the origin and this calibration point. The slope of this line gives the value of parameter a in Eq. (2). The amplitude and the phase θ_{BG} of the background can be determined by measurement of the PA signal of pure N_2, and the noise N can be measured by blocking of the laser light. The amplitude of the background can be regarded as parameter c. The acoustic and electronic noises always contribute to the measured background value. The random noise, however, does not influence the phase of the background. Therefore the value of parameter b in Eq. (2) can be written as

$$b = -2a\sqrt{c^2 - N^2}\cos(\theta_{PA} - \theta_{BG}). \tag{4}$$

Consequently all parameters of the fit function of Eq. (2) can be determined by independent measurements and the concentration x can be calculated from the measured PA signal as follows:

$$x = \left(\frac{U_{PA}{}^2 - c^2}{a^2} + \frac{b^2}{4a^4}\right)^{1/2} - \frac{b}{2a^2}. \tag{5}$$

The limiting sensitivity of the PA detector for NH_3 can be estimated from the standard deviation of the data points in Fig. 4. The average standard deviation, expressed in concentration, was 0.2 ppmV. This value can be regarded as the precision of the measurements and also as the limiting sensitivity at $S/N = 1$. The corresponding minimum detectable absorption coefficient was $\alpha_{min} \approx 3.4 \times 10^{-8}\ cm^{-1}$ and the optical density was $\alpha_{min} l \approx 1.4 \times 10^{-7}$. These numbers clearly indicate the high performance of the present diode-based PA detector for NH_3 detection.

Because the PA signal is proportional to the absorbed light power, it is better to characterize the sensitivity S_{PA} of the PA detector by the expression $S_{PA} = \alpha_{min} P = 1.4 \times 10^{-9}\ cm^{-1}W$, where P is the incident laser power in watts. For a given species and absorption wavelength the sensitivity can be improved by use of lasers with higher power. Because the power of diode lasers currently available is not very high (<50 mW), a sensitive detection technique is crucial. Note that the above expression for the sensitivity is valid only if the linewidth of the exciting light is much smaller than the absorption linewidth. This requirement is always fulfilled for DFB diode laser spectroscopy of gases at ambient pressure.

Kopie bereitgestellt durch Universitaetsbibliothek der Universitaet der Bundeswehr Hamburg

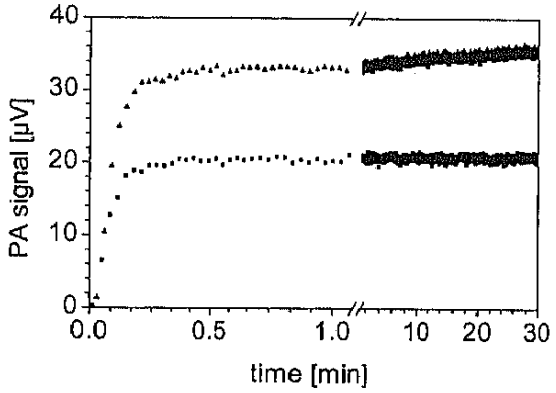

Fig. 6. Comparison of the rise of the PA signal after the flow is switched from pure N_2 to a 50-ppm NH_3–N_2 mixture for a cleaned brass cell (upper curve) and PP cell (lower curve).

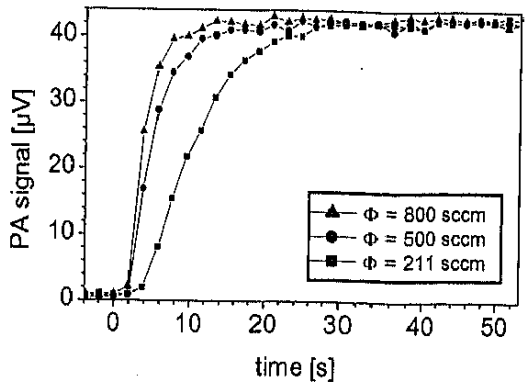

Fig. 7. Response time of the PP detector at different flow rates Φ.

C. Response Time of Photoacoustic Detectors

We measured the response time of the PA detector by suddenly switching the gas flow from pure N_2 to an NH_3–N_2 mixture. A special four-way valve was used, which allowed a change of the flow direction without interrupting the gas flow (see Fig. 1). In this way sudden concentration changes, caused by pressure transients, could be avoided. The time behavior of a PA signal typical for a cleaned cell can be seen in the upper curve of Fig. 6. Because of the fast gas exchange, the PA signal rises nearly instantaneously within a few seconds, but then a rather slow increase follows. The PA signal did not stabilize on a time scale of minutes, as can be seen in Fig. 6.

This behavior is typical for polar molecules in a metal cell. It was proved that adsorption of NH_3 molecules at the cleaned inner surfaces of the PA detector was responsible for this observation.[11] When the incoming concentration suddenly increased, some of the NH_3 molecules were adsorbed, thus reducing the concentration in the gas phase. An inverse process can be monitored when the incoming concentration drops suddenly. In this case NH_3 molecules desorbing from the walls increase the concentration in the gas phase. Therefore reliable concentration measurements can be carried out only after stabilization of the gas-phase concentration. Unfortunately, in this case the response time of the detector will be determined by the time needed for signal stabilization. Although this period can be reduced if a higher-volume flow is applied, it still remains much higher than the gas-exchange time.

It was shown in a recent, detailed study of adsorption and desorption effects of NH_3 measured by the PA technique[11] that these effects can be essentially eliminated if PP is used for the PA detector and the cell walls are heated to 40–50 °C. The lower curve in Fig. 6 indicates the dramatic improvement achieved. The PA signal becomes nearly constant immediately after the fast onset. The response time of the PP detector was investigated with different flows. The curves presented in Fig. 7 show that the rise time of the PA signal corresponds to the flow-through time of the gas mixture. The measured values are in good agreement with a theoretical model that takes into account the gradual increase of concentration that is due to mixing of the old and the new gas components in the acoustic filter part of the detector. The resulting response time of the PA detector at 500-SCCM flow was approximately 10 s for a 50-ppm mixture of NH_3 in N_2. Thus fast changes of NH_3 concentrations at the inlet of the PA detector could be followed essentially in real time.

Generally speaking, the response time of a gas-detection system is limited by the combination of the following factors:

1. the time that is required for a measurement point (including averaging)
2. the gas-exchange time that depends on the volume and the flow velocity
3. the time delay that is due to adsorption–desorption processes.

The time needed for the measurement and the gas exchange can be easily measured or estimated, and they are independent of the concentration and the nature of the gas molecules detected. The time delay resulting from adsorption–desorption processes is different and may depend on the gas species, the material of the cell, the flow rate, and the concentration. Therefore it is difficult to compare different systems with regard to this aspect. Further details can be found in Ref. 11.

4. Discussion

A. Comparison of Photoacoustics and Optical Detection

The comparison of PA gas detection with other established detection methods, such as gas chromatography, mass spectrometry, or FTIR spectroscopy, is quite difficult because of the different physical concepts and sampling methods. Because PA spectroscopy can be regarded as a specific direct detection of absorption, it is straightforward to compare the PA sensor with optical detection by use of the same sample cell. Two papers have been published on a direct

Kopie bereitgestellt durch Universitaetsbibliothek der Universitaet der Bundeswehr Hamburg

Table 1. Comparison of the Optical Multipass and PA NH_3 Sensors

Characteristics	Optical Multipass Sensor	PA Detector
Detection wavelength (nm)	1531.64–1531.70	1531.69
Pressure (Torr)	100	760 (1 bar)
Sensitivity for NH_3 at SNR = 3 (ppm)	0.7	0.6
Sensitivity in optical density	3×10^{-4}	1.4×10^{-7}
Sensitivity in absorption coefficient (cm^{-1})	8.3×10^{-8}	3.4×10^{-8}
Fluctuation (standard deviation) at 5 ppm (ppm)	0.2	0.2
Time of a single measurement (s)	30	2
Gas-exchange time (minimum)	4 min	4 s
Dynamic range	Not indicated	0.2–90000 ppm (linear)
Flow rate (SCCM)	10	300
Measured components	NH_3, CO_2	NH_3
Calibration with gas mixtures	1 point at 5 ppm	3 points (5, 50, 100 ppm)

comparison of these two methods.[9,16] The reported results were controversial; the PA method was found to be ~3 orders of magnitude more sensitive in the first paper and more than 1 order of magnitude worse in the second. Because the first experiment was optimized for PA detection, whereas the second one was optimized for optical detection, these works cannot be used for a reliable comparison of PA and optical absorption methods.

A recent publication on NH_3 detection by diode laser spectroscopy offers a unique possibility for a comparison of the two techniques.[7] In this study the same NH_3 absorption line was used as in the present experiments. Because the measurements were carried out at 100-Torr pressure, two neighboring absorption lines of NH_3 could be distinguished (Ref. 7, Fig. 6) in the wave-number range 6528.70–6529.00 cm^{-1}. The same lines were observed photoacoustically in an earlier study (Ref. 17, Fig. 2c), also performed at 100 Torr in the wave-number range from 6528.3 up to 6529.6 cm^{-1}. At ambient pressure three lines overlap and form one broadband (Ref. 17, Fig. 3c). The peak of this broadband is close to the wavelength of the stronger line observed in Ref. 7, whereas the asymmetric broadening of the line is caused by the second absorption line of NH_3, and the shoulder of the broadband is due to the third absorption line. Only the first two lines are in the wave-number range used in the measurements in Ref. 7.

The main components of the optical sensor were a fiber-coupled 15-mW DFB diode laser, a compact Herriot cell with 36-m path length, and a dual-beam autobalanced InGaAs detector.[7,8] The sample gas was sucked through the multipass cell at a rate of 10 SCCM by a two-stage diaphragm pump at 100-Torr pressure. Because the volume of the Herriot cell was ~0.3 l, a system response time of at least 4 min was expected.

NH_3 concentration measurements were performed in the following way. The laser was scanned over the 0.3-cm^{-1} wave-number range at a rate of 20 Hz. The transmitted light power was measured with a dual-beam autobalanced InGaAs detector, and 500 scans were averaged to give a single measurement. More details on these measurements and data processing can be found in Ref. 7.

The time for a single measurement, including data processing, was ~30 s; the sensitivity of the method was 0.7 ppm at a signal-to-noise ratio (SNR) of SNR = 3. In Table 1 the overall performances of the multipass optical NH_3 sensor and the single-pass PA NH_3 detector are compared. As can be seen, the PA detector is not only considerably simpler and cheaper but also provides a clearly higher sensitivity.

B. Comparison of Photoacoustic Detection with a Diode Laser and a Quantum-Cascade Laser

PA NH_3 concentration measurements with an 8.5-μm DFB QC laser have been published recently.[12] NH_3 absorption at 8.498 μm was used to generate the PA signal. The absorption coefficient of NH_3 is 14.8 cm^{-1} at this IR wavelength. NH_3–N_2 mixtures with different concentrations were measured in a continuous-flow mode of 2 l/h (~33 SCCM). A sensitivity of 100 ppbV (SNR = 1) was reported at 16-mW laser power. The measurements were carried out at 1 bar and 300 K; thus the relevant NH_3 feature of the spectrum contains unresolved absorption lines. The NH_3 feature was scanned, and the integrated PA signal was used as a measure of the NH_3 concentration. The scan time was 10 min for a single concentration measurement.

Real-time concentration monitoring was also performed in this work.[12] A mixture with 100-ppmV NH_3 was injected into the PA detector for short periods between 1 and 200 s. NH_3 absorption–desorption cycles produced a variation of the peak height for identical injection times. The integrated areas remained constant for identical integration times, despite the variation of the peak amplitude. These observations are in agreement with our previous investigations of the adsorption–desorption process in PA NH_3 measurements.[11]

The main characteristics of NH_3 detection with the QC laser and the NIR diode laser are compared in Table 2. The sensitivity of the differential PA detector is ~10 times that of the PA detector used in the QC laser experiments. Because no wavelength scan was applied in the NIR measurements, the time of a

Kopie bereitgestellt durch Universitaetsbibliothek der Universitaet der Bundeswehr Hamburg

Table 2. Comparison of PA NH_3 Detection with QC (IR) and NIR Lasers

Characteristics	QC (IR)	NIR Diode
Detection wavelength (μm)	8.498	1.531
NH_3 absorption coefficient (1 bar) (cm^{-1})	14.8	0.17
Sensitivity for NH_3 at SNR = 1 (ppm)	0.1	0.2
Laser power (mW)	16	42
Operating temperature (deg K)	~50	~300
Mode of operation	cw	cw
Sensitivity of the PA detector (W cm^{-1})	1.4×10^{-8}	1.4×10^{-9}
Time of a single measurement	10 min (wavelength scan)	2 s (single point)
Gas-exchange time (minimum)	Not indicated	4 s
Flow rate (SCCM)	33	300
Measured components	NH_3, H_2O	NH_3
Calibration with gas mixtures	No calibration	3 points (5, 50, 100 ppm)

single measurement was much shorter than in the DFG QC laser case. On the other hand, a wavelength scan delivers more information than a measurement at a fixed wavelength. However, for monitoring just NH_3 in air a single wavelength is sufficient, although the interfering CO_2 absorption line (see Table 1, Line C in Ref. 7) near the selected NIR NH_3 line may disturb the NH_3 measurement below 100 ppbV.

5. Conclusions

PA trace-gas monitoring by use of overtone and combination band excitation with NIR diode lasers can compete with optical multipass sensors operating in the NIR region and with PA detection by use of currently available IR QC lasers. The excellent performance of the PA detector described here is based on a differential cell design, high flow rates, and a novel method of data acquisition and evaluation. The main advantages of PA detection over optical multipass arrangements are a faster response time, a larger linear dynamic range, and simplicity and robustness of the setup. The achievable absorption (and concentration) sensitivities are comparable for the two methods.

PA detection with IR QC lasers is potentially superior to NIR detection because of the substantially higher absorption coefficients in the mid-IR range (up to 2 orders of magnitude). The advantage of the higher absorption coefficient, however, could not be utilized in the NH_3 measurements cited because the adsorption–desorption processes caused problems at the low flow rate used. Reliable NH_3 detection can be carried out only by continuous flow with sufficiently high flow rates.

A disadvantage of PA detection is that wavelength scans cannot be performed so quickly because of the time needed for averaging the acoustic signal. This time is usually ~1 s, and thus at least a few minutes are required for wavelength scans. This is long compared with the scan periods realized in the optical systems, which are in the 10-ms range (and can be even shorter if high-speed photodetectors are used). Therefore optical multipass systems provide a better performance for measurements involving an absorption spectrum that extends over a larger wavelength range. However, the PA detection setup described here, owing to its advantages of a very simple design, high sensitivity, and ease of operation, is ideally suited for monitoring one or several components at fixed wavelengths with high sensitivity.

References

1. D. J. Brassington, "Tunable diode laser absorption spectroscopy for the measurement of atmospheric species," in *Spectroscopy in Environmental Science*, R. J. H. Clark and R. E. Hester, eds. (Wiley, New York, 1995), pp. 85–147.
2. M. Feher and P. A. Martin, "Tunable diode laser monitoring of atmospheric trace gas constituents," Spectrochim. Acta A **51**, 1579–1599 (1995).
3. M. Feher, P. A. Martin, A. Rohrbacher, A. M. Soliva, and J. P. Maier, "Inexpensive near-infrared diode-laser-based detection system for ammonia," Appl. Opt. **32**, 2028–2030 (1993).
4. R. M. Mihalcea, M. E. Webber, D. S. Baer, R. K. Hanson, G. S. Feller, and W. B. Chapman, "Diode-laser absorption measurements of CO_2, H_2O, N_2O, and NH_3 near 2.0 μm," Appl. Phys. B **67**, 283–288 (1998).
5. I. Linnerud, P. Kaspersen, and T. Jaeger, "Gas monitoring in the process industry using diode laser spectroscopy," Appl. Phys. B **67**, 297–305 (1998).
6. D. D. Nelson, M. S. Zahniser, J. B. McManus, C. E. Kolb, and J. I. Jiménez, "A tunable diode laser system for the remote sensing of on-road vehicle emissions," Appl. Phys. B **67**, 433–441 (1998).
7. R. Claps, F. V. Englich, D. P. Leleux, D. Richter, F. K. Tittel, and R. F. Curl, "Ammonia detection by use of near-infrared diode-laser-based overtone spectroscopy," Appl. Opt. **40**, 4387–4394 (2001).
8. M. E. Webber, R. Claps, F. V. Englich, F. K. Tittel, J. B. Jeffries, and R. K. Hanson, "Measurements of NH_3 and CO_2 with distributed-feedback diode lasers near 2.0 μm in bioreactor vent gases," Appl. Opt. **40**, 4395–4403 (2001).
9. M. Fehér, Y. Jiang, P. Maier, and A. Miklós, "Optoacoustic trace gas monitoring with near infrared diode lasers," Appl. Opt. **33**, 1655–1658 (1994).
10. A. Miklós, P. Hess, A. Mohácsi, J. Sneider, S. Kamm, and S. Schäfer, "Improved photoacoustic detector for monitoring polar molecules such as ammonia with a 1.53 μm DFB diode laser," in *Photoacoustic and Photothermal Phenomena: 10th International Conference*, F. Scudieri and M. Bertolotti, eds. (American Institute of Physics, Woodbury, N.Y., 1999), pp. 126–128.
11. A. Schmohl, A. Miklos, and P. Hess, "Effects of adsorption–desorption processes on the response time and accuracy of

Kopie bereitgestellt durch Universitaetsbibliothek der Universitaet der Bundeswehr Hamburg

photoacoustic detection of ammonia," Appl. Opt. **40**, 2571–2578 (2001).
12. B. A. Paldus, T. G. Spence, R. N. Zare, J. Oomens, F. J. M. Harren, D. H. Parker, C. Gmachl, F. Capusso, D. L. Sivco, J. N. Baillargeon, A. L. Hutchinson, and A. Y. Cho, "Photoacoustic spectroscopy using quantum-cascade lasers," Opt. Lett. **24**, 178–180 (1999).
13. J. Henningsen and N. Melander, "Sensitive measurement of adsorption dynamics with nonresonant gas phase photoacoustics," Appl. Opt. **36**, 7037–7045 (1997).
14. J. Henningsen and N. Melander, "A photoacoustic study of adsorption," in *Photoacoustic and Photothermal Phenomena: 10th International Conference*, F. Scudieri and M. Bertolotti, eds. (American Institute of Physics, Woodbury, N.Y., 1999), pp. 78–80.
15. A. Miklós, P. Hess, and Z. Bozóki, "Application of acoustic resonators in photoacoustic trace gas analysis and metrology," Rev. Sci. Instrum. **72**, 1937–1955 (2001).
16. S. Schaefer, M. Mashni, J. Sneider, A. Miklós, P. Hess, H. Pitz, K.-U. Pleban, and V. Ebert, "Sensitive detection of methane with a 1.65 μm diode laser by photoacoustic and absorption spectroscopy," Appl. Phys. B **66**, 511–516 (1998).
17. A. Miklós, Z. Bozóki, Y. Jiang, and M. Feher, "Experimental and theoretical investigation of photoacoustic signal generation by wavelength-modulated diode lasers," Appl. Phys. B **58**, 483–492 (1994).

Kopie bereitgestellt durch Universitaetsbibliothek der Universitaet der Bundeswehr Hamburg

Bestell-Nr: 2002042303112 lok.Nr:
PPN: APOPA
Bestelldatum 23-04-2002-15:55

Subito-Bestellung

normal

Tel: 06221/545984

Mail: peter.hess@urz.uni-heidelberg.de

AK Hess
Physikalisch-Chemisches Institut Unniversitaet Heidelberg
Im Neuenheimer Feld 253
DE-69120 Heidelberg

USER-GROUP-1

Kontaktperson
Mrs Andreas Schmohl
Andreas.Schmohl@urz.uni-heidelberg.de

Kunden-/Zugangsnummer
HSL9801683

Lieferbibliothek:
Universität der Bundeswehr Hamburg
Universitätsbibliothek
Holstenhofweg 85

22043 Hamburg
Germany

Tel. Fax +49 (040) 6541-xxxx
E-Mail: biblio@unibw-hamburg.de

Einzelrechnung
Rechnungsanschrift

Lieferschein / delivery note

odb. Nr. 01 /
Datum / date 24.4.02

Lieferung einer Aufsatzkopie per / delivery of article by
☙ Post /mail ☙ E-Mail /ARIEL ☙ Fax
☙ Eildienst / express delivery
☙ Fernleihe eines Buches - einer Mikroform / lending of book - microform

9 Kopien / copies

Wir berechnen für unsere Lieferung / price EUR 4.00

Rechnung folgt - Bitte veranlassen Sie erst dann eine Zahlung, wenn die Rechnung bei Ihnen eingetroffen ist.
Bills are mailed every three months or according to arrangements.

Verfasser: (Aufsatz) a. Schmohl, a. Mikl s, p. Hess

Titel: (Aufsatz) detection of ammonia by photoacoustic spectroscopy with ssemiconductor lasers

Seiten: 1815-1823

Titel (Monographie/ Zeitschrift)

Applied optics
Washington, DC
Soc.
0003-6935/n

Standort:

PHY 415:Z00797 / MB

Band Heft 41/9

Jahrgang 2002

Lieferform: PDF

Lieferart: E-Mail alt. Post

Lieferung erwünscht bis:
26-04-2002

2002042303112

Bemerkungen:

Wir weisen Sie als Empfänger darauf hin, daß Sie nach geltendem Urheberrecht die von uns übersandten Vervielfältigungsstücke ausschließlich zu Ihrem privaten oder sonstigem Gebrauch verwenden und weder entgeltlich noch unentgeltlich in Papierform oder als elektronische Kopie verbreiten dürfen.
Universität der Bundeswehr Hamburg, Universitätsbibliothek

Kopie bereitgestellt durch Universitaetsbibliothek der Universitaet der Bundeswehr Hamburg