INTEGRATED CAVITY OUTPUT ANALYSIS OF ULTRA-WEAK ABSORPTION

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Abstract

It is demonstrated that direct absorption optical measurements with sensitivities of better than 1 part in a million can be made using pulsed light sources and employing a simple cavity optical configuration. A model is presented which demonstrates that the integrated absorption signal provides a quantitative total attenuation measurement if the absorption cavity mirror reflectivities are known. This approach to making absorption measurement provides a sensitivity comparable to that realized using the time domain Cavity Ringdown approach with a significant reduction in complexity. The approach is demonstrated using the weak $b^1\Sigma_{g(v'=1)}$ - $X^3\Sigma_{g(v''=0)}$ forbidden absorption of oxygen near 689 nm.

Introduction

Since it's introduction as a technique for quantitative optical absorption measurements in the 1980's [1-4], Cavity Ringdown Laser Absorption Spectroscopy (CRLAS, CRDS) has been employed in numerous configurations for spectroscopic studies in chemical physics, and has proven to be an absorption technique of broad application. In Cavity Ringdown spectroscopy, the decay rate of a photon population in an optical cavity is used to obtain the associated total intra-cavity losses (per pass) as a function of the photon frequency. When the cavity losses are dominated by cavity mirror scatter and transmission, the frequency resolved "loss" curve maps out the mirror reflectivity function. When a narrow band absorbing species is present, absolute atomic or molecular absorption intensities can be inferred by subtracting the baseline (non-resonant) losses of the cavity, which are determined while the laser is off-resonance with transitions. The power of the CRLAS method lies in the extremely high sensitivity and simplicity of the technique, together with the fact that it is an absorption-based method, and so can provide absolute attenuation determinations. As such, it is highly desirable for quantitative studies, as absolute concentrations are easily inferred from the absorption data. CRLAS concentration detection limits for many species have been demonstrated to be in the part-per-billion to part per trillion range [5].

Since the introduction of Cavity Ringdown spectroscopy, a number of new, ringdown-based techniques have been developed, including Fourier-transform [6], polarization dependent [7], and pseudo-cw [8] cavity-ringdown spectroscopy. While it may appear that the great sensitivity of the Cavity Ringdown approach results entirely from the temporal analysis of the signal rather than the amplitude analysis of traditional absorption techniques, it is demonstrated here that a comparable sensitivity can be realized using these more traditional direct absorption methods while employing the CRLAS geometry.

In this letter, a new variation of the technique, Integrated Cavity Output Spectroscopy (ICOS), is described which will enable absorption spectra to be obtained through direct attenuation methods, while providing a detection sensitivity comparable to CRLAS. In this approach the transmitted output of the cavity is simply integrated to provide an absorption spectrum as the injection light source is scanned in wavelength. The obvious advantages of this approach over the time domain approach are in system simplicity, cost, and the ability to use broad spectral bandwidth light sources and spectrally resolve the cavity output to produce a real-time broad spectrum image for chemical monitoring applications. In these initial ICOS studies, the basic principles are first discussed and then demonstrated in a proof-of principle experiment employing a frequency scanned pulsed dye laser source. These studies establish the feasibility of the concepts employed in ICOS, and demonstrate the utility of the approach.

Approach

In a conventional Cavity Ringdown experiment, narrowband laser light is coupled into a highly reflective optical cavity, and the decay or "ringdown" time is recorded as a function of the input laser frequency. Total per pass cavity losses are calculated from the measured decay time, and include mirror reflectivity, scattering, and molecular absorption for species located between the mirrors. In ICOS the absorption signal is obtained through the integration of the total signal transmitted through a ringdown type optical cavity cell, in much the same fashion as in conventional absorption measurements. The difference is that the path length in the ICOS approach is effectively infinite, as the light retraces the same path on each cycle. The resulting absorption changes to the integrated output are large, even for very weak absorptions per pass because the absorptions add in time.

The system can be easily modeled assuming a short pulse (or short coherence length pulse) injection through one of the cavity mirrors into the cavity. It is assumed that the incident optical path is aligned with the optical axis of the cavity so that the injected pulse traces over the same path on each round trip cycle within the cavity. The absorption at some frequency resonant with a molecular transition increases for each cycle the wave packet makes within the cavity. On the first pass of the light pulse through the cavity the transmitted signal (the light transmitted through the second cavity mirror) is related to the incident pulse, I_o, by:

$$I_1 = I_o \times T \times T \times \exp^{[-k\times L]} \qquad (1)$$

where T is the transmission coefficient for each mirror (assumed the same) and is equal to 1-R, and k is the absorption coefficient of the molecular absorber (in units of inverse length), and L is the cavity length. The next transmission to the detector follows a round trip cycle in the cavity where the intra-cavity pulse is reduced by two reflections and two more absorption lengths:

$$I_2 = I_o\times T\times T\times R^2\times \exp^{[-3\times k\times L]} \qquad (2)$$

which can be generalized to give the total (integrated) transmitted signal as the summation:

$$I=I_o\times T^2\times \Sigma[R]^{(2n)}\times[\exp^{(-(2n+1)\times k\times L)}] \qquad (3)$$

where the summation is over n, the number of reflections in the cavity. The summation can be approximated by an integral over n (for large n) resulting in;

$$I = I_o\times T^2\times\int[R]^{(2n)}\times\exp^{(-(2n+1)\times k\times L)}\, dn \qquad (4)$$

where the integration is from 0 to infinity. Rearranging terms this can be expressed as;

$$I = I_o\times T^2\times\exp^{(-k\times L)}\times\int[R\times\exp^{(-k\times L)}]^{(2n)}\, dn \qquad (5)$$

Since the term $\exp^{(-k\times L)}$ is simply a constant (typically 0.999+ for applications relevant to this discussion, as well as to the

Cavity Ringdown technique), we can fold it into a new term, R', where;

$$R' = R \times \exp^{(-k\times L)} \qquad (6)$$

which yields;

$$I = I_o \times T^2 \times \exp^{(-k\times L)} \times \int [R']^{(2n)}\, dn \qquad (7)$$

Solving this expression, we get;

$$I = I_o \times T^2 \times \exp^{(-k\times L)} \times [2\times \log(R')]^{-1} \qquad (8)$$

It is useful to consider several special cases. First consider the case in which there is no absorption present within the cavity. In this example the sample cavity is comprised of two mirrors of R= 99.99% (typical of Cavity Ringdown applications), into which a short pulse of light is injected. In the limit where scatter and absorption losses in the cavity mirrors are very small compared to the transmission through the reflective coating,;

$$T \cong (1-R) \qquad (9)$$

and with the assumption of no intra-cavity molecular absorption we have $\exp^{(-k\times L)} = 1$, and $R' = R$.

$$I = I_o \times (10^{-4})^2 \times [2\times \log(.9999)]^{-1} \qquad (10)$$

$$\cong I_o \times 5\times 10^{-5}$$

which returns the physically expected result that of the fraction of I_0 transmitted into the optical cavity ($I_o \times 10^{-4}$), half escapes out through each mirror. The total output from each of the two cavity mirrors is unequal because there is a built-in asymmetry in our model. In practice, however, the difference is small; the difference being a factor of R. Using mirrors with reflectivities of 99.9% or greater makes the difference insignificant.

A second interesting case is seen in adding to the above example a weak molecular absorption of 10^{-6} per cavity pass (i.e. $\exp^{(-k\times L)} = 0.999999$). In this case the integrated transmitted signal is

$$= I_o \times 4.95\times 10^{-5}$$

which represents a change in the transmitted signal of 1% from the earlier result. This demonstrates that in an ICOS experiment, very small absorption changes result in rather large changes in the total transmitted signal, and suggests that it should be able to use **simple direct absorption methods** to make such quantitative measurements.

Simple numerical modeling of the intra-cavity absorption process confirms this result. In Figure 1 the net transmitted signal is plotted as a function of the fractional absorption, **x** , over the range **x** = 0 to **x** = 1×10^{-6} . In this plot the signal refers to the fraction of injected light which the detector sees (integrated in time). In the case where there is no absorption, (x=0) the detector sees half of the total injected light (the other half exits through the second mirror). The plot assumes that the reflectivity is 99.99% for the cavity mirrors.

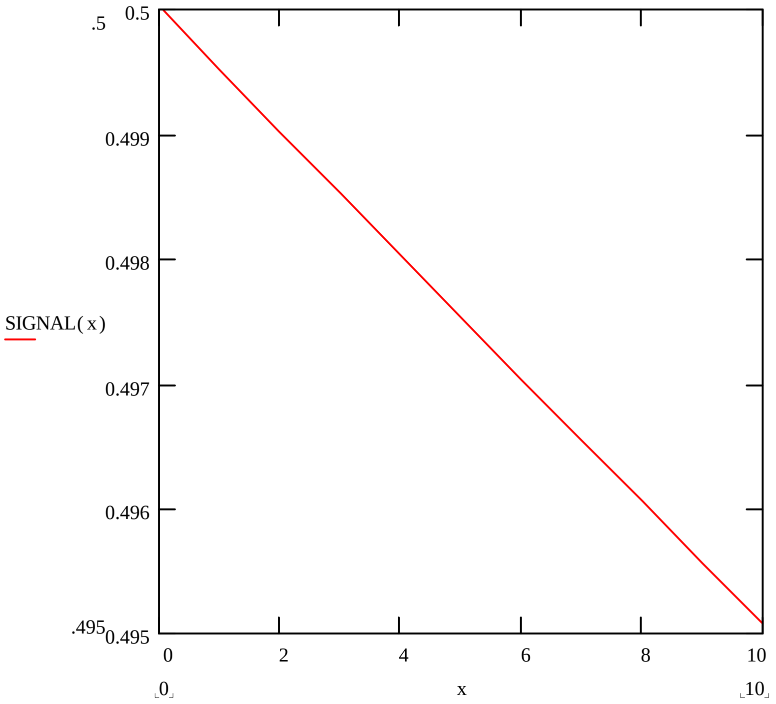

Figure 1. Relative ICOS signal vs intra-cavity absorption ranging from 0 to 10^{-6} fractional absorption per cavity length for mirror reflectivity of R=99.99%. The Y-axis represents the fraction of energy injected into the cavity which is measured by a detector behind one of the cavity mirrors. The X-axis represents intra-cavity absorption per-pass in the cavity. Under these conditions a 1% change in the total integrated signal is observed for a single pass fractional absorption of 10^{-6} .

Thus, if the mirror reflectivity is known it is possible to quantitatively measure per-round trip absorptions of 1 part-per-million as net integrated absorptions of ~1% (for R=99.99%). This result is easily seen to scale with the cavity mirror reflectivity. Using mirrors with reflectivity of 99.9% results in a reduction of sensitivity such that per pass absorption of 10^{-5} is required to produce a 1% change in the ICOS signal. The use of mirrors with higher reflectivities result in a corresponding increase in sensitivity. This detection sensitivity is comparable to that achieved using the time domain CRLAS technique, and the relationship between the mirror reflectivity and the absorption sensitivity is similar [9]. The ultimate sensitivity of this approach will be determined by the noise level of the light source as well as the shot noise level of the signal, however the results presented here demonstrate that even relatively noisy pulsed dye lasers (shot-to-shot variation of ~5-10%) can provide part-per-million per pass sensitivity with modest signal averaging.

Experimental

The model discussed above was tested by making integrated absorption measurements in a cavity configuration using a pulsed dye laser and looking at the weak oxygen absorption bands between

688.5 and 690.5 nm. In the experiments described here both the traditional Cavity Ringdown approach as well as the ICOS approach were utilized in order to compare the results and sensitivities. These tests have shown that the proposed approach is well described by the above model and that the ICOS approach can be used to obtain quantitative absorption information. These tests also provide a measure of the signal to noise levels we can achieve for a known detector.

The initial experimental setup employed a pulsed Nd:YAG laser which is used to pump a pulsed tunable dye laser which provides the wavelength tunable light for the tests. The setup used in this work was essentially the same as has been described in other publications [1] and it is only important to note that no optical alignment was modified in making this comparison. The only change made was in the data processing procedure. The goal of these tests was to demonstrate that an absorption sensitivity similar to that achieved using the Cavity Ringdown Technique could be realized using the simple integrated cavity output, thus reducing the need for fast sampling electronics and making rapid (greater than kHz) data acquisition feasible.

Using a 0.75 cm^{-1} bandwidth Continuum dye laser light source (dye gain broadened above nominal operating specifications), operating around 690 nm, standard CRLAS type Ringdown and integrated absorption measurements of the oxygen $b^1\Sigma_{v=1}$ - $X^3\Sigma_{v=0}$ band, averaging 16 laser shots per point. The data were recorded using a Tektronix TDS 360 digital scope interfaced to a Pentium based PC running Labview data collection software. In the CRLAS tests, the digitized signal was processed and fit to an exponential slope, and the result plotted as per pass absorption (in units of parts-per-million) as a function of the laser wavelength. The resulting data from the Ringdown approach is shown in Figure 2. Following these tests the data analysis procedure was modified so that the total light signal exiting the optical cavity was integrated. the transmitted optical signal was integrated for a period of greater than 5 time constants to produced the ICOS signal. This signal was normalized to the pulse-to-pulse variation in the laser pulse energy by dividing the result by the largest single data point in the pulsed transmitted signal. This normalization approach is adequate for the weak absorptions examined here, however an independent laser power normalization could easily be employed, which would permit the analysis of moderately strong absorptions. The resulting absorption spectrum is plotted as percentage absorption as a function of the laser wavelength and is shown in Figure 3.

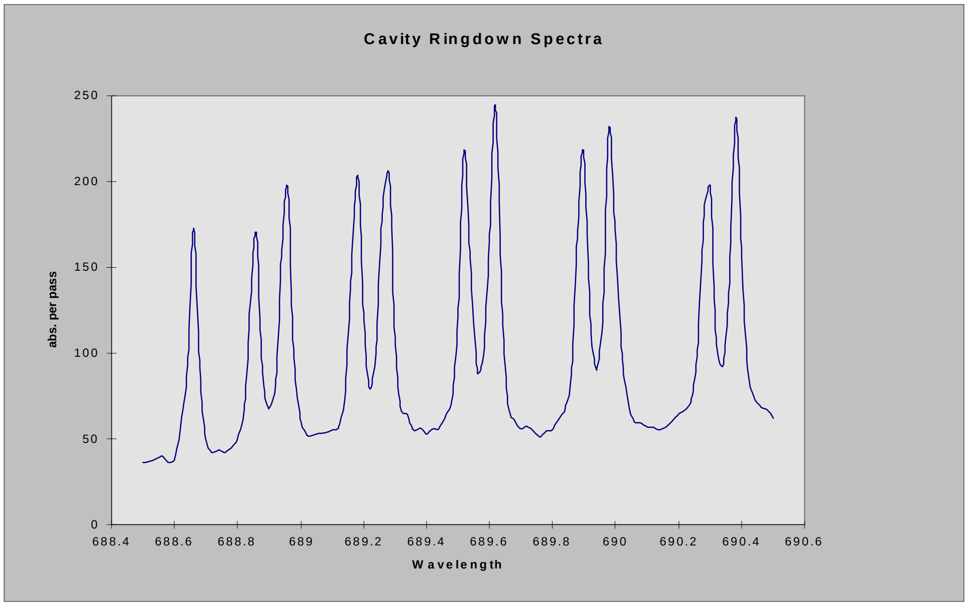

FIGURE 2. Cavity Ringdown spectra of the $b^1\Sigma_{v=1}$ - $X^3\Sigma_{v=0}$ band of molecular oxygen between 688.5 nm and 690.5 nm. The Y-axis is in units of “parts-per-million” absorption per optical pass through the ringdown cavity. Noise level is approximately 5 ppm.

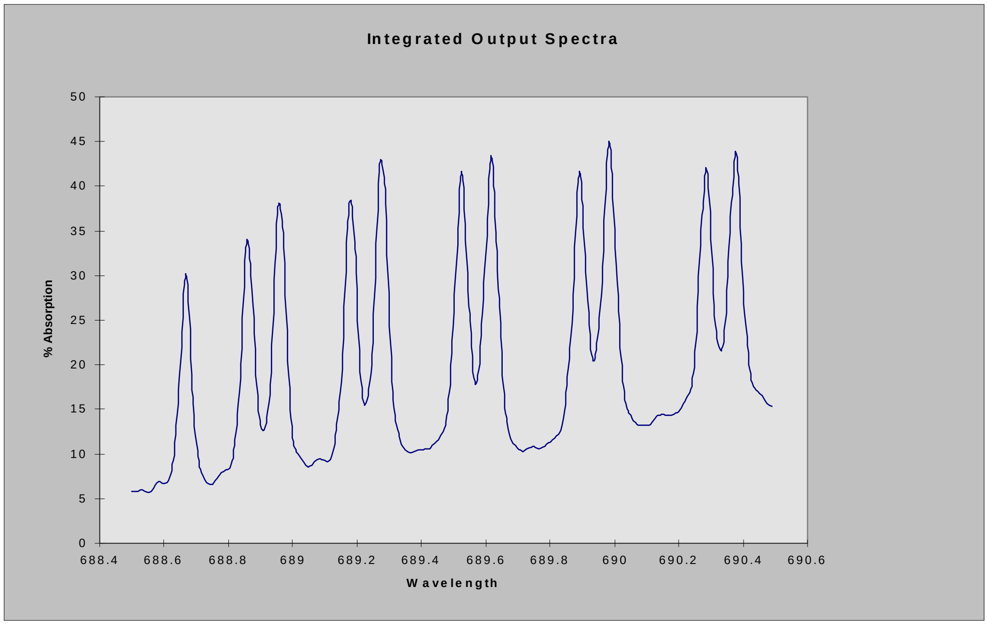

FIGURE 3. Integrated absorption spectra of the same band region as seen in Figure 2. The units on the y-axis are in % absorption.

The direct absorption data seen in Figure 3 demonstrates that the proposed approach does provide a very comparable level of sensitivity to that achieved using the more complex time domain CRLAS technique. The relative signal to noise levels are similar, even though the dye laser experiences rather large pulse amplitude fluctuations. While this approach worked very well, it could result in a problem in dynamic range, however for single pass absorptions not much greater than 5 to 10 times the cavity mirror transmission losses, the effect should not be too important.

The absolute absorption seen in the signal in the integrated output test is approximately 30-40% attenuation on individual lines. Using equation (4) it is possible to calculate the predicted absorption signal strength. Noting that the mirrors had reflectivity of ~99.94% and using the estimated absorption strengths for resolved lines in this band for the estimated laser linewidth of 0.75 cm^{-1} [1], ka = 2×10^{-5} cm^{-1} atm^{-1}, the calculated absorption change is ~ 30% , which is very close to what is observed in Figure 3.

Conclusions

In this letter, the Integrated Cavity Output absorption analysis method has been detailed, and the concepts involved were demonstrated in a proof-of-principle experiment which was carried out using a pulsed dye laser light source. The experiment looked at the absorption signals produced by molecular oxygen between 688.5 nm and 690.5 nm using both the traditional CRLAS technique as well as that of ICOS. The absorption intensities extracted from the ICOS data were found to be in excellent agreement with those obtained with the well established Cavity Ringdown method, and are accurately described by the simple model presented here. This work demonstrates that the ICOS approach can be used to record quantitative absorption signals of weak absorbers at signal collection rates which exceed that possible using the time domain Cavity Ringdown technique. Perhaps even more exciting is that the approach can clearly be used in conjunction with post-cavity spectral resolution of broad band width light sources to provide optical multi-channel array detection of extremely weak absorptions. This approach would be of great importance in the concurrent monitoring of several absorbing species.

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References:

1) O’Keefe, A., Deacon, D.A.G., Rev. Sci. Instrum., **1988**, 59, 2544
2) Ramponi, A.J., Milanovich, F.P., Kan, T., Deacon, D., Appl. Opt., **1988**, 27, 4606
3) O’Keefe, A., Lee, O., American Laboratory, **1989**, December, 19
4) O’Keefe, A., Scherer, J.J., Cooksy, A.L., Sheeks, R., Heath, J., Saykally, R.J., Chem. Phys. Lett., **1990**, 172, 214
5) Jongma, R.T., Boogaarts, M.G.H., Holleman, I., Miejer, G., Rev. Sci. Instrum., **1995**, 66, 2821
6) Engeln, R., and Meijer, G., Rev. Sci. Instrum., **1996**, 67, 2708
7) Engeln, R., Berden, G., vander Berg, E., Meijer, G., J. Chem. Phys., **1997**, 107, 4458
8) Romanini, D., Kachanov, A.A., Sadeghi, N., and Stoeckel, F., Chem. Phys. Lett., 1997, 264, 316
9) Scherer, J.J., Paul, J.B., O’Keefe, A., and Saykally, R.J., Chem. Rev.,**1997**, 97, 25