

# Optical Path Length, Temperature, and Wavelength Effects Simulation on Ozone Gas Absorption Cross Sections towards Green Communications

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**Abstract**—Ozone is a green house gas. Ozone absorption cross sections have been reported with discrepancies and inconsistencies. In this paper, simultaneous effects of the optical path length and temperature variations on ozone gas absorption cross sections are investigated at different wavelengths. HITRAN 2012, the latest available line list on spectralcalc.com simulator, is used in this study to simulate ozone gas absorption cross sections in relation to the simultaneous effects of the optical path length and temperature at the wavelengths of 603 nm and 575 nm. Results obtained for gas cells with the optical path length from 10 cm to 120 cm show that the decrease in temperatures from 313 K to 103 K results in the increase in ozone gas absorption cross sections. At wavelengths of 603 nm and 575 nm, the percentage increase of ozone gas absorption cross sections is 1.22% and 0.71%, respectively. Results obtained in this study show that in the visible spectrum, at constant pressure, ozone gas absorption cross sections are dependent on the temperature and wavelength but do not depend on the optical path length. Analysis in this work addresses discrepancies in ozone gas absorption cross sections in relation to the temperature in the visible spectrum; thus, the results can be applied to get optimal configuration of high accuracy ozone gas sensors.

**Index Terms**—Absorption cross sections, length, ozone, pressure, transmittance, visible spectrum.

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## 1. Introduction

Green communications are the technology directed towards the sustainability of environment and economy<sup>[1]</sup>. Ozone is a primary green house gas. Green house gases are associated with the risk of causing climate changes which results in earth warming<sup>[2]</sup>. Thus, accurate and adequate monitoring of green house gases like ozone is necessary. The ozone gas absorption cross sections are crucial for the accurate measurement of ozone gas concentration<sup>[3]</sup>. However, inconsistencies and discrepancies have been associated with ozone gas absorption cross sections in [4] to [6]. Above 10% discrepancies in absorption cross sections of ozone gas have been reported in [7] and [8]. The dependence of ozone gas absorption cross sections on the temperature was recently investigated by Serdyuchenko *et al.*<sup>[4]</sup>. The authors observed that it is obvious that ozone absorption data is not consistent. Their work was in the wavelength range from 213 nm to 1100 nm and the temperature range from 193 K to 293 K. Results obtained by the authors in the visible spectrum, the wavelength range of 450 nm to 700 nm showed that the decrease in the temperature between 293 K and 193 K results in a small increment (about 1%) in the ozone gas absorption cross sections around 600 nm wavelength<sup>[4]</sup>. This result, however, contradicts the result of El Helou *et al.*, who showed 3% and 6.7% decreases in ozone gas absorption cross sections with the decrease in the temperature between 223 K and 144 K<sup>[6]</sup> in the wavelength range of 540.54 nm to 645.16 nm. In view of these discrepancies, further work on the temperature effect on ozone gas absorption cross sections is inevitable. Furthermore, different lengths of gas cells have been used in the measurement of ozone gas concentration in the visible spectrum: 10 cm, 25 cm, 50 cm<sup>[5]</sup>, 70 cm<sup>[9]</sup>, and 120 cm<sup>[10]</sup>. Differences in the length of gas cells will result in differences in the total volume of gas cells. According to Charles's Law, at constant pressure, the volume of a fixed mass of gas is proportional to its absolute temperature<sup>[11],[12]</sup>; thus, the optical path length variation is examined in the way it affects ozone absorption cross sections in the visible spectrum at different temperatures. In

the literatures, accuracy<sup>[5]</sup>, resolution, and sensitivity<sup>[13]-[20]</sup> have been shown to be dependent on the optical path length. The novelty in this work is to establish the relation between the optical path length and temperature with ozone gas absorption cross sections at different wavelengths. While the absorption spectroscopy is the focus of this manuscript, other spectroscopic techniques for gas detection such as intra-cavity spectroscopy were emphasized in [21].

This paper is organized into five sections. Section 1 is an introduction. This provides background information on which the study is built. Section 2 is a fundamental review to ozone gas absorption cross sections in the visible spectrum. Section 3 focuses on the methodology adopted in this study. In Section 4, results obtained are discussed and analysed. Finally, in Section 5, conclusions are drawn based on the findings in Section 4.

## 2. Review of Ozone Gas Absorption Cross Sections in Visible Spectrum

The relevance of ozone gas absorption cross sections is demonstrated by several research activities devoted towards obtaining the right value of ozone gas absorption cross sections in the visible spectrum<sup>[8],[13],[22]-[24]</sup>. Griggs<sup>[22]</sup> in 1968 found out that the value of ozone gas absorption cross sections he obtained for the visible spectrum were in excellent agreement with Vigroux (5.18×10<sup>-25</sup> m<sup>2</sup>/molecule)<sup>[13],[23]</sup>. Thus, Griggs recommended the previous results obtained by Vigroux<sup>[23]</sup> for use in the Chappuis band<sup>[22]</sup>. Ozone gas has peak absorption in the visible spectrum; in 1988, Brion *et al.*<sup>[7]</sup> in their article reported that Amoroso *et al.*<sup>[25]</sup>, Vigroux<sup>[23]</sup>, and Inn and Tanaka<sup>[8]</sup> were in an agreement on the peak absorption of ozone gas in the visible spectrum at the wavelengths of 603 nm and 575 nm. Thus, simulation results in this work are compared with the peak absorption cross section at 603 nm and ozone gas absorption at 576.96 nm<sup>[7],[13]</sup>. This article investigates the relationship between the temperature and ozone gas absorption cross sections in the visible spectrum, thus, previous work on the temperature effect is also reviewed. Serdyuchenko *et al.*<sup>[4]</sup>, El Helou *et al.*<sup>[6]</sup>, Burrows *et al.*<sup>[26]</sup>, and Burkholder and Talukdar<sup>[27]</sup> investigated the dependence of ozone gas absorption cross sections on the temperature in the Chappuis band. The work by Serdyuchenko *et al.*<sup>[4]</sup> and El Helou *et al.*<sup>[6]</sup> has been discussed in Section 1. Burrows *et al.* reported that ozone gas absorption cross sections decreased with decreasing temperatures at the wavelength range of 370 nm to 500 nm<sup>[26]</sup>. However, the authors observed an increase in ozone gas absorption cross sections as the temperature decreased at wavelengths of above 650 nm<sup>[26]</sup>. Burkholder and Talukdar in their work recorded a variation of less than 1% in ozone gas absorption cross sections between 550 nm and

650 nm wavelengths<sup>[27]</sup>. Measurements of ozone and other trace gases were dependent on the accurate value of absorption cross sections in [28].

## 3. Simulation Software and Methodology

The methodology adopted is online simulation via www.spectralcalc.com. The simulation is for high resolution spectral modelling. HITRAN 2012—the latest available line list on the spectralcalc.com simulator is used in this study to simulate ozone gas absorption cross sections in relation to the effects of varying the temperature and optical path length at the wavelengths of 603 nm and 575 nm. The ranges of the temperature and optical path length considered are between 103 K and 313 K and between 10 cm and 120 cm, respectively.

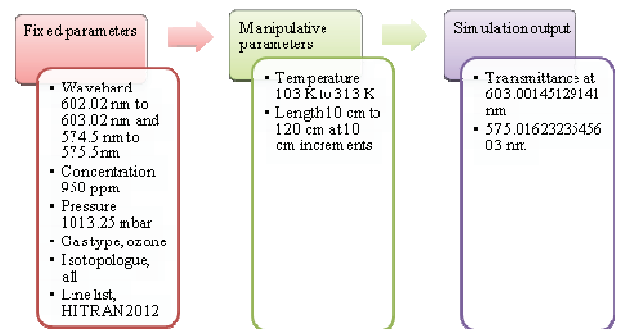


Fig. 1. Summary of spectralcalc.com simulation methodology.

The fixed parameters as shown in Fig. 1 include the wavelength ranges from 602.02 nm to 603.02 nm and 574.5 nm to 575.5 nm, concentration at 950 ppm, and one atmosphere pressure. Ozone gas is selected as the gas of choice. All isotopologues of ozone gas are considered. The output from the simulator is transmittance at 603 nm (actual value is 603.0105702572658 nm) and that at 575 nm (actual value is 575.0162323346030 nm). The methodology is summarized in Fig. 1. The ozone gas absorption cross section  $\sigma$  and deviation  $\Delta\sigma$  are computed using (1) and (2) earlier<sup>[29],[30]</sup>.

$$\sigma = -\frac{10^6 RT_p}{c_{\text{ppm}} N_A PL} \ln T \quad (1)$$

where  $c_{\text{ppm}}$  is the ozone concentration in ppm.  $R$  is the ideal gas constant in atm·m<sup>3</sup>·mol<sup>-1</sup>·K<sup>-1</sup>.  $T_p$  is the temperature in K.  $\sigma$  is the absorption cross section in m<sup>2</sup>/molecule.  $N_A$  is Avogadro's constant in molecule/mol.  $P$  is the pressure in atmosphere atm.  $L$  is the optical path length. And  $T$  is the transmittance.

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

where  $\sigma$  is the ozone absorption cross section at 603 nm.  $\sigma_w$  is the ozone absorption cross section obtained in this work.

## 4. Results and Discussion

Fig. 2 and Fig. 3 show the effects of the temperature and optical path length variations on transmittance for one atmosphere pressure at the wavelengths of 603 nm and 575 nm. The decrease in temperatures from 313 K to 103 K results in a decrease in the transmittance for each gas cell considered. At 603 nm, the decrease is 0.24% and 2.87% for the optical path length of 10 cm and 120 cm, respectively. Similarly, at 575 nm, the decrease is 0.22% for 10 cm and 2.63% for 120 cm, respectively. The longer the gas cell, the higher the decrease in the transmittance is with decreasing temperatures. Also, at a specific temperature, the light transmittance generally decreases with the increase in the optical path length. At 603 nm with the optical path length increased from 10 cm to 120 cm, the decrease in transmittance is 3.78% for the temperature of 103 K and 1.24% for 313 K, respectively. Similarly, at 575 nm with the optical path length increased from 10 cm to 120 cm, the decrease in transmittance is 3.47% for 103 K and 1.15% for 313 K, respectively.

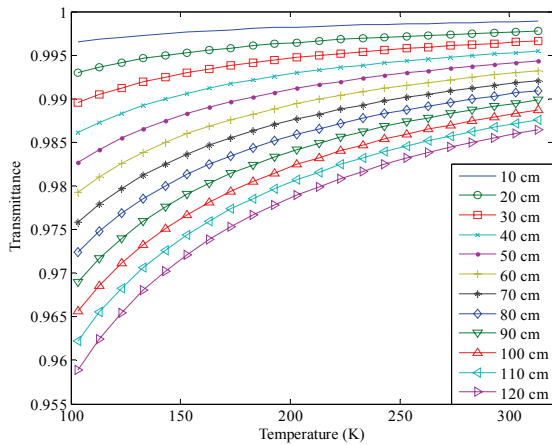


Fig. 2. Effects of the optical path length and temperature variations on transmittance at 603 nm.

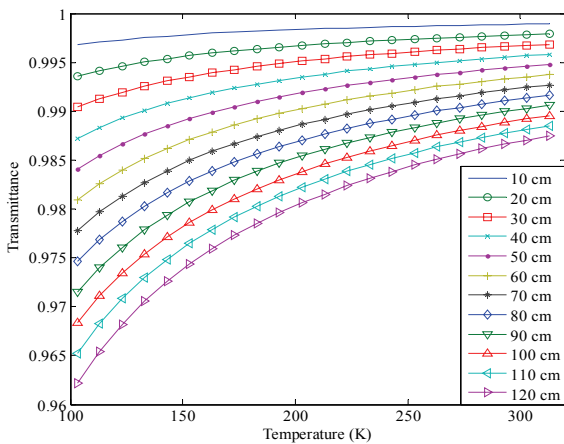


Fig. 3. Effects of the optical path length and temperature variations on transmittance at 575 nm.

Fig. 4 shows the temperature and optical path length effects on ozone gas absorption cross sections at the

wavelengths of 603 nm and 575 nm. Increasing the optical path length from 10 cm to 120 cm has the same effect on ozone gas absorption cross sections. Hence, the effect of the optical path length for each gas cell is overlapping for wavelengths 603 nm and 575 nm, respectively. There are three different responses observed as the temperature is decreased from 313 K to 103 K. Between 313 K and 293 K, the absorption cross sections are a constant value of  $5.1058 \times 10^{-25}$  m<sup>2</sup>/molecule at 603 nm and  $4.7158 \times 10^{-25}$  m<sup>2</sup>/molecule at 575 nm, respectively. For the temperature range of 293 K to 203 K the absorption cross sections are increased from  $5.1058 \times 10^{-25}$  m<sup>2</sup>/molecule to  $5.1569 \times 10^{-25}$  m<sup>2</sup>/molecule at 603 nm and from  $4.7158 \times 10^{-25}$  m<sup>2</sup>/molecule to  $4.7468 \times 10^{-25}$  m<sup>2</sup>/molecule at 575 nm, respectively. For the temperature range of 203 K to 103 K, the absorption cross sections are increased from  $5.1569 \times 10^{-25}$  m<sup>2</sup>/molecule to  $5.1691 \times 10^{-25}$  m<sup>2</sup>/molecule at 603 nm and from  $4.7468 \times 10^{-25}$  m<sup>2</sup>/molecule to  $4.7495 \times 10^{-25}$  m<sup>2</sup>/molecule at 575 nm, respectively. For the temperature range of 193 K to 103 K, the absorption cross sections are a constant value of  $5.1691 \times 10^{-25}$  m<sup>2</sup>/molecule at 603 nm and  $4.7495 \times 10^{-25}$  m<sup>2</sup>/molecule at 575 nm, respectively.

The decrease in temperatures from 313 K to 103 K shows an increase in ozone gas absorption cross sections. At the wavelength of 603 nm, the increased percentage is 1.22%. At 575 nm, the increased percentage is 0.71%. A difference of 0.51% shows that the variation of absorption cross sections is wavelength dependent.

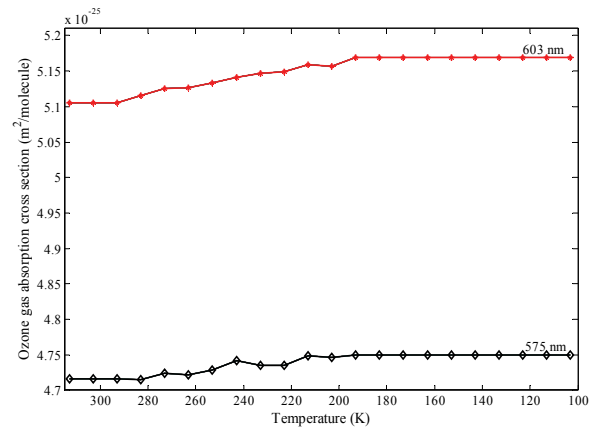


Fig. 4. Effects of the temperature and optical path length on ozone absorption cross sections.

In comparison with previous work, the results are in a good agreement with Serdyuchenko *et al.*<sup>[4]</sup>, who obtained a similar increment of 1%. The increase in the ozone gas absorption cross sections is due to the temperature variation. The electronic ground state, vibrational and rotational distribution states change with temperatures<sup>[31]</sup>. Nonlinearity behaviour is more pronounced at 575 nm, which is observed at temperatures 263 K, 233 K, and 203 K. The peak absorption wavelength of 575 nm in comparison with 603 nm has lower absorption of ozone gas (approximately 8% lower).

The results obtained are further compared with the work of Brion *et al.* ( $5.23 \times 10^{-25} \text{ m}^2/\text{molecule}$ )<sup>[7]</sup> and Vigroux *et al.* ( $5.18 \times 10^{-25} \text{ m}^2/\text{molecule}$ )<sup>[13],[23]</sup> at 603 nm and with Brion *et al.* ( $4.766 \times 10^{-25} \text{ m}^2/\text{molecule}$ )<sup>[7]</sup> and Hearn ( $4.76 \times 10^{-25} \text{ m}^2/\text{molecule}$ )<sup>[32]</sup> at 575 nm. Fig. 5 and Fig. 6 show the deviation with the increase in temperatures from 103 K to 313 K.

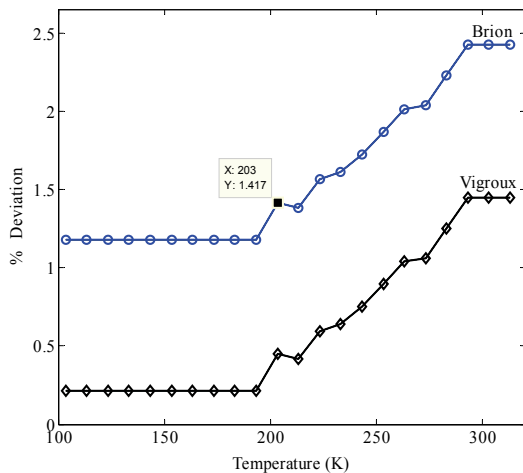


Fig. 5. Deviation of the absorption cross sections from  $5.18 \times 10^{-25} \text{ m}^2/\text{molecule}$  and  $5.23 \times 10^{-25} \text{ m}^2/\text{molecule}$  at 603 nm.

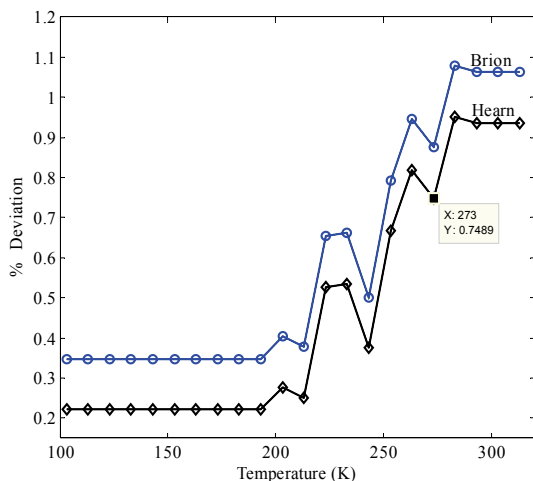


Fig. 6. Deviation from the absorption cross sections of  $4.76 \times 10^{-25} \text{ m}^2/\text{molecule}$  and  $4.766 \times 10^{-25} \text{ m}^2/\text{molecule}$  at 575 nm.

In Fig. 5 the range of deviation at 603 nm is from 0.21% to 1.45% in comparison with that of Vigroux *et al.* and 1.18% to 2.43% in comparison with that of Brion *et al.* Similarly, in Fig. 6, the range of deviation is from 0.22% to 0.94% and 0.35% to 1.06% when compared with those of Hearn and Brion *et al.*, respectively.

In relation to green communications, the results in this study can be applied to enhance the accurate measurement of ozone gas, which will in turn, facilitate adequate monitoring of ozone gas impacts on the environment.

## 5. Conclusions

The temperature and optical path length effects on the ozone gas absorption cross sections were investigated in the

visible spectrum at the wavelengths of 603 nm and 575 nm. The decrease in temperatures from 313 K to 103 K showed a decrease in transmittance for each gas cell considered. The longer the gas cell, the higher the decrease in transmittance was along with the decrease in temperatures. There was an increase in the absorption cross sections along with the decrease in temperatures. The decrease in the absorption cross sections was 1.22% at 603 nm and 0.71% at 575 nm, respectively, which shows the dependence on wavelengths. The increase in absorption was the same for all optical path lengths (10 cm to 120 cm) considered. Thus, the results obtained in this work show that at constant pressure, the ozone gas absorption cross sections are dependent on the temperature and wavelength, but are independent on the optical path length. The study addresses discrepancies that arise in the ozone gas measurement in relation to the temperature effect on the ozone gas absorption cross sections. These results will enhance the accurate measurement and monitoring of ozone gas as a green house gas. It is recommended that the results obtained need to be further verified through experiments.

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