

## On Rayleigh Optical Depth Calculations

BARRY A. BODHAINE

*NOAA/Climate Monitoring and Diagnostics Laboratory, Boulder, Colorado*

NORMAN B. WOOD

*Cooperative Institute for Research in Environmental Sciences, NOAA/Climate Monitoring and Diagnostics Laboratory, Boulder, Colorado*

ELLSWORTH G. DUTTON

*NOAA/Climate Monitoring and Diagnostics Laboratory, Boulder, Colorado*

JAMES R. SLUSSER

*Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, Colorado*

21 January 1999 and 3 May 1999

### ABSTRACT

Many 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. The authors recommend that the calculation of Rayleigh optical depth be approached by going back to the first principles of Rayleigh scattering theory rather than the variety of curve-fitting techniques currently in use. A survey of the literature was conducted in order to determine the latest values of the physical constants necessary and to review the methods available for the calculation of Rayleigh optical depth. The recommended approach requires the accurate calculation of the refractive index of air based on the latest published measurements. Calculations estimating Rayleigh optical depth should be done as accurately as possible because the inaccuracies that arise can equal or even exceed other quantities being estimated, such as aerosol optical depth, particularly in the UV region of the spectrum. All of the calculations are simple enough to be done easily in a spreadsheet.

### 1. Introduction

Modern Rayleigh scattering calculations have traditionally been made by starting with those presented by Penndorf (1957). In Penndorf's paper, the refractive index of air was calculated using the equation of Edlén (1953):

$$(n_s - 1) \times 10^8 = 6432.8 + \frac{2\,949\,810}{146 - \lambda^{-2}} + \frac{25\,540}{41 - \lambda^{-2}}, \quad (1)$$

where  $n_s$  is the refractive index of air and  $\lambda$  is the wavelength of light in micrometers. This equation is for "standard" air, which is defined as dry air at 760 mm Hg (1013.25 mb), 15°C (288.15 K), and containing 300

ppm CO<sub>2</sub>. It is an empirical relationship derived by fitting the best available experimental data and is dependent on the composition of air, particularly CO<sub>2</sub> and water vapor. Next, Penndorf (1957) calculated the Rayleigh scattering coefficient for standard air using the classic equation that is presented in many textbooks (e.g., van de Hulst 1957; McCartney 1976):

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

where  $\sigma$  is the scattering cross section per molecule;  $N_s$  is molecular density; the term  $(6 + 3\rho)/(6 - 7\rho)$  is called the depolarization term,  $F(\text{air})$ , or the King factor; and  $\rho$  is the depolarization factor or depolarization ratio, which describes the effect of molecular anisotropy. The  $F(\text{air})$  term is the least known for purposes of Rayleigh scattering calculations and is responsible for the most uncertainty. The depolarization term does not depend on temperature and pressure, but does depend on the gas mixture. Also,  $N_s$  depends on temperature and pres-

*Corresponding author address:* Barry A. Bodhaine, NOAA/CMDL, R/E/CG1, 325 Broadway, Boulder, CO 80303.  
E-mail: bbodhaine@cmdl.noaa.gov

sure, but does not depend on the gas mixture. The resulting value of  $\sigma$ , the scattering cross section per molecule of the gas, calculated from Eq. (2), is independent of temperature and pressure, but does depend on the composition of the gas. Note that  $N_s$  depends on Avogadro's number and the molar volume constant, and is expressed as molecules per cubic centimeter, and that values for  $n_s$  and  $N_s$  must be expressed at the same temperature and pressure. However, since  $(n_s^2 - 1)/(n_s^2 + 2)$  is proportional to  $N_s$ , the resulting expression for  $\sigma$  is independent of temperature and pressure (McCartney 1976; Bucholtz 1995). Note that the usual approximation  $n_s^2 + 2 \approx 3$  was not included in Eq. (2) in the interest of keeping all calculations as accurate as possible. Results of such calculations were presented by Penndorf (1957) in his Table III. 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.

Soon after Penndorf's paper was published, Edlén (1966) presented a new formula for estimating the refractive index of standard air:

$$(n_s - 1) \times 10^8 = 8342.13 + \frac{2\,406\,030}{130 - \lambda^{-2}} + \frac{15\,997}{38.9 - \lambda^{-2}}, \quad (3)$$

although the maximum deviation of  $n_s$  from the 1953 formula was given as only  $1.4 \times 10^{-8}$ . Edlén (1953, 1966) also discussed the variation of refractive index with temperature and pressure, and also with varying concentrations of  $\text{CO}_2$  and water vapor. In light of the Edlén (1966) revisions, Owens (1967) presented an in-depth treatment of the indexes of refractions of dry  $\text{CO}_2$ -free air, pure  $\text{CO}_2$ , and pure water vapor, and provided expressions for dependence on temperature, pressure, and composition. However, Owens' (1967) main interest was in temperature and pressure variations, and his analysis does not significantly impact our present work because our calculations are performed at the temperature and pressure of "standard" air. Peck and Reeder (1972) further refined the currently available data for the refractive index of air and suggested the formula

$$(n_s - 1) \times 10^8 = 8060.51 + \frac{2\,480\,990}{132.274 - \lambda^{-2}} + \frac{17\,455.7}{39.329\,57 - \lambda^{-2}} \quad (4)$$

for the most accuracy over a wide range of wavelengths. Equation (4) is specified for standard air but at the beginning of their paper, Peck and Reeder (1972) specify standard air as having 330 ppm  $\text{CO}_2$ . Also, they repeat Edlén's (1966) formula, which had clearly defined standard air as having 300 ppm  $\text{CO}_2$ , but state that it applies to air having 330 ppm  $\text{CO}_2$ . Here we will use the equation of Peck and Reeder (1972) and assume that it holds for standard air having 300 ppm  $\text{CO}_2$ .

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. In brief, Young (1981) suggested that the value  $F(\text{air}) = (6 + 3\rho)/(6 - 7\rho) = 1.0480$  be used rather than the value 1.0608 used by Penndorf (1957). This effect alone reduced Rayleigh scattering values by 1.2%; however, it cannot be applied over the entire spectrum because  $F(\text{air})$  is dependent on wavelength. Furthermore, since the depolarization has been measured for the constituents of air (at least in a relative sense), it is possible in principle to estimate the depolarization of air as a function of composition. Bates (1984) and Bucholtz (1995) discussed the depolarization in detail. It appears that currently the best estimates for  $(6 + 3\rho)/(6 - 7\rho)$  use the equations given by Bates (1984) for the depolarization of  $\text{N}_2$ ,  $\text{O}_2$ , Ar, and  $\text{CO}_2$  as a function of wavelength. It is therefore possible to calculate the depolarization of air as a function of  $\text{CO}_2$  concentration.

Bates (1984) gave a formula for the depolarization of  $\text{N}_2$  as a function of wavelength as

$$F(\text{N}_2) = 1.034 + 3.17 \times 10^{-4} \frac{1}{\lambda^2}, \quad (5)$$

and for the depolarization of  $\text{O}_2$  as

$$F(\text{O}_2) = 1.096 + 1.385 \times 10^{-3} \frac{1}{\lambda^2} + 1.448 \times 10^{-4} \frac{1}{\lambda^4}. \quad (6)$$

Furthermore, Bates (1984) recommended that  $F(\text{air})$  be calculated using Eqs. (5) and (6), assuming that  $F(\text{Ar}) = 1.00$ ,  $F(\text{CO}_2) = 1.15$ , and ignoring the other constituents of air.

## 2. 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

$$I(\lambda) = I_0(\lambda) \exp[-\tau(\lambda)/\cos\theta], \quad (7)$$

where  $I_0(\lambda)$  is the extraterrestrial flux at wavelength  $\lambda$ ,  $I(\lambda)$  is the flux reaching the ground,  $\theta$  is the solar zenith angle, and  $\tau(\lambda)$  is the optical depth. Clear-sky measurements of  $I(\lambda)$  as a function of  $\theta$ , and plotted as  $\ln I(\lambda)$  versus  $\sec\theta$ , should yield a straight line with slope  $-\tau(\lambda)$  and intercept  $I_0$  (extrapolated back to  $\sec\theta = 0$ ). An excellent example, along with a discussion of this process, is shown by Stephens (1994) in his Fig. 6.1.

An important point is that  $\tau(\lambda)$ , the total optical depth, may be composed of several components given by

$$\tau(\lambda) = \tau_R(\lambda) + \tau_a(\lambda) + \tau_g(\lambda), \quad (8)$$

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. At this point it should be apparent that in order 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 necessary to calculate only 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

$$\tau_R(\lambda) = \sigma \frac{PA}{m_a g}, \quad (9)$$

where  $P$  is the pressure,  $A$  is Avogadro's number,  $m_a$  is the mean molecular weight of the air, and  $g$  is the acceleration of gravity. Note that  $m_a$  depends on the composition of the air, whereas  $A$  and  $g$  are constants 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 formula (List 1968)

$$\begin{aligned} g \quad (\text{cm s}^{-2}) \\ = g_0 - (3.085\,462 \times 10^{-4} + 2.27 \times 10^{-7} \cos 2\phi)z \\ + (7.254 \times 10^{-11} + 1.0 \times 10^{-13} \cos 2\phi)z^2 \\ - (1.517 \times 10^{-17} + 6 \times 10^{-20} \cos 2\phi)z^3, \end{aligned} \quad (10)$$

where  $\phi$  is the latitude,  $z$  is the height above sea level in meters, and  $g_0$  is the sea level acceleration of gravity given by

$$\begin{aligned} g_0 = 980.6160(1 - 0.002\,637\,3 \cos 2\phi \\ + 0.000\,005\,9 \cos^2 2\phi). \end{aligned} \quad (11)$$

### 3. Approximations for Rayleigh optical depth

Many authors have simply taken Rayleigh scattering cross-section data from Penndorf (1957) over a particular wavelength interval of interest and applied a curve-fitting routine to approximate the data for their own purposes. Some, but not all, of these authors have ap-

plied Young's (1981) correction. Teillet (1990) compared the formulations of several authors and found significant differences among them. It is not the purpose of this paper to survey all of the approximations in use by various authors nor is it to compare accuracies of the various methods; however, a few examples will serve to illustrate some of the difficulties. The simplest approach, taken by many authors, is to fit an equation of the form

$$\tau(\lambda) = A\lambda^{-B}, \quad (12)$$

where  $A$  and  $B$  are constants to be determined from a power-law fit and the equation is normalized to 1013.25-mb pressure. An example was given by Dutton et al. (1994), who performed such a fit over the visible range and provided the equation

$$\tau_R(\lambda) = \frac{p}{p_0} 0.008\,77\lambda^{-4.05}, \quad (13)$$

where  $p$  is the site pressure,  $p_0$  is 1013.25 mb, and  $\lambda$  is in micrometers. Clearly, one problem with this approximation is that it cannot be extrapolated to other parts of the spectrum, particularly the UV, where the power-law exponent is significantly different. To account for the fact that the exponent changes, some authors (e.g., Fröhlich and Shaw 1980; Nicolet 1984) used equations of the form

$$\tau_R(\lambda) = \frac{\text{molecules}}{\text{cm}^2} A\lambda^{-(B+C\lambda+D\lambda^{-1})}, \quad (14)$$

where the term molecules  $\text{cm}^{-2}$  is calculated from the surface pressure, as explained above. This equation is likely to be more accurate over a greater range of the spectrum. A slightly different approach was taken by Hansen and Travis (1974), who suggested the equation

$$\tau_R(\lambda) = 0.008\,569\lambda^{-4}(1 + 0.0113\lambda^{-2} + 0.000\,13\lambda^{-4}), \quad (15)$$

where  $\tau_R(\lambda)$  is normalized to 1013.25 mb. As a final example Stephens (1994) suggested the equation

$$\tau_R(\lambda) = 0.0088\lambda^{(-4.15+0.2\lambda)} e^{(-0.1188z-0.001\,16z^2)}, \quad (16)$$

where the expression is given in terms of altitude (km) above sea level using the standard atmosphere. The point here is that all of these equations were useful for the particular authors over a limited wavelength range and at limited accuracy. Comparing these various equations shows significant differences, especially in the UV (Teillet 1990). More importantly, the differences among these equations can be significantly greater than typical aerosol optical depths found in the atmosphere. In the case of clean conditions at Mauna Loa, it is possible for aerosol optical depth to be calculated as negative values because of these errors.

TABLE 1. Constituents and mean molecular weight of dry air.

Gas	% volume	Molecular wt	% vol $\times$ mol wt
N <sub>2</sub>	78.084	28.013	2187.367
O <sub>2</sub>	20.946	31.999	670.2511
Ar	0.934	39.948	37.311 43
Ne	$1.80 \times 10^{-3}$	20.18	0.036 324
He	$5.20 \times 10^{-4}$	4.003	0.002 082
Kr	$1.10 \times 10^{-4}$	83.8	0.009 218
H <sub>2</sub>	$5.80 \times 10^{-5}$	2.016	0.000 117
Xe	$9.00 \times 10^{-6}$	131.29	0.001 182
CO <sub>2</sub>	0.036	44.01	1.584 36
Mean molecular weight with zero CO <sub>2</sub>			28.959 49 gm mol <sup>-1</sup>
Mean molecular weight with 360 ppm CO <sub>2</sub>			28.964 91 gm mol <sup>-1</sup>

#### 4. Suggested method to calculate Rayleigh optical depth of air

Here we suggest a method for calculation of Rayleigh optical depth that goes back to first principles as suggested by Penndorf (1957) rather than using curve-fitting techniques, although it is true that the refractive index of air is still derived from a curve fit to experimental data. We suggest using all of the latest values of the physical constants of nature, and we suggest including the variability in refractive index, and also the mean molecular weight of air, due to CO<sub>2</sub> 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. Furthermore, it simply makes sense to perform the calculations as accurately as possible.

We should note that the effects of high concentrations of water vapor on the refractive index of air may be of the same order as CO<sub>2</sub> (Edlén 1953, 1966). However, for practical atmospheric situations the total water vapor in the vertical column is small and does not significantly affect the above 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<sub>2</sub> is generally well mixed throughout the atmosphere.

To facilitate the following Rayleigh optical depth calculations, the latest values of Avogadro's number ( $6.022\,136\,7 \times 10^{23}$  molecules mol<sup>-1</sup>), and molar volume at 273.15 K and 1013.25 mb ( $22.4141$  L mol<sup>-1</sup>) were taken from Cohen and Taylor (1995). In order to calculate the mean molecular weight of dry air with various concentrations of CO<sub>2</sub>, the percent by volume of the constituent gases in air were taken from Seinfeld and Pandis (1998), and the molecular weights of those gases were taken from the *Handbook of Physics and Chemistry* (CRC 1997). These results are shown in Table 1. The mean molecular weights ( $m_a$ ) for dry air were calculated from the formula

$$m_a = \frac{\sum (\% \text{Vol} \times \text{MolWt})}{\sum (\% \text{Vol})}. \quad (17)$$

Note that the error arising from the fact that  $\sum (\% \text{Vol})$  is not exactly 100 is negligible. Assuming a simple linear relationship between  $m_a$  and CO<sub>2</sub> concentration,  $m_a$  may be estimated from the equation  $m_a = 15.0556(\text{CO}_2) + 28.9595$  gm mol<sup>-1</sup>, where CO<sub>2</sub> concentration is expressed as parts per volume (use 0.000 36 for 360 ppm).

We recommend starting with Peck and Reeder's (1972) formula for the refractive index of dry air with 300 ppm CO<sub>2</sub> concentration:

$$(n_{300} - 1) \times 10^8 = 8060.51 + \frac{2\,480\,990}{132.274 - \lambda^{-2}} + \frac{17\,455.7}{39.329\,57 - \lambda^{-2}}, \quad (18)$$

and scaling for the desired CO<sub>2</sub> concentration using the formula

$$\frac{(n - 1)_{\text{CO}_2}}{(n - 1)_{300}} = 1 + 0.54(\text{CO}_2 - 0.0003), \quad (19)$$

where the CO<sub>2</sub> concentration is expressed as parts per volume (Edlén 1966). Thus the refractive index for dry air with zero ppm CO<sub>2</sub> is

$$(n_0 - 1) \times 10^8 = 8059.20 + \frac{2\,480\,588}{132.274 - \lambda^{-2}} + \frac{17\,452.9}{39.329\,57 - \lambda^{-2}}, \quad (20)$$

and the refractive index for dry air with 360 ppm CO<sub>2</sub> is

$$(n_{360} - 1) \times 10^8 = 8060.77 + \frac{2\,481\,070}{132.274 - \lambda^{-2}} + \frac{17\,456.3}{39.329\,57 - \lambda^{-2}}, \quad (21)$$

where it must be emphasized that Eqs. (18)–(21) are given for 288.15 K and 1013.25 mb, and  $\lambda$  in units of micrometers.

We recommend that the scattering cross section (cm<sup>2</sup> molecule<sup>-1</sup>) of air be calculated from the equation

$$\sigma = \frac{24\pi^3(n^2 - 1)^2 \left( \frac{6 + 3\rho}{6 - 7\rho} \right)}{\lambda^4 N_s^2 (n^2 + 2)^2}, \quad (22)$$

where  $n$  is the refractive index of air at the desired CO<sub>2</sub> concentration,  $\lambda$  is expressed in units of centimeters,  $N_s = 2.546\,899 \times 10^{19}$  molecules cm<sup>-3</sup> at 288.15 K and 1013.25 mb, and the depolarization ratio  $\rho$  is calculated as follows. Using the values for depolarization of the gases O<sub>2</sub>, N<sub>2</sub>, Ar, and CO<sub>2</sub> provided by Bates (1984), we recommend that the depolarization of dry air be calculated using Eqs. (5)–(6) and the following equation to take into account the composition of air:

$$F(\text{air, CO}_2) = \frac{78.084F(\text{N}_2) + 20.946F(\text{O}_2) + 0.934 \times 1.00 + C_{\text{CO}_2} \times 1.15}{78.084 + 20.946 + 0.934 + C_{\text{CO}_2}}, \quad (23)$$

where  $C_{\text{CO}_2}$  is the concentration of  $\text{CO}_2$  expressed in parts per volume by percent (e.g., use 0.036 for 360 ppm). The results of Eq. (23) for standard air (300 ppm  $\text{CO}_2$ ) are shown in Fig. 1. Note that the value of  $N_s$  in Eq. (22) was calculated from Avogadro's number and the molar volume, and then scaled to 288.15 K according to the formula

$$N_s(\text{molecules cm}^{-3}) = \frac{6.022\,136\,7 \times 10^{23} \text{ molecules mol}^{-1} \cdot 273.15 \text{ K}}{22.4141 \text{ L mol}^{-1} \cdot 288.15 \text{ K}} \times \frac{1 \text{ L}}{1000 \text{ cm}^3}, \quad (24)$$

Finally, we recommend that the Rayleigh optical depth be calculated from the formula

$$\tau_R(\lambda) = \sigma \frac{PA}{m_a g}, \quad (25)$$

where  $P$  is the surface pressure of the measurement site ( $\text{dyn cm}^{-2}$ ),  $A$  is Avogadro's number, and  $m_a$  is the mean molecular weight of dry air calculated from the formula  $m_a = 15.0556(\text{CO}_2) + 28.9595$ , as in Eq. (17). The value for  $g$  needs to be representative of the mass-weighted column of air molecules above the site, and should be calculated from Eqs. (10)–(11), modified by using a value of  $z_c$  determined from the *U.S. Standard Atmosphere*, as provided by List (1968). To determine  $z_c$  we used List's (1968, p. 267) table of the density of air as a function of altitude and calculated a mass-weighted mean above each altitude value, using an average altitude and average density for each layer listed

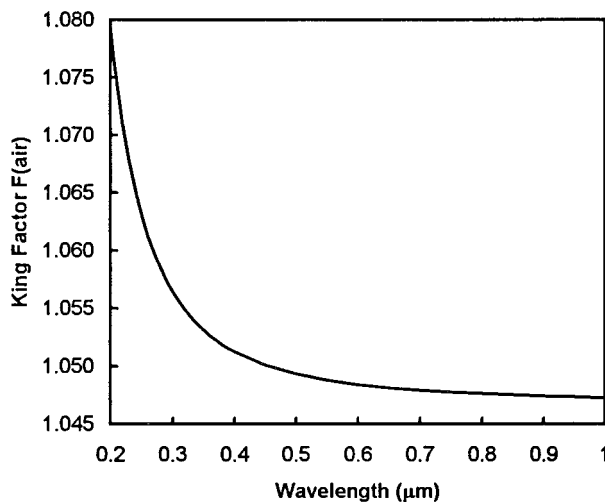


FIG. 1. Depolarization factor for dry air with 300 ppm  $\text{CO}_2$ .

in the table. Next a least squares straight line was passed through the resulting  $z_c$  values up to 10 500 m, giving the following equation:

$$z_c = 0.737\,37z + 5517.56, \quad (26)$$

where  $z$  is the altitude of the observing site and  $z_c$  is the effective mass-weighted altitude of the column. For example, an altitude of  $z = 0$  m yields an effective mass-weighted column altitude of  $z_c = 5517.56$  m to use in the calculation of  $g$ . The resulting values or  $\tau_R$  should be considered the best currently available values for the most accurate estimates of optical depth.

**5. Optical depths of the constituents of air**

As a sensitivity study, the contribution of  $\text{CO}_2$  to the Rayleigh optical depth of air may be estimated as a function of wavelength by using the above formulas expressed for  $\text{CO}_2$ . Owens (1967) gives the refractive index of  $\text{CO}_2$  at 15°C and 1013.25 mb as

$$(n_{\text{CO}_2} - 1) \times 10^8 = 22\,822.1 + 117.8\lambda^{-2} + \frac{2\,406\,030}{130 - \lambda^{-2}} + \frac{15\,997}{38.9 - \lambda^{-2}}, \quad (27)$$

where  $\lambda$  is expressed in units of micrometers as before. Next the scattering cross section of a  $\text{CO}_2$  molecule can be calculated from Eq. (22), where  $N_s = 2.546\,899 \times 10^{19}$  molecules  $\text{cm}^{-3}$  at 288.15 K and 1013.25 mb as before, and the King factor  $F(\text{CO}_2)$  taken to be 1.15, as suggested by Bates (1984). Finally  $\tau(\text{CO}_2, \lambda)$  can be calculated using Eq. (25), where  $m = 44.01$  (the molecular weight of  $\text{CO}_2$ ), and multiplying by 0.000 36 (for a  $\text{CO}_2$  concentration of 360 ppm) to estimate the number of  $\text{CO}_2$  molecules. Note that  $\tau(\text{H}_2\text{O}, \lambda)$  for 44 kg  $\text{m}^{-2}$  column water vapor was calculated in a similar manner using the refractive index of  $\text{H}_2\text{O}$  given by Harvey et al. (1998) and a depolarization ratio of 0.17 for  $\text{H}_2\text{O}$  given by Marshall and Smith (1990). The results of these calculations are shown in Table 2, where the change of optical depth  $\Delta\tau(\text{H}_2\text{O})$  is given for the case where dry air molecules are replaced by  $\text{H}_2\text{O}$  molecules for 44 kg  $\text{m}^{-2}$  column water vapor. Thus for a Rayleigh optical depth of 1.224 for air at 300 nm, a  $\text{CO}_2$  con-

TABLE 2. Optical depths of the constituents of air (standard pressure 1013.25 mb and altitude 0 m).

$\lambda$ (nm)	$\tau$ ( $\text{N}_2 + \text{O}_2 + \text{Ar}$ )	$\tau$ ( $\text{CO}_2$ )	$\tau$ ( $\text{H}_2\text{O}$ )	$\Delta\tau$ ( $\text{H}_2\text{O}$ )
300	1.2232	0.001 031	0.008 654	0.000 189 5
340	0.7163	0.000 605 8	0.004 928	-0.000 029 01
370	0.5015	0.000 424 8	0.003 514	0.000 043 45

centration of 360 ppm would contribute an optical depth about 0.001.

**6. Some example calculations**

Using the above equations we now present example calculations to show new values for the scattering cross section (as a function of wavelength) of dry air containing 360 ppm CO<sub>2</sub>, similar to the presentations of Penndorf (1957) and Bucholtz (1995). In addition we present new values for Rayleigh optical depth for dry air containing 360 ppm CO<sub>2</sub> at sea level, 1013.25 mb, and a latitude of 45°; and at Mauna Loa Observatory (MLO) (altitude 3400 m, pressure 680 mb, and a latitude of 19.533°). The results of these calculations are shown in Table 3.

For those readers who wish to use curve-fitting techniques, we have investigated several different equations similar to those used by other authors, as discussed earlier in this paper. We found that the accuracies of those equations were not sufficient for our purposes, and therefore we looked for a more accurate approach. We find that the equation

$$y = \frac{a + b\lambda^{-2} + c\lambda^2}{1 + d\lambda^{-2} + e\lambda^2} \tag{28}$$

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

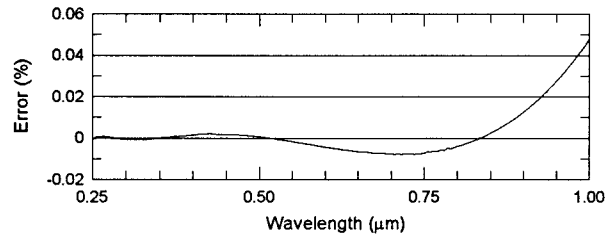


FIG. 2. Percent error for Eq. (29) fit to the scattering cross-section data in Table 3.

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 in Table 3 the best-fit equation is

$$\begin{aligned} \sigma(\times 10^{-28} \text{ cm}^2) &= \frac{1.045\,599\,6 - 341.290\,61\lambda^{-2} - 0.902\,308\,50\lambda^2}{1 + 0.002\,705\,988\,9\lambda^{-2} - 85.968\,563\lambda^2}. \end{aligned} \tag{29}$$

Equation (29) is accurate to better than 0.01% over the 250–850-nm range, and still better than 0.05% out to 1000 nm when fitting the scattering cross-section data in Table 3. In fact, this equation is accurate to better than 0.002% over the range 250–550 nm (see Fig. 2). Best fits for the other two examples provided in Table 3 are

$$\tau_R(\text{sea level, } 45^\circ\text{N}) = 0.002\,152\,0 \left( \frac{1.045\,599\,6 - 341.290\,61\lambda^{-2} - 0.902\,308\,50\lambda^2}{1 + 0.002\,705\,988\,9\lambda^{-2} - 85.968\,563\lambda^2} \right) \text{ and} \tag{30}$$

$$\tau_R(\text{MLO, 3.4 km, 680 mb}) = 0.001\,448\,4 \left( \frac{1.045\,599\,6 - 341.290\,61\lambda^{-2} - 0.902\,308\,50\lambda^2}{1 + 0.002\,705\,988\,9\lambda^{-2} - 85.968\,563\lambda^2} \right). \tag{31}$$

It should be noted that only the leading coefficients in Eqs. (30)–(31) are different from those in Eq. (29). These numerical values represent the values of the  $PA/m_a g$  terms (molecules in the column) given in Eq. (25) for the two cases (taking into account the  $10^{-28}$  factor that was removed from the scattering cross section data to facilitate curve fitting calculations).

**7. Conclusions**

We have presented the latest values of the physical constants necessary for the calculation of Rayleigh optical depth. For the most accurate calculation of this quantity it is recommended that users go directly to first principles and that Peck and Reeder’s (1972) formula be used to estimate the refractive index of standard air. Next, we recommend that Penndorf’s (1957) method be

used to calculate the scattering cross section per molecule of air, taking into account the concentration of CO<sub>2</sub>. 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. Next 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  $g$ . We do not necessarily recommend the use of curve-fitting techniques to generate an equation for estimating Rayleigh optical depth because the inaccuracies that arise can equal or even exceed other quantities being estimated, such as aerosol optical depth. Furthermore, all of the above calculations are simple enough to be done in a spreadsheet if desired, or can easily be programmed in virtually any computer language. However, for those who wish to use a simple

TABLE 3. Scattering cross section (per molecule) and Rayleigh optical depth ( $\tau_R$ ) for dry air containing 360 ppm CO<sub>2</sub>. Rayleigh optical depths are given for a location at sea level, 1013.25 mb, 45° latitude, and at MLO at altitude 3400 m, pressure 680 mb, and latitude 19.533°.

WV ( $\mu\text{m}$ )	$\sigma$ (cm <sup>2</sup> )	$\tau_R$ (sea level, 45°N)	$\tau_R$ (MLO, 680 mb)	King factor
0.250	1.2610E-25	2.7137E+00	1.8264E+00	1.06308
0.255	1.1537E-25	2.4828E+00	1.6710E+00	1.06215
0.260	1.0579E-25	2.2766E+00	1.5322E+00	1.06130
0.265	9.7206E-26	2.0919E+00	1.4079E+00	1.06052
0.270	8.9496E-26	1.9260E+00	1.2962E+00	1.05979
0.275	8.2552E-26	1.7766E+00	1.1956E+00	1.05912
0.280	7.6282E-26	1.6416E+00	1.1048E+00	1.05850
0.285	7.0608E-26	1.5195E+00	1.0227E+00	1.05793
0.290	6.5462E-26	1.4088E+00	9.4813E-01	1.05739
0.295	6.0785E-26	1.3081E+00	8.8038E-01	1.05689
0.300	5.6525E-26	1.2164E+00	8.1868E-01	1.05643
0.305	5.2638E-26	1.1328E+00	7.6238E-01	1.05599
0.310	4.9084E-26	1.0563E+00	7.1092E-01	1.05559
0.315	4.5830E-26	9.8629E-01	6.6379E-01	1.05521
0.320	4.2846E-26	9.2206E-01	6.2056E-01	1.05485
0.325	4.0103E-26	8.6304E-01	5.8084E-01	1.05452
0.330	3.7580E-26	8.0873E-01	5.4429E-01	1.05421
0.335	3.5254E-26	7.5868E-01	5.1060E-01	1.05391
0.340	3.3108E-26	7.1249E-01	4.7952E-01	1.05363
0.345	3.1124E-26	6.6981E-01	4.5079E-01	1.05337
0.350	2.9289E-26	6.3031E-01	4.2421E-01	1.05312
0.355	2.7589E-26	5.9372E-01	3.9958E-01	1.05289
0.360	2.6011E-26	5.5977E-01	3.7673E-01	1.05266
0.365	2.4546E-26	5.2824E-01	3.5551E-01	1.05246
0.370	2.3183E-26	4.9892E-01	3.3578E-01	1.05226
0.375	2.1915E-26	4.7162E-01	3.1741E-01	1.05207
0.380	2.0733E-26	4.4619E-01	3.0029E-01	1.05189
0.385	1.9631E-26	4.2246E-01	2.8432E-01	1.05172
0.390	1.8601E-26	4.0030E-01	2.6941E-01	1.05156
0.395	1.7639E-26	3.7959E-01	2.5547E-01	1.05140
0.400	1.6738E-26	3.6022E-01	2.4243E-01	1.05126
0.405	1.5895E-26	3.4207E-01	2.3022E-01	1.05112
0.410	1.5105E-26	3.2506E-01	2.1877E-01	1.05098
0.415	1.4363E-26	3.0910E-01	2.0803E-01	1.05085
0.420	1.3667E-26	2.9412E-01	1.9795E-01	1.05073
0.425	1.3013E-26	2.8004E-01	1.8847E-01	1.05062
0.430	1.2398E-26	2.6680E-01	1.7956E-01	1.05051
0.435	1.1819E-26	2.5434E-01	1.7118E-01	1.05040
0.440	1.1273E-26	2.4261E-01	1.6328E-01	1.05030
0.445	1.0759E-26	2.3154E-01	1.5583E-01	1.05020
0.450	1.0274E-26	2.2111E-01	1.4881E-01	1.05011
0.455	9.8165E-27	2.1126E-01	1.4218E-01	1.05002
0.460	9.3841E-27	2.0195E-01	1.3592E-01	1.04993
0.465	8.9755E-27	1.9316E-01	1.3000E-01	1.04985
0.470	8.5889E-27	1.8484E-01	1.2440E-01	1.04977
0.475	8.2231E-27	1.7696E-01	1.1910E-01	1.04969
0.480	7.8766E-27	1.6951E-01	1.1408E-01	1.04962
0.485	7.5483E-27	1.6244E-01	1.0933E-01	1.04954
0.490	7.2370E-27	1.5574E-01	1.0482E-01	1.04948
0.495	6.9417E-27	1.4939E-01	1.0054E-01	1.04941
0.500	6.6614E-27	1.4336E-01	9.6480E-02	1.04935
0.505	6.3951E-27	1.3763E-01	9.2624E-02	1.04929
0.510	6.1421E-27	1.3218E-01	8.8959E-02	1.04923
0.515	5.9015E-27	1.2700E-01	8.5475E-02	1.04917
0.520	5.6727E-27	1.2208E-01	8.2161E-02	1.04911
0.525	5.4549E-27	1.1739E-01	7.9006E-02	1.04906
0.530	5.2475E-27	1.1293E-01	7.6002E-02	1.04901
0.535	5.0499E-27	1.0868E-01	7.3140E-02	1.04896
0.540	4.8615E-27	1.0462E-01	7.0412E-02	1.04891
0.545	4.6819E-27	1.0076E-01	6.7811E-02	1.04886
0.550	4.5105E-27	9.7069E-02	6.5329E-02	1.04882
0.555	4.3470E-27	9.3549E-02	6.2960E-02	1.04878

TABLE 3. (Continued)

WV ( $\mu\text{m}$ )	$\sigma$ (cm <sup>2</sup> )	$\tau_R$ (sea level, 45°N)	$\tau_R$ (MLO, 680 mb)	King factor
0.560	4.1908E-27	9.0188E-02	6.0698E-02	1.04873
0.565	4.0416E-27	8.6977E-02	5.8537E-02	1.04869
0.570	3.8990E-27	8.3908E-02	5.6472E-02	1.04865
0.575	3.7627E-27	8.0974E-02	5.4497E-02	1.04861
0.580	3.6323E-27	7.8168E-02	5.2608E-02	1.04858
0.585	3.5075E-27	7.5483E-02	5.0801E-02	1.04854
0.590	3.3880E-27	7.2912E-02	4.9071E-02	1.04851
0.595	3.2736E-27	7.0450E-02	4.7414E-02	1.04847
0.600	3.1640E-27	6.8092E-02	4.5827E-02	1.04844
0.605	3.0590E-27	6.5831E-02	4.4305E-02	1.04841
0.610	2.9583E-27	6.3664E-02	4.2847E-02	1.04837
0.615	2.8618E-27	6.1586E-02	4.1448E-02	1.04834
0.620	2.7691E-27	5.9592E-02	4.0107E-02	1.04831
0.625	2.6802E-27	5.7679E-02	3.8819E-02	1.04829
0.630	2.5948E-27	5.5842E-02	3.7582E-02	1.04826
0.635	2.5128E-27	5.4078E-02	3.6395E-02	1.04823
0.640	2.4341E-27	5.2383E-02	3.5254E-02	1.04820
0.645	2.3584E-27	5.0754E-02	3.4158E-02	1.04818
0.650	2.2856E-27	4.9188E-02	3.3104E-02	1.04815
0.655	2.2157E-27	4.7682E-02	3.2091E-02	1.04813
0.660	2.1484E-27	4.6234E-02	3.1116E-02	1.04810
0.665	2.0836E-27	4.4840E-02	3.0178E-02	1.04808
0.670	2.0213E-27	4.3498E-02	2.9275E-02	1.04806
0.675	1.9612E-27	4.2207E-02	2.8406E-02	1.04804
0.680	1.9035E-27	4.0963E-02	2.7569E-02	1.04802
0.685	1.8478E-27	3.9765E-02	2.6762E-02	1.04799
0.690	1.7941E-27	3.8610E-02	2.5985E-02	1.04797
0.695	1.7424E-27	3.7497E-02	2.5236E-02	1.04795
0.700	1.6926E-27	3.6424E-02	2.4514E-02	1.04793
0.705	1.6445E-27	3.5390E-02	2.3818E-02	1.04792
0.710	1.5981E-27	3.4392E-02	2.3146E-02	1.04790
0.715	1.5533E-27	3.3428E-02	2.2498E-02	1.04788
0.720	1.5101E-27	3.2499E-02	2.1872E-02	1.04786
0.725	1.4684E-27	3.1601E-02	2.1268E-02	1.04784
0.730	1.4282E-27	3.0735E-02	2.0685E-02	1.04783
0.735	1.3893E-27	2.9898E-02	2.0122E-02	1.04781
0.740	1.3517E-27	2.9089E-02	1.9577E-02	1.04779
0.745	1.3154E-27	2.8308E-02	1.9051E-02	1.04778
0.750	1.2803E-27	2.7552E-02	1.8543E-02	1.04776
0.755	1.2463E-27	2.6822E-02	1.8052E-02	1.04775
0.760	1.2135E-27	2.6116E-02	1.7576E-02	1.04773
0.765	1.1818E-27	2.5433E-02	1.7117E-02	1.04772
0.770	1.1511E-27	2.4772E-02	1.6672E-02	1.04770
0.775	1.1214E-27	2.4132E-02	1.6241E-02	1.04769
0.780	1.0926E-27	2.3514E-02	1.5825E-02	1.04768
0.785	1.0648E-27	2.2914E-02	1.5422E-02	1.04766
0.790	1.0378E-27	2.2334E-02	1.5031E-02	1.04765
0.795	1.0117E-27	2.1772E-02	1.4653E-02	1.04764
0.800	9.8642E-28	2.1228E-02	1.4287E-02	1.04762
0.805	9.6191E-28	2.0701E-02	1.3932E-02	1.04761
0.810	9.3817E-28	2.0190E-02	1.3588E-02	1.04760
0.815	9.1515E-28	1.9694E-02	1.3255E-02	1.04759
0.820	8.9283E-28	1.9214E-02	1.2931E-02	1.04758
0.825	8.7120E-28	1.8749E-02	1.2618E-02	1.04757
0.830	8.5021E-28	1.8297E-02	1.2314E-02	1.04756
0.835	8.2986E-28	1.7859E-02	1.2019E-02	1.04754
0.840	8.1011E-28	1.7434E-02	1.1733E-02	1.04753
0.845	7.9095E-28	1.7022E-02	1.1456E-02	1.04752
0.850	7.7235E-28	1.6621E-02	1.1186E-02	1.04751
0.855	7.5429E-28	1.6233E-02	1.0925E-02	1.04750
0.860	7.3676E-28	1.5855E-02	1.0671E-02	1.04749
0.865	7.1974E-28	1.5489E-02	1.0424E-02	1.04748
0.870	7.0321E-28	1.5133E-02	1.0185E-02	1.04747
0.875	6.8715E-28	1.4788E-02	9.9523E-03	1.04746
0.880	6.7154E-28	1.4452E-02	9.7263E-03	1.04746

TABLE 3. (Continued)

WV ( $\mu\text{m}$ )	$\sigma$ ( $\text{cm}^2$ )	$\tau_R$ (sea level, 45°N)	$\tau_R$ (MLO, 680 mb)	King factor
0.885	6.5638E-28	1.4126E-02	9.5067E-03	1.04745
0.900	6.1339E-28	1.3200E-02	8.8841E-03	1.04742
0.905	5.9985E-28	1.2909E-02	8.6880E-03	1.04741
0.910	5.8668E-28	1.2626E-02	8.4972E-03	1.04740
0.915	5.7387E-28	1.2350E-02	8.3117E-03	1.04740
0.920	5.6141E-28	1.2082E-02	8.1312E-03	1.04739
0.925	5.4929E-28	1.1821E-02	7.9556E-03	1.04738
0.930	5.3749E-28	1.1567E-02	7.7848E-03	1.04737
0.935	5.2601E-28	1.1320E-02	7.6184E-03	1.04737
0.940	5.1483E-28	1.1079E-02	7.4566E-03	1.04736
0.945	5.0395E-28	1.0845E-02	7.2989E-03	1.04735
0.950	4.9335E-28	1.0617E-02	7.1455E-03	1.04734
0.955	4.8303E-28	1.0395E-02	6.9960E-03	1.04734
0.960	4.7298E-28	1.0179E-02	6.8505E-03	1.04733
0.965	4.6319E-28	9.9682E-03	6.7087E-03	1.04732
0.970	4.5366E-28	9.7629E-03	6.5706E-03	1.04732
0.975	4.4437E-28	9.5630E-03	6.4360E-03	1.04731
0.980	4.3531E-28	9.3681E-03	6.3049E-03	1.04730
0.985	4.2649E-28	9.1782E-03	6.1770E-03	1.04730
0.990	4.1788E-28	8.9930E-03	6.0524E-03	1.04729
0.995	4.0950E-28	8.8125E-03	5.9310E-03	1.04728
1.000	4.0132E-28	8.6366E-03	5.8125E-03	1.04728

equation and are satisfied with less accuracy, the techniques used to produce Eqs. (29)–(31) may be of interest. As more accurate estimates of the various parameters discussed above become available, the equations of interest may easily be modified.

In some calculations of optical depth it may be desired to take into account the vertical distribution of the composition of air, particularly  $\text{CO}_2$ . 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.

*Acknowledgments.* We thank Gail Anderson for her helpful comments concerning curve-fitting techniques.

## APPENDIX

### Summary of Constants

Values for the constants of nature that have been used in this paper are listed below.

Avogadro's number =  $6.022\,136\,7 \times 10^{23}$  molecules  $\text{mol}^{-1}$

Molar volume at 273.15 K and 1013.25 mb = 22.4141 L  $\text{mol}^{-1}$

Molecular density of a gas at 288.15 K and 1013.25 mb =  $2.546\,899 \times 10^{19}$  molecules  $\text{cm}^{-3}$

Mean molecular weight of dry air (zero  $\text{CO}_2$ ) = 28.9595 gm  $\text{mol}^{-1}$

Mean molecular weight of dry air (360 ppm  $\text{CO}_2$ ) = 28.9649 gm  $\text{mol}^{-1}$

Acceleration of gravity (sea level and 45° latitude)  $g_0(45^\circ) = 980.6160 \text{ cm s}^{-2}$

Mass-weighted air column altitude  $z_c = 0.737\,37z + 5517.56$

## REFERENCES

- Bates, D. R., 1984: Rayleigh scattering by air. *Planet. Space Sci.*, **32**, 785–790.
- Bucholtz, A., 1995: Rayleigh-scattering calculations for the terrestrial atmosphere. *Appl. Opt.*, **34**, 2765–2773.
- Cohen, E. R., and B. N. Taylor, 1995: The fundamental physical constants. *Phys. Today*, **48**, 9–16.
- CRC, 1997: *Handbook of Chemistry and Physics*. D. R. Lide and H. P. R. Frederikse, Eds., CRC Press, 2447 pp.
- Dutton, E. G., P. Reddy, S. Ryan, and J. J. DeLuisi, 1994: Features and effects of aerosol optical depth observed at Mauna Loa, Hawaii: 1982–1992. *J. Geophys. Res.*, **99**, 8295–8306.
- Edlén, B., 1953: The dispersion of standard air. *J. Opt. Soc. Amer.*, **43**, 339–344.
- , 1966: The refractive index of air. *Metrologia*, **2**, 71–80.
- Fröhlich, C., and G. E. Shaw, 1980: New determination of Rayleigh scattering in the terrestrial atmosphere. *Appl. Opt.*, **19**, 1773–1775.
- Hansen, J. E., and L. D. Travis, 1974: Light scattering in planetary atmospheres. *Space Sci. Rev.*, **16**, 527–610.
- Harvey, A. H., J. S. Gallagher, and J. M. H. Levelt Sengers, 1998: Revised formulation for the refractive index of water and steam as a function of wavelength, temperature and density. *J. Phys. Chem. Ref. Data*, **27**, 761–774.
- Hoyt, D. V., 1977: A redetermination of the Rayleigh optical depth and its application to selected solar radiation problems. *J. Appl. Meteor.*, **16**, 432–436.
- List, R. J., 1968: *Smithsonian Meteorological Tables*. Smithsonian, 527 pp.
- Marshall, B. R., and R. C. Smith, 1990: Raman scattering and in-water ocean optical properties. *Appl. Opt.*, **29**, 71–84.
- McCartney, E. J., 1976: *Optics of the Atmosphere*. Wiley, 408 pp.
- Nicolet, M., 1984: On the molecular scattering in the terrestrial atmosphere: An empirical formula for its calculation in the homosphere. *Planet. Space Sci.*, **32**, 1467–1468.
- Owens, J. C., 1967: Optical refractive index of air: Dependence on pressure, temperature and composition. *Appl. Opt.*, **6**, 51–59.
- Peck, E. R., and K. Reeder, 1972: Dispersion of air. *J. Opt. Soc. Amer.*, **62**, 958–962.
- Penndorf, R., 1957: Tables of the refractive index for standard air and the Rayleigh scattering coefficient for the spectral region between 0.2 and 20.0  $\mu$  and their application to atmospheric optics. *J. Opt. Soc. Amer.*, **47**, 176–182.
- Seinfeld, J. H., and S. N. Pandis, 1998: *Atmospheric Chemistry and Physics from Air Pollution to Climate Change*. Wiley, 1326 pp.
- Stephens, G. L., 1994: *Remote Sensing of the Lower Atmosphere*. Oxford University Press, 523 pp.
- Teillet, P. M., 1990: Rayleigh optical depth comparisons from various sources. *Appl. Opt.*, **29**, 1897–1900.
- van de Hulst, H. C., 1957: *Light Scattering by Small Particles*. Wiley, 470 pp.
- Young, A. T., 1980: Revised depolarization corrections for atmospheric extinction. *Appl. Opt.*, **19**, 3427–3428.
- , 1981: On the Rayleigh-scattering optical depth of the atmosphere. *J. Appl. Meteor.*, **20**, 328–330.