

Photochemistry

Radiation and Photolysis

Weeks 5/6

Objectives

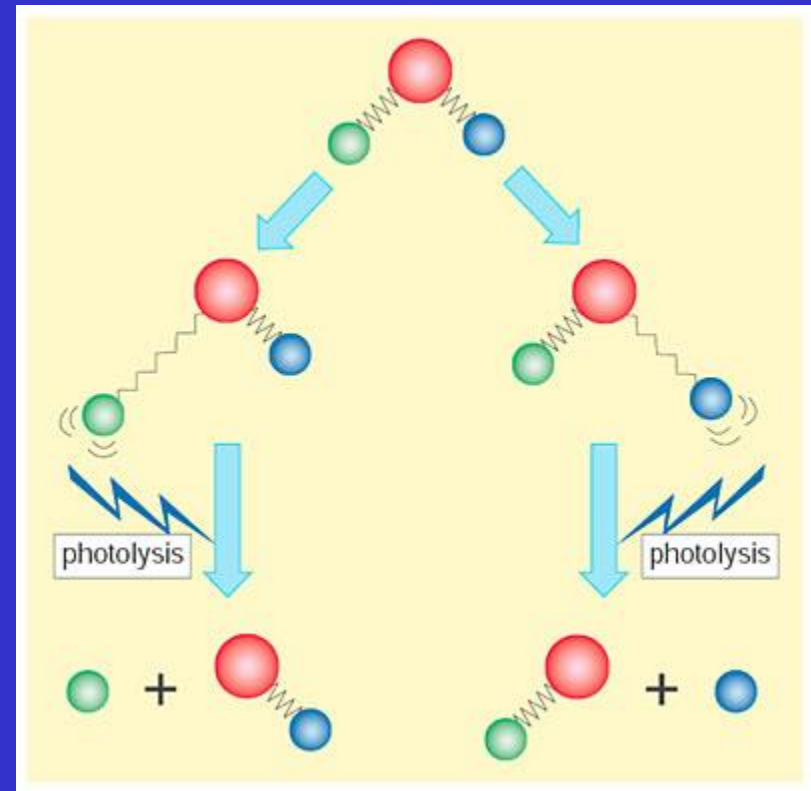
- Review the electromagnetic spectrum
- Review the relationship between energy and wavelength
- Learn about the nature of photolysis
- The Beer-Lambert law

See Page 59-60 in text for example of photolysis

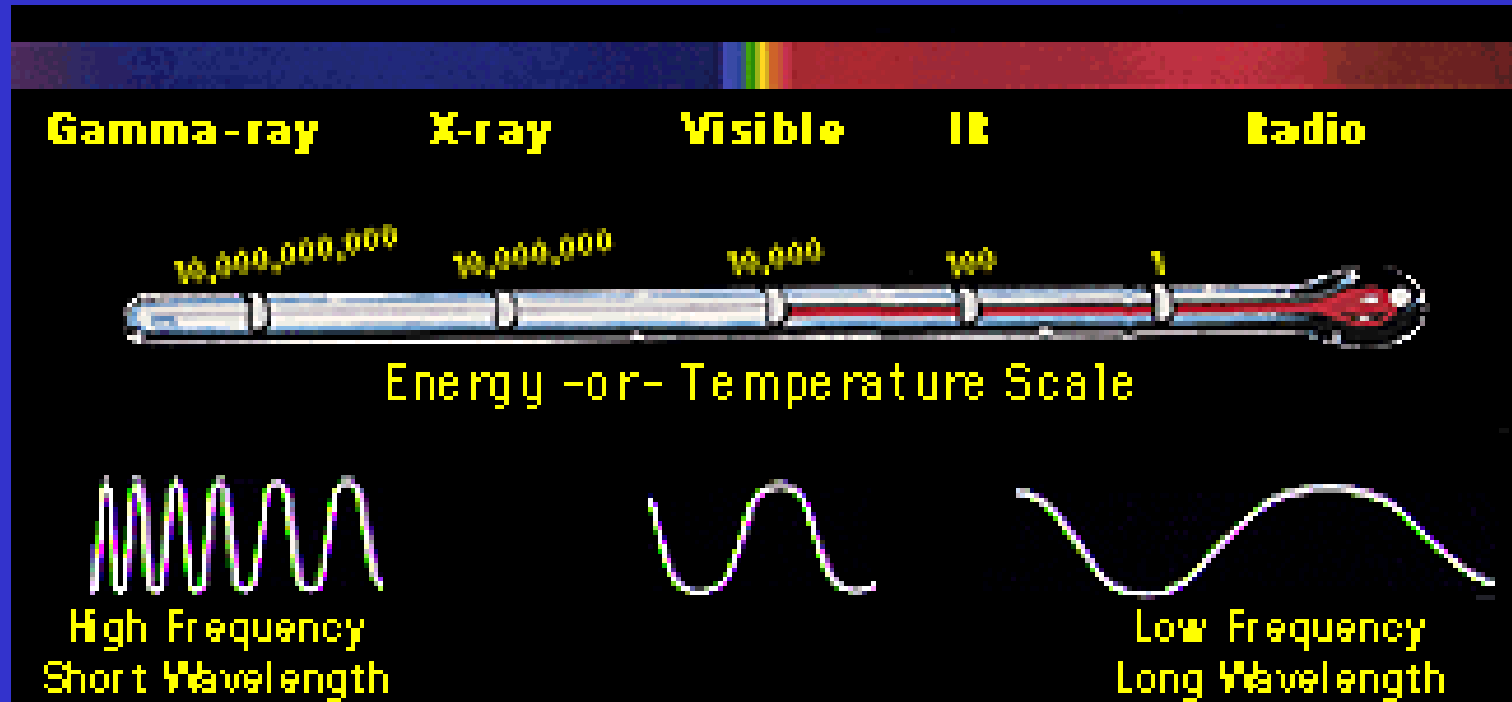
Last time we saw how formation of ozone in the stratosphere is initiated by the photolysis of O_2 in the ultraviolet region of the spectrum. What is photolysis, exactly?

Absorption of a photon by a molecule that results in the breaking of a bond.

Photolysis is a selective process, the breaking of a specific bond based on the energy of the photon (wavelength) and the strength and type of molecular bond (usually covalent)



The Electromagnetic Spectrum



For more information on the electromagnetic spectrum, see this [website](#).

Essentials of Electromagnetic Energy

The "unit" of electromagnetic energy is the photon,

A photon can be thought of as a very tiny particle, but also possesses properties that are like those of a wave (the so-called "wave-particle duality" of light).

Wavelength and frequency are related via the speed of light, which in a vacuum is the same value for all wavelengths:

$$\lambda \nu = c = 3.00 \times 10^8 \text{ m s}^{-1}$$

wavelength x frequency = speed of light

(Checking dimensions
 $\text{m} \times \text{s}^{-1} = \text{m s}^{-1}$)

Wavelength is the distance from peak to peak in a wave, and is always given in units of meters, nanometers ($1 \text{ nm} = 10^{-9} \text{ m}$), micrometers or “microns” ($1 \text{ }\mu\text{m} = 10^{-6} \text{ m}$), and even centimeters ($1 \text{ cm} = 10^{-2} \text{ m}$) or millimeters ($1 \text{ mm} = 10^{-3} \text{ m}$). This is to span the very wide range of wavelengths that are encountered in our daily lives (see Sample Problem in next slide).

Frequency is the number of waves that pass in a second and is typically given as s^{-1} or Hertz (Hz).

Energy = Planck's constant x frequency

Thus, energy of a photon is related to its wavelength via:

$$E = h\nu = hc/\lambda$$

where $h = 6.626 \times 10^{-34}$ Joule seconds (or “J s”)

Energy is sometimes given in Watts (W), which are joules per second, or J s^{-1} . In reality, a Watt is a unit of power, the rate at which energy is done (i.e. energy per unit time)

Sample Problem: A microwave oven puts out radiation at 50 GHz. What is the corresponding energy of the microwave photons? What is the wavelength of the photons? How does a microwave oven heat food anyway?

First note that 50 GHz is a frequency ($\text{Hz} = \text{s}^{-1}$)

$$\begin{aligned} E &= h\nu = (6.626 \times 10^{-34} \text{ J s}) \times (50 \times 10^9 \text{ s}^{-1}) \\ &= 3.313 \times 10^{-23} \text{ J} \end{aligned}$$

$$\lambda\nu = c$$

$$\text{so } \lambda = c/\nu$$

$$\lambda = (3 \times 10^8 \text{ m s}^{-1}) / (50 \times 10^9 \text{ s}^{-1})$$

$$\lambda = 6 \times 10^{-3} \text{ m} (= 6 \text{ millimeters or “mm”})$$

Microwaves heat food by exciting a rotational transition within water molecules. The excited water molecules exchange their energy with other molecules in the food, warming it up.

Sample Problem: A typical laser pointer puts out about 5 mW of red light at a wavelength of 653 nm. How many photons is this in one second?

We are given a power for the laser pointer, 5 mW (5 milliW, or 5×10^{-3} W)

$$5 \times 10^{-3} \text{ W} = 5 \times 10^{-3} \text{ J s}^{-1}$$

Since we're asked for the number of photons in one second, we are dealing with a total energy of 5×10^{-3} J.

Next we calculate the amount of energy in a single 653 nm photon:

$$\begin{aligned} E &= hc/\lambda \\ &= (6.626 \times 10^{-34} \text{ J s}) \times (3 \times 10^8 \text{ m s}^{-1}) / (653 \times 10^{-9} \text{ m}) \\ &= 3.04 \times 10^{-19} \text{ J (per photon)} \end{aligned}$$

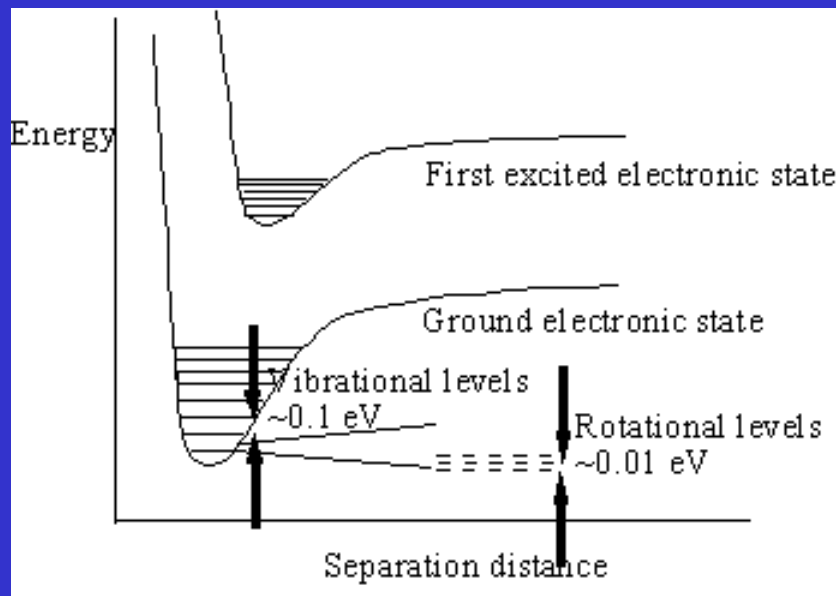
Then,

$$\begin{aligned} \text{Total photons} &= (5 \times 10^{-3} \text{ J}) / (3.04 \times 10^{-19} \text{ J photon}^{-1}) \\ &= 1.64 \times 10^{16} \text{ photons} \end{aligned}$$

The Nature of Photolysis

When a molecule or atom absorbs (or emits) light energy, it must undergo an internal change to account for this change in total energy. That change may be in vibrational, rotational, or electronic energy (i.e., the configuration of the electrons in the molecule). Chemists illustrate the electronic state of a molecule using what is called an "energy level diagram". Energy level diagrams come in many forms, and can be relatively simple to understand, or quite complex.

Here is an example of an energy level diagram for a diatomic molecule:



What determines photolysis rates in the atmosphere?

The photolysis rate (J) for any molecule is determined by a number of factors:

- Absorption cross section, as a function of λ
- Amount of solar radiation, as a function of λ , which depends on season, latitude, time of day, O_3 , O_2 column, and amount of aerosol

To calculate a photolysis rate, one performs a complex integration:

$$J = \int_{\lambda} \sigma(\lambda) \epsilon(\lambda) q(z, \chi, \lambda) d\lambda$$

where σ is the molecular absorption cross-section, ϵ is the "quantum yield", and q is the solar flux (a function of altitude (z), solar zenith angle (χ) and wavelength (λ)).

A photolysis rate is a product of three terms:

(1) Brightness of the source:

“Solar flux”

(2) Ability for a molecule to absorb electromagnetic radiation:

“Molecular absorption coefficient”

(3) The ability for the absorbed energy to break a molecular bond:

“Quantum yield”

All three of these terms vary with wavelength, so we recognize that the photolysis rate will depend strongly on a molecule's interaction with radiation of different wavelengths.

The first thing that we note is that if there isn't enough energy to break a molecular bond, then there won't be photolysis at that wavelength.

Most covalent chemical bonds are about 350-450 kJ mole⁻¹. When we work this out, it corresponds to a wavelength of 340 nm (for the lower energy range) to 265 nm (for the higher energy range). This is in the ultraviolet region of the spectrum.

So unless a bond is relatively weak, photolysis can't occur at visible and longer wavelengths.

Most molecules of atmospheric significance photolyze in the UV,



But some can be dissociated by visible light. These are the ones that have weak bonds.

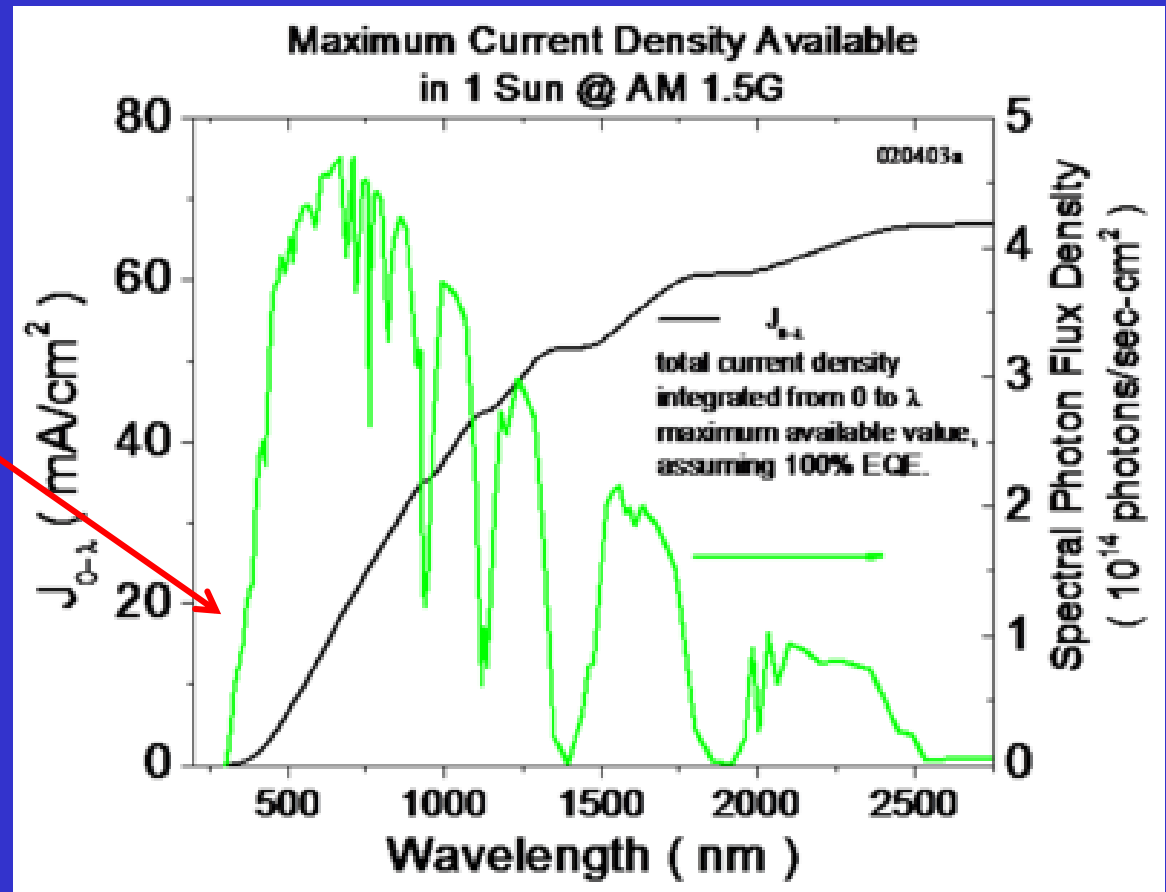


Example - The bond strength for Cl_2 is 243 kJ mole^{-1} , which corresponds to 492 nm , which is in the blue-green portion of the spectrum (so Cl_2 gas tends to look green!)

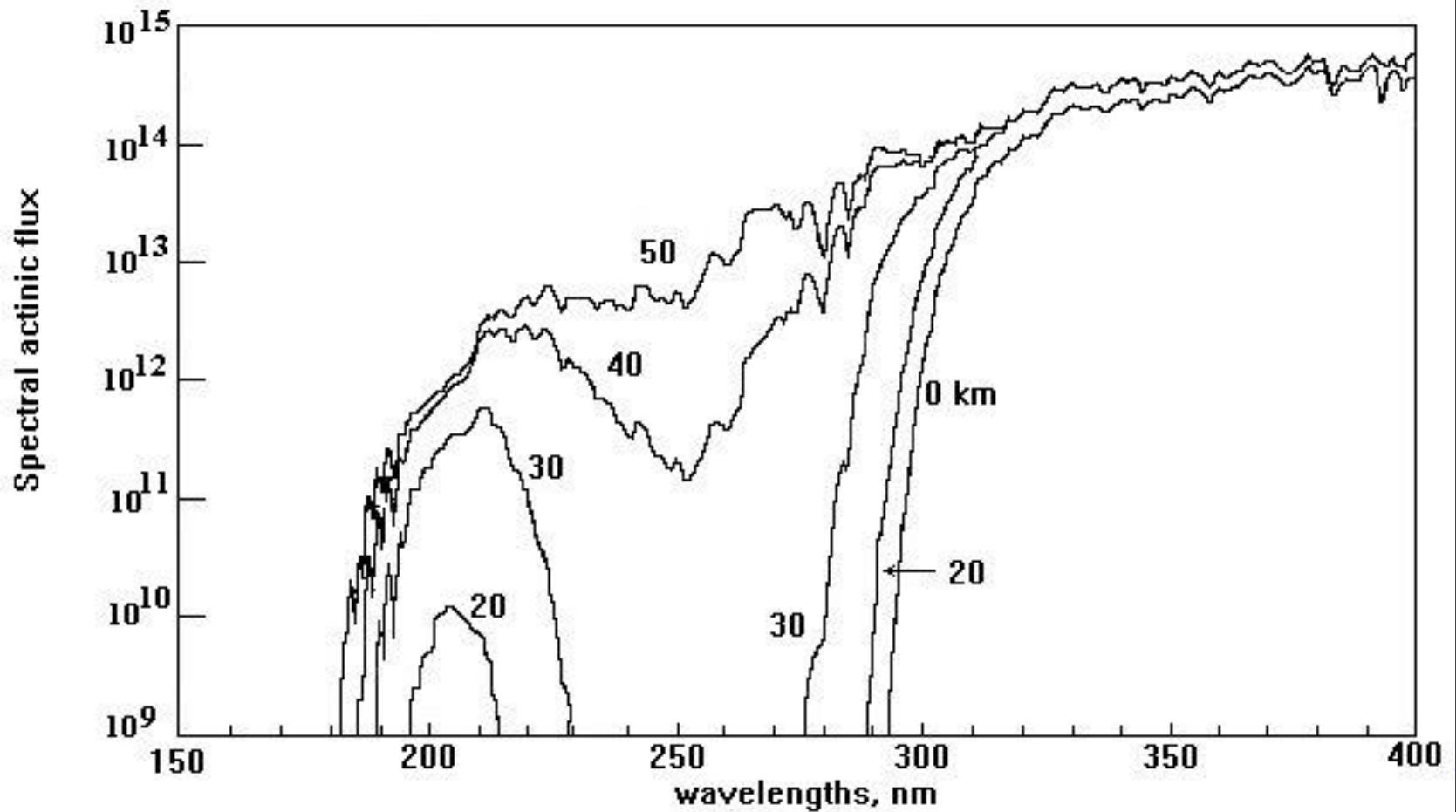
Solar flux at surface

Solar panel manufacturers are quite familiar with the solar spectrum, because it is the basis of their revenue. This figure is from a solar energy web site:

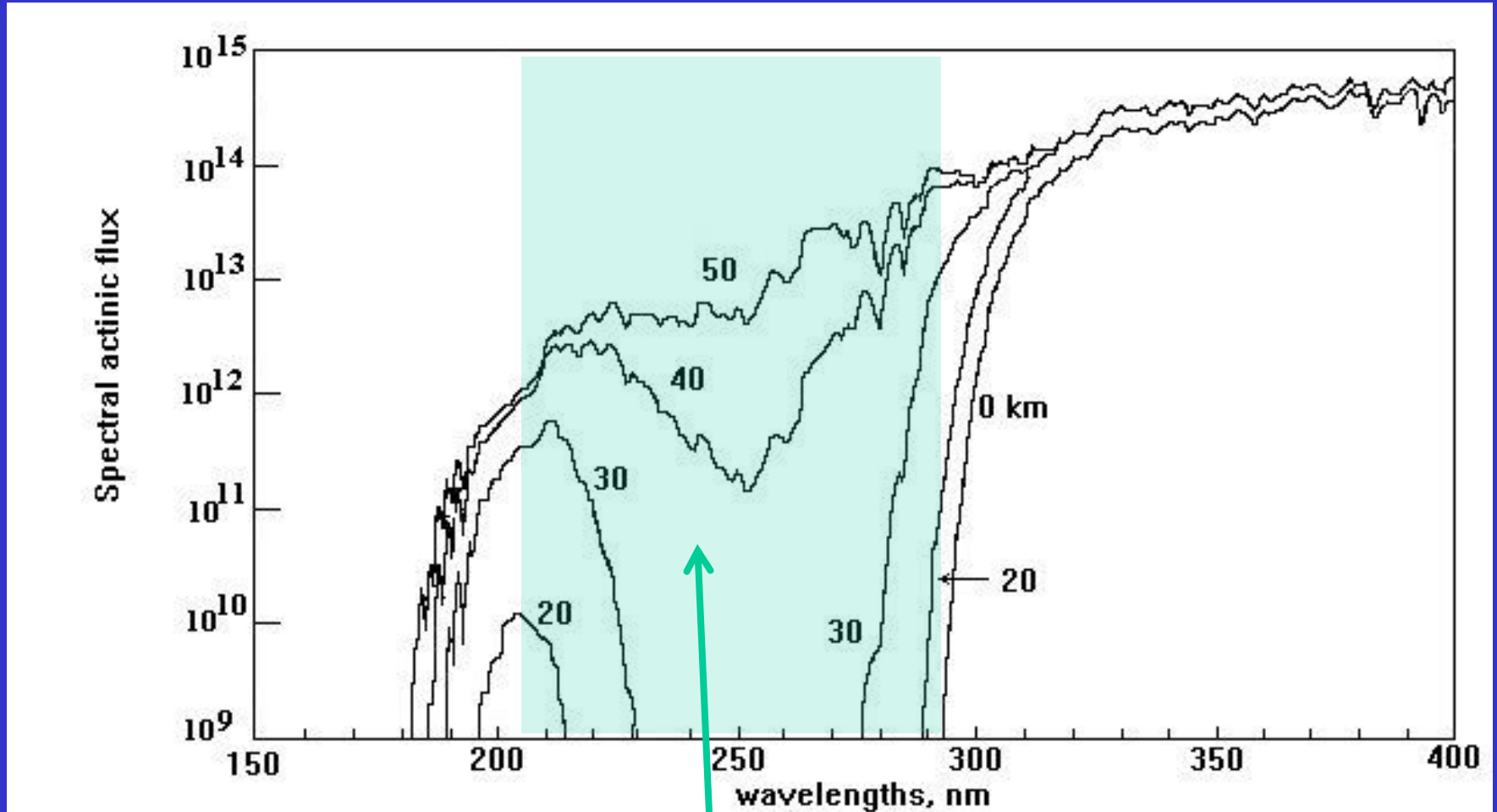
Hard cutoff at 310 nm due to absorption by O_3 in the stratosphere.
(Green is solar flux)



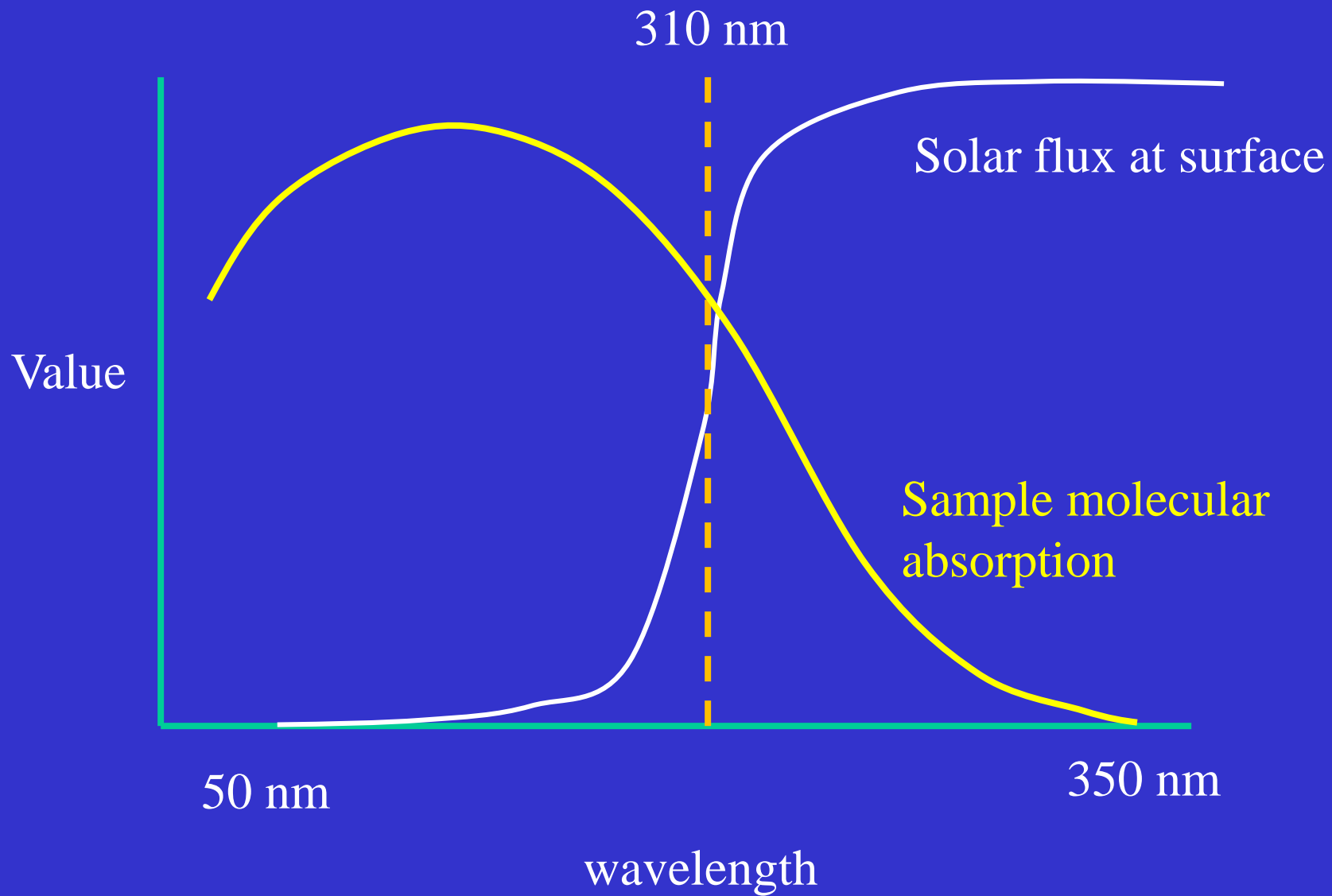
Here is how solar flux varies with altitude

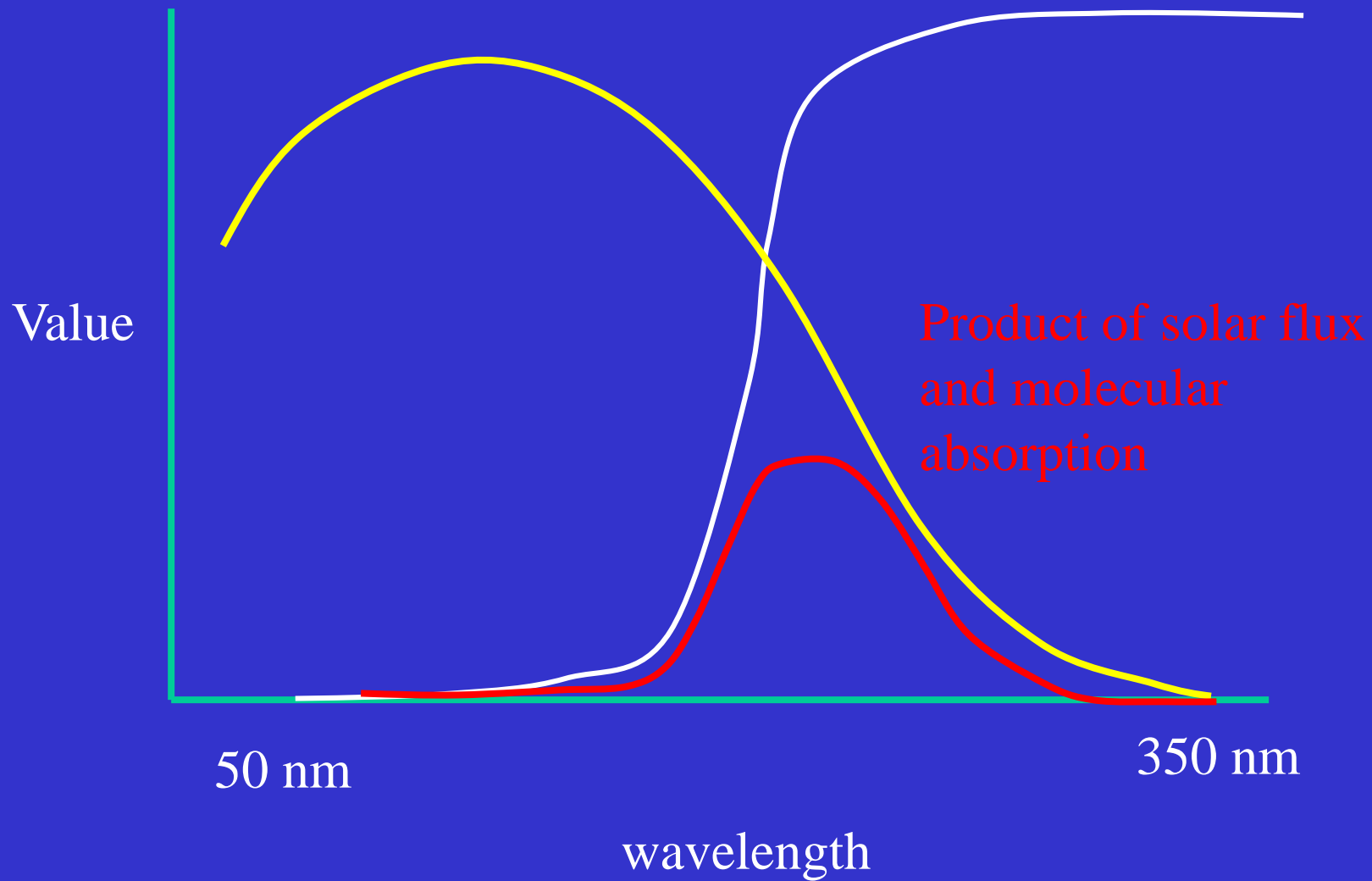


Here is how solar flux varies with altitude

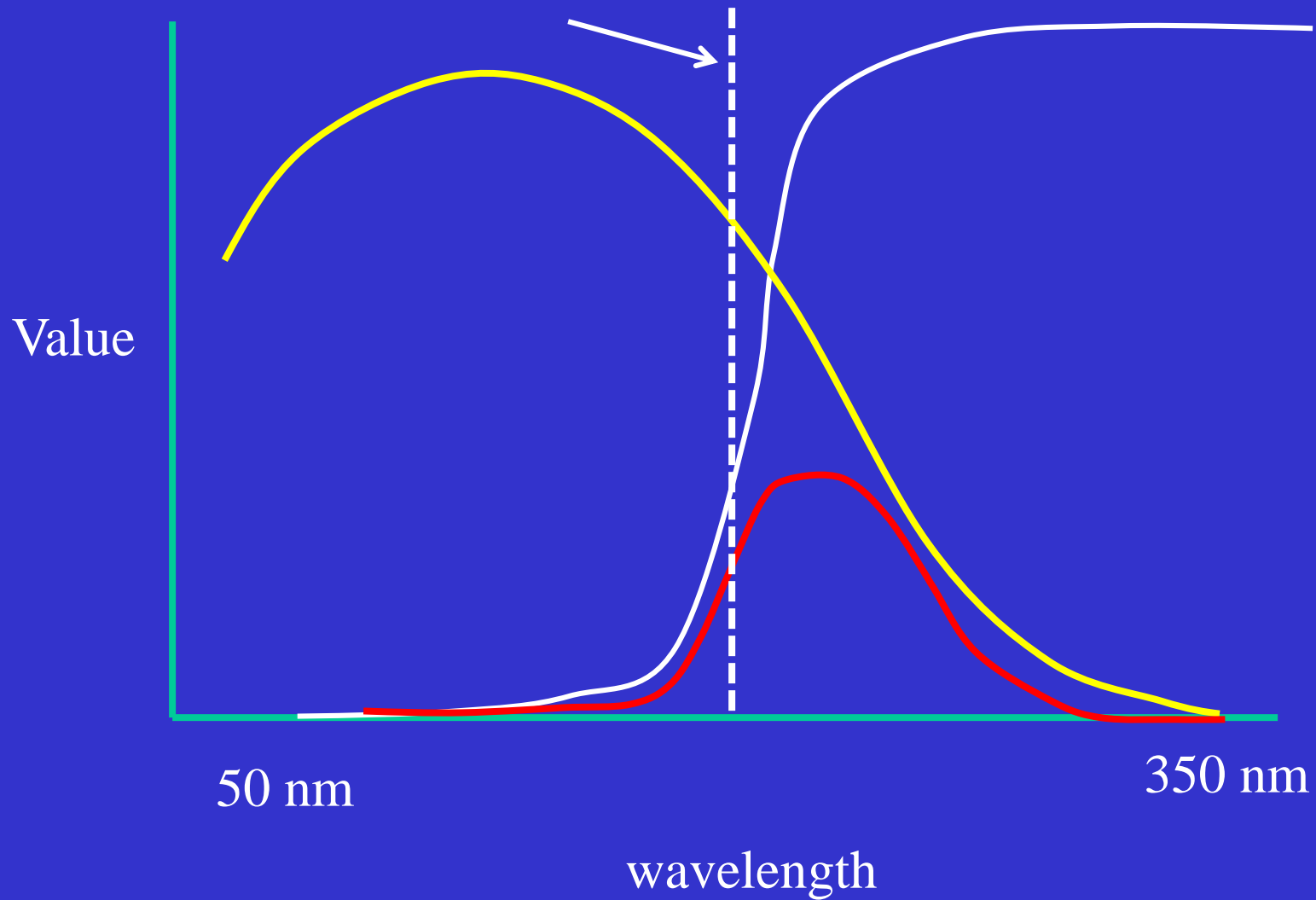


Absorption in this region is due to ozone

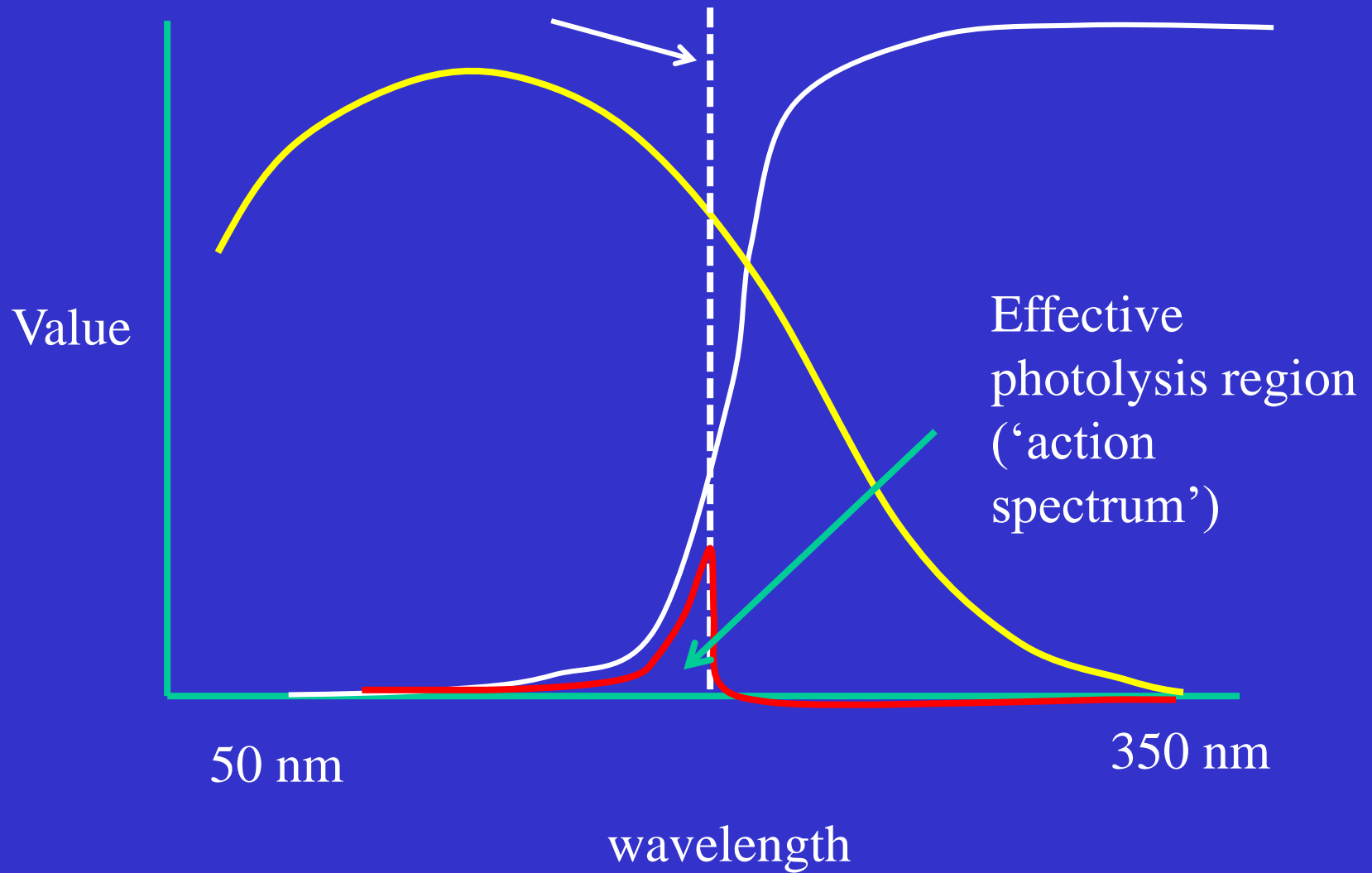




Only wavelengths shorter than this have enough energy to break the bond



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Because sunlight has to pass through the atmosphere, solar flux depends on altitude (there is more high-energy radiation at high altitudes – see page 59)

We can determine the amount of light at any altitude using Beer's Law (also called the Beer-Lambert law), if we know something about the absorbers in the atmosphere and the angle light has to pass through the atmosphere (see page 60-61)

$$I = I_0 \exp(-\sigma \ell n)$$

I = amount of light with absorber present

I_0 = amount of light with no absorber

σ = absorption cross section ($\text{cm}^2 \text{ molecule}^{-1}$)

ℓ = path length (cm)

n = number of absorbers (molecule cm^{-3})

Sample Problem: Column O₃ over midlatitudes has decreased about 4% over the past decade. How much more radiation at 300 nm now reaches the surface? There are about 8×10^{18} O₃ molecules cm⁻² in the column and the absorption cross section of O₃ at 300 nm is 3.4×10^{-19} cm².

If there are 8×10^{18} O₃ molecules cm⁻², then a 4% reduction will leave 7.68×10^{18} cm⁻².

Note that for a column of air, the quantity given is $n \times \ell$ (units of cm⁻²)
Using the Beer-Lambert law,

Original ozone: $I/I_0 = \exp[-(8 \times 10^{18} \text{ molec cm}^{-2})(3.4 \times 10^{-19} \text{ cm}^2)] = 6.59 \times 10^{-2}$

4% less ozone: $I/I_0 = \exp[-(7.68 \times 10^{18} \text{ molec cm}^{-2})(3.4 \times 10^{-19} \text{ cm}^2)] = 7.34 \times 10^{-2}$

Change in radiation at 300 nm: $(0.0734 - 0.0659)/0.0659 = 11\%$ increase!!!