Absorption Cross Section Simulation: a Preliminary Study of Ultraviolet Absorption Spectroscopy for Ozone Gas Measurement

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1.0 INTRODUCTION

“Good up high, bad nearby” is the description of ozone by Environment Protection Agency of United States in 2003 [1]. This is because ozone at stratosphere protects earthy lives from harmful ultraviolet rays from the sun, but ozone at troposphere is a pollutant. Ozone, O\textsubscript{3} is formed by combination of three oxygen atoms. Although ozone is colourless at low concentration, it has distinctive smell. Breathing in ozone is bad for respiratory system [2]. In addition, ozone speeds up paint wear and damages vegetation [3]. Despite that, ozone, if is used properly, can be useful due to its strong oxidising property and environmentally friendly features. Ozone can be applied in gas phase or made soluble in water. The lower the temperature, the higher the solubility [4]. The unstable molecule quickly reverts to oxygen; therefore, it must be generated on site. For instance, ozone may be generated via dielectric barrier discharge [5] on demand.

Abstract

Preliminary study to measure gaseous ozone concentration using ultraviolet absorption spectroscopy is presented. Firstly, background of ozone is introduced. Next, fundamental theory behind ultraviolet absorption spectroscopy is discussed based on Beer-Lambert’s Law and absorption spectrum of ozone. After that, absorption cross section of ozone is simulated via spectralcalc.com. Temperature of system is varied. Peak absorption cross section and peak absorption wavelength are found to be 1.166 \times 10^{-21} \text{ m}^2 \text{ molecule}^{-1} and 255.376 \text{ nm} respectively at 300 K and 0 torr. Absorption cross section in ultraviolet region shows slight variation of at most 1.286 per cent when temperature is changed from 200 K to 300 K. Around room temperature, peak absorption cross section simulated in current work is consistent with previous work, because relative error is found to be small in between 1.630 per cent and 3.087 per cent. Unlike previous work, absorption of light by ozone is detected in ultraviolet region only due to weak absorption in visible region.

Keywords: Absorption spectroscopy; absorption cross section; ultraviolet; ozone gas; spectralcalc.com

Abstrak

Kajian awal untuk mengukur kepekitan gas ozon menggunakan spektroscopy penyerapan ultrawe found to be slightly different with previous work, which was conducted at room temperature. However, around room temperature, peak absorption cross section simulated in current work is consistent with previous work, because the relative error is found to be small in between 1.630 per cent and 3.087 per cent. Unlike previous work, absorption of light by ozone is detected in ultraviolet region only due to weak absorption in visible region.

Kata kunci: Spektroskopi penyerapan; keratan rentas penyerapan; ultrawe nuf; gas ozon; spectralcalc.com

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2.0 PRINCIPLE OF MEASUREMENT

Beer-Lambert’s Law is the fundamental theory behind ultraviolet absorption spectroscopy. Typical experiment setup can be found in literature [6]. Light emitted from a broadband light source is partially absorbed by ozone and received by a spectrometer. The relationship is found in the literature [7]:

\[ A = \alpha N_l c s = \varepsilon \omega c I = \ln(I_0/I) = -\ln T \]  

(1)

\( A \) is optical density, optical depth or absorbance  
\( \sigma \) is absorption cross section of sample in m\(^2\) molecule\(^{-1}\)  
\( N_l \) is Avogadro’s constant, 6.022 \times 10\(^{23}\) molecule mol\(^{-1}\)  
\( c \) is concentration of sample gas of interest in mol m\(^{-3}\)  
\( \omega \) is optical path length of sample  
\( \varepsilon \) is molar absorption coefficient in m\(^2\) mol\(^{-1}\)  
\( I_0 \) is light intensity on sample  
\( I \) is light intensity through sample  
\( T \) is transmittance of light

Based on Equation 1, absorbance (\( A \)) is dependent on concentration (\( c \)), absorption cross section (\( \sigma \)) and optical path length (\( \omega \)). These three parameters causes intensity of light to decrease from \( I_0 \) to \( I \).

2.1 Absorption Spectrum of Ozone

According to Figure 1, absorption spectrum of ozone has a large peak in ultraviolet region (Hartley band) and a small in peak visible region (Chappuis band). Absorption cross section of ozone in visible region (4.14 \times 10^{-25} m\(^2\) molecule\(^{-1}\)) [9] is reported to be more than two thousand times smaller than typical absorption cross section of ozone in ultraviolet region. According to Table 1, peak absorption wavelength in ultraviolet region is typically selected at mercury resonance wavelength at 253.65 nm [10, 11, 12, 13, 14] Absorption cross section in ultraviolet region that are applied previously range from 1.13 \times 10^{-21} m\(^2\) molecule\(^{-1}\) [10] to 1.147 \times 10^{-21} m\(^2\) molecule\(^{-1}\) [14]. This shows disagreement among different authors. This poses difficulty to researcher to select appropriate absorption cross section to calculate ozone concentration accurately using Equation 1. Conducting experiment at peak absorption wavelength is important so that sensor is sensitive to concentration change. Therefore, primary study of ozone sensor is dedicated to simulate peak absorption cross section via spectralcalc.com. The software is a subscription based online high resolution spectral modelling developed by GATS Inc. [15].

3.0 SIMULATION METHODOLOGY

Figure 2 shows input of spectralcalc.com to calculate absorption cross section. Firstly, line list browser in spectralcalc.com is clicked. In this simulation, HITRAN 2008 cross section database is selected. Gas selected for simulation is ozone gas only. Spectral range set for the simulation is from 245.5 nm to 700 nm to determine absorption cross section of ozone in both ultraviolet and visible regions. In the simulator, pressure is fixed at 0 torr. Temperature of gas is set at 300 K. Then, simulation is repeated for temperature at 280K, 260K, 240K, 220K and 200 K respectively.

![Figure 2](image)

**Figure 2** Graphic user interface of line list browser in spectralcalc.com

3.0 RESULTS AND DISCUSSIONS

Simulation results are tabulated in Table 1 and illustrated in Figure 3, Figure 4 and Figure 5 as follow:

![Figure 3](image)

**Figure 3** Absorption cross section per molecule in logarithmic scale of ozone versus wavelength from 245.5 nm to 700 nm at 300 K and 0 torr

Figure 3 shows simulation result in current work. Absorption cross section in ultraviolet region is strongly detected. Compared to previous work in Figure 1 [8], peak at visible region is not noticeable in current work. This is because absorption cross section in ultraviolet region is very much higher than that of visible region.

![Figure 4](image)

**Figure 4** Graph of peak absorption cross section of gaseous ozone versus temperature at pressure of 0 torr
Figure 4 shows the higher the temperature, the lower the absorption cross section. The finding is consistent with previous work [10, 12, 16]. Deviation between maximum point ($\sigma_{200K} = 1.181 \times 10^{-21} \text{ m}^2 \text{ molecule}^{-1}$) and minimum point ($\sigma_{300K} = 1.166 \times 10^{-21} \text{ m}^2 \text{ molecule}^{-1}$) is 1.286 per cent. It is calculated via ($\sigma_{300K} - \sigma_{200K})/\sigma_{200K} \times 100$, where $\sigma_{200K}$ and $\sigma_{300K}$ are absorption cross sections at 200 K and 300 K respectively. Therefore, we conclude that peak absorption cross sections of ozone in ultraviolet region stay almost constant within temperature range from 200 K to 300 K. The finding agrees well with previous work [10, 12] (deviation of at most 1 per cent from 218 K to 298 K). Figure 5 shows peak absorption wavelengths are very close to each other from 200 K to 300 K. The values range from 255.271 nm to 255.48 nm and has mean of 255.34 nm. This agrees well with literature [10, 12, 16] that temperature dependence at Hartley band is small.

Table 1 shows absorption cross section simulated at 300 K in current work ($1.166 \times 10^{-21} \text{ m}^2 \text{ molecule}^{-1}$) is comparable to that of previous work at room temperature. Absorption cross section in literature [14] ($1.147 \times 10^{-21} \text{ m}^2 \text{ molecule}^{-1}$) is in close agreement with current work. Error of previous work relative to current work ranges from 1.630 per cent to 3.087 per cent. Absorption cross section obtained in current work is slightly larger than previous work. The discrepancy may be due to difference in temperature in current work simulation and previous work experiment. Hence, we conclude that ozone has strong absorption in ultraviolet region at 300 K, particularly at wavelength 255.376 nm.

### 4.0 Further Work

Further work is required to verify simulated peak absorption cross section of ozone via experiment. Simulation is done at 0 torr, but experiment may not be practically done at vacuum. Furthermore, temperature of actual experiment may vary from simulation temperature, 300 K. Peak absorption wavelength and peak absorption cross section to be obtained via experiment are expected to deviate slightly from simulation due to temperature and pressure difference.

### 5.0 Conclusion

In conclusion, simulation of ozone absorption cross section via spectralcalc.com is done. Simulation results show peak absorption cross section is $1.166 \times 10^{-21} \text{ m}^2 \text{ molecule}^{-1}$ at 255.376 nm, 300 K and 0 torr. Deviation of absorption cross section is at most 1.286 per cent when temperature is changed from 300 K to 200 K. Temperature effect at Hartley band is negligible as long as ozone is measured at peak absorption wavelength near average of 255.34 nm. Absorption cross section simulated in current work is in close agreement with previous work, due to small relative error of 1.630 per cent to 3.087 per cent. Current work suggests measurement of ozone in ultraviolet region, because absorption cross section of ozone in visible region is too small to be noticed in simulation. Validity of absorption cross sections simulated in current work should be further verified via experiment.

<table>
<thead>
<tr>
<th>Researchers</th>
<th>Temperature (K)</th>
<th>Peak absorption wavelength (nm)</th>
<th>Peak absorption cross section (m$^2$ molecule$^{-1}$)</th>
<th>Relative error (%)$^*$</th>
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<tbody>
<tr>
<td>[10]</td>
<td>295</td>
<td>253.65</td>
<td>$1.13 \times 10^{-21}$</td>
<td>3.087</td>
</tr>
<tr>
<td>[12]</td>
<td>295</td>
<td>253.65</td>
<td>$1.1305 \times 10^{-21}$</td>
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<tr>
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<td>293</td>
<td>253.65</td>
<td>$1.137 \times 10^{-21}$</td>
<td>2.487</td>
</tr>
<tr>
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<td>295</td>
<td>253.65</td>
<td>$1.147 \times 10^{-21}$</td>
<td>1.630</td>
</tr>
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<tr>
<td></td>
<td>200</td>
<td>255.31</td>
<td>$1.181 \times 10^{-21}$</td>
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</tr>
</tbody>
</table>

$^*$ $\sigma_{200K}$ is absorption cross section in previous work experiment. $\sigma_{300K}$ is absorption cross section in current work simulation at 300K via spectralcalc.com
Acknowledgement

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References


