

Detection of NO₂ using Cavity Enhanced Absorption Spectroscopy in 405nm regime

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Abstract— Cavity Enhanced Absorption Spectroscopy is noninvasive technique to detect trace gas species. Here we demonstrate an instrument based on CEAS for detecting the trace gas NO₂, which is having very low concentration in ambient atmosphere. Variation in the concentration of NO₂ in ppb level itself could create great impact on atmosphere. By using high reflectivity DBR mirrors we designed very high finesse optical cavity. Using a 405nm Diode laser as source, Output of the cavity is analyzed using a photomultiplier tube (PMT). NO₂ is having absorption in the region 400-405nm which is also Ozone free zone (absorption of ozone is negligible). By using a Data Acquisition System (DAQ) the output from the PMT is coupled into a computer. Using LabVIEW™ software we interfaced the DAQ and analyzed the data using the same GUI based programming. NO₂ produced in the lab setup was detected using the developed instrument and concentration of the NO₂ is calculated.

Index Terms— CEAS, Laser Spectroscopy, LabVIEW™, Trace gas detection.

1 INTRODUCTION

PRESENCE of NO₂ in atmosphere has shown significant concern in last few decades. Trace gases like Nitrogen dioxide (NO₂) presence have been detected in mid 70's itself [1]. Even a small change in the concentration of NO₂ can cause major effects in earth climate. Nitrogen dioxide (NO₂) is a nasty smelly gas which is always sticky. The major source of Nitrogen dioxide (NO₂) in earth atmosphere is due to the anthropogenic activities. Burning fossil fuel result in the production of Nitrogen dioxide (NO₂) [2]. Most of the nitrogen dioxide in cities comes from motor vehicle exhaust (about 80%). Other sources of nitrogen dioxide are petrol and metal refining, electricity generation from coal-fired power stations, other manufacturing industries and food processing. Nitrogen dioxide is also formed naturally in the atmosphere by lightning and some is produced by plants, soil and water [3]. However, only about 1% of the total amount of nitrogen dioxide found in our cities' air is formed this way. Its presence in troposphere directly leads to photolysis and thus in the formation Ozone O₃ [4].

Breathing Nitrogen dioxide can cause respiratory problems. It can cause inflammation in linings of lungs and also it can reduce the immunity to lungs diseases. Ultimately results in wheezing, coughing, colds, flu and bronchitis.

Early in-situ and Laboratory measurement of NO₂ in the 405nm region is done by CRDS (Cavity Ring Down Spectroscopy) method [5]. The high relevance of NO₂ is demonstrated in past years. Here we report the laboratory generation and detection of NO₂ in 405nm region using CEAS technique. In-situ measurement of NO₂ can be done in many ways, CEAS

(Cavity Enhanced Absorption Spectroscopy) is one of the method used to find the trace gases concentration [6]. Usually DOAS (Differential Optical Absorption Spectroscopy) or chemiluminescence methods are used for measurements [7].

2 METHODOLOGY

2.1 Measurement Principles

The weak light absorption coefficient as function of optical frequency in a medium is governed by the Beer's law.

$$I(\nu) = I_0(\nu) \exp(-\alpha(\nu)L) \quad (1)$$

Where $I_0(\nu)$ and $I(\nu)$ are the incident and transmitted intensities and $\alpha(\nu)$ is the absorption coefficient. The absorption coefficient $\alpha(\nu) = N\sigma(\nu)$, where $\sigma(\nu)$ and N are the cross section and number density of the absorbing species in the medium respectively. In CEAS system light from laser is transmitted through a stable optical cavity resonator composed of two dielectric mirrors. Light in the cavity is reflected back and forth between the high reflective dielectric mirrors and slowly leaks out to the detector. This results in a long photon residence time and very long effective path length for photon in the cavity. This long effective path length arising from long photon residence time is the source of the sensitivity of the technique. Following the analysis done in for optical cavity of length d with an approximation of small loss per pass and high reflectivities of the mirrors, $\text{Loss} \rightarrow 0$, $R \rightarrow 1$, absorbing the scattering effects to the calibrated effective mirror reflectivity the absorption coefficient can be approximated to

$$\alpha(\nu) = 1/d (I_0/I - 1)(1 - R(\nu)) \quad (2)$$

This equation is widely used in CEAS instrument for detection of trace species.

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2.2 Instrument

The setup mainly consists of a diode laser of 405nm (Laser Glow) which is having high stability over time (RMS- 1% over 4 hours). Monochromatic light from the laser is made to fall on the HR mirror after passing through an iris to separate the central part of the Gaussian beam. High Reflectivity Dielectric coated DBR mirrors (LayerTec GmbH) are used in the cavity. Only a 0.05% of the incoming light will transmit through the mirror for the wavelength 405nm, resulting in a high finesse cavity. Light exiting from the 2nd cavity mirror is passing through an iris in order to reduce the stray light. Finally made to fall on a PMT (Hamamatsu). The output from the photo-multiplier tube and the Photodiode (PD) is sent to an A/D converter (NI DAQ USB 6009). The output from PD is used to monitor the laser power fluctuations to make sure that the absorption measured by the instrument is not due to the laser output intensity fluctuations.

A Labview based software controls and automates the CEAS instrument operation and provides the real time light absorption measured by the instrument averaged at desired time interval. The DAQ read 1000 Sample/second, from the single channel during the CEAS operation. For a 1 second acquisition averaging time the DAQ roughly average 40 samples and write the value with corresponding time stamp to a text file. The CEAS instrument collects and process raw voltage readings simultaneously from PMT and PD, which corresponds to the laser light intensity falling on corresponding detector. If the PD that monitors laser power, shows considerable fluctuation in its voltage readings (indicating laser power fluctuation for any reason) then the I_0 , I in equation (2) should be corrected using this PD reading appropriately before calculating the absorption coefficient.

3 EXPERIMENT

Nitrogen dioxide was produced in the lab using reduction of concentrated Nitric acid by copper,

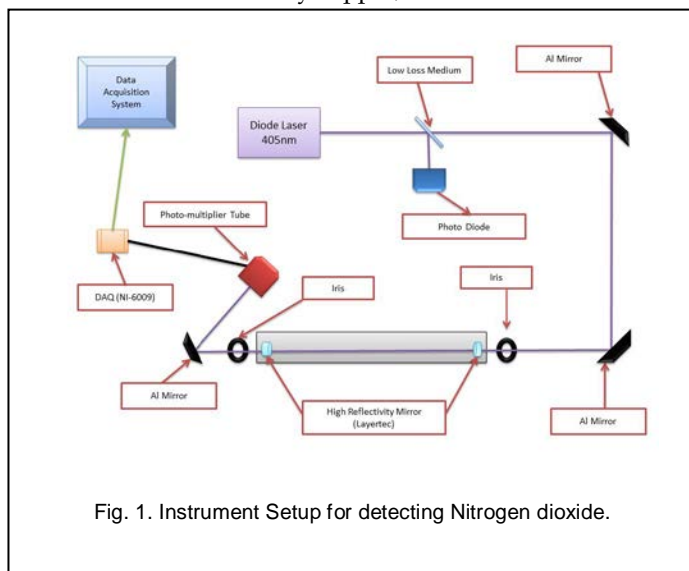
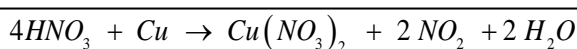


Fig. 1. Instrument Setup for detecting Nitrogen dioxide.



NO_2 is prepared in a chamber and it is connected to the instrument using Teflon pipe and a valve. Initially the cavity is made vacuum using a rotary vane pump. The output from the cavity is monitored in PC.

After a 2-3 minutes pump was disconnected from the cavity and nitrogen dioxide is extracted from the chamber to cavity using a diaphragm pump (5L/m). Output data was saved and after some time when the nitrogen dioxide inside the chamber is fully extracted, output signal seems to gain intensity. Since NO_2 is sticky we used vacuum pump again to evacuate. The output signal gained to the initial condition in a small interval of time.

A Photo diode is used to monitor the stability of laser during the experiment. Light from reflected from a low loss optic medium placed inline to the light path was used for this. Fortunately PD didn't shows considerable variation during the measurement. The laser was very stable during the measurement.

4 RESULT & DISCUSSIONS

4.1 Experimental Results

Figure 2 shows the real time PMT signal output voltage of the instrument. The graph clearly shows the changes in the cavity output. Initially cavity is in vacuum condition and when NO_2 is introduced in to the cavity using diaphragm pump, output intensity decreased and this clearly shows the detection of NO_2 .

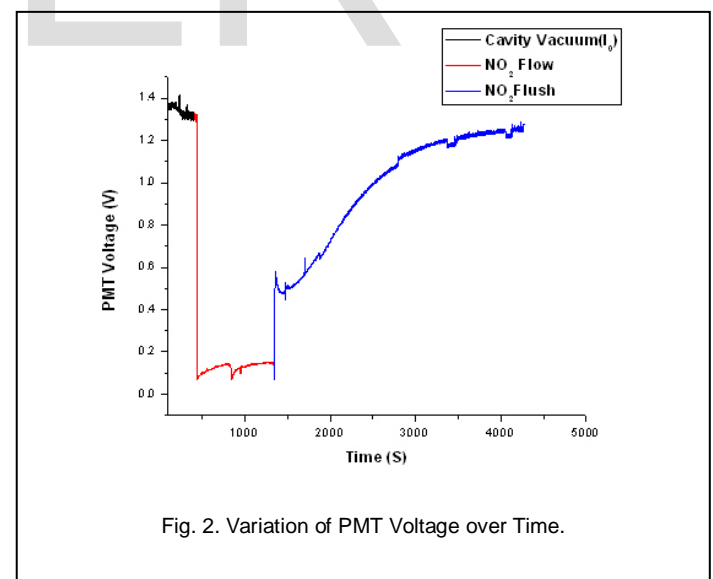
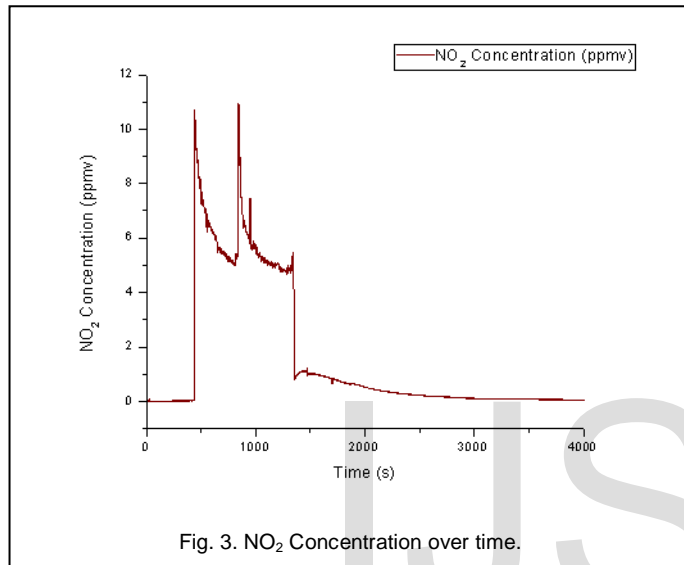


Fig. 2. Variation of PMT Voltage over Time.

NO_2 has high absorption cross section in the 405nm region [8]. The data acquisition system (NIDAQ USB 6009) is very fast which collect samples at a rate of 1000 samples/s, also the acquisition averaging time was 1 second, so it will show random noise fluctuations too. But the output voltage was very smooth without any random fluctuation, indicating that laser and entire system was stable during the measurement. The number density of NO_2 is calculated by the linear least square fit of absorption

coefficient which is calculated using equation (1) and pre measured absorption cross sections corresponding to laser wavelength taken from the Mainz database. The theoretical mirror reflectivity value is used in the above calculation. Reflectivity can be calibrated using a low loss optic medium [9]. Here we used special type of cavity alignment, in which the dielectric mirrors are placed inside the cavity chamber base plate, other than usual method of placing mirrors at the end side of the cavity which is usually used in CEAS methods. The laser light is coupled in to the cavity by the help of an AR coated window placed at the end of the cavity chamber. So the cavity will not be misaligned during evacuation and sample extraction. The stability of entire system is clear from the smooth behavior of PMT output.



4.2 Further Researches

The purpose of the instrument is accurate in-situ concentration measurement of NO₂ with the help of IBBCEAS instrument and will be published soon. The both instruments run in a way that one will be used for calibrating the other one respectively.

CONCLUSION

The CEAS instrument has been constructed in the 405nm region. The NO₂ is generated in the lab using reduction of concentrated Nitric acid by copper. Concentration of NO₂ is measured using CEAS setup. The entire system was stable during the measurement, so there is no need of laser intensity fluctuation correction to the measured concentration. The measured stable PMT output voltage confirms that the new alignment method is free from misalignment during evacuation and sample extraction.

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