

Cavity ring-down optical spectrometer for absorption measurements using pulsed laser sources

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We have developed a technique which allows optical absorption measurements to be made using a pulsed light source and offers a sensitivity significantly greater than that attained 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. Narrowband absorption spectra are recorded by scanning the output of a pulsed laser (which is injected into the optical cavity) through an absorption resonance. We have demonstrated the sensitivity of this technique by measuring several bands in the very weak forbidden $b \Sigma_g^- - X \Sigma_g^-$ transition in gaseous molecular oxygen. Absorption signals of less than 1 part in 10^6 can be detected.

INTRODUCTION

The study of molecular absorption and emission of radiation is of great importance in basic and applied science. Much of our knowledge of the geometrical and electronic structure of various molecules and molecular clusters stems from optical absorption studies performed in either bulk samples or, more recently, in molecular beam expansions. Apart from fundamental questions of structure, etc., this information provides the necessary optical tools to design experimental probes of remote populations and processes such as the make-up of our atmosphere and the chemical processes occurring in hostile (e.g. combustion) environments. In some situations, especially involving small diatomic and triatomic species where fluorescence yields are high, emission measurements can be more sensitive since they measure the appearance of a small signal rather than a small change in a large signal. For many applications involving large polyatomic molecules, however, absorption measurements are potentially superior to those based on optical emission since rapid quenching (through energy redistribution processes) of the excited upper state formed by absorption of a photon will occur resulting in a greatly reduced emission quantum yield.

For some applications, such as some atmospheric pollution analysis and the optical probing of flames, the use of direct absorption measurements is often impractical since the absorbing species is present in only trace amounts or the sample path length is very short. In the limit of weak absorption the transmitted

optical intensity decreases exponentially with absorption path length, in accordance with Beer's law, where the exponential decay constant, k , is the absorption coefficient at the frequency of the incident beam. 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% and, as a rule, such precision absorption measurements require sophisticated optical systems and sources (often laser based) which have a stable output intensity. The required intensity stability has been achieved using several types of continuous lasers (e.g. infrared lasers¹⁻⁵ diode lasers^{6,7} and tunable cw dye lasers⁸) using experimental configurations which typically employ some form of frequency modulation to discriminate against low frequency noise. The same degree of success 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 large, greater than 10%, requiring a greater detector dynamic range and reducing the effective signal resolution. In addition, the short pulse widths of such lasers, typically 10-30 nsec, makes it very difficult to modulate the frequency for differential analysis. Because of these limitations sensitive absorption measurements have not been made over the full spectral range accessible using non-linear frequency conversion techniques.

For the applications in which fluorescence emission analysis is not practical some means of increasing the sensitivity of absorption detection is required. In the limit of very weak absorption, when the absorbing sample is optically thin (dilute sample) the signal is increased in direct proportion to the sample path length. For this

reason long paths are almost universally used in air pollution spectroscopic analysis. To increase the net absorption the multipass optical cell was developed⁹⁻¹⁴, which has, in some cases, increased the effective sample length to several hundred meters.

Other applications, such as the analysis of samples with small geometrical cross sections (e.g. molecular beams), present greater difficulty since they require that the same small volume is to be repeatedly probed. Recently, several innovative examples of optical multipass systems suitable for use with a molecular beam sample have been proposed¹⁴⁻¹⁶ although most allow only a few passes and the most optimistic design¹⁴ promises a maximum of about 100 passes. The problem in such conventional approaches lies in the requirement for the light beam to traverse distinct paths for each pass. The circumvention of this requirement would make possible an almost unbounded effective sample length.

We have developed a new technique, which allows an increase of several orders of magnitude in sensitivity over existing techniques for the wide spectral region accessible with tunable pulsed lasers. In addition, the approach represents a significant departure from the classical optical multipass cell and offers a wide range of utility. A schematic representation of the system configuration is shown in Figure 1. The principle of operation is based, not on the measurement of the absorbed signal strength for a given sample path, but of the time rate of absorption of a sample located within a closed optical cavity. A pulse of light is coupled into a closed linear or ring optical cavity from which a small (a few parts per million) portion is outcoupled each transit cycle. The rate of decrease in the outcoupled signal is determined by the total cavity loss and the sample absorption. The absorption measurement is then based upon the measurement of a signal decay and the numerical fitting of the loss rate. This approach offers several notable advantages. First, the sensitivity of the technique increases as the sample absorption decreases since the exponential decay time lengthens and the signal waveform will be spread over an increased number of data points (for a fixed sampling rate). The ultimate sensitivity is limited by the finite mirror loss within the cavity. In addition, the sample size required is modest since the beam retraces itself each cycle. For a two-mirror confocal linear cavity the beam passes through a

waist in the center which permits resolved sampling of spatially well-defined samples.

The system described here is, in part, a multipass absorption cell with (for typical laser intensity decay time constants of tens of microseconds) effective path lengths of 10^4 meters. The ability to sample such large paths with a small (1 meter cavity) optical system makes this approach useful in atmospheric or combustion analysis, especially in studies where spatially resolved sampling of trace constituents is desired. This non-conventional approach also may be applied to the analysis of species within a molecular beam by locating the beam at the cavity waist of the cell.

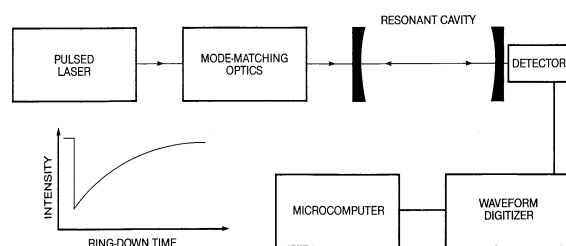


FIG.1 Schematic representation of the experimental layout used to evaluate the cavity lossmeter absorption technique. A 10 ns optical pulse from a dye laser pumped by a nitrogen laser is mode matched to the sample absorption cavity and coupled into it by weak transmission through the cavity mirrors ($T \approx 10^{-4} - 10^{-5}$). 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.

I. PRINCIPLES OF OPERATION

Progress in optical absorption and spectroscopic technology has made possible the development of high sensitivity absorption spectrometers capable of detecting total losses approaching the 10 ppm region¹⁻⁸. These approaches typically require frequent calibration and careful attention to detail, which reduces their attraction as general purpose techniques. Although the specific details vary, all of these techniques boil down to a comparison of transmitted to incident intensities.

An alternative approach, originally designed to make precise determinations of laser mirror absorption loss, was developed by Herbelin et al.¹⁷ who worked out a method of measurement based on the finesse of a resonant optical cavity. This approach uses a cw probe laser which is intensity modulated and transversely mode matched into a resonator formed of a pair of mirrors. The phase of the modulation of the transmitted beam is measured, and compared to the phase of the incident beam. Since each of the injected photons bounces back and forth in the resonator for a time before it is lost, the transmitted photons are delayed on the average by the ring-down time of the cavity, shifting the phase of the transmitted radiation. This phase shift is inversely related to the sum of the reflection losses in the resonator. The losses within the cavity can be determined to a precision on the order of 100 ppm/round trip pass. If the empty cavity space between the mirrors is replaced with an absorbing medium and the mirror loss is assumed to be negligible the system becomes an absorption spectrometer. For a cavity length of 1 meter the above sensitivity translates to a minimum detectable absorption of $\sim 10^{-6} \text{ cm}^{-1}$.

The major limitation on the precision of this technique is the noisy character of the transmitted laser intensity. The accuracy of the determination of the phase of the transmitted beam is limited by this noise source¹⁸; practical limitations on the signal integration time restrict this approach to precisions on the order of 50 ppm/pass. The noise present in the transmitted beam is intrinsic to this technique. Fabry-Perot analysis shows that transmission will occur only when one of the laser modes (which occur at integer multiple frequencies of $c/2L_{\text{probe}}$ where L_{probe} is the length of the probe laser cavity) matches the frequency of one of the cavity modes. Since the two cavity lengths are vibrating independently, the modes of the two cavities will match up periodically to permit some transmission, but at random times. Although the phase shifts of the individual transmitted photons is fixed, the phase of the transmitted beam is obscured in the random intensity noise.

Anderson *et al.*¹⁹ addressed this problem by configuring the detection electronics in a triggered mode of operation and waiting for the modes to overlap before starting the data acquisition. The detector monitoring the transmitted beam triggers on the electronics when longitudinal mode

matching has occurred in one of these coincidences, permitting the intensity to build up in the test cavity so that a signal is observed on transmission. Triggered by the "light is present" observation at the detector, a fast optical switch shuts off the probe laser beam, and the ring-down time is measured. The sum of the losses in the test cavity is related to the ring-down time. A precision of about 5 ppm was demonstrated with this method. Although this reconfiguration of the electronics reduces the signal noise, the problem of the random mode coincidences remains, producing intensity fluctuations, intermittent delays between successive signals, and occasional nonexponential decays.

The technique described here also measures the decay time of the test cavity, but avoids the problems associated with the requirement of longitudinal mode coincidences by using short optical pulses so that every pulse of the probe laser enters the cavity with no additional intensity fluctuation or time delay. As a result, the sensitivity and data rate improve, and the technical requirements of the system are greatly relaxed. By ensuring that each laser pulse produced and sent to the system will be coupled into the cavity it becomes feasible to use pulsed lasers with low duty cycles (10-100 Hz). The use of such laser sources greatly increases (through non-linear conversion) the spectral range which is available to this technique. A repeatability better than 1 ppm is realized using the device described in this paper.

The key to the successful operation of this technique for optical absorption measurements is the use of a laser pulse with a coherence length so short that no interference can become established in the test cavity. In the short pulse regime, the Fabry-Perot theory cited above breaks down, permitting any frequency to be injected into the test cavity. As discussed in the next section, operation in this regime ensures that every pulse of the probe laser enter the cavity, producing stable and reproducible operation, and continuous frequency scanning becomes possible without jumping from mode to mode as the frequency is scanned.

II. THEORY OF CAVITY COUPLING

In optimizing the performance of a ring-down resonator, it is important to tailor the characteristics of the source laser to the resonator. A major requirement is to drive energy

into the resonator efficiently and with small intensity fluctuations. The fluctuation in the energy deposited into the resonator on each laser pulse can be calculated in the frequency domain without too much effort.

We describe the input light pulse by the Fourier transform $E(\nu)$ of its field amplitude $E(t)$. For the source laser radiation, the input field is quasi periodic in the round trip time $2L_s/c$ of the laser resonator cavity (certainly not strictly periodic due to the time variation of the gain, the high round trip losses, and the presence of amplified spontaneous emission). Since the input laser pulse generally is many times longer than the round trip time in its resonator, the emission will be made up of multiple longitudinal modes whose width is small compared to their spacing. For a pulsed dye laser, for example, the 15 ns pulse length is approximately 10 times longer than the round trip time. The width of the longitudinal modes in the emission spectrum will therefore be on the order of 0.1 times $c/2L_s$ in the limit of strict periodicity. We therefore express the input field as a sum of modes whose amplitudes a_i are all different, but whose form $s(\nu-\nu_i)$ is independent of the mode index:

$$E(\nu) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt E(t) e^{-i2\pi\nu t} = \sum_i a_i s(\nu - \nu_i), \quad (1)$$

where $\nu_i = ic/2L$. The acceptance function $C(\nu)$ of the absorption cavity, which is the ratio of the excited field in the cavity to the incident field, is the well known Airy function, which becomes a sum of separated modes $c(\nu-\nu_m)$ for high Q cavities. Ignoring the overall coupling coefficient into the cavity, we find

$$C(\nu) = \frac{te^{i2\varphi}}{2ie^{i\varphi} \sin \varphi + \Gamma} \simeq \sum_m c(\nu - \nu_m), \quad (2)$$

where t is the field coefficient for transmission, $\Gamma = 1-r^2$ is the cavity loss (assuming two mirrors), r is the field coefficient for reflection, $\varphi = 2\pi\nu L_c/c$, L_c is the cavity length, and $\nu_m = mc/2L_c$.

The energy W coupled into the resonator on a given pulse is therefore proportional to the square

of the product of (1) and (2), integrated over frequency.

$$\begin{aligned} W &\propto \int d\nu |E(\nu)C(\nu)|^2 d\nu \\ &= \int d\nu \sum_{ij} a_i a_j^* s(\nu - \nu_i) s^*(\nu - \nu_j) \\ &\quad \times \sum_{mn} c(\nu - \nu_m) c^*(\nu - \nu_n). \end{aligned} \quad (3)$$

Since the modes are well separated, the $i \neq j$ and $m \neq n$ terms in the sum vanish. For this application, the cavity modes have very high Q. Since they are much narrower than any other frequency structure, $c^2(\nu - \nu_m)$ can be approximated as a delta function, which allows the integral to be performed easily. This is equivalent to ignoring the variation of the laser spectrum across the cavity acceptance function $C(\nu)$ which is a very good approximation.

$$W \propto \sum_{im} |a_i|^2 |s(\nu_m - \nu_i)|^2 \equiv \sum_{im} A_i S(\nu_m - \nu_i), \quad (4)$$

where A_i and $S(\nu_m - \nu_i)$ have been defined in an obvious change in notation. We are interested in the fluctuations in this quantity, so we must calculate the ensemble average of W and W^2 over many laser pulses.

The ensemble average of (4) is

$$\langle W \rangle \propto \sum_i A_i \left\langle \sum_m S(\nu_m - \nu_i) \right\rangle = \sum_i A_i M \langle S \rangle, \quad (5)$$

where $\langle S \rangle$ is the average over one free spectral range of the source laser cavity, and $M (=L_s/L_c)$ is the number of test cavity modes in the same range. The ensemble average of the square of (4) is

$$\begin{aligned} \langle W^2 \rangle &\propto \sum_{ij} A_i A_j \left\langle \sum_{mn} S(\nu_m - \nu_i) S(\nu_n - \nu_j) \right\rangle \\ &= \sum_{i=j} A_i^2 \left\langle \sum_{mn} S(\nu_m - \nu_i) S(\nu_n - \nu_i) \right\rangle \\ &\quad + \sum_{i \neq j} A_i A_j \left\langle \sum_m S(\nu_m - \nu_i) \right\rangle \left\langle \sum_n S(\nu_n - \nu_j) \right\rangle. \end{aligned} \quad (6)$$

We have separated the ensemble averages in the second term by ignoring the correlations. This has the effect of increasing the calculated level of fluctuation, making this estimate an upper value. The second term can be simplified using the

average of S as in (5). In the first term, we break up the sum over m and n into two pieces summing over m = n and m ≠ n. The first piece is related to the average of S². The second piece is a sum of autocorrelations of S at frequencies shifted by multiples of c/2L_c.

$$\begin{aligned} \langle W^2 \rangle &\propto \sum_i A_i^2 M \langle S^2 \rangle \\ &+ \sum_i 2A_i^2 \left(\sum_{m=n+1} \langle S(v_m - v_i) S(v_n - v_i) \rangle \right. \\ &\left. + \sum_{m=n+2} \langle \quad \rangle + \dots \right) + \sum_{i \neq j} A_i A_j M^2 \langle S \rangle^2. \end{aligned} \quad (7)$$

The autocorrelations are negligible if the width of the laser modes is smaller than c/2L_c. We will make this approximation in the following calculation.

In evaluating the sums in (5) and (7), we will take the approximation that the source laser has a mean number N of modes of equal amplitude (A). The root mean square relative fluctuation in the energy coupled into the cavity is

$$\begin{aligned} \frac{W_{\text{rms}}^2}{\langle W \rangle^2} &= \frac{\langle W^2 \rangle - \langle W \rangle^2}{\langle W \rangle^2} \\ &= \frac{\sum_i A_i^2 M \langle S^2 \rangle + \sum_{i \neq j} A_i A_j M^2 \langle S \rangle^2 - \sum_{ij} A_i A_j M^2 \langle S \rangle^2}{\sum_{ij} A_i A_j M^2 \langle S \rangle^2} \\ &= \frac{1}{N} \frac{M \langle S^2 \rangle - M^2 \langle S \rangle^2}{M^2 \langle S \rangle^2}. \end{aligned} \quad (8)$$

Assuming a Gaussian form for S(v_m - v_i) with a width dominated by the pulse length τ,

$$S(v_m - v_i) \propto \exp[-2\pi^2 \tau^2 (v_m - v_i)^2], \quad (9)$$

we can calculate the relative RMS fluctuations analytically

$$\frac{W_{\text{rms}}}{\bar{W}} \leq \frac{1}{\sqrt{N}} \sqrt{\frac{\sqrt{\pi} - P}{P}} \approx \frac{1}{\sqrt{NP}} \quad (P \ll 1), \quad (10)$$

where P = 2L_c/cτ is the number of sample cavity modes which fit within the bandwidth of a single laser mode. This result is intuitively appealing in that it shows the fluctuation to be inversely

proportional to the square root of the number of modes that are coupled into the sample cavity. The ≤ sign signifies that we have dropped the correlation terms in equation (6). The constant in the P dependent factor in (10) depends somewhat on the model chosen in (9) for the mode functions. For small P, the fluctuation amplitude increases. For large P, the above analysis breaks down due to the neglect of the correlation terms, but we know in this case that the fluctuations become very small since the leading edge of the laser pulse no longer overlaps with the trailing edge within the cavity.

We take as a numerical example the instrument used for the measurements described here. This cavity lossmeter system has a 1 m test cavity with total losses per pass of Γ = 1.2x10⁻⁴, driven by a 15 ns dye laser pulse of bandwidth ≅ 0.05 nm, produced by a laser cavity 25 cm long. The test cavity modes are separated by 150 MHz, and are 18 kHz wide, which is enough like a delta function for the above approximation to be correct. The source laser produces approximately N = 62 longitudinal modes separated by 600 MHz, each with a width we have not measured, but which is somewhat greater than 70 MHz, the transform limit. In this case, P lies in the range from 0.5 to perhaps 1.0, and the fluctuation of the energy coupled into the cavity is predicted to be less than about 15%. The observed fluctuation is about 10%. This performance is sufficient for easy measurement and alignment. If however, the laser bandwidth were significantly narrowed or the cavity shortened, the above analysis shows that the fluctuations would increase.

We have made the assumption for this calculation that the different cavity modes fall at stochastically independent frequencies. The opposite, correlated, limit is also of some interest. If the mode separations of the laser and sample cavity are approximately equal, the correlations will be strong. In this case, one can simply fold the laser mode spectrum into a single "effective mode" by translating the laser modes in units of the test cavity free spectral range. If the mode separations are incommensurate, the effective mode can have an effective bandwidth as large as N times an individual laser mode bandwidth. This has the effect of reducing the fluctuations linearly in N rather than as the square root in equation (10). We have also assumed that the end mirrors act as reflecting surfaces forming a single resonant cavity. In fact, the rear surfaces

of both mirrors contribute small reflections, even after anti-reflecting coating, and form three weakly coupled cavities. A comprehensive discussion of this effect is beyond the scope of this paper.

A system we have fabricated for operation in the infrared between 1.8 microns and 600 nm falls into this latter category. This system has $N \cong 7$ and $P \cong .2$, but the mode separations of both cavities are about 380 MHz. The observed fluctuations are less than about 5% on this system, showing that the effective mode, which is about 70 MHz wide, always overlaps a couple of cavity modes, which would not happen if the seven modes were effectively independent.

An advantage of the pulsed laser lossmeter is that the operating wavelength of the system is widely and easily tunable, simply by tilting the laser grating, keeping all other alignments and parameters constant. The system described here has been scanned over a wavelength range of several hundred angstroms without showing any reduction in precision. It has been operated throughout the visible and near IR regions of the spectrum with consistently good results. By contrast, since the alternative approaches use a CW beam, they must use an optical modulator or Pockels cell switch. Although in principle a tunable CW laser could be used, tuning is made much more difficult by the requirement to change the setup of the modulator or Pockels cell at each new wavelength of operation. While step-by-step wavelength changes are possible with considerable effort, continuous wavelength scanning is in practice impossible. Because of this, frequency tuning has never been attempted with the earlier techniques.

Several other conditions must also be satisfied for the device to work properly. Of course, the laser frequency must match the high reflection band of the cavity mirrors. The transverse mode of the probe laser must also be matched into the measurement cavity. This can be a problem for pulsed lasers since their transverse mode quality is generally much poorer than that of the continuous lasers because of their high gain. We chose an amplified pulsed dye laser (the Molelectron DL II Model 12 dye laser pumped by the UV12 Nitrogen laser) to drive the system because the amplifier acts as an active spatial filter, cleaning up the transverse mode profile to the point where it can be used in the lossmeter without further spatial filtering. Although a beam of poorer quality could be used in this type of

system, the number of modes excited in the test cavity will be larger, which produces two ill effects. First, the footprint of the light in the mirrors is larger, diminishing the spatial resolution of the method. Second, the transmitted light becomes modulated in amplitude and spatial extent due to the beating of the modes, which presents problems in the data analysis. Designing the probe laser mode to match well with the TEM_{00} mode of the cavity eliminates these two problems.

When the above conditions are met, the same fraction of each and every laser pulse will enter the test cavity, and the stored energy will decay away with a time constant characteristic of the sum of the losses traversed by the light in the cavity. A detector is placed behind one of the cavity mirrors so that a signal is generated proportional to the light transmitted through the mirror. That signal is amplified if necessary, and digitized at a sufficiently high rate in an analog to digital converter. The digitized information is transferred to a microcomputer which extracts the decay information by fitting the signal to an exponential. The results are displayed to the operator on a monitor.

A 12 bit, 10 MHz transient digitizer is used to collect the data. A maximum of 8192 points are taken each time the digitizer is triggered. The digitizing rate limits the sensitivity of the system to losses below about 5%. The machine is operated in "pre-trigger" mode so that at least 32 samples of the baseline are retained before the start of the laser pulse to aid in the reduction of the data by the computer. The digitizer is plugged into a "CAMAC" dataway and can be commanded by the computer to transfer the digitized data to the computer for storage.

The computer fits the data to an exponential decay

$$y(t) = C_1 + C_2 \exp[-(t-t_0)/\tau] \quad (11)$$

by a linear least squares fit to the log of the data after the baseline value has been subtracted, calculates the losses of the mirrors, and displays the results to the operator on a monitor. It can also scan the laser wavelength over a predetermined range at a rate set by the operator, and display the losses thereby obtained as a function of wavelength.

The loss measurement obtained by this method is an accurate description of 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 gas sample enclosed within the cavity. We have measured absorption to a precision of better than 1 ppm.

III. SYSTEM PERFORMANCE

The cavity lossmeter system we have described here is both versatile and sensitive. We have looked at the very weak atmospheric oxygen absorptions around 6300 Å and 6900 Å. A schematic representation of the general experimental configuration used in this investigation is shown in Figure 1. A 4 mJ pulse from the nitrogen laser is used to pump the dye laser containing an oscillator-amplifier cell configuration and using either the dye DCM or RB/NBAP for output at 6300 Å or 6900 Å respectively. The system is operated at a repetition rate of about 15 Hz. The output of the dye, typically 10^{-4} J, is mode matched to the optical cavity as discussed in Section 2 and injected through one of the cavity mirrors. Ideally, the mirrors are coated for maximum reflection in the spectral region of interest resulting in a minimum loss from the cavity (and a minimum of energy coupled in). The mirror coatings used in the present study were not centered at the band centers resulting in an increased loss in each case and, as will be seen, a somewhat reduced sensitivity. The total round trip cavity loss due to mirror transmission at 6900 Å was found to be about 450 ppm, while that at 6300 Å was about 75 ppm.

We have measured absorptions due to the doubly forbidden $b^1\Sigma_g^+ - X^3\Sigma_g^-$ intercombination transitions in O_2 to demonstrate the performance of the system. This band system has been extensively studied by Babcock and Herzberg²⁰ and others.^{21,22} Two factors result in the greatly reduced intensity of this transition. The symmetry of the electronic states involved in the transition, $^1\Sigma_g^+ - ^3\Sigma_g^-$, does not permit electric dipole radiation so the transition must occur through a magnetic dipole interaction. In addition, the transition violates the selection rule for spin conservation, reducing its intensity by another factor of about 10^{-3} . The transition probability, A_{bX} , for this system is reported to be 0.07 sec^{-1} [Ref. 23] which is about a factor of 10^8 less than that expected for ordinary electric dipole radiation. The b-X magnetic dipole intercombination transition is made up of doublet R and P branches, $R, ^RQ, P,$ and PQ , with the first two of these forming a red

degraded bandhead. Because of its natural abundance in the atmosphere, this oxygen transition has been used as an atmospheric probe of density and temperature^{24,25} and the absorption strengths for resolved individual rotational components of the 0-0 vibronic band have been determined. The thermal distribution of population over the lowest energy levels is reflected in the intensity variation of rotational components and, at the temperature of our measurement, $T=300 \text{ K}$, will display a maximum at about $K=8$. In absorption out of the $v=0$ level of the ground electronic state the Franck-Condon factors favor the vertical 0-0 transition over the 1-0 or 2-0 bands by the ratios 0.931:0.066:0.003.²³ These bands have origins at 7619.3 Å, 6882.5 Å, and 6286.6 Å respectively (see Table I). The band oscillator strengths for the 0-0 and 1-0 transitions have been calculated²⁶ to be, $f_{0-0} = 2.5 \times 10^{-10}$, and $f_{1-0} = 2 \times 10^{-11}$.

TABLE I. Transition energies, wavelengths, and Franck-Condon factors for several absorption bands of the O_2 b-X system.

$X(0)-b(v')$	Transition energy (cm^{-1})	Wavelength (Å)	Franck-Condon factor
$v' = 0$	13122	7619	0.931
1	14526	6882	0.066
2	15903	6287	0.003
3	17253	5795	7×10^{-5}

Using the dye laser configured with only an intracavity telescope to narrow the output bandwidth to about 1 cm^{-1} (estimated from the observed signal bandwidth), we have measured the absorption spectra of oxygen in its natural abundance in air (20%) over the spectral ranges from 6270 Å - 6330 Å (2-0 band), and 6860 Å - 6950 Å (1-0 band). The cavity loss at each wavelength (step intervals of 0.1°) was averaged over 8 laser pulse decay measurements. Typical results for the 1-0 and 2-0 bands are shown in Figures 2 and 3 where the P and PQ branch components are indicated above the absorption peaks. Transitions not attributed to the O_2 b-X system can be seen in Figure 3 especially at wavelengths shorter than the transition bandhead at 6276 Å. These lines have not been positively identified but are believed to be due to trace amounts of NO_2 present in the air sample during the measurement. The signal fluctuation seen in Figure 3 is about ± 1 ppm for an average of 8 ring down measurements.

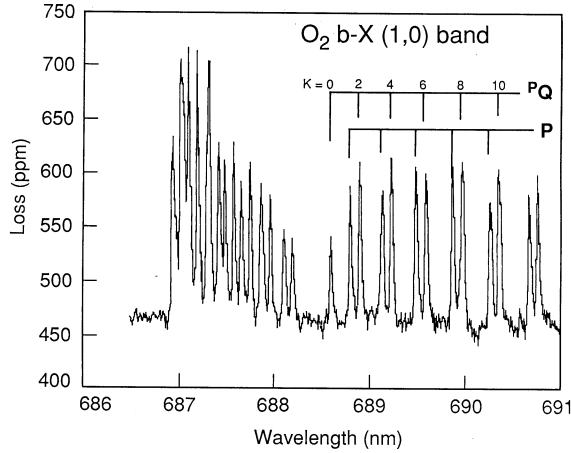


FIG. 2 Absorption spectrum of air in the spectral region between 6860 Å and 6910 Å taken at 0.1 Å steps which shows the (1,0) band of the O_2 $b^1\Sigma_g^- - X^3\Sigma_g^-$ system. Components of the PQ and the P branches are indicated above. The loss scale (per pass) on the left refers to measurements made with a 1 cm^{-1} laser bandwidth which is much greater than the pressure broadened transition bandwidth of 0.047 Å . The baseline loss signal ($\approx 460\text{ ppm}$) is high since this spectral region lies on the edge of the cavity mirror's HR coating bandwidth. The data acquisition time was about 1 second per point.

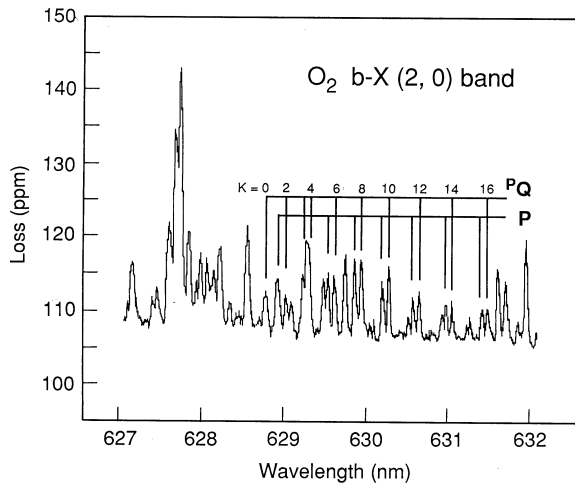


FIG. 3 Absorption spectrum of air in the spectral region between 6270 Å and 6330 Å taken at 0.1 Å steps showing the (2,0) band of the O_2 $b^1\Sigma_g^- - X^3\Sigma_g^-$ system. Some components of the PQ and P branches are indicated above. Some of the lines not designated as PQ or P lines are due to impurities in the air (probably NO_2). The most distinct of these impurity signals are those lying at wavelengths shorter than the bandhead at 6278 Å. The baseline loss signal ($\approx 110\text{ ppm}$) reflects a much better matching of the dielectric mirror coating with the wavelength range of interest. The data acquisition rate was the same as that used to collect the data shown in Figure 2.

The measured peak absorption for one of the strongest K components, the $P(K=8)$ line, is, from Fig. 2, about 160 ppm per 200 cm cavity round trip, i.e. an absorption coefficient, $k_a = 8.0 \times 10^{-7}\text{ cm}^{-1}$. To estimate the true absorption coefficient for this transition we must account for the large bandwidth of the laser relative to the transition width. The line shape of the transition is a Voigt line function, determined by both collisional and Doppler broadening at STP and has been measured for this band to be 0.047 cm^{-1} .²⁷ Assuming the laser bandwidth to be 1 cm^{-1} (as estimated from the measured O_2 linewidths) the absorption coefficient expected for narrowband operation (matching of laser frequency bandwidth with that of the molecular absorption) would be

$$K_a = 1.7 \times 10^{-5}\text{ cm}^{-1}. \quad (12)$$

There are few direct measurements of absorption strengths for resolved individual lines for this band system, however Kalshoven et al.²⁴ have measured the absorption strength of the $P(27)$ line of the 0-0 band at 7683.8 Å for very long path lengths over the temperature range covering $260\text{ K} < T < 290\text{ K}$, and have used its variation as a probe of gas temperature. The absorption coefficient for this line at a temperature of 300 K (corresponding to the present measurements) can be estimated, by modest extrapolation of their measurements, to be $k = 1 \times 10^{-5}\text{ cm}^{-1}$. By accounting for the population difference in the two rotational levels and taking into account the difference in Franck-Condon factors for the two bands, this extrapolated value can be scaled to yield an estimated absorption coefficient for the $K=8$ component of the 1-0 band. The ratio of population in the $K=8$ level to that of the $K=27$ level can be determined by calculating the partition functions for each level at the temperature of interest (the total rotational partition function cancels out in the ratio). Electronic absorption intensities for a system in thermal equilibrium can be expressed as the product of the line strength S_J and the Boltzmann factor. The line strength factor differs from the usual $(2K+1)$ degeneracy term and depends upon the change in J as well as the change in electronic orbital angular momentum for the transition. The S_J , or Honl-London factor,²⁸ for a P branch line is, for this transition, given by J ($=K$). The relative intensity of each P branch component is given by the expression

$$P(K)_{\text{intensity}} \propto (K) \times \exp[-B \times K \times (K+1)/kT] \quad (13)$$

where K denotes the rotational level of interest, B is the rotational constant for the state, and kT at room temperature is about 208 cm⁻¹. Since all excitation is occurring from the v=0 level of the O₂ ground electronic state, the B value for this state,²³ B=1.437 cm⁻¹, is the appropriate constant to use in calculating line strengths for either band (1-0 or 2-0) observed. Using these numbers the ratio of populations in the (K=8)/(K=27) levels is 4.86/0.15 = 32 at room temperature. In addition to the change in absorption strength due to population differences the signal is also modified by the difference in Franck-Condon factors of the 0-0 and 1-0 bands. As noted above, the 0-0 band is stronger than the 1-0 band by a factor of 0.931/0.066 = 14.1. The net scaling factors to be applied to the result of Kalshoven *et al.*²⁴ to obtain an estimate of the absorption coefficient for the P(8) component of the 1-0 band are

$$\begin{aligned} (\text{calc.})k_a(K=6)_{1-0} &= (1 \times 10^{-5} \text{ cm}^{-1} \times 32)/14.1 \\ &= 2.25 \times 10^{-5} \text{ cm}^{-1}, \end{aligned} \quad (14)$$

or about 30% greater than the measured value. The difference between the estimated and measured coefficients is consistent with a small error in our estimation of the laser linewidth and perhaps variation in sample temperature which has a strong effect upon the absorption strength of the P(27) line used in the comparison. The measured value of k allows an absorption cross section to be calculated since we know the absorption coefficient and sample density (5 × 10¹⁸ cm³) giving a value of

$$\sigma = 3.4 \times 10^{-24} \text{ cm}^2 \quad (15)$$

which can be compared to the value^{29,30} for an allowed diatomic transition, $\sigma = 3 \times 10^{-15} \text{ cm}^2$, for absorption by the NO molecule at 215 nm.

For other laboratory applications the cavity may be either enclosed within a vacuum chamber which contains the sample of interest or a sample chamber can be located within the optical cavity. In the second approach special care must be taken to ensure that the chamber windows do not introduce an unacceptable level of loss either through direct absorption, scatter, or by reflection.

Many potential applications, such as in the analysis of reaction products in a flow tube or species in a molecular beam, will involve small sample paths of cm's or mm's. We can estimate the sensitivity in such applications by scaling the results obtained for the forbidden oxygen transition using an absorption sensitivity of 1 ppm per pass. Assuming an allowed absorption cross section of $\sigma = 10^{-16} \text{ cm}^2$, we have for species AB,

$$10^{-6}/\text{cycle} < \sigma \times [AB] \times [L] \quad (16)$$

where [AB] and [L] are the species concentration and sample length utilized in the measurement. Rearranging this we have

$$10^{10} \text{ cm}^{-2} < [AB(\text{cm}^{-3})] \times [L \text{ cm}] \quad (17)$$

which gives, for example, a minimum species concentration of 10¹¹/cm³ for a path length of 1 mm (e.g. a molecular beam source). Such numbers correspond to bulk densities and must be corrected for the overall partition function of the species of interest. Absorption measurements at this sensitivity would be useful as a state selective probe in many gas phase reaction studies where the species of interest does not fluoresce to an appreciable extent.

DISCUSSION

The optical absorption technique described here allows sensitive measurements to be made using a pulsed light source. Because the technique is based upon the determination of the rate of absorption in a sample rather than the absolute amount of absorption, it is perfectly suitable for applications using pulsed lasers which typically display significant pulse to pulse intensity variations. Since the measurement is not made within the laser cavity the technique can be employed throughout the spectral range covered by the laser fundamental as well as that accessible using non-linear frequency conversion techniques and is limited in sensitivity only by the reflectivity of the mirrors used to form the absorption cavity.

The theory underlying the operation of such a cavity lossmeter presented in Section II describes the relationship between the source laser mode density and that of the absorption cell cavity and indicates the advantages and limitations of this approach. For laser pulse widths comparable to or less than the round trip optical transit time within the absorption cavity the frequency mode

matching is not important. For laser pulse widths much greater than the cavity transit time, however, the optical coupling depends strongly upon the laser bandwidth and the matching of the laser and sample cavities. To avoid significant mode matching problems, the size of a given optical cavity will then determine an upper limit to the spectral resolution which may be achieved. For typical pulsed laser systems with pulsed lengths of 10 nsec, transform limited ($\cong 20$ MHz) spectral measurements should be possible using sample cavities (the sample need not fill the cavity) of less than 2 meters length. Such spectral resolution should be sufficient for many measurements in the visible.

The technique has several advantages over the conventional multipass cell approach:

1. It has a demonstrated high sensitivity of better than 10^{-6} per pass which, for a 1-m sample cavity, gives a minimum absorption coefficient of 10^{-8} cm^{-1} .
2. It offers effective path lengths greater than 10 km. for a meter length cavity with an easily aligned optical system.
3. The absorption cell is a mode matched optical cavity into which the light is coupled. All of the probe light passes through a beam waist at the center of the cavity which can be positioned so as to sample small sample sources such as molecular beams and can typically provide several thousand passes through the beam intersection volume (beam waist cross section $< 1 \text{ mm}^2$).
4. The technique is based upon a pulsed measurement and so can be used to provide time resolved absorption measurements with an update frequency determined by the laser source and the absorption rate of the sample.

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