Atmospheric Processes ATSC4010 Fall 2014 Jeff Snider

Everything You Wanted to Know about Light Absorption, But Were Afraid to Ask

Attenuation of Radiant Energy by Absorption

The basis for this is a differential equation (Beer's Law), developed by the August Beer (1825-1863), a German physicist and mathematician.

We imagine a radiant flux, represented by F, attenuated by a differential amount (dF) during passage through matter along a differential path length dx.

$$\frac{dF}{F} = -\sigma \cdot \rho \cdot dx$$

Application of Beer's Law to the atmosphere necessitates that we adopt "z" as the coordinate, that the absorber's density be allowed to vary vertically, and that an absorber's wavelength-dependent crossection (σ_λ) be accounted for. Adopting these requirements, and using the atmospheric flux distribution function (ϕ_λ), in place of F (Jacob, Chapter 7), we get Equation 1.

$$\frac{d\varphi_\lambda}{\varphi_\lambda} = \sigma_\lambda \cdot \rho(z) \cdot dz \qquad (1)$$

Equation 1 envisions a flux propagating through the atmosphere, perpendicular to the Earth's surface. We note that dz is negative (dz <0) for a radiant flux propagating downward into the atmosphere.

On the next page we will be integrating Equation 1. That integration requires an integration limit. From consideration Planck's Radiation Law and the Sun-Earth orbital geometry, we can formulate the upper integration limit. It is commonly known as the extraterrestrial flux. We symbolize the extraterrestrial flux as $\phi_\lambda(\infty)$.

$$\varphi_\lambda(\infty) = \frac{R_S^2}{d^2} \cdot \frac{2\pi \cdot hc^2}{\lambda^5 \cdot \left(exp\left(\frac{hc}{\lambda k T_S} \right) - 1 \right)}$$

Attenuation Radiant Energy by Absorption - Continued

In integral form, Beer's Law (Equation 1) looks like this

$$\int_{\varphi_\lambda(z)}^{\varphi_\lambda(\infty)} \frac{1}{\varphi_\lambda} \cdot d\varphi_\lambda = \sigma_\lambda \cdot \int_z^\infty \rho(z) \cdot dz \,.$$

In the previous equation we have assumed that the crossection does not vary with altitude. With integration, we have this

$$\phi_\lambda(z) = \phi_\lambda(\infty) \cdot \exp(-\delta(z)) \qquad \text{(2a)}$$

where the quantity

$$\delta(z) = \sigma_\lambda \cdot \int_z^\infty \rho(z) \cdot dz \qquad \text{(2b)}$$

is defined as atmosphere's optical depth. We note, from Equation 2b, that the optical depth is the product of absorber crossection and absorber column mass.

If we parameterize the absorber's density as $\rho(z) = \rho(0) \cdot \exp(-z/h)$, we derive optical depth as an altitude-dependent function

$$\delta(z) = \sigma_\lambda \cdot h \cdot \rho(0) \cdot \exp(-z/h) \,. \qquad \text{(3)}$$

Summarizing:

1) The shortwave (solar) flux is attenuated by absorption occurring within the Earth's atmosphere. For the cloud-free atmosphere (we have ignored clouds here), the absorption occurs within a few, relatively narrow, wavelength intervals.

2) Both oxygen and ozone absorb solar ultraviolet photons and thus attenuate the shortwave flux at ultraviolet wavelengths; water vapor attenuates solar photons in the near infrared.

3) Attenuation by absorption, in part, explains why the shortwave flux, at the surface, is diminished relative to the extraterrestrial flux (see Figure 7-7 on the next page).

4) Beer's Law (Equation 1) is an example of a physical law, expressed in a differential form. The integral form of Beer's Law (Equation 2a-2b) describes altitude- and wavelength-dependent attenuation due to gaseous absorption.

5) Equations 2a-2b represent a model for absorption by atmospheric gases.

6) Crossection (σ_λ) is a wavelength-dependent property of the absorbing gas. Crossection can be evaluated empirically (spectroscopy), or it can be developed from theory. The latter is one of the topics addressed by quantum mechanics.

7) In this document, crossection (σ_λ) has dimension square meter per kilogram. Hence, optical depth is dimensionless. I.e., crossection times column mass is dimensionless.

8) Optical depth is positive definite; i.e., $\delta \geq 0$. Optical depth's lower-limit ($\delta = 0$) corresponds to negligible crossection or negligible column mass.

9) Optical depth values equal to 1, 2, 3... correspond to altitudes where the radiant flux is attenuated by the factor e^{-1}, e^{-2}, e^{-3}, etc. (Calculator note: $e^{-1} \approx 0.37$; $e^{-2} \approx 0.14$; $e^{-1} \approx 0.05$).

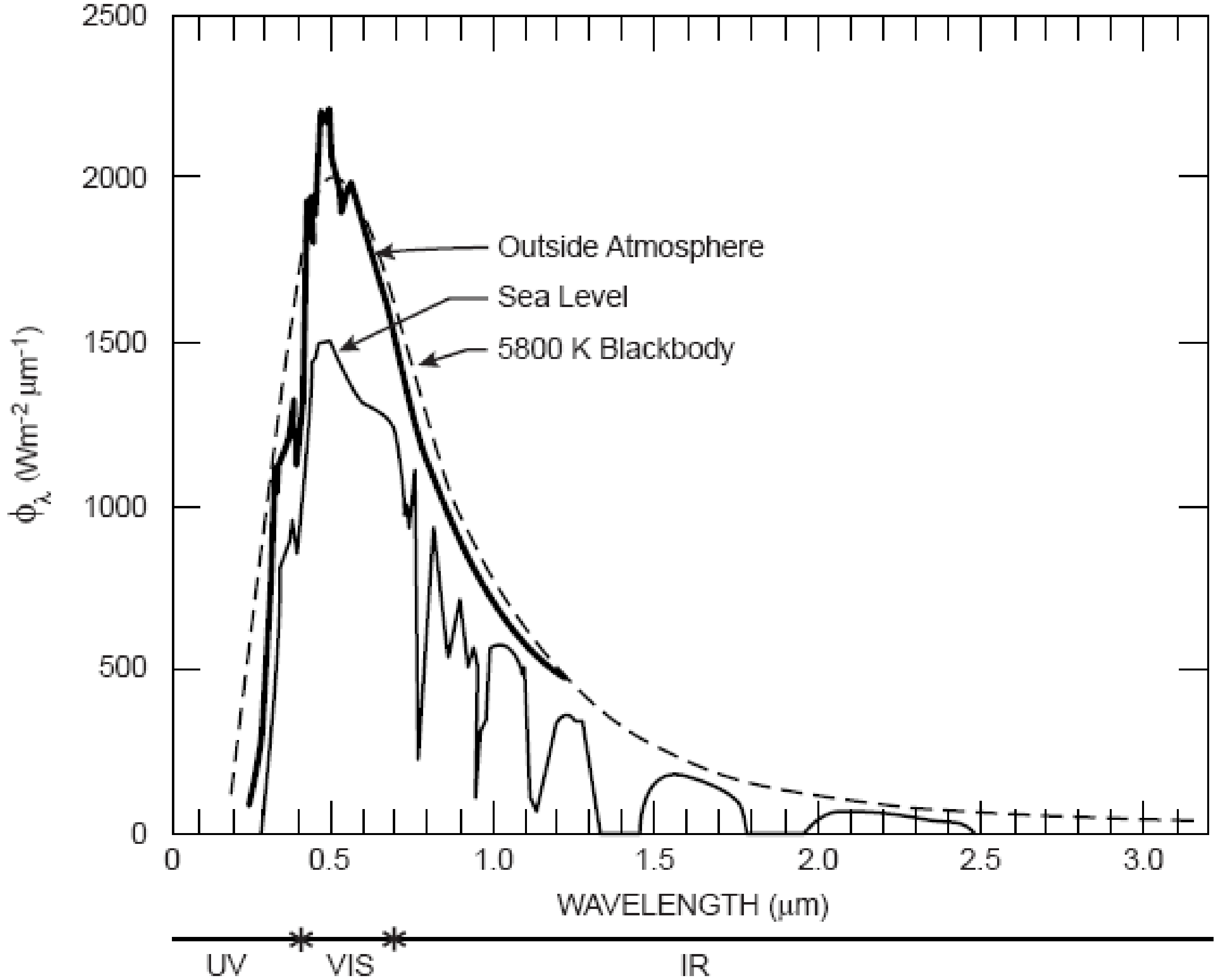
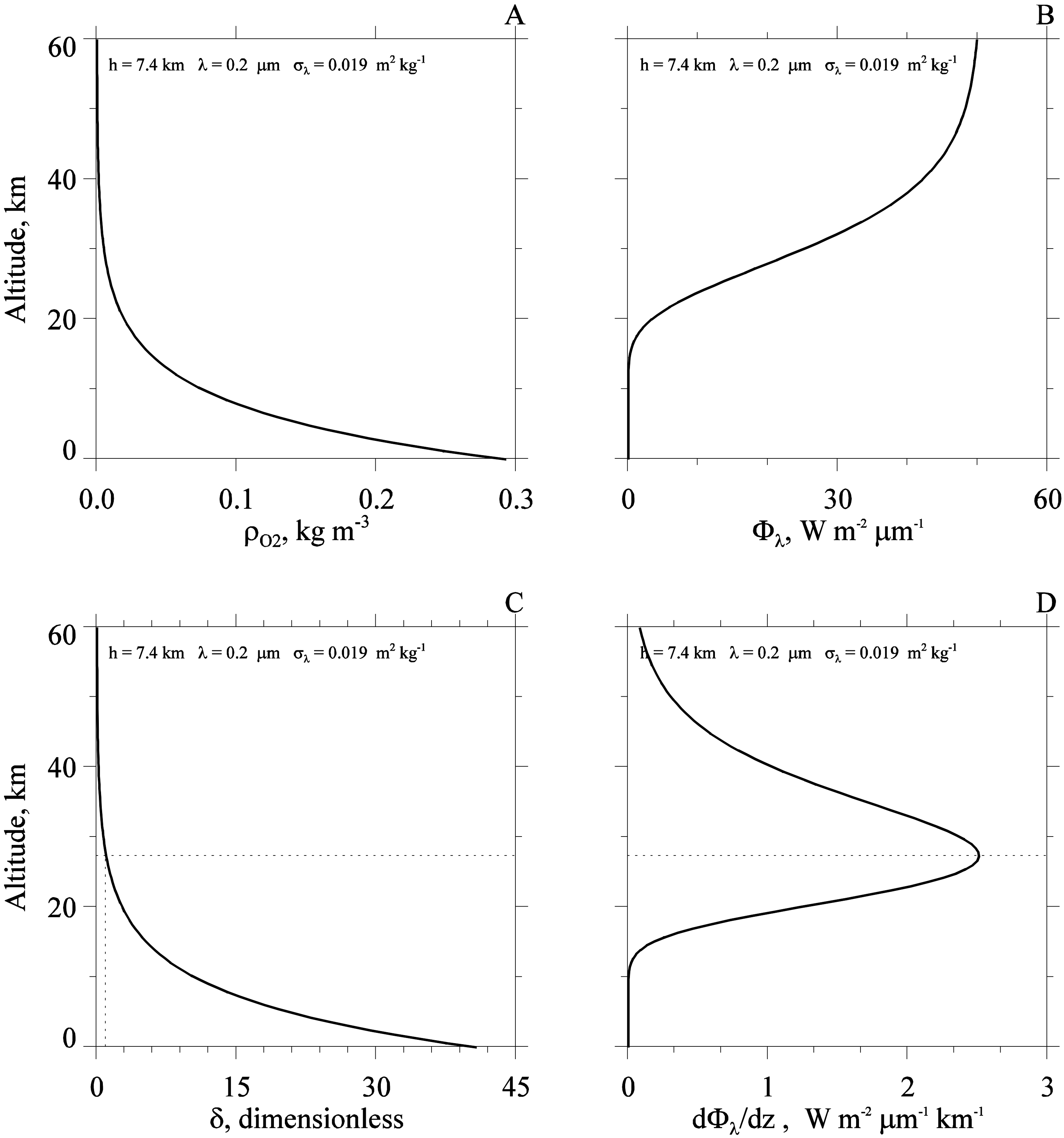


Figure 7-7 Solar radiation spectra measured from a satellite outside Earth's atmosphere (in bold) and at sea level.


A
B
C
D
h = 7.4 km λ = 0.2 μm σ$_\lambda$ = 0.019 m^2 kg^{-1}
Altitude, km
0
20
40
60
0.0
0.1
0.2
0.3
ρ$_{O2}$, kg m^{-3}
0
30
60
Φ$_\lambda$, W m^{-2} μm^{-1}
0
15
30
45
δ, dimensionless
0
1
2
3
dΦ$_\lambda$/dz , W m^{-2} μm^{-1} km^{-1}

The Vertical Derivative of the Radiant Flux

In some applications, for example studies of the stratospheric energy budget and stratospheric chemistry, we are interested in how the radiant flux varies with altitude. Building on what we have developed, particularly Equation 2a, the flux's variation with altitude can be formulated as a derivative

$$\frac{d\varphi_\lambda}{dz} = \frac{d}{dz}\left(\varphi_\lambda(\infty)\cdot exp\left(-\delta(z)\right)\right)$$

By applying the Chain Rule, to the exponential form of Equation 2a, we can formulate the vertical derivative as

$$\frac{d\varphi_\lambda}{dz} = -\varphi_\lambda(z)\cdot\frac{d\delta(z)}{dz}.$$

Now, if we substitute Equation 2b for the optical depth, we have the following

$$\frac{d\varphi_\lambda}{dz} = -\varphi_\lambda(z)\cdot\frac{d}{dz}\left(\sigma_\lambda\cdot\int_z^\infty \rho(z)\cdot dz\right)$$

$$\frac{d\varphi_\lambda}{dz} = \varphi_\lambda(z)\cdot\frac{d}{dz}\left(\sigma_\lambda\cdot\int_\infty^z \rho(z)\cdot dz\right)$$

Assuming that the crossection is independent of altitude, and according to the Fundamental Theorem (calculus), the last equation simplifies to

$$\frac{d\varphi_\lambda}{dz} = \varphi_\lambda(z)\cdot\sigma_\lambda\cdot\rho(z) \qquad (4)$$

The Vertical Derivative of the Radiant Flux - Continued

From Equation 4, we see that the flux derivative ($d\varphi_\lambda / dz$) is a *convolution* of two opposing effects. The first is the tendency for the flux to *decrease* with *decreasing* altitude (absorption) and the second is the *decrease* of gas density with *increasing* altitude (hydrostatics).

A plot of $d\varphi_\lambda / dz$ versus altitude is provided (Figure D). This formulation of $d\varphi_\lambda / dz$ uses Equation 4, with Equations 2a and 3 providing the functional form of $\varphi_\lambda(z)$ (plotted in Figure B), density parameterized as $\rho(z) = \rho(0) \cdot \exp(-z/h)$ (plotted in Figure A), and O_2's crossection at $\lambda = 0.2$ μm (in the ultraviolet). The plot shows a maximum, so our concept of two opposing effects (absorption and hydrostatics) is sound.

In the following discussion of Figure D, we will refer to altitudes smaller than the $d\varphi_\lambda / dz$ maximum ("small altitude"), and to altitudes larger than the $d\phi_\lambda / dz$ maximum ("large altitude").

We attribute the decrease of $d\varphi_\lambda / dz$, at small altitude, to the attenuation of the flux (absorption), and we attribute the decrease of $d\varphi_\lambda / dz$, at large altitude, to the decrease of mass density with increasing altitude (hydrostatics).

What's so Important about Optical Depth Equal to One?

The plots (Figures A, B, C and especially D) demonstrate, for a particular case (O_2 absorbing ultraviolet photons), that $d\varphi_\lambda / dz$ maximizes at an optical depth equal to one ($\delta = 1$). We can use that result to establish a general relationship between altitude and absorber properties (crossection, density and scale height).

We define z' as the altitude of the $d\phi_\lambda / dz$ maximum. At the maximum we have this

$$\left(\frac{d^2 \varphi_\lambda}{dz^2} \right)_{z'} = 0$$

From Equation 4, we have,

$$\left(\frac{d}{dz} \left(d\varphi_\lambda / dz \right) \right)_{z'} = \left(\frac{d}{dz} \left(\varphi_\lambda(z) \cdot \sigma_\lambda \cdot \rho(z) \right) \right)_{z'} = 0$$

Assuming, as before, that the crossection is independent of altitude, we have

$$\left(\frac{d}{dz} \left(\varphi_\lambda(z) \cdot \rho(z) \right) \right)_{z'} = 0$$

According to the product rule (calculus), we have

$$\varphi_\lambda(z') \cdot \left(\frac{d}{dz} \rho(z) \right)_{z'} + \rho(z') \cdot \left(\frac{d}{dz} \varphi_\lambda(z) \right)_{z'} = 0 \qquad (5)$$

What's so Important about Optical Depth Equal to One? - Continued

There are two derivatives in Equation 5. One of those follow from our density parameterization ($\rho(z') = \rho(0) \cdot \exp(-z'/h)$)

$$\left(\frac{d}{dz}\rho(z)\right)_{z'} = \rho(0) \cdot (-1/h) \cdot \exp(-z'/h) = -\frac{\rho(z')}{h}$$

and the other comes from Equation 4

$$\left(\frac{d}{dz}\varphi_\lambda(z)\right)_{z'} = \varphi_\lambda(z') \cdot \sigma_\lambda \cdot \rho(z').$$

Plugging the derivatives into Equation 5, we have

$$-\varphi_\lambda(z') \cdot \frac{\rho(z')}{h} + \rho(z') \cdot \varphi_\lambda(z') \cdot \sigma_\lambda \cdot \rho(z') = 0$$

Canceling common factors, we have

$$-\frac{1}{h} + \sigma_\lambda \cdot \rho(z') = 0.$$

Substituting the density parameterization into the previous equation, we have

$$-\frac{1}{h} + \sigma_\lambda \cdot \rho(0) \cdot \exp(-z'/h) = 0.$$

Solving for the altitude that the derivative maximizes, we get an expression for the altitude of the $d\phi_\lambda / dz$ maximum.

$$z' = h \cdot \ln\left(\sigma_\lambda \cdot \rho(0) \cdot h\right). \qquad (6)$$

Substitution of Equation 6 into Equation 3 establishes that $d\varphi_\lambda / dz$ is a maximum at the altitude (z') that the optical depth is equal to one. It follows that what we see in Figures C and D, with $d\varphi_\lambda / dz$ maximizing at $\delta = 1$, is a general phenomenon.