Combined Effects of Temperature and Optical Path-Length on Ozone Gas Absorption Cross Section at 257.34nm and 279.95nm in Relation to Green Communications

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ABSTRACT— The value of ozone absorption cross section (OACS) is a key parameter used in the configuration of gas sensors. Sadly, the variations of certain parameters among others such as temperature, pressure, and optical path-length in a given spectrum can affect the values of OACS. As a result, there have been several discrepancies in the value of OACS. Recently, the simultaneous effects of optical path-length were investigated in the visible spectrum. Hence, there is the need to also carry out the same investigation in the UV spectrum. So, in this paper, we have reported the combined variation effects of temperature (100 *K*–350 *K*), and optical path-length (0.75 cm–130 cm) on OACS in the UV spectrum. We used the method of optical absorption spectroscopy as deployed in a model software called Spectralcalc. The software comprising the HITRAN12 latest line list was used to simulate OACS values. Simulated results were obtained using the latest available line list on the HITRAN12 Spectralcalc simulator. Our obtained results were slightly different from those reported for the visible spectrum but followed a similar trend, in that it showed a decrease in the OACS with an increase in the temperature from 100 *K* to 350 *K* at 279.95 nm and 257.34 nm by 1.09 *%* and 1.43 *%* respectively. While optical path-length had zero effect on it. We, therefore, conclude that at constant pressure, OACS depends on both temperature and absorption wavelength but not on optical path-length. The analysis reported in this work only seeks to address the differences in the OACS relative to temperature in the UV spectrum. So, the results obtained in this paper can be used to optimally configure ozone gas sensors to obtain an accurate measurement.

KEYWORDS: Absorption cross section, absorption spectroscopy, optical path-length, ozone gas, temperature, UV.

I. INTRODUCTION

Ozone as a greenhouse gas among others contributes to the earth's warming. This gas has some good advantages to the earth's inhabitants, especially in the stratosphere, where it acts as a giant sunshade shielding the earth from harmful ultraviolet radiations that can affect both plants, animals as well as certain inanimate bodies [1]. However, on the contrary, in the troposphere where life exists, ozone gas if found anywhere above a threshold value of 100 ppb constitutes negative effects on the earth's inhabitants [2]. For this sole reason, the National air quality standard has set a thresh hold of 75 ppb beyond which the concentration of ozone must not exceed [3], [4]. There is therefore the need for accurate measurement.

Photonics which is the technology that uses light to obtain the measurement of certain parameters can also be deployed in optical sensors for the measurement of ozone gas concentration. Light is one of the agencies through which this can be done. The absorption of light occurs in four major regions of the

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electromagnetic spectrum. These bands are Chappius, Hartley, Huggins, and Wulf band. When light is passed through a gascell (for instance, containing ozone gas) of concentration x ppb, the extent to which photons of the light are absorbed defines the absorption cross section of the gas. Hence the term ozone gas absorption cross section (OACS). Previous works have reported measurements of ozone in the troposphere using optical sensors, such as cavity-enhanced absorption Spectroscopy [5], cavity ring-down spectroscopy (CRDS) [6], and Photo-acoustic Sensors [7].

Most importantly, certain parameters are known to affect the rate of light absorption by ozone gas. Among other parameters that can affect gases as seen in Charles and Boyle's law [8] are concentration, temperature, pressure, volume, and optical pathlength (Optical Pathlength is simply the distance traveled by light in the gas cell during measurement). In a more recent work [9], the effect of temperature and optical path-length on OACS in the visible spectrum was reported at an absorption wavelength of 603 nm and 575 nm with gas cell optical path-length from 10 cm to 120 cm. Result obtained showed that an increases in the temperature from 103 K to 313 K resulted in a decrease in the OACS. The percentage decrease was 1.22% and 0.71%, at 603 nm and 575 nm respectively. While optical path-length variation was found to have no effect on the OACS [9]. The question arising was, what could possibly be the effect of these parameters in the UV spectrum (Hartley band)?

Of the afore mention bands, the Hartley band has the strongest absorption of light in the UV spectrum, hence a high OACS [10] Therefore, ozone gas concentration in the atmosphere could be efficiently measured in the Hartley band (between 200 to 300 nm). 257.34 nm [11] and 279.95 nm [12] being in the Hartley band have also shown strong absorption cross section of ozone in the UV. To a large extent, in the Hartley band, ozone gas has a unique property that allows very strong absorption of UV radiation. At an absorption wavelength of 253.65 nm, a thin line of mercury is reproduced thereby making its corresponding value of absorption cross section a standard for the atmospheric monitoring of the globe.

Progressive research has been carried out in a bid to improve accuracy in the measurement of ozone gas concentration. In commercial ozone sensors, the absorption cross section is very useful in the measurement of ozone concentration. The absorption cross section of Hearn 1.147×10^{-17} (m^2/molecule) at 253.65 nm was re-determined, thereafter, an absorption cross section of 1.127×10^{-17} (m^2/molecule) was proposed [11]. This value of cross section was aimed at measuring ozone with decreased uncertainties. However, to obtain an accurate measurement of ozone concentration in the future, an absorption wavelength and cross section of 257.34 nm, 1.107×10^{-17} (m^2/molecule) respectively was suggested [13].

Furthermore, in ozone measurement, an error can be introduced if the range of light transmittance goes against the linearity of the Beer-Lamberts law that governs the measurement of ozone concentration. As a result, for linearity's sake, an alternative wavelength and absorption cross section of 279.95 nm and 4.077×10^{-18} (m^2/molecule) has also been reported [14]. There is a required value of transmittance that is expected to minimize error in the concentration measurement of ozone gas.

From Charles Law, other factors such as temperature, pressure, and the optical path-length can affect this measurement. Though the simultaneous effects of temperature and optical path-length on the OACS in the visible spectrum have been reported [9]. Hence, borrowing leave from this recently reported work in the visible spectrum, we propose to also evaluate the effects of temperature and optical path-length on ozone gas absorption cross section in the UV spectrum (specifically, Hartley band) at wavelengths 257.34 and 279.95 nm. Since our related work [9] considered 10cm to 120cm and 103 k to 313 k, we decided to vary our optical path-length from the least path-length (0.75 cm) [14] and a little beyond the highest value of the path-length

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(126 cm) used in [13]. Also, we extended our range a little further compared to [9].

Therefore, we varied our measurement from 100 I to 350 *K* and from 0.75 cm to 130 cm temperature and optical path-length respectively. We also adopt absorption spectroscopy for measurement as it is most preferred compared to other techniques [15]. One major reason is its immunity to interferences from electromagnetic waves. Also, in the measurement of ozone concentration this technique can be deployed in electrically discharged locations safely [15], [16]. Simulated results were obtained using the latest available line list on the HITRAN12 Spectralcalc simulator. The results obtained were similar to [9], in that they showed a decrease in the OACS with an increase in the temperature from 100 *K* to 350 *K* at 257.34 and 279.95 nm by 1.43 % and 1.09 %, respectively. While optical path-length had zero effect on it. Simulation results obtained only demonstrates that at constant pressure, OACS depends on both temperature and absorption wavelength but not on optical path-length. The analysis reported in this work only seeks to address the differences in the OACS relative to temperature in the UV spectrum. So, results obtained it this paper can be used to optimally configure ozone gas sensors to obtain accurate measurement.

II. Simulation and Methodology

The methodology we have adopted for this work is absorption spectroscopy. Simulated results were obtained using the latest available line list on the HITRAN12 Spectralcalc simulator. First, we set the wavelength to 257.34 nm and 279.95 nm on the gas cell simulator (For each of the absorption wavelengths we simulate results). Second, the pressure and concentration were fixed at 1013.25mbar and 950ppm respectively [9], [12]. Third, values of optical path-length were then inserted beginning from 0.75cm – 130cm while the temperature was then varied from 100K – 350K for each optical path-length. Four, output from the simulator was the transmittance.

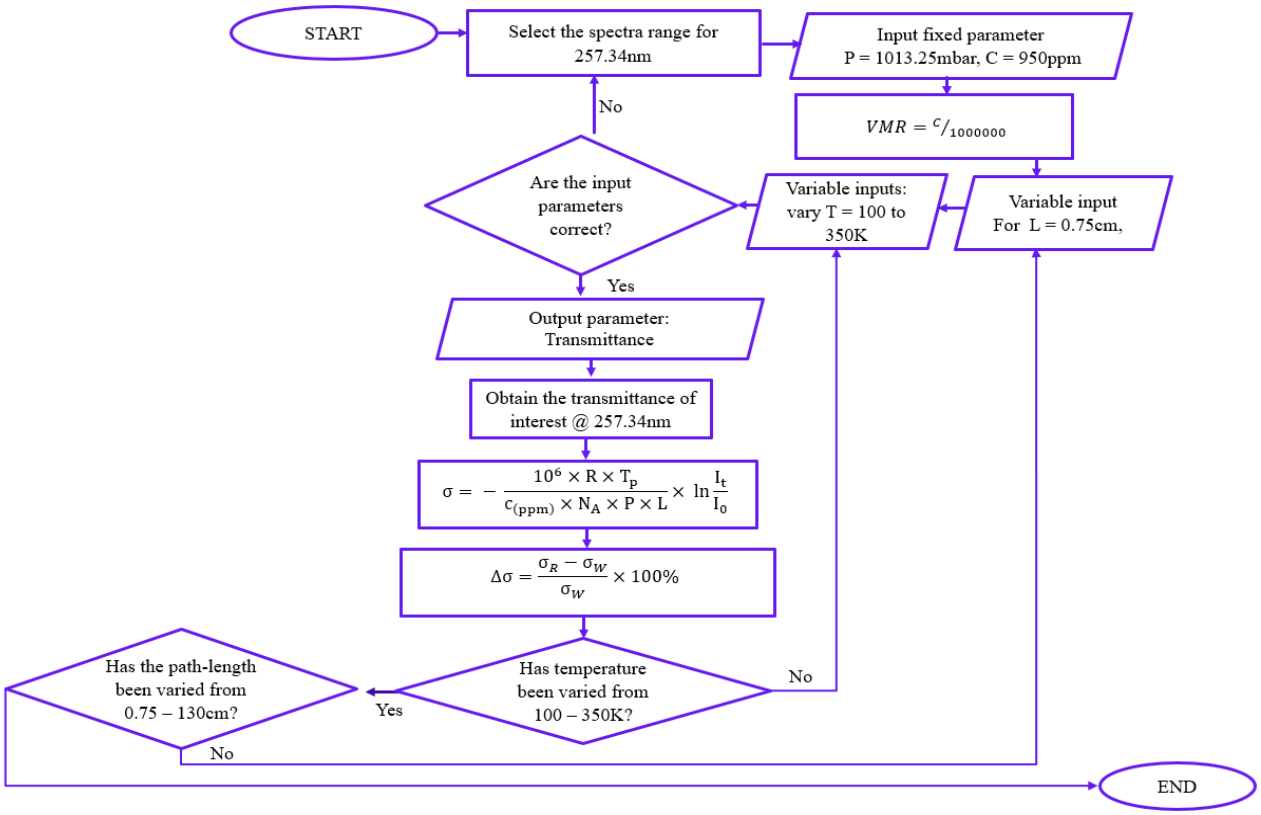

Fig. 1. Simulation Flow Chart

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Figure 1 clearly describes the flow process of the simulation. The transmittance seen on the flow chart is used to determine the OACS as seen in Eq. (2) and (3). The transmittance is the measure of the ratio of the output photons passing through the gas cell and the input light photons. Refer to the Eq. (1). When the entire loop process described in the flow chart is completed for the first absorption wavelength 257.34 nm, it is repeated for the second, 279.95 nm.

A. *Mathematical Modelling*

1) *OACS Response to Temperature*

The workings of the gas cells in the optical sensor used in our research are governed by the Beer-Lambert law. The law demonstrates the effect of the input and output parameters of light on gas measurement, which is expressed in Eq. (1). It gives a mathematical relationship between three parameters such as the optical path-length "L" , concentration of the gas sample"c", and the absorbance "A"

$$A = \varepsilon \times L \times c \text{[17]} \tag{1}$$

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

$$\frac{I_t}{I_o} = 10^{-\varepsilon CL} \text{ [12], [17]} \tag{2}$$

In this regard, the transmittance (T_r), can be expressed as,

$$T_r = \frac{I_t}{I_o} \text{[12], [17]} \tag{3}$$

$$-lnT_r = \frac{\sigma N_A\, Plc}{10^6 RT} \text{ [12]} \tag{4}$$

The values of the transmittance obtained from the simulator were applied and the absorption cross section was then calculated using the Eq. (4) [9].

Since our focus is to determine the response of the ozone absorption cross section (σ) to both varying temperature and optical path-length, we made it the subject of the relation as shown in Eq. (4) below.

$$\sigma = -\frac{10^6 RT}{c \times N_A \times l} \times l_n \frac{I_t}{I_o} \tag{5}$$

Substituting Eq. (3) into (5) we get,

$$\sigma = -\frac{10^6 RT}{c \times N_A \times l} \times l_n T_r \tag{6}$$

The range of temperature values over which the ozone absorption cross section response would be determined is from 100K – 350K. Now, for each optical path-length (l) beginning from $0.75\,cm$ to $130\,cm$, the temperature is varied over 26 temperatures with its minimum and maximum values as $100\ K$ and $350\ K$, respectively. Where σ_{100} and σ_{350} are the absorption cross sections at $100\,K$ and $350\,K$ respectively, T_{100} and T_{350} are the minimum and maximum temperatures, $T_{r_{100}}$ and T_{350} are the transmittances at $100K$ and $350K$ at a fixed optical path-length (l_f), $\Delta\sigma$ is the resultant change in the absorption cross section as the temperature is varied from $100K$ to $350K$, R is the ideal gas constant: 8.205746×10^{-5} (atm m^3/mol×K), N_A is Avogadro's constant: 6.02214199×10^{23} (molecule/mol).

For each optical path-length, Eq. (7) and (8) show the ozone absorption cross section at the minimum and maximum values of temperature.

$$\sigma_{100} = -\frac{10^6 RT_{100}}{c \times N_A \times l_f} \times l_n T_{r_{100}} \tag{7}$$

$$\sigma_{350} = -\frac{10^6 RT_{350}}{c \times N_A \times l_f} \times l_n T_{r_{350}} \tag{8}$$

We compute the total change in the ozone absorption cross section as follows:

$$\Delta\sigma = \frac{\sigma_{350} - \sigma_{100}}{\sigma_{100}} \times 100 \tag{9}$$

We then substitute the equivalents of σ_{100} and σ_{350} in Eq. (7) and (8) into Eq. (9) to obtain

$$\Delta\sigma = \frac{\left(-\frac{10^6 RT_{350}}{c \times N_A \times l} \times l_n T_{r_{350}}\right) - \left(-\frac{10^6 RT_{100}}{c \times N_A \times l} \times l_n T_{r_{100}}\right)}{\left(-\frac{10^6 RT_{100}}{c \times N_A \times l} \times l_n T_{r_{100}}\right)} \times 100 \tag{10}$$

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$$\Delta\sigma = \frac{10^6 R\left(T_{350} l_n T_{r_{350}} - T_{100} l_n T_{r_{100}}\right) / c \times N_A \times l}{10^6 R T_{100} \times l_n T_{r_{100}} / c \times N_A \times l} \times 100 \quad (11)$$

By further simplifying Eq. (11), we have the Eq. (12) which is the model that expresses the temperature effect on the absorption cross section of ozone at each given optical path-length.

$$\Delta\sigma = \frac{T_{350} l_n T_{r_{350}} - T_{100} l_n T_{r_{100}}}{T_{100} \times l_n T_{r_{100}}} \times 100 \quad (12)$$

2) *OACS Response to Optical Path-Length*

From Eq. (4) above, we can also derive the change in the ozone gas absorption cross section as the optical path-length was varied from 0.75 cm to 130 cm for each temperature ranging from 100 *K*–350 *K* as follows. Eq. (13) and (14) give the absorption cross section of ozone gas at the minimum and maximum value of optical at 0.75 cm and 130 cm respectively. Where; $\sigma_{0.75}$ and σ_{130} are the absorption cross sections at the minimum and maximum optical path-lengths of 0.75 cm and 130 cm, respectively, $T_{r_{0.75}}$ and T_{130} are the transmittances at $0.75cm$ and $130cm$ at a fixed temperature (T_f), and $\Delta\sigma$ is the resultant change in the absorption cross section as the temperature is varied from 0.75 cm to 130 cm

$$\sigma_{0.75} = -\frac{10^6 R T_f}{c \times N_A \times l_{0.75}} \times l_n T_{r_{0.75}} \quad (13)$$

$$\sigma_{130} = -\frac{10^6 R T_f}{c \times N_A \times l_{130}} \times l_n T_{r_{130}} \quad (14)$$

To determine the total resulting change in the absorption cross section, Eq. (15) does that.

$$\Delta\sigma = \frac{\sigma_{130} - \sigma_{0.75}}{\sigma_{0.75}} \times 100 \quad (15)$$

Further substitution of the equivalents of $\sigma_{0.75}$ and σ_{130} in Eq. (13) and (14) into Eq. (15) results in Eq. (16).

$$\Delta\sigma = \frac{\frac{l_n T_{r_{130}}}{l_{130}} - \frac{l_n T_{r_{0.75}}}{l_{0.75}}}{\frac{l_n T_{r_{0.75}}}{l_{0.75}}} \times 100 \quad (16)$$

$$\Delta\sigma = \frac{l_{0.75}}{l_n T_{r_{0.75}}} \left(\frac{l_n T_{r_{130}}}{l_{130}} - \frac{l_n T_{r_{0.75}}}{l_{0.75}}\right) \times 100 \quad (17)$$

By expanding Eq. (17), we then arrive at Eq. (18) which is the model that mathematically explains the optical path-length effect on ozone gas absorption cross section.

$$\Delta\sigma = \left(\frac{l_{0.75} l_n T_{r_{130}}}{l_{130} l_n T_{r_{0.75}}} - 1\right) \times 100 \quad (18)$$

Finally, these cross section values were then carefully analyzed to see their response to the varying parameters. These procedures were repeated for each of the wavelengths (257.34 nm and 279.95 nm respectively).

III. RESULTS AND DISCUSSION

As seen in Fig. 2, at 257.34 nm, the effect of temperature on the cross section can be broken down into five stages. Decreasing the temperatures from 350 *K*–300 *K* and 190 *K*–100 *K*, the absorption cross section was invariant as it remained constant at 1.107×10^{-17} (m^2/molecule) and 1.123×10^{-17} (m^2/molecule), respectively. For 300 *K*–250 *K*, a 0.98% increase from 1.107×10^{-17} (m^2/molecule) to 1.118×10^{-17} m^2/molecule was recorded. Subsequently, for 250 *K*–240 *K*, 0.15% decrease from 1.118×10^{-17} m^2/molecule to 1.116×10^{-17} m^2/molecule 240 *K*–220 *K*, 0.10% increase from 1.116×10^{-17} (m^2/molecule) to 1.117×10^{-17} (m^2/molecule). 220 *K*–200 *K*, 0.21% decrease from 1.117×10^{-17} (m^2/molecule) to 1.115×10^{-17} (m^2/molecule) and lastly, a percentage increase of 0.71% was recorded as the cross section increased from 1.115×10^{-17} (m^2/molecule) to 1.123×10^{-17} (m^2/molecule). Generally, the OACS increased by 1.43% as the temperature was reduced from 350 *K*–100 *K*.

However, at a higher absorption wavelength of 279.95 nm, as seen in Fig. 3, the absorption cross section rather decreased by 1.09% with a decrease in temperature from 350K – 100K which is contrary to what we recorded at 254 nm [10] and 257.34 nm (there, the cross section increased with decreasing temperature). This

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shows that the absorption cross section is wavelength-dependent.

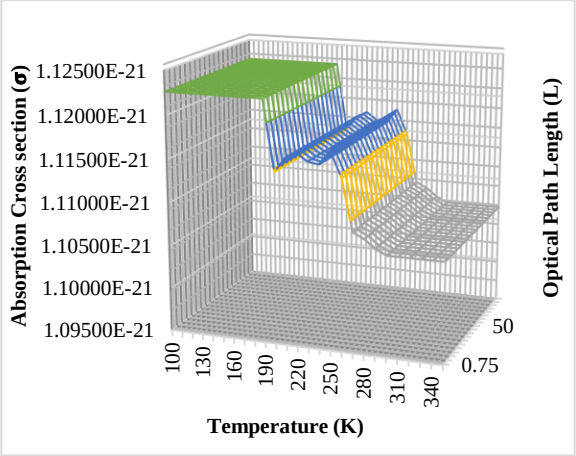

Fig. 2. Simultaneous effects of temperature and optical path-length on OACS at 257.34 *nm*

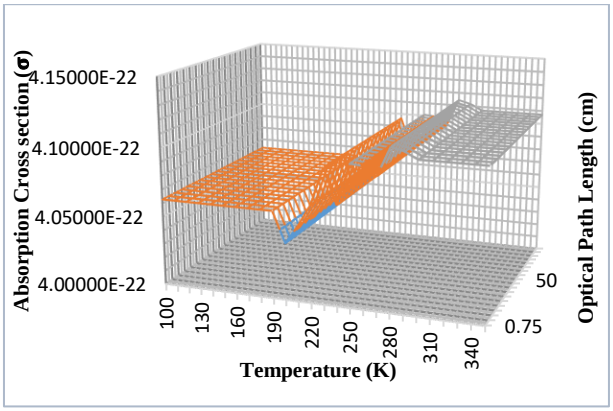

Fig. 3. Simultaneous effects of temperature and optical path-length on OACS at 279.95 *nm*

The simultaneous effect of temperature and the gas cell length on the ozone absorption cross section has been sectioned into Seven. It was invariant at temperatures of 350*K*–300*K* and 190*K*–100*K* with constant values of 4.107×10^{-18} (m^2/molecule) and 4.063×10^{-18} (m^2/molecule), respectively. Further decrease in the temperature from 300*K*-280*K* as well as 270*K*–250*K*, led to a 0.17% increase in the cross section from 4.107×10^{-18} (m^2/molecule) to 4.114×10^{-18} (m^2/molecule) and 4.094×10^{-18} (m^2/molecule) to 4.101×10^{-18} (m^2/molecule) respectively. 280*K*–270*K*, 0.50% decrease from 4.114×10^{-18} (m^2/molecule) to 4.094×10^{-18} (m^2/molecule). 250*K*–240*K*, 0.72% decrease from 4.101×10^{-18} (m^2/molecule) to 4.071×10^{-18} (m^2/molecule). 240*K*–230*K*, 0.62% increase from 4.071×10^{-18} (m^2/molecule) to 4.097×10^{-18} (m^2/molecule). 230*K*–200*K*, at this range of temperature, the ozone absorption cross section was affected the most by a percentage decrease of 1.38% from 4.097×10^{-18} (m^2/molecule) to 4.041×10^{-18} (m^2/molecule). Finally, we also recorded a 0.54% increase in the absorption cross section as the temperature was lowered from 200 *K*–190 *K* raising the cross section to 4.063×10^{-18} (m^2/molecule) from 4.041×10^{-18} (m^2/molecule).

Table 1. Summary on the Range of Temperatures for which the Ozone Absorption Cross Section Is Least and Most Affected.

Wavelength (*nm*)	Temperature (*K*)	Effect on OACS (σ)	Percentage Change %
257.34	300–250	Most affected by an increase	0.98
	240–220	Least affected by a small increase	0.10
279.95	230–200	Most affected by a decrease	1.38
	300–280	Least affected by a small increase	0.17

From Table 1, it is best to measure ozone concentration at such a temperature range where the OACS is least affected. Thus, we suggest the range of 240*K*–220*K*, 300*K*–280*K* for measurement as the OACS is least affected by only 0.10% and 0.17% at 257.34 nm and 279.95 nm respectively. For the effect of optical path-length variation on the absorption cross section at 257.34 nm and 279.95 nm, we noticed that the effect is overlapping and is the same for each optical path-length from 0.75 – 130cm. In summarily, varying the optical-path-length has zero effect on the OACS at 257.34 nm and 279.95 nm.

Finally, from Fig. 2 and 3, there is a decrease in the OACS with an increase in the temperature from 100*K* to 350*K* at 279.95 nm and 257.34 nm by 1.09 % and 1.43 % respectively which is similar to what was reported in [9] where results

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revealed a decline in the OACS (with 1.22% and 0.71%) as temperature increases at 603 nm and 575 nm respectively. However, in both cases, optical path-length was found to have no effect on the OACS.

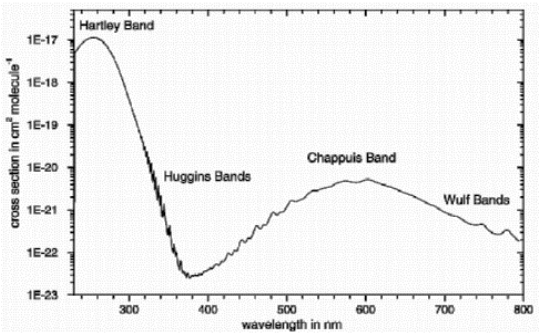

Fig. 4. Ozone Spectrum Showing Absorption Cross Section Versus Wavelength [10]

Also looking at Fig. 4 reported by [10], our results showed some consistencies as the OACS dropped from 1.43% (257.34 nm) to 1.09 % (279.95 nm) as it approached the Huggins band. Same applied to the OACS in [9] as it moves towards the Chappuis band.

A. *Validation of Results*

1) *Temperature Effect on OACS*

At 257.34 nm, fixed optical path-length, $l = 130cm$; varied temperatures from 100 K to 350K, with maximum and minimum values at: $T_{350} = 350K$ and $T_{100} = 100K$ respectively; Transmittance, $l_nT_{r_{350}} = -28.6549$; $l_nT_{r_{100}} = -101.751$; $\Delta\sigma$ is computed as follows

$$\Delta\sigma = \frac{T_{350}l_nT_{r_{350}} - T_{100}l_nT_{r_{100}}}{T_{100}\times l_nT_{r_{100}}} \times 100 \quad (12)$$

$$\Delta\sigma = \frac{(350 \times -28.6549) - (100 \times -101.751)}{100 \times -101.751} \times 100$$

$$\Delta\sigma = -1.43\%$$

At 279.95 nm, fixed optical path-length, $l = 130cm$; varied temperatures from 100K to 350K, with maximum and minimum values at: $T_{350} = 350K$ and $T_{100} = 100K$ respectively; Transmittance, $l_nT_{r_{350}} = -10.6359$; $l_nT_{r_{100}} = -36.8237$;

$$\Delta\sigma = \frac{T_{350}l_nT_{r_{350}} - T_{100}l_nT_{r_{100}}}{T_{100} \times l_nT_{r_{100}}} \times 100$$

$$\Delta\sigma = \frac{(350 \times -10.6359) - (100 \times -36.8237)}{100 \times -36.8237} \times 100$$

$$\Delta\sigma = 1.09\%$$

The -1.43% and 1.09% change in the absorption cross section obtained via the mathematical model is the same as what was reported for the simulated results.

2) *Optical Path-Length Effect on Ozone Sas Absorption Cross Section*

From Eq. (18), as derived in the mathematical model earlier, the effect of varying optical path-lengths on the ozone absorption cross section can be determined thus:

$$\Delta\sigma = \left(\frac{l_{0.75}l_nT_{r_{130}}}{l_{130}l_nT_{r_{0.75}}} - 1\right) \times 100 \quad (18)$$

At 257.34nm; fixed temperature at $T = 100K$, varied optical path-lengths from 0.75cm to 130cm with maximum and minimum values at: $l_{0.75} = 0.75cm$ and $l_{130} = 130cm$ respectively; Transmittance, $l_nT_{r_{0.75}} = -0.59703$; $l_nT_{r_{130}} = -101.751$

$$\Delta\sigma = \left(\frac{l_{0.75}l_nT_{r_{130}}}{l_{130}l_nT_{r_{0.75}}} - 1\right) \times 100$$

$$\Delta\sigma = \left(\frac{0.75 \times -101.751}{130 \times -0.59703} - 1\right) \times 100$$

$$\Delta\sigma = 0\%$$

At 279.95 nm; fixed temperature at $T = 100K$, varied optical path-lengths from 0.75cm to 130cm with maximum and minimum values at: $l_{0.75} = 0.75cm$ and $l_{130} = 130cm$, respectively; Transmittance,

$l_nT_{r_{0.75}} = -0.21244$; $l_nT_{r_{130}} = -36.8237$

$$\Delta\sigma = \left(\frac{l_{0.75}l_nT_{r_{130}}}{l_{130}l_nT_{r_{0.75}}} - 1\right) \times 100$$

$$\Delta\sigma = \left(\frac{0.75 \times -36.8237}{130 \times -0.21244} - 1\right) \times 100$$

$$\Delta\sigma = 0\%$$

The 0% effect of optical path-length on the absorption cross section obtained from the

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mathematical model shows is the same as what was reported via simulation.

IV. CONCLUSION

This paper investigated absorption cross section dependence on both temperature and optical path-length at 257.34 nm and 279.95 nm. spectralcalc online software simulation revealed that OACS increased by 1.43% with decreasing temperature from 350 K – 100 K while it was found to decrease by 1.09% with decreasing temperature from 350 K – 100 K. However, in the Hartley band with reference to 257.34 nm and 279.95 nm, variation in the optical path-length has no effect on the OACS. We, therefore, conclude that at constant pressure, OACS depends on both temperature and absorption wavelength but not on optical path-length. The analysis reported in this work only seeks to address the differences in the OACS relative to temperature in the UV spectrum. Thus, the results obtained in this paper can be used to optimally configure ozone gas sensors to obtain an accurate measurement. Accurate measurement of ozone gas as a greenhouse gas is essential to promoting the drive towards achieving green communication.

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