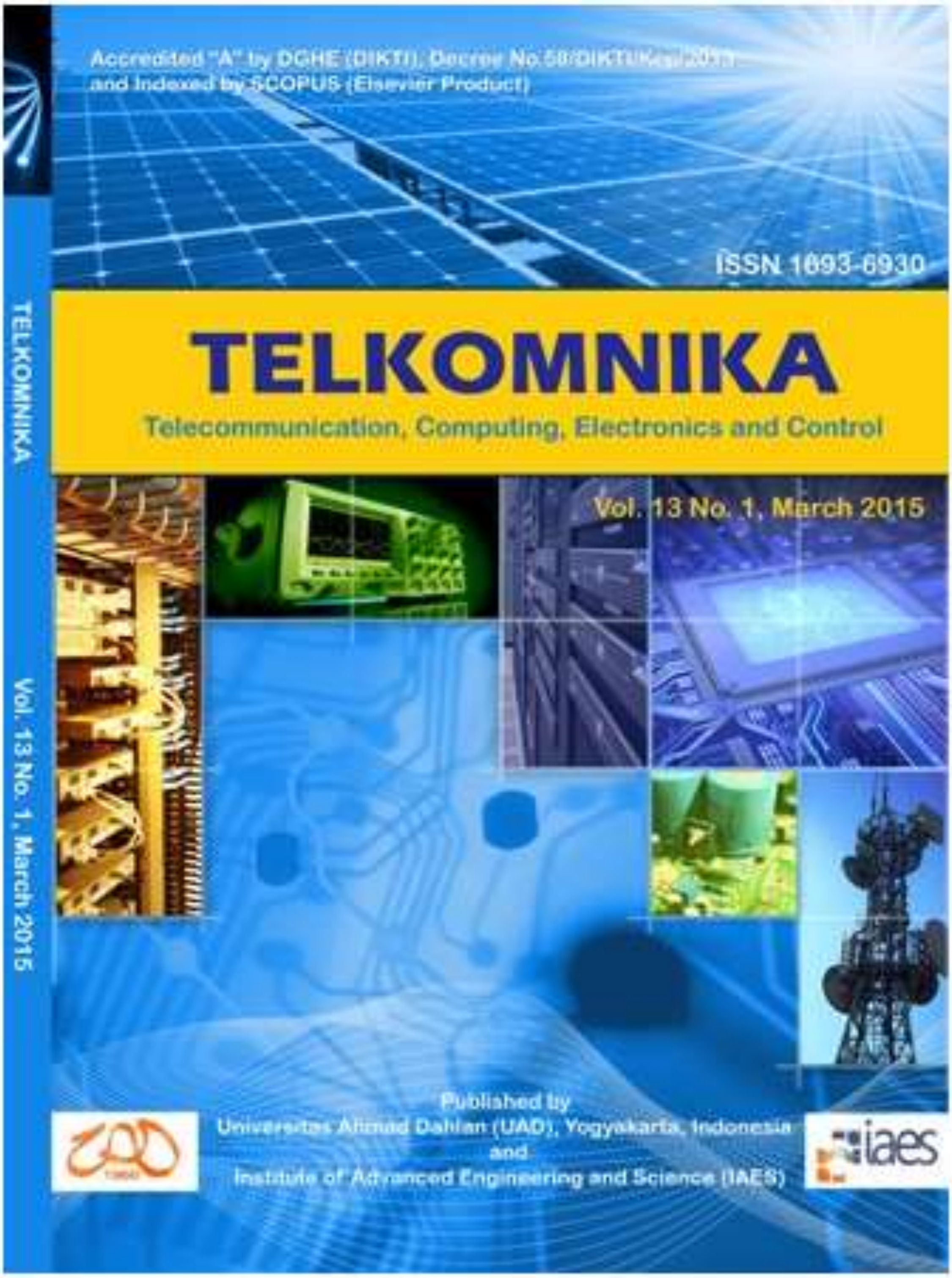

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Varying Effects of Temperature and Path-length on Ozone Absorption Cross-section

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Abstract

Inconsistencies in the absorption cross section of ozone have been observed. Hence, for accurate measurement, we have reported the combined effects of varying optical path-length and temperature on the ozone gas absorption cross section (OACS) at 334.15nm. Adopting optical absorption spectroscopy, results of the (OACS) have been simulated using spectralcalc simulator with HITRAN 12 has the latest line list. OACS increased by 52.27% as the temperature increased from 100K to 350K while it was slightly affected by a 0.007% decrease varying the path-length from 0.75cm-130cm.

Keywords*: ozone; absorption spectroscopy; absorption cross section; path-length; temperature*

1. Introduction

The hazardous effects of ozone gas on plants and animals as well as other susceptible inanimate objects have been reported [1-4]. In the stratosphere, ozone gas helps to prevents harmful UV radiation from reaching the earth which can cause cancer and as well impose danger to plants. Ozone as a green gas has been known to contribute immensely to the global warming. On the contrary, ozone gas exhibits negative properties in the troposphere. National growth in the economy of any country can lead to the emission of the carbon foot print of Ozone gas [5]. Anthropogenic activities results in the local generation of ozone gas in the troposphere such as transportation industries, information technology, manmade machine and electrical garment [6-8]; putting earth's life in danger. Tropospheric ozone can result in environmental pollution. Hence, the need to accurately measure ozone concentration in the troposphere. Among other measurement techniques, optical absorption spectroscopy has been considered to yield accurate measurement of ozone gas, as it can be deployed in electrically discharged area, function without consumables, immune to electromagnetic waves, and it is not corroded during the dissociation of O_3. In a bid to measure the concentration of ozone, several inconsistencies in the value of ozone absorption cross section (OACS) have been reported [9-11]. Absorption cross section is very indispensable in the determination of ozone concentration.

2. Overview of Absoption Cross Section Dependance in the Huggins Band

Temperature effect on the OACS in the Huggins band is very indispensable in the retrieval of ozone profiles from the Global Ozone Monitoring Experiment (GOME) [12], within the spectra range of 300-370nm. Furthermore, a precise knowledge of the ACS dependence on temperature is used to determine the rate of atmospheric photolysis as well as how much ozone contributes to the balance of the atmospheric earth warming. In fact, absorption cross section is so important in the determination of ozone concentration. The reason is because, absorption cross section is used in calculating the ozone concentration in commercial ozone sensors, such as 2B Technologies Ozone Monitor model 106-M. The OACS dependence on temperature in the 231-794nm range was reported by [13]. Between temperatures of 202K and 293K, the ACS measurement was determined with the aid of the GOME Flight Model (FM) satellite spectrometer. As reported, OACS varying the temperature in the Huggins band depends

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strongly on the wavelengths with differences way up to 30% as well as 70% for maximum and minimum spectra formation around 335nm [14]-[15]. Orphal and Chance reported various absorption cross sections of seven trace gases (ozone gas inclusive) relevant for HITRAN in both the UV and the visible spectrum, at temperatures and pressures ranging from 200K-300K and 1-1000 mbar respectively. Within the Huggins band (320-350nm), the cross section was found to be extremely dependent on temperature which was in good agreement (1-2%) with those of Bass and paur; Brion *et al.*

In the Huggins band, the extreme high dependence of the ozone absorption cross section (OACS) on temperature [16],[12] and pressure [14] has been reported. Likewise, the effects of path-length on sensor sensitivity and response time [7],[17],[18] as well as sensor resolution has also been experimented[19].Authors of [20], observed that an increase in the sensors path length can further improve the sensitivity of the sensor thereby improving its ability to determine the measurement of far lower concentrations of ozone. In the ultraviolet region, several path-lengths have been used experimentally such as, 0.75, 10 and 15cm [21],[22],[10] 5cm [23], 4 and 80cm [24] 8 and 80cm [19], 126cm [7]. However, the combined simultaneous effect of both path-length and temperature on the OACS has not been considered yet, which is the focus of this paper.

3. Simulation and Methodology

The spectralcalc.com online simulator has been used to simulate several values of ozone absorption cross sections in response to the varying effects of path-length and temperature at an absorption wavelength of 334.2nm. The most recent available line list on the HITRAN12 data base with about 47 analytes, 120 isotopologues for each analyte and has a wider coverage from the microwave to the visible spectrum. The temperature was varied over the range of 100K-350K while the path-length from 0.75cm-130cm. However, the pressure and the concentration were fixed at 1013.25mbar and 950ppm respectively as shown in Figure 1. The transmittance is the output from the spectralcalc simulator (given by Equation 1 and 2) with which the absorption cross section is been evaluated.

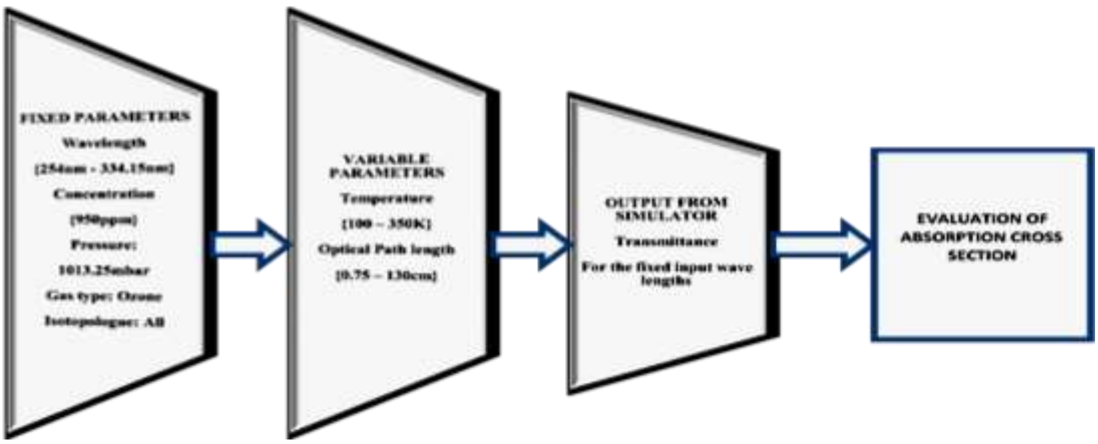

Figure 1. Block diagram of the entire spectralcal.com simulation procedure

$$\frac{I_L(\lambda)}{I_O(\lambda)} = T_r \qquad (1)$$

Also as seen in [26], the transmittance shows a strong relation with the absorption cross section as expressed in Equation 2

$$\ln T_r = \frac{-\sigma N_A P l c}{(10^6 RT)} \qquad (2)$$

For the absorption wavelength of 334.15nm, the nearest value obtained by the simulator is 334.1470073320352nm, with their equivalent transmittances for all varied temperatures and path-lengths. As giving by [17], the OACS(σ) as well as the deviation ($\Delta\sigma$) are hence evaluated using;

$$\sigma = - \frac{10^6 \times R \times T}{c_{(ppm)} \times N_A \times P \times L} \times ln \frac{I_L}{I_0} \quad (3)$$

$$\Delta\sigma = \frac{\sigma_R - \sigma_W}{\sigma_W} \times 100\% \quad (4)$$

Where, I_I, input light intensity; L, optical path length of the medium ( ); C, concentration of ozone(*ppm*); P, pressure (*mbar*); T, absolute temperature ( ); T_r, transmittance; R, ideal gas constant: $8.205746 \times 10^{-5} (atm\ m^3/mol \times K)$; N_A, Avrogadro's constant: $6.02214199 \times 10^{23} (molecule/mol)$; σ, ozone absorption cross-section($cm^2/molecule$); I_0, the incident light intensity; $\Delta\sigma$, percentage deviation; σ_W, Absorption cross sections of this work and σ_R, Absorption cross section of referenced and other related works.

4. Discussion of Results

Figure 2 shows how the transmittance at 1atm and 950ppm is being affected by both temperature and gas cell length variation in the Huggins band at 334.15nm absorption wavelength. As seen in Figure 2, the transmittance is affected by temperature and optical path length. Reducing the path length from 130cm-0.75cm, the value of transmittance increased with increase in temperature from 100K to 350K. At a gas cell length of 0.75cm, 0.01% increase was recorded while 1.69% increase was recorded at 130cm length. Therefore, decrease in the optical path length will lead increase in the transmittance as the temperature increases. We also observed that at each temperature (100K-350K), the value of the transmittance increased with reduction in the path length from 130cm-0.75cm. At 100K and 350K it increased by 0.99% and 1% respectively. The higher the temperature, the higher the transmittance. The lower the optical path length, the higher the transmittance. These are in good agreement with the Beer-lamberts law as shown in Equation 2. In the visible spectrum, David *et al.* reported the same conclusion as ours on the effectsof optical path length and temperature on the transmittance.

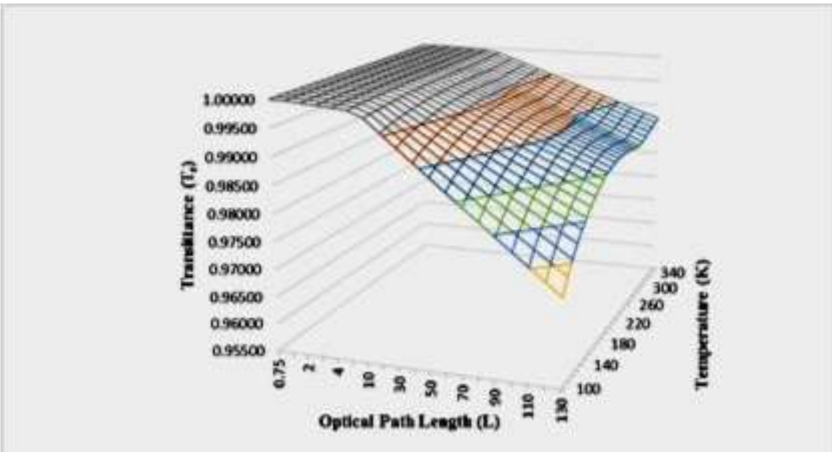

Figure 2. Effect of temperature and optical path length on the transmittance at 334.15nm

In the Huggins band, the ozone gas absorption cross section is also affected by temperature variation only while opticalpath length variation does no effect to it as shown in the Figure 3. The absorption cross section increased with increased temperature from 100K-350K by 52.27%. An irregular change was found between gas cell lengths of 0.75cm-20cm while a regular change was seen from 20cm-130cm. This effect of temperature has been sectioned into two. Between 20cm-130cm path lengths, with temperatures decrease ranging from 350K to 300K as well as 190K to 100K, the absorption cross section was found to be invariant with values of $4.978 \times 10^{-21} m^2/molecule$ and $3.269 \times 10^{-21} m^2/molecule$ respectively. This shows that; above room temperature and lower temperatures (190-100K), the OACS is not affected. However, between 300K-190K, a decrease of 52.27% in the cross section was recorded from $4.978 \times 10^{-21}\, m^2/molecule$to $3.269 \times 10^{-21} m^2/molecule$ within path lengths of 20cm and 130cm. This implies that within the room temperature and as low as about 189K, the OACS is affected. For each temperature 100K to 350K, the absorption cross section was found to decrease in value slightly by 0.007% as the optical path length was increased from 0.75cm to 130cm. The absorption cross section is $3.26968 \times 10^{-21} m^2\,/molecule$ and $3.26931 \times 10^{-21} m^2/molecule$ at 100K, 0.75cm gas cell length and 350K, 130cm gas cell length respectively. This is not the case at 254nm [25] where the increased optical path length has no effect on the ozone absorption cross section.

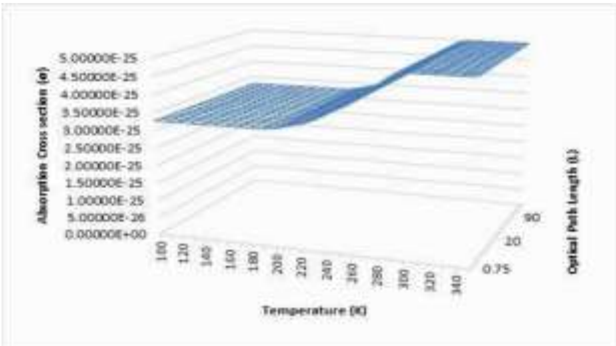

Figure 3. Simultaneous effect of sensing parameters on the ozone absorption cross section at 334.15nm

The absorption cross section as seen in the Figure 3 shows a very strong temperature dependence which is in good agreement with [2]. This results were further compared with previous works such as Hearn ($4.27 \times 10^{-21} \mathrm{m}^2/\mathrm{molecule}$), Molina & Molina ($4.46 \times 10^{-21} \mathrm{m}^2/\mathrm{molecule}$) and Bass & Paur ($4.7 \times 10^{-21} \mathrm{m}^2/\mathrm{molecule}$). The deviation at 334.15nm as shown in Figure 4, was from 36.4 to -10.4%, 30.60% to -14.2% and 43.75 to -5.6% for each of them respectively. The large deviations is as a result of the large discrepancies in the cross sections giving by Hearn, Molina & Molina and Bass & Paur at 334.15nm. Moreover they were reported at different temperatures.However, around 270K, deviations of 2.93%, 1.54% and 0.67% were observed from the cross sections of Hearn, Molina & Molina and Bass & Paur as shown in Figure 4.

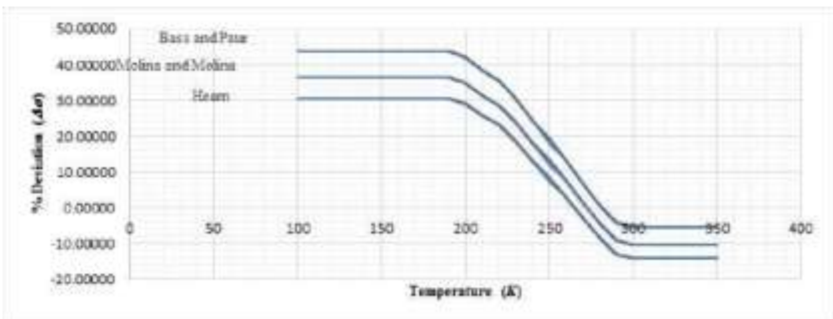

Figure 4. Deviation of ozone absorption cross section from those of Hearn, Molina & Molina and Bass & Paur at 334.15nm

5. Conclusion

At an optical path-length of 0.75cm, a 0.01% increase was recorded while 1.69% increase was recorded at 130cm length. So, a decrease in the optical path length will lead to an increase in the transmittance with a corresponding increase in the temperature.At each temperature (100K-350K), the value of the transmittance increased with reduction in the path length from 130cm-0.75cm. For the OACS, it increased by 52.27% with increase in temperature from 100K-350K has been presented. This large percentage increase of 52.27% indicates a huge dependence of the OACS on the temperature in the Huggins band at 334.15nm. Likewise the OACS was only slightly affected by increased path-length from 0.75cm-130cm. Now, for accuracy in the measurement of ozone gas in the HUGGINS band, we have proposed these results. However, we recommend that this procedure be carried out experimentally to compare with simulated results obtained in this work.

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References

[1] NRC (National Research Council). Emergency and Continuous Exposure Guidance Levels for Selected Submarine Contaminants. Washington, DC: National Academy Press. 2008; 2.
[2] Mc Donnell MJ, Pickett STA, Pouyat RV. The application of the ecological gradient paradigm to the study of urban effects, in Humans as components of ecosystems: subtle human effects and the ecology of populated areas. *Springer Verlag, New York.* 1993: 175-189.
[3] L Ye *et al.* Effects of ozone and drought on biomass allocation of four seedlings in South China. *Adv. Mater. Res.* 2014; 867: 2478-2484.
[4] JD Fuentes, TH Roulston, J Zenker. Ozone impedes the ability of a herbivore to find its host. *Environ. Res. Lett*. 2013; 8: 1-6.
[5] H Tang, J Pang, G Zhang, M Takigawa, G Liu. Mapping ozone risks for rice in China for years 2000 and 2020 with flux-based and exposure-based doses. *Atmos. Environ*. 2014; 86: 74-83.
[6] A Vibenholt, PA Clausen, P Wolkoff. Chemosphere Ozone reaction characteristics of indoor floor dust examined in the emission cell “FLEC”. *Chemosphere.* 2014.
[7] Maria, L De, Bartalesi D. A Fiber-Optic Multisensor System for Predischarges Detection on Electrical Equipment. 2012; 12(1): 207-212.
[8] Ayanoglu E. Editorial Launching IEEE Transactions on Green Communications and Networking. *IEEE Transactions on Green Communications and Networking*. 2017; 1: 1-2.
[9] Inn EC, Tanaka Y. Absorption Coefficient of Ozone in the Ultraviolet and Visible Regions. *JOSA.* 1953; 43(10): 870-872.
[10] TCE. Marcus *et al.* Alternative Wavelength for Linearity Preservation of Beer-Lambert Law in Ozone. 2015; 57(4): 1013-1016.
[11] J Viallon, S Lee, P Moussay, K Tworek, M Petersen, RI Wielgosz. Accurate measurements of ozone absorption cross-sections in the Hartley band. 2015: 1245-1257.
[12] Burrows JP, Richter A, Dehn A, Deters B, Himmelmann S, Voigt S, Orphal J. Atmospheric RemoteSensing Reference Data from GOME. 2. Temperature-Dependent Absorption Cross Sections of O_3 in the 231-794 nm range, *J. Quant. Spectrosc. Ra.* 1999; 61: 509-517.
[13] Burrows JP, Dehn A, Deters B, Himmelmann S, Richter A, Voigt S, Orphal J. Atmospheric RemoteSensing Reference Data From GOME□: Part 1. Temperature-Dependent Absorption Cross-Sections of No in the 231-794 Nm. 1998; 60(6): 1025-1031.
[14] Paur RJ, AM Bass. *The ultraviolet cross-sections of ozone: The measurements in Atmospheric Ozone.* Proceedings of the Quadrennial Ozone Symposium in Halkidiki, Greece, D. Reidel, Hingham, Mass. 1985: 611-616.
[15] LT Molina, MJ Molina. Absolute Absorption Cross Sections of Ozone in the 185- to 350nm Wavelength Range. 1986; 91.
[16] A Serdyuchenko, V Gorshelev, M Weber, W Chehade, JP Burrows. High spectral resolution ozone absorption cross-sections-Part 2□: Temperature dependence. *Atmos. Meas. Tech.* 2014; 7: 625-636.
[17] David M, Ibrahim MH, Idrus SM, Ngajikin NH, Izam A, Ching T, Marcus E. Optical Path Length, Temperature, and Wavelength Effects Simulation on Ozone Gas Absorption Cross Sections towards Green Communications. 2016; 14(3): 1-6.
[18] Keeffe SO, Fitzpatrick, C, Lewis E. An optical fibre based ultra violet and visible absorption spectroscopy system for ozone concentration monitoring. 2007; 125: 372-378.
[19] Degner M, Damaschke N, Ewald H. UV LED-based Fiber Coupled Optical Sensor for Detection of Ozone in the ppm and ppb Range. 2009: 95-99.
[20] Keeffe SO, Fitzpatrick C, Lewis E. Ozone measurement using an optical fibre sensor in the visible region. 2005: 758-761.

[21] Hearn AG. The Absorption of Ozone in the Ukra-Violet and Visible Regions of the Spectrum. 1961; 78: 932-940.
[22] Parkinson WH, Yoshino K, Freeman DE. Absolute Absorption Cross Section Measurements of Ozone and the Temperature Dependence at Four Reference Wavelengths Leading to Renormalization of the Cross Section between 240 and 350 nm. 1988: 1-35.
[23] T Ching, E Marcus, MH Ibrahim, NH Ngajikin, AI Azmi. Sensors and Actuators B□: Chemical Optical path length and absorption cross section optimization for high sensitivity ozone concentration measurement. *Sensors Actuators B. Chem.* 2015; 221: 570-575.
[24] Daumont D, Brion J, Charbonnier J, Physique, DC, Malicet J. Ozone UV Spectroscopy I□: Absorption Cross-Sections at Room Temperature. *Journal of Atmospheric Chemistry*. 1992; 15: 145-155.
[25] Enenche Patrick, Michael David, AO Caroline, Salihu Alhaji Bala, Abolarinwa Joshua Adegboyega, Adeiza James Onumanyi. *Comparative Study of the Effect of Sensing Parameters on Ozone Gas Absorption-Cross-Section*. 2nd International Engineering Conference IEC. 20; 1: 284-290.