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THEORETICAL COMPARISON OF THE CAVITYDECAYCONSTANT FOR NITROGEN DIOXIDE IN A PULSED CAVITY RING DOWN SPECTROSCOPY USING THE PHOTON BULLET MODEL AND CAVITY TRANSFERFUNCTION IN THE TIME DOMAIN

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Abstract

Simulations of cavity transfer function and photon bullet model are performed for an arbitrary cavity of length 30 cm and mirror reflectivity of 99.98% using Mat lab programming. The time constant value thus obtained using the two functions for different concentrations of Nitrogen Di Oxide(NO_2) at 532 nm was found to be different.The Photon bullet model gives a higher value of concentration dependent time constant as compared to the cavity transfer function. The empty cavity time constant was found to be 2.485 μsec and 3 μsec for transfer function and bullet model respectively.

KeyWords: *Cavity ring down Spectroscopy (CRDS), Photon Bullet model,Transfer function,Gas concentration, parts per billion(ppb),Fabry-Perot cavity.*

1. Introduction

Cavity ring down spectroscopy (CRDS),a very sensitive absorption spectroscopic technique was developed by O'Keefe and Deacon in 1988(1). It employs an optical cavity like a Fabry-Perot cavity formed between two highly reflective concave mirrors in which a laser beam is trapped. If the cavity supports the laser beam, it will be reflected many times and will slowly lose power due to mirror imperfections. The intensity of the beam in the cavity is probed as a function of time after the initial laser pulse by measuring the intensity of the light leaking from the back mirror.

When an absorbing species(like a gas)is present within the cavity the decay in intensity will be faster. The quantitative analysis of CRDS to deduce the concentration can be done by the fundamental photon bullet model as well as the cavity response function. Both the models yield an exponential decay depending on the number density of the species enclosed. The focus of the present paper is to employ the two functions viz the photon bullet model and the transfer function and obtain the time constants for the empty cavity as well as for different concentrations of the gas. The results were compared and the reasons for the deviations were analyzed.

2.Photon bullet model

From photon bullet model(2) approach the envelop of the intensity of the output from a ring down curve is an exponential decay with respect to time which is characterized by the cavity losses, due to the mirrors, diffraction loss as well as due to the absorption of the analyte present.

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When a light pulse with intensity I_{in} is directed into the cavity, it initially encounters the first mirror. The input mirror can either reflect or transmit the radiation through the first mirror, with respective probabilities of R and T, such that R + T = 1. After transmission through the first mirror the light travels through the cavity, where it may be absorbed or scattered by the sample. The probability that a photon will be transmitted through the cavity on the first pass is therefore given by the Beer-Lambert law. A fraction T of the first pulse is then transmitted through the second mirror before being detected. The detected intensity from the first pass through the cavity is

$$I_0 = I_{in} \cdot T^2 \cdot \exp[-\sigma(\nu)Nd]$$

in which d is the path length through the absorbingspecies. After another round trip of the cavity, the intensity is decreased further by reflection at each mirror and absorption or scattering in the cavity. The remaining intensity is

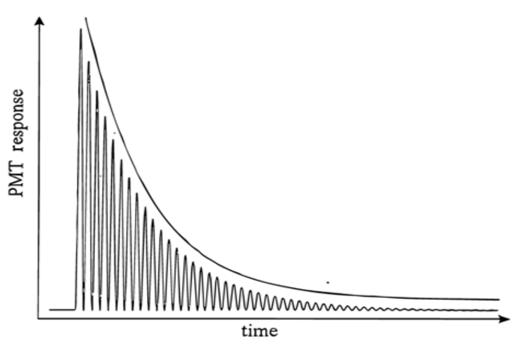
$$I_1 = I_0 \cdot R^2 \cdot \exp[-2\sigma(\nu)Nd]$$

After n round trips the intensity at the detector is therefore given by

$$I_n = I_0 \cdot R^{2n} \cdot \exp[-2n\sigma(\nu)Nd]$$

$$= I_0 \cdot \exp[-2n(\sigma(\nu)Nd - \ln R)]. \quad \text{--1`}$$

Fig 1a shows the output at the detector and fig 1b is the pictorial representation of the photon bullet model



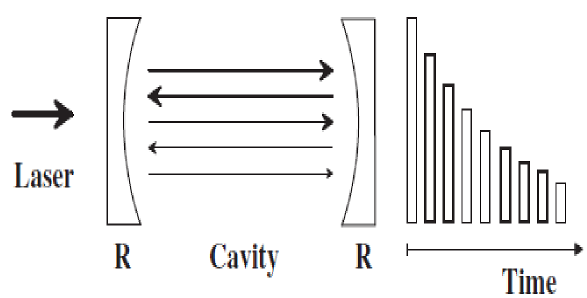


Figure 1a **Figure 1b**

3.Transfer function of the Ring down cavity:

The theoretical description of a cavity response to a pulsed excitation can be done either by time domain(3) or frequency domain analysis. The time domain approach has been proved to be a convenient choice to obtain a specific ring down detail. Consider a Fabry Perot cavity of length L constituting of mirrors with identical field reflectivity R and transmittivity T respectively.Here we obtain the ring down signal for a mechanically stable cavity excited by a pulsed laser field where the cavity is transversely mode matched to the TEM_{00} mode. This makes the analysis simple by considering the signal features in one dimension along the cavity.

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The cavity response function can be expressed as a Green's function G(t)(4)

$$G(t) = \sum_{n=0}^{\infty} T^2 R^{2n} \delta(t-(n+1/2)tr)$$

δ(t) is Kronecker-delta function and t_r is the cavity round trip time with velocity c and n, the number of round trips made by the light within the cavity. As we know that for every round-trip some part of the light escapes out of the cavity depending on the output mirror transmittivity T, we write the output field due to an arbitrary excitationof the input field E_{in} as

$$E_{out} = \sum_{n=0}^{\infty} T^2 R^{2n} Ein(t-(n+1/2)tr)$$

A Fabry Perot cavity has its own cavity response function depending on the cavity parameter and is independent of the Laser characteristics.In the time domain analysis of the cavity's response to an excitation we considerthe Fourier transform limited Gaussian input pulsewhich is represented as

$$E_{in}(t) = A \exp(-at^2)\exp(-i\omega t)$$

where $A = 4\sqrt{4} \ln 2/(\pi\tau p^2$) the complex amplitude and $a=2 \ln 2/ \tau p^2$ is the coefficient determining the pulse duration τpin FWHM.The transmitted output field is written as follows

$$E_{out}(t)=\sum_{n=0}^{\infty} T^2 R^{2n} A \exp\left[-a\left(t-\left(n+\frac{1}{2}\right)tr\quad\right)^2\right]\exp[-i\omega(t-(n+1/2)tr)]$$

$$=T^2 A exp\left[-i\omega\left(t-\frac{tr}{2}\right)\right]\sum_{n=0}^{\infty} R^{2n}\exp\left[-a\left(t-\left(n+\frac{1}{2}\right)tr\quad\right)^2\right]\exp[in\Omega tr]$$

here the Laser frequency ω is compared to the that of the cavity resonance $\omega_c=2\pi N/tr$

whereΩ is the detuning between the cavity and the input laser given by $\Omega = \omega-\omega_c$,which is used to determine the off resonance and on resonance conditions.

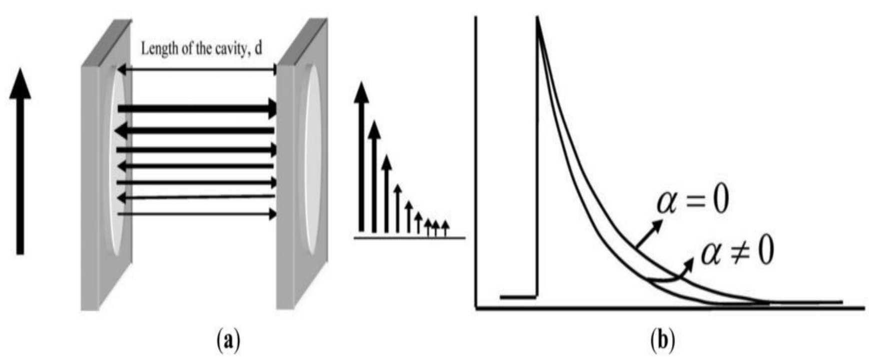

Figure 2a and 2b Pulsed CRDS for Dirac-delta function and the decay profile with and without an absorber

Since it is the output intensity that decays with time we deduce the time constant of an empty cavityfrom the following equation

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$$\mathrm{Iout(t)} = T^2 I_o \mathrm{mod}\{\sum_{n=0}^{\infty} R^{2n} \exp\left[-a\left(t-\left(n+\frac{1}{2}\right)tr\right)^2\right] \exp[in\Omega tr]\}^2 \quad (2)$$

When the cavity is filled with the analyte the reflectivity and transmittivity of the mirrors get modified as given(5)

$$R \rightarrow R\, e^{-\alpha l} = R\, e^{(-N\sigma l)} \& T^2 \rightarrow T^2 e^{-\alpha l} = T^2 e^{(-N\sigma l)}$$

where$l$is the length of the cavity filled with the analyte(typically a gas), N is the number density of the analyte in molecules/cm^3,σ is the frequency dependent absorption coefficient of the analyte.

$$\mathrm{Iout(t)} = T^2 e^{-(N\sigma l)} I_o \mathrm{mod}\ \{\sum_{n=0}^{\infty} R^{2n} \exp(-N\sigma l) \exp\left[-a\left(t-\left(n+\frac{1}{2}\right)tr\right)^2\right] \exp[in\Omega tr]\}^2 \quad (3)$$

4.Results and Discussion

The mathematical equations (1) & (2) are simulated for an arbitrary cavity of length 30 cm.Fig 3a is an overlay graph of both the models where it is very evident that the bullet model offers a higher value of time constant than that of the transfer function model.The analysis is extended to NO_2 at 532 nm whose absorption cross section is $1.65*10^{-19} cm^2\ molecule^{-1}$.The transfer function is simulated using equation(3) and the bullet model is simulated using equation (1) for the gas filled cavity.Fig 3b,3c,3d,3e &3f are the overlay graphs with increasing gas concentration.It is evident that the τ value decreases with increasing concentration as there is an increase in the absorption within the cavity.The tabulated resultes of increasing concentration from 1100 ppb to 3000 ppb are shown in Table 1.

The photon bullet model appears to be straight forward which shows that decay signal is a true exponential. The amplitude and phase effects with in the cavity are not considered in the photon bullet model and hence gives a higher intensity as well as time constant value.The cavity is a frequency selective filter where it can sustain particular modes.The transfer function considers the response of the cavity to the input laser pulse and also the input pulse width and cavity detuning.This makes the output intensity transient peak fall as compared t the bullet model there by impacting the decay time constant.The application of cavity ring down spectroscopy for quantitative analysis of a gas need to be determined precisely and hence it is apt to consider the transer function model for this purpose.

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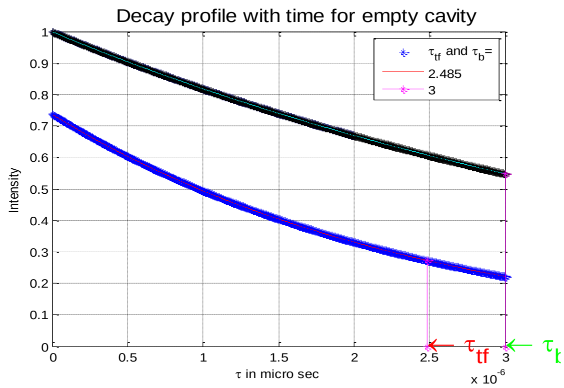

Fig: 3a

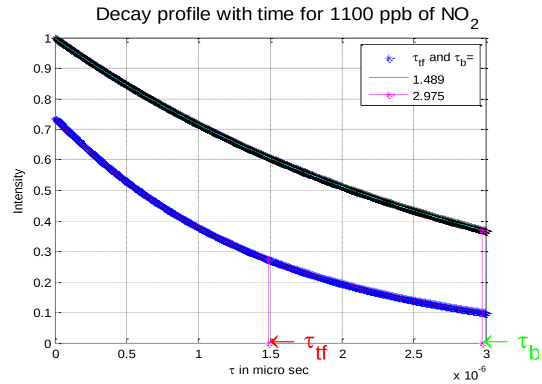

Fig:3b

Over lay graph of Bullet model and transfer function for (3a) empty cavity and(3b) 1100 ppb

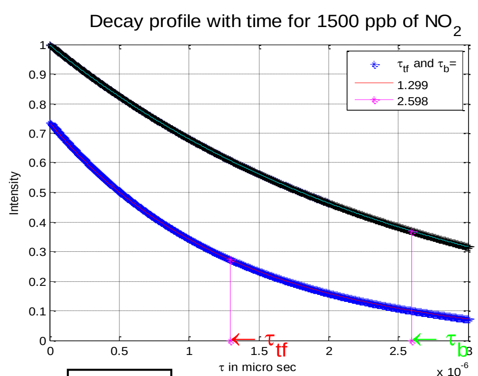

Fig 3c

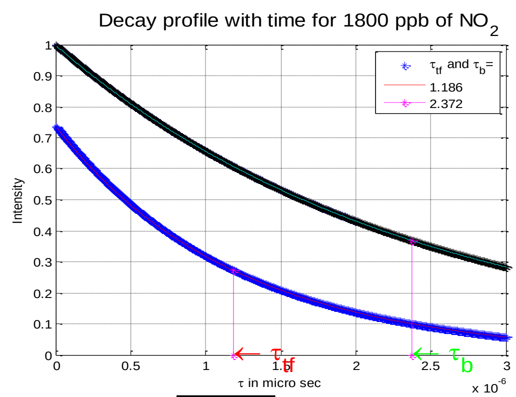

Fig 3d

Over lay graph of Bullet model and transfer function for (3c) 1500 ppb and(3d) 1800 ppb

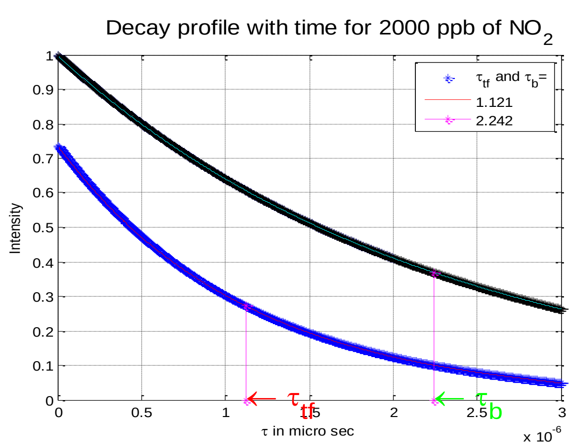

Fig 3e

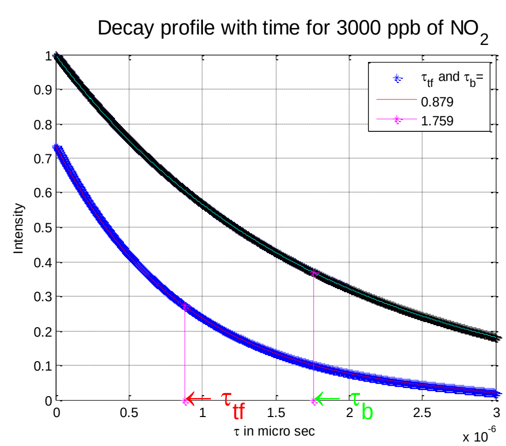

Fig 3f

Over lay graph of Bullet model and transfer function for (3e) 2000 ppb and(3f) 3000 ppb

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Table:1

Gas Concentration in ppb	Time constant value in µ sec using Transfer function	Time constant value in µ sec using Bullet model
Empty cavity	2.485	3
1100	1.489	2.975
1200	1.436	2.871
1300	1.387	2.774
1400	1.342	2.683
1500	1.299	2.598
1600	1.259	2.518
1700	1.221	2.443
1800	1.186	2.372
1900	1.152	2.305
2000	1.121	2.242
2100	1.091	2.182
2200	1.062	2.125
2300	1.035	2.071
2400	1.01	2.02
2500	0.985	1.971
2600	0.962	1.925
2700	0.94	1.88
2800	0.919	1.838
2900	0.899	1.797
3000	0.879	1.759

6.Conclusions:

Pulsed cavity ring down spectroscopy is a proven technique for the quantitative measurements of a gas.The theory of cavity transfer function gives a convincing result where we can quantify the concentration of a gas from the obtained time constant values.

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