

# Lecture 7 – Photolysis, part 2

ATOC/CHEM 5151

# Photolysis, review

- Recall that there are three components we need to consider:
  1. The molecule's absorption cross-section ( $\sigma$ )
  2. The quantum yield ( $\Phi$ )
  3. The number of photons present ( $F$ )

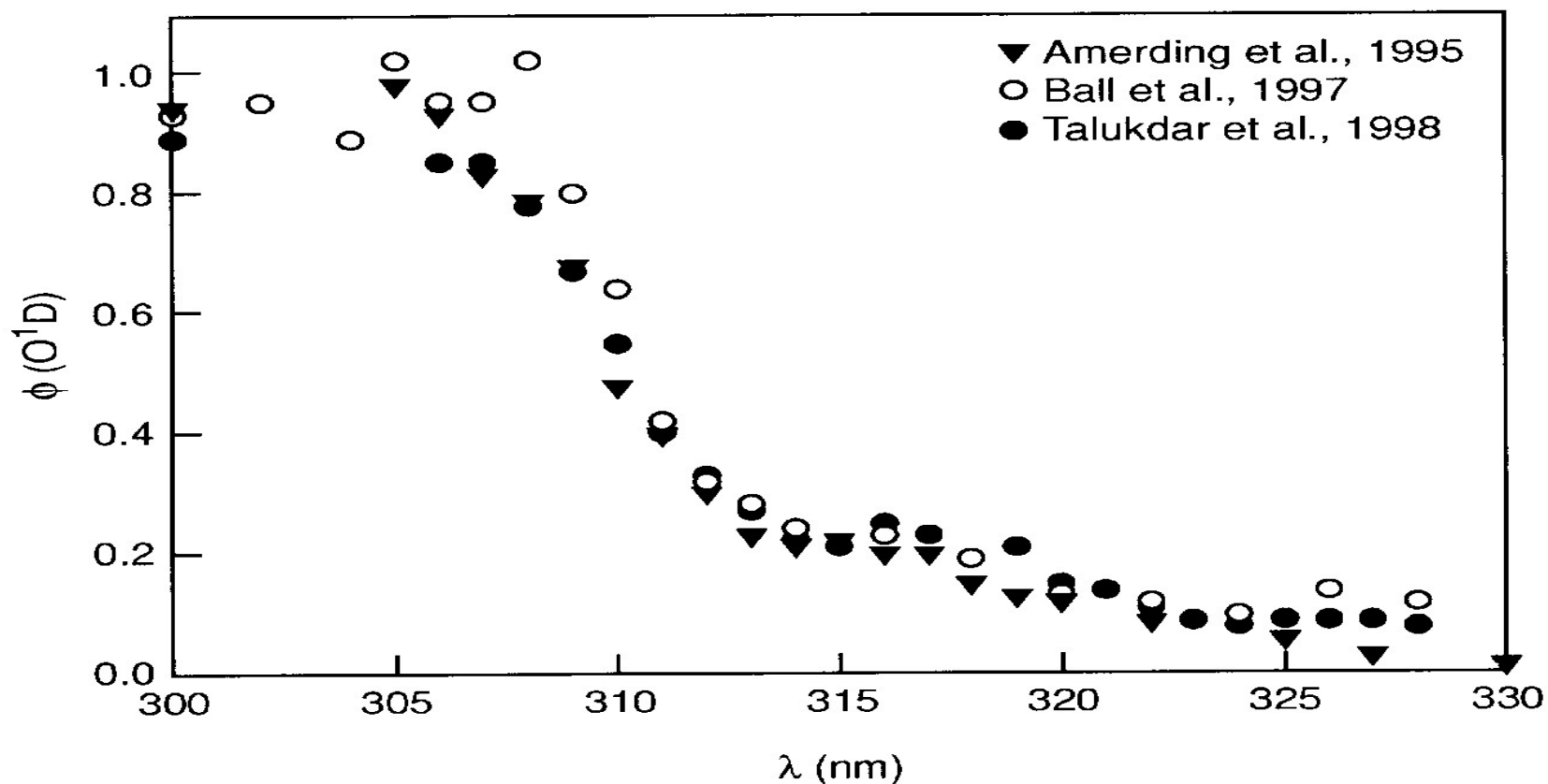
# Quantum Yield

# molecules photolyzed/# photons absorbed

**Why isn't this simply one or zero?**

Note: Must be measured; very hard to calculate.

# Quantum yield, example 1



**FIGURE 4.9** Some measurements of the quantum yields for production of  $O(^1D)$  in the photolysis of  $O_3$  at 298 K.

# Quantum yield, Example 2a

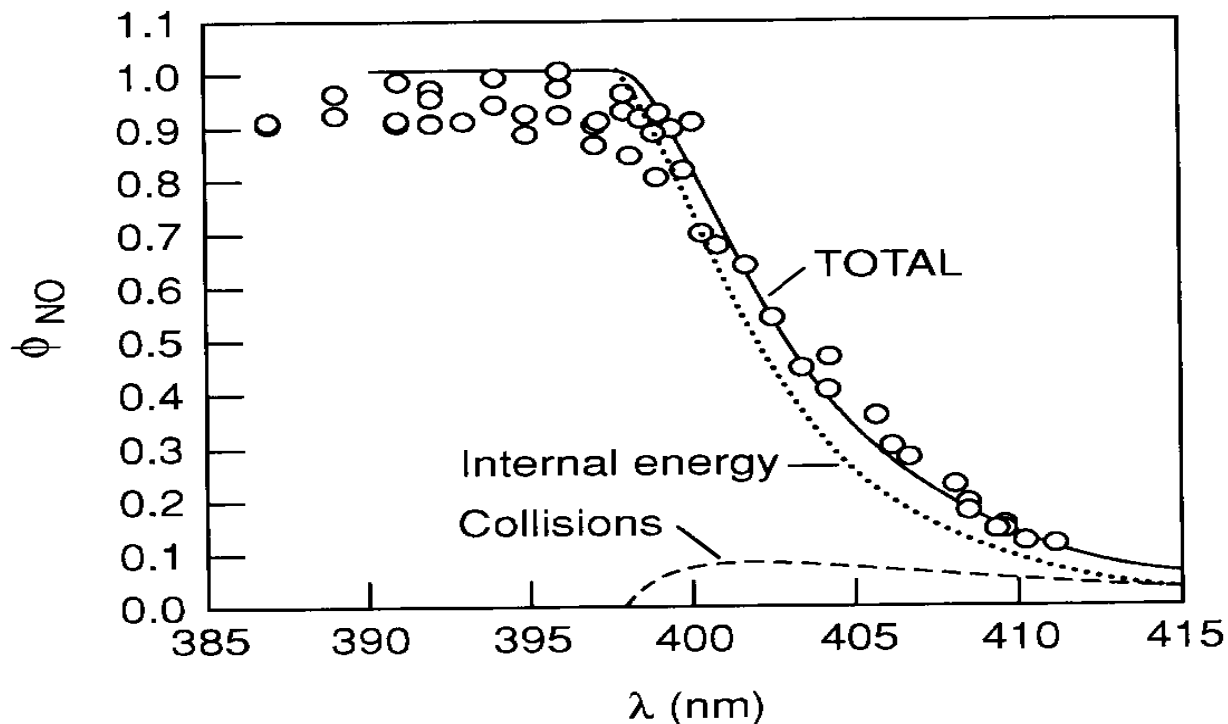
TABLE 4.10 Calculated Wavelengths (nm) for NO<sub>2</sub> Photolysis Below Which the Fragments Shown Can Be Produced<sup>a,b</sup>

NO	Oxygen atoms		
	<sup>3</sup> P	<sup>1</sup> D	<sup>1</sup> S
X <sup>2</sup> Π	397.8	243.9	169.7
A <sup>2</sup> Σ <sup>+</sup>	144.2	117.4	97

<sup>a</sup> From Okabe (1978).

<sup>b</sup> Assuming no contribution from internal energy of the molecule.

# Quantum yield, example 2b



**FIGURE 4.12** Quantum yields for NO production in the photolysis of  $\text{NO}_2$  at 298 K. Calculated quantum yields due to internal energy (dotted line), the calculated dissociation due to collision (dashed line), and the sum of these two calculations (solid line) are also shown (adapted from Roehl *et al.*, 1994).

# Beer-Lambert Law

- Simple model to quantify absorption of light
- $I = I_0 \exp(-n\ell\sigma)$

$n \equiv$  number of absorbers  
( $\text{cm}^{-3}$ )

$\ell \equiv$  pathlength (cm)

$\sigma \equiv$  absorption cross-section  
( $\text{cm}^2 \text{ molec}^{-1}$ )

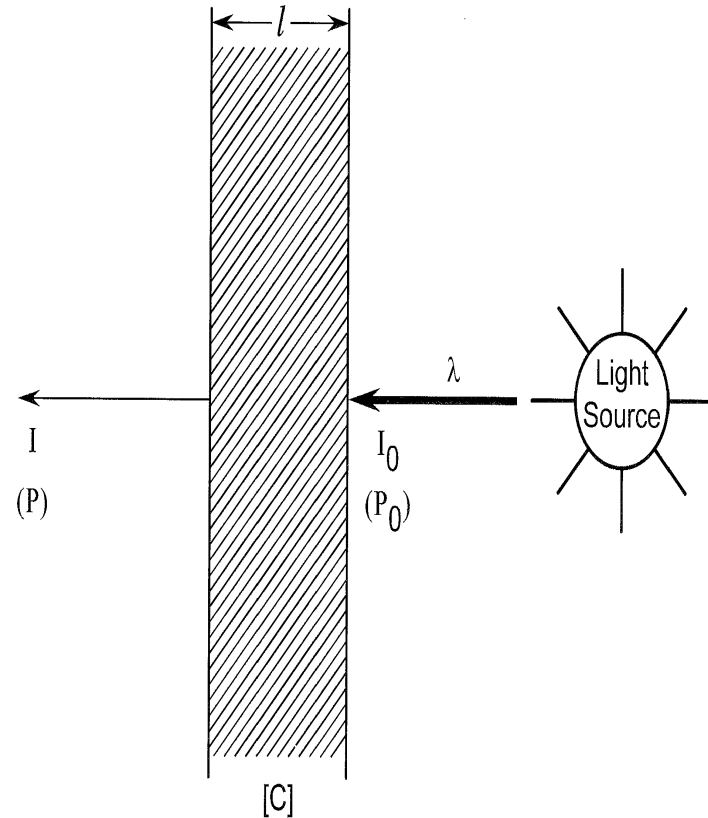
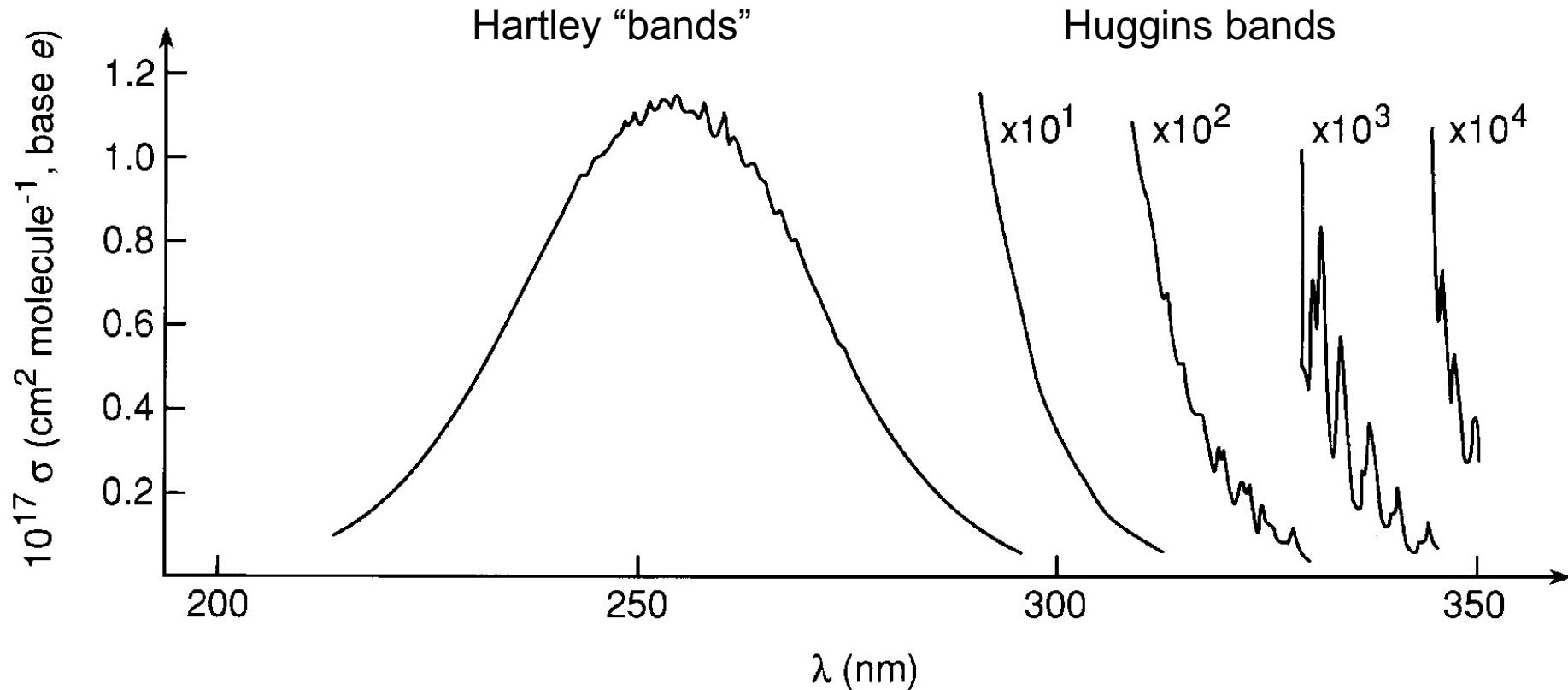


FIGURE 3.11 Schematic diagram of experimental approach to the Beer-Lambert law.

# An example: ozone



**FIGURE 4.7** UV absorption of  $\text{O}_3$  at room temperature in the Hartley and Huggins bands. At the longer wavelengths, each curve has been expanded by the factor shown. (Adapted from Daumont *et al.*, 1989.)



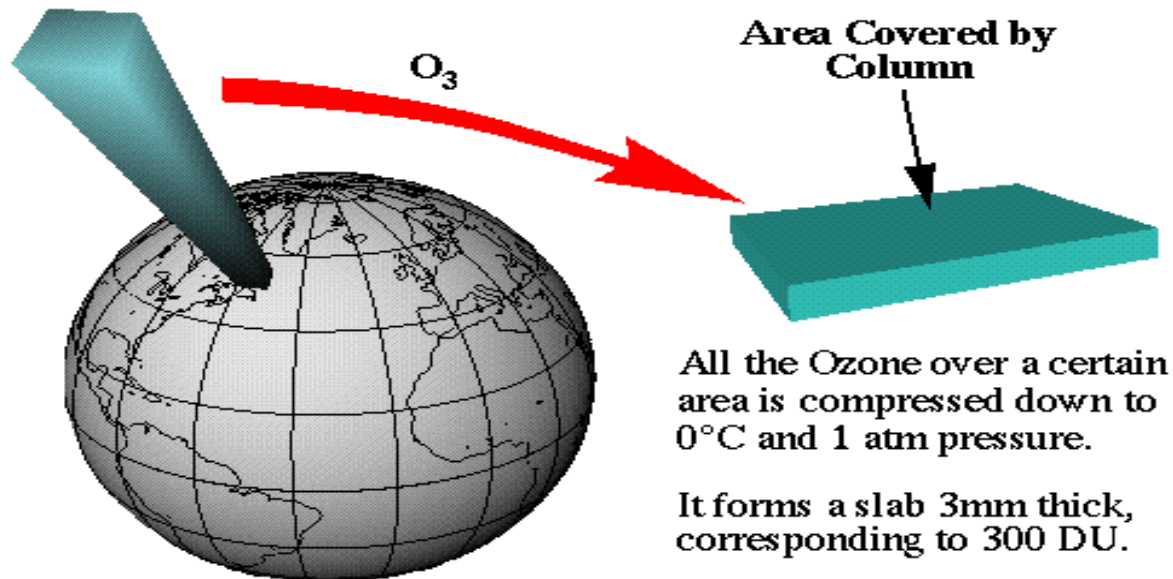
# Ozone example, part 2

Ozone is a particularly important absorber of UV radiation. Let's look at  $\lambda = 250$  nm where  $\sigma = 1.13 \times 10^{-18}$  cm<sup>2</sup> molec<sup>-1</sup> (at 298K)

I have an ozone instrument with a path length of 30 cm and a light source at 250 nm. There is 50 ppb of ozone outside. How much absorption will there be? [Note that density is about  $2.5 \times 10^{19}$  molec cm<sup>-3</sup>].

# Column ozone

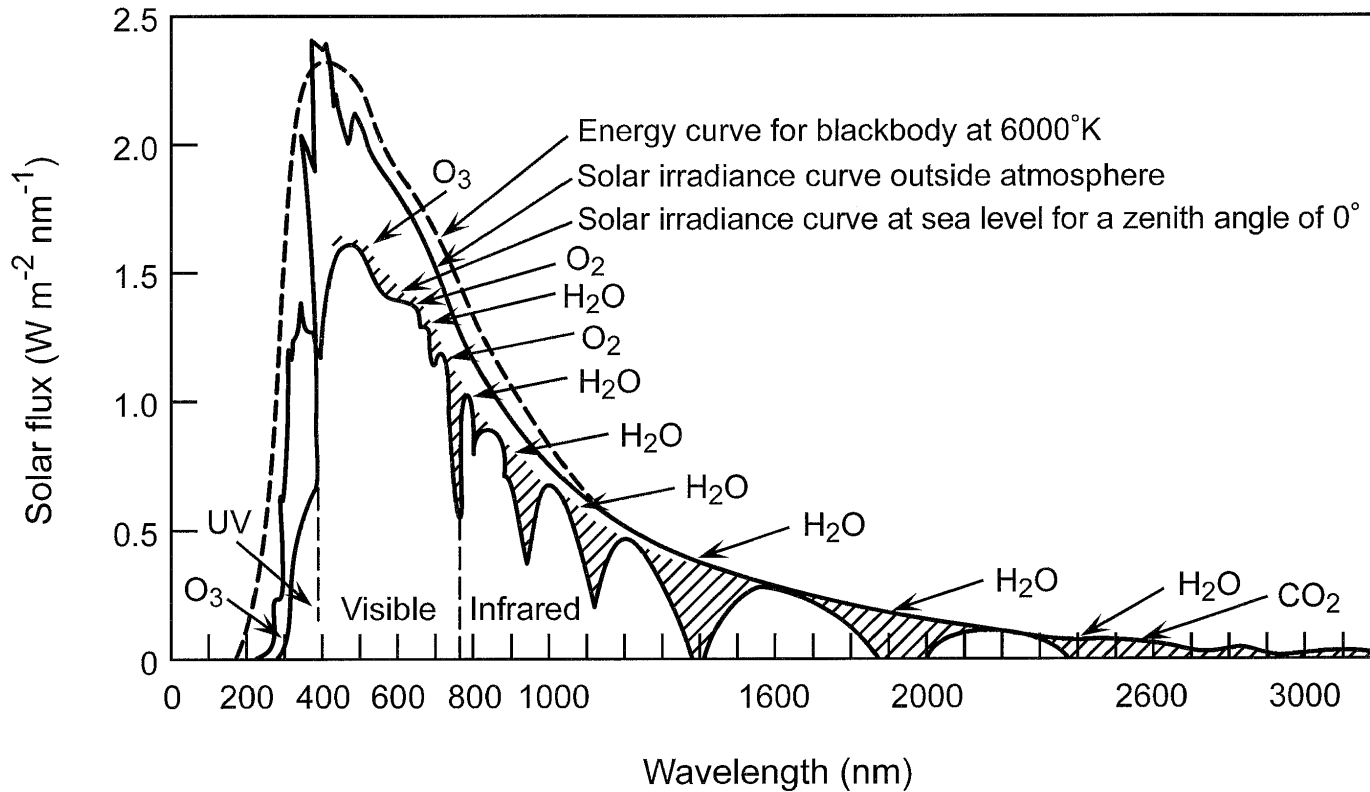
What matters in the atmosphere is the column amount of the absorber of interest.



# Column Ozone, part 2

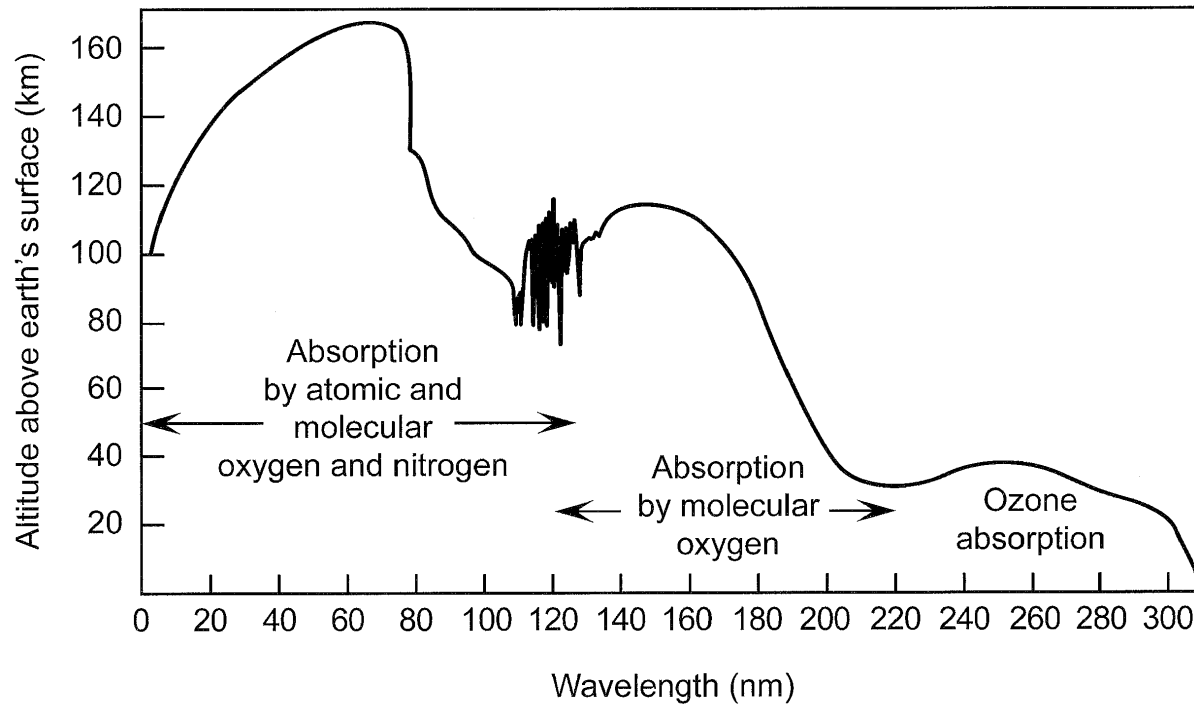
Given the ozone column amount of 300 DU, how much radiation at  $\lambda = 250 \text{ nm}$  makes it to the surface?

# Solar Flux



**FIGURE 3.12** Solar flux outside the atmosphere and at sea level, respectively. The emission of a blackbody at 6000 K is also shown for comparison. The species responsible for light absorption in the various regions ( $\text{O}_3$ ,  $\text{H}_2\text{O}$ , etc.) are also shown (from Howard *et al.*, 1960).

# Removal of solar radiation



**FIGURE 3.13** Approximate regions of maximum light absorption of solar radiation in the atmosphere by various atomic and molecular species as a function of altitude and wavelength with the sun overhead (from Friedman, 1960).

# Calculating J

$$J = \int_{\lambda} F \sigma \Phi d\lambda$$

$$\sigma = \sigma(\lambda, T)$$

$$\Phi = \Phi(\lambda, T)$$

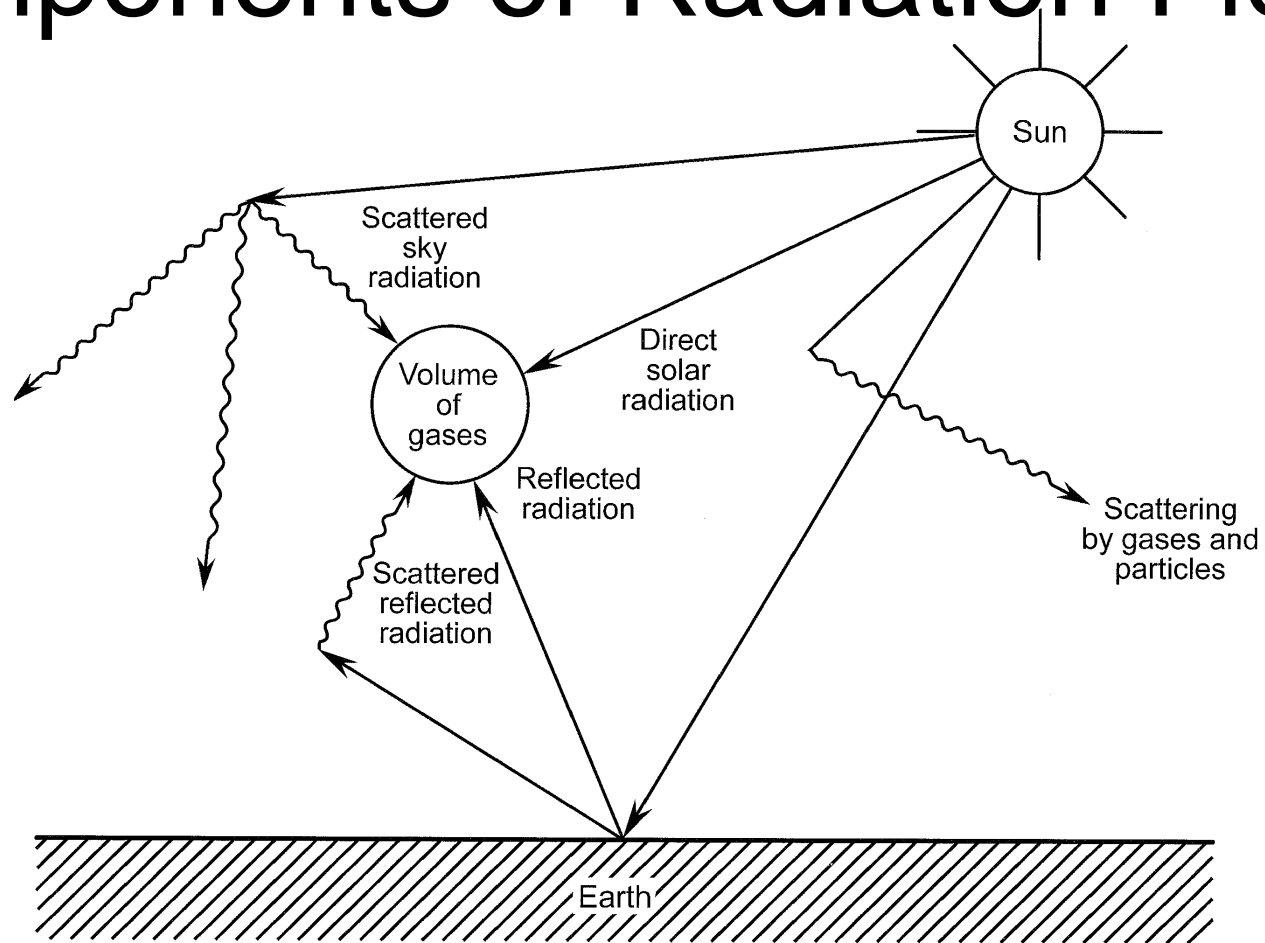
$$F = F(\lambda, z, \text{lat}, \text{albedo}, N_{\text{O}_3}, N_{\text{O}_2}, \text{aerosol})$$

altitude

columns

**Actinic Flux**

# Components of Radiation Field



**FIGURE 3.16** Different sources of radiation striking a volume of gas in the atmosphere. These sources are direction radiation from the sun, radiation scattered by gases and particles, and radiation reflected from the earth's surface.

# Variation of Actinic Flux with Altitude

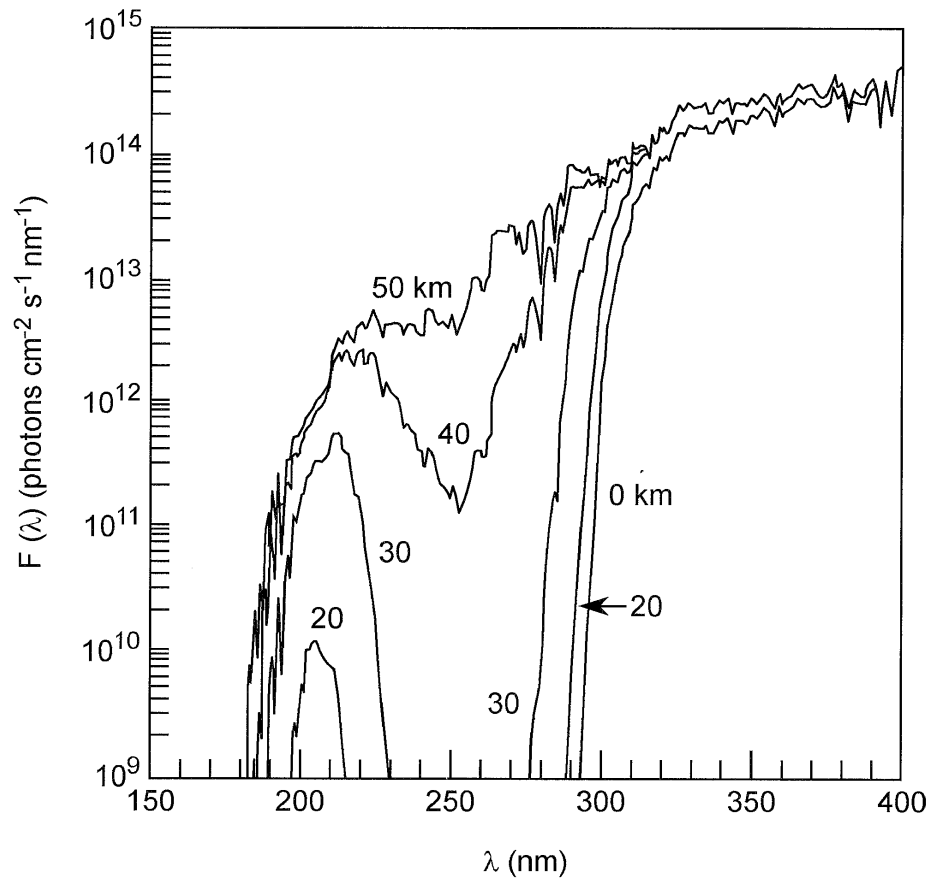


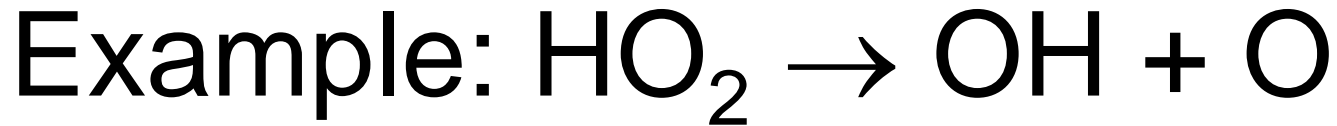
FIGURE 3.32 Calculated actinic fluxes as a function of altitude for a solar zenith angle of  $30^\circ$  and a surface albedo of 0.3. (From DeMore *et al.*, 1997.)



# How to calculate actinic flux

$$F_z = F_\infty \exp[-\sum_i(\sigma_i N_i)] = \\ F_\infty \exp[-(\sigma_{O_3} N_{O_3} + \sigma_{O_2} N_{O_2})]$$

This calculation must be done over the wavelength interval of importance for the molecule of interest.



$\lambda$ (nm)	$\sigma(\text{O}_2)$	$\sigma(\text{O}_3)$	$F_\infty$	$F_{32\text{km}}$	$\sigma(\text{HO}_2)$	$J_\lambda$
230	$2.55 \times 10^{-23}$	$1.75 \times 10^{-17}$	$5.58 \times 10^{13}$	$7.7 \times 10^4$	$2.45 \times 10^{-18}$	$1.9 \times 10^{-13}$
240	$7.78 \times 10^{-24}$	$2.75 \times 10^{-17}$	$6.57 \times 10^{13}$	3.4	$1.35 \times 10^{-18}$	$4.6 \times 10^{-18}$
250	--	$3.50 \times 10^{-17}$	$6.55 \times 10^{13}$	0	$6.0 \times 10^{-19}$	0

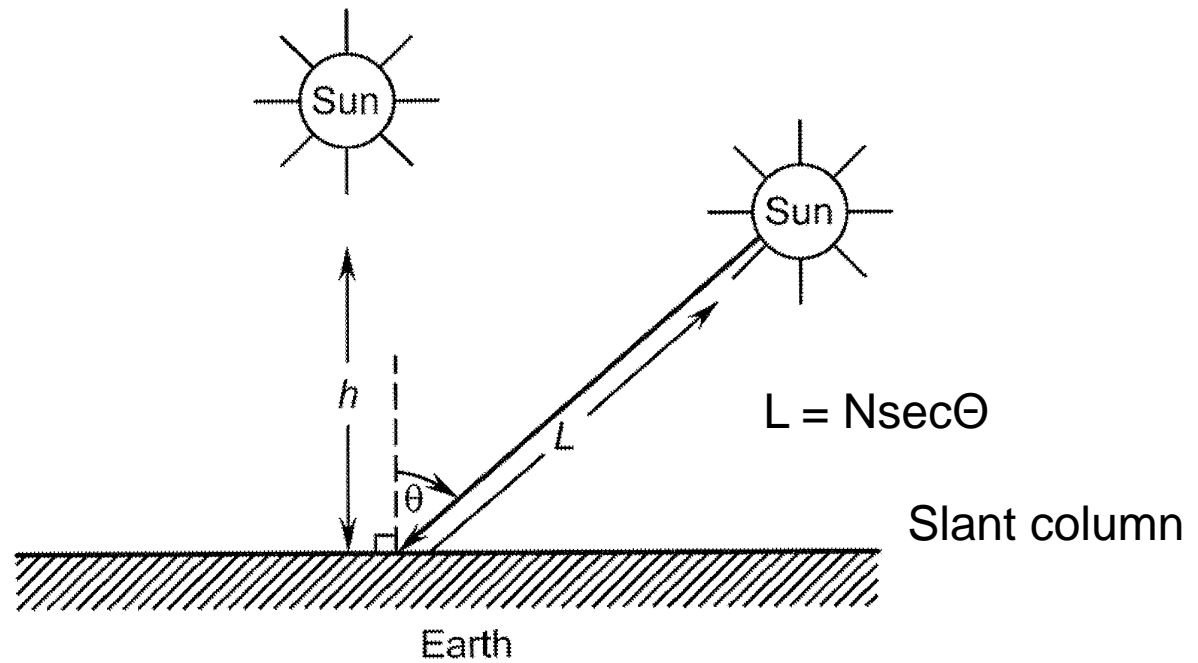


The entire wavelength range of interest extends from 190 – 250 nm.

If we did the same calculation for all wavelength bins:

$$J_{\text{total}} = \sum_{\lambda} J_{\lambda} = 5.2 \times 10^{-7} \text{ s}^{-1}$$

# Sun Angle



**FIGURE 3.14** Definition of solar zenith angle  $\theta$  at a point on the earth's surface.

# Variation of Solar Zenith Angle

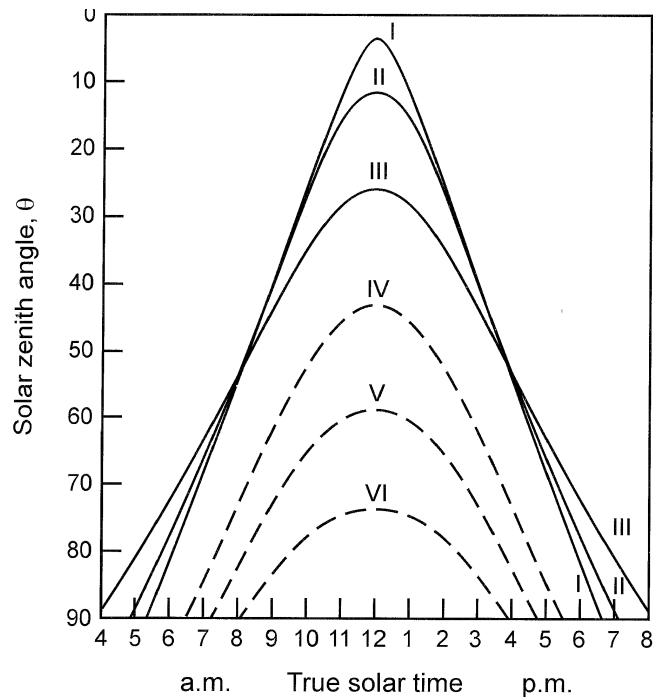


FIGURE 3.22 Effect of latitude on solar zenith angle. On the scale of true solar time, also called apparent solar time and apparent local solar time, the sun crosses the meridian at noon. The latitudes and seasons represented are as follows: I, 20°N latitude, summer solstice; II, 35°N latitude, summer solstice; III, 50°N latitude, summer solstice; IV, 20°N latitude, winter solstice; V, 35°N latitude, winter solstice; VI, 50°N latitude, winter solstice (from Leighton, 1961).

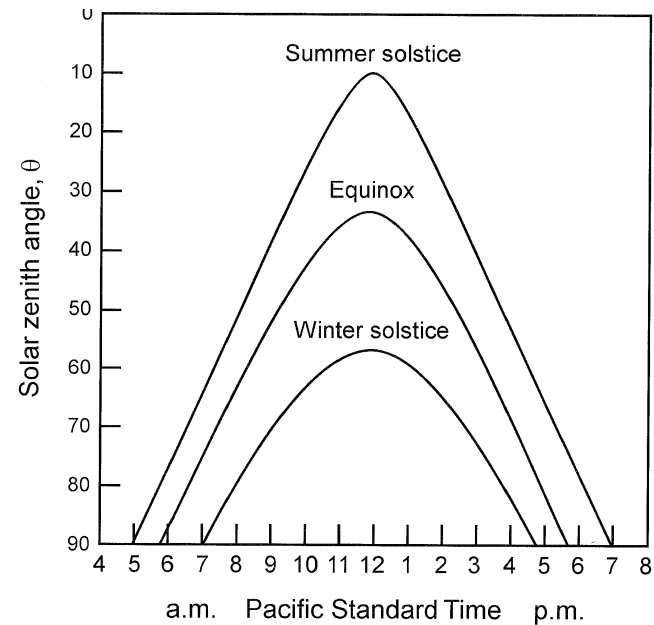


FIGURE 3.23 Relation between solar zenith angle and time of day at Los Angeles, California (from Leighton, 1961).

# Actinic Flux vs. Wavelength

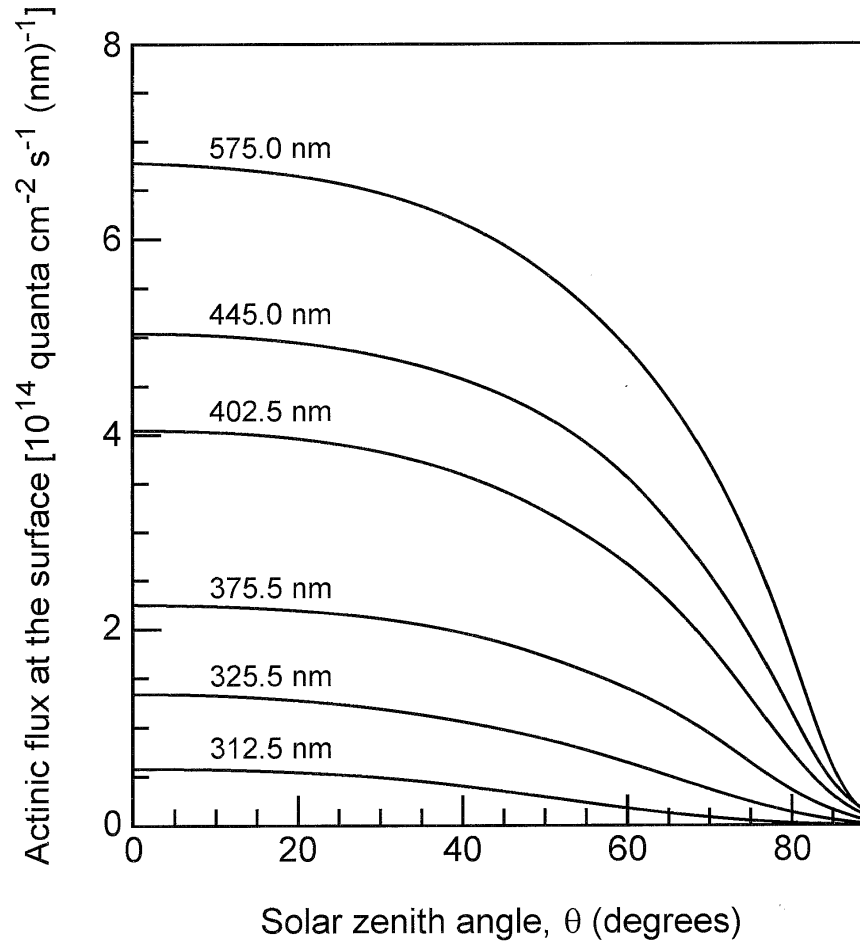


FIGURE 3.21 Calculated actinic flux centered on the indicated wavelengths at the earth's surface using best estimate albedos as a function of solar zenith angle (from Madronich, 1998).

# Light attenuation by scattering

To make a completely correct calculation of  $J$ , need to account for scattering, both by gas molecules and by aerosols.

Generally we use “optical depth”,  $\tau$ , instead of column amounts:

$$I = I_0 e^{-\tau}$$

Note that  $\tau = 1$  means  $I/I_0 = 0.37$

# Scattering components

$$\tau = \tau_{\text{abs}} + \tau_{\text{Ray}} + \tau_{\text{part}}$$

Rayleigh scattering for air,

$$\sigma \approx 4 \times 10^{-28} / \lambda^4 \text{ cm}^2 \text{ molec}^{-1}$$

Scattering by particles is complex; we can't do justice here – depends on size and phase.



# Attenuation components

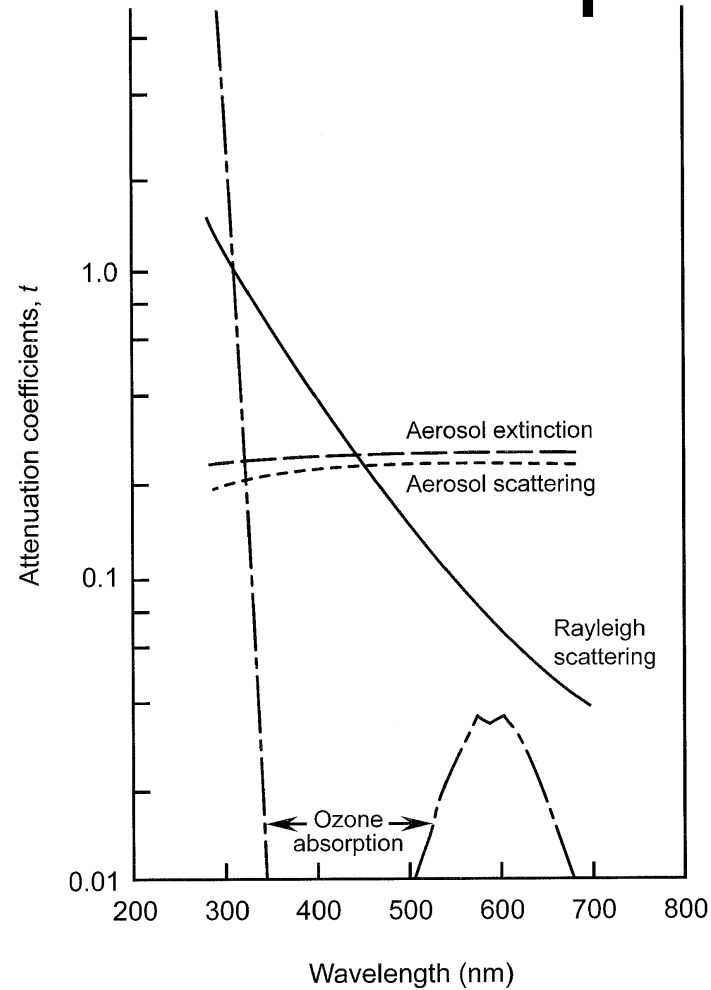


FIGURE 3.15 Attenuation coefficients ( $t$ ) for light scattering (Rayleigh scattering) and absorption (ozone absorption) by gases and for scattering and scattering plus absorption (aerosol extinction) by particles [from Peterson (1976) and Demerjian *et al.* (1980)].