

for many of the compounds studied vs. the mole % ratio of each particular solvent system. Each of these plots shows that  $\nu\text{C}=\text{O}$  shifts with change in the mole % ratio of the solvent.

## CONCLUSIONS

The rotational isomer distribution of carbonyl-containing compounds changes with change in the polarity of the solute/solvent system. The more polar form of the solute increases in concentration as the concentration of the more polar solvent increases in concentration. There is a general correlation where  $\nu\text{C}=\text{O}$  decreases in frequency with increase in polarity ( $\delta_t$ ) of the solvent, but there are exceptions. Hydrogen bonding between the solvent proton and the carbonyl oxygen atom also decreases the  $\nu\text{C}=\text{O}$  frequency.

Steric factors of  $\alpha$ -halo or  $\alpha$ -oxy atoms for the *gauche* carbonyl rotational isomer hinder the interaction of the solvent with the positive site of the canonical solute form,

which weakens the  $\text{C}=\text{O}$  bond. Thus, *gauche*  $\nu\text{C}=\text{O}$  does not decrease in frequency as much as does the *cis*  $\nu\text{C}=\text{O}$  mode for the *cis* rotational isomer in the particular solvent system.

The  $\nu\text{C}=\text{O}$  mode decreases in frequency in the order of increased polarity of the solvent: hexane, carbon tetrachloride, chloroform, and dimethyl sulfoxide. Intermolecular hydrogen bonding between the chloroform proton and the carbonyl oxygen atom of the solute causes  $\nu\text{C}=\text{O}$  to shift to lower frequency. Polar solvents such as dimethyl sulfoxide induce more of the canonical form—which lengthens and weakens the carbonyl group—than do less polar solvents. The  $\nu\text{C}=\text{O}$  frequencies do not appear to correlate with AN numbers of the solvent.

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# The Assessment of Laser Photoacoustic Spectroscopy as the Analytical Tool for Studying the Potato Sprout Suppressants Carvone and Pulegone

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$\text{CO}_2$  laser photoacoustic spectroscopy in combination with the resonant cell has been used to determine the absorption cross sections of the sprouting suppressants pulegone and carvone in order to evaluate the prospects of this technique for practical application during the storage of harvested potatoes. Maximal values found at room temperature are  $0.06 \text{ atm}^{-1} \text{ cm}^{-1}$  and  $0.04 \text{ atm}^{-1} \text{ cm}^{-1}$  for pulegone and carvone respectively, corresponding to detection limits of 200 and 150 ppbv. At  $\text{CO}$  laser wavelengths, a 1 ppb detection limit has been derived.

Index Headings:  $\text{CO}_2$  laser photoacoustic spectroscopy; Sprouting suppressants; Carvone; Pulegone.

## INTRODUCTION

Photothermal methods rely on the various effects induced in the sample (and its surroundings) by the absorption of the modulated electromagnetic radiation, such as refractive index gradient, surface deformation, acoustic emission, phase change, etc. One of these—i.e., the photoacoustic effect—involves the conversion of photon energy absorbed by the sample into sound by means of

collisional relaxation, followed by generation of a pressure wave which is detected by a sensitive microphone.

The ability of laser photoacoustic spectroscopy and related photothermal techniques to provide the measurement of ultra-low absorption in gas, liquid, and solid phases has led to numerous applications in various areas of scientific research.<sup>1,2,3</sup> The magnitude of the pressure wave is linearly proportional to the absorption coefficient of the studied sample (for values of the absorption coefficient below the onset of saturation), the power of the radiation source, and the concentration (six orders of magnitude is not exceptional) of the investigated species. In addition, the intrinsically high speed of response and the ease of sampling make this method very suitable for real-time analysis. *In situ* concentration monitoring at the sub-ppbv level for several gaseous atmospheric pollutants has already been performed under realistic conditions. Quite recently, the photoacoustic method in combination with the powerful carbon dioxide laser (infrared region around  $10 \mu\text{m}$ ) has also been applied in order to study the time evolution of ethylene metabolism in stressed *Cymbidium* flowers<sup>4,5,6</sup> and in the inundated *Rumex* plants; an ultimate detection sensitivity of 10 ppt has been attained in these experiments.

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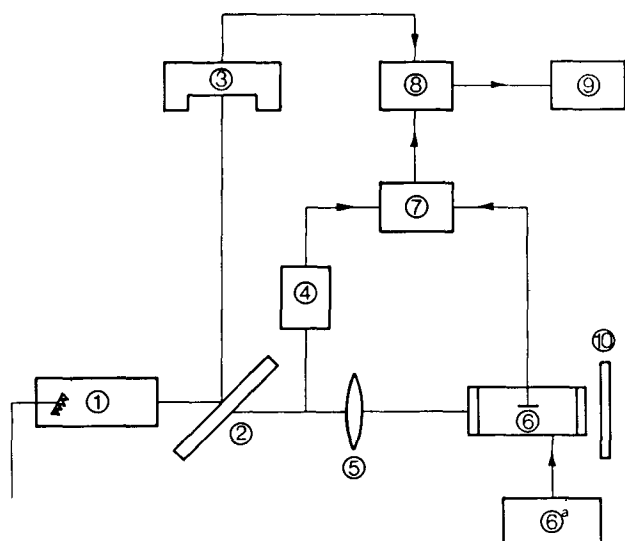


FIG. 1. The experimental setup used in this study. (1) Tunable laser; (2) beamsplitter; (3) power detector; (4) chopper; (5) lens; (6) photoacoustic cell with microphone; (6a) gas handling system; (7) lock-in amplifier; (8) ratiometer; (9) data registration; (10) beam stop.

Storage of potatoes at 2–4°C in the post-harvest period prevents sprouting. However, at such low temperatures the concentration of reducing hexoses in commonly used potato cultivars reaches undesirably high levels, leading to the well-known Maillard reaction during processing. In order to avoid this, potato tubers are stored at elevated temperature (7–10°C) and treated with a mixture of chemicals such as propham and chlorpropham. Although no evidence of hazardous effects (at the applied concentration) for humans, due to such treatment, has ever been collected, intensive research attempts, aimed at finding alternative sprouting inhibitors of plant origin, are being carried out. Carvone and pulegone, found in the essential oils of many plants, have emerged as possible candidates.<sup>7</sup> Studying the dose-effect relationship of these volatiles as potential controllers of sprout growth requires a technique capable of a low detection limit and high resolution. The absorption coefficients of carvone and pulegone at CO<sub>2</sub> laser wavelengths have therefore been determined with the use of photoacoustic spectroscopy.

## EXPERIMENTAL

A schematic diagram of the experimental setup is shown in Fig. 1. The radiation of a power-stabilized CO<sub>2</sub> waveguide laser emitting 2 W is modulated by a Photon Technology International OC 4000 chopper. A CO<sub>2</sub> spectrum analyzer from Optical Engineering is used to monitor the emission line of the laser. The lens system ensures that the diameter of the laser beam at the output coupling mirror equals that in the photoacoustic cell. This latter is a stainless-steel cylinder (50 mm in diameter and 300 mm long)—terminated on both ends by end caps with ZnSe windows—that accommodates another tube (8 mm diameter and 230 mm long) that serves as an acoustic resonator at 555 Hz. A ring with four miniature hearing-aid electret microphones (Knowless 1760) is mounted in the middle of the resonator tube. The generated signal is synchronously detected at the modulated frequency

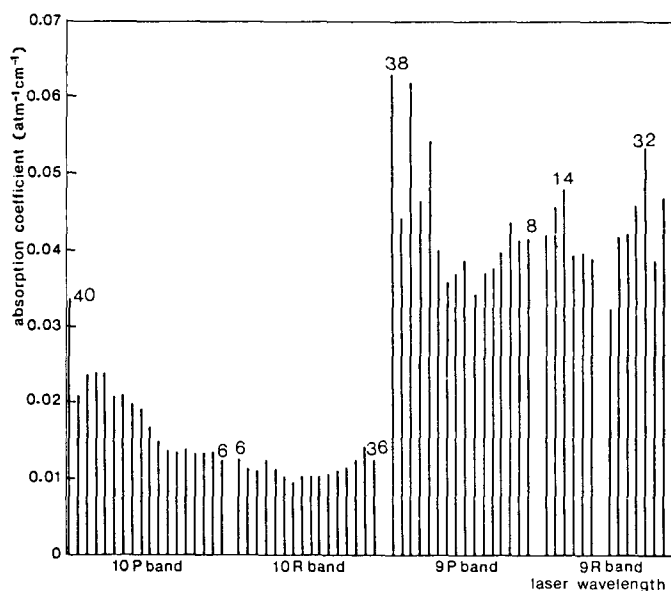


FIG. 2. The normalized spectrum of pulegone vapor at the atmospheric pressure and room temperature plotted vs. CO<sub>2</sub> laser wavelength.

by an Ithaco 3961 lock-in amplifier with a bandwidth of 1 Hz. A gaseous mixture of sprout suppressant is prepared in the following way: A known amount of liquid is injected into an evacuated cylinder of 70 L, where it vaporizes (vapor pressures of pulegone and carvone are 18 and 16.6 Pa at 298 K) before being buffered with an ultrapure nitrogen to a total pressure of 1000 mbar at a temperature of 295 K. From this reservoir, the homogeneous gaseous mixture can easily be admitted into the evacuated photoacoustic cell.

In order to determine the absolute values of the absorption coefficients, the photoacoustic cell had to be calibrated first. This was achieved with the use of the signal produced by a known concentration of test gas containing ethylene [precisely known value of 36 atm<sup>-1</sup> cm<sup>-1</sup> at the 10P (14) laser line] in pure nitrogen. The signal was vectorially corrected for the coherent laser background contribution that occurred when the cell was filled with an infrared nonabsorbing gas (nitrogen), due to the optical losses (and hence the heating) in cell windows. The typical background level (measured with nitrogen as a fill gas) was 1–2 μV for each watt of the incident power and was practically independent of the laser wavelength.

## RESULTS AND DISCUSSION

The photoacoustic spectra were recorded at some sixty discrete laser emission lines in the wavelength region from 9 to 11 μm, with the cell kept at room temperature and at atmospheric pressure. Inspection of pulegone (C<sub>10</sub>H<sub>16</sub>O) absorption spectra recorded in the liquid phase<sup>8</sup> reveals bands at 1035 and 935 cm<sup>-1</sup>. In the case of carvone (C<sub>10</sub>H<sub>16</sub>O), two strong peaks centered at 1100 and 880 cm<sup>-1</sup> are observed,<sup>8</sup> but this falls outside the spectral region covered by the CO<sub>2</sub> laser emission; however there is some absorption near 1050 cm<sup>-1</sup>.

Figure 2 shows the experimentally determined absorption coefficient  $\alpha$  in atm<sup>-1</sup> cm<sup>-1</sup> units (1 m/N 1010

atm<sup>-1</sup> cm<sup>-1</sup>) for pulegone obtained with the static fill (nonflowing) sample in the gas phase, plotted against the laser wavelength from the 10P to 9R band of the laser. The value of  $\alpha$  (atm<sup>-1</sup> cm<sup>-1</sup>) is calculated from the measured lock-in signal  $S(V)$  and the power  $P(W)$  (measured by a calibrated Coherent Radiation 210 thermopile detector behind the photoacoustic cell) reaching the gas in the cell according to the relationship:

$$\alpha = S/(PRc) \quad (1)$$

where  $c$  is the concentration (measured in atm; for example, 1 ppb is 10<sup>-9</sup> atm), and  $R$  (V cm<sup>-1</sup>/W) is the cell responsivity factor obtained through the calibration with a 120-ppb certified mixture of ethylene in nitrogen.

The maximum value of the absorption coefficient for pulegone is 0.06 atm<sup>-1</sup> cm<sup>-1</sup> at the 9P (38) laser transition, corresponding to a frequency of 1029.44 cm<sup>-1</sup>. The spectrum is rather congested, with the absorption dominating the 9- $\mu$ m region. For comparison, the value of the maximal absorption coefficients for simple molecules, such as ethylene and ammonia, is 500 to 1000 times larger under the same conditions. The peak absorption for carvone (0.045 atm<sup>-1</sup> cm<sup>-1</sup>) is also in the 9P band, [centered at the 9P (22) transition]; furthermore, spectral features in the 10- $\mu$ m band are less pronounced.

From the experimentally determined values of the absorption cross sections, the detection sensitivity of the present experimental setup can be derived. Direct comparison of our data with those obtained previously with ammonia, ethylene, and many other gases<sup>9,10</sup> provides an ultimate detection limit of 150 to 200 ppbv for pulegone and carvone (in the nonflowing regime) at the CO<sub>2</sub> laser wavelengths with the sample at room temperature and with a laser power of 1 W. Further improvement in sensitivity is made possible by using an intracavity arrangement<sup>5</sup> (the photoacoustic cell is placed within the optical cavity of the laser, thereby being exposed to power levels 100 times larger than those in effect when the extracavity configuration is used), as has already been demonstrated.<sup>6</sup> Operating the photoacoustic cell as a heat pipe at elevated, instead of ambient, temperature provides an additional enhancement, as has been shown with geraniol<sup>11</sup> and malathion<sup>12</sup> pesticides as the test specimens.

A sub-ppbv detection limit sensitivity can be readily anticipated if a strong radiation source emitting at shorter wavelengths becomes available. Both carvone and pulegone have very strong absorption bands at 1700 and 1650 cm<sup>-1</sup>—a spectral region that is accessible to CO lasers. Various types of conventional,<sup>13,14</sup> electrochemically tuned,<sup>15</sup> and radio-frequency-excited carbon mon-

oxide lasers<sup>16</sup> emitting more than a watt of power at a large number of lines between 3 and 6  $\mu$ m are available at present. Since the CO laser can be tuned into a resonance with both resonant transitions mentioned above, an ultimate detection limit close to 1 ppb may be anticipated.

In conclusion, laser photoacoustic spectroscopy has been shown to have potential usefulness in the monitoring of low concentrations of carvone and pulegone in real time. The characteristic spectral fingerprints of several other volatile organic sprout suppressants in the infrared region suggest that they too can be studied efficiently with the same cell and lasers.

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