International Journal of Advances in Applied Sciences (IJAAS)
Vol. 11, No. 2, June 2022, pp. 97~106
ISSN: 2252-8814, DOI: 10.11591/ijaas.v11.i2.pp97-106

The concurrent upshot of optical path-length and pressure on O_3 absorption cross-section in relation to green communication

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Article Info

Article history:

Received Aug 4, 2021
Revised Apr 23, 2022
Accepted May 20, 2022

Keywords:

Absorption cross-section
Green communication
Optical path length
Ozone gas
Pressure
Visible spectrum

ABSTRACT

Ozone gas is a greenhouse gas. Accurate measurement of its concentration is dependent on the right value of the ozone gas absorption cross-section. In the literature, discrepancies and inconsistencies have been however linked with ozone gas absorption cross-section. In the literature, information on the pressure effect on pressures less than 100 mbar and greater than 100 but less than 1000 mbar is not available for the visible spectrum. Thus, creating an information gap that this manuscript is intended to fill up. This is the problem that has been addressed in this present work. The method of simulation with SpectralCalc is the method adopted for the present work. HITRAN 2012 simulator, available on spectralcalc.com, was used in simulating the ozone gas absorption cross-section to determine the simultaneous effect of optical path length and pressure at two peak wavelengths in the visible spectrum. Simulation outcomes were obtained for an optical path length of 10 cm to 120 cm showing that the optimum absorption cross-section value of 5.1084×10^{-25} m^2/molecule at 603 nm and 4.7182×10^{-25} m^2/molecule at 575 nm for gas cells length between 10 cm and 120 cm are obtained at peak points. Pressure values at which ozone gas absorption cross-section becomes a constant value of 5.1058×10^{-25} m^2/molecule at 603 nm and 4.7158×10^{-25} m^2/molecule at 575 nm is optical path length dependent. The percentage difference between 5.1084×10^{-25} m^2/molecule and 5.1058×10^{-25} m^2/molecule is 0.05% for all lengths of gas cells considered. Similarly, the percentage difference between 4.7182×10^{-25} m^2/molecule and 4.7158×10^{-25} m^2/molecule is also 0.05% for all lengths of gas cells considered. These results are relevant for high-accuracy and high-precision ozone gas measurements. Furthermore, efficient measurement of ozone gas is a direct enhancement of green communication.

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1. INTRODUCTION

Accurate measurement of ozone concentration as a greenhouse gas has become crucial in light of the aftermath effect of exposure to an unsafe quantity of ozone gas [1], [2]. The measurement of ozone gas concentration depends on the accuracy of the ozone gas absorption cross-section [3], [4]. In the literature,

however, discrepancies and inconsistencies have trailed values of ozone gas absorption cross-section [5], [6]. Above 10% discrepancies in ozone gas absorption cross-section have been reported [7], [8]. Several parameters such as temperature [9], pressure [10] sampling frequency [11], and absorption wavelength [6] have been investigated previously in relation to the ozone gas absorption cross-section. Marcus *et al.* investigated the effect of pressure on ozone gas absorption cross-section in the ultraviolet (UV) [12]. At a peak absorption wavelength of 255.442 nm, a pressure range of 101.3250 mbar to 303.9750 mbar has been shown to have no effect on the peak absorption cross value of 1.148×10^{-21} m^2/molecule. Similarly, Voigt *et al.* studied the dependence of ozone gas absorption cross-section on pressure. In their publication, it was shown that pressure values of 100 mbar and 1000 mbar for temperature values between 203 K and 293 K do not affect ozone absorption cross-section for absorption wavelength between 230 nm and 850 nm [10]. However, information on the pressure effect on pressures less than 100 mbar and greater than 100 but less than 1000 mbar is not available for the visible spectrum in the literature. Thus, creating an information gap that this work is intended to fill up. This is the problem that has been addressed in this present work. In addition, ozone gas concentration has been measured using varying lengths of gas cells in the visible spectrum: 10 cm, 25 cm, 50 cm [6], 70 cm [13], and 120 cm [10]. Variation in the length of gas cells will result in variation in gas cell total volume. Robert Boyle in Boyle's law had stated that pressure and volume of a gas are inversely related [14]–[16]. Since the variation in the length of the gas cell will result in total volume variation, the concurrent upshot of optical path length and pressure at 603 nm and 575 nm on the ozone absorption cross-section is therefore investigated in the visible spectrum.

2. OZONE GAS ABSORPTION CROSS-SECTION: AN OVERVIEW

The authors had previously established in [4] according to literature that error free measurement of ozone gas is dependent upon ozone gas absorption cross-section [3]. And this has led to lots of research efforts to investigate the accurate value of ozone gas absorption cross-section [4]. High accuracy and high precision measurement of ozone gas concentration have become a necessity in light of the revised exposure safety limit of ozone gas. The earlier exposure of 0.1 ppm of ozone gas in the workplaces in the US [17], was revised to 0.075 ppm in 2008 [18], [19]. International Health and Safety Standards have also placed a limit of 0.05 ppm to 0.10 ppm of ozone concentration in the air [20]. Ozone gas absorption coefficient (ε) is dependent on absorption cross-section according to the following relationship: $\varepsilon = \sigma \times N_A$; N_A is Avogadro's constant with a value of 6.02214199×10^{23} (molecule/mol) [21]. There have been lots of research efforts to obtain correct value of absorption cross-section of ozone gas in the visible spectrum [8], [22]–[25]. Grigg's results [23] were in very good agreement with the results obtained by Vigroux; Griggs thus, recommended Vigroux results [24] to be used in the Chappuis band [23]. In 1988, Brion [7] showed that Amoruso [26], Vigroux [24] and Tanaka [8] agree well on 603 nm and 575 nm as the peak absorption of ozone gas in the visible spectrum. Numerical outcomes obtained by simulation in this work were compared with previous work with peak absorption cross-section at 603 nm and ozone gas absorption at 576.96 nm [7], [22]. The authors had previously defined (1) and (2) that were used in calculating the absorption cross-section (σ) of ozone gas in this work [11], [27]–[30].

$$\sigma = -\frac{10^6 \times R \times T_P}{C_{PPM} \times N_A \times P \times L} \times \ln T \quad (1)$$

Where, c(ppm) = Ozone concentration in ppm, R = Ideal gas constant (atm m^3 mol^{-1} K^{-1}), T_p = temperature (K); σ = Absorption cross-section (m^2/molecules), N_A = Avogadro's constant (molecule/mol), P = pressure in atmosphere (atm), L = Optical path length (m), T = Transmittance.

$$\frac{\sigma - \sigma_w}{\sigma_w} \times 100\% \quad (2)$$

Where, σ = ozone absorption cross-section at 603 nm, σ_w = absorption cross-section obtained in this work.

3. SIMULATION SOFTWARE AND METHODOLOGY

The methodology adopted for this work is the use of an online simulator known as Spectralcalc. Spectralcalc.com is an online simulator used for high-resolution spectral modeling. The gas cell simulator's main option was used primarily for the simulation of absorption cross-section as shown in Figure 1 and Figure 2. On the gas simulator main option, Figure 1 shows the observer sub-option. Simulation of transmittance was carried out on the observer sub-option within a wavelength range of 0.60202 μm to 0.60302 μm and 574.5 nm to 575.5 nm. In Figure 2, the gas cell sub-option is displayed. With the gas cell,

sub-option ozone gas was selected as the gas of choice and the value of 10 cm to 120 cm was imputed as the length of the gas cell. Ozone gas concentrations of 950 ppm and 293 K were considered at room temperature [31] and pressure values in mbar were varied between 10 mbar and 1000 mbar. HITRAN 2012 from HITRAN database was used for all simulations. It is the latest available line list on Spectralcalc.com simulator. For all simulations, an actual spectral line from Spectralcalc.com approximated as 603 nm is 603.00145129141 nm and at 575 nm (actual value is 575.016232354603 nm). Figure 3 is a summary of the methodology employed.

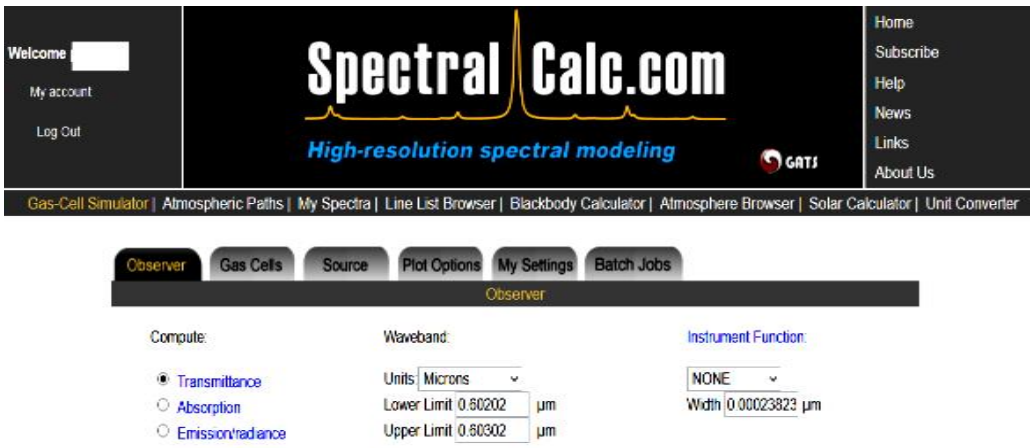

Figure 1. Gas cell simulator: observer sub-option

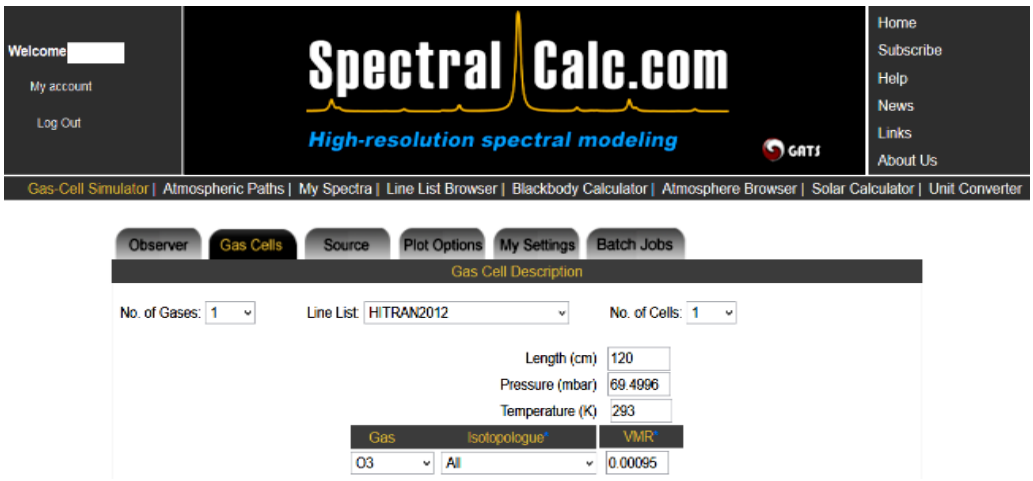

Figure 2. Gas cell simulator: gas cell sub-option

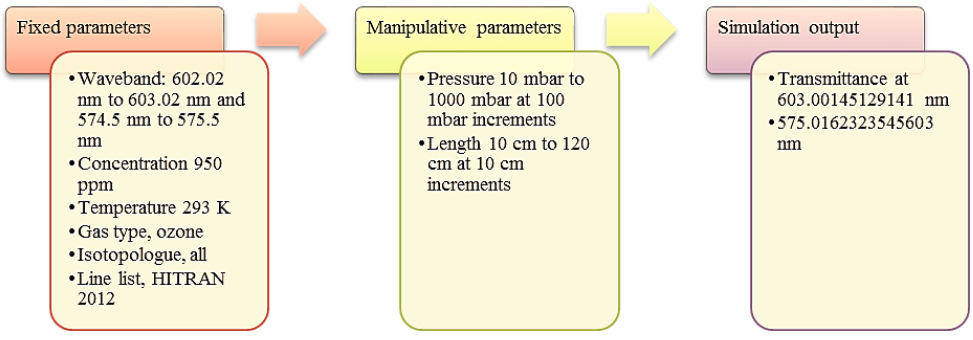

Figure 3. Simulation methodology using Spectralcalc.com simulator

4. RESULTS AND DISCUSSION

The results section is divided into two parts. In the first part discussions and results on the relationship between pressure and admittance are presented. In the second part, the results on pressure effect and optical path length on ozone gas absorption cross-section at 603 nm and 575 nm are presented. In our discussion, results obtained for pressure effect on ozone gas absorption cross-section at 603 nm and 575 nm for pressure values less than 100 mbar and greater than 100 mbar but less than 1000 mbar are novel to this work.

The effect of optical path length on transmittance for pressure values between 10 mbar and 1000 mbar is shown in Figures 4 and 5. At low-pressure values, there was a convergence towards a transmittance value of 1 for all gas cells. Transmittance reduces with increasing pressure and with an increase in gas length. The range of transmittance at 10 mbar was between 0.999856 to 0.999988 and 0.985714 to 0.998802 at 1000 mbar at 603 nm. Similarly, for 575 nm wavelength, at 10 mbar, the range of transmittance is 0.999867 to 0.999989 and 0.986798 to 0.998893 at 1000 mbar.

The simulation was carried out in stages. The first stage was at an interval of 100 mbar for all gas cells. The exception to this is between 10 mbar and 100 mbar. This is depicted in Figure 6 and Figure 7. Figure 6 and Figure 7 show the simulation results for the effect of variation in pressure and length of the gas cell on ozone gas absorption cross-section in the visible spectrum at 603 nm and 575 nm respectively. The initial simulation was between a pressure range of 10 mbar and 1000 mbar. The results show that the absorption cross-section for all gas cells increases from a pressure of 10 mbar until a maximum point which depends on the optical path length of the gas cell.

After the optimum or maximum point is attained, the absorption cross-section becomes a constant. Further simulations were carried out to obtain a precise optimum point for each gas cell and corresponding values of pressure at these points. Figure 6 and Figure 7 were further used to identify the region of the maximum position for each gas cell. The next stage simulation was at an interval of 10 mbar. Figures 8, 9, and 10 are for the wavelength of 603 nm. Figure 8 was obtained for lengths of 90 cm to 120 cm by simulating a pressure increment of 10 mbar between 10 mbar and 100 mbar. Figure 9 shows the simulation results at a pressure increment of 10 mbar between 10 mbar and 500 mbar for gas lengths of 20 cm to 80 cm.

Figure 10 is the simulation results for the gas cell of 10 cm. A simulation between 700 mbar and 1000 mbar, was at a step of 10 mbar. For 575 nm wavelength, similar simulations were carried out. Each gas cell was however treated separately with respect to the location of the maximum point identified in Figure 7. At 603 nm, the absorption cross-section for all gas cells considered at 10 mbar is approximately 5.1060×10^{-25} m^2/molecule while 5.1084×10^{-25} m^2/molecule is the absorption cross-section value at the maximum points. Similarly, at a wavelength of 575 nm, the absorption cross-section for all gas cells considered at 10 mbar is approximately 4.7160×10^{-25} m^2/molecule while 4.7182×10^{-25} m^2/molecule is the absorption cross-section value at the maximum points.

Table 1 shows the pressure values at the maximum absorption cross-section for each gas cell for both 603 nm and 575 nm wavelengths. Figure 11 shows the length of gas cells and corresponding values of pressures where the absorption cross-section became a constant value of 5.1058×10^{-25} m^2/molecule at 603 nm and 4.7158×10^{-25} m^2/molecule at 575 nm.

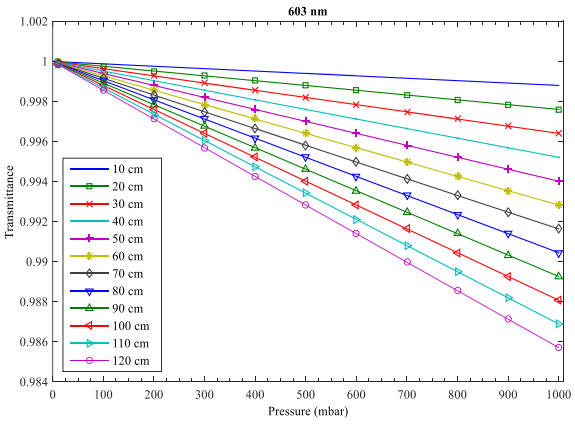

Figure 4. Effect of variation of optical path length and pressure on transmittance at 603 nm

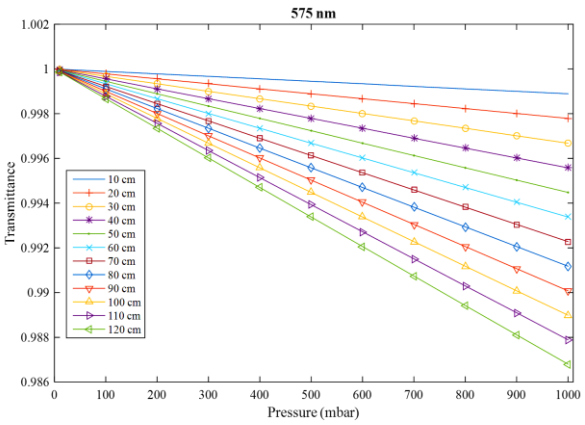

Figure 5. Effect of variation of optical path length and pressure on transmittance at 575 nm

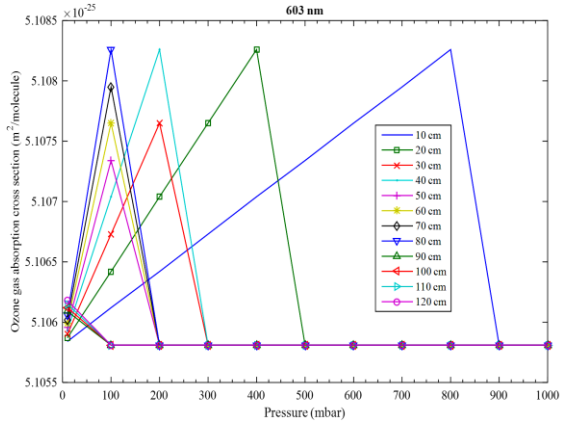

Figure 6. Effect of variation of optical path length and pressure (100 mbar) on ozone cross-section at 603 nm

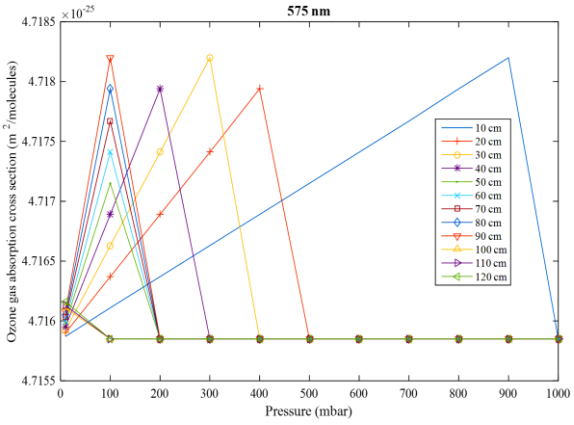

Figure 7. Effect of variation of optical path length and pressure (100 mbar) on ozone cross-section at 575 nm

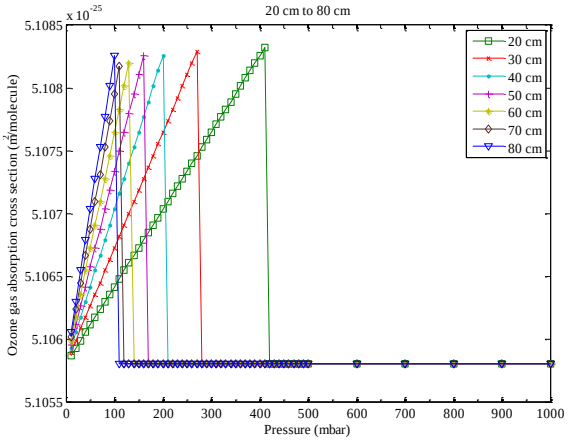

Figure 8. Effect of variation of optical path length and pressure (10 mbar) on ozone cross-section for 20 cm to 80 cm at 603 nm

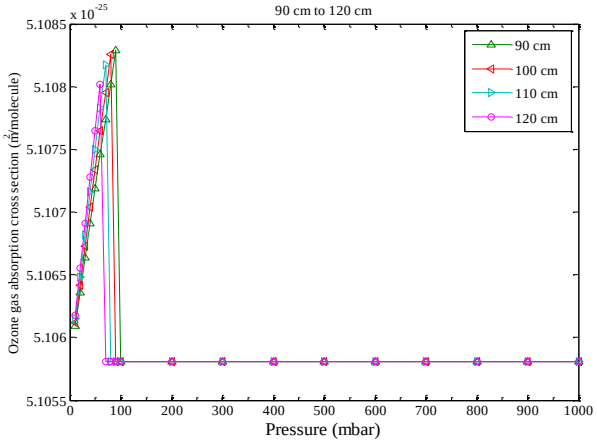

Figure 9. Effect of variation of optical path length and pressure (10 mbar) on ozone cross-section for 90 cm to 120 cm at 603 nm

Figures 12, 13, and 14, show the deviation of absorption cross-section in each gas cell from 5.18×10^{-25} m^2/molecule at 603 nm [22], [24]. The range of deviation in percentage is from 1.40% at the maximum points to 1.45% at the points where the absorption cross-section is constant. The percentage difference of 0.05% in deviation will be of significance for high accurate and high precision measurements of ozone gas measurements.

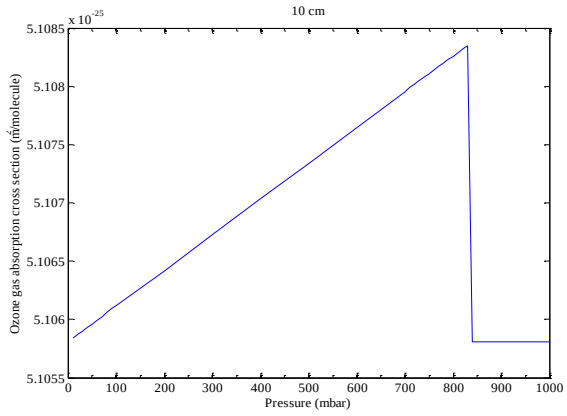

Figure 10. Effect of variation of optical path length and pressure (10 mbar) on ozone cross-section for 10 cm

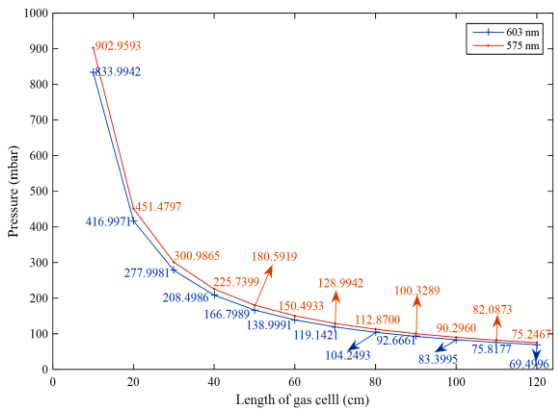

Figure 11. Pressures values for each gas cell where ozone absorption cross-section becomes constant value of 5.1058×10^{-25} m^2/molecule at 603 nm

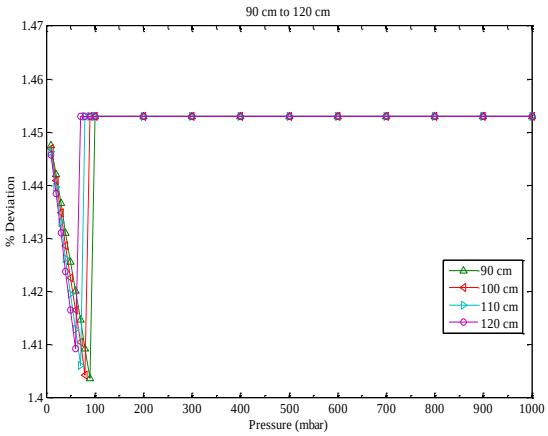

Figure 12. Deviation from absorption cross-section from 5.18×10^{-25} m^2/molecule at 603 nm for 90 cm to 120 cm

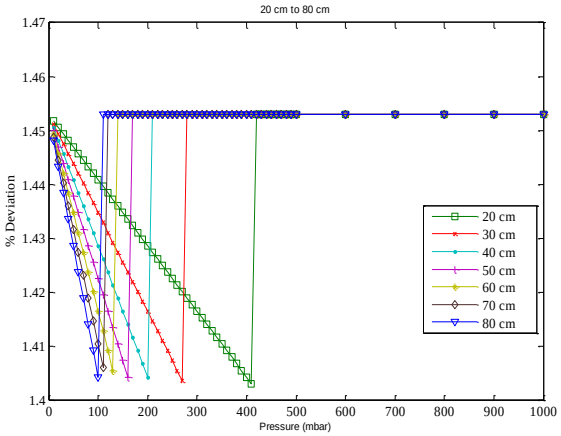

Figure 13. Deviation from absorption cross-section from 5.18×10^{-25} m^2/molecule at 603 nm for 20 cm to 80 cm

By comparing the pressure values obtained for both 603 nm and 575 nm, for each gas cell, 8.27% is the percentage difference of each corresponding value of either pressure value at peak points or pressure values at points where absorption cross-section becomes constant. This value is very close to the percentage difference of 8.82%, which is the percentage difference between the absorption cross-section of 5.18×10^{-25} m^2/molecule at 603 nm [22], [24] and 4.76×10^{-25} m^2/molecule [7], [32] at 576.96 nm. Thus, the absorption cross-section is wavelength-dependent. The last stage of the simulation was to identify the precise pressure value (up to four decimal points) at maximum points and pressure values where absorption cross-section became constant.

Table 1. Pressure values at maximum absorption cross-section for each gas cell

Values	Presssure (mbar)	Ozone absorption cross-section (m^2/molecule)	Presssure (mbar)	Ozone absorption cross-section (m^2/molecule)	Presssure (mbar)	Ozone absorption cross-section (m^2/molecule)
		10 cm		20 cm		30 cm
603 nm	833.9941	5.1084E^{-25}	416.9970	5.1084E^{-25}	277.9980	5.1084E^{-25}
575 nm	902.9592	4.7182E^{-25}	451.4796	4.7182E^{-25}	300.9864	4.7182E^{-25}
		40 cm		50 cm		60
603 nm	208.4985	5.1084E^{-25}	166.7988	5.1084E^{-25}	138.9990	5.1084E^{-25}
575 nm	255.7398	4.7182E^{-25}	180.5918	4.7182E^{-25}	150.4932	4.7182E^{-25}
		70 cm		80 cm		90 cm
603 nm	119.1420	5.1084E^{-25}	104.2492	5.1084E^{-25}	92.6660	5.1084E^{-25}
575 nm	128.9941	4.7182E^{-25}	112.8699	4.7182E^{-25}	100.3288	4.7182E^{-25}
		100 cm		110 cm		120 cm
603 nm	83.3994	5.1084E^{-25}	75.8176	5.1084E^{-25}	69.4995	5.1084E^{-25}
575 nm	90.2959	4.7182E^{-25}	82.0872	4.7182E^{-25}	75.2466	4.7182E^{-25}

For all lengths of optical gas cells considered, the common pressure value where the absorption cross-section becomes constant is 833.9942 mbar for 603 nm and 902.9593 mbar at 575 nm. The results obtained on pressure effect on ozone gas absorption cross-section at 603 nm and 575 nm for pressure values less than 100 mbar and greater than 100 mbar but less than 1000 mbar are novel to this work. Voigt *et al.* establish that for the 120 cm gas cell, ozone absorption cross-section was constant at both 100 mbar and 1000 mbar [10].

This in comparison to the results obtained for the 120 cm gas cell with our simulation shows very good agreement. A constant value of absorption cross-section for the 120 cm gas cell begins at 69.4996 mbar for 603 nm and 75.2467 mbar for 575 nm. This thus confirms other results obtained in this article. According to them, there was no variation in absorption cross-section ozone in relation to pressure due to the rather short lifetime ozone gas in the upper electronic states [10]. Constant ozone gas absorption cross-section or no pressure effect is attributed to upper electronics states of ozone which has a short lifetime [10].

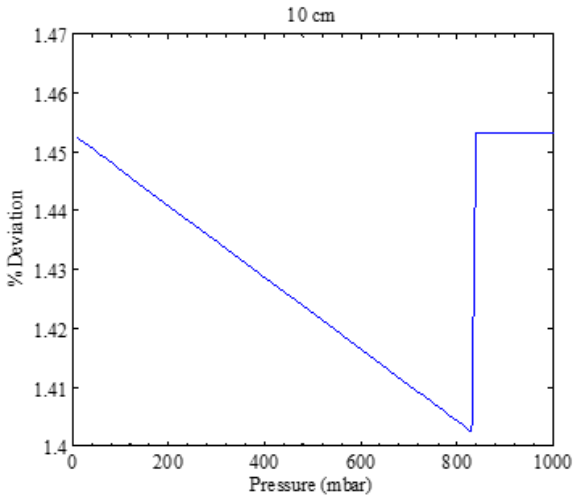

Figure 14. Deviation from absorption cross-section from 5.18×10^{-25} m^2/molecule at 603 nm for 10 cm

Similarly, in comparison with 5.23×10^{-25} m^2/molecule at 603 nm [6], the range of deviation in percentage is from 2.38% at the maximum points to 2.43% at the points where the absorption cross-section is constant. This also yields a percentage difference of 0.05%. Similarly, at a wavelength of 575 nm, range of deviation from 4.76×10^{-25} m^2/molecule [7], [29] in percentage is from 0.89% at the maximum points to 0.94% at the points where the absorption cross-section is constant. The percentage difference of 0.05% in deviation will be of significance for high accurate and high precision measurements of ozone gas measurements. Similarly, in comparison with 4.766×10^{-25} m^2/molecule at 575 nm [7], the range of deviation in percentage is from 1.01% at the maximum points to 1.06% at the points where the absorption cross-section is constant.

This also yields a percentage difference of 0.05%. The results thus obtained in this work compliment the work done previously by Marcus *et al.* in the UV [12] and that by Voigt *et al.* Hence, simultaneous effect of pressure and optical path length not previously available in the literature for pressures less than 100 mbar and greater than 100 but less than 1000 mbar is now made available through this work [29]. This is the novelty of this present work. In addition, efficient measurement of ozone gas as a greenhouse gas will promote and enhance the realization of green communication.

5. CONCLUSION

In this article, we have simulated absorption cross-section measurement for ozone a greenhouse gas in the visible spectrum at 603 nm and 575 nm peak wavelengths. The absorption cross-section obtained has shown the dependence of ozone gas absorption cross-section on pressure, optical path length, and sampling wavelength. Both optimum and constant values of ozone absorption cross-section occur at different pressure values depending on the optical path length of the gas cell and sampling wavelength. In complimenting the works of Marcus *et al.* and Voigt *et al.* on pressure effect on ozone gas absorption cross-section: it is seen from the results that pressure value at which pressure has no effect on ozone gas absorption cross-section for a 120 cm gas cell begins at 69.4996 mbar; that for a 10 cm gas cell begins at 833.9942 mbar at 603 nm. While at 575 nm, pressure value at which pressure has no effect on ozone gas absorption cross-section for a 120 cm gas cell begins at 75.2466 mbar; that for a 10 cm gas cell begins at 902.9593 mbar. Thus, the longer the optical path length, the more the effect of pressure is reduced. These results obtained on pressure effect on ozone gas absorption cross-section at 603 nm and 575 nm for pressure values less than 100 mbar and greater than 100 mbar but less than 1000 mbar are novel to this work. Results obtained are essentially relevant for high precision and high accuracy measurement of ozone gas absorption cross-section in relation to green communications.

ACKNOWLEDGEMENTS

The authors would like to thank Universiti Teknologi Malaysia (UTM) for sponsoring this work under Research University Grant (RUG) Scheme, grant no: 05J60 and 04H35. The Ministry of Higher Education (MOHE) Malaysia is acknowledged for provision of Fundamental Research Grant Scheme

(FRGS) grant no: 4F317 and 4F565. The Nigerian Education Trust Fund (ETF) is also acknowledged for the financial support giving through Tertiary Education Trust Fund (TET-Fund).

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