

Development of a Phase Shift-, Fourier Transform- Cavity Ring Down Spectrometer

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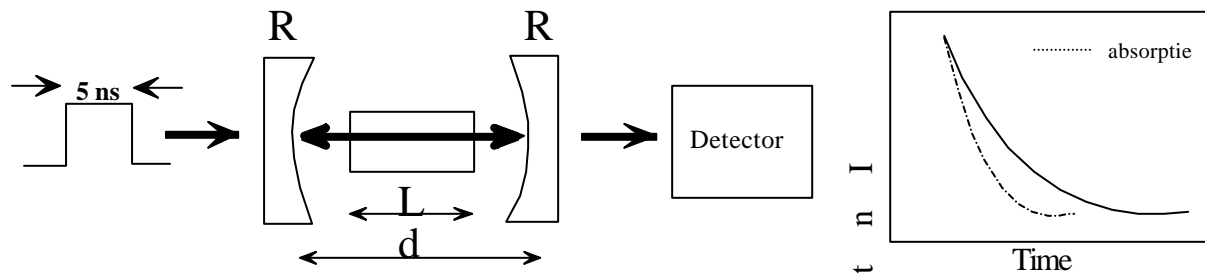
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Abstract

The possibilities for combining two Cavity Ring Down Spectroscopy (CRDS) techniques were studied. The objective is to lay the grounds for the development of a sensitive broad band, gas phase, cw, optical absorption spectrometer. CRDS is a type of multi-pass absorption spectroscopy. In CRD the "lifetime" of light intensity in an optical resonant cavity is related to the loss in the cavity [5]. This loss is due to the mirrors' non-ideal reflectance and to the absorption of the gas inside the cavity. Therefore CRD can be used to determine with high sensitivity the reflectance of mirrors as well as densities, temperature, pressure of the medium between the mirrors

PS-CRD is a cw based technique, in which the light being coupled to the cavity is modulated and a Phase Shift is detected, which is related to the loss in the cavity. This has been demonstrated experimentally with a ring-dye laser [2]. Here we demonstrate this same technique with a low power diode laser, detecting loss due to absorption in part of a weak O₂ band (A-band) of up to few ppm/cm. The Signal to Noise Ratio (SNR) was studied as a function of modulation frequency and depth. A LabView program was developed in order to control the experiment from the computer via GPIB [1].

FT-CRD has been demonstrated with a broad band pulsed dye laser as source [3]. In that work the light exiting the cavity was coupled into a Michelson-type interferometer and the time dependence acquired for a range of path differences. Loss at every wavelength could be deduced from this. In this work is demonstrated in theory how PS- and FT-CRD can be combined, creating an absorption spectrometer that can be used with a broad band (e. g. white light) cw source, that could measure loss in a resonant cavity for the different wavelengths by detecting a phase. The possibility of coupling the light from a modulated optical cascaded arc into a confocal optical cavity was also tested. The arc could be modulated up to 20kHz, 10% depth. For lower frequencies higher depths are possible. The results strongly indicate that the light can be coupled, but they are not yet conclusive.



[Fig. 1]- Schematic representation of a pulsed CRD experiment. d is the distance between the mirrors, and L the path over which absorption is considered.

Theory of the PS- and FT- CRD Symbiosis

Conventional Cavity Ring Down (CRD) Spectroscopy

The multi-pass absorption technique CRD can be implemented by measuring the rate of decay in intensity of a light pulse in an optical cavity. The most elementary way to understand this is to consider an optical cavity consisting of two highly reflective mirrors and a light pulse that is coupled into this cavity [5].

If the reflectance R of the mirrors is very close to unity, then only a small fraction of the intensity of the incoming beam is coupled into the cavity, $(1-R)$, an aspect intrinsic to the CRD technique. Consider then this pulse that has entered the cavity. It will be reflected back and forth inside the cavity, and if there is not any absorbing medium between the mirrors, then the only losses will occur at the mirrors, due to their finite transmittance. In approximation we can go from these discrete changes in intensity to a continuous change, that is, considering the intensity as a function of time. We then have that (in approximation), the intensity for a given frequency ν decreases exponentially in time:

$$I(\nu, t) = I(\nu, t_0) \cdot e^{-\frac{t}{\tau_0(\nu)}} \quad [1]$$

in which τ_0 is given by:

$$\tau_0(\nu) = \frac{d}{c[\ln(R(\nu))]} \quad [2]$$

If there are absorbing species in the region L between the mirrors, (see fig. 1), there will be losses due to absorption and scattering. In gas phase, scattering can usually be neglected as compared to absorption (scattering cross-sections are much smaller), and so a further term due to absorption is introduced in the denominator for τ .

$$\tau(\nu) = \frac{d}{c[(1-R(\nu)) + N_p S(\nu)L]} \quad [3]$$

considering homogeneous absorption at ν over a distance L , by a density N_p . N_p can then be calculated after measuring τ :

$$N_p S(\nu)L = \frac{d}{c} \left[\frac{1}{\tau(\nu)} - \frac{1}{\tau_0(\nu)} \right] \quad [4]$$

an expression most useful when analysing data in CRD measurements. It also implies that, in order to determine $N(\nu)$, there must be a measure or estimate/calculation for τ_0 , that is, the ring down time without absorption¹. This can be done by measuring τ without any absorbing species in the cavity, or at a wavelength on which we are sure to have no absorption (that is, one could measure against the *baseline*).

This is a simple approach to CRD, one can find more detail by looking at the electromagnetic solutions

¹ in the case of a spectrum, it will in general correspond to τ measured from the baseline.

for an optical cavity [13], of course. But the expressions derived here are the ones currently used and this model is enough to understand the basis of the theory.

Phase Shift CRD

As compared to normal CRDS, performed with a pulsed laser, the use of a cw light source (in PS-CRD) brings a clear advantage. When using a non-stabilised cavity, which goes in and out of resonance in time, cw light can be coupled more efficiently to the cavity and a low power output laser can be used. On the other hand, a cw light source generally has a much narrower bandwidth, therefore increasing the spectral resolution of the measurement. Consider a coherent light beam, modulated in intensity:

$$I(\nu, t) = I_0(\nu)(1 + a(\nu) \sin(\Omega t)) \quad [5]$$

If this light interacts with an atomic or molecular system with discrete energies, exciting a particular state, fluorescence will take place, due to the finite lifetime of the excited state. Duchinsky [7] has proven already in 1933 that the intensity of such fluorescence will be modulated in time with the same frequency Ω , but delayed (or phase-shifted) in relation to the incident light modulation. This phase shift was related to the lifetime:

$$\tan\phi = -\Omega\tau \quad [6]$$

The modulation depth is also attenuated:

$$a'(\nu) = a(\nu) \frac{1}{\sqrt{1 + \Omega^2\tau^2}} \quad [7]$$

In an optical cavity, for each ν (or resonant mode) a “lifetime” or decay time can be defined, for a light beam intensity $I(\nu, t)$ or even a single photon². This is nothing more than the *Ring Down Time* already discussed, which in turn can be related to absorption.

In theory it is possible to retrieve the ring down time τ either by measuring the phase shift ϕ or the decrease in modulation depth, α'/α . But in practice, it proves to be much more feasible to measure ϕ . This brings us to the necessity of using phase sensitive detectors. The most sensitive and appropriate solution that current electronics has to offer is the Lock-in Amplifier (LIA), a device capable of retrieving the intensity and phase³ of a modulated signal, at a defined frequency, and which can be buried in as much as 60db of noise ([8], [9], [10], [20]).

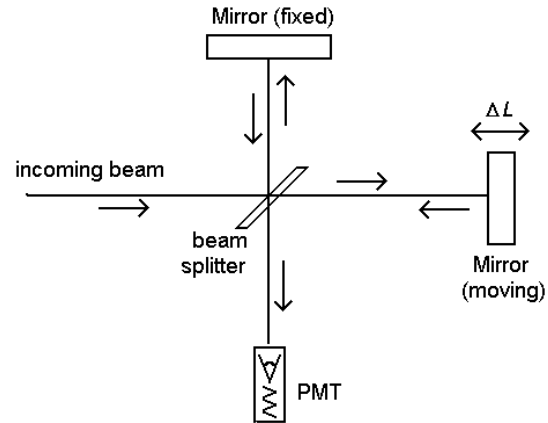
Fourier Transform CRD

In FT-CRD one uses a broadband light source, with a spectral intensity distribution $I(\nu)$, which is coupled into the cavity. The light source is pulsed, as in conventional CRD, and the time evolution of the light leaking out of the cavity is recorded. One does not observe one exponential decay at the detector, as light in all

² In the classical limit, the situation is not distinguishable, for $I(\nu) \propto N_{\text{Photons}}(h\nu)_{\text{Photon}}$, so the decay time is the same, because it is evaluated in terms of a ratio I_0 / I_t .

³ Phase as compared to a reference.

wavelengths is present and $\tau = \tau(\nu)$. So it is necessary to resolve the different wavelengths. In FT spectroscopy, this is done with an interferometer, Michelson-type.



[Fig 2] - Schematic representation of a Michelson-type interferometer, which can be used for Fourier Spectrometry. The mirror scans along ΔL . The PMT registers the signal for this of values in ΔL , separated by a step δx . The *FFT* (numerical *Fast Fourier Transform*) of this set will be the spectral composition of the incoming beam. The maximum frequency obtainable is $1/(2\delta x)$ (Nyquist Theorem) and the max. resolution $1/\Delta L$.

By scanning along ΔL and acquiring the time dependent signal, one obtains the Fourier Transform of the spectral profile, in the ‘distance’ space. This data can in turn be treated numerically in order to yield the Inverse Fourier Transform, which will be the spectral distribution (in frequency space). We get $I(\nu, \delta)$, so that we can retrieve the ring down time for each ν ([1]), and calculate the absorption/density.

Fourier Transform - Phase Shift CRD Spectroscopy

We intend to use the advantages of a broad band light source, proper of FT-CRD spectroscopy, while measuring a relative phase shift (on cw) instead of transients (on pulse), a feature proper to PS-CRD spectroscopy. If it proves possible to use (e.g.) white light, not only a broader spectral range is available, as also costs for the source may be reduced. In this case, the spectral range for the analysis is determined by the reflectivity profile of the mirrors, and one may even consider using sets of mirrors to cover a broader spectral range.

The mathematical details are presented in [1]. The light going in now would be:

$$I_{in}(\nu, t) = I_0(\nu)[1 + a(\nu) \sin\Omega.t] \quad [8]$$

The light leaking out, when in resonance, according to expressions above: [9]

$$I_{out}(\nu, t) = I_0(\nu) \left[1 + \frac{a(\nu)}{\sqrt{1 + \tan^2[f(\nu)]}} \sin(\Omega.t + f(\nu)) \right]$$

The light at the detector, where both beams come together: [10]

$$I_{det}(\Delta L, t) = A(\Delta L) + B(\Delta L) \sin\Omega.t + C(\Delta L) \cos\Omega.t$$

That is, $I(\Delta L, t)$ consists of a DC component and two separable AC components, which can be seen as the in-

phase and out-of-phase components. A Lock-In Amplifier can retrieve both these components, that is, B and C for each position ΔL . It can be proven [report] that the cosine Fourier Transforms of those two sets of values will be:

$$\mathfrak{S}_{\cos}[B(\Delta L)](v) = \frac{I_0(v)\mathbf{a}(v)}{\sqrt{1 + \tan^2[\mathbf{f}(v)]}} \cos \mathbf{f}(v) \quad [11a]$$

$$\mathfrak{S}_{\cos}[C(\Delta L)](v) = \frac{I_0(v)\mathbf{a}(v)}{\sqrt{1 + \tan^2[\mathbf{f}(v)]}} \sin \mathbf{f}(v) \quad [11b]$$

And by simply dividing both transforms $\tan \mathbf{f}$ is obtained:

$$\frac{\mathfrak{S}_{\cos}[C(\Delta L)](v)}{\mathfrak{S}_{\cos}[B(\Delta L)](v)} = \frac{\sin \mathbf{f}(v)}{\cos \mathbf{f}(v)} = \tan \mathbf{f}(v) \quad [12]$$

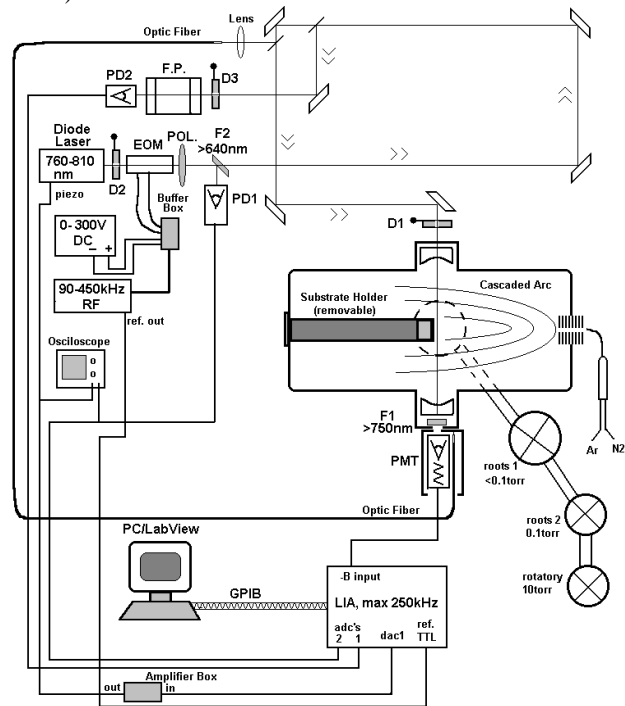
And \mathbf{f} can be related to the Ring Down Time \mathbf{t} $\tan \mathbf{f}(v) = -\Omega \tau(v)$, and the latter to absorption:

$$\mathbf{t}(v) = \frac{d}{c[\ln(R(\mathbf{n})) + \sum_j A_j^{abs}(v)]} \quad [13]$$

Experimental Results

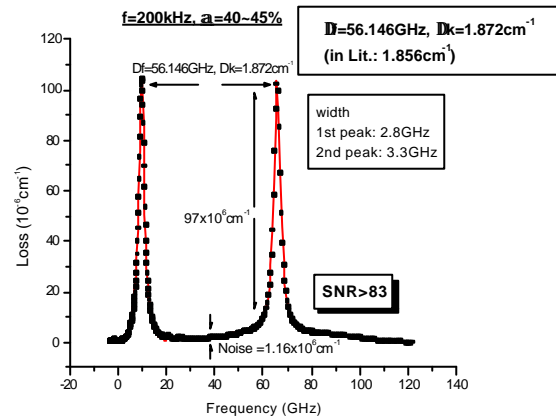
Testing PS-CRD technique

To become acquainted with the technique a part of the absorption spectrum of atmospheric O_2 was scanned. These were the “weak” rotational transitions in the $b^1 \Sigma_g^+ (v' = 0) \leftarrow X^3 \Sigma_g^- (v'' = 0)$ band of $^{16}O_2$ (A-Band).



[Fig 3] - Semi-conceptual sketch of the setup. A plasma deposition chamber (with cascaded arc) was used in order to have vacuum.

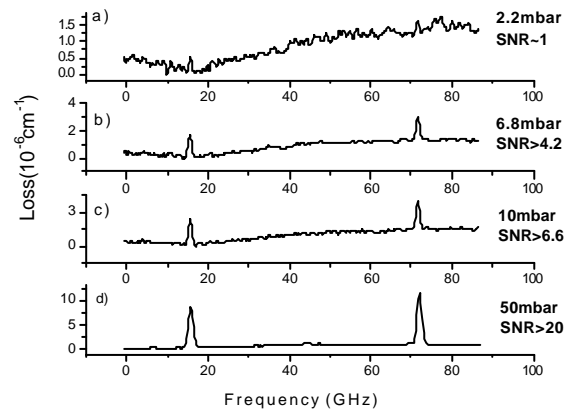
Here we use absorption *per unit length*, or *loss*, which is just $A(v)/d = \alpha(v) L/d$, or $A(v) = \alpha(v) L$ which is the case. So *loss* is the attenuation coefficient in Lambert-Beer law.



[Fig. 4] - Obtained *Loss* for two O_2 lines at 765.4-765.5 nm, with a modulation frequency of 200kHz and depth around 45%. The *signal to noise ratio*, SNR, is measured taking the smallest peak and the maximum local variation (noise). The peak height is measured relative to a *baseline*. According to [12], these peaks are supposed to have the same height. Doppler broadening is calculated to be 0.028 cm^{-1} . The width of the Lorentz fits (0.093 cm^{-1}) is 3.3 times higher (pressure broadening).

Using the peak values from the graph, one can make a first estimate on the cross-section for this absorption, considering 0.2 bar of O_2 . For this line, at 765.4nm, 13065 cm^{-1} , it yields $S(v) \approx 1.92 \cdot 10^{-27} \text{ m}^{-2}$. This is approximate to values from literature [11], though it is just an estimate.

By fitting one of the peaks to a Voigt profile, we can extract estimates for Doppler and Pressure broadening. The Voigt profile is a convolution between Gauss and Lorentz profiles. The correspondent widths (1st peak), converted to cm^{-1} , are 0.028 cm^{-1} for Gauss (Doppler) and 0.087 cm^{-1} for Lorentz (pressure) profiles. This compares to an expected 0.028 cm^{-1} and 0.05 cm^{-1} , respectively (room temperature, 1 bar and at $\sim 760 \text{ nm}$). We now can be relatively sure that the measured absorption values can be related to density, and the phase shift signal is usable for absorption measurements.



[Fig 5] - Comparison of absorption for pressures in the limit of sensitivity of the technique. Separation (in v) between peaks remains unaltered, as expected. It is possible to notice a correlation in the signal for 2.2mbar, though the peaks are at noise level.

To determine the sensitivity of such technique, the absorption peaks were measured at consecutive lower

pressures. The limit was reached at about 2.5-3mbar vessel pressure, i. e., 0.5mbar O₂, or an absorption *loss* of $1 \times 10^{-6} \text{ cm}^{-1}$.

The cross section for this weak absorption in O₂ is very small when compared to regular, common cross section values. For example, in transitions in/from CH, NO, or N₂(A), the σ is 9 orders of magnitude higher. This in turn implies that the lowest densities detectable for the referred species are about 9 orders of magnitude lower! The next table presents an estimate to summarise this, if we consider the lowest detectable pressure for O₂ to be 1mbar (= 0.2x5mbar):

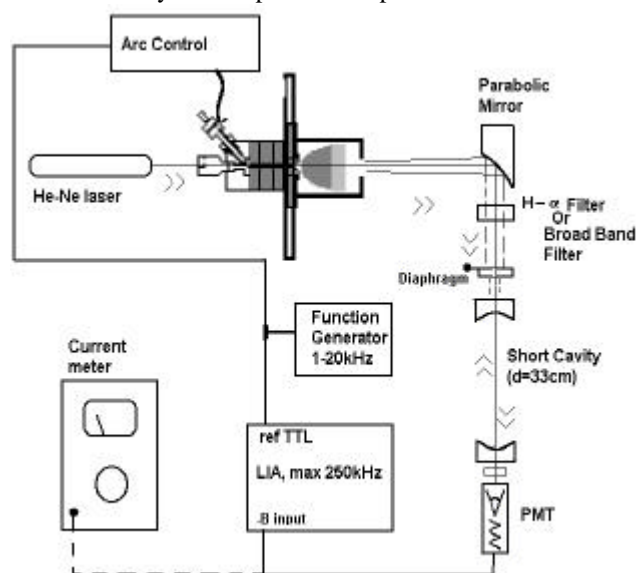
Molecule	Cross Section(cm ²)	Lowest pressure (mbar)	Lowest density (cm ⁻³)
O ₂ (A-Band)	$\sigma_{\text{O}_2} \approx 2 \times 10^{-23}$	~1	$\sim 3 \times 10^{16}$
CH(A ← X-band)	$\sigma_{\text{CH}} \approx 1 \times 10^{-14}$	$\sim 2 \times 10^{-9}$	$\sim 6 \times 10^7$

This provides a basis to compare the possibilities of such technique, which has proven to be fairly high-sensitive.

The Cascaded Arc as a White Light Source

The Setup

Due to time limitations, only a brief experimental study was undertaken on the feasibility of the optical cascaded arc as a light source to be used with an optical resonant cavity. The experiment is pictured below.



[Fig 6] The Optical Cascaded Arc ran on Argon (radiation power~50W). The current was modulated up to 20kHz, with about 10% modulation depth. However, the experiment was carried at 10kHz, because the overall modulated signal improves significantly for lower frequency.

Results

The first result in the experiments with the arc is that it can be modulated up to 20kHz via the current. On the other hand, results for PS-CRD on Signal to Noise Ratio dependence on modulation frequency [1] showed that is possible to obtain absorption signal at 20kHz. This suggests a possibility to use the arc as source. The second result is the suggestion that the cavity may be “ringing” on the light from the arc. The light at both mirrors was measured using a narrow band pass filter (H- α line), so

that only the light for which the mirrors were highly reflective could be coupled into the optical cavity.

Mirrors	SNR on current meter	Modulated Signal Magnitude	Phase Shift (LIA)
1	2	~100 μ V	30°-33°
2	2	~10 μ V	28°-40°

A reduction by only a factor of 10 is observed. If the cavity is ringing, in theory no reduction would be observed, except for the finite efficiency. Anyway, from the previous experiments, we would not expect to observe a much better efficiency in the coupling in of the light. So far, there are two possibilities. One would be that the cavity is effectively ringing, there is build up of energy between the mirrors, and the observed intensity for the modulated light is much stronger (50x) than would be considering one reflection backwards by each of the two mirrors. Less optimistic, it can be to consider the amount of stray light to increase when using the two mirrors. This could be because the front mirror of the cavity would reflect back most light, and this would scatter back from the diaphragm, and by some more reflection (on the table, etc) would reach the PMT. In this case, when replacing the mirror, though completely tilted, the same amount of stray light would be expectable. But this is not observed, with a fully misaligned cavity there is no detectable intensity. So the first possibility is fairly acceptable. However, one also observes the phase signal to be too unstable to be used. For this cavity, with $d=33\text{cm}$ and $R=99.8\%$, at 10kHz: $\tau_0 = 0.5\mu\text{s}$; $\phi = 0.3^\circ$. This is to be compared to an experimental uncertainty (error ‘bar’) of about 12° in phase. Therefore, it is necessary to improve the signal so that at least ϕ will be bigger than it’s uncertainty.

Conclusions

- It is now proven in theory that PS-CRD and FT-CRD spectroscopy can be combined, using the devices proper to each.
- It was found experimentally that the vibrations on the cavity actually improve the quality of the signal, contrary to most diagnostics. This indicates a potential of PS-CRD to be used in vacuum/plasma vessels, in which pumps and associated vibrations are always present.
- The dynamic range for our PS-CRD setup is between 1 and 110 ppm/cm (*Loss*). For a “fully allowed” transition such as A ← X in CH, the lowest density measurable is around 10^7 cm^{-3} !
- The optical cascaded arc can be modulated up to 20kHz via the current. On the other hand, signal was obtained with monochromatic PS-CRD for the lowest frequency of 20kHz. Therefore a phase shift may be measurable with a white light source. This is an important step towards the combination of PS- and FT- CRD. It also means that an Electro-Optic Modulator may be dispensed.
- There is strong indication that light from the arc can be coupled into an optical cavity. However, the

experiment was not tested for reproducibility. More experiments have to be performed in order to draw definite conclusions.

Finally, a word of acknowledgement. To B. Husken, H. Jong and R. v.d. Sande for all the technical support.

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