Photoacoustic Measurements of Agriculturally Interesting Gases and Detection of \( \text{C}_2\text{H}_4 \) 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 \( \text{C}_2\text{H}_4 \) in air. Improvements made to achieve this sensitivity are reported, and this low limit is applied to the detection of the \( \text{C}_2\text{H}_4 \) 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, \( \text{CO}_2 \); 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 \( \text{CO}_2 \) 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 (\( \text{C}_2\text{H}_4 \)), 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 \( \text{C}_2\text{H}_4 \) production of an orchid flower is investigated and described. Also, measurements of the absorption coefficients of important agricultural gases on the \( \text{CO}_2 \) laser lines are given.

THE \( \text{CO}_2 \) WAVEGUIDE LASER

The \( \text{CO}_2 \) waveguide laser emits at wavelengths of 9–11 \( \mu \text{m} \) in the infrared. The four branches of the ro-vibrational \( P \) and \( R \) transitions of \( \text{CO}_2 \) produce radiation at 90 laser lines.\(^8\)-\(^10\) A hollow dielectric waveguide tube of \( \text{SiO}_2 \) 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 \( \text{CO}_2 \) 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 \( \text{NaCl} \) windows at the Brewster angle. The windows are attached to aluminum holders and heated to prevent hygroscopic dressing. 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 \( \text{NaCl} \) 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 \( \text{ZnSe} \) end mirror at one end and a line-selecting grating (150 L/mm, blazed at 10.6 \( \mu \text{m} \)) 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 \( \text{CO}_2 \) laser operation we used a mixture of \( \text{He} : \text{N}_2 : \text{CO}_2 \) 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 \( \text{TEM}_00 \) 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 stability\(^11\) (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 the line selection of three branches (10\( P \), 10\( R \), 9\( P \)) of the \( \text{CO}_2 \) laser. Only the 9\( R \) 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...
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.\(^1\) - \(^6\) 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,\(^6\) 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 \((N/m^2 = \text{Pascal})\); \(\alpha\) 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 \((\text{watt})\); \(\omega_0 = 2\pi V_0 = (\pi c/L)\) \((\text{resonance frequency})\); and \(L\) the length of the resonator tube. For a given cell geometry

\[
F(\omega_0) = \frac{(\gamma - 1)LQG}{\omega_0 V} \tag{1}
\]

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

\[
Q = \frac{2S}{2\pi R(d_w + (\gamma - 1)d_h)} \tag{2}
\]

Here, \(S\) stands for the cross section of the resonator tube, \(R\) for the radius of the tube, and \(d_h = (2\mu/\rho c)^{1/3}\) for the thermal boundary layer, \(d_w = (2K/\rho c_{j}c)^{1/3}\) for the viscous boundary layer; \(\mu\) is the viscosity coefficient, \(K\) the conductivity coefficient, and \(\rho\) the density of mass.

The dependence of \(F\) and \(Q\) on the length and diameter of the resonator is obvious, i.e., \(Q \propto R/L\) and \(F \propto L^4R\). 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 theory\(^6\) 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 \((300 \text{ mm})\) with a diameter of \(6 \text{ mm}\).

![Fig. 1. Experimental arrangement for the photoacoustic measurements of C\(_2\)H\(_4\) emitted from orchid flowers. The hydrocarbons present in the compressed air are dissociated into CO\(_2\) and H\(_2\)O 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\(_2\)H\(_4\) photoacoustic signal. Because of the time scale of the experiments the total setup is connected to a computer.](image-url)

![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.](image-url)
TABLE I. Characteristics of the resonator: length, 300 mm; diameter, 6 mm; outer dimensions: length, 450 mm; diameter, 58 mm; volume, 1.2 dm³.

<table>
<thead>
<tr>
<th>Diameter (mm)</th>
<th>Length (mm)</th>
<th>F</th>
<th>Q Theor. (x10⁴)</th>
<th>Q Exp. (x10⁴)</th>
<th>Q Exp.</th>
<th>F Corrected (x10⁴)</th>
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<td>6</td>
<td>300</td>
<td>11.2</td>
<td>22.0</td>
<td>7.1 ± 0.4</td>
<td>16.4 ± 0.5</td>
<td>9.5 ± 0.7</td>
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<td>9</td>
<td>300</td>
<td>7.3</td>
<td>33.9</td>
<td>5.6 ± 0.3</td>
<td>28.7 ± 0.8</td>
<td>6.6 ± 0.5</td>
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<td>12</td>
<td>300</td>
<td>5.2</td>
<td>45.8</td>
<td>3.1 ± 0.2</td>
<td>34.0 ± 1.0</td>
<td>4.1 ± 0.3</td>
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<tr>
<td>18</td>
<td>300</td>
<td>3.0</td>
<td>65.9</td>
<td>2.0 ± 0.10</td>
<td>46.6 ± 1.4</td>
<td>2.8 ± 0.2</td>
</tr>
<tr>
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<td>7.9</td>
<td>31.1</td>
<td>3.8 ± 0.2</td>
<td>17.1 ± 0.5</td>
<td>6.9 ± 0.5</td>
</tr>
<tr>
<td>9</td>
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<td>47.7</td>
<td>2.8 ± 0.14</td>
<td>27.2 ± 0.8</td>
<td>5.0 ± 0.4</td>
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<td>64.7</td>
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<td>17.5 ± 0.5</td>
<td>3.0 ± 0.2</td>
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<tr>
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<td>101.0</td>
<td>0.78 ± 0.04</td>
<td>41.0 ± 1.3</td>
<td>1.9 ± 0.14</td>
</tr>
</tbody>
</table>

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/ω. Above 1 kHz we have a constant noise level (Brownian noise) of 1 μV/√Hz (vacuum 0.5 μV/√Hz). The cell constant is F ∝ L³/R or F ∝ 1/(R · ω²). Due to this, the signal-to-noise ratio is proportional to ω below 1 kHz and 1/ω 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 × 58 mm (length × 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 μV/√Hz. At atmospheric pressure the acoustic background noise is 1 μV/√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 μV/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 CH₄ 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, α = 30.4 atm⁻¹ cm⁻¹. The photoacoustic cell shows a linear response, for the investigated range of mixtures of CH₄ with N₂ from 100 ppm (parts per million) to 1 ppb (parts per billion, 10⁻⁹).

We have investigated various resonator diameters and lengths. For the shorter resonator tube of 150 mm, the outer cell dimensions are 225 × 58 mm (length × diameter). The results are shown in Table II and Fig. 2. In this table the cell constant F is multiplied by √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 (√2 x rms value).
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 $5.0 \times 10^{-9}$ cm$^{-1}$ (1 Hz bandwidth and 1 W laser power). The detection limit for 7 W laser power is thus $7.1 \times 10^{-10}$ cm$^{-1}$, yielding a limit of 20 ppt (parts per trillion, $1 \times 10^{12}$) for C$_2$H$_4$.

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 $\tau$ of $12.4$ min. The buffer volume at the entrance port of the cell largely affects the replenish time $\tau$. 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, length $75$ mm), we found a $\tau$ 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 ($R = 750$ 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$_2$H$_4$ 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). As a consequence of the superposition of different pressure-broadened C$_2$H$_4$ transitions, a strong absorption is obtained at the 10P14 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 $v_1 \rightarrow v_2$ and $2v_2 \rightarrow v_3$. These transitions are weak, and the lower levels are barely populated (~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$_2$H$_4$, 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$_2$H$_4$ (for CO$_2$ at the 10P14 laser line, $\alpha = 2.1 \times 10^{-3}$ atm$^{-1}$ cm$^{-2}$; 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
absorption on a KOH-based scrubber. In this way concentrations below 1 ppm CO₂ can be achieved. Another way is to use the infrared N₂O laser lines, which have no coincidences with the CO₂ difference band transitions. Absorptions at N₂O laser lines are given by Lambeau et al.²⁵ for C₂H₄. A disadvantage is the 3× lower output power of the N₂O laser and its spectral range. The third method utilizes the phase information of the photoacoustic response to suppress the CO₂ signal. The CO₂ molecules in the photoacoustic cell, excited by CO₂ laser radiation to the v₃ level, undergo resonant collisions with N₂ molecules producing the v = 0 → v = 1 vibrational transition of N₂; the vibrational energy is exchanged between CO₂ and N₂. This N₂ vibrational level has a long relaxation time (N₂, τ = 0.3 ms atm²)²³ C₂H₄, τ = 138 μs Torr²³). In comparison with a chopping period of 1.8 ms, the vibrational-translational relaxation of the CO₂ (due to collisions with N₂, τCO₂-N₂ = 12.8 μs atm)²⁴ in combination with the high concentration of CO₂ (~1%) yields a phase shift of the signal with respect to the acoustic signal of ethylene. A combined signal for a CO₂-C₂H₄ 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 C₂H₄ absorption, and thus a mixture of CO₂ and C₂H₄ in air is measured on two CO₂ laser transitions. One obtains four pieces of information, i.e., the CO₂-C₂H₄ mixture phase shift and absorption strength on both lines. From this, with known absorption coefficients for both lines, the CO₂ and C₂H₄ 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 C₂H₄ concentration.

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 C₂H₄ 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 C₂H₄ (air pollution) formed during combustion processes and found, for example, in car exhaust gases.²⁰

In most laboratories the standard procedure for analysis of C₂H₄ concentrations is gas chromatography with flame ionization detection. For this apparatus the detection limit is 5 nanoliter/liter (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 C₂H₄ production, the orchids are normally placed in a closed volume to accumulate the produced C₂H₄, after which a sample is extracted every hour²⁸ and measured by a gas chromatograph. However, during the accumulation time the C₂H₄ production rate can be influenced by changes in concentration of CO₂, C₂H₄, and O₂. 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

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**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.

**Fig. 7.** Initial changes in ethylene concentration and calculated ethylene production following emasculation of various orchid species (temperature, 22°C; relative humidity, ~50%). E = time of emasculation. In the insert, the prompt increase of ethylene production of Phalaenopsis after emasculation is shown.
orchid flower, as measured with our setup. Orchids are chosen because they show a low level emission of C$_2$H$_4$ 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 "emasculating" (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$_2$O. A KOH-based scrubber inserted between the sampling cell and the photoacoustic cell eliminates H$_2$O and CO$_2$ without influencing the C$_2$H$_4$ 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 $\tau = 14$ min ($1/e$ time). This $\tau$ 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$_2$H$_4$ production of a single flower (0.02 to 0.3 nL/g/h).

The C$_2$H$_4$ concentration is measured on the 10P14 (strong C$_2$H$_4$ absorption) and 10P12 (weak C$_2$H$_4$ absorption) CO$_2$ laser lines, at 949.48 cm$^{-1}$ ($\alpha = 30.4$ atm$^{-1}$ cm$^{-1}$) and 951.19 cm$^{-1}$ ($\alpha = 4.31$ atm$^{-1}$ cm$^{-1}$), respectively.

In Fig. 5 the ethylene production of the Cymbidium orchid after emasculation is shown as a function of time. The C$_2$H$_4$ 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 coloring of the labellum (lip), the second one with wilting of the flower. An intact flower shows these symptoms (coloration and wilting) over a much longer time span (10-15 days). The C$_2$H$_4$ 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$_2$H$_4$ 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 (Cymbidium orchid) over a much longer time span (10-15 days). The C$_2$H$_4$ concentration in the outlet flow from an intact reference flower shows no significant changes during the experiment.

Fig. 8. Changes in C$_2$H$_4$ production following emasculation of cymbidium flowers under conditions of low (~50%) and high (~100%) relative humidity. $E =$ time of emasculation.
TABLE III. Continued.

<table>
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<th>Line no.</th>
<th>Frequency [cm⁻¹]</th>
<th>O₃ error</th>
<th>H₂S error</th>
<th>CH₂Br₂ error</th>
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<td>9R40</td>
<td>1090.0283</td>
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</table>

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 CaCl₂ and by putting some CaCl₂ grains inside the sampling cell. This lowers the RH to 50%. For both experiments the H₂O 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 C₂H₆ production is shown in Fig. 8. For the high RH, the normal response to emasculation is diminished; i.e., neither increase of C₂H₆ production nor lip coloration and wilting occur. These and other experiments with chemicals which influence the wilting process are described elsewhere.\textsuperscript{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 O₃, H₂S, 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 N₂ (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 N₂. The measurements are performed at 300 K and at atmospheric pressure; the results are listed in Table III.

Ozone. High concentrations of ozone (O₃) are harmful to plants. In urban areas, levels of 0.08–0.2 ppm O₃ are produced from motor exhaust gases in a photochemical reaction.\textsuperscript{30} For instance, visible injury to leaves of ornamental plants occurs after exposure to 0.1 ppm O₃ during one hour.\textsuperscript{31}

For determination of the O₃ 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 CO₂ laser (12.7 atm⁻¹ cm⁻³; see Ref. 32), which is
in agreement with the excitation of the ν₃ vibrational level of O₂. The estimated detection limit is 0.06 ppb (1 W laser power, S/N = 1).

**Hydrogen Sulphide.** An exposure of 7–9 days to 0.3 ppm H₂S inhibits the growth and reduces the weight of spinach. Hydrogen sulphide is contained in effluent water of the potato flour industry. H₂S is a weak absorber at CO₂ laser wavelengths. The concentration used was 0.4% H₂S in nitrogen. The photoacoustic spectrum (Fig. 10) yields absorption towards the 9R branch as expected from diode laser measurements. The band center νₛ of H₂S lies at 1183 cm⁻¹, with a red-shifted wing towards the CO₂ laser region. This yields in the largest absorption at the 9R34 CO₂ laser line (4.1 × 10⁻³ atm⁻¹ cm⁻¹) with a minimum detectable concentration of 170 ppb (1 W, S/N = 1).

**1,2-Dibromoethane.** CH₂Br.CH₂Br is used as a cheap but dangerous chemical to produce C₂H₄ “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 C₂H₄. Br₂, which produces C₂H₄ and ZnBr₂ in a reaction with zinc. C₂H₄Br₂, however, is a carcinogen, and small drops could reach the fruit, together with the C₂H₄; therefore sensitive detection is required. In Fig. 11 the absorption coefficients measured at a mixture of 0.14% in N₂ are shown. The strong absorption in the 9R CO₂ laser band (1064–1088 cm⁻¹) is in agreement with earlier results taken from infrared spectra. The band center of the νₛ is at 1087 cm⁻¹. The absorption at the 9R26 CO₂ laser line (1.0 atm⁻¹ cm⁻¹) results in a detection limit of 0.4 ppb (1 W, S/N = 1).

**Ethylacetate.** Experiments with gas chromatography and mass spectrometry have shown that certain chemicals are indicative of the deterioration process of fresh or stored meat and meat products. Ethylacetate (CH₃CO₂CH₂CH₃) is one of the volatile constituents associated with the spoilage of various meat products, beef, pork, poultry, and fish. 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 strength of 12.2 atm⁻¹ cm⁻¹, which estimates a detectable concentration of 0.06 ppb (1 W, S/N = 1).

**DISCUSSION**

In this paper we have presented a laser photoacoustic system which is able to detect a minimum absorption coefficient of α_min = 7.1 × 10⁻¹⁰ cm⁻¹, corresponding to a concentration of 20 parts per trillion of C₂H₄ in air. This extremely low limit was applied to detect the C₂H₄ 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 C₂H₄ 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 C₂H₄ 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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35. S. Gentiloni, Scienza e Dossier 4, 22 (1986).