Behaviour of Ozone Absorption Cross Section to Change in Optical path length and Pressure in the UV

By

J. A. Onyeodili, P. Enenche, M. David, J. A. Abolarinwa, and H. B. Salahu
Department of Telecommunication Engineering,
School of Electrical Engineering Technology,
Federal University of Technology Minna, Nigeria
Email: jacmakeliz@yahoo.com1

ABSTRACT
The effect of optical path length (OPL) and pressure variation on the ozone gas absorption cross section (OACS) is been reported. The current available line list on the spectralcalc online simulator tool was used to simulate the results obtained. Simulation results show that at 255.442 nm where the absorption of light is at its peak, the OACS maintained a value of $1.148E-21\ cm^2/molecule$ *as the pressure was changed successively from 0.1 to 3.0 atm while the OPL is increased from 0.75 cm through 130 cm. However, at a higher wavelength of 296.73nm where light absorption is weakest in the UV, both OPL and pressure variation had no effect on the OACS as it maintained a constant value of* $6.156E-23\ cm^2/molecule$*. Therefore, OACS is independent on pressure and OPL.*

Key words: Absorption cross section, pressure, optical path length, Optical absorption spectroscopy and transmittance

INTRODUCTION

Photons are known to travel faster than electrons. In the previous century electronics was the order of the day just as photonics is making much waves in this 21st century. It uses the application of light to arrive at certain desired outcome [1]. Hence, photonics can be used for the measurement of several gas concentrations [2].

Ozone gas is one of the major determinant of the greenhouse effect. It is found majorly in the stratosphere where it acts as a sunshade that prevents harmful ultraviolet radiation from reaching earth's inhabitors, as well as in the troposphere causing harm to bodies in the earth surface [3]. The oxidizing property of ozone is the reason for the harzadious effects it places on earth's bodies as well as plants and animal. This of course results in environmental pollution [4].

Therefore, there is the need to accurately measure and monitor the concentration of ozone gas in the troposphere. Currently, the National Air Quality Standard (NAQS) are responsible for setting threshhold limits beyound which the atmospheric ozone concentration must not exeed to maintain good environmental sanity [5].

Knowing the harzardious effect of tropospheric ozone, Green Communication has stepped in to reduce the atmospheric ozone content so as to protect humman life. Green communication helps to provide relevant data set that can foster accurate concentration measurement of atmospheric ozone [6].

Achieving accuracy in the concentration measurement of ozone gas for excellent atmospheric monitoring is not possible without the provision of adequate value of ozone absorption cross section (OACS). It is so indispensable in the measurement of gas concentration at specific pressures and temperatures [7]. Globally, the OACS proposed by [8] has been very vital for the monitoring of atmospheric ozone [9]. Earlier works carried out on the proposing of OACS [7] [10] [11] [12] [13] and [14].

PRESSURE EFFECT ON OZONE ABSORPTION CROSS SECTION

Absorption cross section of ozone has been known not to depend on pressure. Within absorption wavelengths of 230 – 850 *nm*, varying the pressure from 100 to 1000 *mbar*, was found to have zero effect on the OACS [15]. Likewise at an optical path length of 20 *cm*, Marcus reported the effect of varying pressure on the ozone gas absorption cross section. With temperature fixed at 300 *K*, it was observed that at 255.442nm, 1.148×10^{-21} (m^2/mol) is the maximum OACS on which the variation of pressure from 0.1 to 3.0 *atm* (≃100 – 3000 *mbar*) had no effect on it. However, optical path length was not varied alongside with the pressure [16]. Measurement of ozone was found to be highly accurate at high pressures when longer optical path lengths are used at 296.73 *nm* as well as 302.15 *nm* [8].

OPTICAL PATH LENGTH AND CONCENTRATION EFFECT ON OZONE ACS

Optical path length is the same as gas cell length. Therefore, the length of the gas cell length is equivalent to the optical path length. If the length of a gas cell is 10 *cm*, then the optical path length is 10 *cm* likewise. Research have shown that shorter gas cell lengths are suitable for high concentration ozone measurement which indicates how sensitive a sensor is [2] [18] [23]. The choice of the optical path length is wavelength dependent and while it is true that shorter path length is good for high concentration measurement, longer path length is suitable for lower concentration measurement [2]. Various optical path lengths that have been used for ozone concentration measurements. From the table you will discover that shorter optical path lengths such 0.75cm to 10 could measure higher concentrations [8] [17] [18], while longer ones could detect lower concentration as well small changes in concentration [7] [19] [20] and [21]. Therefore, since optical path length choice could affect ozone concentration measurement, then there is the need to investigate the way changing path length affects the OACS.

METHODOLOGY

The Model gives the flow of the simulation process. The input parameters, both variable and fixed are expressed by equations. The simulation shows the varying effect of pressure on the OACS at fixed optical path length. For each optical path length (0.75 – 130 *cm*), the pressure will be varied from 0.1 – 3.0 *atm*. While certain parameters such as temperature and concentration are held constant at 298 *K* (being room temperature) and 950 *ppm*. This concentration was carefully chosen to be 950 *ppm*. The reason is shorter 0.75 *cm* is suitable for high concentration measurement while longer path length effectively measures low concentration. The output of the spectralcalc is transmittance. This transmittance value will then be used to calculate the absorption cross section and then evaluation on how pressure and path length variation can be done. The simulation was carried out for $255.442\ and\ 296.73nm$ respectively in response to the varied effects of pressure and Path-length at 0.1 – 3.0 atm and 0.75cm to 130cm.

Spectralcalc.com simulation

These are the input parameters required for the simulation process at peak and week absorption wavelengths 255.442 and 296.73nm respectively.

255.442nm spectral range: 0.255 to 0.255662 μm

296.73nm spectral range: 0.296 to 0.296957μm

Fixed parameters

Temperature: $T = 298K$,

Concentration: $C = 950ppm$

Variable parameters

Pressure: $P = 0.1\ to\ 3.0\ atm$, 0.1 step size

Optical path length: $l = 0.75\ to\ 130\ cm$

Gas: O_3

Line List: *HITRAN2012* available on the spectralcalc.com [25]

Mathematical Model: Absorption cross section response to pressure

The methodology adopted to carry out this work is the optical absorption spectroscopy. This method is generally governed by the Beer-Lambert's equation given by equation 3.1, [22].

$$-lnT_r = \frac{\sigma N_A Plc}{10^6 RT}$$

(3.1)

But the transmittance (T_r), can be expressed as;

$$T_r = \frac{I_t}{I_o}$$

(3.2)

Being that our focus is to determine the response of the OACS (σ) to both varying temperature and optical path length, we made it the subject of the relation as shown in equation 3.3 below.

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

(3.3)

Substitute equation 3.2 into 3.3 we get;

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

(3.4)

The range of pressure over which the OACS response would be determined is from 0.1 atm – 3.0 atm. Now, for each optical path length (l) starting from 0.75 cm to 130 cm, the pressure is varied over 30 pressures with its maximum and minimum values as 0.1 atm – 3.0 atm respectively.

Where; $\sigma_{0.1}$ and $\sigma_{3.0}$ are the OACS at 0.1 atm – 3.0 atm respectively, $P_{0.1}$ and $P_{3.0}$ are the minimum and maximum pressures, $T_{r_{0.1}}$ and $T_{3.0}$ are the transmittances at 0.1 atm and 3.0 atm at a fixed optical path length (l_f), $\Delta\sigma$ is the resultant change in the ACS as the pressure is varied from 0.1 atm to 3.0 atm, R is the ideal gas constant: $8.205746 \times 10^{-5}\ (atm\, m^3/mol \times K)$, N_A is Avogadro's constant: $6.02214199 \times 10^{23}\ (molecule/mol)$.

For each optical path length, equations (3.5) and (3.6) shows the OACS at the minimum and maximum values of pressure.

$$\sigma_{0.1} = -\frac{10^6 RT}{c \times N_A \times P_{0.1} \times l_f} \times l_n T_{r_{0.1}}$$

(3.5)

$$\sigma_{3.0} = -\frac{10^6 RT}{c \times N_A \times P_{3.0} \times l_f} \times l_n T_{r_{3.0}}$$

(3.6)

To compute the total change the ozone absorption cross section, equation 3.7 does that.

$$\Delta\sigma = \frac{\sigma_{3.0}-\sigma_{0.1}}{\sigma_{0.1}} \times 100$$

(3.7)

We then substitute the equivalents of $\sigma_{0.1}$ and $\sigma_{3.0}$ in equations 3.5 and 3.6 into equation 3.7

$$\Delta\sigma = \left(\frac{l_n T_{r_{3.0}}}{P_{3.0}} - \frac{l_n T_{r_{0.1}}}{P_{0.1}}\right)\frac{P_{0.1}}{l_n T_{r_{0.1}}} \times 100$$

(3.8)

By further simplifying equation 3.8, we have the equation 3.9 which is the model that expresses the pressure effect on the OACS at each given optical path length.

$$\Delta\sigma = \left(\frac{P_{0.1} l_n T_{r_{3.0}}}{l_{130} l_n T_{r_{0.1}}} - 1\right) \times 100$$

(3.9)

Absorption Cross Section Response to Optical Path Length

From equation 3.4 above, we can also derive the change in the OACS as the optical path length was varied from 0.75 cm to 130 cm for each pressure ranging from 0.1 atm – 3.0 atm as follows; Equations 3.10 and 3.11 gives the OACS 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 OACS 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 0.75 cm and 130 cm at a fixed pressure (P_f), and $\Delta\sigma$ is the resultant change in the OACS as the path length is varied from 0.75 cm to 130 cm.

$$\sigma_{0.75} = -\frac{10^6 RT_f}{c \times N_A \times P_f \times l_{0.75}} \times l_n T_{r_{0.75}}$$

(3.10)

$$\sigma_{130} = -\frac{10^6 RT_f}{c \times N_{A \times P_f} \times l_{130}} \times l_n T_{r_{130}}$$

(3.11)

To determine the total resulting change in the ACS, equation 3.13 does that.

$$\Delta\sigma = \frac{\sigma_{130}-\sigma_{0.75}}{\sigma_{0.75}} \times 100$$

(3.12)

Further substitution of the equivalents of $\sigma_{0.75}$ and σ_{130} in equations 3.10 and 3.11 into equation 3.12 results in equation 3.13. Simplifying further we get,

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

(3.13)

By expanding equation 3.13, we then arrive at equation 3.14 which is the model that mathematically explains the optical path length effect on OACS.

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

(3.14)

RESULTS AND DISCUSSIONS

Pressure and optical path length effects on OACS at 255.442nm

This work was focused at reporting the effects that pressure and optical path lengths variation have on the OACS. The pressure was varied from 0.3 to 3.0 atm (101.33 – 3039.75 $mbar$) with a step size of 0.1, while the path length was varied over 15 values from 0.75 to 130 cm. For the optical path length, the authors considered 0.75 and 5 cm, to see the effect that shorter path lengths could have on the OACS. Furthermore, a step size of 10, was implemented from 10 – 130 cm optical path lengths. In the end, the effects of varying pressure and optical path length is reported thus.

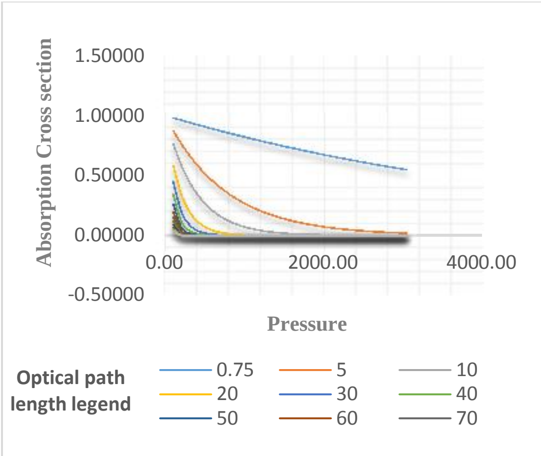

Figure 0.1 effects of pressure and optical path length on transmittance at 255.442 *nm*

The author has established earlier, that the output of the spectralcalc simulator is the Transmittance. Without the transmittance, the OACS cannot be determined. At 255.442 *nm*, as shown in Figure 4.1 the transmittance was observed to slop downwards linearly by 0.0002 $mbar^{-1}$ to 0.48 at 0.75*cm* path length as the pressure increased from 101.33 – 3039.75 *mbar*. However, for optical path lengths (OPL) ranging from 5 to 130 *cm*, the transmittance sloped downward with a curve to 0.00 transmittance value. Zero transmittance indicates total absorption of light by the ozone gas sample. Hence, increase in the OPL from 0.75 to 130 *cm* leads to decrease in the transmittance to zero as the pressure is increased from 101.33 – 3039.75 *mbar*.

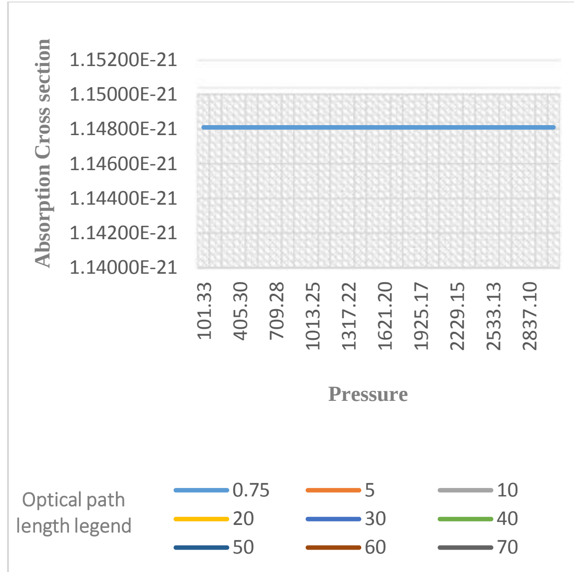

Figure 0.2 effects of pressure and optical path length on the OACS at 255.442 *nm*

Based on the values of the transmittances obtained, the OACS was determined and graphically presented as shown in Figure 4.2 clearly. The OACS was found to maintain a constant value of $1.148E-21\ cm^2/molecule$ as the pressure and OPL increased from 101.33 – 3039.75 *mbar* and 0.75 – 130 *cm* respectively. This report shows that pressure and OPL variation have zero effects on the OACS which is consistent with the work of [16] who reported the independence of pressure (0.1 to 3.0 *atm*) on OACS at 255.442 *nm* and an OPL of 20 *cm*.

Pressure and optical path length effects on OACS at 296.73 nm

At a higher absorption wavelength of 296.73 *nm* as shown in Figure 4.3 graphically, the transmittance response to varying pressure and OPL is unlike what was reported at 255.442 *nm*. Here, the transmittance sloped downwards linearly as the OPL increased from 0.75 to 10 *cm* as the pressure increased from 101.33 – 3039.75 *mbar*. However from OPL of 20 to 130 *cm*, the transmittance sloped downward with a curve with increasing pressure. It sloped from 0.904 to 0.049 at 70 *cm*. However, from 80 – 130 *cm*, the transmittance was observed to decrease to 0.00 as the pressure increased from 101.33 – 3039.75 *mbar*. This implies that at longer OPL beyond 70 *cm*, increase in the pressure will result in zero transmittance – almost a complete absorption of light by the ozone gas.

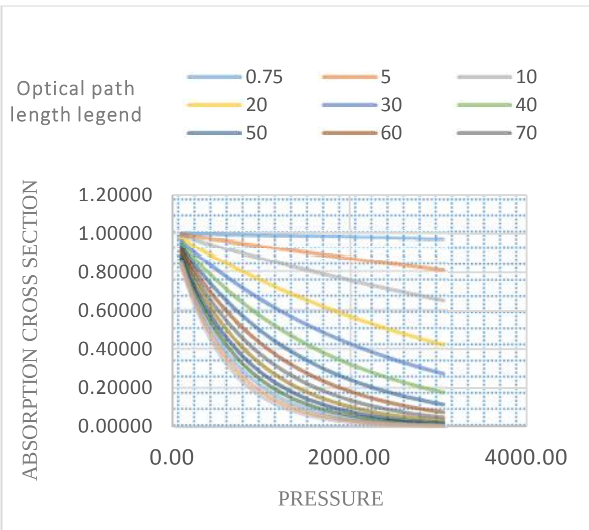

Figure 0.3 effects of pressure and optical path length on transmittance at 296.73 nm

The transmittance was in turn used to estimate the OACS. Figure 4.4 graphically describes the effects of pressure and OPL on the cross section of ozone gas. As the OPL and pressure increased from 0.75 – 130 *cm* and 101.33 – 3039.75 *mbar* respectively, the OACS remained constant at $6.156\text{E}-23\, cm^2/molecule$. This confirms the assertion that pressure does not depend on the OACS. Likewise, as presented in Figure 4.4, variation of OPL too has no effect on the OACS.

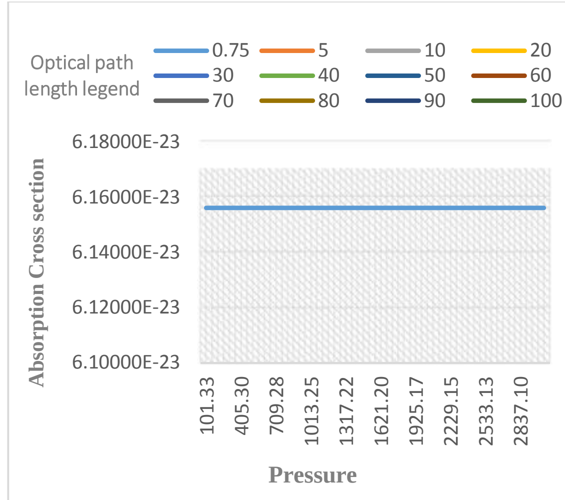

Figure 0.4 effects of pressure and optical path length on the OACS at 296.73 nm

The effects of the variation of pressure and optical path lengths on the OACS have been reported in this thesis. While the optical path length was fixed for each value ranging from 0.75 – 130 *cm*, the pressure was varied from 0.1 – 3.0 *atm*. At 255.442*nm* and 296.73*nm*, the author reported that the OACS remained constant at a value of $1.148\text{E}-21\, cm^2/molecule$ and $6.156\text{E}-23\, cm^2/molecule$ respectively as the pressure and optical path length are been varied.

The mathematical model was used to validate this assertion as the results generated via simulation were in perfect agreement with those obtained via the mathematical model.

REFERENCES

[1] Significant Technologies Bhd. sdn. “Optical Fiber Communication System” In *FOA’S Certified Fiber Optic Technologist (Cfot) Training*. pp4–5, 2014.

[2] Keeffe, S. O., Fitzpatrick, C., & Lewis, E. “Ozone measurement using an optical fibre sensor in the visible region” 758–761, 2005.

[3] Fuentes, J. D., T'ai, H. R. and Zenker, J. "Ozone Impedes the Ability of a Herbivore to find its Host", *Environmental Research Letters*. 8(1), 014048, 2013.

[4] Oyama, S. T. "Chemical and Catalytic Properties of Ozone", *Catalysis Reviews*, *42*(3), 279–322, 2000. https://doi.org/10.1081/CR-100100263.

[5] Berger, F., Ghaddab, B., Sanchez, J. B., & Mavon, C. "Development of an ozone high sensitive sensor working at ambient temperature", *Development Of An Ozone High Sensitive Sensor Working At Ambient Temperature*, *307*, 2011, 12054. https://doi.org/10.1088/1742-6596/307/1/012054

[6] Ockwell, D., and Whitmarsh, L. "Grass-Roots Engagement", 1–23, 2016. https://doi.org/10.1177/1075547008328969

[7] Daumont, D., Brion, J., Charbonnier, J., Physique, D. C., & Malicet, J. "Ozone UV Spectroscopy I : Absorption Cross-Sections at Room Temperature", *Journal of Atmospheric Chemistry*, *15*, 145–155, 1992.

[8] Hearn, A. G. "The Absorption of Ozone in the Ukra-violet and Visible Regions of the Spectrum", *78*, 932–940, 1961.

[9] Viallon, J., Lee, S., Moussay, P., Tworek, K., Petersen, M., & Wielgosz, R. I. "Accurate measurements of ozone absorption cross-sections in the Hartley band", 1245–1257, 2015.

[10] Inn, E. C. and Tanaka, Y. "Absorption Coefficient of Ozone in the Ultraviolet and Visible Regions", *JOSA. 43(10)*, 870–872, 1953.

[11] Vigroux, E. "Contribution À L'étude Expérimentale De L'absorption De L'ozone, Par Ernest Vigroux", Masson, 1953.

[12] Griggs, M. "Absorption Coefficients of Ozone in the Ultraviolet and Visible Regions", *The Journal of Chemical Physics*, 49(2), 857-859, 1968.

[13] Brion, J., Chakir, A., Daumont, D., Malicet, J. and Parisse, C. "High-Resolution Laboratory Absorption Cross Section of O_3", Temperature Effect. *Chemical Physics Letters*. 213(5-6), 610-612, 1993.

[14] Keeffe, S. O., Fitzpatrick, C., & Lewis, E. "An optical fibre based ultra violet and visible absorption spectroscopy system for ozone concentration monitoring", *125*, 372–378, 2007. https://doi.org/10.1016/j.snb.2007.02.023

[15] Voigt, S., Orphal, J., Bogumil, K. and Burrows, J. "The Temperature Dependence (203–293 K) of the Absorption Cross Sections of O3 in the 230–850 nm Region Measured by Fourier-Transform Spectroscopy", *Journal of Photochemistry and Photobiology A: Chemistry*. 143(1), 1-9, 2001.

[16] Marcus et al., "Pressure Effect Simulation for Ozone Absorption Cross Section", IGCESH2014, 2014.

[17] Marcus, T. C. E., David, M., Yaacob, M., Salim, M. R., Hussin, N., Ibrahim, M. H., Raja, P. "Alternative Wavelength for Linearity Preservation Of Beer – Lambert Law In Ozone", *57*(4), 1013–1016, 2015. Https://Doi.Org/10.1002/Mop

[18] Marcus, T., E. Ching, Ibrahim, M. H., Ngajikin, N. H., & Azmi, A. I. "Sensors and Actuators B: Chemical Optical path length and absorption cross section optimization for high sensitivity ozone concentration measurement", *Sensors & Actuators: B. Chemical*, *221*, 570–575,

2015b. https://doi.org/10.1016/j.snb.2015.07.005

[19] Hintsa E. J., G. P. Allsup, C. F. Eck, D. S. Hosom, M. J. Purcell, A. A. Roberts, D. R. S., & Sholkovitz, A. E. R. "New Ozone Measurement Systems for Autonomous Operation on Ocean Buoys and Towers", 1007–1016, 2004.

[20] Degner, M., Damaschke, N., & Ewald, H. "UV LED-based Fiber Coupled Optical Sensor for Detection of Ozone in the *ppm* and ppb Range", 95–99, 2009.

[21] Maria, L. De, & Bartalesi, D. "A Fiber-Optic Multisensor System for Predischarges Detection on Electrical Equipment", *12*(1), 207–212, 2012.

[22] David, M., Ibrahim, M. H., Idrus, S. M., Ngajikin, N. H., Izam, A., Ching, T., & Marcus, E. "Optical Path Length , Temperature , and Wavelength Effects Simulation on Ozone Gas Absorption Cross Sections towards Green Communications", *14*(3), 1–6, 2016.

[23] Aoyagi, Y., Takeuchi, M., Yoshida, K., Kurouchi, M., Araki, T., Nanishi, Y., Sugano, H., Ahiko, Y. and Nakamura, H. "High-Sensitivity Ozone Sensing Using 280 nm Deep Ultraviolet Light-Emitting Diode for Detection of Natural Hazard Ozone", *Journal of Environmental Protection.* 3(8), 695, 2012.

[24] Enenche Patrick, Michael David, A.O. 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*, vol 1, 284 – 290, 2017.

[25] *SpectralCalc.com High-resolution Spectral Modeling*, GATS, Inc., Newport News, access online on 22 February 2014 from http://www.spectralcalc.com/info/about.php

http://www.atbuftejoste.com/index.php/joste/article/view/575/pdf_376