

IR RADIATION BASED OPTICAL EMISSION METHOD OF SINGLET OXYGEN CONCENTRATION MEASUREMENT FOR CHEMICAL OXYGEN IODINE LASER AND STUDYING THE EFFECTS OF PARAMETRIC VARIATIONS.

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ABSTRACT

A very critical parameter for the efficient performance of chemical oxygen iodine laser (COIL) is Yield of Singlet Oxygen (SO). Singlet Oxygen(SO) is required not only for pumping as well as dissociation of iodine molecules. Hence, the output power and efficiency of this laser strongly depends on the yield of $O_2(a^1\Delta)$ in singlet oxygen generator (SOG).

Keywords: Chemical Oxygen Iodine Laser, Singlet Oxygen Yield, Data Acquisition Hardware

I INTRODUCTION

The chemical oxygen iodine laser (COIL) is the only chemical laser based on the electronic transitions. It emits at 1315 nm on the transition between the spin-orbit levels of the ground state configuration of the iodine atom. Here near resonant energy transfer takes place from a singlet delta oxygen [$O_2(a^1\Delta)$] molecule to an atomic iodine atom. The singlet delta oxygen molecules $O_2(a^1\Delta)$ are produced by the chemical reaction between chlorine and basic hydrogen peroxide solution.

Hence, detection of SO is very much essential for COIL performance optimization. It is important to accurately measure the absolute density of $O_2(a^1\Delta)$.

The flowing medium gas lasers such as chemical oxygen iodine laser (COIL) employing various gas effluents and chemical reagents offer high flexibility, advantages in cost, beam quality, and power scalability. This is a highly potential laser source finding wide-ranging applications in both military and civil fields.

Chemical lasers like COIL are an excellent choice for strategic and tactical operations, considering the capabilities of high output power and operation at near-infrared wavelength which allows for better beam propagation in turbulent atmospheric conditions. The COIL is also of interest for use in commercial applications because it is a continuous-wave (CW) scalable laser with a fiber-deliverable wavelength (1.315 μm) [1], some commercial industrial applications are shipbuilding, automotive manufacturing, underwater cutting, and cutting tasks associated with decommissioning and decontaminating nuclear facilities ¹.

It has been estimated that approximately 5 $O_2(a^1\Delta)$ molecules are required to transform a single I_2 molecule into 2 $I^*(^2P_{1/2})$ atoms [2]. Therefore, the efficiency and power of COIL are greatly dependent on the amount of

$O_2(a^1\Delta)$ present in the laser. Much effort in COIL development has gone towards finding more efficient and less hazardous methods of producing large densities of $O_2(a^1\Delta)$ and a variety of schemes have been developed, including wet chemical reactions, electric discharges, optical pumping, and alternate energy transfer methodologies.

Several methods have been developed to measure singlet oxygen, including emission spectroscopy [3], tunable diode laser absorption spectroscopy [4], Raman scattering [5], intracavity laser absorption spectroscopy (ICLAS) [6], electron spin resonance (ESR)[7], and resonance enhanced multiphoton ionization (REMPI).

II SINGLET OXYGEN APPLICATIONS

- a. Used in the field of Photo-chemistry as a reagent.
- b. Used in medicine: Photo Dynamic Therapy (PDT), Photohemolysis etc.
- c. Photohemolysis: photochemical damage to the RBC membrane promotes cation efflux, leading to swelling of the cells and eventually rupture.
 - Used in Drug Industries (anti cancer drugs like Anthraquinone etc)
 - Used in food processing (anti fungus etc.)
 - Atmospheric pollution control / cleaning.
- d. 1O_2 generated in the lower atmosphere by the action of sunlight on *polycyclic aromatic hydrocarbons* (PAH) may be involved. PAH is a large class of organic pollutants released in the atmosphere by natural sources
 - **As a pumping source for iodine laser**
 - As a laser medium (Liquid laser)

III METHODS FOR MEASURING THE $O_2(a^1\Delta)$ CONCENTRATION

So far, the methods used in COIL belong mostly to 3 categories.

3.1 Spontaneous Raman method: [2]–[4] measures the $O_2(a^1\Delta)$ yield [i.e., $O_2(a^1\Delta) / O_2(a^1\Delta) + O_2(x^3\Sigma)$] by comparing the line intensity of $O_2(a^1\Delta)$ and that of $O_2(x^3\Sigma)$ in the Raman spectrum.

Advantage

1. Immune to the window contamination and
2. Easy variation in the geometry of detection system.

Disadvantages

1. To obtain the absolute $O_2(a^1\Delta)$ concentration this method needs an accurate measurement of N_2 flow as the diagnostic standard, and
2. The measuring system is too costly for most practical purposes.

3.2 Absorption spectroscopy method: including diode-laser based absorption[5],[6] and cavity ring-down spectroscopy,[7] has a relatively large error, because the $O_2(a^1\Delta)$ concentration was indirectly obtained from the Cl_2 utilization and the $O_2(x^3\Sigma)$ concentration determined, respectively, by violet absorption near 325 nm and $O_2(x^3\Sigma) \rightarrow O_2(b^1\Sigma)$ absorption near 763 nm.

Disadvantages

1. Relatively large error
2. The measuring system is quite costly, as require extra laser sources.

3.3 IR radiation based optical emission method: by which the $O_2(a^1\Delta)$ concentration was determined through monitoring the IR radiation at 1.27 μm , is historically a common type of diagnostics for $O_2(a^1\Delta)$ with no need of an extra light source.

Advantage

1. No need of an extra light source
2. Low cost
3. Best suitable for laboratory application

Disadvantages

1. Calibration procedures are complicated

IV OPTICAL EMISSION MODEL

Singlet Oxygen emits at 1.27 μm , for which non-contact type optical emission based measurement scheme can be applied. Optical emission based measurement scheme comprises of an interference filter and a suitable photo detector compatible with the emission wavelength [8].

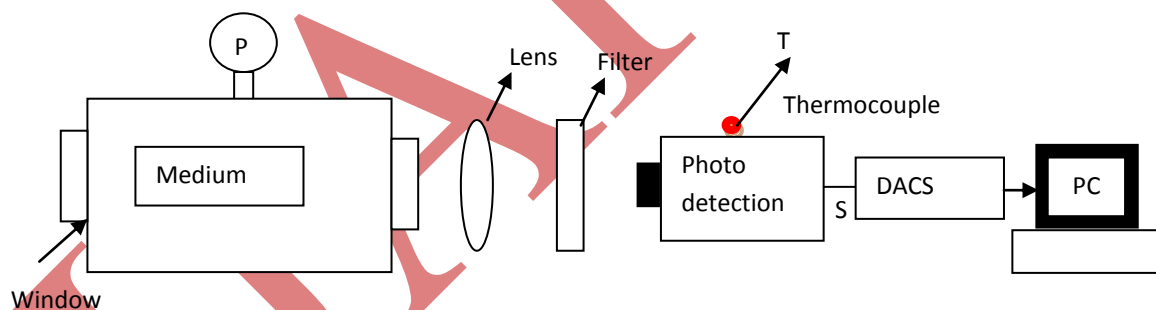


Fig.1: Schematic of optical emission based singlet oxygen measurement

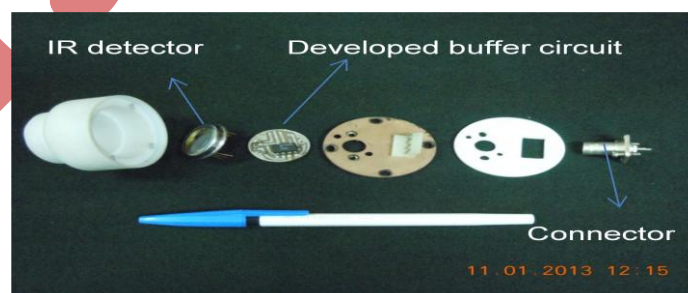


Fig 2: Parts of disassembled optical emission detection unit

V BASIC CONCEPT FOR SO CONCENTRATION MEASUREMENT USING IR RADIATION METHOD [9]

In experiments Optical Scheme for Singlet Oxygen Measurement using the IR radiation method, the electric signal S (mV) from an IR radiation receiving apparatus is related to the absolute concentration O_2 ($a^1\Delta$)

$$S = R_{es} \eta h \nu AV [O_2 (a^1\Delta)]$$

$$S = R_{es} \eta h \nu AV \frac{P_a}{kT}$$

Define an IR detective coefficient, K' as

$$K' = R_{es} \eta h \nu AV$$

$$S = K \frac{P_a}{kT} \quad \text{We obtain} \quad K' = K \frac{P_t X_a}{kT}$$

where R_{es} (mV/W) is the responsivity of the radiation receiving apparatus, η the coupling efficiency, defined as the ratio of the radiation power received by the radiation receiving apparatus, $h\nu$ is the photon energy at 1.27 μm , V the volume of the optical cell, A the Einstein coefficient, k the Boltzmann constant, P_a and X_a the partial pressure and molar percentage of O_2 ($a^1\Delta$), respectively, and P_t and T the total pressure and gas temperature, respectively. Hence, the absolute concentration and partial pressure of O_2 ($a^1\Delta$) are readily calculated through measuring S and T .

5.1 Salient features of selected diagnostics & Data Acquisition hardware:

We have chosen:

- InGaAs PIN photodiode, Model: G8370-10, Make: Hamamatsu, with large active area (dia. 10 mm),
- Suitable lens and filter (1.27 μm) with appx. One inch dia. The filter's spectral center is located at 1.27 $\mu\text{m} \pm 5 \text{ nm}$ and its bandwidth is 28 nm which is much greater than the pressure and Doppler broadening widths of O_2 ($a^1\Delta$) so that its emission profile width can be neglected.
- Advantech card 4019, 4520 (Range : 0-10 V)
- Pressure sensors: Metran (Tensoresistor type)
- Thermocouple Type: K
- Data flow Scheme: Serial comm. (10samples/sec)
- Software: Advantech Adam view & lab view
- PC based analysis

O_2 ($a^1\Delta$) was produced by gaseous chlorine and BHP liquid in the Jet SOG and then flowed through the brass tube, appx. one inch in dia., incorporating proper space and fitting of lens and filter, emitting 1.27 μm photons for all space within Diagnostic hardware.

VI EXPERIMENTAL CALCULATIONS (IN DEVELOPED SOFTWARE)

Responsivity R_{es} (mV/W) = 0.8 (at $\lambda=1.27\mu\text{m}$),

The coupling efficiency $\eta = 0.8$,

$h\nu$ is the photon energy at $1.27 \mu\text{m} = 6.634 \times 10^{-34} \times 3 \times 10^8 / 1.27 \times 10^{-6} = 15.67 \times 10^{-20}$,

V the volume of the optical cell $= A \cdot L$, where A is the area of the cylindrical cell (dia. 1 inch $= 2.54 \text{ cm} = 2.54 \times 10^{-2} \text{ m}$) & L is the length of the cell (4 inch $= 4 \times 2.54 \times 10^{-2} \text{ m}$),

Hence $V = \pi r^2 L = 3.14 \times (2.54 \times 10^{-2} / 2)^2 \times 4 \times 2.54 \times 10^{-2} = 0.5 \text{ m}^3$,

A the Einstein coefficient, Relationship between the Einstein coefficient of emission A & Einstein coefficient of absorption B is given by $A/B = 8\pi h / \lambda^3$,

Hence $A = 8B\pi h / \lambda^3 = 2.31 \times 10^{-4} \text{ s}^{-1}$, k the Boltzmann constant $= 1.38 \times 10^{-23} \text{ J/K}$

IR detective coefficient, K'

$$K' = R_{\text{es}} \eta h \nu A V$$

$$K' = 0.8 \times 0.8 \times 15.67 \times 10^{-20} \times 2.31 \times 10^{-4} \times 0.5 = 11.58 \times 10^{-24}$$

The signal generated by the detector is 60 mV corresponding to the singlet oxygen emission, but the range of DACS cards is 0-10 V, So I designed & developed a low noise amplifier (Gain = 100) circuit (figure 3) for converting it into the required range.

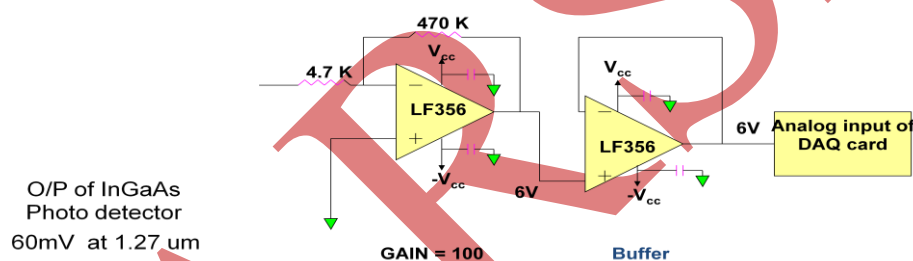


Fig.: 3 Low Noise Amplifier Circuit

Hence $[O_2(a^1\Delta)] = S/K' = 6V / 11.58 \times 10^{-24} = 5.18 \times 10^{23} \text{ moles m}^{-3}$,

$$\text{Singlet oxygen yield } Y = \frac{[O_2(a^1\Delta)]}{[O_2]_{\text{TOTAL}}} = \frac{[O_2(a^1\Delta)]}{[O_2(a^1\Delta)] + [O_2(X^3\Sigma)]} = \frac{P_{\Delta}}{P_O},$$

where P_{Δ} is partial pressure of SO concentration,

We have, $P_{\Delta} = P_a = [O_2(a^1\Delta)] kT = 5.18 \times 10^{23} \times 1.38 \times 10^{-23} \times 323 = 2310 \text{ Pa} = 2310 / 133.3 \text{ torr} = 17 \text{ torr}$

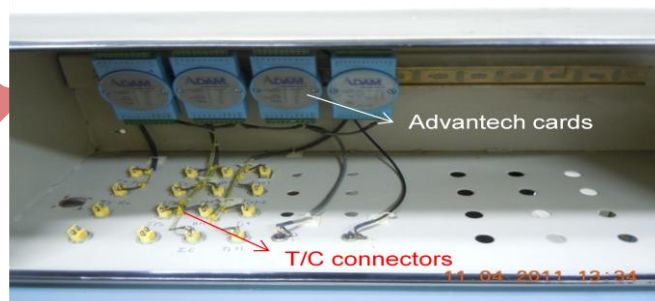


Fig 4: Control panel for temperature measurement through DACS (Data Acquisition & Control System)

And P_O is partial pressure of oxygen in the diagnostic infrared radiative cell, which is calculated for the known values of chlorine & buffer gas nitrogen flow rates (Dalton's Law) & is calculated approx. 25 torr.

Therefore we achieved Yield = $17/23 = 0.74$ or 74%.

The IR signal S , total pressure P and temperature T at the optical cell, were all recorded in real time by an (A/D) card inserted in a computer.



Fig 5: control panel for SO concentration, pressure measurement

VII RESULTS AND DISCUSSIONS

Effect of gaseous fuel @ const. u_g (15 ms^{-1})

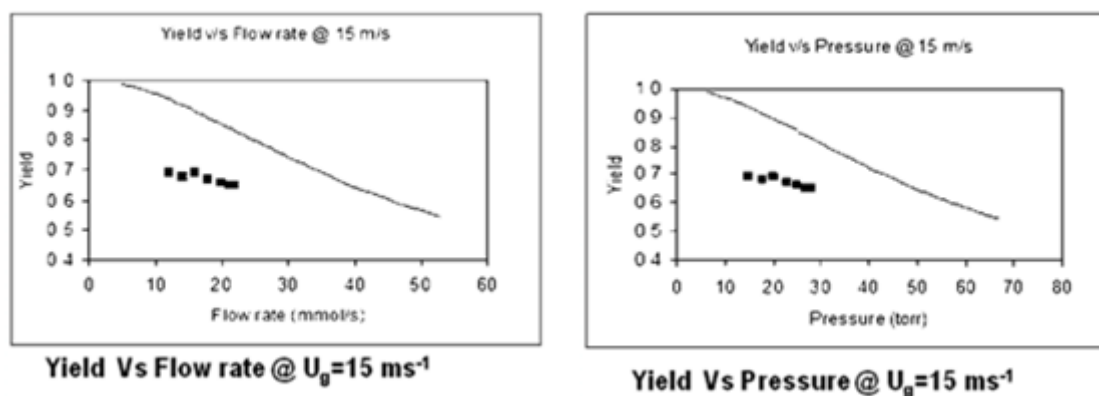


Fig 6: (a) Yield vs. Flow rate (b) Yield vs. Pressure

The detected photo emission signal S depends on the partial pressure of O_2 ($a^1\Delta$) and the calibration factor of the system. However, since the calibration and the actual measurement are made in different locations, the optical geometries and optical characteristics are different.

P_o is calculated for the mathematically known values of nitrogen (buffer gas) and chlorine gas flow rates using the Dalton's Law.

The developed optical diagnostic system has been used regularly during the COIL experiments for the Yield measurement of SO. On the basis of the numerous experiments conducted we got SO yield approximately 74%.

Discussion 1: From fig. 6 (a) it is clear that when we increase the flow rate of the chlorine gas, the total partial pressure of the all gases increased (according to the Dalton's Law) & the partial pressure of the total oxygen P_o is reduced. Hence yield of singlet oxygen is increased ($Y = P_{\Delta} / P_o$)

Discussion 2: From fig. 6 (b) it is clear that when we increase the pressure inside the SOG, yield of singlet oxygen is increased ($P_a = [O_2(a^1\Delta)]kT$, $Y = P_a / P_o$).

VIII CONCLUSIONS

This optical scheme has the advantages of simpleness and by incorporating the IR radiation method this gives the best suitable method for measuring the SO concentration $[O_2(a^1\Delta)]$.

Theoretically we achieve about 90% SO Yield, but on the basis of experiments by using the above mentioned measurement method we achieve only 74%. A lot of future work is under progress for increasing the SO Yield upto 90% or more for the efficient high power COIL system by changing the different parameters in design approach of different subsystems of COIL like Singlet Oxygen Generator (SOG), Chlorine Utilization, mixing of the diluents gases like He etc by varying the composition of $KOH:H_2O_2$.

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