Effect of Nitrogen dioxide for environmental gas detection using Pulsed Cavity ring down spectroscopy

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***Abstract* — *Global climate awareness is an important prerequisite for the benefit of the living species. A balance of the green house gases would make the terrestrial climate friendly and problem free. In this context ground based spectroscopic measurement of atmospheric gases play a major role .Nitrogen oxides present in the atmosphere react with water leading to acid rains. Atmospheric photo chemistry induces a complicated mechanism between Nitrogen oxides which impact the Ozone abundance. Detection of environmental gases by optical methods have proved to be the fastest and reliable detection techniques and Cavity Ring Down Spectroscopy in particular has proved to meet the requirements of being non invasive , portable, instantaneous and precise without interference with other species. It can detect weak absorptions as well as diluted species. The use of high reflectivity mirrors of the order of 99.99% enables the increase in effective path lengths of the light within the cavity and hence contribute to ultra high sensitivities. The purpose of this paper is to emphasis on Nitrogen Di oxide ,an important green house gas. Theoretical simulations are performed for NO_2 at two different wavelengths(447 nm and 532 nm) based on the technique of Cavity ring down spectroscopy(CRDS). The empty cavity ring down time constant τ_0 and the concentration dependant ring down time constant τ are obtained through simulations. The analysis is done for increasing cavity lengths from 40 cm to 90 cm at 447 nm and 532 nm. The results have shown that the time constant difference (τ_0 - τ) increases with gas concentration and is unique at each wavelength due to the dependence on absorption cross-section.*

Keywords — *Cavity ring down spectroscopy(CRDS), time constant ,parts per billion(ppb),Absorption cross-section, Nitrogen di oxide, Beer-Lamberts law.*

I. INTRODUCTION

A major advantage of laser-spectroscopic gas analysis is the capability of remote measurements where precise sensitivity is required. The potential problems of off-line methods, like short atmospheric life time of a particular trace gas , contamination during sample storage and the inability to allow for instantaneous feedback, can be avoided with online methods. Laser light can detect and distinguish specific molecules which vibrate and rotate at distinct frequencies which is a characteristic of their composition and structure. The crucial features in a gas sensor for Environmental monitoring are the sensitivity in the parts per billion and trillion ranges and the ability to discriminate interference of other polluting gases[1].

II. BRIEF OVERVIEW OF THE TECHNIQUE OF CRDS

Pulsed CRDS is a direct absorption, highly sensitive, versatile technique suitable for the analysis of a wide range of gases. The technique has already been proved to be largely immune to shot-to-shot variations in the laser intensity and benefits from tremendously long effective path lengths through the sample over a bench top[2]. Classical absorption techniques are based on the measurements of the decrease in the light beam intensity as the beam passes through an absorbing medium. For a weak and homogenous absorption, the intensity decay follows the Beer-Lambert's law

$$I(\nu) = Io(\omega)\exp(-k(\omega)l_{abs})$$

where $Io(\omega)$ is the input light intensity , $k(\omega)$ is the absorption coefficient which is related to the absorbing medium and l_{abs} is the absorption path length[3]. In CRDS it is the time taken for the initial intensity to fall to 1/e of the initial value that is quantified in to the concentration of the analyte. It is a general practice of measuring the time constant for the empty cavity referred as τ_o and then τ for the same cavity with an anlayte present. The optical absorption is evaluated by the measurement of a time constant rather than intensity ratio using the Beer-Lambert's law.

III. MEASUREMENT OF RING DOWN TIME CONSTANTS

CRDS involves the measurement of photon lifetime traversing the optical cavity. Here a laser pulse bounces back and forth across the cavity if the propagation vector of the input pulse is perpendicular to the surface of the mirrors. High reflectivity mirrors makes the cavity absorb negligible amount and transmit the remaining amount of light. On every pass the light pulse loses some part of its initial energy. So after passing the output mirror for the first time, we can say that the outgoing intensity will be given by $I_{in} T^2$ where I_{in} is the initial input intensity and T is the mirror transmission. For every transmission the light intensity leaking through the rear mirror would fall by a factor of R^2.So the exponential decay in the intensity with time resembles a ringing pattern [4]. When the resonator is filled with a gas sample that obeys Beer's law it would increase the losses in the cavity and hence decrease the time constant.

Light Intensity inside the empty cavity decays by the formula

$$I(t)= I_o \exp(-t/ \tau_o)$$

Where I_o is the intensity of the Initial detected light , τ_o is the time it takes for the intensity to reach to 1/e of I_o. With the presence of absorber the ring-down time will decrease , hence

$$I(t) = I_o \exp(-t/ \tau - \alpha ct)$$

where ‘α’ is the molecular absorption coefficient of the gas enclosed within the cavity.

$\alpha(\lambda) = N \sigma(\lambda) =(L/c)[(1/ \tau)-(1/ \tau_o)]$

Where $\tau_o = d/(c(1-R))$ (1)

$N \sigma(\lambda) =(L/c)[(1/\tau)-(1/\tau_o)]$

$N =(L/c) (\sigma(\lambda)) [(1/\tau)-(1/\tau_o)]$ [ref 5]

we can as well rewrite the above equation as

$(1/\tau)-(1/\tau_o)= N c \sigma(\lambda)$ (2)

$1/\tau =1/\tau_o + N c \sigma(\lambda)$ (3)

Eq.(2) shows that the time constant difference varies directly with the absorption coefficient of a gas.

IV. RESULTS AND DISCUSSION

According to HITRAN database 2008 [6] NO_2 exhibits a broad band absorption from 300 to 650 nm. The absorption cross-section of NO_2 at 447 nm is $4.4667*10^{-19} cm^2$/molecule [7] and that at 532 nm is 1.45 $*10^{-19}$ cm^2/molecule.[8]. The empty cavity ring down time constant τ_0 is obtained from Eq.1 and the concentration dependant time constant τ is obtained from Eq.3.The τ values are simulated for different concentrations viz. 0.1 ppb,0.5 ppb,1 ppb and 10 ppb with increasing cavity length from 40 cm to 90 cm at the two wavelengths. The time constant difference is also obtained and a graph is plotted for the values thus obtained. Figure 1a -1d are the plots showing that the time constant difference **(τ_0- τ)** is unique and can be used for gas detection depending on the Laser wave length and mirror reflectivities. It is also evident that given a concentration the gas can also be identified

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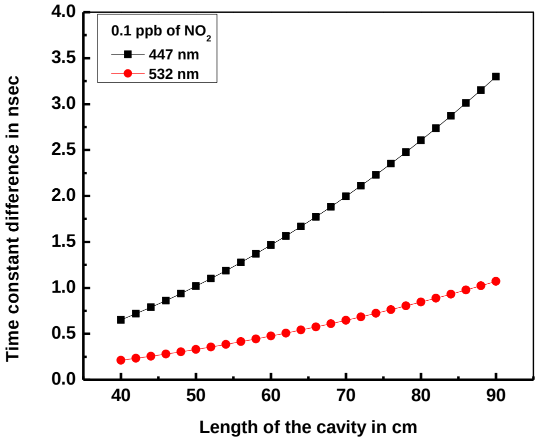

Figure 1a

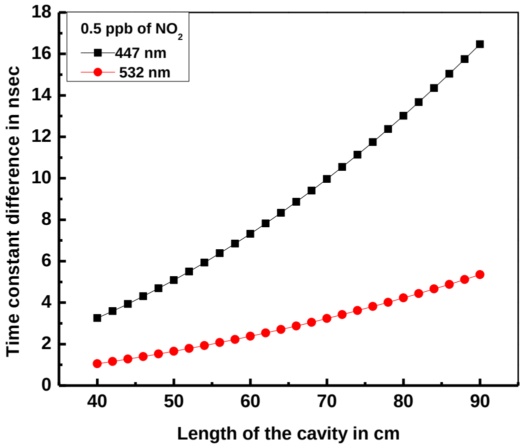

Figure 1b

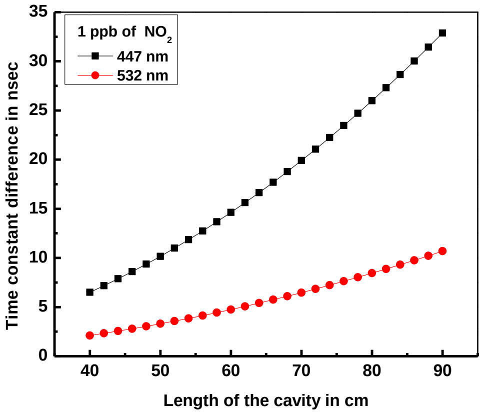

Figure 1c

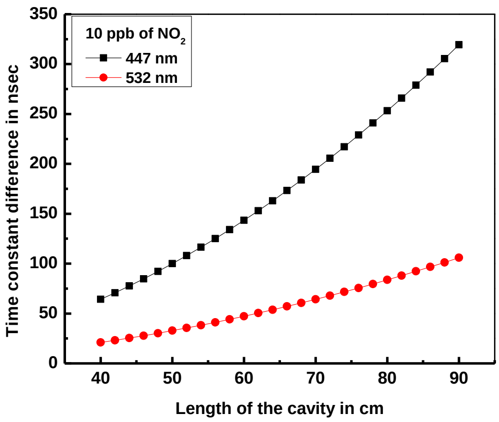

Figure 1 d

V.TABLE I
$(\tau_0 - \tau)$ OF NO_2 (447 NM, 0.1, 0.5,1 AND 10 PPB'S (EFFECTIVE MIRROR REFLECTIVITY OF 0.9997)

Concentration of the Gas	$(\tau_0 - \tau)$ ns (L=40 cm)	$(\tau_0 - \tau)$ ns (L=90 cm)
0.1 ppb	0.65	3.29
0.5 ppb	3.25	16.46
1ppb	6.50	32.87
10 ppb	64.21	319.34

TABLE II
$(\tau_0 - \tau)$ OF NO_2 (532 NM,0.1, 0.5,1 and 10 PPB's (EFFECTIVE MIRROR REFLECTIVITY OF 0.9997)

Concentration of the Gas	$(\tau_0 - \tau)$ ns (L=40 cm)	$(\tau_0 - \tau)$ ns (L=90 cm)
0.1 ppb	0.21	1.06
0.5ppb	1.05	5.34
1 ppb	2.11	10.68
10 ppb	21.03	105.87

VI. CONCLUSIONS

It is evident from the observations that the time constant difference $(\tau_0 - \tau)$ is unique for a gas at a given concentration and wavelength. The concentration dependant time constant decreases with an increase in absorption cross-section of the gas. Thus the Cavity ring down technique opens new perspectives in the field of environmental gas detection.

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