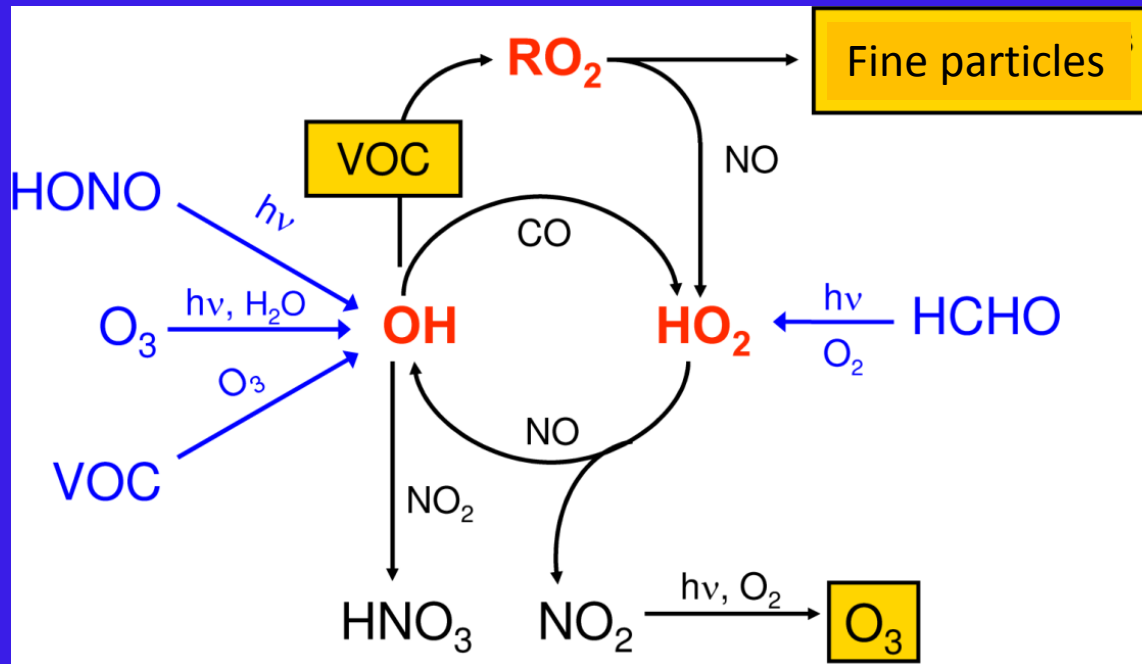# Week 7 – Chemical 'families' and introduction to Atmospheric Photochemistry

Atmospheric chemists handle complex sequences of reactions by examining the behavior of various compounds by "family."

We've seen 'odd oxygen' (or O_x) used to define the sum of $O + O_3$ – this is most important in the upper atmosphere (stratosphere + mesosphere). Other "families" that will be useful include:

"odd nitrogen" ($NO_x = NO + NO_2 + NO_3$)

"odd hydrogen" ($HO_x = HO + HO_2$)

Halogens chlorine and bromine ($Cl_x = Cl + ClO$, $Br_x = Br + BrO$)

Sulfur ($SO_x = SO + SO_2$)

We'll look at these problems somewhat separately, although we acknowledge that there are couplings and feedbacks between the various families.

Nitrogen and sulfur are the primary agents responsible for acidic fog and precipitation ("acid rain")

NO_x destroys ozone in the stratosphere but is a critical agent for ozone production in the troposphere.

$HO_x = HO + HO_2$ is the most important catalyst for oxidation, determining the atmospheric lifetimes for most long-lived species. HO_x is also important in the stratosphere.

Cl_x and Br_x destroy ozone in the stratosphere and in the troposphere.

The linkages between these families are complex – here is a 'simple' diagram showing how NO_x and HO_x interrelate in the troposphere.

Let's start with something a little more simple. What is the fate of an organic compound in an oxidizing atmosphere?

We'll consider methane, CH_4

Naively, we would expect slow "combustion" of methane in an atmosphere loaded with oxygen.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

The problem is that oxygen doesn't really react with methane in a single step – combustion is a process that involves multiple 'intermediate' reactions that eventually will oxidize methane to CO_2 and water, but there are some interesting products that pop up along the way, and these can have important implications – for health, visibility, and the chemical state of the atmosphere.

So what does the 'oxidation' of methane look like, and what are the important intermediates? First, we note that methane is a fairly stable molecule, so it doesn't react with just any old molecules. In fact, it reacts only with radicals (atoms or molecules with an unpaired electron). The hydroxyl (OH) is the most important species that initiates the oxidation of methane (and most other organic compounds in the atmosphere);

$$CH_4 + OH \rightarrow CH_3 + H_2O \qquad \text{(initiation reaction)}$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \quad \text{(recombination reaction)}$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \qquad \text{(extraction reaction)}$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \qquad \qquad .$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad \text{(reformation of OH)}$$

Let's take a closer look – note that some reactions produce species that are consumed in the next step – we call these 'intermediates'. The colors below track the evolution of the hydrocarbon intermediates as they are progressively oxidized. Note, even after four steps, we are still a few steps away from carbon dioxide!
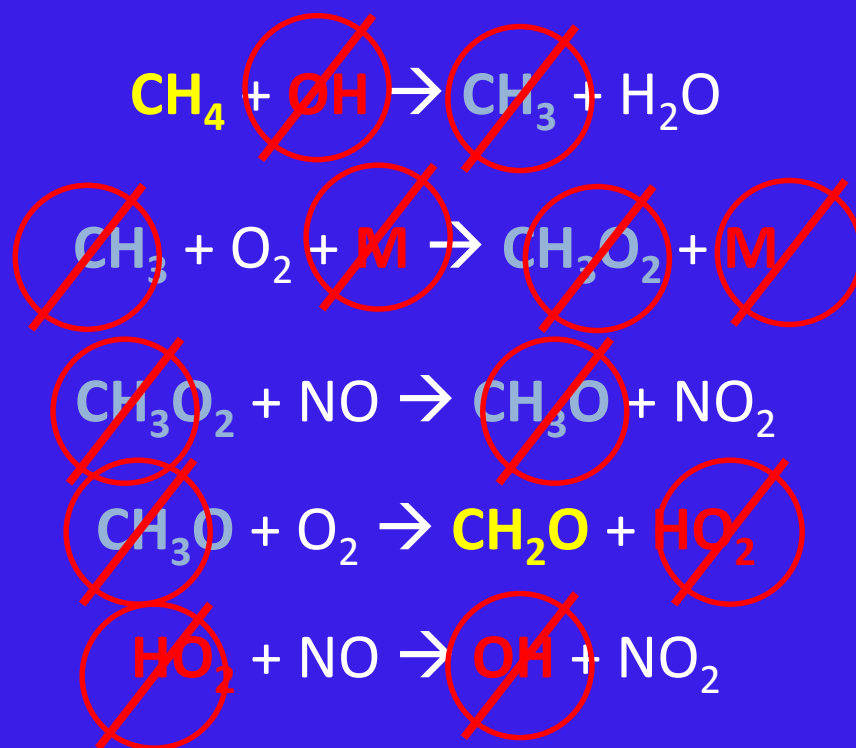
$$CH_4 + OH \rightarrow CH_3 + H_2O$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

Red colors below identify species that are critical to the reaction scheme, but are themselves not consumed. We call these species "catalysts," since they are important for the overall reaction cycle to continue, but are themselves not consumed, so they are present for the next round of reactions. Notice our 'friend' M. This is simply "air" (mainly N_2 and O_2). We will see that M is a bit different than the other catalysts OH and HO_2 because it doesn't ever change forms.

$$CH_4 + OH \rightarrow CH_3 + H_2O$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

To determine the over 'net' result of these five reactions, we can cancel out species that appear on both sides of the overall reaction.

$$CH_4 + OH \rightarrow CH_3 + H_2O$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

Overall reaction: $CH_4 + 2O_2 + 2NO \rightarrow CH_2O + H_2O + 2NO_2$

$$CH_4 + 2O_2 + 2NO \rightarrow CH_2O + H_2O + 2NO_2$$

This overall (or 'net') reaction is more interesting than simple formation of CO_2 and H_2O. It produces a new hydrocarbon, formaldehyde, which is more toxic than methane and one that might survive long enough in the atmosphere to be of concern for air quality.

Even worse, we see that two nitric oxide (NO) molecules have been converted into nitrogen dioxide (NO_2). Both NO and NO_2 are highly toxic, but what NO_2 does next is highly problematic:

$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$
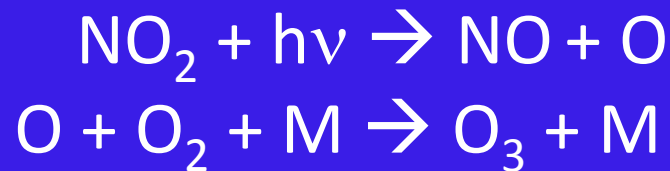
The photolysis of NO_2 (a process that can only take place in sunlight) thus rereleases NO so that it can participate in another series of reactions with other hydrocarbons (and essentially converts it into a catalyst for additional oxidation reactions).

$$CH_4 + 4O_2 + 2h\nu \rightarrow CH_2O + H_2O + 2O_3$$

Photochemical smog!

Nature has taken a single – mainly harmless – molecule of methane and turned it into formaldehyde, a toxic molecule, and two ozone molecules. Ozone is important for absorbing UV light, but direct contact is very harmful for living things.

So why is NO_2 formation so important in the troposphere?

Recall that O_2 only absorbs at wavelengths shorter than about 240 nm. So there is no easy way to make ozone in the lower atmosphere.

NO_2 absorbs in the visible portion of the spectrum, and because the NO bond in NO_2 is weak, these photons have enough energy to break up the molecule, releasing an O atom that then forms O_3. NO_2 photolysis is the main source of O_3 in the troposphere, and O_3 is the source of OH, the main oxidant in the atmosphere. It's safe to say that there would be much greater buildup of pollutants in the lower atmosphere were it not for NO_2. But it's also fair to say that adding NO_2 to the atmosphere would not be a good idea, since it's toxic (as is too much ozone).
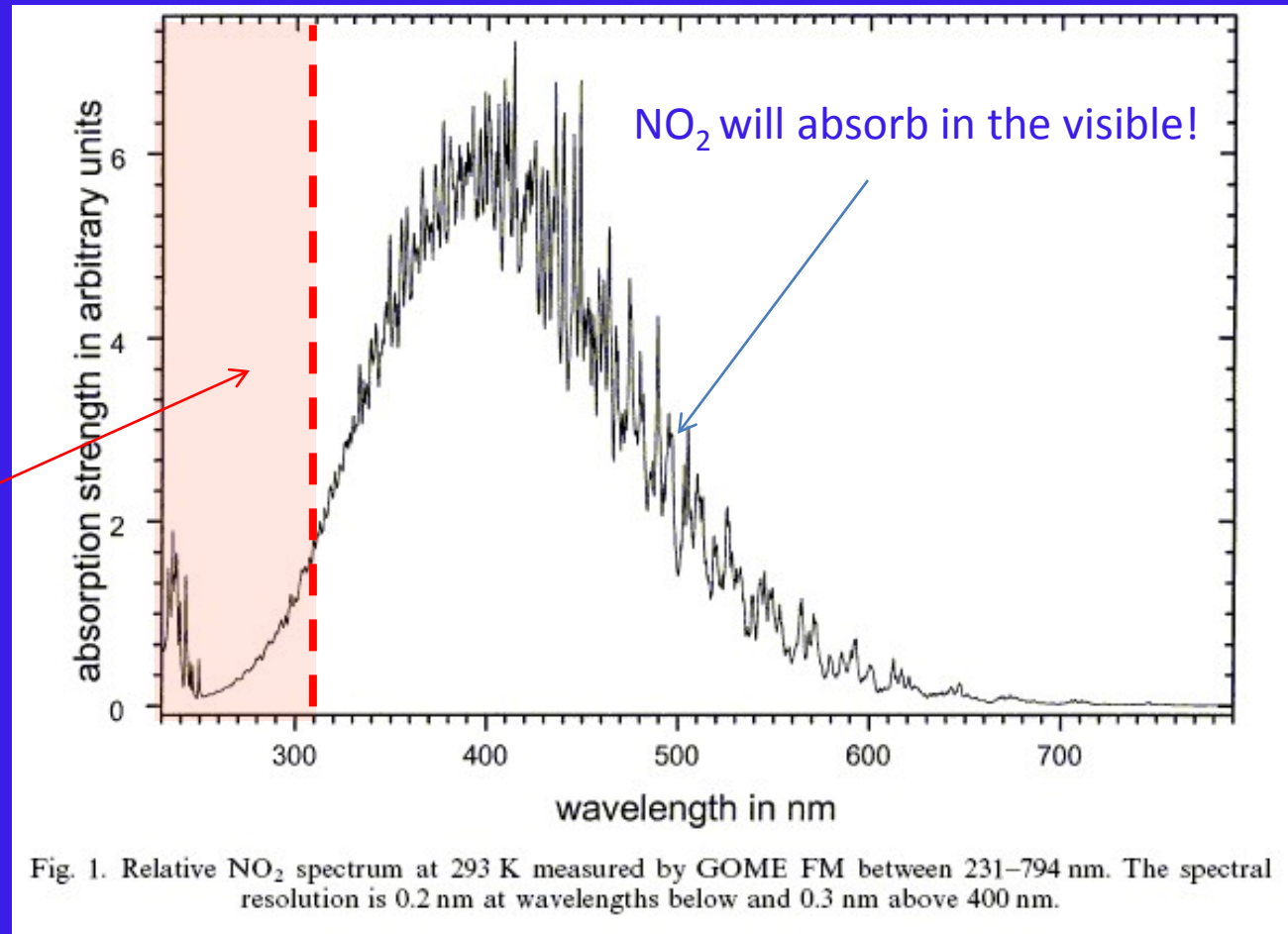
Recall that a photolysis rate is the integral of a product of solar flux, molecular absorption cross section, and the 'quantum yield' of the process. For NO_2, from the figure below, we note that we don't have to worry about wavelengths shorter than 310 nm if we are in the lower atmosphere, because these are all absorbed by ozone in the stratosphere.

(the red shaded region below is the sunlight reaching Earth's surface).

Solar Radiation Spectrum
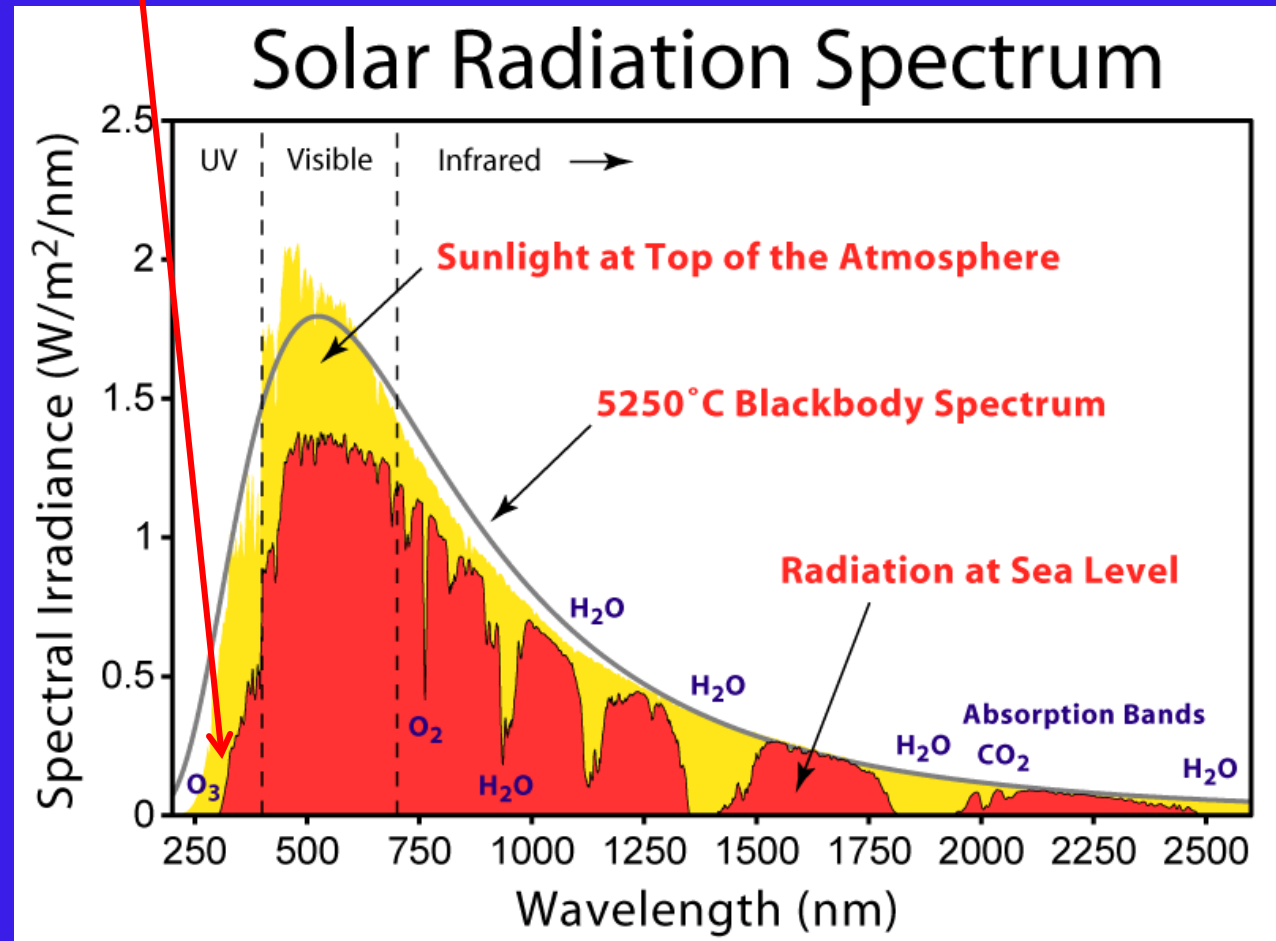
When we look at the absorption spectrum of NO_2, we see that it will absorb in the visible region.

NO_2 will absorb in the visible!

No sunlight reaches Earth's surface at UV wavelengths

Fig. 1. Relative NO_2 spectrum at 293 K measured by GOME FM between 231–794 nm. The spectral resolution is 0.2 nm at wavelengths below and 0.3 nm above 400 nm.

We can approximate the curve below as a series of step values over finite ranges – let's say 25 nm, just for illustration.

These values are:

310-335, 2.7
335-360, 4.2
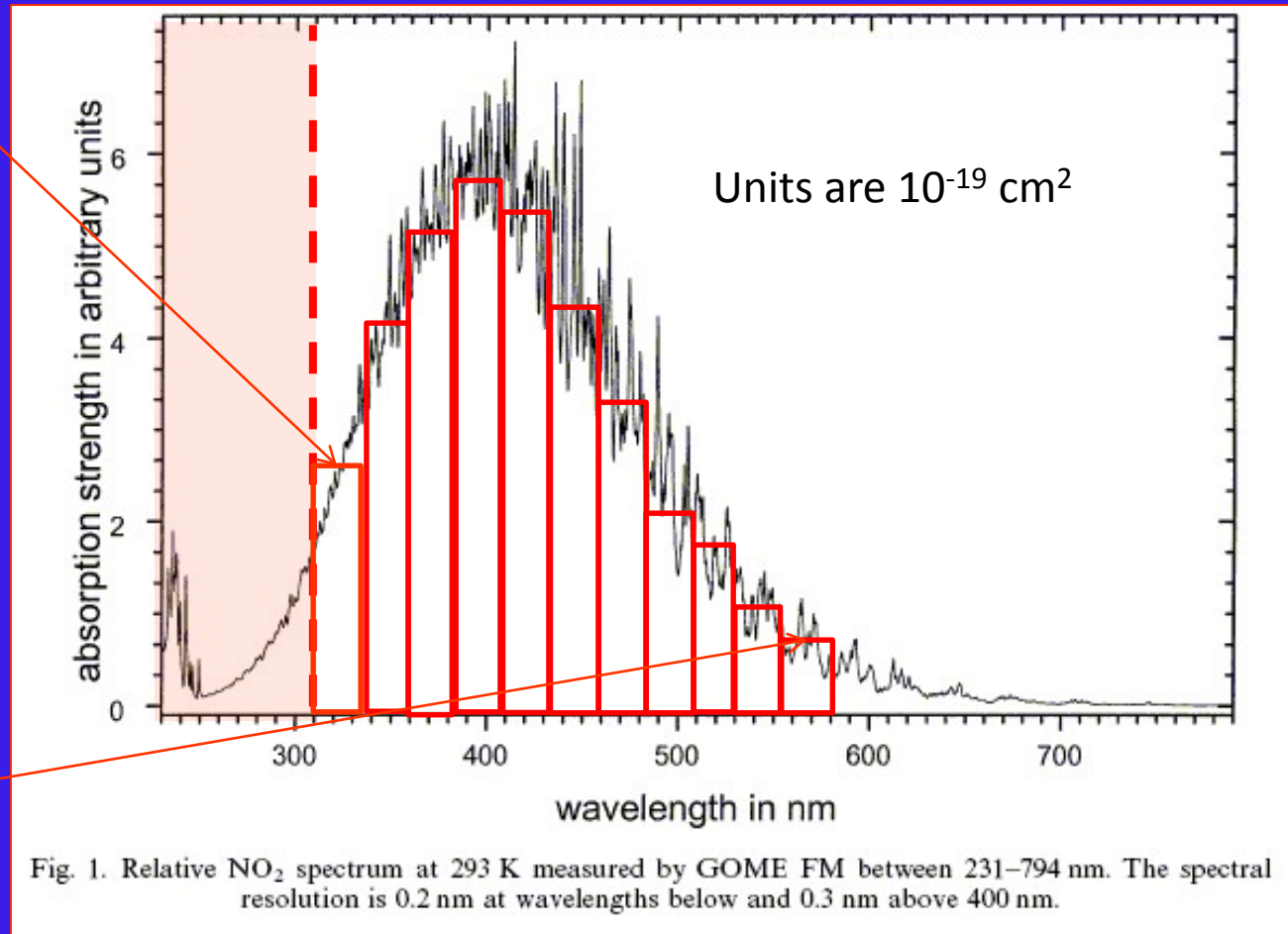360-385, 5.1
385-410, 5.8
410-435, 5.2
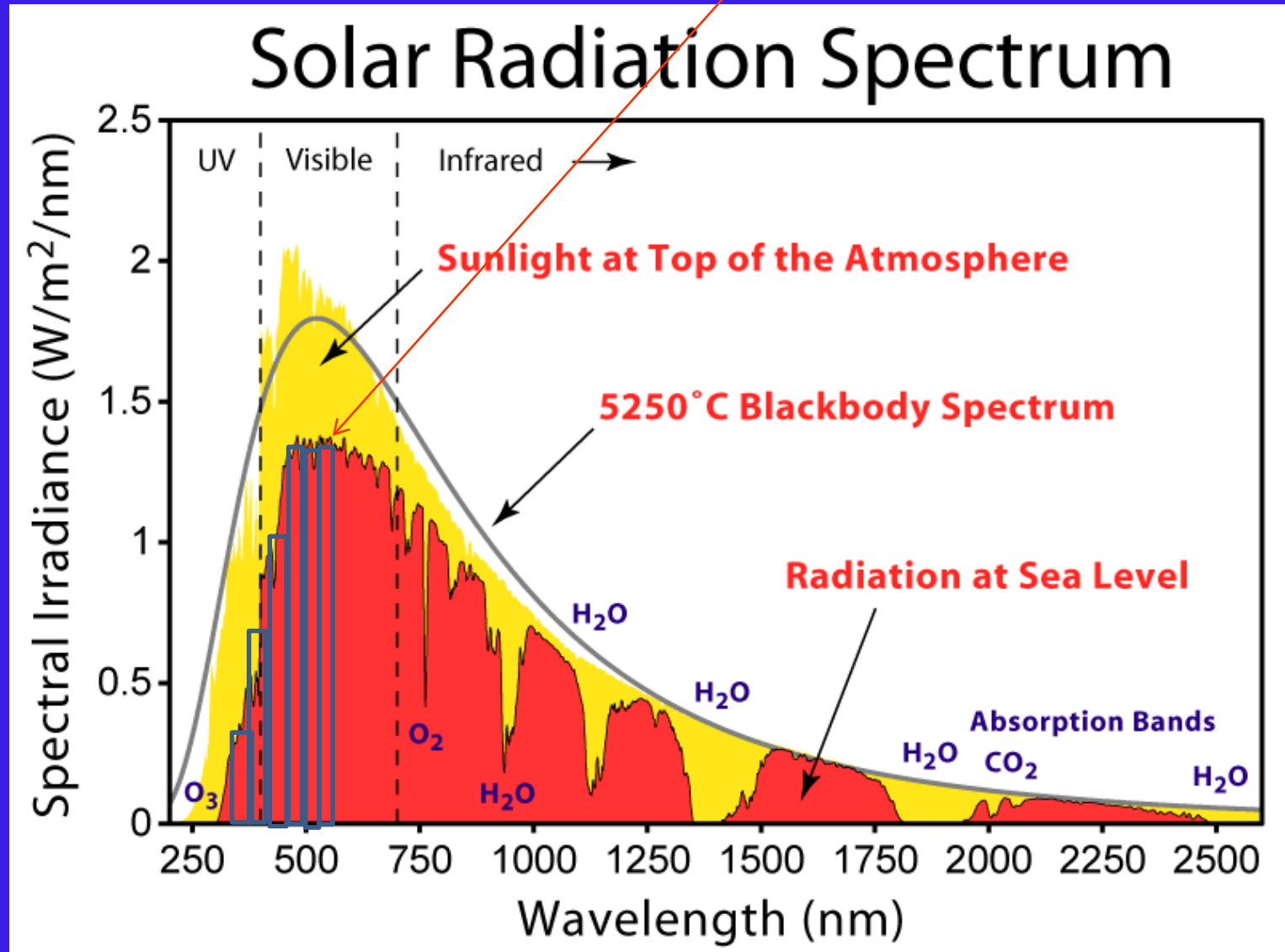435-460, 4.4
460-485, 3.3
485-510, 2.1
510-535, 1.7
535-560, 1.2
560-585, 0.9

Units are 10^{-19} cm^2

Fig. 1. Relative NO_2 spectrum at 293 K measured by GOME FM between 231–794 nm. The spectral resolution is 0.2 nm at wavelengths below and 0.3 nm above 400 nm.

It's a little harder to do this for the solar spectrum, but we can try.

Solar Radiation Spectrum

So, let's say these are our results:

Wavelength range	NO_2 cross section (A)	Solar flux (B)	Product (AxBxC)
310-335 nm	2.7×10^{-19} cm^2	0.3 W m^{-2} nm^{-1}	2×10^{-22} W
335-360 nm	4.2	0.5	5.3×10^{-22} W
360-385 nm	5.1	0.7	8.9×10^{-22} W
385-410 nm	5.8	0.9	13×10^{-22} W
410-435 nm	5.2	1.1	12×10^{-22} W
435-460 nm	4.4	1.25	13.8×10^{-22} W
460-485 nm	3.3	1.34	11×10^{-22} W
485-510 nm	2.1	1.34	7.0×10^{-22} W
510-535 nm	1.7	1.34	5.7×10^{-22} W
535-560 nm	1.2	1.34	4.0×10^{-22} W
560-585 nm	0.9	1.34	3.0×10^{-22} W

Note: 1 cm^2 = 10^{-4} m^2

And $\Delta\lambda$ = 25 nm for all points

The sum of the results in the right column = 86 x 10^{-22} W = 8.6 x 10^{-21} W

So, using this step-wise summation (which is one way to approximate an integral), we find that the J_{NO2} = 8.6 x 10^{-21} W. These units that are particularly useful, so let's convert to photons per second:

$$1\ W = 1\ J\ s^{-1}$$

But we have to assume a wavelength in order to figure out how many photons this corresponds. Let's just use the average wavelength 425 nm. At this wavelength, using E = hν, we find that 1 J = 2.14 x 10^{18} photons. Converting,

$$J_{NO2} = 8.6\ x\ 10^{-21}\ J\ s^{-1}\ x\ 10^{18}\ photons\ J^{-1} = 0.018\ s^{-1}$$

This is almost right. The actual value is 0.011 s^{-1}. Can you determine why this might be the case? Think about the portion of the integration that we've neglected (the quantum yield!).
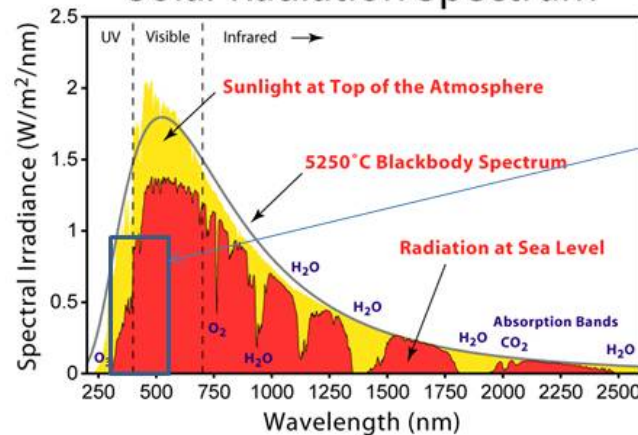
For Homework 10, do the same calculation that I just did, except instead of 10 boxes, just use one. It's not as accurate, but you should be able to get an answer that is close. Note that you have to use the wavelength range 300-550 nm, which is a bigger step – instead of 25 nm, you will have a step $\Delta\lambda$ = 250 nm.
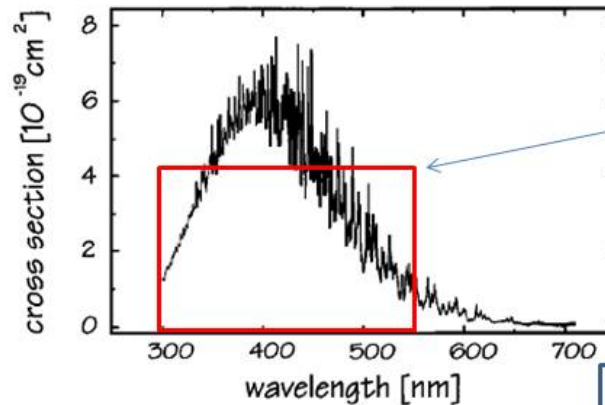
$\sigma_{avg} = 4.3 \times 10^{-19}$ cm^2

$$J = \int I_\lambda \times \sigma_\lambda \times d\lambda \sim I_{avg} \times \sigma_{avg} \times \Delta\lambda$$

Solar Radiation Spectrum

$I_{avg} = 1.0$ W m^{-2} nm^{-1}