

# TRACE GAS ANALYSIS BY PULSED LASER ABSORPTION SPECTROSCOPY

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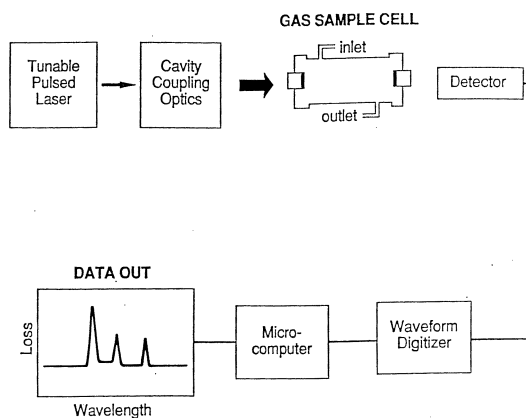
## ABSTRACT

Optical absorption measurements of trace level (ppb) pollutants in ambient air samples and chemical reaction products in laboratory flow reactors have been made using a new technique employing pulsed laser sources. This new technique allows optical absorption measurements to be made using either broad band or narrow band pulsed lasers and offers a temporal resolution and absorption detection sensitivity significantly greater than can be attained by using stabilized continuous light sources. The technique is based upon the measurement of the rate of absorption rather than the magnitude of absorption of a light pulse confined within a closed optical cavity. The decay of the light intensity within the cavity is a simple exponential with loss components due to mirror loss, broadband scatter (Rayleigh, Mie), and molecular absorption. We present measurements that demonstrate the great sensitivity of this technique and the utility of this approach as a sensitive probe of complex chemical environments.

Optical techniques based upon atomic and molecular absorption and fluorescence are routinely used for the in-situ analysis of environmental samples both in the field and in the laboratory. For many applications involving large polyatomic molecules, absorption measurements are potentially superior to those based on optical emission of which the quantum yield could be reduced by the rapid quenching of the excited upper state through energy redistribution processes. To study these systems, sensitive new optical absorption techniques are needed.

In the limit of weak absorption the transmitted optical intensity ( $I$ ) decreases exponentially with absorption pathlength ( $l$ ) in accordance with Beer's law,

$$I = I_0 e^{-kl}$$
, where the exponential decay constant,  $k$ , is the absorption coefficient at the frequency of the incident beam and  $I_0$  is the incident intensity. The ability to accurately measure the ratio of  $I$  to  $I_0$  typically limits the measurement to minimum losses of 0.01% to 0.001%. As a rule, such precision absorption measurements require sophisticated



**FIGURE 1.** Schematic representation of the experimental layout used to evaluate the Cavity Lossmeter absorption technique. A 10 ns optical pulse from a dye laser pumped by a nitrogen laser is mode matched to the sample absorption cavity and coupled into it by weak transmission through the cavity mirrors ( $T \approx 10^{-4}$  -  $10^{-5}$ ). The light coupled in is trapped in a closed cavity with the only loss mechanisms being intracavity absorption and transmission loss at the mirror surfaces. A signal proportional to the intracavity optical intensity is obtained by measuring the transmitted signal through the rear mirror. This signal is digitized and fit to an exponential waveform to obtain the ring-down time constant, which can be expressed as a loss per pass.

optical systems and sources that have stabilized output intensity. In the most sophisticated laboratory systems, the required intensity stability has been achieved by using several types of continuous lasers

(e.g. infrared lasers<sup>1-5</sup>, diode lasers<sup>6,7</sup>, and tunable cw dye lasers<sup>8</sup>. Typical experimental configurations also employ some form of frequency modulation to discriminate against low frequency noise.

The same level of sensitivity has not yet been possible for experimental systems based upon pulsed laser sources for several reasons. First, the pulse to pulse amplitude variation of most pulsed laser sources is typically larger than 10%. Therefore, the detectors used need a greater dynamic range and their effective signal resolution suffers. In addition, frequency modulation techniques are not feasible with the short pulsewidths (typically 10 to 30 nsec) of these lasers. Because of these limitations, sensitive absorption measurements have not been made over the full spectral range accessible only with the combination of pulsed lasers and non-linear frequency conversion techniques.

The Cavity Lossmeter system (Deacon Research, Palo Alto, CA) employs a new technique that allows an increase of several orders of magnitude in sensitivity of absorption measurement over existing techniques while taking the advantages of pulsed laser sources. Its sensitivity is better than 0.0001% (1 ppm) and its operation range is between 0.0001% and about 5%. Its spectral range is limited only by the availability of short pulse (several tens of nanosecond or shorter) lasers and high reflectors (better than 99% reflectivity) at a given wavelength.

#### *Principles of operation*

Details of the development and design of the basic Cavity Lossmeter system described here have been discussed in a recent paper<sup>9</sup>. A schematic representation of the system approach and configuration is shown in *Figure 1*. The technique is

based on the measurement of the rate of absorption of a tailored light pulse by a sample located within a closed optical cavity consisted of two parallel, aligned mirrors with very high reflectivity. A pulse of light is coupled into the cavity from which a small portion (~50 parts-per-million) is transmitted through one of the mirrors on each transit cycle and directed into a photodetector. The measured intensity of the small, out-coupled light pulse is proportional to that of the circulating pulse within the cavity. In the absence of any other loss mechanism, the rate of intra-cavity intensity loss is

$$dI/dt = C_t \times c/L \times I \quad (1)$$

where  $C_t$  is the coefficient of transmission for the mirrors at the laser wavelength,  $c$  is the speed of light, and  $L$  is the cavity length. The solution to this differential equation is a simple exponential

$$I = I_0 \times \exp[-C_t \times c/L \times (t-t_0)] \quad (2)$$

where  $I_0$  is the initial intensity injected into the cavity at time  $t_0$ . It can be seen that additional losses in the cavity simply add to the magnitude of the decay constant,  $C_t$ .

In order to make the determination of the loss rate, the signal is amplified, digitized, and transferred to a microcomputer. The computer extracts the exponential decay time ( $\tau$ ) of the signal and calculates the total loss ( $\Gamma$ ) of the cavity according to

$$\Gamma = 1 - \exp(-2L/c\tau) \cong 2L/c\tau \quad (3)$$

The loss obtained by this method is the sum of the losses experienced by the light stored in the cavity, including losses at the mirrors due to absorption, scatter, diffraction, and transmission as well

as the absorption due to the sample enclosed within the cavity.

The absorption measurement is then based upon the measurement of a signal decay time and the determination of the loss rate. There are several significant advantages to making the absorption measurement in the time domain. First, the sensitivity of the technique increases as the sample absorption decreases since the exponential decay time lengthens and becomes easier to determine. The ultimate sensitivity is limited by the finite mirror loss within the cavity. In addition, the sample size required is modest since the beam exactly retraces itself each cycle. For a two mirror cavity the beam passes through a waist in the center which permits spatially resolved sampling of small samples.

Narrow band absorption spectra are recorded by scanning the output of a pulsed laser through the selected spectral region containing an absorption resonance. In the most basic design, the entire space between the two cavity mirrors serves as a sample cell. In more sophisticated adaptations, the "sample" (e.g. a discharge, flame or a molecular beam source) would be located between the two mirrors. The loss of an "empty" reference cavity is determined first and is later subtracted from that of the cavity with the sample in presence. The difference is attributed to the loss of the sample.

#### *Applications*

The system described here is, in part, a closed path multipass absorption cell with effective pathlength of  $10^4$  meters. The ability to sample such large paths with a small (ranging from 0.2 to 5 meter cavity size) optical system makes this approach useful in atmospheric or combustion analysis, especially in studies where spatially resolved sampling of trace

constituents is desired. One promising area of application is atmospheric monitoring of various pollutants. A number of such species can be detected by visible or near UV absorption analysis. Because the absorption coefficients at various wavelengths are known for a large number of important pollutants, it is a simple task to transform the measured absorption signal to an absolute concentration. Since the equivalent path length over which the measurement is made is very long (10 - 20 km), the sensitivity is excellent.

In order to characterize the performance of the basic configuration of the Cavity Lossmeter, we have made survey scans of ambient air using a 1 meter cavity length. Our earliest studies were of the red optical absorptions of molecular oxygen. These bands are due to the strongly forbidden  $b^1\Sigma_u^- - X^3\Sigma_g$  transition in  $O_2$  known as the atmospheric bands of oxygen. Components of this transition have been used for Lidar probes of the atmosphere and have been well characterized. We used several very weak vibronic components of this system to characterize the capabilities of this technique and representative spectra are shown in a recent paper<sup>9</sup>. Throughout the visible, and particularly in the longer wavelength regions, components of  $H_2O$  vibrational overtone transitions can be seen. Two representative spectra are shown in Figure 2. These spectra are due to very weak overtone combination bands<sup>10</sup>. We have also recorded the overtone spectra of organic species such as propane at room temperature. The typical spectra observed for large organic overtones is quite broad, as is seen by other techniques such as intra-cavity dye laser absorption<sup>11</sup>.

These examples help illustrate the sensitivity of the Cavity

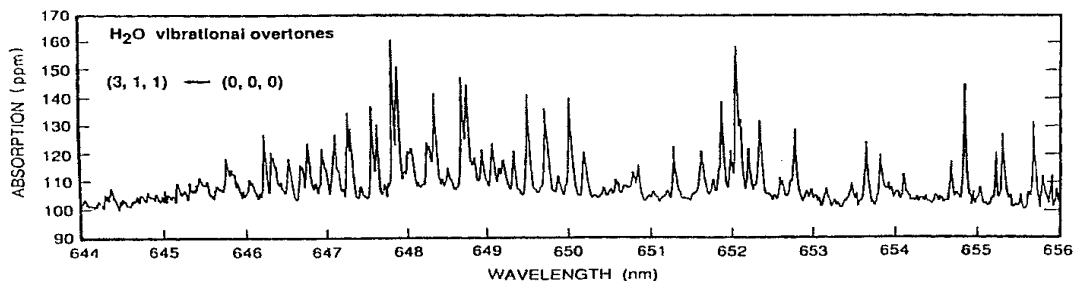
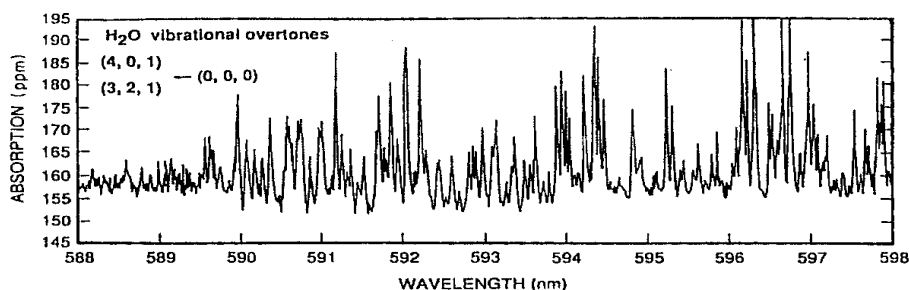


FIGURE 2. Absorption spectrum of air in the spectral region between 5880 Å and 5980 Å, and between 6440 Å and 6560 Å taken at 0.1 Å steps which shows several combination overtone bands due to absorption by the H<sub>2</sub>O molecule. The loss scale (per pass) on the left refers to measurements made with a 1 cm<sup>-1</sup> laser bandwidth, which is greater than the pressure broadened transition bandwidth. The baseline loss signal ( $\approx 100$ -150 ppm) is due to the transmission loss of the mirrors used. The data acquisition time was about 1 second per point.

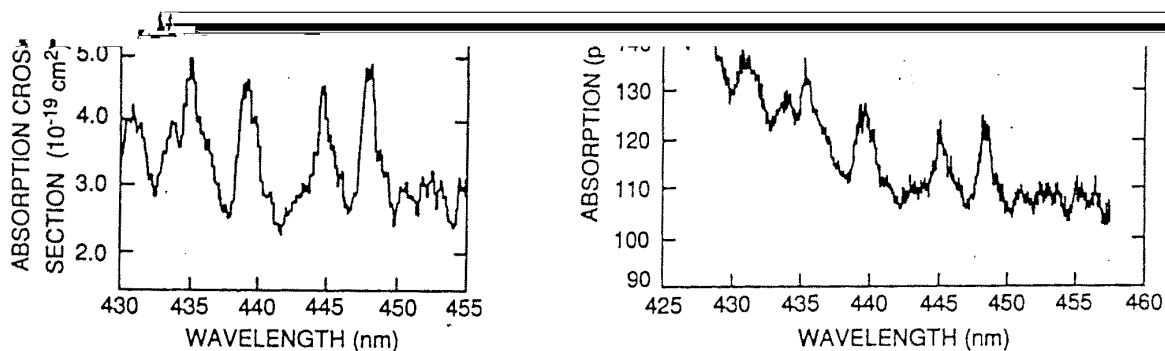
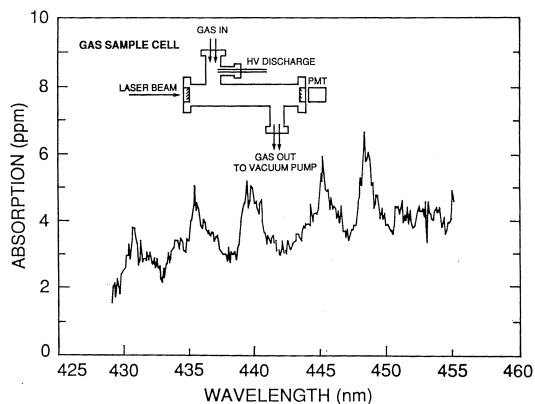


FIGURE 3. Absorption spectrum of air in the spectral region between 4250 Å and 4600 Å taken at 0.1 Å steps showing the absorption bands due to trace levels of NO<sub>2</sub> present in the air. The spectrum shown in (a) is a reproduction of that obtained by reference 12 and provides the absorption cross section as a function of wavelength throughout this region. The spectrum shown in (b) is obtained using the Cavity Lossmeter. The sloping baseline at the short wavelength end is the result of the gradual change in the mirror reflectivity function and would normally be subtracted from a sample spectrum. We have not done this subtraction to demonstrate the gradual variation of this function. The data acquisition rate was the same as that used to collect the data shown in Figure 2. (Figure 3 reproduced with permission from Ref. 12.)



**FIGURE 4.** Absorption spectrum produced by an electrical discharge in a nitrogen/oxygen mixture. The features seen are attributed to the  $\text{NO}_2$  molecule. The average product molecule density is estimated to be  $\approx 8 \times 10^{-10} \text{ cm}^{-3}$ .

Lossmeter for making measurements of atmospheric pollutants. The  $\text{NO}_2$  molecule provides an excellent example of such species since it is important in the atmospheric chemistry of urban areas and has absorption bands in the visible region, which can be used for concentration measurements. The absorption spectra of  $\text{NO}_2$  from 430-455 nm has been measured and the absorption coefficient determined as a function of wavelength over this range<sup>12</sup>. We have measured the absorption spectra of ambient laboratory air over the same spectral range; typical results are presented in Figure 3. Figure 3a shows the  $\text{NO}_2$  absorption cross section as a function of wavelength (reproduced with permission from Ref. 12). The mirror pair used in our analysis was coated for peak reflectivity at  $\sim 460$  nm. The increasing baseline seen in our spectra towards shorter wavelength results from the increasing mirror transmission. In normal operation this baseline would be subtracted out, however this figure is a typical example of the reflection function for the types of mirrors used. The change in reflectivity is very gradual and is only easily perceived when scans of this width are made.

The measured absorption (per 100-cm pathlength) at 448 nm is about 20 ppm, giving an absorption

coefficient ( $k_a$ ) of  $2 \times 10^{-7} \text{ cm}^{-1}$ . Since the absorption cross section ( $\sigma$ ) at the same wavelength is  $5 \times 10^{-19} \text{ cm}^2$ ,<sup>12</sup> the concentration of  $\text{NO}_2$  is:

$$[\text{NO}_2] = k_a / \sigma = 4 \times 10^{11} \text{ molecules cm}^{-3}$$

or about 16 ppb.

We have also slightly modified the optical arrangement to permit the analysis of gas phase chemical reaction products. To illustrate one such configuration we have measured the production of  $\text{NO}_2$  from the reaction of excited atoms and molecules formed in a weak electrical discharge in an air gas mixture. The mirrors that comprise the closed optical cavity were used as vacuum chamber windows for the 50 cm long cell containing the gas flow (0.3 - 5 Torr total pressure) and electrical discharge. The mirrors were mounted on soft o-rings in a housing so that they can be independently adjusted and aligned to the input laser beam. A slow flow of air was passed through a 300 volt discharge at a pressure of 0.5 Torr and drifted down the axis of the cell. Figure 4 is the spectrum with the mirror transmission baseline subtracted for clarity. The same features seen in Figure 3 are present in Figure 4 and, as above, a calculation of the average  $\text{NO}_2$  density results in

$$[\text{NO}_2] = 8 \times 10^{10} \text{ molecules cm}^{-3}.$$

Because the reaction products are flowing down the axis of the cell the product density will vary with position. In another configuration the absorption spectra could be used to determine product concentrations as a function of position (or time in a reaction flow tube).

The absorption technique employed by the Cavity Lossmeter has several important features that will make it an attractive approach for a variety of applications. First, it is much more sensitive than any other direct absorption technique in the visible range and offers effective pathlengths of several tens of kilometers. The estimated minimum detectable absorption, based upon a minimum of  $10^{-7}$  loss per pass through a 100 cm cell, is  $\sim 10^{-9}$   $\text{cm}^{-1}$ . In addition, it can provide a measurement with a temporal resolution of less than  $10^{-3}$  sec for single pulse determinations. Although the system requires the use of a laser, it is compact and reasonably insensitive to vibrations, and can be operated as a mobile sensor. Finally, the system can be run in either a broadband (over several tens of nm) scanning mode or a narrowband high resolution mode depending upon the laser used. These features suggest that the area of greatest potential application are in the analysis of atmospheric gases such as various pollutants, or in the area of gas purity analysis, such as for electronics materials production. Such applications may include the

analysis of industrial stack emissions, the monitoring of chemical production gas flows, or mobile determinations of selected species.

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