Comparative Study of the Effect of Sensing Parameters on Ozone Gas Absorption-Cross-Section

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ABSTRACT

Obviously in this 21st century, photonics is causing a major revolution. As a result in this work, we zeroed in on one of the applications of photonics, which is sensor based. In this paper, the simultaneous effect of the variation of optical path length and temperature on the absorption cross section of ozone at 334.15nm referenced wavelengths in the UV is proposed. To actualise accuracy in measurements, optical absorption spectroscopy has been adopted via an online real time Spectralcalc.com simulation software. The simulated Absorption cross-section (ACS) results show a 1.67% increase with decreasing temperature from 350K – 100K. However, increase in the optical path-length from 0.75cm – 130cm has no effect on the ozone ACS. Results obtained are relevant to Green Communications.

Keywords: *Absorption cross section, absorption spectroscopy, optical path length, ozone, temperature, wavelength.*

1 INTRODUCTION

Photonics is the technology of light that controls, uses and manipulates light in order to get a desired outcome. It consist of several technologies such as optics, lasers, quantum electronics, fibers, detectors, materials. Basically, Photonics is photon engineering. The 20th century was revolutionized by electronics. However, in this 21st century, Photonics is doing the same since light (photon) travels faster than electrons. Photonics finds excellent application in Communications as in Fiber based and Free Space. Military applications in setting up a Range Finder. It is applied in sensors; for gas, chemical, fuel, distance, pressure, fluid level and gyro sensing. In medical field it is tailored toward LASIK, Endoscope, Dental surgery as well as Industrial applications for Precision cutting. In Lighting photonics also finds application for entertainment, display and signage (Significant Technologies Bhd. sdn., 2014). The scope of this work would be centered on the sensor application aspect of photonics, ozone sensing.

Ozone sensing has to do with the detection and measurement of the concentration of atmospheric ozone profiles. Ozone naturally exist in the stratosphere and also found in the troposphere due to anthropogenic activities. Electrochemical sensors, semiconductor sensors and fiber optic sensors, are the three generic methods for sensing ozone. Due to the advantages fiber optic sensors have over the others, we have chosen to use optical absorption spectroscopy which is a fiber based sensor. The values of absorption cross section have been known to be very useful in the detection of ozone and other gases present in the atmosphere at certain temperatures and pressures (Daumont et al., 1992). In the context of ozone shielding of ultraviolet light, absorption cross section is the ability of a sample to absorb photon of certain wavelengths and polarization. In a bid to obtain an accurate value of the absorption cross section of ozone, several works have been carried out and among these are those of (Hearn, 1961, Inn and Tanaka, 1953, Vigroux, 1953a , Daumont et al., 1992, Keeffe et al., 2007). However in 1961, Hearn established a fact that ozone is characterized with a special property to strongly absorb Ultra-violet radiation especially in the Hartley Band and particularly at $253.65nm$, as it relatively reproduces a mercury line (in air) which has led to a wide acceptance of the absorption cross section value of ozone at $253.65nm$. Globally, this (ACS) has become particularly important for the monitoring of atmospheric ozone (Viallon et al., 2015).

Despite this reference value of the absorption cross section of ozone proposed by (Hearn, 1961), there have been so much discripancies and inconsistencies in the value of cross section of obtained by various reseachers. This is due to the unstable nature of Ozone gas and other uncertainties that ensue during its measurement. Hence, this has posed a very big challenge to researchers as it is very difficult to accurately determine the concentration of Ozone gas.

Ozone gas has been known to play a very major role in the green house effect as it plays two major roles on the balancing of the earth's temperature by the absorption of the solar ultra violet radiations and the infra red radiations giving up by the surface of the earth. As a very strong oxidizing agent it can be use in environmental treatement (Jodpimai et al., 2016). It also helps to prevent harmful ultra violet radiations from reaching the earth which can result to cancer and the destruction of both terrestial and aquatic lifes. Unfortunately, ozone has a very strong oxidising property which makes it dangerous to both animate and inanimate bodies, it also has been known to cause severe problem of air pollution (Oyama, 2000). In the present day, the detection of the presence of Ozone as a pollutant in the atmosphere has really posed a serious challenge. For this singular reason, a threshold of 75ppb has been set by the National Air Quality Standard (NAQS) founded by the United states' environmental protection agency (US EPA) to be the allowable atmospheric concentration of Ozone (Berger et al., 2011). The World Meterological Angency (WMO) and Enviromental Protection Angency(EPA) would not be able to accurately detect the atmospheric concentration of ozone without certain value of ozone absorption cross section. Also the value of cross section is used for the configuration of the gas sensors so as to obtain accurate measurement.

Moreover, atmospheric transmission both in the visible and in the ultraviolet region would not be possible without this value of absorption cross section. Due to the positive and dangerous properties of ozone gas, we are faced with a greater demand to develop an accurate economical ozone monitoring system by adopting some telecommunication technique.

In a bid to improve on the accuracy of the absorption cross section of ozone, Optical Telecommunication finds an expression in this subject as the technique of Optical Absorption Spectrocopy can be used to effectively determine the absorption cross section of ozone gas.

2 SENSING PARAMETERS EFFECT ON OZONE ABSORPTION CROSS SECTION

2.1 TEMPERATURE EFFECT ON THE ABSORPTION CROSS SECTION

The temperature effect on the absorption cross section of ozone in the UV region is very necessary in the determination of ozone profile by latest modern day remote sensing devices. The temperature effect on the cross section stems from the changes that occur in the distribution of population within the electronic state of the ground having states of rotational vibrations.

The changes of the absorption cross section of ozone that results from the variations of temperature had been a main focus of study due to possibility of remotely sensing ozone with various applications. In the early time, an absorption cross section of $1.147 \times 10^{-17} cm^2/molecule$at 253.65nm mercury line in the Hartley band at 295K and $4.27 \times 10^{-17}\ cm^2/molecule$ at 334.15nm in the Huggins band at 293K (Hearn, 1961).

Yoshino et al., reported that the effect of temperature is negligible, Burrows et al., observed that at wavelength below $260nm$ the absorption cross section of ozone obviously increases with a decrease in temperature (Burrows et al., 1999) which is consistent with (Molina and Molina, 1986) (Daumont et al., 1992, Vallon et al., 2015).

The authors David et al., carried a work on the simultaneous effects of temperature and optical variation on the absorption cross section of ozone at wavelengths of 603 nm and 575 nm only in the visible spectrum. The work was simulation based. At a fixed concentration of 950ppm and pressure at 1atm, the optical path length was varied from 10 – 120cm as well as the Temperature from 313 K to 103 K. From the results they obtained it was reported that as the temperature decreased from 313 K way down to 103 K, the absorption cross section increased by a percentage of 0.71% and 1.22% for 575 nm and 603 nm respectively with optical path length within the range 10cm – 120cm (David et al., 2016). Parkinson et al., in their work determined the dependence of the absolute absorption cross section of ozone on temperature at four different reference wavelengths such as; 238.3nm, 245.8nm, 253.7nm as well as 263.7nm respectively. The absorption cross section at temperatures of 195, 228, and 293K was determined. It was observed that at 253.7nm, the cross section values are only efficient for measurements at room temperature and are not suitable at lower temperatures. The results obtained were used to normalize the cross section value of ozone from 240– 350nm. Also they reported that a cross section of $1.15 \times 10^{-17} cm^2$ is anticipated 253.7nm with path length of 10cm with a vapor pressure of 2.5mTorr (Parkinson et al., 1988). Increase in the absorption cross section was recorded with decrease in temperature ranging from 295K through 195K this results happens to be consistent with that of (Molina and Molina, 1986). Molina and Molina, also experimented the effect of temperature from 226 through 298K with wavelengths ranging from 190 – 270nm. They recorded that the temperature dependence in the Hartley band around wavelength of 250nm was vivid as there was a noticeable increase in the absorbance by 1% with decrease in temperatures from 298 way down to 226K but at longer wavelengths specifically above 270nm a huge temperature dependence was reported (Molina and Molina, 1986). This inconsistencies in the value of the absorption cross section of ozone owing to the temperature difference is yet being worked upon by various researchers in a bid to resolve this all-time challenge.

Near 250nm and at 253.65nm, a change of 2% in the ozone absorption cross section was reported within the range of 193K and 293K Serdyuchenko et al., 2014).

2.2 Optical Path length, Pressure and Concentration effect on Ozone ACS

Optical path length is the distance traveled by light in a sample of a gas cell. Generally, the shorter the optical path length, the higher the ozone concentration measurement observed leading to a lager absorption cross section which indicates better sensor sensitivity (Ching et al., 2014, Ching et al., 2015a); Aoyagi et al., 2012). Range of ozone concentration measurement is dependent on the optical path length (Marcus et al., 2016) and the ozone sampling wavelength. An increase in the sensors path length can improve further of the sensitivity of the sensor thereby improving its ability to determine the measurement of far lower concentrations of ozone (Keeffe et al., 2007, David et al., 2013). Hearn, at high pressures, recorded that with longer path length the measurement was more accurate than those of shorter path length at 296.73nm and 302.15nm respectively. For Hearn's measurements, the tubes used for absorption purpose were made from materials of fused silca with their respective lengths as 0.75, 10 and 15cm. The fused silca material was used so as to prevent the loss of ozone gas as a result of the surface of the measurement apparatus (Hearn, 1961).

Daumont et al., kept the value of pressure constant as low as $\simeq 4.05 \times 10^{-2}\,Torr.$ in one of their measurements which was independent of temperature. This condition could only enable the measurements of high absorption cross sections value of $\simeq 10^{-17} cm^2$, associated with 100cm optical path length making it relevant to 254nm absorption wave length (Daumont et al., 1992). A 40cm reflective cell (80cm optical path length) was used to measure the standard deviation in the concentration of ozone gas around 0.03ppm as well as 0.003ppm for 4cm. (Marcus et al., 2015)at four absorption wave lengths all in the UV region, 10cm path-length, 300K as well as pressure fixed at $0\,Torr$ between concentrations of $357\ and\ 971\ \mu LL^{-1}$, reported a cross section of $4.077 \times 10^{-18} cm^2$. At the end Measurement of ozone concentration above transmittance of 0.2165 has been recommended by Marcus for high measurement accuracy alongside an excellent Beer-Lambert relation (Marcus et al., 2015). An absorption wavelength at 254nm along with an absorption path length of 126cm can be used to effectively detect changes in the ozone concentration from 0.05 ppm through 0.3 ppm (less than 2ppm) resulting from predisgarges that emanate from electrical equipment (Maria & Bartalesi, 2012). A setup was made using two low cost 255nm LEDs having robust light source, two reflective gas cells of 4 and 40cm (8 and 80cm for transmission type gas cell) for the detection of ozone concentration (Degner et al., 2009). While the former is applicable to handheld devices measuring from some ppb to approximately 100ppm, the latter is suitable for stationary systems with a potential to detect ozone from a range of some ppb to about 10ppm. This shows that sensors resolution is increased by an increase in the optical path length. It was also reported that the SNR of a measuring system influences the resolution concentration and the optical path length. Under temperature of several hundreds of degree, the system has been designed to withstand such while working perfectly.

Two equations were developed from the existing Beer-Lambert equations that can be used to obtain higher sensitivity measurements by the optimization of the optical path length and the absorption cross section (Ching et al., 2015a). At 253.65nm, an optimized path length of 4.941cm was proposed for the measurement of ozone concentration between 500ppm and 1000ppm at a pressure of 1atm as well as temperature of 300K. Optimized path length of 4.998 cm suitable for 713 ppm (Ching et al., 2015a), 10cm for absorption wavelength near 254.03nm of concentration values between 357ppm and 971ppm (Marcus et al.,2015). Hence, there is the need for optimization of optical path length to provide for higher sensor sensitivity measurement for certain concentrations of ozone.

Therefore, the novelty of our work is to determine how both temperature and optical path-length variation affect the ozone absorption cross section at constant pressure and concentration at 254nm absorption wavelength.

3 METHODOLOGY AND SIMULATION

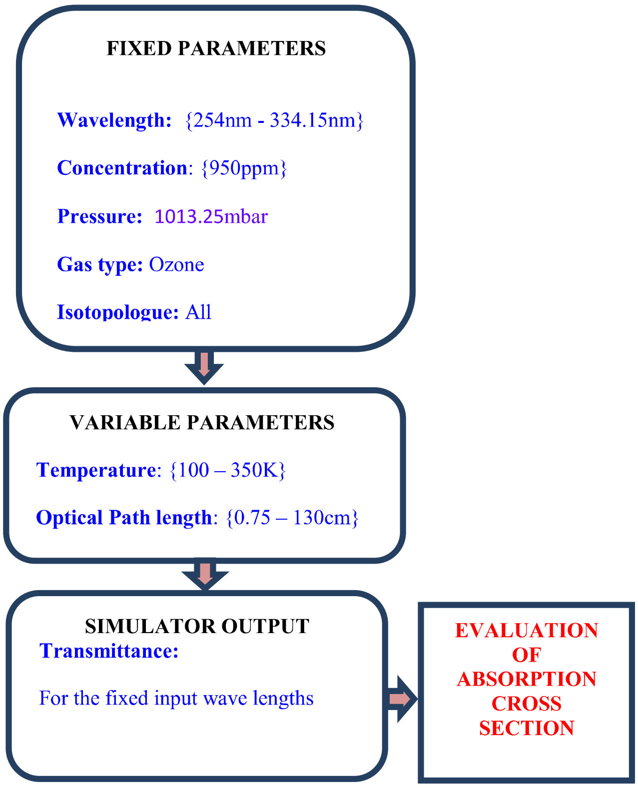

Figure 3-1 Block diagram of the entire Spectralcal.com Simulation Procedure

The methodology that will be implemented to carry out this work is an online simulator accessible through www.spectralcalc.com. The software offers a platform to model a system with high spectral resolution via simulation. The figure 3-1 gives the description of the necessary input parameters needed to calculate the ozone gas absorption cross section. For the purpose of optimum result HITRAN 2012 data base on the spectralcalc.com gas cell simulator will be used in this work to do the simulation on the absorption cross section of ozone at four reference wavelengths which are; $254, 257.34, 279.95\ and\ 334.15nm$ respectively in response to the varying effect of temperature and optical Path-length at (100 – 350K) and path-lengths at (0.75 to 130cm). As seen in figure 3-1, for this work, in order to determine the effect of temperature and optical path length on the absorption cross section of ozone, based on the reviews we have done so far, the concentration is fixed at 950ppm and the pressure at 1013.25mbar (as guided by previous literatures). The chosen range of temperature and optical path length for the variations were considered so that the simultaneous effects of these parameters on the absorption cross section can be properly observed.

The step size for the optical path length variation was meticulously chosen for better analysis. The 0.75cm path length was the least we found from literatures centered on the UV (Hearn, 1961) while Others are within the range of 1 – 15cm. Nevertheless, a few considered higher path lengths up to 126cm (Maria & Bartalesi, 2012). In a bid to cover a wider range, a variation from 0.75cm to 130cm was considered. No regular step size was used from 0.75cm – 10cm, as inputs of; 0.75, 1, 2, 3, 4, 5 and 10cm were varied first. However, a step size of 10 was used from 10 to 130 subsequently. (Degner et al., 2009).

The wavelengths as fixed parameters take on the input values (λ) given below while the optical path length as well as temperature are being varied simultaneously.

On the spectralcalc.com simulator, the closest absorption wavelength for 254nm (2.540022474601436e-01) was the actual value we used. The simulator's output is Transmittance. From the value of the transmittance (T_r) obtained as the simulator's output, the absorption cross section (σ) is then computed alongside the deviation (Δσ) with the equations (4) and (5) respectively.

3.1 BEER-LAMBERT LAW

The modus operandi of the gas cells in this optical sensor is governed by the Beer-Lambert law as it is an established principle that can ease measurement (Ching et al., 2014). The law demonstrates the effect that input and output parameter of light have on the gas measurement which can be expressed by equation (1). It gives an express mathematical relationship amongst three parameters such as: the optical path-length"L", concentration of the gas sample"c", and the absorbance "A"

$$A = \varepsilon \times L \times c$$
(1)

The concentrations of ozone can thus be calculated by using the values generated and displayed on the spectrometer by applying a variation of the Beer-Lambert law featuring the Decadic absorption coefficient which is expressed as:

$$\frac{I_{L(\lambda)}}{I_{O(\lambda)}} = 10^{-\varepsilon CL}$$
(2)

But, $\frac{I_{L(\lambda)}}{I_{O(\lambda)}} = T_r$

$$\ln T_r = \frac{-\sigma N_A Plc}{(10^6 RT)} \qquad (3)$$

The Beer-Lambert law indicates that there is an exponential reduction in the intensity of light that travels through the gas sample provided that certain parameters such as temperature, pressure and gas concentration remain invariant as seen in equation (3). The question emerging from equation (3) that we are considering is what happens to the absorption cross section of light passing through a sample when the temperature is not invariant as well as the path length.

To compute the value of the absorption cross section (σ) and the deviation (Δσ) equations 4 and 5 will do.

$$\sigma = -\frac{10^6 \times R \times T_p}{c_{(ppm)} \times N_A \times P \times L} \times \ln \frac{I_t}{I_0}$$
(4)

$$\Delta\sigma = \frac{\sigma_R - \sigma_W}{\sigma_W} \times 100\% \quad \text{(David et al., 2016)} \qquad (5)$$

Where:

I_L, is the light intensity at known wavelength transmitted via;

L, optical path length of the medium (gas cell) (m)

C, which is the concentration of the gas sample (mol/dm^3)

P, pressure (atm)

T, absolute temperature (K)

T_r, transmittance of light. $(0 < T_r < 1)$ $(unitless)$

R, ideal gas constant: 8.205746×10^{-5} $(atm\, m^3/mol \times K)$

N_A, Avrogadro's constant: $6.02214199 \times 10^{23} (molecule/mol)$

σ, ozone absorption cross-section $(m^2/molecule)$

I_O, the incident light intensity

ε, molar absorption coefficient$(m^2/mole)$.

σ_R, referenced absorption cross section (254nm) and

σ_W, absorption cross section for this work.

4 RESULTS AND DISCUSSION

From the simulated results obtained, Figure 4-2 indicates that the transmittance at an absorption wavelength of 254nm is both affected by temperature and optical path length. The decrease in the transmittance tends to be more obvious as the path length and the temperature increase. A gradual decline from 99.93% to 87.4% in the transmittance was observed form 0.75cm to 10cm. Subsequently, a very drastic decline to almost zero transmittance was also recorded from 10cm to 130cm as the temperature increased from 100K to 350K. Therefore, at 950pplm and 1atm, increase in the optical path length (0.75cm to 10cm) as well as temperature (100K to 350K) leads to fall in the value of transmittance form its maximum (0.85) to its minimum (≃0.00).

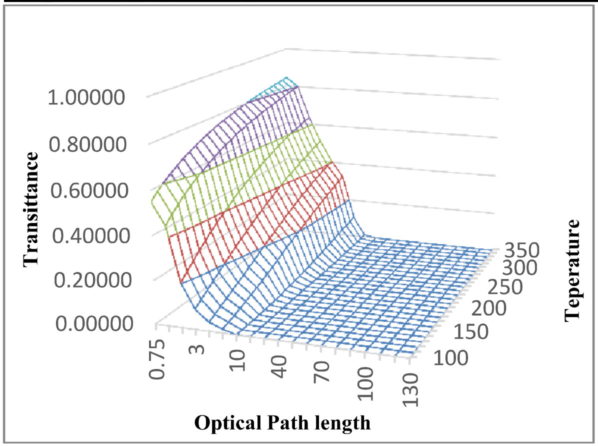

Figure 4-1 Effect of Temperature and Optical path length on the Transmittance at 254nm

Figure 4-3, explains the simultaneous effect of optical path length and temperature on ozone absorption cross section at an absorption wave length of 254nm, 1atm, 950ppm. Varying the temperature and the optical path length over the rages; 100K to 350K and 0.75cm to 130cm respectively. The absorption cross section of ozone was observe to increase by 1.67% as the temperature was decreased from 350K to 100K which is consistent with previous work that have been done in the UV. As seen from the figure 4-2, the temperature effect on the cross section can be broken down into six sections. 350K – 300K, the absorption cross section was invariant with its value at $1.124 \times 10^{-17}(cm^2/molecule)$. 300K – 280K, an increase of 0.19% in the absorption cross section was recorded, from $1.124 \times 10^{-17}(cm^2/molecule)$ to $1.126 \times 10^{-17}(cm^2/molecule)$. 280K – 270K, a decrease of 0.21% in the cross section was noticed from $1.126 \times 10^{-17}(cm^2/molecule)$ to $1.124 \times 10^{-17}(cm^2/molecule)$. 270K – 210K, another 1.11% increase in the absorption cross section from $1.124 \times 10^{-17}(cm^2/molecule)$ to $1.137 \times 10^{-17}(cm^2/molecule)$. 210K – 200K, a very minute decrease of 0.04% from $1.137 \times 10^{-17}(cm^2/molecule)$ to $1.136 \times 10^{-17}(cm^2/molecule)$. 200K – 190, a very obvious increase of 0.61% was recorded from $1.136 \times 10^{-17}(cm^2/molecule)$ to $1.143 \times 10^{-17}(cm^2/molecule)$. Finally, from 190K to 100K, the absorption cross section again remained constant at a value of $1.143 \times 10^{-17}(cm^2/molecule)$. For the optical path length effect on the absorption cross section at 254nm, we noticed that the effect is overlapping and the same for each gas cell length from 0.75 – 130cm.

Comparing this work with previous ones, we found our work to be in good agreement with Serdyuchenko et al., who recorded an increase in the absorption cross section of about 1 – 2% as against the 1.67% increase we reported. The nonlinearity observed at certain points in figure 4-3, is due to the deviation from Beer-lamberts law that occurs at 254nm which is consistent with what Marcus *et al* reported (Marcus *et al.,* 2015).

Furthermore, we compared our obtained results with the works of Hearn with $1.147 \times 10^{-17}(cm^2/molecule)$, Vallon *et al.* with $1.124 \times 10^{-17}(cm^2/molecule)$, Molina & Molina with $1.157 \times 10^{-17}(cm^2/molecule)$, Daumont with $1.131 \times 10^{-17}(cm^2/molecule)$ and Yoshino with $1.145 \times 10^{-17}(cm^2/molecule)$ all at an absorption wavelength of 254nm. The figure 6-2, gives a perfect description of what happens to the absorption cross section as the temperature is increased from 100K to 350K.

At 254nm, a deviation of 0.34% to 2.05%, 1.22% to 2.93%, and 0.17% to 1.87% were recorded when compared with those of Hearn, Molina and Molina, Yoshino respectively. While in comparison to those of Vallon *et al.* and Daumont *el al.*, the deviation were -1.14% to 0.27% as well as -1.10 to 0.58 respectively. Therefore, this deviation justifies the fact that temperature variation affects the absorption cross section of ozone only between the temperature ranges of 300K to 190K in descending order. Adding also that between temperatures of 350K and 300K, as well as 190K and 100K, temperature is of no effect on ozone absorption cross section. We have been able to only report the results obtained at 254nm as the others are currently been worked upon.

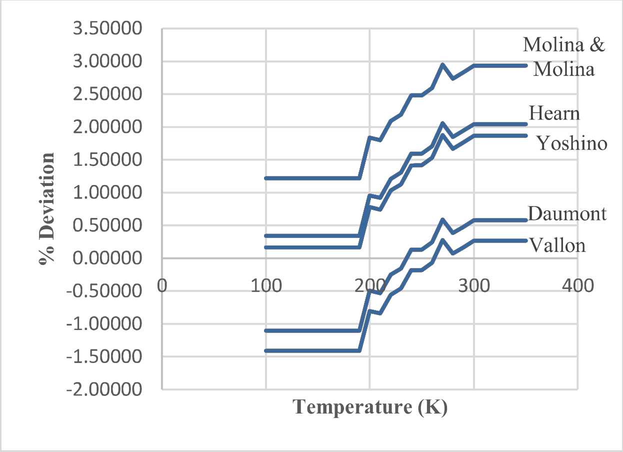

Figure 4-2 Deviation of ozone absorption cross section from other works

Green communications would find these results useful as we have provided more data set that can be used to improve on the accuracy in the measurement of ozone concentration. Thereafter, based on accurate obtained measurements, caution can be given to control anthropogenic activities in the troposphere.

5 CONCLUSION

As parts of the attributes of green communication which include: effective efficient utilization of energy by improving power efficiency, optimal allocation of power with sizable gain, older equipment upgrade for better energy-efficient products and employing management system in a bid to boost efficiency – developing the understanding of man to take on the green mind set and

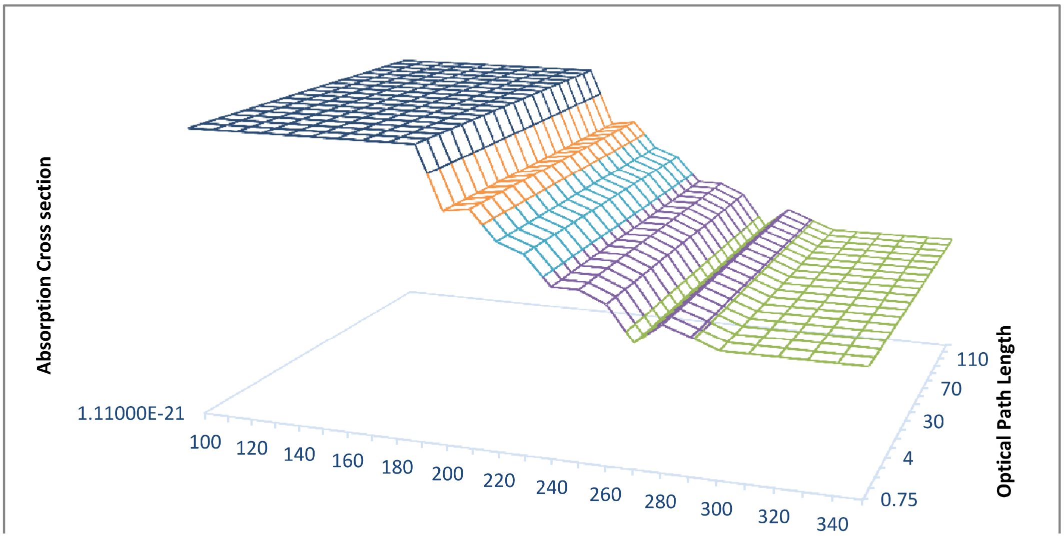

Figure 5-1 Simultaneous effect of sensing parameters on the ozone absorption cross section at 254nm

behavior through public enlightenment campaign – on systems that sponsor the release of ozone in the troposphere, therefore the results of this work would take the later aspect of the afore mentioned attributes in a bid to improve on green communications. Hence, the WMO, EPA as well as the Ground based-Satellite Sensing Network would find our result relevant in determining the ozone profile of the atmosphere. Furthermore, it is worthy of note that this results can be used for sensor configuration due to the fact that the accuracy of a sensor is dependent on the ACS. The ACS also determines the SNR of the sensor which signifies its potency in the detection of ozone gas.

We recommend that this work be done via experimental procedures

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