

Attenuation of UV-C Solar Radiation as a Function of Altitude ($0 \leq z \leq 100$ km): Rayleigh Diffusion and Photo Dissociation of O₂ Influence

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How to cite this paper: Pinedo-Vega, J.L., Ríos-Martínez, C., Navarro-Solís, D.J., Dávila-Rangel, J.I., Mireles-García, F., Saucedo-Anaya, S.A., Manzanares-Acuña, E. and Badillo-Almaraz, V. (2017) Attenuation of UV-C Solar Radiation as a Function of Altitude ($0 \leq z \leq 100$ km): Rayleigh Diffusion and Photo Dissociation of O₂ Influence. *Atmospheric and Climate Sciences*, 7, 540-553.

<https://doi.org/10.4236/acs.2017.74039>

Received: September 15, 2017

Accepted: October 20, 2017

Published: October 23, 2017

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Abstract

In this paper, we present an analysis of attenuation for UV-C radiation ($\lambda \leq 290$ nm) as a function of the altitude z ($0 \leq z \leq 100$ km) by calculating the interaction ratio between the UV-C radiation and the molecular species susceptible of interact with UV-C radiation. The Rayleigh scattering spectral cross sections were calculated, the UV-C spectral cross sections of the species susceptible of interact with UV-C radiation and the UV extra-terrestrial (*ETR*) solar spectrum were standardized with wavelength steps of 1 nm, and The International Standard Atmosphere model (ISO 1972) was adapted to calculate the molecular density. These data were utilized to calculate the photodissociation and Rayleigh scattering ratios as a function of the altitude and to determine to what measure the photodissociation and the Rayleigh diffusion were determinants of the attenuation of UV-C radiation. It became clear that the photo dissociation of O₂ is the primordial mechanism of attenuation for the UV-C radiation, but the Rayleigh diffusion appears like a mechanism that encreases the photon flux, raising the performance of the O₂ photodissociation. The attenuation capacities of N₂O, CO₂ and water vapor (H₂O) over the UV-C radiation are all similar, although smaller (less than 0.6%), and this is due to their low concentration. The O₃, has the theoretical greater attenuation capacity, but it is found in mid-range altitudes ($15 \leq z \leq 40$ km), where the residual UV-C photons has almost vanished by O₂ photo dissociation or Rayleigh diffusion, so the real effect over the UV-C attenuation is minimum.

Keywords

UV-C Radiation, Rayleigh Scattering, O₂ Photodissociation

1. Introduction

It is well known that UV-C radiation does not reach the surface of the Earth. However, there is no precise knowledge about its spectral attenuation.

The attenuation of UV radiation, in general, is the result of the interaction of the photons with the species or molecules that are susceptible to interact. The photons extinguish themselves upon reacting, transferring their energy to the molecules either causing the breaking of their molecular bonds or the dissociation of the molecule. Due to its nature, this type of interaction is called photodissociation.

The spectral photodissociation ratio $R_\lambda(z)$ can be defined as the number of molecular photodissociation produced by the solar radiation of each wavelength λ at any altitude in the atmosphere. This must be proportional to the spectral photon flow $\phi_\lambda(z)$ and to the molecular density $N(z)$ of each chemical species at z altitude

$$R_\lambda(z) = \phi_\lambda(z)N(z)\sigma_\lambda \quad (1)$$

σ_λ known as the cross section, represents the probability of reacting or of molecular photodissociation which is specific to each wavelength λ for each molecular species.

The total photodissociation ratio at each altitude z is the integral of the spectral photodissociation ratio

$$R(z) = \int R_\lambda(z) d\lambda = \int \phi_\lambda(z)N(z)\sigma_\lambda d\lambda \quad (2)$$

The attenuation of the residual spectral photon flux at each altitude z can be calculated by subtracting the number of reactions of photodissociation from the spectral photon flux at the altitude $z+1$

$$\phi_\lambda(z) = \phi_\lambda(z+1) - R(z+1) \quad (3)$$

The initial spectral photon flux $\phi_{0\lambda}$ can be calculated from the spectral irradiance $I_{0\lambda}$ received at the top of the atmosphere or ETR spectrum

$$\phi_{0\lambda} = \frac{I_{0\lambda}}{E_\lambda} \quad (4)$$

where, $E_\lambda = \frac{hc}{\lambda}$, is the photon energy, h the Planck constant and c the speed light in vacuum.

The molecular density at altitude z can be expressed in terms of the pressure and the average temperature with the equation

$$N(z) = \frac{P(z)N_A}{MRT(z)} \quad (5)$$

where, $N_A = 6.0221415 \times 10^{23}$ molecules/mol is Avogadro's number, $M = 28.96644 \times 10^{-3}$ kg/mol is the air molecular weight at TP standard and R is the specific gas constant $R = 287.05$ J/K · kg.

A priori, one can assume, in accordance with hydrostatic law, that the decrease of the pressure with the altitude is exponential in nature; nevertheless, because of photodissociation reactions, layers in the atmosphere with different temperature gradients λ_n alternate. The temperature in the stratosphere, for example, can be characterized through three temperature gradients—the lower one positive, the highest one negative, and an isothermal layer in between—until reaching the mesopause.

The temperature gradients λ_n have an approximately linear nature in each layer n of the atmosphere

$$\frac{dT}{dz} = \lambda_n \quad (6)$$

Through integration, the temperature inside the layer n can be expressed as

$$T(z) = T_n + \lambda_n(z - z_n)$$

where T_n y z_n are the temperature and altitude base of each layer.

According to The International Standard Atmosphere, between 0 and 100 km the standard atmosphere is comprised of 8 layers [1].

For a layer with gradient $\lambda_n \neq 0$, the molecular density is given by

$$N(z) = \frac{N_A}{M} \frac{P_n}{RT_n} \left(1 + \frac{\lambda_n(z - z_n)}{T_n} \right)^{-\frac{g}{\lambda_n R}} \quad (8)$$

where g is the acceleration due to gravity.

While for one isothermal layer $\lambda_n = 0$, or one without a temperature gradient the molecular density is given by

$$N(z) = \frac{N_A}{M} \frac{P_n}{RT_n} e^{-\frac{g}{T_n R}(z - z_n)} \quad (9)$$

The species susceptible to reacting with UV-C radiation are O₂, O₃, CO₂, H₂O and N₂O. The corresponding cross sections are consulted in The MPI-Mainz UV/VIS Spectral Atlas [2].

The first claim of this paper is to determine to which measure these molecular species are determinant in the attenuation of the UV-C radiation. The region for the study of the attenuation of UV-C radiation is the homosphere ($0 \leq z \leq 100$ km). The homosphere—the region in which the composition of air and the molecular weight are approximately constant—contains 99.79% of the total mass reported in the atmosphere, and it is also the region where the molecular species susceptible to reacting with UV-C radiation reside.

In this paper, the homosphere is discretized in 100 m steps and the attenuation of UV-C radiation has been restricted to the perpendicular diffusion towards the surface of the Earth.

2. Materials and Methods

2.1. ETR Solar Spectrum

The Gueymard extraterrestrial (*ETR*) spectrum $I_{0\lambda}$ ($\text{W}/\text{m}^2 \cdot \text{nm}$) was used, due to it being the only one found in literature that begins in 0.5 nm. The Gueymard spectrum covers the spectral region from 0.5 nm to 280 nm in 1 nm steps, 280 to 400 nm in 0.5 nm steps, from 400 nm to 1705 nm in 1 nm steps, 5 nm steps from 1705 nm to 4000 nm, and variable steps beyond 4000 nm [3].

The integral of the Gueymard spectrum is equal to $1366.1521372347 \text{ W}/\text{m}^2$, which is in the same order as the Solar Constant $I_0 = 1366.1 \text{ W}/\text{m}^2$ [4]. The UV-C irradiance is $10.712521 \text{ W}/\text{m}^2$, representing 0.7841% of the whole solar spectrum. In **Figure 1** the UV-C region of the Gueymard spectrum is presented.

By the Gueymard spectrum having variable wavelength steps, in this paper the spectrum was standardized with wavelength steps of 1 nm centered on multiples of 0.5 nm. The error propagated by this standardization was evaluated by comparing the integrals of the original and the homologated spectrums. The difference between the original integral of UV-C irradiance and the standardized integral of UV-C irradiance was $0.132 \text{ W}/\text{m}^2$, which equals a relative error of 0.1272%.

2.2. Cross Sections

In **Figure 2** the cross sections of the principal molecular species of the atmosphere that absorb UV radiation are presented.

The cross section of O_2 (black line) extends until 250 nm and given its concentration in the atmosphere (0.20953) it is one of the most determinant species in the attenuation of the UV-C radiation between 0 and 244 nm.

Under 150 nm, the most important cross sections are those of N_2O and CO_2 (magenta and blue line). Nevertheless, the capacity for attenuation of these species cannot be too important, due to their low concentrations in the atmosphere

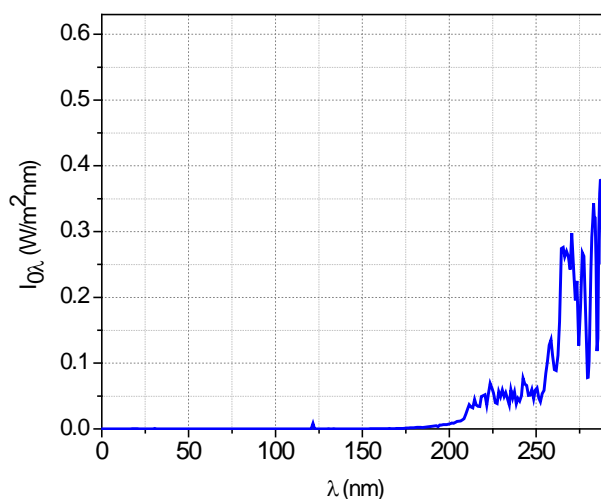


Figure 1. Solar UV-C spectrum. Source: Gueymard (2004).

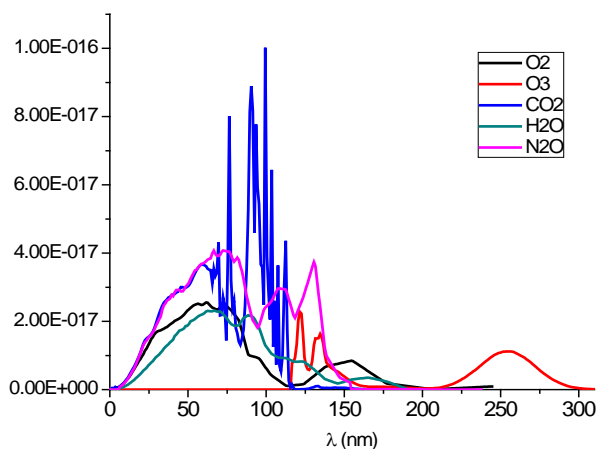


Figure 2. Cross sections of molecular species in the atmosphere which are susceptible to reacting with the UV-C radiation [2].

(fractions 3.15×10^{-7} and 4×10^{-4} respectively) and because in this region the solar ETR irradiance is only 0.01522 W/m^2 (0.14% of UV-C irradiance) (See **Figure 1**).

The water vapor cross sections (navy line) are important up until 200 nm, but given their relatively reduced concentration in the troposphere, they also cannot have an important attenuation capacity for the UV-C radiation.

The ozone, for its part (red line), is the only species whose cross sections are important between 200 nm and 300 nm, the region of the spectrum in which the ETR solar irradiance is in the range of 10 W/m^2 ; although its concentration is relatively reduced (3.5×10^{-7}), the ozone must play a significant role in the attenuation of the UV-C radiation.

2.3. Rayleigh Scattering

Another phenomenon that must influence the attenuation of the radiation UV-C is the Rayleigh scattering or the Rayleigh diffusion.

The Rayleigh scattering theory was proposed at the end of XIX century by John William Strutt (British physicist known like Lord Rayleigh). Using Electromagnetic Theory Rayleigh assumed that the molecules of the air, at being pushed into their excited state by the electromagnetic radiation of the sun, are converted into oscillating dipoles that re-emit the radiation in 4π steradians.

The expression for the Rayleigh scattering cross section σ_R for standard air –790 mm Hg, 15°C and containing 300 ppm CO_2 is the Penndorf equation [5] presented like the classic equation in many textbooks (e.g. [6])

$$\sigma_R(\lambda) = \frac{24\pi^3 (n_s^2 - 1)^2}{\lambda^4 N_s^2 (n_s^2 - 2)^2} \left(\frac{6 + 3\delta}{6 - 7\delta} \right) \quad (10)$$

where n_s is the refractive index of air, $N_s = 2.54743 \times 10^{19} \text{ cm}^{-3}$ is the air

molecular standard density, $F_D = \left(\frac{6+3\delta}{6-7\delta}\right)$ is the depolarization term or the King factor and δ is the depolarization factor which describes the effect of molecular anisotropy.

For the refractive index n_s , Peck and Reeder [7] proposed the formula for 300 ppm CO₂

$$(n_s - 1)_{(300)} \times 10^8 = 8060.51 + \frac{2480990}{132.274 - \frac{1}{\lambda^2}} + \frac{17455.7}{39.32957 - \frac{1}{\lambda^2}} \quad (11)$$

Scaling for the desired CO₂ concentration in ppm

$$(n_s - 1)_{(\text{CO}_2)} = (n_s - 1)_{(300)} (1 + 0.54(\text{CO}_2 - 0.0003)) \quad (12)$$

Figure 3 presents the behavior of the refractive index of air n_s for 300 and 380 ppm CO₂. The numerical differences in the calculation of n_s with both concentrations are so small that the graphics overlap. Discontinuities are observed under 160 nm—this simply gives an account of which expressions from Peck and Reeder were deduced for values of $\lambda > 200$ nm. Thus, the Rayleigh scattering cross sections are only reliable for wavelengths $\lambda > 200$ nm.

The King factor depends on air composition and wavelength radiation. According to Bates [8]

$$F_D = \frac{78.084F(\text{N}_2) + 20.946F(\text{O}_2) + 0.934 + 1.15 \times C_{\text{CO}_2}}{78.084 + 20.946 + 0.934 + C_{\text{CO}_2}} \quad (13)$$

where

$$F(\text{N}_2) = 1.034 + 3.17 \times 10^{-4} \left(\frac{1}{\lambda^2}\right) \quad (14a)$$

$$F(\text{O}_2) = 1.096 + 1.385 \times 10^{-3} \left(\frac{1}{\lambda^2}\right) + 1.448 \times 10^{-4} \left(\frac{1}{\lambda^4}\right) \quad (14b)$$

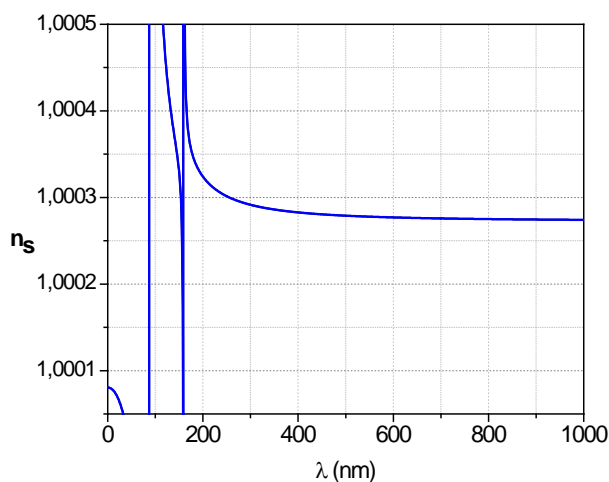


Figure 3. Refractive index of air n_s for CO₂ 300 and 380 ppm.

$$F(\text{Ar}) = 1 \quad (14c)$$

$$F(\text{CO}_2) = 1.15 \quad (14d)$$

Figure 4 shows the Rayleigh cross sections calculated using the Peck and Reeder refractive index n_s and Bates King factor. The discontinuities for $\lambda < 200$ nm reappear.

In **Table 1**, we present the values of σ_R reported by Penndorf [5], Bodhain [9] and Bucholtz [10] as well as the values calculated using the Equations (10)-(14) for the concentrations of CO₂ 360, 380 and 400 ppm. The differences between authors are around 10^{-27} cm²; meanwhile the differences for the different concentrations of CO₂ are around 10^{-29} cm². For the purpose of the calculations of attenuation of UV-C radiation, those minute differences do not cause a great impact.

2.4. Limitations

The spectral cross sections available in literature present important differences between authors and no one author has uniform wavelength steps. It is known that the cross sections vary with temperature, but it was not possible to take into account this dependence, seeing as no data exists that permits taking the gamma temperatures that exist in the atmosphere. The majority of the cross sections used in this work were measured at 298 K, with exceptions of the higher part of the spectrum of O₂, whose cross sections were measured at 202 and 243 K, and

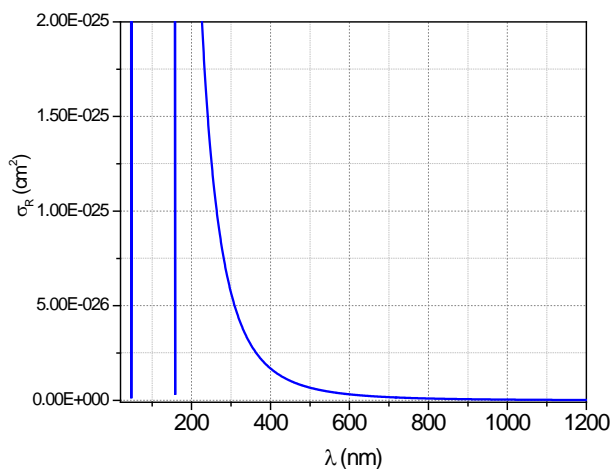


Figure 4. Rayleigh scattering cross sections.

Table 1. Rayleigh cross section comparison.

λ (μm)	$\sigma_r(\lambda)$ Penndorf [5]	$\sigma_r(\lambda)$ Bodhaine [9]	$\sigma_r(\lambda)$ Bucholtz [10]	$\sigma_r(\lambda)$ CO ₂ = 360ppm	$\sigma_r(\lambda)$ CO ₂ = 380pp	$\sigma_r(\lambda)$ CO ₂ = 400ppm
0.250	1.259E-25	1.2610E-25	1.259E-25	1.25707E-25	1.25707E-25	1.25707E-25
0.300	5.642E-26	5.6525E-26	5.642E-26	5.64514E-26	5.64515E-26	5.64516E-26
0.400	1.689E-26	1.6738E-26	1.673E-26	1.67498E-26	1.67498E-26	1.67498E-26

the cross sections of CO₂ which were measured at 310 K.

In the case of the ozone, values for the cross sections which are under 110 nm were not found. Nevertheless, under this wavelength the Irradiance is equal to only 0.00517 W/m², in such a way that the error generated due to the omission of this region must be very small. In the case of the Rayleigh scattering cross section the only reliable values are those calculated for wavelength $\lambda > 200$ nm, with this in mind the Rayleigh scattering for this wavelength was omitted.

The ETR solar spectrum and the cross sections were standardized into wavelengths through interpolation and/or extrapolation and into wavelength steps of 1 nm were situated values of 0.5 nm. The error generated was evaluated by comparing the integral of the original and homologated spectrums. The relative differences between the integrals under the curve from the reported cross sections and the standardized cross sections were: in the case of O₂: 9.818×10^{-5} , in the case of the O₃: -0.01599; in the case of CO₂: 0.040026, in the case of N₂O: 5.3782×10^{-5} , and in the case of H₂O: 0.00243.

3. Results

3.1. UV-C Attenuation by the O₂

The cross sections of O₂ were utilized: Brion [11] from 0 to 120 nm, Ackerman [12] from 120 to 170 nm, Brion [11] from 170 to 250 and Bogumil [13] from 250 to 444 nm. The molecular density was calculated using Equations (8)-(9) and the degradation of the photons flow was calculated by Equations (3)-(4).

In **Figure 5(a)** the photodissociation ratio of O₂ is presented as a function of altitude, considering the O₂ as the only species that produces attenuation of the UV-C radiation. Two regions of interaction between the UV-C radiation and O₂ molecules are observed, one in the upper layers of the homosphere ($z > 80$ km), and the other between 0 and 40 km—which is approximately the region in which one would find the distribution of the ozone in the atmosphere.

In **Figure 5(b)**, UV-C Irradiance is presented as a function of the altitude that corresponds to the residual flow of UV-C radiation reacting strictly with the O₂. Between 100 and 80 km, the molecules of O₂ only attenuate around 18% of the UV-C radiation. Between 80 km and 50 km, it is observed that the residual quantity of the UV-C radiation is constant. Left is an irradiance of 8.79 W/m² of the 10.71 W/m² which are produced from the sun. Between 40 and 0 km, the O₂ attenuates another 76.4% of the UV-C irradiance which is composed of lower energy photons. Nevertheless, if the UV-C radiation interacts exclusively with the O₂ it would not be able to attenuate completely with the UV-C radiation given that on the Surface of the Earth (sea-level), a residual irradiance around 0.6 W/m² (5.6% of the UV-C ETR).

Partial conclusion, the O₂ is not the only species that prevents the UV-C radiation from reaching the surface of the Earth.

3.2. UV-C Attenuation by the Rayleigh Diffusion

In **Figure 6(a)**, the density of the Rayleigh scattering of the UV-C radiation with

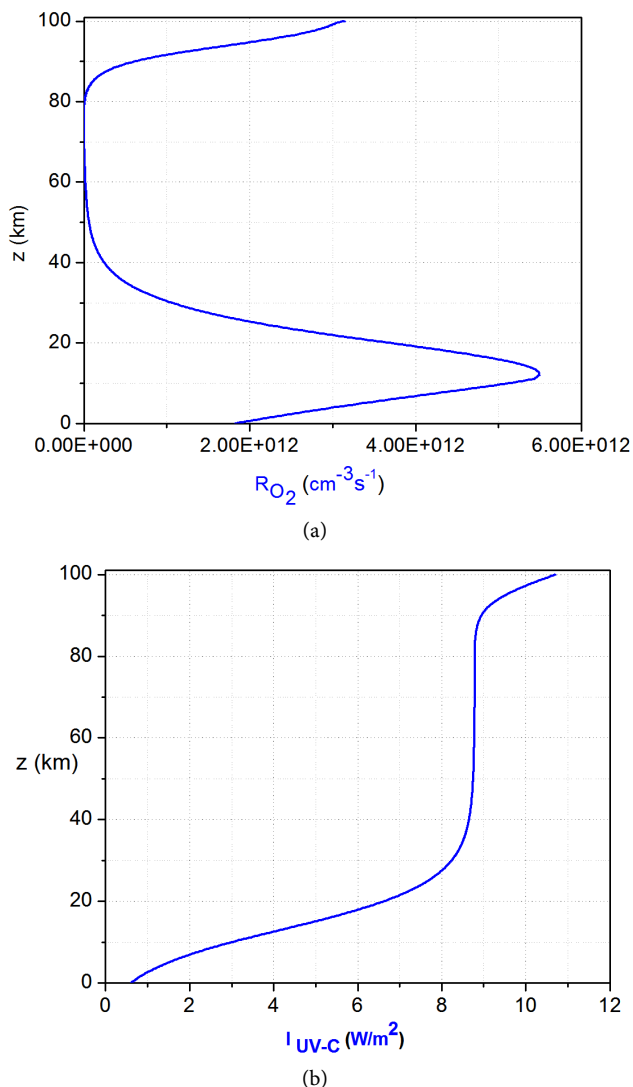


Figure 5. (a) Density of the reactions to the interaction of UV-C radiation and the O_2 molecules; (b) Residual irradiance from the UV-C radiation upon reacting with O_2 molecules.

the air molecules is presented as a function of the altitude while taking into consideration exclusively the Rayleigh Diffusion as the only mechanism for the attenuation of the UV-C radiation. In **Figure 6(b)** eqs. the UV-C Irradiance is presented as a function of the altitude that corresponds to the residual flow of the diffused UV-C radiation. One can observe that the scattering is practically null for greater altitudes and begins to be important only under 40 km. This is due to the increase of molecular density: $N(40 \text{ km}) = 7 \mp 10^{16} \text{ cm}^{-3}$ and $N(0 \text{ km}) = 2.54 \times 10^{19} \text{ cm}^{-3}$.

If the Rayleigh Diffusion was the only process of attenuation for the UV-C radiation, an irradiance equal to 1.65 W/m^2 would manage to reach the surface of the Earth. Nevertheless, this would be sufficient enough to attenuate 85% of the UV-C radiation.

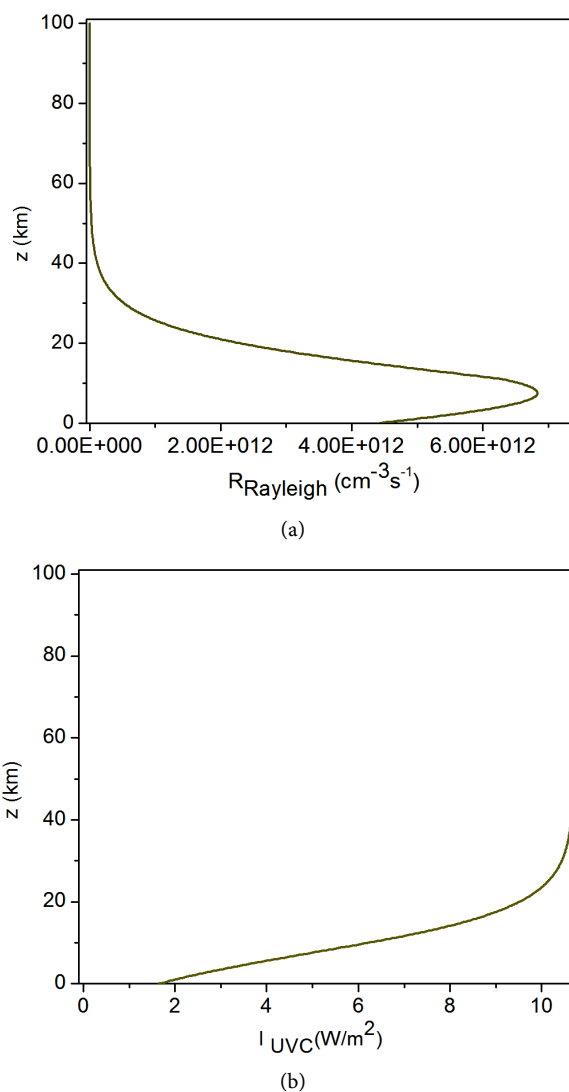


Figure 6. (a) Density of the reactions of the Rayleigh diffusion with the UV-C radiation; (b) Residual Irradiance of the UV-C radiation due to the Rayleigh diffusion

3.3. UV-C Attenuation by the O_2 Considering the Rayleigh Diffusion

In **Figure 7(a)** the total photodissociation ratio is presented in between the UV-C radiation and the molecules of O_2 as a function of the altitude considering the Rayleigh diffusion. One can observe that the photodissociation ratio of O_2 increases quantitatively and rises slightly in altitude; in other words, the Rayleigh diffusion improves the performance of the photodissociations.

In **Figure 7(b)**, the UV-C irradiance is presented as a function of the altitude corresponding to the residual flow of the radiation from the UV-C radiation upon reacting with O_2 , taking into account the Rayleigh diffusion. The Irradiance that reaches the surface of the earth has diminished. From being $0.6 \text{ W}/\text{m}^2$ without considering Rayleigh diffusion, it diminished to $0.14 \text{ W}/\text{m}^2$. Nevertheless, it is not zero because the ozone is still left to be considered and the

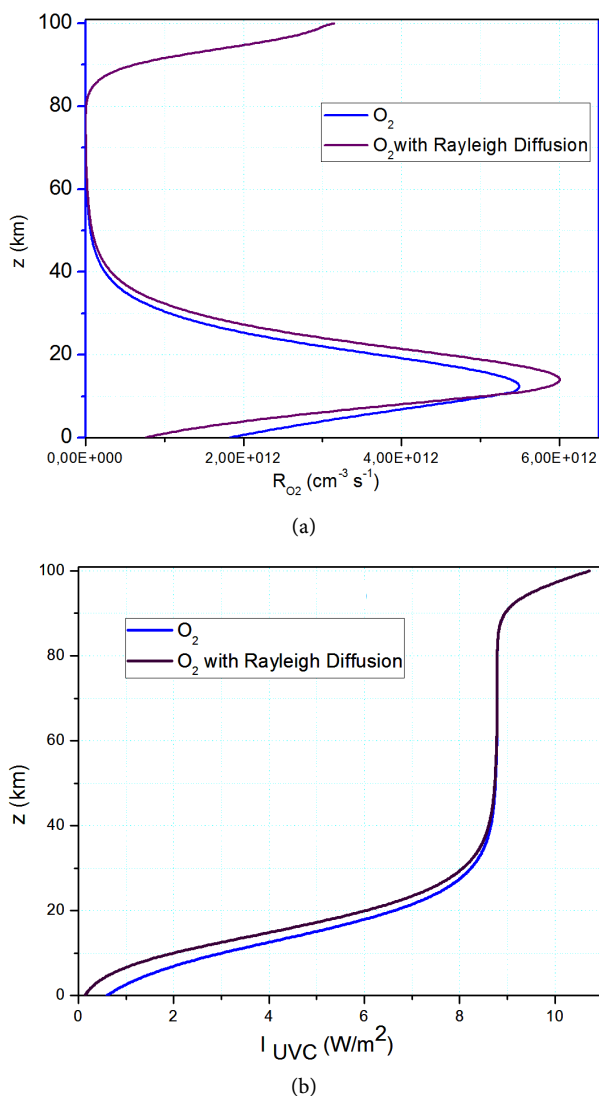


Figure 7. (a) The densities of the reactions between UV-C radiation and the O_2 molecules considering the Rayleigh diffusion (violet line) and without considering the Rayleigh diffusion (blue line); (b) The residual irradiance of the UV-C radiation upon reacting with the O_2 molecules with and without Rayleigh diffusion.

ozone cross sections are important for the upper section of the UV-C range (see **Figure 1**).

3.4. Attenuation of the UV Radiation Spectrum: Ozone's Role in UV Attenuation

In **Figure 8** the degradation of the UV radiation spectrum is presented as a function of the altitude making the molecular dissociation of O_2 and O_3 and the Rayleigh diffusion intervene. Between 100 and 80 km, the degradation of the spectrum is imperceptible; however, the spectrum degradation is evident under 40 km. The UV-C range ($0 \leq \lambda \leq 290$ nm) extinguishes itself completely, this is due to the photodissociation of the O_2 molecules that were reinforced or assisted

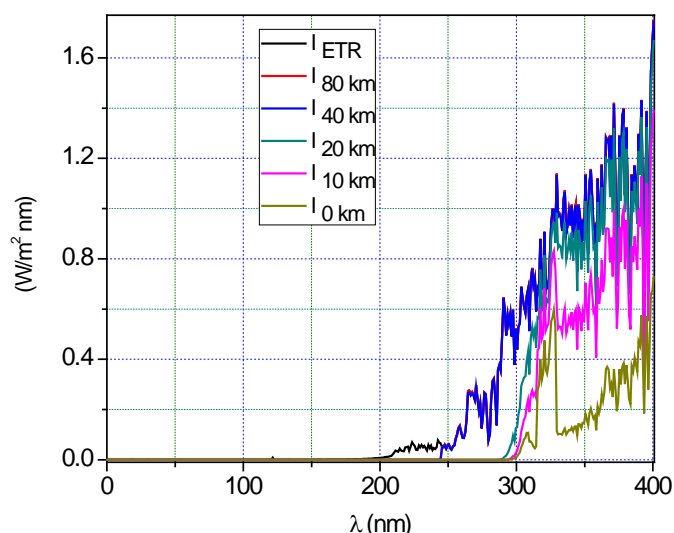


Figure 8. UV spectral irradiance for different altitudes, causing the photodissociation of the O_2 , of the O_3 , and the Rayleigh diffusion to intervene.

by the Rayleigh diffusion and by the O_3 .

To simulate the actions of the ozone, a profile of the concentration of the columns of the ozone was taken randomly, characteristic of a region with a value of 238 DU. In fact, it is the ozone that completes the elimination of the residual 0.14 W/m^2 of the photodissociation of O_2 .

On the other hand, the UV-B range, at ground level ($z = 0$) only leaves 3.0529 W/m^2 of the ETR UV-B irradiance (18.6707 W/m^2); meanwhile the UV-A irradiance only 23.3126 W/m^2 at ground level of the ETR UV-A irradiance (83.584 W/m^2). This is a good approximation of what goes on.

3.5. UV-C Attenuation by N_2O , CO_2 and Water Vapor

Although under the wavelength of 150 nm the cross sections of these molecular species are elevated (Figure 1), due to its low concentration and the fact that the irradiance of the spectrum in this region is very weak, these species are not important in the attenuation of the UV-C radiation. If the attenuation is due to these exclusively, the reduction of the UV-C radiation would be around 0.06 W/m^2 .

4. Conclusions

Combining the air's Rayleigh diffusion and photodissociation of O_2 , the profile of dissociations of O_2 as a function of the altitude was obtained to describe the attenuation of the UV-C radiation in the atmosphere. This method demonstrates that the dissociations of O_2 occur in two regions of the atmosphere. In this altitude, 18% of the UV-C radiation is attenuated through the photodissociation produced by photons of high energy ($\lambda \leq 240 \text{ nm}$). These photodissociations contribute to the elevation in the temperature of the lower part of the ionosphere, but at these altitudes the liberated atoms of oxygen don't produce molecules

from the ozone, which is succinctly due to the low molecular density of O₂. The region where the largest attenuation of the UV-C radiation is produced is distributed between the troposphere and the stratosphere, having maximum grounds for attenuation at 18 km.

The method is not enough achieved because the absence of cross section for the span of temperatures in the atmosphere. Even so it explains why the UV-C doesn't arrive to the Earth surface gives relevance to the Rayleigh diffusion like a mechanism that increases the photon flux, raising the performance of the O₂ photodissociation.

The profile of the photodissociation ratio of O₂ is similar to the conditions for distribution of O₃ in the atmosphere. This permits the explanation that the ozone resides in the stratosphere because that is where the majority of the photodissociation ratio of O₂ exists.

Additionally, this paper permits the emphasis that not only the photodissociation of O₃ is what contributes to the generation of the temperature gradient in the stratosphere. In fact, the number of photodissociation of O₂ is four times the number of photodissociation of O₃. This is meanwhile the photodissociation ratio of O₂ of one column of the atmosphere about 1 cm² from the surface is

$$R_T(\text{O}_2) = \int R_{\text{O}_2}(z) dz = 1.48 \times 10^{16} \text{ cm}^{-2} \cdot \text{s}^{-1}$$

The total number of the photodissociation of O₃ is

$$R_T(\text{O}_3) = \int R_{\text{O}_3}(z) dz = 3.64 \times 10^{15} \text{ cm}^{-2} \cdot \text{s}^{-1}$$

On the other hand, given that 1 DU = 3.64 × 10¹⁵ O₃ molecules per cm² $R_T(\text{O}_3)$ implies the destruction of 0.135 DU of O₃ per second.

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