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RESEARCH ARTICLE

Study of time constant variation with concentration of a Gas in a Pulsed - Cavity Ring Down Spectroscopy.

Y. Seetha Mahalakshmi*[1], P. Madhusudana Rao[1]and S. Surendra Babu[2].

1. Department of Physics, Jawaharlal Nehru Technological University, Hyderabad, India.
2. Directorate of Laser Systems, Research Centre Imarat, Hyderabad, India.

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Corresponding Author

Y. Seetha Mahalakshmi.

Abstract

Pulsed-Cavity Ring down Spectroscopy(CRDS) is a promising technology capable of being self-calibrating besides being non-invasive and compact. This paper describes the basic principles of CRDS and summarizes the main application of it to gas detection at parts per billion level(ppb).In the present work, concentration of a gas is deduced basing on the Beer-Lamberts law and the time constant thus obtained for the three atmospheric gases NO_2, SO_2 and NO_3 are studied at 1 part per billion concentration. Variationsin time constant for the three gases with varying concentration of the Gas from 100 ppb to 3000 ppb are studied. It is observed that with increasing concentration the time constant difference increased showing a more observable value.

Introduction:-

With a huge urge towards urbanization, the development of Smart Sensors for trace gas detection whose sensitivity is typically of the order of parts per billion has attracted the attention of contemporary researchers. These sensors are useful in monitoring the gas concentration in real time applications such as human health monitoring, hazardous environment assessment and precise control of industrial process, etc. Among various types of gas detection techniques, Cavity Ring down Spectroscopy (CRDS) is the most promising as well as accurate one. CRDS is a promising technology capable of being self-calibrating besides, being non-invasive and rapid. It guarantees accurate molecular count within milliseconds. Light from a pulsed laser is fed into a high finesse optical cavity, where the photons bounce back and forth losing intensity gradually following an exponential decay. The total distance travelled by the photons before their energy tends to zero will be few kilometres which gives the extended sensitivity of the technique. The technique has no spectral region limitations as far as mirrors, sources and detectors are available. CRDS is a high-sensitivity technique for the measurement of absorption of gases, which has been applied primarily to studies of species that are either very dilute or very weakly absorbing [1].In the present work time constant for an empty cavity of length 65 cm as well as with the analyte present has been calculated using the Beer-Lambert's law. The difference in time constants for various gas concentrations are calculated and the results are analyzed. The transit time of the photons inside the cavity has been optimized in consideration with the pulse width of the laser source and concentration of the gas to be detected.

Methods:-

Optical Resonator selection:-

One of the parameters of concern in a CRDS technique is of the resonator configuration. The optical resonator cavity consists of two parallel mirrors at distance L, each having reflectivity R and a radius of curvature r_1 and r_2.There are many possible choices of these parameters which can form the resonator but not all of them give rise to a stable configuration. In general for a resonator to be stable it is necessary to satisfy the following relation [2]

$$0 < \left(1 - \frac{L}{r}\right)\left(1 - \frac{L}{r2}\right) < 1 \quad \text{Eq. (1)}$$

OR $0 < g_1 g_2 < 1$ where $g_1 = 1 - L/r_1$ and $g_2 = 1 - L/r_2$ are the g-parameters of the resonator. It is convenient to visualize the optical resonator in the g-diagram also referred as stability diagram as shown in figure 1[2].

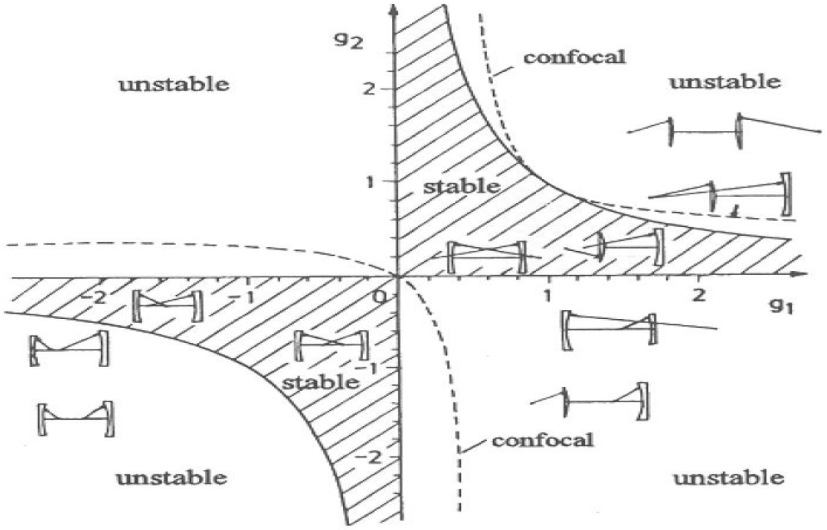

Figure 1:-Resonator stability diagram in terms of g-parameters

All cavity configurations are unstable unless they correspond to points located in the area enclosed by a branch of the hyperbola $g_1 g_2 = 1$ and the coordinate axes. The origin of the diagram represents the confocal system.For practical implementations of CRDS one can use the following rule to choose L and r_i.

$$0 < L < 2ri$$

Laser Source selection:-

While designing an optical resonator the relationship between the spectral widths of the incident light $\Delta\omega_{laser}$ (laser pulse) the absorption line to be studied ω_{abs} and the distance of the neighboring longitudinal modes need to satisfy the following condition[3].

$$\omega_{abs} > \Delta\omega_{laser} > \Delta\omega_{modes}$$

In the above relation if $\omega_{abs} > \Delta\omega_{laser}$ is not satisfied we will end up at a place where only a small fraction of the input laser intensity is absorbed. This results in a decay which is not a single exponential leading to an under estimated absorption coefficient. On the other hand the relation $\Delta\omega_{laser} > \Delta\omega_{modes}$ is straightforward. An optical resonator can sustain light of a discrete set of frequencies ω_n which are defined by the resonator round trip time t_r or length L. When we consider that the injected light is purely a Gaussian mode then the longitudinal modes that sustain within the cavity would be $\omega_n = 2\pi n/t_r$ and spacing between the modes would be $\Delta\omega_n = 2\pi/t_r$. It is required that the spectral width of the laser pulse overlaps with one of the narrow sustained cavity modes for spectroscopic studies. The width of a TEM_{00} mode for a con focal cavity at the center of the cavity is given by

$$\omega_o = \sqrt{((L\lambda)/\pi)}$$

Where ω_o is the beam waist which specifies the spatial resolution of CRDS. The relation $\omega_{abs} > \Delta\omega_{laser}$ imposes that the upper state life time of the absorber be greater that the cavity roundtrip time t_{rt}. The upper state life time decreases with pressure as the particles are more likely to be perturbed due to collisions, and so it is highly necessary to adjust the length such that upper state life time or the relaxation time of the absorber be less than t_{rt}.

2.3 Measurement of lifetimes

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-Lamberts law

$$I(\nu) = Io(\omega)\exp(-k(\omega)l_{abs}) \quad \text{Eq. (2)}$$

Where Io (ω) is the input light intensity, k(ω) is the absorption coefficient which is related to the absorbing medium and l_{abs} is the absorption path length[3].In cavity ring down technique, the cavity life time τ is defined as the time taken for the initial intensity to fall to 1/e of the initial value. It is a general practice of measuring the time constant for the empty cavity referred as τ_o and that of the same cavity with an anlayte present.

Results and discussion:-

In a CRDS experiment the photon bounces back and forth across the cavity if the propagation vector of the input pulse is perpendicular to the surface of the mirrors. The mirror reflectivities are arbitrarily taken to be.99.97% in the present analysis. This 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. 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 outside the empty cavity decays exponentially and can be expressed as

$$I(t) = I_o \exp(-t/\tau_o) \quad (3)$$

Where I_o is the initial light intensity, 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

$$I(t) = Io \exp(-t/\tau - \alpha ct) \quad (4)$$

where 'α' is the molecular absorption coefficient of the analyte (typically a gas).Evaluation of the time constants of the cavity filled with absorbing species τ (λ) and of the empty cavity $\tau_o(\lambda)$ respectively allows the determination of the species' absorption coefficient $\alpha(\lambda)$ at the laser wavelength λ.

$$\alpha(\lambda) = N\,\sigma(\lambda) = (1/c)[(1/\tau)-(1/\tau_o)] \quad (5)$$

$$[(1/\tau)-(1/\tau_o)] = N\,\sigma(\lambda)\,c \quad (6)$$

$$1/\tau = (1/\tau_o) + N\,\sigma(\lambda)c \quad (7)$$

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

Here N is the concentration of the analyte present in the resonator and σ (λ) is its absorption cross-section, $\alpha(\lambda)$ the absorption coefficient of the gas ,*c* is the speed of light and *L* the cavity length. The concentration of the species can be deduced by scanning the laser wavelength in the absorption spectra of the species. The value of the time constant is obtained from Eq. [7] and can be used to deduce a relation between (τ_o-τ) and the concentration from which one can obtain a valuable information of the analyte. Hence the concentration *N* of the species could be retrieved giving the absorption cross-section of the absorbing species or vice-versa. The most promising analytical application of CRDS is in the field of trace gas analysis. NO_2,SO_2 and NO_3 are major air polluting agents[6] which impact the environment even at parts per billion level. The two spherical mirrors are chosen to have radius of curvature 1meter and are of identical reflectivity 99.97%.

Eq. [6] has been simulated to assess the above mentioned gases. For this analysis a cavity with a length of 65 cm has been chosen arbitrarily. The reflectivities of the cavity mirrors were fixed at 99.97% (300ppm loss)

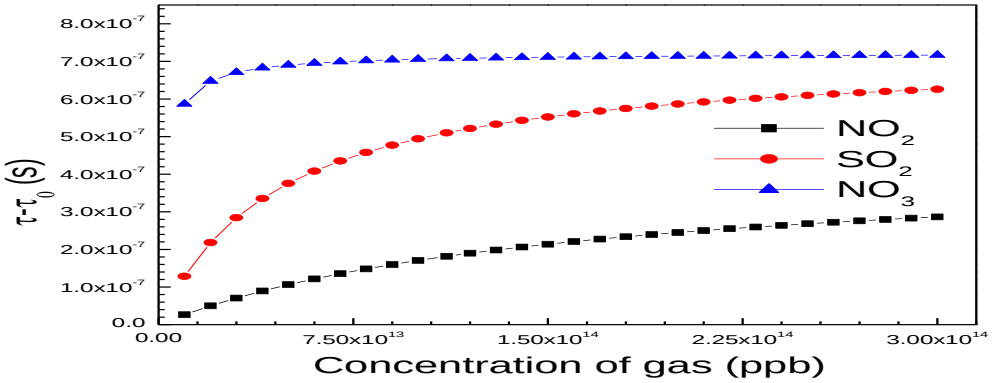

Figure 2:-

Variation of time constant with increasing concentration (100ppb to 3000ppb) of gases SO_2, NO3 and NO_2.

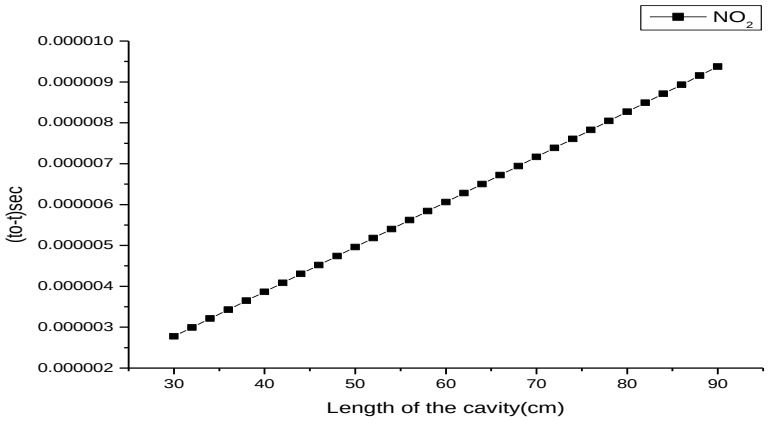

Figure 3:-Variation of time constant difference with respect to length of the cavity for a concentration of 1 ppb and mirror reflectivity 99.95%

It is evident from figure 2 that the time constant for NO_3varies from 7.05 µsec to 7.21 µsec. For the same range of concentration SO_2 showed a marked variation of 4.94µsec to 7.11 µsec. Also the wave length dependent absorption cross section $\sigma(\lambda)$ of a gas affects the time constant at a particular concentration. The more the value of $\sigma(\lambda)$the more is the decay constant of the gas**.** Figure 3 shows that difference in the time constant shows a linear response with respect to cavity length. The following table shows the time constant variation at 1 ppb for the three different gases. It is observed that NO_3 with a higher absorption cross section among the three shows a pronounced difference as compared the other two gases.

Table:1:-Acomparison of time constant variation of SO_2,NO_3 and NO_2 for a cavity of length 65 cm ,Reflectivity 99.97% at 1ppb concentration

Mirror Reflectivity %)	Empty Cavity Decay Time(µsec))	Gas Studied	Absorption Cross-Section($cm^2molecule^{-1}$)	τ_o-τ (µsec)
99.97	7.222	NO_3	$2.0*10^{-17}$(at 667 nm)	7.05
99.97	7.222	SO_2	$1.0*10^{-18}$(at 290 nm)	4.94
99.97	7.222	NO_2	$5.0*10^{-19}$(at 448 nm)	3.75

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