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Study of damping, saturation and surface losses on low level detection of NO_2 using time resolved pulsed photo acoustic technique

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ABSTRACT

The time resolved pulsed photo-acoustic (PA) spectrum of atmospheric pollutant gas (NO_2) buffered in two different mediums is reported. The closed window PA resonance cell made of stainless steel filled with highly pure NO_2 gas mixed with air and nitrogen separately to study the role of buffer gases for the generation of radial modes of higher frequency and damping effect in the same cavity. The energy storage phenomena of the resonant cavity is explained using coupled oscillator theory. The second harmonics i.e. $\lambda = 532$ nm pulses obtained from Q-switched Nd: YAG laser having 7 ns pulse width is used to excite the resonant modes of the cavity. The losses corresponding to radial and longitudinal modes are estimated experimentally and found to have a good agreement with their corresponding theoretical values. The dependence of saturation behavior of NO_2 as an artifact of the PA cell along with gas molecules at different values of the incident laser energy has been discussed for the first time. In addition, we have successfully demonstrated the effect of damping on the quality factor-Q of the cavity which is not only responsible for generation of higher order modes but also decide the low level detection of the PA system. The developed PA sensor helped us to achieve minimum detection concentration of NO_2 of the order of 0.213 ppbV and 1.2 ppbV.

1. Introduction

Measurement of trace green house gases such as NO_2, CO_2, CH_4 etc. play a very important role to monitor the level of pollution in the atmosphere. NO_2 is the pollutant gas which is emitted from automobile exhausts, industrial boilers and electrical power generators. The oxidation of nitric oxide (NO) in the presence of ozone in the atmosphere is responsible for the generation of NO_2 and leads to promote the formation of acidic aerosols which harms the vegetation and buildings. In addition, NO_2 is released by high energy materials (HEM) which have a wide absorption spectrum in UV–vis–IR range [1–5]. There is a growing interest in laser-based analytical techniques for remote trace detection of nitrogen dioxide NO_2. Absorption spectroscopy, Raman spectroscopy along with Photo-acoustic spectroscopy in the infrared (IR) region are some of the important techniques employed for trace gas analyses. However, all these techniques need tunable UV–vis–IR laser sources. Due to long natural life time and strong absorption band of NO_2 at 532 nm, it provides very efficient collision energy transfer mechanism from excited levels [2–9]. The NO_2 molecules are excited by green pulses of Nd: YAG laser in a resonant photo acoustic (PA) cell and obtained PA signal is used to determine the low level concentration. However, pure NO_2 mixed with N_2, He or Ar etc. as a buffer gas is used to ascertain the low level of detection [10]. It is also observed that in case of Ar as a buffer the strength of PA signal almost becomes double. But effect of buffer gas also play important role to control the *Q*-factor of the cavity and some of the selected gases support to generate higher order radial modes in the cavity.

The present study describes a modified approach to study the effect of damping factor, saturation and surfaces losses on generation of higher order acoustic signals, *Q*-factor and very low level detection of NO_2 gas in the closed window cell. It is based on the saturation behavior of different types of radial and longitudinal PA modes as an artifact of PA system and NO_2 gas buffer in the air and Nitrogen. Moreover, the focus was given to analyze the losses in the resonant cavity on the basis of *Q* factor for the first order (010) radial and the second order (002) longitudinal modes. The experimentally ascertained value of *Q*-factor is of the order of 108 when air is used as a buffer medium. However, it goes down to 65 when air is replaced by pure N_2 as a buffer and inferred due to damping effect only. The second harmonics $\lambda = 532$ nm pulses of 7 ns pulse width obtained from *Q*-switched Nd: YAG laser with repetition rate 10 Hz is used to excite these modes in the PA cell. The amplitude of the PA signal in frequency domain is obtained by Fast Fourier Transform (FFT). The indigenously developed data acquisition system provides the direct information about all the excited acoustic modes of PA cell. Also, it is interesting to note that when NO_2 is buffered in air provides first radial mode (010) at 4275 Hz,

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while the second longitudinal mode (002) occurred at 2100 Hz frequency. However, when NO_2 is buffered in N_2 then additional higher order radial modes i.e. 2nd and 3rd order at 8050 and 11500 Hz frequencies, respectively, are also present.

The modified PA system with different Q-values with good signal to noise ratio (*SNR*) helped us to achieve low detection limit of the order of at 0.213 ppbV and 1.2 ppbV in air and N_2 respectively.

2. Experimental set-up and signal processing:

Fig. 1 shows the schematic experimental layout of PA system. The closed window PA cell is made of stainless steel and designed and fabricated in the laboratory itself. The cell's internal diameter is 9.4 cm and its average length is 15 cm [10]. The second harmonic i.e. λ=532 nm of *Q*-switched Nd: YAG laser (Model Spit, Germany) is used to record the PA spectrum of NO_2 gas molecules. The PA signal is detected by a pre-polarized microphones having responsivity 50 mV/Pa (BSWA, China). The microphone is placed at the center of the cell. The output signal of the microphone is fed to the preamplifier which is coupled to the 200 MHz Oscilloscope (Tektronix U.S.A.). The USB /GPIB interfacing is used for data acquisition through Boxcar integrator (Stanford Instruments Inc., USA). The data analysis is done using software made in lab-view. The NO_2 gas buffered in air and N2 under different pressure are used to record the PA spectrums.

The basic principle of photo acoustic spectroscopy with resonant cylindrical cells is described in details elsewhere [6–15]. The inhomogeneous wave equation of the sound pressure in the lossless cylindrical resonator is given by

$$\frac{d^2P(r,t)}{dt^2} - c^2\nabla^2 P(r,t) = (\gamma-1)\frac{dH(r,t)}{dt} \tag{1}$$

where c, γ and *H* are the sound velocity, the adiabatic coefficient of the gas and the heat density deposited in the gas by light absorption, respectively. The solution of Eq. (1) is given by the series:

$$P(r,t) = \sum_{n=0}^{\infty} A_{n,m}\, e^{imw_0 t} P_n(r) \tag{2}$$

The dimensionless eigen modes distribution of cylindrical resonator is the solution of the homogeneous wave equation which can be expressed as:

$$P_n(r,t) = P_n(r)e^{iw_n t} \tag{3}$$

where W_n is the resonance frequency of the cavity resonator, $P_n(r)$ is

$$P_n(r) = P_{mnq}(r,\varnothing,z) = J_m(K_r\, r)\cos(K_z z)\{{}^{\cos(m\varnothing)}_{\sin(m\varnothing)}\} \tag{4}$$

It is assumed that the deposited heat density directly depends on input laser power (*E*). Then amplitude A_n of the Photo acoustic signal in case of pulsed laser can be written as

$$A_n = \frac{(\gamma-1)\, L\ fn\ P_n\,(r_m)\alpha\, E}{V} \tag{5}$$

where *fn* is the normalized overlap integral which describes the effect of the spatial overlap between the propagating laser beam and the pressure distribution of the *n*th acoustic eigen modes and *L*, *V*, α and γ are the length and volume of the resonator, the PA absorption coefficient of the sample and adiabatic constant of the buffer gas respectively [7,14]

The acoustic resonant modes generated within the cylindrical cells can be described as

$$F_{mnq} = \frac{c}{2}\left(\left(\frac{\propto_{mn}}{R}\right)^2 + \left(\frac{q}{L}\right)^2\right)^{1/2} \tag{6}$$

where *c* is the sound velocity, α_{mn} is the *n*th zero of the derivative of the *m*th Bessel function at $r=R$, where *R* and *L* represent the radius and the length of the cylinder, respectively. The normal modes are separated into longitudinal (q), radial (n) and azimuthal (m) modes. Due to strong coupling between the high vibrational levels of X^2A_1 ground state and $^2B_2$ or $^2B_1$, the optical stored energy entirely contribute to the sample heating regardless of whether the excited level belong to the $^2B_2$ or $^2B_1$ state. Therefore the dependence of the PA signal on the absorbed energy will not change in the entire visible range. NO_2 is excited to the $^2B_2$ state due to absorption of 532 nm and its excitation energy is lost to photo acoustic signal generated by V–T and V–V relaxations of NO_2 in collisions with air molecules [8–13].

3. Results and discussion:

This section is divided into five parts; Section 3.1 deals with PA modes in time and frequency domains; Section 3.2 deals with the study of PA signal based on input laser energy; Section 3.3 deals

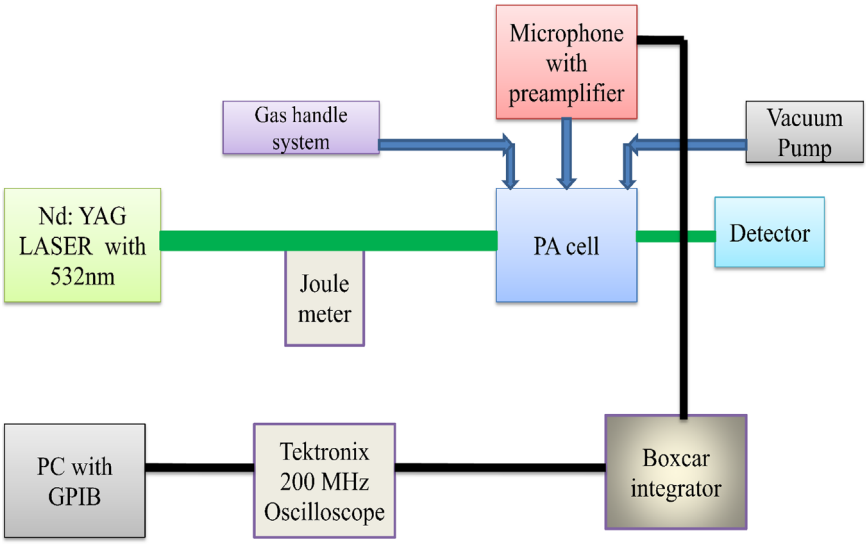

Fig. 1. Experimental set-up.