Photoacoustic Spectroscopy in Trace Gas Monitoring

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1 INTRODUCTION

A gaseous molecule that absorbs electromagnetic radiation is excited to a higher electronic, vibrational, or rotational quantum state. Generally, depopulation of this quantum state to lower lying states occurs either via fluorescence or via collisions; the latter gives rise to a temperature increase of the gas due to energy transfer to translation. This nonradiative relaxation process occurs when the relaxation time can compete with the radiative lifetime of the excited energy levels. Radiative decay has a characteristic lifetime of $10^{-7}$ s at visible wavelengths as compared to $10^{-2}$ seconds at 10 $\mu$m. For nonradiative decay these values depend on the pressure ($\tau$ inversely proportional to the pressure) and can vary strongly at atmospheric pressures ($10^{-3}$ – $10^{-8}$ s).

By modulating the radiation source at an acoustic frequency, the temperature changes periodically, giving rise to a periodical pressure change. The modulated pressure will result in an acoustic wave, which can be detected with a sensitive microphone. The amplitude of the detected sound is proportional to the concentration of the probed molecules. Laser-based photoacoustic detectors are able to monitor trace gas concentrations at atmospheric conditions with orders of magnitude better sensitivity as compared to conventional scientific instrumentation; in addition, they are able to monitor noninvasively and on-line under dynamic conditions.

2 HISTORICAL OVERVIEW

The photoacoustic effect was first reported by Alexander Graham Bell in 1880\(^{(1)}\); he discovered that thin discs emitted sound when exposed to a rapidly interrupted beam of sunlight. In a later experiment,\(^{(2)}\) he removed the eye piece of a commercial spectroscope and placed absorbing substances at the focal point of the instrument. The substances were put in contact with the ear by means of a hearing tube (Figure 1) and he found ‘good’ sounds in all parts of the visible and invisible electromagnetic spectrum of the sun. Other publications on this phenomenon followed this first work; we mention here the works of Röntgen,\(^{(3)}\) Tyndall,\(^{(4)}\) and Preece.\(^{(5)}\)

However, owing to the lack of a quantitative description overview, attention is focused onto the description of devices and equipment; they determine the detection limits and selectivity. Applications are discussed with emphasis on environmental monitoring, medical applications and biological applications (such as post-harvest physiology, plant physiology, microbiology, and entomology).
and the lack of sensitive microphones, the interest in the photoacoustic effect soon declined.

In 1938, Viegerov refined the photoacoustic technique for the first spectroscopic gas analysis; thereafter Pfund and Luft measured trace gas absorption spectra with an infrared broadband light source down to the part per million level. By the end of the 1960s, after the invention of laser, the scientific interest expanded again. In 1968, Kerr and Atwood utilized laser photoacoustic detection to obtain the absorption spectrum of small gaseous molecules. Owing to the high spectral brightness of lasers and improved phase-sensitive lock-in techniques to amplify the acoustic signal, they were able to determine low concentrations of air pollutants. Kreuzer demonstrated that it was possible to detect concentrations of 10 ppbv (1ppbv = $1 \times 10^6$) of methane in nitrogen, using an intensity-modulated infrared (3 µm) He–Ne laser. Patel demonstrated the potential of the technique by measuring the NO and H2O concentrations at an altitude of 28 km with a balloon-borne spin-flip Raman laser. From hereon, the photoacoustic effect was introduced into the field of trace gas detection with all its environmental, biological, and medical applications.

### 3 DEVICES AND EQUIPMENT

#### 3.1 Nonlaser Light Sources

Lasers are not essential to operate photoacoustic gas detection systems. Although the spectral power density of broadband infrared lamps is orders of magnitude lower as compared to lasers, they have substantial advantages such as wide wavelength coverage, reliability, and cost effectiveness. Such infrared lamp sources in combination with various photoacoustic detection schemes are commercially available for trace gas detection at ppmv levels for a wide range of molecular gases such as CO, CO2, NO, N2O, SO2, CH4, C2H4, and C3H8. Such design is a direct result of the developments made by Luft and coworkers in the 1950s and 1960s.

The infrared-lamp-based gas analyzer uses a photoacoustic detection scheme that is able to detect a specific gas out of a multicomponent gas mixture avoiding cross interferences. In this instrument, selectivity is achieved by comparing the direct absorption in a sample cell to that in a reference cell (Figure 2). After passing the sampling cells, each attenuated light beam enters a second detection cell, filled only with the gas of interest (e.g. CO2); the detection cells are interconnected via a membrane connected to a capacitance. Since the dual beam is modulated by a chopper, the difference in acoustic energy reflects the difference in absorption and thus the concentration difference between sample cell and reference cell. Selection of wavelength occurs by the species under investigation itself in such a way that all wavelengths at which absorption occurs are simultaneously active. When there is no spectral overlap from other gases, additional absorptions in the sample cell will not contribute to the acoustic signal; the light passes the detection cell unattenuated. When a specific compound, e.g. H2O, causes spectral overlap, an extra cell can be placed in the light path filled with the interfering gas. This cell completely attenuates
Infrared gas analyzer with photoacoustic detection scheme to detect a specific gas out of a multicomponent gas mixture thereby avoiding cross interference (ABB GmbH, Frankfurt). Light from the infrared source is split into two paths. The chopper modulates the intensity for both paths. The filter volume in each path serves to filter out light of wavelengths not needed for the detection process; they can be filled with gases, the absorption spectra of which do not overlap with those of the species under scrutiny. M1 and M2 serve as measuring cell and reference cell, respectively. With the help of the equalizer, both light intensities become equal before entering the last cell. The last cell consists of two compartments with a membrane in between. Both compartments are filled with the gas under investigation so that all wavelengths characteristic for this gas contribute to the signal. If the attenuation differs in M1 from that in M2, the membrane starts to oscillate with the frequency of the chopper. This oscillation (typically a few hertz) is detected capacitively.

Instead of using optical filters, if photoacoustic detection is also combined with Fourier transformed infrared (FTIR) spectroscopy higher spectral resolution can be achieved. FTIR is a widely used method for obtaining broad infrared spectra of a sample. Infrared radiation is split in a Michelson interferometer where half of the light passes through to a fixed mirror and the other half is reflected toward a moving mirror. The two beams recombine and pass through a gas cell where the sample absorbs light at molecule-specific frequencies. Instead of using a large volume multipass cell, a small volume (30 mL) photoacoustic cell is used. In this way sensitivity of gas-phase FTIR is improved to sub-ppmv levels for a wide range of gases.

Nowadays, light emitted diodes (LEDs) are an intermediate alternative with reduced spectral range, but with increased power density as compared to infrared lamps (Figure 4). LEDs are very convenient sources for PA since they are small in size and have low power consumption. The full width at half maximum (FWHM) of the emission spectrum is typically 10–20% of its peak wavelength, and is sufficient for most single optical filters in a rotation cartwheel before the light passes through the photoacoustic gas sampling cell, the specific infrared wavelength is selected at which the gas of interest has its strongest absorption bands. Such a system can measure concentrations of up to five component gases and water vapor in any air sample. Detection limit is gas dependent, but is typically in the sub-ppmv region. Such instruments require no consumables and very little maintenance, and are therefore ideally suited for permanent monitoring tasks (environment and industrial).

Figure 3  Light from an infrared light source is reflected off a mirror and is passed through a mechanical chopper and then through one of the optical filters in the filter wheel (LumaSense Technologies, Denmark). The gas being monitored selectively absorbs the light transmitted by the optical filter, causing an increase in the temperature of the gas. The filter wheel turns so that light is transmitted through the next optical filter, and the new signal is measured. The number of times this step is repeated is dependent on the number of gases being measured. The response time is 30 s if five gases and water vapor are measured.
gas measurement. LED output is easily modulated by current pulsing with frequencies up to several megahertz; its brightness and on/off contrast do not decline as modulation frequency is increased as with traditional blackbody emitters. With mid-infrared LEDs photoacoustic trace gas detection is performed in the 3–7 µm wavelength range, using a cantilever instead of a microphone. Detection at the low ppmv levels can be achieved for gases such as methane, propane, CO₂, and SO₂ in 1 s sample integration time.

3.2 Laser Light Sources

High spectral brightness renders cw (continuous wave) laser sources ideally suitable for photoacoustic trace gas detection. In contrast to direct absorption techniques, the photoacoustic signal is proportional to the laser power. From the Lambert–Beer law one finds for small absorptions

\[ P = P_0 e^{-\sigma N l} \Rightarrow P_0 - P \approx P_0 \sigma N l \]  

with \( P_0 \) and \( P \) are the laser power before and after the photoacoustic cell, respectively; \( \sigma \) the absorption cross section per molecule (cm²), \( N \) the number of absorbing molecules per cubic centimeter, and \( l \) the absorption path length (cm). The absorbed power \( (P_0 - P) \) is converted into acoustic power recorded by a microphone. As can be seen from this equation, for small absorptions, the generated acoustical signal is proportional to the incoming laser power (high laser powers are advantageous) and the gas concentration (linearity of the signal). A nonlinear absorption response occurs only in focused high power laser beams as a result of saturation. Normally, the pumping rate to a higher rovibrational level is proportional to the laser light intensity; in the case of saturation it exceeds the collisional de-excitation rates.

Besides sensitivity, lasers achieve high selectivity. The first practical lasers that were used to detect trace gases were CO₂ lasers. At present, photoacoustic detection goes together with laser light sources ranging from the infrared to the visible and UV, including both cw and pulsed lasers.

In the mid-infrared wavelength region, cw CO₂ (wavelength region from 9 to 11 µm) and CO lasers (4.6–8.2 µm) were among the most used. The developments in solid-state physics and nonlinear optics have expanded the potential for photoacoustic spectroscopy to other wavelength regions. The recent availability of high power (cw and pulsed), quantum cascade lasers (QCLs) operating at room temperature with power levels
up to 1 W has boosted photoacoustic spectroscopy in the mid-infrared wavelength region. Even more, single-mode tuning ranges, approaching 300 cm\(^{-1}\), are now achievable from commercially available external cavity QCL products. QCLs operate in the mid-infrared wavelength region from 3.5 to 24 µm.\(^{(16,17)}\) For the 2.5–5 µm region, cw periodically poled lithium niobate optical parametric oscillators (PPLN-OPOs) have become available at high power (several watts) level and narrow linewidth. Nowadays, OPOs are pumped by high power, near-infrared lasers with excellent spectroscopic properties (narrow linewidth, Gaussian beam profile, fast wavelength scanning), which the OPO can convert into the mid-infrared wavelength region due to its instantaneous nonlinear effects.\(^{(18)}\)

In the wavelength region around 1.5 µm, ‘Telecom’ diode lasers have the advantage of small size, reliability, and low costs. Owing to their low power, the combination with photoacoustic spectroscopy is not always very favorable. However, the development of fiber amplifiers in this wavelength region could overcome this disadvantage. Telecom lasers are well suited to be used in gas sensing instruments in which the sensitivity is limited to the ppmv range. These lasers are tunable only over a limited wavelength region, but larger tuning ranges can be obtained by external cavity setups (external cavity diode laser). The near-infrared diode lasers have the main disadvantage that they operate at the weak overtone absorption bands instead of the strong fundamental vibrational absorption bands located in the mid-infrared wavelength region. In the 650–1000 nm (near-infrared wavelength region), cw titanium sapphire ring lasers have been used intensively for high-resolution studies of weak overtone absorption spectra of molecular gases. High overtone spectroscopy profits from sensitive photoacoustic detection, since one deals with high vibrational excitation, where fluorescence-based techniques do not work. Electronic spectroscopy with light sources in the visible or in the ultraviolet does not immediately ask for photoacoustic detection because other techniques [e.g. laser-induced fluorescence (LIF) or resonance-enhanced multiphoton ionization (MPI)] provide more powerful means.

In general, the highest sensitivities of photoacoustic detection have been achieved with modulated cw lasers, but then photoacoustic spectroscopy can also be performed using pulsed lasers. By combining pulsed lasers with gated photoacoustic detection in a boxcar integrator, the pulse character of the generated signal allows suppression of signals from other sources arriving at other times at the detector (piezo transducer or microphone). However, owing to the high pulse intensities in the laser pulse, absorptions by molecular gases can be nonlinear (multiphoton absorption, saturation) generating pulse-to-pulse signal fluctuations and thereby reducing detection sensitivity.\(^{(19)}\) Cw lasers are more sensitive (up to a factor 10\(^2\)) in trace gas detection when compared to pulsed lasers. Therefore, if no other arguments prevail, the use of cw lasers is recommended.

### 3.3 Photoacoustic Cells

#### 3.3.1 Nonresonant Cells

To perform trace gas detection, an ideal photoacoustic cell should amplify the generated sound originating from the molecular gas absorption, and reject any acoustic (and electric) noise and in-phase infrared absorption from other materials. Interfering gases should be distinguished by spectroscopic or physical methods. For gas-phase measurements, the resonant cells are combined with modulated cw lasers and lock-in amplifiers; pulsed lasers are combined with piezoelectric detectors and boxcars. The need for selective amplifiers arises from the necessity to lower acoustic and electric noise levels thus improving the signal-to-noise ratio. Other requirements for photoacoustic cells are low gas consumption and a fast response; for this the active volume of the cell should be small so that no dilution can take place when the trace gas and its carrier flow through the acoustic cell. If we consider a nonresonant, cylindrical cell, its performance can be expressed as its efficiency to convert absorbed photon energy into acoustic energy, i.e. \( p_{\text{gas}} = F \Delta P \), with \( p_{\text{gas}} \) the generated acoustic pressure in the gas and \( \Delta P \) derived from Equation (1). The cell constant \( F \) (Pa m W\(^{-1}\)) can be derived by

\[
F_{\text{nonresonant}} = \frac{G(\gamma - 1) l_{\text{nr}}}{2\pi \nu V_{\text{nr}}} \tag{2}
\]

where \( l_{\text{nr}} \) and \( V_{\text{nr}} \) are the length and the volume of the cell, respectively, \( \gamma \) the specific heat constant, \( \nu \) the modulation frequency, and \( G \) a geometrical factor on the order of one. From the above formula, one can derive that \( F \) is independent of the cell length. The diameter should be as small as possible to generate high signals, just large enough to allow proper alignment of the incident light beam. To minimize the detection of absorption by the cell windows, one has to maximize the cell length; the energy absorbed by the windows is then distributed over a larger volume. The photoacoustic signal decreases with higher modulation frequencies; therefore, it is advantageous to use low modulation frequencies.

#### 3.3.2 Resonant Cylindrical Cells

In a resonant cell, the modulation frequency is chosen to match one of the resonant frequencies of the cell. This produces a standing, amplified, sound wave in the resonator. For a gas-type resonant cell, two varieties...
of acoustical resonators have found widespread use: the Helmholtz resonator and the cylindrical resonator excited in a longitudinal, radial and/or azimuthal mode (Figure 5).

For cylindrical resonant cells, one has to multiply the cell constant $F$ (Equation 2) with the quality factor $Q$ of the generated acoustic resonance:

$$F_{\text{resonant}} = \frac{G(\nu - 1)l_r Q}{2\pi V_r}$$

where $l_r$ and $V_r$ are the length and the volume of the acoustic resonator, respectively; $Q$ equals the ratio of the energy stored in the acoustical standing wave over the energy losses per cycle. For resonant cylindrical cells, one can derive for the cell constant $F_{\text{resonant}} \propto \sqrt{l_r/R}$, where $R$ is the radius of the resonator.$^{(20)}$ Cell geometries with large diameter-to-length ratios, to excite the resonance in the radial or azimuthal acoustic mode, possess high $Q$ values and high resonance frequencies; they have, however, low $F$ values. Photoacoustic cells with high $Q$ values are sensitive to long-term drifts, for example, because of thermal expansion if the temperature is not carefully controlled. Such cells require active locking of the modulation frequency on the resonance frequency of the cell. In longitudinally excited resonators, a smaller acoustic gain, as a consequence of a relatively low $Q$ value, is compensated for by the signal gain due to the smaller diameter (Figure 6).

The resonant acoustical amplification is limited by various dissipation processes, which can be divided into surface and volume effects. Main surface losses are viscous and thermal losses at the resonator surface, microphone losses, and acoustic wave scattering losses at obstacles inside the cell. The less-important volumetric losses are radiation losses, free-space viscous and thermal losses, and dissipative relaxation processes within the absorbing gases. For a cylindrical resonator, the resonant frequencies are given by Miklos et al.$^{(22)}$

$$v_{\text{amp}} = V_s \left[ \left( \frac{a_{\alpha \nu n}}{d} \right)^2 + \left( \frac{p}{2f} \right)^2 \right]^{1/2}$$

where $V_s$ is the sound velocity of the gas inside the cavity, $d$ the cell diameter, $l$ the axial length, $p = 0, 1, 2, 3 \ldots$ axial mode numbers, $a_{\alpha \nu n}$ is the $n$th root of the derivative of the Bessel function, and $dJ_n/dr = 0$ at $r = R$ (e.g. $a_{00} = 0, a_{01} = 1.2197, a_{10} = 0.5861,$ and $a_{11} = 1.6970$).

### 3.3.3 Helmholtz Resonant Cells

Another type of resonant cell is a Helmholtz resonator, it consists of a closed volume (cavity) connected via a long narrow tube to the microphone volume (Figure 7). It is the acoustic equivalent of a mechanical oscillator composed of a mass (long tube) and a spring (cavity). The oscillation frequency ($v_H$) of the system depends on the length ($l_H$) and cross section ($A_H$) of the tube (or duct) and the volume ($V_H$) of the cavity via the following relation:

$$v_H = V_s \left( \frac{A_H}{V_H} \right)^{1/2}$$

where $V_s$ is the velocity of sound.$^{(23)}$ Although the acoustical response of such a resonator is somewhat lower as compared to the response of the cylindrical resonators described above, this type of resonator has some advantages when low or high temperatures are needed. Microphones have a limited operating temperature range around room temperature. When gases are investigated at low (e.g. 80 K) or high (>350 K) temperatures, it is advantageous to have a homogeneous temperature distribution across the gas volume while the microphone operates at room temperature. The temperature gradient is over the long narrow tube of the resonator at which end the microphone is placed.

### 3.4 Photoacoustic Detectors

#### 3.4.1 Microphones

Pressure detection methods are widely available ranging from the large membranes as in the earliest designs of Luft$^{(8)}$ to piezoelectric transducers operating at megahertz frequencies. Normally, for photoacoustic detection of gases audio microphones are used. Microphones range

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Figure 6 Two photoacoustic cell types successfully used in trace gas detection. (a) A banana-shaped cell, where the laser beam enters from the left through a Brewster window (BW) to leave the central part \( l = \lambda / 2 \) of the resonator at the right BW.\(^\text{(21)}\) The position of the microphone M is indicated. The two pieces of length \( \lambda / 4 \) before and after the bends serve to suppress the window signal. The total length of the banana cell amounts to \( \lambda \). In the bends, the gas inlet and gas outlet (Gi and Go) are shown. (b) The open-organ-pipe cell; the main part is manufactured of a block of massive brass to suppress surrounding noise.\(^\text{(20)}\) The central organ pipe acts as an open resonator with length \( \lambda / 2 \); the resonator tube has a highly polished, gold-coated inner surface to minimize wall heating by stray light. The central position of the gas inlet (Gi) is essential to obtain short measuring times; only the resonator volume of 2.8 mL must be replenished before an independent concentration measurement can be performed. TAC: \( \lambda / 4 \) tunable air columns to suppress window signal. NF: \( \lambda / 4 \) notch filter to suppress acoustic in coupling of noise via gas inlet.

Figure 7 Sketch of a photoacoustic Helmholtz resonator.\(^\text{(24)}\)

from very small size (1 mm membrane) for hearing aid purposes behind the ear, to large size (25 mm membrane) very sensitive (1000 mV Pa\(^{-1}\)) professional microphones with a spectrally flat response to sound pressure (Bruel and Kjaer microphones). The small size microphones (such as from Knowles) have mostly a peak in acoustic amplitude response around 1 kHz with a typical response of 10 mV Pa\(^{-1}\). Besides that the latter are low cost, they have the advantage that they do not take up so much acoustic energy as compared to large size microphones.\(^\text{(20)}\) This is important in the case of resonant acoustic cells, for which increased friction losses will lower the quality factor of the resonator and, thus, the generated acoustic amplitude.

3.4.2 Quartz Tuning Fork

In gas-phase spectroscopy, the common approach is to use a resonant photoacoustic cell and accumulate the absorbed energy in the gas. However, an alternative developed approach is to store the absorbed energy in a sensitive element. A well-suited material for this is a high-Q crystal quartz element with piezoelectric properties. These elements are mass produced and inexpensive; every electronic watch or clock is built around a high-Q quartz crystal frequency standard. Usually, it is a quartz tuning fork (TF) with a resonant frequency close to 32.768 Hz (Figure 8). The mode at this frequency corresponds to a symmetric vibration (the prongs move in opposite directions). The antisymmetric vibration is
Figure 8 Optical configurations for photoacoustic signal detection with a TF: (a) the laser beam is perpendicular to the TF plane; (b) the laser beam is in the TF plane; (c) an acoustic resonator (sound tube) is added to enhance the signal. The laser beam is directed through the tube. The pressure antinode is in the center at the location of the tuning fork between the two pieces of the tube.

piezoelectrically inactive. These quartz TFs have recently become widely used for atomic-force and optical near-field microscopy and therefore their properties have been carefully analyzed. A typical watch TF has a Q value of 20,000 in vacuum; at normal atmospheric pressure, this is lower (∼8000) because of the viscous properties of air. Besides, its amplitude depends also on the pressure, which could be a drawback for studying mixtures or unknown components. The typical energy accumulation time at atmospheric pressure is 250 ms, which is quite longer than any practical gas-filled resonator.

The special features using a TF are as follows: (i) ambient acoustic noise is very low above 10 kHz; (ii) external sound will always excite both prongs of the TF and, as a result, will not excite the piezoelectrically active mode, in which the two prongs move in opposite directions; (iii) the width of the TF resonance at normal pressure is 4 Hz, and only frequency components in this narrow spectral band can produce efficient excitation of the TF vibration; (iv) the gas sampling volume is extremely small (0.15 mm³).

3.4.3 Cantilever-type Optical Microphone

Microphones, where the flexible membrane is strained over a frame or the pressure sensor is a thinner portion in a metal plate, are not very sensitive and the response is not linear. This is due to the fact that the material has to stretch out radially under the pressure variations. A cantilever-type pressure sensor has been proposed as shown in Figure 9. The cantilever size is 2 mm × 4 mm and made out of silicon. The cantilever moves like a flexible door because of its extreme thinness (5 µm) and the pressure variations in the surrounding gas. The frame around the silicon cantilever is thick (380 µm) and there is a narrow (30 µm) gap between the frame and the cantilever on three sides. As the pressure varies, the...

Figure 9 (a) The dimensions of the cantilever and the gap between the cantilever and frame. (b) The setup containing the cantilever is in principle the same setup as the nondispersive setup in Figure 2, but now with a cantilever detection setup. It consists of three cells: the reference cell, sample cell, and photoacoustic cell. The photoacoustic cell acts as a detector and includes high concentration of the gas to be detected. The cell is divided into two parts, A and B, which are separated by the cantilever and its frame. The position of the cantilever is proportional to the pressure difference between the cell parts A and B. The displacement of the cantilever end is measured continuously with a Michelson-type interferometer.
The movement of the free end of the cantilever can be about two orders of magnitude greater than the movement of the middle point of the tightened membrane under the same pressure variation. The larger sensitivity to pressure fluctuations means that it can also become more sensitive to flowing gases. The displacement of the cantilever is easily detected using optical interferences. With this setup, a detection limit of 0.9 ppmv for ethylene, 0.3 ppmv for methane, and 0.1 ppmv for carbon dioxide was achieved with a mechanically chopped blackbody radiator.

### 3.5 Special Designs

In the past, special designs have been developed for longitudinally, azimuthally, and radially resonant photoacoustic cells,\(^{22,27–29}\) even without windows\(^{30}\) to improve sensitivity.

In order to improve the selectivity, the combination of the Stark or Zeeman effect with photoacoustic detection represents an interesting solution for specific molecules such as ammonia (NH\(_3\))\(^{31,32}\) and nitric oxide (NO).\(^{33}\) The change in absorption at a specific laser frequency depends on the shift and splitting of the molecular absorption lines of the species under investigation. Although the method does not suffer from interference problems within multicomponent gas mixtures, there are some limitations. The detection is limited to molecules with a permanent electric or magnetic dipole moment; in addition, the shift or splitting of the lines should be observable within the pressure broadened Lorentzian profile at the overlap with the laser frequency. For ammonia at the 10R8 transition of the 12\(^{12}\)CO\(_2\) laser, these requirements are satisfied; Thöny and Sigrist\(^{31}\) showed that the absorption cross section changed by a factor of two at atmospheric pressure by applying an electric field of 16.7 kV cm\(^{-1}\).

Another way to improve the sensitivity for detection of a specific gas is changing the temperature. By increasing the temperature, the vapor pressure of, e.g. oil with low vapor pressure is increased, thereby improving the sensitivity. An elegant cell has been designed by Jalink and Bicanic,\(^{34}\) who combined a photoacoustic cell and a heat pipe keeping the microphone and windows at room temperature. In addition, a Helmholtz resonant photoacoustic cell (Figure 10) has been developed by Kästle and coworkers for quantitative, temperature-dependent investigations on fatty acids. The temperature of the water bath was varied between 278 and 350 K with a cold finger and two immersion heaters, while the temperature of the microphone was kept constant with a cooling/heating device.\(^{35}\)

![Figure 10](image)

**Figure 10** Photoacoustic cell applied for temperature-dependent investigations on fatty acids. The temperature of the water bath was varied between 278 and 350 K with a cold finger and two immersion heaters, while the temperature of the microphone was kept constant with a cooling/heating device.\(^{35}\)

3.6 **Sensitivity, Selectivity, Limitations, Interference, Detection Limits**

Laser-based absorption spectroscopy performs well in terms of sensitive and selective detection of trace gases and it allows on-line measurements. Its high sensitivity and selectivity are due to several important factors. Firstly, the narrow linewidth of lasers gives a high spectral power density as compared to broadband light sources. Especially for cw lasers, this linewidth is typically much narrower than the molecular absorption lines. This causes the total laser emission to be attenuated by the gas sample under investigation, instead of only a small fraction, as it is the case in broadband absorption. Thus, the absorption signal increases strongly because of its narrow linewidth. In addition, the selectivity improves because it enables a wavelength scan over an absorption feature. This helps to distinguish the target molecule from interfering compounds and background signals. Selectivity enhances further by the unique spectral absorption spectrum of each molecule, which corresponds to different rovibrational transitions of the molecule. Spectroscopic gas detection probes the internal structure of the molecule, whereas other techniques such as mass spectrometry assess only a global property of the investigated compound.

In the infrared fingerprint wavelength region (2.5–25 µm), molecules have strong absorption lines. Combined with highly sensitive spectroscopic methods, gases can be detected at trace levels below the ppbv range (1 ppbv = 1 × 10\(^{-9}\)). Here, a number of spectroscopic methods will be compared and applications will be shown for a variety of gases.

In the 1970 and 1980s fixed-frequency CO\(_2\) and CO lasers dominated the detection of molecular gases in the mid-infrared because of their high power (photoacoustic signal is proportional to the laser power) and wide wavelength coverage. One good example is the Q-branch...
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Figure 11  Absorption coefficients (atm\(^{-1}\) cm\(^{-1}\)) of C\(_2\)H\(_4\) at the CO\(_2\) laser lines in the 9–11 μm wavelength region.\(^{(37)}\) Owing to pressure broadening of the individual rotational lines of ethylene, there is a strong overlap at specific CO\(_2\) laser lines.

the \(\nu_7\) band of C\(_2\)H\(_4\) in the 10 μm region. The 10P\(_{14}\) CO\(_2\) laser line is in exact resonance (Figure 11) with this Q-branch and this resulted in an extremely low detection limit of 6 pptv (1 pptv = 1 : 10\(^{12}\)) for C\(_2\)H\(_4\) in nitrogen.\(^{(36)}\) Alternatives to fixed-frequency gas lasers at that time were liquid-nitrogen-cooled lead-salt diode lasers and color center lasers, generating only a few milliwatts of tunable laser radiation and subsequent low photoacoustic signals.

Over the past two decades, the selective detection of molecular gases improved strongly with the development of QCLs and OPOs. The invention of the QCL in 1994\(^{(38)}\) made it possible to operate current-driven diode-like lasers at room temperature\(^{(39)}\) in the mid-infrared wavelength region from 3 μm to as long as 20 μm.\(^{(16,40)}\) The first cw, quasi-phase matched, singly resonant OPOs, using PPLN crystals suitable for trace gas detection, were developed in 1996.\(^{(18)}\)

In order to have a maximum signal-to-noise ratio and, thus, an excellent sensitivity, one has to take into account the acoustical noise spectrum. The theoretical minimum acoustical noise results from random pressure fluctuations and their frequency distribution due to Brownian motion. The total power of these pressure fluctuations is constant, but the noise spectrum depends on the \(Q\) value of the acoustical resonance of the photoacoustic cell; a high \(Q\) value will significantly amplify noise power at these resonances. However, often this Brownian noise level is below what is produced by other noise sources such as electronic amplifier noise and external acoustical noise from the surroundings; their power decreases with increasing frequency. It is then advantageous to utilize a resonant cell to improve the signal-to-noise ratio. The resonance frequency might be chosen such that contributions from Brownian noise and amplifier/external noise become comparable. At resonance, external acoustical noise within the cell will be amplified at a high \(Q\) value. Here, acoustical shielding helps; that is, a proper cell wall construction (massive), material choice (brass) and good design of in- and outlet ports are required. For the latter, λ/4 notch filters (λ the acoustical wavelength) are positioned in line with the gas in- and outlet (Figure 6). In practice, by mounting a B&K 4179 condenser microphone on a well-shielded resonant (\(Q = 40\)) photoacoustic cell, the noise level of the complete system quoted by the manufacturer (microphone and amplifier) was one order of magnitude lower.\(^{(20)}\)

By definition, noise components do not possess a fixed phase relation with the periodical modulation of the light intensity. However, external perturbing sources may have a fixed phase relation, for example, the directly generated acoustical sound caused by chopping the light beam. They must be minimized in the same way as the external acoustical noise. In the case of a mechanical chopper, a good choice of the chopper position and removal of objects in the neighborhood of the chopper wheel are advantageous. A more serious problem is formed by the photoacoustic background signal; absorption of the light beam in the window material or light scattered/ reflected from the resonator wall causes a signal at the frequency of the modulated light beam. In resonant...
cells, using λ/4-tubes next to the windows can diminish window signals. These tubes, placed perpendicular to the resonator axis close to the windows, are tuned to the resonator frequency and act as notch interference filters for the window signals (see Figure 6). Influence of scattered light on the photoacoustic background signal can be minimized by use of highly reflecting, polished resonator wall material with a good thermal conductivity. In the case of infrared light, a polished gold-coated copper wall of the acoustical resonator has been found to work satisfactorily.

Amplifying photoacoustic signals using resonant cells, optical multipass arrangements, high laser powers, microphone arrays, reduced noise, and so on, are all used to reach the best sensitivity for molecular gas absorption. The sensitivity to trace a specific compound depends strongly on its spectroscopic properties. For example, closely spaced rotational absorption lines within a Q-branch of a strong vibrational transition help to reach low detection limits of such a gas.

Other effects can strongly limit the sensitivity or the accuracy of the photoacoustic signal. Reactive gases such as ozone are very difficult to quantify in absolute concentrations, although they exhibit a very strong absorption cross section in the infrared wavelength region, resulting in sub-ppb detection limits. Ozone is highly reactive, thus interactions with tubing walls, sampling cuvettes, and the photoacoustic cell induce rapidly decreasing ozone concentrations. In spite of these limitations, successful studies have been performed to quantify atmospheric ozone concentrations with CO2 laser\(^{(41)}\) and more recently with QCLs\(^{(42)}\). The nitrogen molecule (N\(_2\)) has a long vibrational lifetime of its first excited vibrational mode (\(\approx 1\) ms at 1 atmosphere at \(v_l = 2200\) cm\(^{-1}\)). Using kilohertz modulation of the laser beam, a phase shift may occur in the generated photoacoustic signal. Since, the detection with a lock-in amplifier is phase sensitive, this will result in a significantly reduced photoacoustic signal. A well-known example is the kinetic cooling effect of CO2 at CO2 laser wavelengths (9–11 \(\mu\)m).\(^{(43–45)}\) CO2 has a hot-band absorption in this wavelength region and is excited to the \(v_3\) vibrational level, which is almost resonant with the first vibrational level of N\(_2\) (Figure 12). Therefore, under atmospheric conditions, the energy absorbed by CO2 will only slowly be converted into a temperature and pressure increase of the gas.

N\(_2\) is not unique; similar effects can be observed with oxygen also. An example is CH\(_4\) \(v_4\) vibrational band at 1306.2 cm\(^{-1}\). This is the lowest vibrational mode of CH\(_4\); the collisional relaxation lifetime is therefore large compared to the lifetime of other molecules with a smaller energy gap between their lowest vibrational modes and the ground state. The adjacent \(v_2\) mode too (1533 cm\(^{-1}\)) becomes thermally populated (rate constant 13 \(\mu\)s\(^{-1}\) atm\(^{-1}\)).\(^{(46)}\) Oxygen has a near resonant vibrational level (1554 cm\(^{-1}\)) and only 170 collisions are needed to transfer energy to the vibrational mode of O\(_2\) (rate constant \(\approx 28\) \(\mu\)s\(^{-1}\) atm\(^{-1}\)).\(^{(47)}\) Since this is a rather fast process, most energy is deposited into O\(_2\) and then relaxes slowly to the ground vibrational state; in the case of pure O\(_2\), the average number of collisions required for relaxation to the ground state is \(8.3 \times 10^7\) (at standard temperature and pressure \(5 \times 10^9\)

---

**Figure 12** Vibrational energy level diagram for atmospheric species important in the transfer of energy absorbed by CO2 at 10.6 \(\mu\)m. The indicated relaxation times have been determined for the 1962 US Standard Atmosphere at sea level, assuming a relative humidity of 30\%.\(^{(41)}\) Note that the energy is given in kelvin, 1K = 0.695030 cm\(^{-1}\).
collisions per second take place). The much larger number density of O₂ as compared to CH₄ creates a buffer of vibrational energy leading to an effective transient cooling of the translational degrees of freedom. Owing to the needed high modulation frequency around 1 kHz in photoacoustics, this transient cooling by O₂ is observed as an amplitude decrease and a phase change.

 Addition of H₂O or SF₆ molecules (notorious relaxers) can reverse the situation. An example is shown with the strong rotational–vibrational absorption band of CO₂ at 4.23 μm. To overcome the slow vibrational relaxation of the excited CO₂ levels, 4% of SF₆ gas was added to the atmospheric mixture (Figure 13). In this way, it was possible to detect CO₂ down to 7 ppbv using 20 mW of the OPO light.(48)

 In other cases, limitations are caused by the presence of a complex mixture of gases to be investigated. Gases spectroscopically interfere if molecular absorption lines are close to each other. The most abundant infrared absorbing gases are water and carbon dioxide. To overcome such interferences, detection can be performed at reduced pressure, thereby reducing the pressure broadening. Gases can also be separated by gas chromatographic methods, selective trapping inside a cold trap (e.g. water),(49) or by a specific chemical reaction (e.g. removal of CO₂ by making KOH to react with K₂CO₃, and water with CaCl₂). In most cases, a small amount of the interfering compound remains present. To address this issue, a multicomponent analysis is necessary.

4 APPLICATIONS

4.1 Atmospheric Applications

Early attempts were made to measure stack gas emissions from power plants with laser photoacoustics. Owing to the high amount of nitrogen oxide compounds (NO and NO₂) in the emissions, they have a significant contribution in photochemical smog formation and acidification of the soil. To reduce the total amount of NO in the stack gas, NH₃ is added in the exhaust gas toward the chimney. Using a voluminous catalyst, NO reduction (within the stack gas) takes place. In order to check the performance and to avoid an excess of ammonia injection, the ammonia concentration in the chimney is monitored. For this, a CO₂-laser-based photoacoustic detection system was successfully applied for in situ monitoring of ammonia concentrations.(50) Owing to the difficulty, that is, hostile environment halfway up the chimney (vibrations, temperature fluctuations, etc.), concessions have to be made as to the sensitivity of the apparatus. With a nonresonant photoacoustic cell at 125°C a detection limit of 1 ppmv NH₃ was achieved in a multicomponent gas mixture containing 10–15% CO₂.

Another example of a mobile system was developed and used in a field campaign by Sigrist and Marinov.(51) Installed in a small trailer, the stress on the equipment is less severe. Thanks to this approach the system has been operational for years and has been applied for several field campaigns in urban and rural environments. For example, as part of an atmospheric pollution measurement campaign, they performed in situ measurements of NH₃, C₂H₄, and CO₂ concentrations at the mouth of a freeway tunnel with a time resolution of 1 min over a period of five weeks. Peak concentrations were observed at 600 ppb, 400 ppbv, and 1000 ppmv for NH₃, C₂H₄, and CO₂, respectively. Owing to these multicomponent gas mixtures, cross sensitivities in the absorption coefficients are induced and as a result detection limits are higher, as compared to those based on extrapolation from larger quantities of trace gases in a clean buffer gas. A mathematical analysis of the photoacoustic spectra of multicomponent mixtures is based on the weighted least squares fit of the measured spectra with spectra from pure compound spectra. The latter spectra are separately taken from trace gas mixtures in pure nitrogen or air.

More recently, photoacoustic measurements have been performed by using UV/visible light for the detection of important atmospheric gas of ozone. A frequency quadrupled Nd:YAG laser at 266 nm and a dual-cell photoacoustic detection system were used for the measurement of ozone concentration. The first cell contained the total gas sample while the gas entering the apparatus. With a nonresonant photoacoustic cell at 125°C a detection limit of 1 ppmv NH₃ was achieved in a multicomponent gas mixture containing 10–15% CO₂.

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Figure 13 Increase of photoacoustic signal as a consequence of the absorption of CO₂ is shown as a function of the added SF₆ concentration. The effect is shown for the R16 and R50 CO₂ line. (48)
the second cell was ozone-free using a catalyst. The calibrated instrument had a 100 pptv detection limit and was installed at a regional environmental monitoring station to be operated in parallel with a commercial UV-absorption-photometry-based ozone monitoring instrument. While good agreement between the readings of the two systems was found, the photoacoustic system outperformed its optical-absorption-based counterpart as far as minimum detectable concentration and measurement accuracy are concerned.

For the detection of NO₂, photoacoustic functions at its best in the visible or infrared wavelength regions, where it has a low-lying electronic transition in the blue-violet region around 400 nm, next to its vibrational absorption band in the infrared. A sub-ppbv detection limit has been achieved with external cavities QCLs at 6 µm in combination with photoacoustic detection. A much cheaper, smaller, and cost-effective approach is to use blue LEDs or blue diode lasers, which achieved detection limits of 1 ppmv and 200 pptv, respectively. The effective use of the blue light, a more efficient acoustic excitation, and a better shielding of surrounding noise counted for the better detection limit of the blue diode laser approach as compared to the LED approach.

A large variety of laboratory-based photoacoustic studies on trace gasses can be found elsewhere. A disadvantage of lab-based systems is that they can still be rather bulky and costly and difficult to transport. Nowadays, complete photoacoustic systems are integrated into durable, man portable, computer-size boxes, protected from dust, precipitation, and damage, making it applicable in field measurements. One example is the measurement of ambient ammonia concentration in the lower ppbv concentration range. Ammonia is the third most abundant nitrogen compound in the atmosphere and plays a significant role in cloud and rainwater chemistry. Typical ammonia sources include livestock, fertilizers, soils, forest fires, humans, animals, oceans, industry, and traffic. The main emission source is the use of animal manure and fertilizers for agricultural soils (responsible for more than 80% of the total ammonia emission). The photoacoustic

![Figure 14](image-url)

**Figure 14** Flight track from September 19, 2006: size- and color-coded by the ethene mixing ratios measured by laser photoacoustic spectroscopy below 1000 m. The color scale is truncated at 2 ppbv to bring out the smaller plumes in the graph. The white triangles show ethene point sources in the 2004 Texas Commission on Environmental Quality (TCEQ) inventory, with the size proportional to the source strength.
instrument is based on a wavelength-modulated, near-infrared, room-temperature-operated diode laser and a photoacoustic cell in its longitudinal resonance mode, with compact electronics for fully automated, long-term operation. The photoacoustic cell was made of polyvinylidene fluoride to reduce ammonia adsorption effects. Cross sensitivities (from atmospheric water vapor) were suppressed by using a multi wavelength approach. The system featured highly reliable, automatic operation, achieving a detection limit of 50 ppbv for ammonia.

Another laser-based photoacoustic instrument was developed and used for aircraft measurements of ethene from industrial sources near Houston (Figure 14). This instrument provided 20-s measurements with a detection limit of ~0.7 ppbv. In flight, data collected from this instrument were compared with gas chromatographic measurements, which agreed within 15% on an average. Ethene fluxes from a chemical complex near Houston could be quantified during 10 different flights. The average measured fluxes were one order of magnitude higher than the regulatory emission inventories indicate.

4.2 Chemical Detection of Warfare Agents and Explosives

Over the past decades, the global rise in terrorism and its threats against public places (markets, airports) has increased the awareness for the development of sensitive detectors for the early detection of the presence of explosive chemicals and also chemical warfare agents such as sarin affecting the nerve system. Such chemicals have a large amount of rotational and vibrational modes that are populated at room temperature; therefore, these molecules have no spectrally resolved lines but broadband absorption structures centered around vibrational transitions. An example is given in Figure 15 for TNT. For such broadband structures, broadly tunable lasers are needed. In the past, CO and CO₂ lasers in combination with photoacoustic spectroscopy have been used for the detection of vapors of explosives. However, both these laser sources are step tunable, and neither of them is able to access the strong absorption features specific for molecules such as TNT. The development of QCLs can fulfill these criteria, as they have continuous tunability and can be designed for specific wavelength regions ranging from 3 to 20 μm. In an external cavity configuration they have a wide wavelength coverage (~100 cm⁻¹) at high power (>100 mW up to watts). Combined with photoacoustic spectroscopy such a sensor can be specific and sensitive, because the targets for such detectors must exhibit acceptable receiver operational characteristics (ROC) to assure detection at very low levels without an unacceptable level of false alarms.

4.3 Biological and Agricultural Applications

4.3.1 Plant Physiology

It is a fortunate coincidence that the ubiquitously active plant hormone, ethylene (C₂H₄), is, in particular, easy to detect with CO₂-laser-based photoacoustics. Ethylene is the only known gaseous plant hormone; it is involved in virtually all aspects of the plant life starting from seed germination through growth and flowering, until fruit ripening and plant senescence. The biosynthesis in plants is well understood, leading from the amino acid methionine over two intermediates, S-adenosyl-methionine and amino-cyclo-propane-carboxylic acid, to C₂H₄. Ethylene is produced by plant tissue as a response to many external factors such as wounding, pathogen attack, light/temperature stress, chilling, and drought. Modern gas chromatographic systems can be used in many instances, but still lack the time resolution and extreme sensitivity of photoacoustic spectroscopy. With a detection limit of 10 pptv and a short time constant of about 10 s, photoacoustic detection is ideally suited to obtain an insight into C₂H₄-triggered plant physiological properties. Examples of recent investigations are listed elsewhere.

Numerous studies of the cellular and molecular biology of plants are using Arabidopsis thaliana as the model system. This is an organism about which much is already known, that is, easily manipulated, genetically tractable, and offers the ability for fast and efficient testing of hypotheses. By using Arabidopsis as a reference system, we gain knowledge to move forward with molecular biological and genetic analyses on many physiological processes involving ethylene. With laser-based detection, the dynamics of many processes that take place in plants become easily visible. For example, ethylene released by...
Arabidopsis displays a circadian rhythm (high emission during the light and low emission during dark) with a peak in the mid-subjective day. When the plants were grown for six days in a succession of light (16 h) and dark (8 h) and afterwards were kept in continuous light for several days, they showed an ethylene pattern as would follow the light–dark periods (Figure 16). (66)

One of the major environmental factors influencing crop productivity is flooding. Tolerant species often possess ‘escape’ mechanisms such as fast underwater growth that minimizes the duration of total submergence. However, at early vegetative stages, even in ‘deep-water’ types of rice, such escape is precluded by a lack of sufficiently vigorous shoot elongation for resurfacing. Survival of submergence under these circumstances depends on intrinsic physiological and biochemical tolerance. Screening of cultivars is needed by plant breeders, agrotechnology, and biotechnology to achieve sustainable improvements in the productivity of rice farming in the rainfed lowland of Southeast Asia. (67)

Submergence is not an easily quantified stress compared with, for example, cold, heat, pollution, since it cannot be assessed by one simple analysis. This is because it involves exclusion and entrapment of several key gases and interference with illumination. Normal rates of respiration and photosynthesis are affected; differences in submergence tolerance are reflected also in a different reaction to low oxygen concentrations. Precise measurements of fermentation rates can result in a powerful tool to shed some light on submergence stress. Fermentation in plant tissue was studied by the use of photoacoustic techniques, through detection of ethanol and acetaldehyde. It was shown that young rice seedlings of various species show different degrees of tolerance toward submergence, which is expressed by different fermentation rates under anaerobic and submergence conditions. (67,68)

### 4.3.2 Postharvest Physiology

To delay the effects of aging and ripening, many harvested crops are stored under reduced oxygen concentrations thereby lowering the respiration rate and the rate at which metabolic processes take place. However, when the oxygen concentration falls below a certain limit, crops switch to fermentation, an alternative method to generate the energy needed to sustain their vital functions. This anaerobic metabolism converts glucose, via several intermediate steps, into acetaldehyde, which is then quickly reduced to ethanol. As accumulation of these products in the tissue may affect the quality of the crop, it is necessary to control the rate of fermentation during storage. The concentration of the volatile in the headspace is an accurate quantitative indicator to assess the rate of fermentation. The noninvasive nature of laser-based trace gas detection renders it suitable for applications in this field of postharvest physiology. Moreover, the high sensitivity combined with fast analysis allows one to study an individual piece of fruit so that metabolic activity may be followed in real time. (69) Here, we give an example on a single piece of red bell pepper (Figure 17). The crop is placed in a glass container that is connected to the flow-through system, leading the released metabolites to the photoacoustic cells. Storage conditions are simulated by supplying the sample with a premixed flow of oxygen and nitrogen, while the storage temperature is controlled using a refrigerator. Returning a pepper from anaerobic conditions to oxygen conditions caused a peak in the acetaldehyde. The high velocity with which the process takes place caused the authors to conclude that the effect is mainly due to the peroxidative action of the enzyme catalase. (70,71)

### 4.3.3 Microbiology

The growth of all organisms depends on the availability of mineral nutrients and nitrogen is one of the most required in many biological reactions. Although the earth’s atmosphere contains nearly 80% of nitrogen gas, this is unavailable for use by most organisms, being an inert molecule. In order for nitrogen to be used for growth it must be ‘fixed’ (combined) in the form of ammonium or nitrate ions. This conversion process is known as nitrogen fixation and is exclusively performed by prokaryotes (bacteria) using an enzyme complex called nitrogenase. (72)

Acetylene reduction is the most widely used method for measuring the nitrogenase activity. (73) It is based on
the nitrogenase property to reduce compounds with a triple bond. Thus, by reducing nitrogen to ammonia, the nitrogenase reduces acetylene to ethylene. Both these gases can be measured with high sensitivity by gas chromatography with flame ionization detection. However, owing to its higher sensitivity and fast time response (about 20 s), laser photoacoustic spectroscopy offers the advantage of monitoring small changes in the nitrogenase activity of low amounts of biomass in real time. Photoacoustics was applied for the first time to investigate the nitrogenase activity in a sample of the heterocystous cyanobacterium *Nodularia spumigena*.(74) The on-line monitoring allows measurements under constant conditions, which eliminates artifacts caused by changes in the concentrations of O₂ or CO₂ due to respiration or photosynthesis during incubation. Changes in light intensity and temperature induce fast response in the nitrogenase activity. Knowing the level of saturation of the enzyme at different light intensities is important when rates of acetylene reduction are converted to rates of nitrogen fixation. At 35 °C and above this temperature, the nitrogenase activity is inhibited, most probably because the nitrogenase, or because of the other substrate generating enzyme systems (ATP and e⁻) like the electron transport chain, breaks down irreversibly (Figure 18).

![Figure 17](image1.png) **Figure 17** Acetaldehyde (AA) and ethanol (EtOH) emission of a red bell pepper under zero oxygen conditions. The pepper is inserted into the anoxic environment at \( t = 1.5 \) h. The plateau in the acetaldehyde emission indicates that there is a continuous ongoing fermentation process in which the production of acetaldehyde is the intermediate step and ethanol the final product. Postanoxic addition of as low as 0.4% O₂ leads to a dramatic increase of acetaldehyde emission. In the presence of oxygen, ethanol is enzymatically converted back into ethanol. For clarity, acetaldehyde concentration has been multiplied by 10.(69)

![Figure 18](image2.png) **Figure 18** Response of cyanobacteria *N. spumigena* (see photo) to change of temperature from 10 to 37 °C under light conditions. Significant instability in the nitrogenase activity is observed at 35 °C, leading to a short inhibition tendency at 37 °C, followed by a drastic decrease.
Methane has been recognized as one of the principal greenhouse gases, next to CO\textsubscript{2}. Its estimated contribution to the enhanced greenhouse effect varies between 15% and 20% depending on the time window for which the calculation is made. Natural sources are responsible for the major part of the global methane flux\textsuperscript{(75)} Some arthropods (i.e. millipedes, cockroaches, termites, and scarab beetles) are believed to contribute up to 25% of the total budget\textsuperscript{(76)}

Gas chromatography allows measurement of methane release of single animals only after incubation for several hours. Consequently, these measurements cannot provide information about the dynamic character of the gas emission. Infrared absorption measurements featuring fast response time permitted observation of the dynamics of CO\textsubscript{2} emissions. Besides CH\textsubscript{4} and CO\textsubscript{2} emissions from insects, water vapor release has been the subject of many studies. Information about water loss dynamics in insects is based on theoretical modeling, sensitive weighing, and relatively slow direct water vapor measurements\textsuperscript{(77)} With laser photoacoustic detection, Bijnen et al.\textsuperscript{(49)} showed that cockroaches at rest show a regular breathing pattern to optimize oxygen uptake and reduce water loss. Respiration patterns of cockroaches and beetles have been recorded in which microbiologically produced methane was found to be coemitted with CO\textsubscript{2} and water vapor (Figure 19).

Combining an OPO with photoacoustic spectroscopy, CO\textsubscript{2} emissions even from small insects could be detected. For this the OPO was made tunable in the 3.9–4.8\textmu m infrared wavelength region, covering the strong rotational–vibrational absorption band of CO\textsubscript{2} at 4.23\textmu m. With this system, it was possible to detect CO\textsubscript{2} with a sensitivity of 7 ppbv using 20 mW OPO power. They demonstrated in real time the CO\textsubscript{2} emission in exhaled air of a single ant (Lasius niger) and individual fruit flies (Drosophila melanogaster, Figure 20).\textsuperscript{(79)}

Another application of the OPO photoacoustics was the monitoring of isotope methane (\textsuperscript{12}CH\textsubscript{4} and \textsuperscript{13}CH\textsubscript{4}) emissions by plants. The study was initiated by an earlier study\textsuperscript{(80)} containing the finding that terrestrial plants can produce a large amount of methane in aerobic conditions. This finding was re-examined using an independent test performed with OPO spectroscopy.\textsuperscript{(81)} For this study, \textsuperscript{13}C labeled plants were grown under controlled conditions in a hermetically sealed plant growth chamber (3.5 m\textsuperscript{3}) specifically designed for atmospheric isotope labeling. When investigating possible methane emission, it is preferable to use \textsuperscript{13}C labeled plants, since the natural background concentration of \textsuperscript{13}C-methane is 20 ppbv compared to 1.7 ppmv of \textsuperscript{12}C-methane. Methane shows a very pronounced absorption spectrum around 3000 cm\textsuperscript{-1},
which is dominated by the strong $\nu_3$ band and in which the band centers of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ are shifted 10 cm$^{-1}$ among each other. Figure 21 depicts the measurement of a $^{13}$C-methane-enriched sample and the comparison with a spectral simulation. It was shown that there is no evidence for substantial aerobic methane emission by terrestrial plants.

### 4.4 Human Health, Noninvasive Breath Analysis

Since ancient times, it is known that the smell of exhaled air can be used as an indicator for several processes taking place in the human body.\cite{82,83} Uncontrolled diabetes produces a sweet, fruity odor, advanced liver diseases entail a musty, fishy reek, failing kidneys bring about an urine like smell, and a lung abscess can be brought to light by its putrid stench. In the past, several attempts to use trace gas detection of exhaled air have been performed with variable success because of the nonsufficient detection limits of the detectors available. Gases produced in the body are transported to the lungs and are diluted (in rest, healthy persons exhale approximately 1000 L h$^{-1}$) before being exhaled. To measure them, it is necessary to enrich the air samples by adsorbing the gases onto an agent and releasing the concentrated gas at a certain moment rendering the measurements less accurate and difficult to reproduce.

Laser photoacoustic spectroscopy offers several advantages over such gas chromatographic–mass spectrometric analysis. Owing to its high sensitivity, it allows single breath collection from a small sampling volume (few hundred milliliters) with no preconcentration steps needed. A summary of several compounds out of more than 300 present in breath with their physiological origin and biological–pathological indication is given elsewhere.\cite{84,85} Many of these compounds have a

![Figure 20](image)

**Figure 20** (a) Real-time CO$_2$ emission of a small ant (*Lasius niger*, weight 3.7 mg). Analysis of the ants’ respiration shows a periodic release of CO$_2$, on an average every 90 s. (b) CO$_2$ release of a fruit fly (*Drosophila melanogaster*, weight 1.4 mg). The comparison of the CO$_2$ trace from the fruit fly with the background (without fly) shows that the CO$_2$ release does not drop to zero. The accuracy of the CO$_2$ detection shows that the CO$_2$ peaks vary in amplitude and frequency.\cite{79}
PHOTOACOUSTIC SPECTROSCOPY IN TRACE GAS MONITORING

Figure 21 Calculated methane spectrum from the Hitran database\textsuperscript{14} for 2 ppmv $^{12}$CH$_4$ (dashed line) and 2 ppmv $^{12}$CH$_4$ enriched with 400 ppmv $^{13}$CH$_4$ (solid line). Measured spectrum of 2 ppmv $^{12}$CH$_4$ enriched with 400 ppmv $^{13}$CH$_4$ (○).

well-defined biochemical pathway and can be monitored in real time by photoacoustics.

Here, measurements of the effects of UV radiation on the human skin are presented to illustrate the possibilities of photoacoustic trace detection in this field. Under stress conditions (e.g., ionizing radiation, toxic chemical substances, and diseases), the production of free radicals in the body is significantly increased. Subsequently, the capacity of the free radical scavengers in the body is overloaded and a chain of chemical reactions is activated. This leads ultimately to cell membrane damage that plays an important role in the aging processes and pathogenesis of some diseases such as cancer, Alzheimer, and atherosclerosis. The cell damage is accompanied by the production of small hydrocarbons, such as ethane, pentane, and ethylene, that can be easily measured using photoacoustics.\textsuperscript{86} A small amount of air is sampled from the exhaled air and cleaned from CO$_2$ (typically 5%), water vapor, and other spectroscopically interfering gases such as acetone and ethanol. The test persons are measured while resting under a solar bench.\textsuperscript{87} With the UV radiation on, a steady increase of the exhaled ethylene is observed with a 2 min time delay (Figure 22). The increase continues until the solarium is switched off after 15 min (being the maximum exposure time advised). In the subsequent decrease of ethylene emission, two decays can be distinguished: a fast and a slow decay. The first decay is caused by the washout of ethylene from the blood; the second decay results from ethylene stored in the body tissue. The dynamics of the system, i.e., transport of gases through the body, yield information for pharmacokinetic research.\textsuperscript{88,89} In order to determine the locally induced damage, a specially designed cell was placed on the skin. Immediately after the start of the UV exposure, a steady and constant production of ethylene in the skin was observed. Combining the two results, one concludes that the slow increase in ethylene signal in the exhaled air is caused by the buffering effect of the human body.

Figure 22 Ethylene emission from the human lungs induced by UV radiation from a solar bench. As product of lipid peroxidation, ethylene is found in low amounts in the exhaled air. The time during which the skin is irradiated (in total 15 min) is indicated by the black bar. Shielding the body from UV radiation using Lexan prevents generation of ethylene.\textsuperscript{87}

5 COMPARISON WITH OTHER SPECTROSCOPIC METHODS IN TRACE GAS MONITORING

Fast and sensitive trace gas detection is not exclusively reserved for photoacoustics. In general, all spectroscopic
techniques are able to monitor gas absorptions on a subsecond time scale. However, depending on the type of application not all techniques possess a high sensitivity. Air pollution can be very well studied with long-path light absorption techniques rendering low detection limits. A broadband light source or widely tunable laser is directed toward a receiver over an open path in the atmosphere. Such methods derive their sensitivity from long-path absorption thereby integrating over hundreds of meters. Laser-based photoacoustic detection has the advantage to trace gases locally and can therefore also be used in laboratory studies. Other laser-based techniques which can also achieve a high sensitivity within a small volume of gas are based on high finesse cavities, such as cavity ring down spectroscopy (CRDS) or cavity-enhanced absorption spectroscopy (CEAS). The latter combines very accurate decay time measurements of light pulses and a high Q optical cavity resulting in long effective absorption lengths. In comparison with these techniques, laser photoacoustics has the advantage that it is background free: it is not relying on a decrease of the transmitted light but on an increase from the zero baseline, i.e. on a collisional release of energy after absorption. Other background free and therefore strongly competitive techniques are LIF and MPI. These techniques are extremely sensitive owing to the high collection efficiency of photomultipliers and ion-counters; both can be applied locally within a small gas volume. LIF and laser photoacoustics are complementary in energy release. The advantage of LIF is that it can also detect free radicals (e.g. OH) with relatively low laser powers. MPI can be very selective and sensitive for molecules with a higher mass. A restriction of LIF is the lifetime of the excited levels. As stated in the introduction, the competition between collisional relaxation and radiative decay restricts LIF mainly to the visible and the UV part of the electromagnetic spectrum.

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ABBREVIATIONS AND ACRONYMS

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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>BW</td>
<td>Brewster Window</td>
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<tr>
<td>CEAS</td>
<td>Cavity-Enhanced Absorption Spectroscopy</td>
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<tr>
<td>CRDS</td>
<td>Cavity Ring Down Spectroscopy</td>
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<tr>
<td>cw</td>
<td>Continuous Wave</td>
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<tr>
<td>FTIR</td>
<td>Fourier Transformed Infrared</td>
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<td>FWHM</td>
<td>Full Width at Half Maximum</td>
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<td>LEDs</td>
<td>Light Emitted Diodes</td>
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<td>LIF</td>
<td>Laser-Induced Fluorescence</td>
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<td>Multiphoton Ionization</td>
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<td>NF</td>
<td>Notch Filter</td>
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<td>PPLN-OPOs</td>
<td>Periodically Poled Lithium Niobate Optical Parametric Oscillators</td>
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<td>QCL</td>
<td>Quantum Cascade Laser</td>
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<td>ROC</td>
<td>Receiver Operational Characteristics</td>
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<td>TAC</td>
<td>Tunable Air Column</td>
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<td>TCEQ</td>
<td>Texas Commission on Environmental Quality</td>
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<td>TF</td>
<td>Tuning Fork</td>
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<td>TNT</td>
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