

3.2.10. RAYLEIGH OPTICAL DEPTH CALCULATIONS

Introduction

A variety of different techniques are used for the calculation of Rayleigh optical depth in the atmosphere. In some cases, differences among these techniques can be important, especially in the UV region of the spectrum and under clean atmospheric conditions. It is recommended that Rayleigh optical depth be calculated from first principles of Rayleigh scattering theory rather than the variety of curve fitting techniques currently in use. This approach requires the accurate calculation of the refractive index of air based on the latest published measurements. Small inaccuracies in Rayleigh optical depth calculations can equal or even exceed other quantities being estimated, such as aerosol optical depth, particularly in the UV region of the spectrum. The procedure described here was presented by *Bodhaine et al.* [1999].

Rayleigh scattering calculations for air have traditionally been made using the method of *Penndorf* [1957] where the refractive index was calculated for "standard" air (760 mm Hg, 15° C) using the equation of *Eddén* [1953], and the scattering cross section per molecule was calculated using the classical equation presented in many textbooks [e.g., *van de Hulst*, 1957; *McCartney*, 1976]. This calculation includes the depolarization term, or the King factor, which describes the effect of molecular anisotropy and is the least well known for these purposes. Results of such calculations were presented by *Penndorf* [1957]. It is this table of values that has been used by many workers in the field to estimate Rayleigh optical depths, usually by some curve fitting routine over a particular wavelength range of interest.

Possible errors in the depolarization term were considered by *Hoyt* [1977], *Fröhlich and Shaw* [1980], and *Young* [1980, 1981]. The correction proposed by *Young* [1981] had been accepted for modern Rayleigh scattering calculations in atmospheric applications. However, *Bates* [1984] and *Bucholtz* [1995] discussed the depolarization in detail as a function of the individual constituents, and as a function of wavelength, and presented new values.

Optical Depth

A quantity of fundamental importance in atmospheric studies is the optical depth (or optical thickness). This quantity has been discussed by numerous authors [e.g., *Dutton et al.*, 1994; *Stephens*, 1994] and is derived from the exponential law of attenuation variously known as Bouguer's law, Lambert's law, or Beer's law. For purposes of illustration only, Bouguer's law may be simply written as:

$$I(\lambda) = I_0(\lambda) \exp(-\tau(\lambda) / \cos \theta) \quad (1)$$

where $I_0(\lambda)$ is the extraterrestrial flux at wavelength λ , $I(\lambda)$ is the flux reaching the ground, θ is the solar zenith angle, and $\tau(\lambda)$ is the optical depth. Clear-sky measurements of $I(\lambda)$ as a function of θ , and plotted as $\ln I(\lambda)$ against $\sec \theta$, should yield a straight line with slope $-\tau(\lambda)$ and intercept I_0 (extrapolated back to $\sec \theta = 0$). An important point is that $\tau(\lambda)$, may be composed of several components given by:

$$\tau(\lambda) = \tau_R(\lambda) + \tau_a(\lambda) + \tau_g(\lambda) \quad (2)$$

where $\tau_R(\lambda)$ is the Rayleigh optical depth, $\tau_a(\lambda)$ is aerosol optical depth, and $\tau_g(\lambda)$ is the optical depth due to absorption by gases such as O_3 , NO_2 , and H_2O . In principle it is possible to measure $\tau(\lambda)$ and then derive aerosol optical depth by subtracting estimates of $\tau_R(\lambda)$ and $\tau_g(\lambda)$. In practice, however, arriving at reasonable estimates of these quantities can be difficult, particularly during fairly clean atmospheric conditions such as those found at Mauna Loa, Hawaii. To isolate the individual components of optical depth it is necessary to provide accurate estimates of Rayleigh optical depth.

Rayleigh optical depth is relatively easy to calculate once the scattering cross section per molecule has been determined for a given wavelength and composition because it depends only on the atmospheric pressure at the site. That is, it is only necessary to calculate the total number of molecules per unit area in the column above the site, and this depends only on the pressure, as shown in the formula:

$$\tau_R(\lambda) = \sigma \frac{PA}{m_a g} \quad (3)$$

where σ is scattering cross section per molecule, P is the pressure, A is Avogadro's number, m_a is the mean molecular weight of the air, and g is the acceleration due to gravity. Note that m_a depends on the composition of the air, whereas A is a constant of nature. Although g may be considered a constant of nature, it does vary significantly with height and location on the earth's surface and may be calculated according to the formulas of *List* [1968].

Rayleigh Optical Depth of Air

Bodhaine et al. [1999] outlined a method for the calculation of Rayleigh optical depth that goes back to first principles as suggested by *Penndorf* [1957] rather than using curve fitting techniques, although the refractive index of air is still derived from a curve fit to experimental data. All of the latest values of the physical constants of nature were used, and the effects of CO_2 on the refractive index and the mean molecular weight of air were included, even though these effects are in the range of 0.1-0.01%. It should be noted that aerosol optical depths are often as low as 0.01 at Mauna Loa. Since Rayleigh optical depth is of the order of 1 at 300 nm, it is seen that a 0.1% error in Rayleigh optical depth translates into a 10% error in aerosol optical depth.

The effects of high concentrations of water vapor on the refractive index of air may be of the same order as for CO_2 [*Eddén*, 1953, 1966]. However, for practical atmospheric situations the total water vapor in the vertical column is small and does not significantly affect the calculations. Furthermore, the water vapor in the atmosphere is usually confined to a thin layer near the surface, which significantly complicates the calculation, whereas CO_2 is generally well mixed throughout the atmosphere.

It is recommended that *Peck and Reeder's* [1972] formula for the refractive index of dry air with 300 ppm CO_2 be used after corrections have been applied for the actual CO_2 concentration of the air. Next the scattering cross section per molecule of air should be calculated from the classical equation using the same temperature and pressure as were used for refractive index (1013.25 mb and 288.15 K). Note that the scattering cross section per molecule is independent of pressure and temperature.

The depolarization should be calculated taking into account the CO₂ concentration. Finally the Rayleigh optical depth can be calculated using Equation (3), taking into account the effect of CO₂ concentration on the average density of air, the surface pressure, and the effective value of gravitational acceleration using the correct latitude and the correct mass-weighted mean altitude of the column of air above sea level. By following these guidelines it is possible to calculate the Rayleigh optical depth as a function of wavelength for any point at ground level or in the atmosphere at any location on the earth.

Some Example Calculations

Using the previous equations *Bodhaine et al.* [1999] presented a table of values of Rayleigh scattering cross section, and of Rayleigh optical depth for dry air containing 360 ppm CO₂ at sea level, 1013.25 mb, and at latitude 45°; and at MLO (altitude 3400 m, pressure 680 mb, and latitude 19.533°). For those readers who wish to use curve-fitting techniques, *Bodhaine et al.* [1999] investigated several different equations similar to those currently in use by other authors. They found that the accuracies of those equations were not sufficient and therefore looked for a better approach. They found that the equation

$$y = \frac{a + b\lambda^{-2} + c\lambda^2}{1 + d\lambda^{-2} + e\lambda^2} \quad (4)$$

gives excellent accuracy. This five-parameter equation falls in the class of "ratio of polynomials" commonly used in curve-fitting applications. It gives an excellent fit in this case because the general form of the data being fit by the equation is also a ratio of polynomials. For the scattering cross section data the best fit equation is:

$$\sigma (\times 10^{-28} \text{ cm}^2) = \frac{1.0455996 - 341.29061\lambda^{-2} - 0.90230850\lambda^2}{1 + 0.0027059889\lambda^{-2} - 85.968563\lambda^2} \quad (5)$$

Equation (5) is accurate to better than 0.01% over the 250-850 nm range, and still better than 0.05% out to 1000 nm. In fact, this equation is accurate to better than 0.002% over the range 250-550 nm. Best fits for sea level at 45°N, and for MLO are:

τ_R (sea level, 45°N) =

$$0.0021520 \bullet \frac{1.0455996 - 341.29061\lambda^{-2} - 0.90230850\lambda^2}{1 + 0.0027059889\lambda^{-2} - 85.968563\lambda^2} \quad (6)$$

and:

τ_R (MLO, 3.4 km, 680 mb) =

$$0.0014484 \bullet \frac{1.0455996 - 341.29061\lambda^{-2} - 0.90230850\lambda^2}{1 + 0.0027059889\lambda^{-2} - 85.968563\lambda^2} \quad (7)$$

It should be noted that the leading coefficients in Equations (6) and (7) are the only difference from Equation (5). These numerical values represent the columnar density for the two cases.

Conclusion

For the most accurate calculation of Rayleigh optical depth it is recommended that users employ first principles and that *Peck and Reeder's* [1972] formula be used to estimate the refractive index of standard air. Next, *Penndorf's* [1957] method should be used to calculate the scattering cross section per molecule of air, taking into account the concentration of CO₂. In most cases the effects of water vapor may be neglected. The recommendations of *Bates* [1984] were used for the depolarization of air as a function of wavelength. Finally the Rayleigh optical depth should be calculated using the atmospheric pressure at the site of interest. Note the importance of taking into account variations of g . Curve fitting techniques are not necessarily recommended for estimating Rayleigh optical depth because the inaccuracies that arise can equal or even exceed other quantities being estimated, such as aerosol optical depth. However, for those who wish to use a simple equation and are satisfied with less accuracy, the techniques used to produce Equations (5)-(7) may be of interest.

In some calculations of optical depth it may be desired to take into account the vertical distribution of the composition of air, particularly CO₂ and H₂O. In this case a layer-by-layer calculation may be done using the estimated composition for each layer, and then the total optical depth may be estimated by summing the optical depths for all of the layers.