Photoacoustic Measurements of Agriculturally Interesting Gases and Detection of C_2H_4 below the PPB Level

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We present a laser photoacoustic system which is able to detect a minimum absorption coefficient of $7.1 \times 10^{-10} \text{ cm}^{-1}$ corresponding to a concentration of 20 parts per trillion of C_2H_4 in air. Improvements made to achieve this sensitivity are reported, and this low limit is applied to the detection of the C_2H_4 emission of a single orchid flower after emasculation. In addition, the absorption coefficients and detection limits of the following agriculturally interesting gases are measured: ozone, hydrogen sulphide, 1,2 dibromoethane, and ethylacetate.

Index Headings: Infrared; Lasers, CO_2 ; Spectroscopic techniques.

INTRODUCTION

In daily agricultural practice there is a need for a fast, sensitive monitor for trace gases under atmospheric conditions. Gas chromatographs have neither the sensitivity nor the fast response needed. Laser photoacoustic spectroscopy is suitable for monitoring trace gases in the atmosphere. Studies in the infrared CO_2 laser region have demonstrated strong spectroscopically selective absorption coefficients for several gases.¹⁻⁷

In this paper we describe an experimental setup, the laser and the photoacoustic cell, for sensitive detection of these gases. One of these gases, ethylene (C_2H_4), is of special interest in agriculture. It is an atmospheric air pollutant produced by cars and various industrial burning processes. Ethylene is also produced by plants and flowers themselves. It acts as a gaseous hormone which influences the ripening of fruit, the wilting of flowers, and the abscission of leaves. Plants are sensitive to ethylene, and accumulation of this gas in storage chambers or during transport can cause damage to plants. The influence of emasculation on the C_2H_4 production of an orchid flower is investigated and described. Also, measurements of the absorption coefficients of important agricultural gases on the CO_2 laser lines are given.

THE CO_2 WAVEGUIDE LASER

The CO_2 waveguide laser emits at wavelengths of 9–11 μm in the infrared. The four branches of the ro-vibrational P and R transitions of CO_2 produce radiation at 90 laser lines.⁸⁻¹⁰ A hollow dielectric waveguide tube of SiO_2 permits transmission of the electromagnetic radiation with a very small attenuation. Because of this configuration, the overall size of the laser can be reduced, which is an advantage over a conventional CO_2 laser. The quartz waveguide tube typically has an inner diameter of 3 mm (outer 7 mm) and a discharge length of 45 cm.

On both ends of the tube we attached NaCl windows at the Brewster angle. The windows are attached to aluminum holders and heated to prevent hygroscopic downgrading. The laser is cooled with water around the discharge tube. The dc discharge is driven by a high-voltage power supply, and the positive output is connected to the center electrode; both side electrodes are grounded through a current stabilizer. Commercially available tungsten electrodes (for welding purposes) were used here. Because of their low sputtering susceptibility, they cause no degradation of the tube and windows (>1700 h operating time). During the mentioned operating interval the output power of the laser decreases by 40%. This response is mainly caused by the optical quality loss of the NaCl windows, which are affected by the high intracavity laser intensity. The end reflectors of the laser cavity are a piezo-electrically driven partially (70% or 90%) reflecting ZnSe end mirror at one end and a line-selecting grating (150 L/mm, blazed at 10.6 μm) at the other end. The gas inlet (at both ends) and outlet (at the center) are formed by 2-mm openings in the waveguide tube at the positions of the electrodes. Mirrors and discharge tube are aligned with a He-Ne laser. Final adjustment of optimum laser power is made with screws supporting the waveguide tube.

For CO_2 laser operation we used a mixture of He : N_2 : CO_2 in a proportional ratio of 6:1:1 at a pressure of 80 mbar. The 55-cm resonator length yields a free spectral range (FSR) of 270 MHz. The maximum laser output power is 9 W in the TEM₀₀ mode, and the tunability includes 90 discrete laser transitions.

Due to the quartz rods connecting both end mirrors of the laser and the compensating thermal expansion design, the laser has a good frequency stability¹¹ (better than 1 MHz over a period of 100 s). In order to stabilize the laser power, a fraction of the laser output is modulated and deflected to a pyro-electric element. This signal is compared to a reference level, and the difference signal is fed back to the current stabilizer to correct the discharge current. In this way a power stability of $1:10^4$ has been achieved.

For photoacoustic measurements, the laser is tuned by computer (Apple IIe). The motor control for the grating and the high-voltage supply for the piezo are computer driven to give maximum gain of the laser at a particular laser line. In this way it is possible to control line selection of three branches (10P, 10R, 9P) of the CO_2 laser. Only the 9R branch does not yield single line operation, due to closer spacing of laser transitions and the low resolution of the grating. The latter is caused by the small

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FIG. 1. Experimental arrangement for the photoacoustic measurements of C_2H_4 emitted from orchid flowers. The hydrocarbons present in the compressed air are dissociated into CO_2 and H_2O by a catalyst. Before the air enters the photoacoustic cell, a scrubber of KOH removes the CO_2 from the airflow, to prevent interference of gas absorption signals with the C_2H_4 photoacoustic signal. Because of the time scale of the experiments the total setup is connected to a computer.

inner diameter of the laser tube and the consequently lower number of grooves of the grating, which are effective for the frequency selection. This problem can be overcome by connecting a computer-controlled spectrum analyzer to the system.

GENERATION OF THE PHOTOACOUSTIC SIGNAL

A long open cylindrical resonator with a relatively small diameter inside a large cell volume is used as a photoacoustic resonance cell (Fig. 1). We excite the first longitudinal mode in this resonator. Due to the geometrical restriction of the long narrow tube we can describe the acoustic behavior of the resonator according to electrical transmission line theory.¹²⁻¹⁶ In this theory it is assumed that the acoustic wavelength is much larger than the cross dimensions of the tube. Therefore, the plane acoustic wave propagation can be modeled by the one-dimensional analogue of the electrical current flow in a transmission line. Following this theory,¹⁶ a cell constant F , only dependent on the geometry of the cell, can be defined at resonance frequency $p = F(\omega = \omega_0)\alpha W$, with p the pressure response of the cell ($N/m^2 = \text{Pascal}$); α the absorption coefficient at one atmosphere pressure of the gas at the CO_2 laser wavelength ($\text{atm}^{-1} \text{cm}^{-1}$); W the laser power (watt); $\omega_0 = 2\pi\nu_0 = (\pi c/L)$ (resonance frequency); and L the length of the resonator tube. For a given cell geometry

$$F(\omega_0) = \frac{(\gamma - 1)LQG}{\omega_0 V} \quad (1)$$

where $\gamma = C_p/C_v$ is the specific heat ratio, V the volume of the resonator, G a geometrical factor of order 1, and Q the quality factor of the system. Q is the ratio between the energy stored in the acoustic wave and the losses per cycle of this acoustic wave. It can be calculated as

$$Q = \frac{2S}{2\pi R(d_r + (\gamma - 1)d_h)} \quad (2)$$

Here, S stands for the cross section of the resonator tube, R for the radius of the tube, and $d_r = (2\mu/\rho\omega)^{1/2}$ for the

FIG. 2. Comparison between the theoretical and the experimental values of the cell constant (F) as a function of the diameter and length of the resonator.

thermal boundary layer, $d_h = (2K/\rho\omega c_p)^{1/2}$ for the viscous boundary layer; μ is the viscosity coefficient, K the conductivity coefficient, and ρ the density of mass.

The dependence of F and Q on the length and diameter of the resonator is obvious, i.e., $Q \propto R/L^{1/2}$ and $F \propto L^{1/2}R$. To create an optimum acoustic signal it is important to have a resonator with a large length and a small diameter. The narrowing of the diameter and the increase of the length of the tube are restricted by the divergence of the laser beam over the length of the cell. Equation 1 is a first approximation for the behavior of the cell constant F at resonance frequency. The more extended theory¹⁶ shows a dependence of the cell constant F for L and R , as shown in Fig. 2. In comparison with the first approximation, F is increased by $\sim 15\%$; the geometrical factor G accounts for this.

Photoacoustic Cell Construction. As mentioned before, we use an open end tube type of resonator, excited in its first longitudinal mode (Fig. 1). The resonator is placed coaxially inside a larger cell. To achieve an optimum signal, we have chosen a long absorption pathlength (300 mm) with a diameter of 6 mm.

TABLE I. Characteristics of the resonator: length, 300 mm; diameter, 6 mm; outer dimensions: length, 450 mm; diameter, 58 mm; volume, 1.2 dm³.

Electrical noise (4 microphones) at 560 Hz	0.5 $\mu\text{V}/\sqrt{\text{Hz}}$
Acoustical background noise at 560 Hz	1 $\mu\text{V}/\sqrt{\text{Hz}}$
Background signal	20 $\mu\text{V}/\text{W}$
Cell response ($Q = 16.4$)	$(5.0 \pm 0.4) \times 10^3 \text{ Pa cm/W}$
Limiting sensitivity of the cell	$5.0 \times 10^{-9} \text{ cm}^{-1}\text{W}/\sqrt{\text{Hz}}$
Limiting sensitivity of the system (7 W laser power, 1 Hz bandwidth)	$7.1 \times 10^{-10} \text{ cm}^{-1}$

In order to obtain a maximized signal-to-noise ratio, a resonance frequency around 1 kHz is necessary. The $1/f$ amplifier noise determines the noise level up to 1 kHz, showing a frequency behavior of $1/\omega$. Above 1 kHz we have a constant noise level (Brownian noise) of $1 \mu\text{V}/\sqrt{\text{Hz}}$ (vacuum $0.5 \mu\text{V}/\sqrt{\text{Hz}}$). The cell constant is $F \propto L^2/R$ or $F \propto 1/(R \cdot \omega^2)$. Due to this, the signal-to-noise ratio is proportional to $\sqrt{\omega}$ below 1 kHz and $1/\sqrt{\omega}$ above 1 kHz.

This approach is in contrast to other experiments^{17,18} with a large diameter-to-length ratio for the cell geometry, to excite the resonance in the radial or azimuthal acoustic mode with high Q values and high resonance frequencies. The loss of acoustic signal caused by the relatively low Q value in our system is compensated by the signal gain due to the small diameter.

The outer cell dimensions are (for the 300-mm-long resonator) $450 \times 58 \text{ mm}$ (length $\times$ diameter). Both ends of the outer tube are closed with Brewster windows mounted on aluminum holders. Laser power absorption of the ZnSe windows of the cell generates an acoustic signal which is picked up by the microphone. When the ratio of buffer to resonator diameter is larger and the buffer length equals one quarter of the resonator length, the acoustic coupling to the resonator is minimized.

The acoustic signal from the windows is in phase and at the same frequency as the gas absorption signal. Therefore, it is not filtered out by the lock-in amplifier connected to the microphone; thus a background signal proportional to the laser power is produced. At resonance frequency, acoustic fluctuations with arbitrary phase are seen as noise on the signal (1 Hz bandwidth).

The inner wall of the argentine resonator tube is polished. It is centered inside the outer stainless steel tube by Teflon® spacers. One massive spacer is positioned at one end to prevent bypassing of air in the flow system, the other partially open to avoid the formation of closed volumes. Gas is admitted and exhausted through two

ports located near the ends of the resonator tube. Thus, the perturbation of the acoustic resonator amplitude by the noise of the air flow is minimized.

There are four Knowles electret BT-1754 miniature microphones used in the cell (sensitivity 10 mV/Pa each). They are coupled to the resonator by holes (1 mm diameter) positioned on the central perimeter of the resonator. The electrical signals are added before they are connected to the lock-in amplifier. The battery-fed microphones are mounted in a Teflon® ring pulled over the resonator tube. It is of significant importance to prevent air leakage of the ac pressure signal from inside the resonator tube along the Teflon® microphone holder, since minute spacing between the holder and resonator tube produces a dramatic decrease of the microphone signal and the Q value.

Operating Conditions. The cell parameters are given in Table I. The measurements are performed at a pressure of 1 atm. In the infrared region the molecular absorption lines are pressure broadened to a width of 4 GHz. Short-term frequency stabilization of the laser is therefore less important.

The limiting electrical noise measured at the resonance frequency is $0.5 \mu\text{V}/\sqrt{\text{Hz}}$. At atmospheric pressure the acoustic background noise is $1 \mu\text{V}/\sqrt{\text{Hz}}$ (at resonance frequency) under normal working conditions; the room noise level was 73 dB (A). No increase of the noise level is observed when the very stable laser produces a photoacoustic signal. A photoacoustic background signal of $5 \mu\text{V}/\text{W}$ is observed, in phase and at resonance frequency, if the cell is filled with pure N₂.

The sensitivity of the cell is tested by measuring the C₂H₄ absorption for several CO₂ laser lines. The absorption strengths for these lines at atmospheric pressure are known.¹ The strongest absorption is at the 10P14 CO₂ laser line, $\alpha = 30.4 \text{ atm}^{-1} \text{ cm}^{-1}$. The photoacoustic cell shows a linear response, for the investigated range of mixtures of C₂H₄ with N₂, from 100 ppm (parts per million) to 1 ppb (parts per billion, $1:10^9$).

We have investigated various resonator diameters and lengths. For the shorter resonator tube of 150 mm, the outer cell dimensions are $225 \times 58 \text{ mm}$ (length $\times$ diameter). The results are shown in Table II and Fig. 2. In this table the cell constant F is multiplied by $\sqrt{2}$ to find the peak value from the rms pressure amplitude. In comparison to the theoretical results, the experimental Q values are lower. These increases of losses per cycle of the acoustic wave (see definition of Q value) are due to the air leakage between microphone mount and resonator tube and the imperfection of the resonator wall tube.

TABLE II. Characteristics of various diameters and lengths of the resonator. Cell constant F is given in Pa cm/W ($\sqrt{2} \times \text{rms value}$).

Resonator						
Diameter [mm]	Length [mm]	F Theor. ($\times 10^3$)	Q Theor.	F Exp. ($\times 10^3$)	Q Exp.	F Corrected ($\times 10^3$)
6	300	11.2	22.0	7.1 ± 0.4	16.4 ± 0.5	9.5 ± 0.7
9	300	7.3	33.9	5.6 ± 0.3	28.7 ± 0.8	6.6 ± 0.5
12	300	5.2	45.8	3.1 ± 0.2	34.0 ± 1.0	4.1 ± 0.3
18	300	3.0	65.9	2.0 ± 0.10	46.6 ± 1.4	2.8 ± 0.2
6	150	7.9	31.1	3.8 ± 0.2	17.1 ± 0.5	6.9 ± 0.5
9	150	5.1	47.7	2.8 ± 0.14	27.2 ± 0.8	5.0 ± 0.4
12	150	3.7	64.7	0.80 ± 0.04	17.5 ± 0.5	3.0 ± 0.2
18	150	2.2	101.0	0.78 ± 0.04	41.0 ± 1.3	1.9 ± 0.14

FIG. 3. Photoacoustic pressure amplitude of the resonator (diameter, 9 mm; length, 300 mm) as a function of the chopping frequency. A Q value of 16.4 is obtained around the resonance frequency of 560 Hz in a mixture of C_2H_4 in N_2 .

When we correct the experimental cell constants F with the ratio between the theoretical (calculated with the extended transmission line theory) and experimental Q value, we find a good agreement with theoretical behavior (Fig. 2). For the resonator dimensions of 300 mm length and 6 mm diameter we measure a sensitivity of $5.0 \times 10^{-9} \text{ cm}^{-1}$ (1 Hz bandwidth and 1 W laser power). The detection limit for 7 W laser power is thus $7.1 \times 10^{-10} \text{ cm}^{-1}$, yielding a limit of 20 ppt (parts per trillion, $1:10^{12}$) for C_2H_4 .

The total cell volume was 1.2 dm^3 (see Table I). For flowing conditions, however, it is advantageous to reduce the active volume of the cell. Especially if the flow is smaller than 1 L/h, the replenish time for the 1.2 dm^3 cell becomes impractical. The buffer volume is 198 cm^3 (diameter 58 mm, length 75 mm), yielding a $1/e$ time constant τ of 12.4 min. The buffer volume at the entrance port of the cell largely affects the renewal time τ . The renewal time was measured with the use of the above-mentioned solid Teflon® spacer near the entrance port. Reducing the buffer volume to 24 cm^3 (diameter 20 mm,

FIG. 4. Ethylene absorption coefficient at CO_2 laser wavelengths (see also Ref. 1).

FIG. 5. Ethylene production versus time of a single *Cymbidium* orchid flower. After removal of the pollinia (emasculation), a small increase in ethylene production is observed and an advanced senescence process (second increase in ethylene production). The flow rate was 0.9 L/h, the fresh weight of the flower 2.3 g. The production of the intact flower was not changed during the course of the experiment.

length 75 mm), we found a τ of 2 min. However, an increased acoustical noise level of $2 \mu V/\sqrt{\text{Hz}}$ was observed, due to the gas flow.

EXPERIMENTAL SETUP

The laser and the photoacoustic cell as described above form the essential parts of the experimental setup. The resonance of the photoacoustic cell is excited by a chopped laser beam. The frequency of the chopper is phase stabilized to prevent jitter across the acoustic resonance curve (Fig. 3). The diverging infrared laser beam is converged by a curved mirror ($R = 750 \text{ mm}$) placed at its focal length from the laser exit. In this way, a slightly focused laser beam is passed through the photoacoustic cell without wall interactions.

The linearity and the absorption strength were tested with C_2H_4 diluted in N_2 . At CO_2 laser wavelengths, the absorption strength of ethylene at S.T.P. (300 K, 1 atmosphere) is well known (Fig. 4).¹ As a consequence of the superposition of different pressure-broadened C_2H_4 transitions,¹⁹ a strong absorption is obtained at the $10P_{14}$ laser line. Because of the large spacing between the laser transitions (one each 1.5 cm^{-1}), strong differences of absorption occur.

In ambient air, one finds CO_2 concentrations of 330 ppm. Under the practical conditions of an agricultural application (e.g., in greenhouses) this level rises (to about 1%). This forms a serious practical problem. The CO_2 molecule possesses vibrational difference band transitions $v_1 \rightarrow v_3$ and $2v_2 \rightarrow v_3$. These transitions are weak, and the lower levels are barely populated ($\sim 1\%$) at room temperature. However, due to their exact coincidence of ro-vibrational transitions with the CO_2 laser lines and the relatively high concentration of CO_2 in comparison to trace gases like C_2H_4 , the related photoacoustic signal can exceed the trace signal by many orders of magnitude. A 1.5% concentration of CO_2 has an absorption strength comparable to 1 ppm C_2H_4 (for CO_2 at the $10P_{14}$ laser line, $\alpha = 2.1 \times 10^{-3} \text{ atm}^{-1} \text{ cm}^{-1}$; see Refs. 20 and 21).

There are a few ways to overcome this problem. The first is to remove the CO_2 from the flowing sample by

FIG. 6. The orchid flower and its emasculation. An insect leaving the flower removes the anther cap and pollinia, which serves as an indication for the flower to start its senescence process.

absorption on a KOH-based scrubber. In this way concentrations below 1 ppm CO_2 can be achieved. Another way is to use the infrared N_2O laser lines, which have no coincidences with the CO_2 difference band transitions. Absorptions at N_2O laser lines are given by Lambeau *et al.*¹⁹ for C_2H_4 . A disadvantage is the $3\times$ lower output power of the N_2O laser and its spectral range. The third method utilizes the phase information of the photoacoustic response to suppress the CO_2 signal. The CO_2 molecules in the photoacoustic cell, excited by CO_2 laser radiation to the ν_3 level, undergo resonant collisions with N_2 molecules producing the $\nu = 0 \rightarrow \nu = 1$ vibrational transition of N_2 ; the vibrational energy is exchanged between CO_2 and N_2 . This N_2 vibrational level has a long relaxation time (N_2 , $\tau = 0.3 \text{ ms atm}$; C_2H_4 , $\tau = 138 \mu\text{s Torr}^{23}$). In comparison with a chopping period of 1.8 ms, the vibrational-translational relaxation of the CO_2 (due to collisions with N_2 , $\tau_{\text{CO}_2-\text{N}_2} = 12.8 \mu\text{s atm}$)²⁴ in combination with the high concentration of CO_2 ($\sim 1\%$) yields a phase shift of the signal with respect to the acoustic signal of ethylene. A combined signal for a CO_2 - C_2H_4 mixture is less than the sum of both individual amplitudes (vectorially added). The zero phase of the two-phase vector lock-in amplifier is adjusted to pure C_2H_4 absorption, and thus a mixture of CO_2 and C_2H_4 in air is measured on two CO_2 laser transitions. One obtains four pieces of information, i.e., the CO_2 - C_2H_4 mixture phase shift and absorption strength on both lines. From this, with known absorption coefficients for both lines, the CO_2 and C_2H_4 concentration can be extracted (see also Ref. 25). We have used this last approach for our measurements, which has the advantage that a high laser power can be used and no partial failure of the scrubber can falsify the C_2H_4 concentration.

FIG. 7. Initial changes in ethylene concentration and calculated ethylene production following emasculation of various orchid species (temperature, 22°C ; relative humidity, $\sim 50\%$). E = time of emasculation. In the insert, the prompt increase of ethylene production of Phalaenopsis after emasculation is shown.

APPLICATIONS

Ethylene and Flowers. For investigation of the ethylene emission of orchid flowers, the photoacoustic method is used in a flowing air system. Plant physiologists are interested in C_2H_4 as a plant growth regulator.^{26,27} As a gaseous hormone produced by the plant itself, it causes ripening of fruit, growth inhibition of plants, wilting of flowers, and yellowing and abscission of leaves. These effects are also caused by exogenous C_2H_4 (air pollution) formed during combustion processes and found, for example, in car exhaust gases.²⁰

In most laboratories the standard procedure for analysis of C_2H_4 concentrations is gas chromatography with flame ionization detection. For this apparatus the detection limit is 5 nanoliter/liter ($\text{S/N} = 1$) (our detection limit amounts to 0.03 nL/L). Orchids, which are sensitive to ethylene, are known to produce ethylene just before or during the wilting process.²⁸ Because of the low C_2H_4 production, the orchids are normally placed in a closed volume to accumulate the produced C_2H_4 , after which a sample is extracted every hour²⁸ and measured by a gas chromatograph. However, during the accumulation time the C_2H_4 production rate can be influenced by changes in concentration of CO_2 , C_2H_4 , and O_2 . Another disadvantage of this method is that rapid changes in production are not observable. These drawbacks can be avoided by using the more sensitive photoacoustic method with its flowing air system.

In Fig. 5 is shown the ethylene production of a single

FIG. 8. Changes in C_2H_4 production following emasculation of cymbidium flowers under conditions of low ($\sim 50\%$) and high ($\sim 100\%$) relative humidity. E = time of emasculation.

orchid flower, as measured with our setup. Orchids are chosen because they show a low level emission of C_2H_4 during the wilting process. The production can be manipulated by removal of the pollinia and the anther cap (under natural conditions, this is caused by insects leaving the flower, for example). This "emasculation" (see Fig. 6) is a signal for the orchid to start its fructification and senescence processes.

The flowers are placed in a small glass sample cell (80 cm^3 , Fig. 1) with in- and outlet ports and a port to allow emasculation. Before flowing air is admitted to the flower in the cuvette, the gas is led through a catalyst in order to remove any trace of hydrocarbons present. The catalyst is a copper tube (length = 6 m) filled with platinized aluminum oxide at 350°C , which causes the hydrocarbons to dissociate into CO_2 and H_2O . A KOH-based scrubber inserted between the sampling cell and the photoacoustic cell eliminates H_2O and CO_2 without influencing the C_2H_4 concentrations. A flow controller before the sampling volume is set to 0.9 L/h . The flow velocity minimizes accumulation of the produced gases in the sampling cell. The total renewal time of the gas content in the system (sampling cell, scrubber, and photoacoustic cell) is $\tau = 14\text{ min}$ ($1/e$ time). This τ value is small compared to the biological time response of the treated flowers (one to several hours). However, the flow rate is low enough to yield a measurable signal for the C_2H_4 production of a single flower (0.02 to 0.3 nL/g/h).

The C_2H_4 concentration is measured on the $10P14$ (strong C_2H_4 absorption) and $10P12$ (weak C_2H_4 absorption) CO_2 laser lines, at 949.48 cm^{-1} ($\alpha = 30.4\text{ atm}^{-1}\text{ cm}^{-1}$) and 951.19 cm^{-1} ($\alpha = 4.31\text{ atm}^{-1}\text{ cm}^{-1}$), respectively.

In Fig. 5 the ethylene production of the Cymbidium orchid after emasculation is shown as a function of time. The C_2H_4 concentration increases within 3 h after emasculation, peaking at about 8 h. After a decline the concentration exhibits another peak after 40 h.

The first peak coincides with a red coloration of the labellum (lip), the second one with wilting of the flower. An intact flower shows these symptoms (coloration and

FIG. 9. The ozone (O_3) absorption coefficient at the CO_2 laser wavelengths.

wilting) over a much longer time span (10–15 days). The C_2H_4 concentration in the outlet flow from an intact reference flower shows no significant changes during the experiment.

Besides this Cymbidium orchid flower, other orchid species have been investigated (Fig. 7). Treated in the same way as the Cymbidium, the Oncidium orchid also produces a relatively small C_2H_4 peak shortly after emasculation (1.5 nL/g/h), followed by a more pronounced increase accompanying senescence. The start of the second peak depends on the freshness of the flower (i.e., for fresh flowers after several days, for older ones immediately).

In Phalaenopsis and Epidendrum there is only a gradual increase of ethylene production, starting almost immediately after emasculation and developing into a more pronounced increase starting at about 12 h. This production increase lasted for several days and coincided with wilting.

We have also investigated the influence of the relative humidity (RH) of the air flowing over the flower (Cym-

FIG. 10. Hydrogen sulphide (H_2S) absorption coefficient at the CO_2 laser wavelengths.

TABLE III. Absorption coefficients ($\text{atm}^{-1} \text{cm}^{-1}$).

Line no.	Frequency [cm^{-1}]	O_3 error $\pm 9\%$	H_2S error $\pm 8\%$ ($\times 10^{-3}$)	$\text{C}_2\text{H}_4\text{Br}_2$ error $\pm 8\%$	$\text{C}_4\text{H}_8\text{O}_2$ error $\pm 9\%$
10P50	914.4192				1.08
10P48	916.5817				0.93
10P46	918.7183	0.029	0.059	0.193	0.96
10P44	920.8291	0.031	0.062	0.146	1.02
10P42	922.9142	0.028	0.085	0.117	1.08
10P40	924.9739	0.031	0.085	0.094	1.10
10P38	927.0083	0.027	0.083	0.075	1.11
10P36	929.0174	0.029	0.097	0.053	1.16
10P34	931.0014	0.028	0.078	0.040	1.20
10P32	932.9604	0.030	0.081	0.035	1.15
10P30	934.8944	0.029	0.078	0.031	1.04
10P28	936.8037	0.030	0.083	0.031	0.93
10P26	938.6882	0.030	0.097	0.031	1.00
10P24	940.5480	0.030	0.085	0.030	0.86
10P22	942.3833	0.028	0.092	0.030	0.89
10P20	944.1940	0.027	0.107	0.031	1.01
10P18	945.9802	0.027	0.111	0.033	1.00
10P16	947.7419	0.029	0.116	0.035	0.94
10P14	949.4793	0.029	0.132	0.037	0.62
10P12	951.1922	0.029	0.183	0.036	0.42
10P10	952.8808	0.027	0.142	0.037	0.26
10P8	954.5450	0.028	0.159	0.035	0.20
10P6	956.1849	0.031	0.173	0.037	0.18
10P4	957.8005	0.032	0.194	0.038	0.16
10R2	963.2631		0.28		0.16
10R4	964.7689	0.035	0.30	0.034	0.15
10R6	966.2503	0.038	0.22	0.036	0.15
10R8	967.7072	0.049	0.54	0.036	0.15
10R10	969.1395	0.057	0.44	0.033	0.16
10R12	970.5472	0.062	0.46	0.033	0.16
10R14	971.9302	0.078	0.50	0.031	0.17
10R16	973.2885	0.099	0.51	0.031	0.18
10R18	974.6219	0.128	0.57	0.030	0.20
10R20	975.9304	0.148	0.61	0.029	0.22
10R22	977.2139	0.127	0.60	0.028	0.22
10R24	978.4722	0.162	0.64	0.027	0.23
10R26	979.7054	0.159	0.70	0.027	0.25
10R28	980.9132	0.20	0.65	0.026	0.27
10R30	982.0955	0.21	0.60	0.024	0.29
10R32	983.2522	0.46	0.64	0.025	0.31
10R34	984.3832	0.25	0.68	0.025	0.33
10R36	985.4883	0.30	0.69	0.024	0.37
10R38	986.5673	0.35	0.70	0.025	0.39
10R40	987.6201	0.41	0.68	0.025	0.42
10R42	988.6466	0.36			0.44
10R44	989.6465				0.46
9P46	1021.0569				0.69
9P44	1023.1893	4.9			0.81
9P42	1025.2978	4.9	0.96	0.20	0.96
9P40	1027.3821	5.9	0.47	0.20	1.18
9P38	1029.4420	8.5	0.48	0.19	1.50
9P36	1031.4774	7.0	0.52	0.19	1.94
9P34	1033.4880	3.6	0.67	0.18	2.5
9P32	1035.4736	5.4	0.61	0.17	3.2
9P30	1037.4341	6.2	0.56	0.18	4.0
9P28	1039.3693	8.7	1.09	0.20	4.9
9P26	1041.2790	5.9	0.54	0.21	6.2
9P24	1043.1634	0.83	0.98	0.23	7.3
9P22	1045.0216	2.0	0.68	0.28	8.5
9P20	1046.8542	4.6	0.57	0.32	9.7
9P18	1048.6608	6.2	0.65	0.35	10.6
9P16	1050.4412	8.9	0.61	0.40	11.9
9P14	1052.1955	12.4	0.58	0.58	12.0
9P12	1053.9235	11.1	0.73	0.54	12.2
9P10	1055.6250	6.3	1.06	0.55	12.1
9P8	1057.3001	12.7	0.86	0.62	12.2
9P6	1058.9487	9.2	0.83	0.78	12.2
9R4	1067.5391				
9R6	1069.0140	0.87	1.22	1.15	6.9
9R8	1070.4623	0.53	1.80	1.18	5.9
9R10	1071.8837	0.28	1.95	1.28	5.1

TABLE III. Continued.

Line no.	Frequency [cm^{-1}]	O_3 error $\pm 9\%$	H_2S error $\pm 8\%$ ($\times 10^{-3}$)	$\text{C}_2\text{H}_4\text{Br}_2$ error $\pm 8\%$	$\text{C}_4\text{H}_8\text{O}_2$ error $\pm 9\%$
9R12	1073.2784	0.23	1.65	1.36	4.4
9R14	1074.6464	0.21	1.76	1.25	4.0
9R16	1075.9878	0.167	2.0	1.51	3.6
9R18	1077.3025	0.139	2.1	1.26	3.3
9R20	1078.5906	0.157	2.3	1.45	3.1
9R22	1079.8522	0.190	2.5	1.46	2.8
9R24	1081.0874	0.30	3.9	1.38	2.7
9R26	1082.2962	0.185	2.4	2.0	2.5
9R28	1083.4987	0.196	3.8	1.93	2.4
9R30	1084.6351	0.173	3.1	1.39	2.4
9R32	1085.7654	0.176	3.2	1.42	2.3
9R34	1086.8697	0.178	4.1	1.48	2.2
9R36	1087.9483	0.046	3.4	1.29	2.2
9R38	1089.0011		4.0		2.4
9R40	1090.0283				

bidium). To obtain a high RH inside the sampling cell, one flushes the air through water. Water is also present in the sampling cell; in this way an RH of 100% (23°C) is measured. In a control measurement, a low RH is obtained by passing the air through a column of CaCl_2 and by putting some CaCl_2 grains inside the sampling cell. This lowers the RH to 50%. For both experiments the H_2O concentration in the photoacoustic cell is not changed, due to the scrubber of KOH between the sampling cell and the photoacoustic cell. The influence of the RH on the C_2H_4 production is shown in Fig. 8. For the high RH, the normal response to emasculation is diminished; i.e., neither increase of C_2H_4 production nor lip coloration and wilting occur. These and other experiments with chemicals which influence the wilting process are described elsewhere.²⁹

Other Trace Gases of Interest to Agriculture and Their Absorption Coefficients. The laser photoacoustic system described above is used for measurements of the absorption coefficients of O_3 , H_2S , 1,2-dibromoethane, and ethylacetate. Each of these compounds is chosen in view of its agricultural interest.

Before measurement of the absorption coefficients of various gases, the photoacoustic system is tested with highly purified N_2 (99.995%) on all laser lines to ensure that no unwanted absorption of impurities occurs. Small microphone signals due to either low absorption coefficients or low concentration are corrected for the background signal observed for pure N_2 . The measurements are performed at 300 K and at atmospheric pressure; the results are listed in Table III.

Ozone. High concentrations of ozone (O_3) are harmful to plants. In urban areas, levels of 0.08–0.2 ppm O_3 are produced from motor exhaust gases in a photochemical reaction.³⁰ For instance, visible injury to leaves of ornamental plants occurs after exposure to 0.1 ppm O_3 during one hour.³¹

For determination of the O_3 absorption coefficient, ozone was pronounced by a Fischer ozone generator (Model 501) with a percentage of 0.58% in oxygen. The mixture was rarefied with nitrogen to 18 ppm ozone. The results are shown in Fig. 9 and Table III. The strongest absorption is at the P(8) laser line of the 9.4- μm band of the CO_2 laser ($12.7 \text{ atm}^{-1} \text{cm}^{-1}$; see Ref. 32), which is

FIG. 11. 1,2-dibromoethane ($\text{CH}_2\text{Br}:\text{CH}_2\text{Br}$) absorption coefficient at the CO_2 laser wavelengths.

in agreement with the excitation of the ν_3 vibrational level of O_3 . The estimated detection limit is 0.06 ppb (1 W laser power, $\text{S/N} = 1$).

Hydrogen Sulphide. An exposure of 7–9 days to 0.3 ppm H_2S inhibits the growth and reduces the weight of spinach.³³ Hydrogen sulphide is contained in effluent water of the potato flour industry. H_2S is a weak absorber at CO_2 laser wavelengths. The concentration used was 0.4% H_2S in nitrogen. The photoacoustic spectrum (Fig. 10) yields absorption towards the 9R branch as expected from diode laser measurements.³⁴ The band center ν_2 of H_2S lies at 1183 cm^{-1} , with a red-shifted wing towards the CO_2 laser region. This yields in the largest absorption at the 9R34 CO_2 laser line ($4.1 \times 10^{-3}\text{ atm}^{-1}\text{ cm}^{-1}$) with a minimum detectable concentration of 170 ppb (1 W, $\text{S/N} = 1$).

1,2-Dibromoethane. $\text{CH}_2\text{Br}:\text{CH}_2\text{Br}$ is used as a cheap but dangerous chemical to produce C_2H_4 "on the spot" in an orchard. The ethylene is applied to citrus fruits to make them look sweet and mature. Cheaper than the purchase of gas bottles is the use of liquid $\text{C}_2\text{H}_4\text{Br}_2$, which produces C_2H_4 and ZnBr_2 in a reaction with zinc. $\text{C}_2\text{H}_4\text{Br}_2$, however, is a carcinogen,³⁵ and small drops could reach the fruit, together with the C_2H_4 ; therefore sensitive detection is required. In Fig. 11 the absorption coefficients measured at a mixture of 0.14% in N_2 are shown. The strong absorption in the 9R CO_2 laser band ($1064\text{--}1088\text{ cm}^{-1}$) is in agreement with earlier results taken from infrared spectra.³⁶ The band center of the ν_3 is at 1087 cm^{-1} . The absorption at the 9R26 CO_2 laser line ($1.0\text{ atm}^{-1}\text{ cm}^{-1}$) results in a detection limit of 0.4 ppb (1 W, $\text{S/N} = 1$).

Ethylacetate. Experiments with gas chromatography and mass spectrometry^{37,38} have shown that certain chemicals are indicative of the deterioration process of fresh or stored meat and meat products. Ethylacetate ($\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$) is one of the volatile constituents associated with the spoilage of various meat products, beef, pork, poultry, and fish.^{39–41} For ethylacetate we used a mixture of 23 ppm in nitrogen. The absorption coefficients are given in Table III and are shown in Fig. 12; the largest absorption is at the 9P12 laser line with a

FIG. 12. Ethylacetate ($\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$) absorption coefficient at the CO_2 laser wavelengths.

strength of $12.2\text{ atm}^{-1}\text{ cm}^{-1}$, which estimates a detectable concentration of 0.06 ppb (1 W, $\text{S/N} = 1$).

DISCUSSION

In this paper we have presented a laser photoacoustic system which is able to detect a minimum absorption coefficient of $\alpha_{\min} = 7.1 \times 10^{-10}\text{ cm}^{-1}$, corresponding to a concentration of 20 parts per trillion of C_2H_4 in air. This extremely low limit was applied to detect the C_2H_4 emission of a single orchid flower after emasculation. More sensitive to ethylene than the gas chromatographic apparatus used nowadays, the photoacoustic system allows the discovery of a different behavior of the flower than expected. However, due to the low C_2H_4 production of the orchid, depending on the weight of the flower (weight ± 4 grams), a decrease of the air flow was necessary to increase the C_2H_4 concentration to a detectable level. This factor and the large volume of the photoacoustic cell resulted in a long delay time before the acoustically measured concentration was as high as the concentration in the sampling cell. Reducing this volume resulted in a significant shortening of this interval.

Other sensitive photoacoustic resonant systems, excited in their radial or azimuthal mode, are at a disadvantage here; due to their large volumes they will have a consequently long delay time and high gas consumption. The gas chromatograph has the advantage of a small volume and low gas consumption. A further decrease of the photoacoustic cell volume is made possible by reducing the resonator length and consequently the buffer volume. Owing to this approach, the investigation of smaller biological samples becomes interesting. Another advantage of the shorter resonator length is the more efficient use of a relatively expensive laser setup by placing more photoacoustic cells behind each other. More biological long-run experiments can then be executed in one session.

An increase in sensitivity can be realized by placing the photoacoustic cell in the laser cavity. Due to the flexible construction of our laser, it is possible to make a photoacoustic intracavity setup with ± 100 W laser power available. A rigid construction, stable laser power,

curved mirror, lens, and intracavity chopping are necessary to obtain this result. Measurements on gases with weaker absorption and lower detectable concentrations will become accessible, which will further extend the versatility of the photoacoustic detection technique.

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