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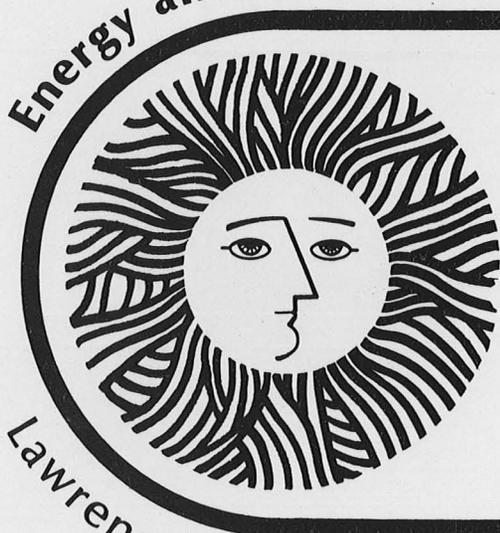
Sensitive Optoacoustic Detection of Carbon Monoxide by Resonance Absorption

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SENSITIVE OPTOACOUSTIC DETECTION OF CARBON MONOXIDE
BY RESONANCE ABSORPTION

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ABSTRACT

Sensitive (0.15 ppm) and unambiguous detection of carbon monoxide is reported and a comparison of acoustically resonant and nonresonant detectors is given. The pressure dependence of the optoacoustic signal is discussed in the context of atmospheric absorption.

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The carbon monoxide molecule (CO) is of interest for a variety of reasons. CO plays a crucial role in the $CO-OH-CH_4$ cycle responsible for cleansing the troposphere.[1] It is a dangerous air pollutant and has been implicated in the formation of smog.[2] It is one of the main constituents of the atmospheres of Venus and Mars, and has been detected in interstellar clouds. In addition, the CO molecule is of fundamental spectroscopic and biomedical interest.

The most widely used techniques for the detection of CO are: 1) conventional infrared absorption. This approach suffers from interference, particularly from N_2O, and although adequate for many applications, it is incapable of ultra-low concentration detection. 2) Gas chromatography, which is highly sensitive, but is elaborate and time-consuming.

We have combined the concept of optical resonance absorption with laser optoacoustic spectroscopy to achieve sensitive and interference-free detection of CO.

We used a cw gas discharge CO laser capable of oscillating on transitions in the fundamental $1 \to 0$ band of CO,[3] around 4.75 μm, as well as on higher vibrational bands. Operation on transitions in the $1 \to 0$ band was essential because only these transitions are resonantly, and hence strongly, absorbed by CO molecules in their ground vibrational state. Laser transitions in higher vibrational bands are generally not resonant with those in the fundamental $1 \gets 0$ band; and while resonant with hot band transitions, the latter produce very little absorption at typical ambient temperatures.

Table I lists the laser lines used and the typical powers available in single-line operation. In addition to three $1 \to 0$ lines, we have investigated the $P_{2-1}(12)$ transition, which, of all observed hot band laser transitions, was closest to resonance with a $1 \gets 0$ absorption line, having an offset of 0.045 cm^{-1} from the $P_{1-0}(18)$ line.[4] Typical full widths at half maximum for lines in the $1 \gets 0$ band in air at atmospheric pressure are 0.10 at 0.14 cm^{-1}.[5] Although the absorption at this hot band wavelength is weaker than for the $1 \to 0$ laser transitions, this is compensated for by the higher power obtainable. However, comparison of the performance of the system when using the $P_{2-1}(12)$ transition to that using the $1 \to 0$ transitions will reveal many of the advantages of the resonant absorption case.

A standard electro-optic modulation system, consisting of a CdTe Pockels cell and quarter-wave plate and polarizer, was used to obtain

vibration-free intensity modulation of the laser light. Good extinction was achieved, but the maximum transmission through the system was only 67%. All laser powers quoted herein were measured at a point before attenuation by the modulation optics.

Two types of optoacoustic cells were investigated for comparison: an acoustically nonresonant cell which was operated in its 1/f frequency response region, and a resonant cell which was driven at the frequency of its first radial resonance.

The nonresonant cell was made of copper, with a cavity 7.6 cm long and 2.5 cm in diameter. NaCl flats were used as cell windows. A General Radio model 1962-9601 1-inch electret condenser microphone (sensitivity 11 mV/Pa) was used as the detector. For isolation from sound and vibrations, the cell was mounted in lead blocks, surrounded by acoustical shielding material, and enclosed in a plywood box resting on rubber foam. This made acoustical noise negligible compared to electrical noise.

We chose to operate at 25 Hz, where both the optoacoustic cell response and the noise spectrum have a 1/f frequency dependence. At this frequency the rms noise was approximately 270 $nV/Hz^{\frac{1}{2}}$. When measuring small concentrations we used a 10 sec time constant on our lock-in amplifier, resulting in a noise level of 35 nV rms. Over a long period of observation the output fluctuated over a ± 50 nV span, and we took this as the limitation on signal measurement imposed by noise.

The system was calibrated by measuring the optoacoustic signals for gas mixtures of known CO concentration. We used gas mixtures from National Bureau of Standards having concentrations 49.3 ± 0.5, 95 ± 0.9, and 476 ± 5 ppm and certified mixtures from Matheson having concentrations 6,

11, and 29 ppm (all ± 5%) of CO in N_2. Mixtures of other concentrations were prepared by diluting the NBS mixtures with N_2.

The dependence of optoacoustic signal on CO concentration in the nonresonant cell for the four transitions investigated is summarized in Table I, and illustrated in Fig. 1 for the $P_{1-0}(11)$ transition. Above a certain background-equivalent concentration, and up to the maximum concentration investigated, 476 ppm, the signal is proportional to CO concentration. Below the background-equivalent concentration, the signal approaches a nonzero value of $\sim$ 0.04 μV/mW for all four transitions as concentration approaches zero. This is an optoacoustic signal which disappears when the laser beam is blocked. It is also observed with pure N_2 in the cell. We attribute this background signal to heating of the walls and/or windows of the cell by the beam, which has a 1 cm diameter at $1/e^2$ intensity traversing the cell.

In practice our limit of lowest detectable concentration for the nonresonant cell was set by the background signal, which allowed the detection of $\sim$ 1.5 ppm for the three resonant transitions. For the $P_{2-1}(12)$ transition, the CO absorption is much weaker but the power available was much larger, so that at a given concentration the observed signal to noise ratio was comparable to that for the resonant transitions. However, the higher power resulted in an increase in the background signal which was equivalent to a CO concentration of 15 ppm. Additional disadvantages of this nonresonant transition will be pointed out later.

The other optoacoustic cell used in this experiment was an acoustically resonant brass cylindrical cavity 10.8 cm in length and diameter. The first radial resonance of this cell occurred at 3952 Hz, with a Q

(defined as the resonant frequency divided by the full width at $1/\sqrt{2}$ response) of 760. A Knowles model BT-1759 miniature electret microphone with built-in FET preamplifier was attached to the wall midway down the length of the cell. This microphone had roughly the same calibration as the GR microphone but was found to be six to seven times noisier when compared under identical circumstances. However, it had the advantage that it could be easily incorporated into a resonant cell without significantly degrading the Q of the resonances. Acoustical noise isolation precautions similar to those used with the nonresonant cell were taken. The peak noise excursions at the resonant frequency with a 10 sec time constant were ± 5.5 nV.

With the resonant cell, for the $P_{1-0}(10)$ transition we observed a signal of 7.5 nV/(mW ppm), which, with a noise level of 5.5 nV and a typical laser power of 5 mW, gives a signal to noise ratio of unity at a concentration of 0.15 ppm. The minimum detectable concentration was limited only by electrical noise, with no background signal observable. By comparison, for the same laser transition, the nonresonant cell would give a signal to noise ratio of unity at 0.4 ppm, but had a background-equivalent concentration of 1.5 ppm.

We investigated the dependence of the optoacoustic signal on pressure for both cells, since in the presence of interference, use of low pressure might be desirable. For the acoustically nonresonant cell, as the pressure of the $CO-N_2$ mixture was reduced from 760 torr to 75 torr, the signal observed for the resonant $1 \rightarrow 0$ laser transitions was found to be nearly independent of pressure, increasing slightly as pressure was decreased. This is reasonable since in the pressure-broadened regime,

for constant percentage of absorbing gas, the absorption coefficient at line center remains constant. Below 75 torr the signal fell off rapidly as Doppler broadening began to dominate, causing the absorption coefficient at line center to decrease in proportion to the pressure. For the optically nonresonant transition, $P_{2-1}(12)$, in the range from $\sim$ 200 torr to 760 torr the signal was observed to fall off linearly with decreasing pressure due to the narrowing of the absorption line. At lower pressures the signal appeared to vary as a higher power of pressure. For an interfering species whose absorption line did not coincide closely with the laser line, the optoacoustic signal would have a pressure dependence similar to that described for the $P_{2-1}(12)$ transition. By lowering the pressure, the interfering absorption line is narrowed, and unless it is in very close coincidence with the laser wavelength, its absorption will be decreased. In contrast, the absorptivity of the resonantly absorbing gas to be detected remains constant, independent of pressure, until Doppler broadening begins to dominate. Hence, selectivity is improved as pressured is decreased.

In the case of the acoustically resonant cell, even for an optically resonant transition, the signal was found to depend linearly on pressure, even though the absorbed power is independent of pressure in the pressure-broadened regime. The reason is that as pressure decreased, the Q of the acoustical resonance decreases. Although the sensitivity of this system to an interfering species will then be decreased relative to the resonantly absorbing gas by decreasing the pressure, the signal to noise ratio will be degraded.

Thus, it appears that the acoustically nonresonant cell has an advantage for low pressure operation, since the signal, and hence signal to noise ratio, remains constant as pressure is decreased, whereas for the resonant cell, it falls off linearly with decreasing pressure. Also, the background signal, which limits the sensitivity of the nonresonant cell at atmospheric pressure, has been found to depend approximately linearly on pressure, and would be less troublesome for low pressure operation.

To assess the effect of interference from atmospheric absorption, we estimated atmospheric absorption coefficients for each of the laser transitions from computer-generated atmospheric transmission spectra.[6] For atmospheric pressure, temperature of 296°K, and relative humidity of 65%, these coefficients were compared to our estimated absorption coefficients to obtain equivalent CO concentrations which would result in the same absorption. The equivalent concentrations were 0.25 ppm for $P_{1-0}(9)$, 0.09 ppm for $P_{1-0}(10)$, 0.08 ppm for $P_{1-0}(11)$, and 0.43 ppm for $P_{2-1}(12)$. Due to the 0.25 cm^{-1} resolution folded into the computed spectra,[6] the equivalent CO concentrations may be somewhat higher for the $P_{1-0}(9)$ and $P_{1-0}(10)$ transitions, since these appear to lie close to the centers of atmospheric absorption lines, where finite resolution would result in an underestimate of the absorption coefficient. On the other hand, the $P_{1-0}(11)$ and $P_{2-1}(12)$ absorption coefficients are more likely to be overestimated since these lines lie far from the centers of atmospheric absorption lines.

While the atmospheric absorption coefficient for the $P_{2-1}(12)$ transition is not large, it appears as a high equivalent CO concentration due to the weak absorption of CO at that wavelength. Use of low pressures

to eliminate this interference is not practicable because, as discussed above, it is not a resonantly absorbed transition.

Of the four transitions we have investigated, $P_{1-0}(11)$ offers the best combination of sensitivity and freedom from interference.

Recent combustion studies have shown that N_2O can be a serious interferer in determining the concentration of CO with monitoring instruments using broad-band, incoherent light sources (e.g., nondispersive infrared analyzers.)[7] The interference stems from the overlap of the 4.5 μm and 4.67 μm absorption bands of N_2O and CO, respectively. This finding motivated us to test the selectivity of our detector since, in principle, detection by resonance absorption should result in the unambiguous determination of CO concentration. We tested a mixture of 4200 ppm of N_2O in N_2 at atmospheric pressure using our acoustically nonresonant detector and observed no signals above the usual background level. We also tested a mixture of 4200 ppm of N_2O and 49 ppm of CO and found that the observed optoacoustic signals did correspond to those obtained for 49 ppm of CO in the complete absence of N_2O.

No attempt was made to increase our detectivity beyond 0.15 ppm. This sensitivity was limited in part by the low output power of our laser. In this connection, it is of interest to note that a chemical laser capable of emitting almost one Watt on transitions in the $1 \rightarrow 0$ band of CO has been reported.[8] The use of such laser would easily extend our detectivity to the sub-ppb level.

REFERENCES

1. N. D. Sze, Science <u>195</u>, 673-675 (1977).

2. K. Westberg, N. Cohen, and K. W. Wilson, Science <u>171</u>, 1013-1015 (1971).

3. N. Djeu, Appl. Phys. Lett. <u>23</u>, 309-310 (1973).

4. T. R. Todd, C. M. Clayton, W. B. Telfair, T. K. McCubbin and J. Plíva, J. Mol. Spectrosc. <u>62</u>, 201-227 (1976).

5. R. T. Ku, E. D. Hinckley, and J. O. Sample, Appl. Opt. <u>14</u>, 854-861 (1976).

6. R. J. Nordstrom, J. H. Shaw, W. R. Skinner, J. G. Calvert, W. H. Chan, and W. M. Uselman, "Computer-Generated Long-Path Air Spectra," EPA-600/3-77-026, available from Environmental Sciences Research Laboratory, E.P.A., Research Triangle Park, North Carolina 27711.

7. C. D. Hollowell and G. W. Traynor, to be published.

8. W. Q. Jeffers, H. Y. Ageno, C. E. Wiswall, and J. D. Kelley, Appl. Phys. Lett. <u>29</u>, 242-244 (1976).

Table I. Performance of the system using the acoustically nonresonant cell.
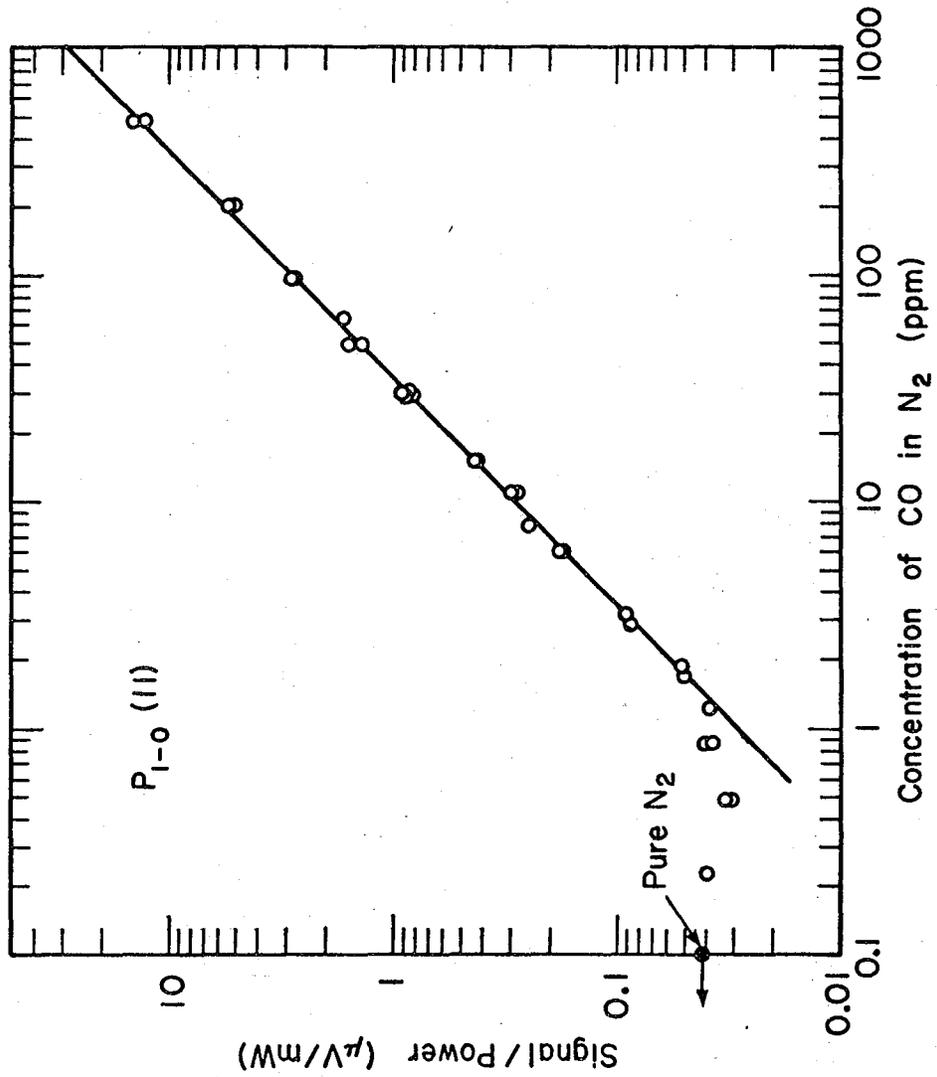
Laser Transition	Typical Output Power (mW)	Optoacoustic Signal per unit power per unit CO concentration (nV/(mW ppm))	Noise-equivalent CO concentration (ppm)	Background-equivalent CO concentration (ppm)
$P_{1-0}(9)$	2	31.2	0.8	1.5
$P_{1-0}(10)$	5	27.7	0.4	1.5
$P_{1-0}(11)$	5	28.9	0.4	1.5
$P_{2-1}(12)$	51*	3.9	0.3*	15

*Maximum rather than the typical power, obtained by optimizing the lasing gas mixture for

$2 \rightarrow 1$ transitions. Noise-equivalent concentration computed using the maximum power value.

FIGURE CAPTION

Fig. 1   Concentration dependence of nonresonant optoacoustic signal

for $P_{1-0}(11)$ transition.

Fig. (1)

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