# DETECTION OF TRACE GASES BY MEANS OF THE INFRARED LASER PHOTOACOUSTIC TECHNIQUE

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A b s t r a c t. In recent years numerous studies have demonstrated the feasibility of the infrared laser photoacoustic spectroscopy (PAS) for agricultural, biological, medical and environmental applications. The photoacoustic spectroscopy is one of the most valuable analytical methods in gas detection, owing to the high sensitivity, high selectivity and the capability of in situ detection. A great number of trace gases can be detected and monitored with the photoacoustic method combined with various molecular gas lasers. These measurements can be done continuously, simultaneously over long periods and with high time resolution.

In the Bonn laboratory a highly sophisticated photoacoustic detection system is available, including computer control for automatic selection of laser frequencies and adaptation of the signal detection unit to varying operation conditions of the spectrometer. The data taken during the measurement are stored, processed and displayed by the computer. These features are available for the photoacoustic spectrometer using the $CO_2$-laser as well as the CO-, CO-overtone- and furthermore the $N_2O$-laser.

In our experiments a spectrometer consisting of either the $CO_2$-laser or the CO-overtone laser and the resonant photoacoustic cell placed intracavity has been used. For example we have reached a detection limit of 30 ppt for ethylene ($C_2H_4$) and 37 ppt for methane ($CH_4$). Our photoacoustic work profits from the collaboration with the research group of Professor J. Reuss in Nijmegen (The Netherlands). The photoacoustic detection method using the $CO_2$-laser as powerful source has been developed to a high degree of perfection in the Nijmegen group.

K e y w o r d s: trace gases, infrared laser photoacoustic technique

## INTRODUCTION

The requirements for precision in measurement of trace gases lead to the establishment of detection techniques based on lasers [10]. The infrared laser photoacoustic technique provides possibilities for the sensitive and selective determination of environment and climate relevant gases and therefore the investigation of the toxicological effects of these gases. These measurements can be carried out under atmospheric pressure conditions.

The need for trace gas analysis in different fields of the agricultural and biological sciences is self-explanatory. Hence the range of potential applications is quite large [7,9,13]. Our research group at the Institut für Angewandte Physik der Universität Bonn uses the photoacoustic spectroscopy for the detection of environmental trace gases. Furthermore the sensitive determination of the gaseous plant hormone ethylene is suitable for the

investigation of plants influenced by different stress factors. Actually we investigate the effect of elevated $CO_2$-concentrations on the ethylene exhaust by kohlrabi plants. This work is carried out within a collaboration with the group of Professor F. Lenz at the 'Institut für Obst- und Gemüsebau der Universität Bonn'. In the foreground of another envisaged project is the evaluation of the role of ethylene, butane and methane in the special replant disease of apple.

In the following sections the method is introduced and the basic features are pointed out. Experimental details and spectroscopic applications are discussed.

### TECHNIQUE

There are numerous small molecules that exhibit strong absorption lines in the infrared spectral region. These absorption bands are due to vibrational-rotational transitions in molecules. Detection techniques based on molecular absorption are often used in the infrared wavelength region. It is called the fingerprint region since a large number of molecules show a characteristic pattern of absorption lines by which various gases can be identified. Accidental coincidences between emission frequencies of the lasers used and the molecular transitions are required in case of using fixed frequency lasers.

In our research group there are various molecular gas lasers available that can be combined with the photoacoustic technique: $CO_2$-, $N_2O$- and CO-laser (CO-$\Delta v=1$ laser). By means of these lasers vibration-rotation transitions of many molecules become accessible. Due to the limited operating range of these fixed frequency lasers in the mid-IR, photoacoustic spectroscopy was limited to the range around $10\,\mu m$ ($CO_2$- and $N_2O$-laser) and to $5$-$8\,\mu m$ ('normal' CO-laser). The unique asset of our group is the CO-overtone laser (CO-$\Delta v=2$ laser) which has been used outside the field of fundamental research for the first time [12]. Due to the fact that this laser is available only since a short time (so far the only other places

where such lasers are in operation are Würzburg, Boulder/Colorado and Louvain la Neuve), no systematic photoacoustic detection measurements have been carried out. The newly developed CO-overtone laser now extends to 2.8-4.1 $\mu m$ and gives us additional 330 laser transitions [1]. This opens up a very interesting range for the photoacoustic sensing since the vibrations of CH-, OH- and NH-groups in molecules are falling into this spectral range.

The spectral range of the above mentioned lasers and the number of available laser lines is shown in Table 1. The $CO_2$- and the CO-$\Delta v=1$ laser can also be operated with rare isotopomers thus increasing the number of lines significantly. In Table 2 a list of molecules with absorption bands covering the range of concerning laser transitions is shown. Several gases have already been detected photoacoustically [2,4,6,8,11].

**T a b l e 1.** Spectral range of infrared lasers

| Laser | Wavelength range ($\mu m$) | Energy range ($cm^{-1}$) | Number of lines |
|---|---|---|---|
| $N_2O$ | 11.1-10.3 | 970-900 | 80 |
| $CO_2$ | 10.8-9.2 | 920-1100 | 100 |
| CO ($\Delta v=1$) | 8.4-4.8 | 1200-2100 | 400 |
| CO ($\Delta v=2$) | 4.1-2.6 | 3800-2500 | 330 |

In general the photoacoustic setup can be operated in intracavity or extracavity configuration. Both the intracavity and extracavity setup consist of four main components: laser, photoacoustic cell, mechanical chopper and computer. In an extracavity setup the photoacoustic cell is placed outside the laser resonator whereas the photoacoustic cell is located inside the cavity in an intracavity setup. In Fig. 1 a scheme of our intracavity photoacoustic setup is depicted.

Outline of the experimental setup:

By means of a mechanical chopper the laser beam is modulated with audio frequencies (10-10 000 Hz). The laser beam passes the photoacoustic cell containing the sample under investigation. In case of a coincidence between the laser wavelength and

**T a b l e  2.** Detectable molecules relevant for agricultural biology

| Compound | Laser | | |
|---|---|---|---|
| | $CO_2$ | CO ($\Delta v=1$) | CO ($\Delta v=2$) |
| Hydrocarbons | ethylene ($C_2H_4$) <br> 1,3 butadien ($C_4H_6$) | methane ($CH_4$) <br> propylene ($C_3H_6$) <br> 1,3-butadien ($C_4H_6$) | methane ($CH_4$) <br> ethane ($C_2H_6$) |
| Chlorofluorocarbons | trichlorofluoromethane ($CCl_3F$) <br> dichlorodifluoromethane ($CCl_2F_2$) | | |
| Hydrochlorofluorocarbons | chlorodifluoromethane ($CHClF_2$) | | |
| Hydrochlorocarbons | vinyl chloride ($C_2H_3Cl$) <br> dichloroethane ($C_2H_4Cl_2$) | vinyl chloride ($C_2H_3Cl$) | |
| Aldehydes and ketones | acetaldehyde ($C_2H_4O$) | formaldehyde ($CH_2O$) <br> acetone ($C_3H_6O$) <br> acetaldehyde ($C_2H_4O$) | formaldehyde ($CH_2O$) <br> acetone ($C_3H_6O$) <br> acetaldehyde ($C_2H_4O$) |
| Alcoholes | methanol ($CH_4O$) <br> ethanol ($C_2H_6O$) <br> isopropyl-alcohol ($C_3H_8O$) | | methanol ($CH_4O$) <br> ethanol ($C_2H_6O$) |
| Inorganic molecules | ozone ($O_3$) | carbon monoxide (CO) <br> carbon dioxide ($CO_2$) | carbon dioxide ($CO_2$) |
| Inorganic molecules (with nitrogen) | ammonia ($NH_3$) | nitric oxide (NO) <br> nitrogen dioxide ($NO_2$) <br> nitrous oxide ($N_2O$) | nitrous oxide ($N_2O$) |
| Inorganic molecules (with sulphur) | hydrogen sulphide ($H_2S$) | sulphur dioxide ($SO_2$) | |
| Pesticides | methyl bromide ($CH_3Br$) <br> trichloroethylene ($C_2HCl_3$) <br> perchloroethylene ($C_2Cl_4$) | methyl bromide ($CH_3Br$) | methyl bromide ($CH_3Br$) |
| Aromatics | benzene ($C_6H_6$) <br> toluene ($C_7H_8$) | benzene ($C_6H_6$) <br> toluene ($C_7H_8$) <br> xylene ($C_8H_{10}$) | toluene ($C_7H_8$) <br> xylene ($C_8H_{10}$) |
| Acids | formic acid ($CH_2O_2$) | acetic acid ($C_2H_4O_2$) | formic acid ($CH_2O_2$) |
| Others | sulphur hexafluoride ($SF_6$) <br> tetrafluoromethane ($CF_4$) | acrolein ($C_3H_4O$) <br> phosgene ($COCl_2$) | hydrogen chloride (HCl) <br> hydrogen cyanide (HCN) |
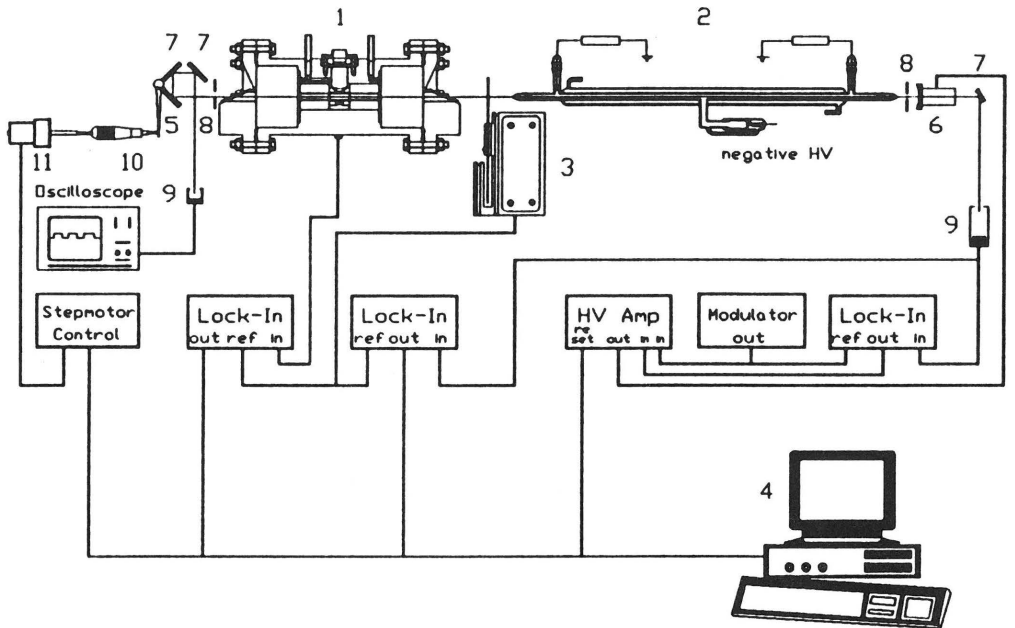
**Fig. 1.** Experimental setup. 1 - photoacoustic cell, 2 - infrared laser, 3 - chopper, 4 - computer, 5 - grating, 6 - piezo-mounted mirror, 7 - mirror, 8 - iris, 9 - pyroelectric detector, 10 - micrometer screw, 11 - stepmotor.

an absorption line of the gas molecules the radiation energy is absorbed and transferred to thermal movement of the molecules by intermolecular collisions. Consequently a periodic change of pressure occurs in the photoacoustic cell which can be detected by a sensitive microphone. The signal is processed by a phase sensitive amplifier (Lock-In amplifier).

A brief description of the resonant photoacoustic cell illustrates its performance (a detailed description of the photoacoustic cell used is in [3]). The open acoustic resonator which is similar to an organ-pipe is inside the body of the photoacoustic cell. The modulated laser beam excites an acoustic wave in the resonator. The interference between the waves propagating back and forth results in a standing acoustic wave provided that the modulation frequency and the resonance frequency of the first longitudinal acoustic mode coincide. The pressure amplitude in the resonator is then increased by constructive interference. The miniature electret microphone is coupled to

the middle of the resonator tube by a small hole. The laser beam enters the photoacoustic cell through the Brewster-windows which are separated from the resonator by the buffer volumes. The reason is to realize a closed resonant photoacoustic cell which can be operated under flow conditions and to suppress acoustic signals due to Brewster-window absorption. Small buffer volumes provide a short response time to changes of the gas concentration. The adaptation of the diameter of the resonators in the photoacoustic cell to the waist of the laser beam is possible by means of exchangeable modules enclosing the resonators. This enables us to use the same photoacoustic cell for the intracavity setup as well as for the extracavity setup.

The photoacoustic detection method has been developed to a high degree of perfection in the Nijmegen group. Their $CO_2$-laser photoacoustic detection system reaches detection sensitivities for ethylene in dilutions of $< 10^{-11}$ at ambient pressures [5]. Therefore to start with we reproduced an experiment

that was based on a waveguide $CO_2$-laser which is certainly the most powerful and easy to operate molecular gas laser. In addition an experimental setup was realized in which the $CO_2$-laser has been replaced by the CO-overtone laser.

### RESULTS AND DISCUSSION

We combined the intracavity photoacoustic detector with both the $CO_2$-laser and the CO-overtone laser. By using the intracavity setup we can take advantage of the much higher power inside the cavity of the laser. In general the photoacoustic signal is proportional to the laser power. This fact becomes aparent in Eq. (1). Commonly the microphone response is subdivided into three factors each describing different properties of the experimental setup or sample.

$$S = \Delta E \, f_{ac} \, F_{mic} \qquad (1)$$

The absorbed energy per pulsetrain $\Delta E$ of laser light passing through the photoacoustic cell is proportional to the laser power and the absorption coefficient of the sample. The factor $f_{ac}$ expressing the acoustical performance of the experimental setup is composed of physical parameters of the sample, such as molecular mass, viscosity, thermal capacity and thermal conductivity, and the geometry of the photoacoustic cell. Finally the factor $f_{mic}$ hints at the microphone responsivity.

In case of background noise limiting the sensitivity of the $CO_2$- and CO-overtone laser photoacoustic detector the corresponding refinement of the method as described above might gain another one to two orders of magnitude in sensitivity. Besides it opens up the opportunity to verify a compact spectrometer practicable for field studies. Nevertheless some weak laser lines might disappear because of the introduction of additional losses by placing the photoacoustic cell into the resonator. This is especially crucial when using the CO-overtone laser since it has a lower gain than the $CO_2$-laser and the ordinary CO-laser. Fortunately the

laser lines causing the fingerprint of methane, nitrous oxide and formaldehyde are strong enough to overcome these additional losses as will be seen from the spectra below.

In the Bonn laboratory there is a highly sophisticated photoacoustic detection system available, including computer control for automatic changes of laser frequencies and setting of Lock-In amplifier parameters depending on varying operation conditions of the spectrometer. The data taken during the measurement are stored, processed (e.g., calculation of the normalized signal) and displayed by the computer. These features are available for the $CO_2$-laser photoacoustic spectrometer as well as for the CO-overtone laser photoacoustic spectrometer.

For example for ethylene ($C_2H_4$) and benzene ($C_6H_6$) a characteristic pattern of absorption strength can be observed for the $CO_2$-laser transitions in the 9-11 $\mu m$ infrared wavelength region. This is illustrated in Fig. 2a and 2b where the absorption coefficient is plotted versus the wavelength. The strongest absorptions occur on the 10P (14) laser line (ethylene) and the 9P (30) laser line (benzene). The sensitivity of the spectrophone for ethylene and benzene diluted in nitrogen is 30 ppt and 450 ppt, respectively. Correspondingly the spectra of methane ($CH_4$), nitrous oxide ($N_2O$) and formaldehyde ($CH_2O$) have been recorded with the CO-overtone laser photoacoustic spectrometer. The photoacoustic spectra of methane and formaldehyde are plotted in Fig. 2c and 2d, respectively. The obtainable sensitivity is 30 ppt (methane), 370 ppt (nitrous oxide) and 250 ppt (formaldehyde), (see Table 3).

From the latter spectra problems inherent in the photoacoustic spectroscopy become obvious. The absorption lines in the shorter wavelength region are mainly due to water absorption whereas the influence of water absorption is neglegible in the other spectral region. The reason is that the laser transitions of the CO-overtone laser are only partially falling into an atmospheric window.

**Absorption coefficient [1/atm cm]**
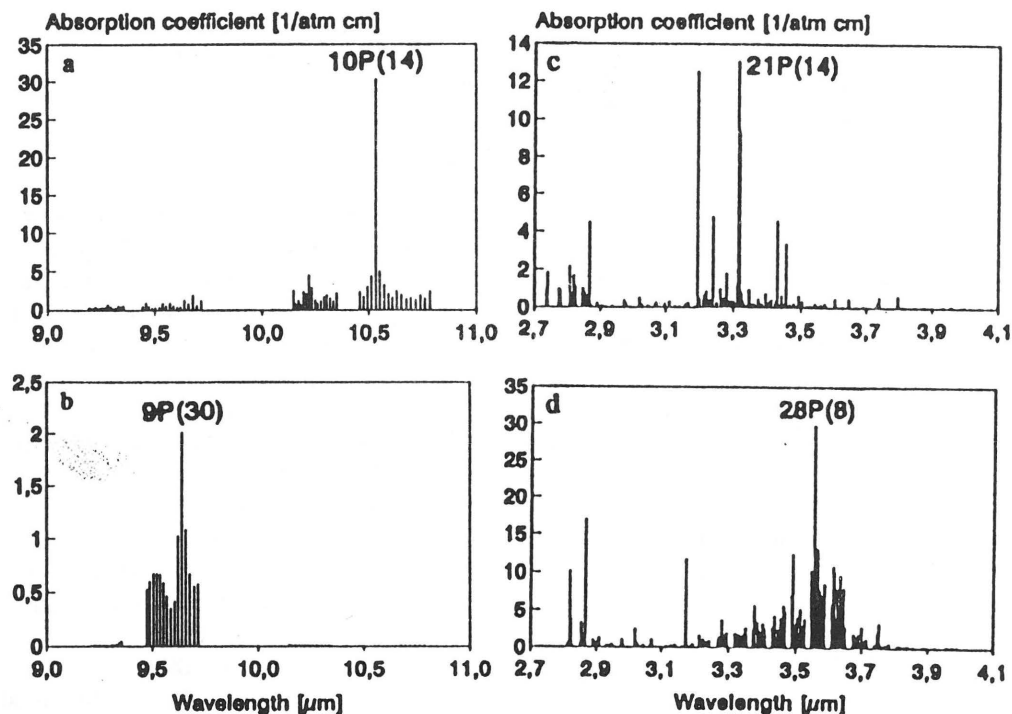
**Absorption coefficient [1/atm cm]**

Fig. 2. Photoacoustic spectrum of ethylene (a), benzene (b), methane (c) and formaldehyde (d).

In contrast to this there is no overlap between water absorption bands and the emission range of the $CO_2$-laser. The cross sensitivity to interfering gases such as water has to be eliminated during the measurement of the relevant gas either by using a cooling trap or catalyst. The function is to freeze out certain gas components or to crack bindings in infrared active molecules. It is also possible to utilize computer calculations based on specially developed algorithms in order to get rid of the contribution of disturbing gases affecting the measurement.

CONCLUSIONS

The potential use of the photoacoustic sensing has been demonstrated by many scientists. Numerous trace gases important for agricultural biology can be detected and monitored with the photoacoustic method combined with various molecular gas lasers, e.g., CO-, CO-overtone-, $CO_2$- and $N_2O$- laser. For some molecules the detection limit is in the sub-ppb range under normal pressure conditions.

The results presented in this paper have been obtained with a $CO_2$- and a CO-overtone laser integrated in a computer controlled photoacoustic spectrometer. This enables us to detect both concentrations and changes of concentrations of gases down to dilutions as they occur in the atmosphere around a plant/soil system. Further improvements of

**T a b l e 3.** Detection limits of various gases in the $CO_2$- and CO- overtone laser wavelength range

| Molecule | Detection limit ($\mu g/m^3$) |
|---|---|
| Ethylene ($C_2H_4$) | 0.03 |
| Benzene ($C_6H_6$) | 1.40 |
| Methane ($CH_4$) | 0.02 |
| Nitrous oxide ($N_2O$) | 0.64 |
| Formaldehyde ($CH_2O$) | 0.29 |

the spectrometer include an intracavity setup with enhanced sensitivity. Exemplifying we report the detection limit for ethylene and benzene with the $CO_2$-laser based system and for methane, formaldehyde and nitrous oxide with the CO-overtone laser photoacoustic spectrometer. To our knowledge the sensitivity for methane, formaldehyde and nitrous oxide is the best reported so far. The CO-overtone laser represents a very promising light source for the photoacoustic spectroscopy since the CH-, NH- and OH-vibrations are falling into its frequency range. It was the first time that this light source was applied to the photoacoustic spectroscopy.

## ACKNOWLEDGEMENT

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