



## *Project Summary*

# Effect of Collisional Lifetime in Optoacoustic Detection of Pollutant Gases

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**The optoacoustic technique shows promise for pollution monitoring due to its small size and high sensitivity. This technique is fundamentally different from most spectroscopy in that absorbed energy is measured indirectly as a pressure change in the surrounding gas. Not all the absorbed energy is detected as a pressure change, the actual value depending on the collisional and thermal relaxation times. This research shows that relaxation effects in carbon dioxide begin to reduce the optoacoustic signal below 100 torr. At 50 torr the optoacoustic signal contains only half the absorbed energy. Collisional and thermal relaxation times of 7.5 m sec and 0.1 m sec are shown to correctly predict the decrease in the optoacoustic signal.**

**A new calibration technique employing a piezoelectric crystal was developed for this research. The piezoelectric calibration was necessary because the microphone sensitivity varied by a factor of 3 as a function of total gas pressure. This technique is generally applicable in accounting for changes in microphone sensitivity.**

***This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).***

### **Introduction**

The optoacoustic signal resulting from absorption of radiation by a confined gaseous absorber depends on the collisional relaxation time,  $t_c$ , of the absorber. Existing mathematical models of the physical processes involved in the generation of the photoacoustic signal,  $S$ , predict the dependence of  $S$  on  $t_c$  as well as other system parameters such as  $t_r$  and  $t_t$ , the radiative relaxation time and thermal relaxation time, respectively. Experimental documentation of corresponding values of  $S$  and the pressure in an optoacoustic cell can be used to infer values of the relaxation times. The technique to be discussed is generally applicable to characterizing optoacoustic response for specific gas mixtures. Results of characterization can be used in optimizing system response with respect to detection of trace gases in air.

### **Results**

A  $\text{CO}_2$  laser was used as a source of radiation to illuminate a gaseous absorber contained in a cylindrical cell. An electret microphone was mounted at the cell wall. Modulation of the laser radiation by a mechanical chopper resulted in small pressure changes that were recorded as a function of the total pressure in the cell.

Microphone sensitivity was noted to vary as the total cell pressure was changed over the range of 10 to 760 torr. The optoacoustic cell was calibrated

by the use of a piezoelectric crystal attached to the cell wall. Changes in crystal length in response to an applied electric field caused precise volume and, hence, pressure changes in the cell. Calibration data depended on the frequency of modulation of the laser radiation and on the cell pressure.

The main experiment consisted of recording the corrected microphone response as a function of total pressure. This data was then compared to a mathematical model for optoacoustic response and values of  $t_c$ ,  $t_r$ , and  $t_t$  were predicted. The model expression was taken from the work of L. Rosengren as published in *Infrared Physics*, 13, 173 (1973). Rosengren's expression was used to fit the experimental data. The relaxation times were determined from the experimental data using a standard chi-squared minimization program. For pure CO<sub>2</sub>, the CO<sub>2</sub> laser radiation at 10.6 microns was used to obtain the values:  $t_c = 7.5$  microsec;  $t_r = 0.002$  sec and  $t_t = 0.11$  sec. The thermal relaxation time  $t_t$  was determined to be  $0.10 \pm 10\%$  sec by an alternative technique. Values of  $t_c$  published by other experimenters ranged from 7.5 to 12.0 microsec.

Additional experiments were performed using pure N<sub>2</sub>O as the absorber and the P(16) and P(24) CO<sub>2</sub> laser lines in the 10 micron band. These experiments show the variation in optoacoustic signal as cell pressure is reduced. A decrease in collisional broadening of the absorbing gas with reduced pressure changes the position of the laser line relative to the absorption profile. This in turn alters the optoacoustic signal as a function of pressure.

## Conclusions

This report establishes a procedure by which the relaxation times corresponding to radiative, collisional and diffusional processes can be estimated. Applied to optoacoustic detection of trace gases, the procedure shows the potential for optimizing optoacoustic signal response. The means devised for calibrating electret microphone response is appropriate for more general use in accounting for changes in microphone sensitivity.

*This Project Summary was authored by William McClenny who is also the EPA Project Officer (see below).*

*The complete report, entitled "Effect of Collisional Lifetime in Optoacoustic Detection of Pollutant Gases," was authored by Wolfgang Christian, who was formerly with Allegheny College, Meadville, PA 16335 and is now with Earlham College, Richmond, IN 47374.*

*The above report (Order No. PB 81-173 312; Cost: \$6.50, subject to change) will be available only from:*

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