Beltsville PBL Air Quality Modeling Atmospheric Chemistry
Solar Actinic Flux Measurements, Photolysis, Simulation and Impact on Air Quality
(William Stockwell/Rosa Fitzgerald)

Objective: The photolysis of nitrogen dioxide (NO_2), ozone (O_3), formaldehyde (HCHO) and other trace gases is a major factor that determines atmospheric composition. Students will learn the factors that determine photolysis frequencies and rates. Solar radiation provides the actinic flux that produces photolysis. The sun's temperature and composition affect the extraterrestrial solar radiation flux. Atmospheric factors, such as stratospheric ozone and aerosol scattering affect the actinic flux that reaches the planetary boundary layer (PBL). The measurement of actinic flux and the calculation of photolysis frequencies from spectrally resolved actinic flux, absorption cross-sections and quantum yields will be discussed. The student will calculate photolysis frequencies, apply them to make first-order estimates of ozone concentrations in the PBL. In addition calculated photolysis frequencies will be used later in modeling assignments of this workshop.

Photolysis Physics

Ultraviolet and visible photons have sufficient energy to cause chemical transformations known as photolysis. Photolysis is a major driver of the chemical transformations that occur in the atmosphere. Four important reactions that affect the formation of air pollutants are shown below.

$NO_2 + h\nu \rightarrow O(^3P) + NO$	Leads to the ozone production.
$O_3 + h\nu \rightarrow O(^1D) + O_2$	Leads to the formation of hydroxyl radical (HO).
$HCHO + h\nu \rightarrow 2\ HO_2 + CO$	Produces HO_2 radicals.
$HCHO + h\nu \rightarrow H_2 + CO$	Reduces production of HO_2.

The photolysis rates of these and other trace gases depend on their concentrations, [C], and a photolysis rate coefficient J (units of frequency). J is not a photolysis rate (too many people in the literature get this wrong). The general equation for the photolysis rate of some substance X is given by the following expression where [X] is the concentration of X. Note the minus sign which is used by convention because there is a loss of X.

$$\frac{d[X]}{dt} = -J_x[X]$$

A photolysis frequency is determined by the available photon flux, the absorption spectrum of the substance and the quantum yield which is the probability of a molecule reacting following the absorption of a photon.

The energy of a photon is given by the following equations where E is energy, h Planck's constant, ν is frequency, c is the speed of light and λ is wavelength.

$$E = h\nu$$

The product of frequency and wavelength is equal to the speed of light.

$$\lambda\nu = c$$

The relationship between wavelength and frequency is obtained by combining these two equations to obtain the following equation.

$$E = \frac{hc}{\lambda}$$

The higher the frequency or the shorter the wavelength the greater the photon energy. And photons with higher energy are more likely to cause photochemical reactions.

Photolysis occurs when a molecule absorbs radiation that excites it from a bound state to an unbound state that dissociates, Figure 1.

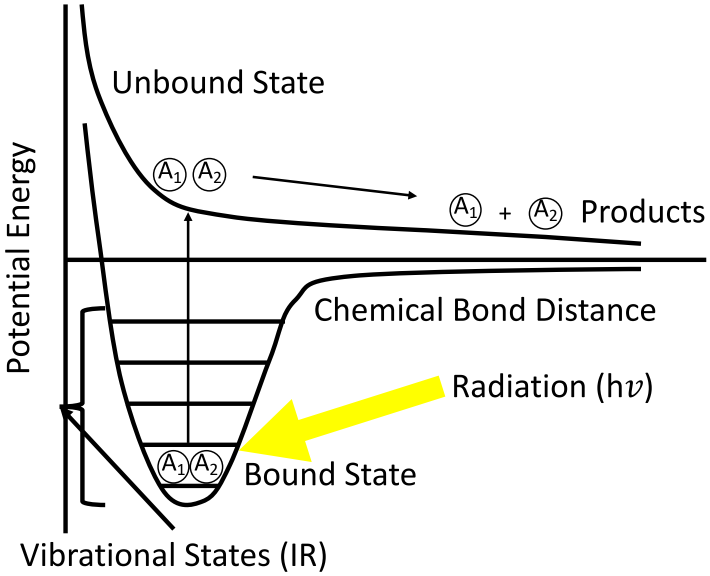


Figure 1. Photolysis of a stable molecule (A1-A2). Radiation is absorbed that the molecule is excited into an unstable unbound state that dissociates.

The equation for J is given below;

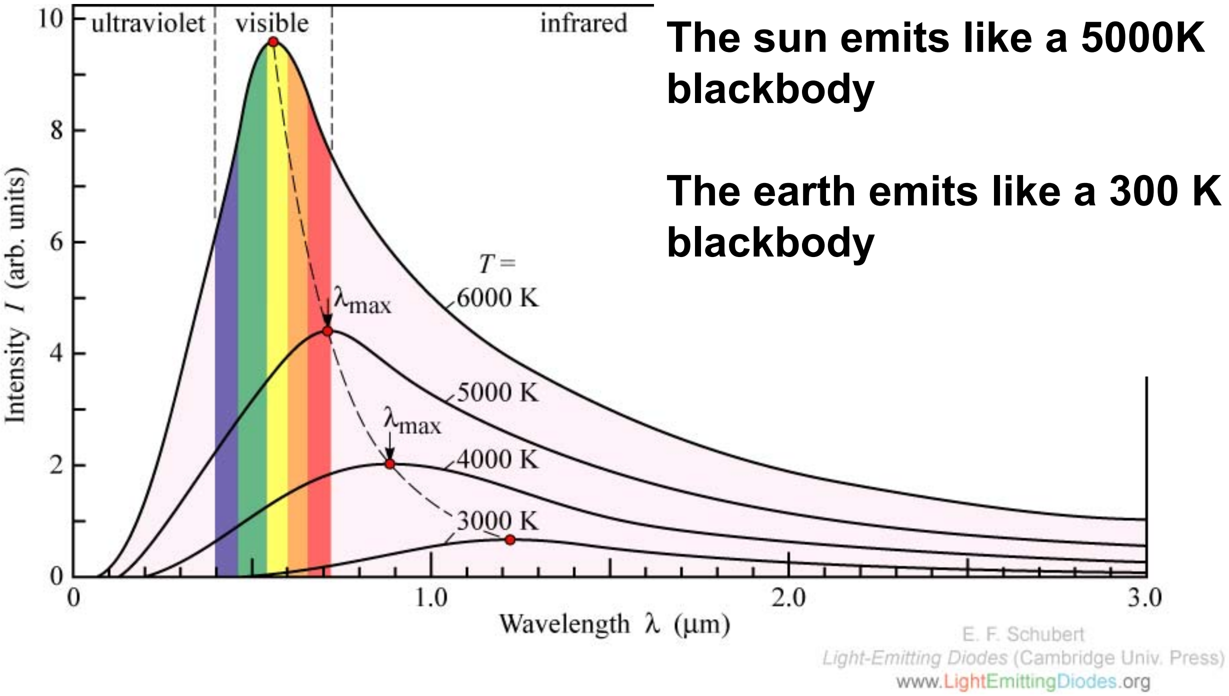
$$J = \int \{I(\lambda) \times \sigma(\lambda) \times \varphi(\lambda)\} d(\lambda)$$

Where J is the photolysis frequency, I is the actinic flux, σ is the absorption cross-section, φ is the quantum yield and λ is wavelength. The integration is performed over all wavelengths that contribute to the photolysis of a substance. The wavelengths of radiation that typically contribute to photolysis in the lower troposphere range from near 300 to 700 nm but for higher altitudes more energetic radiation with lower wavelengths may contribute. Note that typically the equation is converted to a sum as shown below where I, σ and φ are averaged over the wavelength step, $\Delta\lambda$.

$$J = \sum\{I_{avg} \times \sigma_{avg} \times \varphi_{avg}\} \times \Delta\lambda$$

Actinic flux, absorption cross-sections and quantum yields

Actinic flux is the flux of photons entering a spherical volume element of air. The sun's radiation to a good approximation emits radiation as a blackbody A blackbody emits radiation with a spectrum depends on its temperature, T. The hotter the temperature, the more radiation emitted, and the quantity emitted follows an expression of ~ T^4 and the hotter the temperature the shorter the wavelength (greater the frequency) of the peak, Figure 2.



The sun emits like a 5000K blackbody

The earth emits like a 300 K blackbody

E. F. Schubert
Light-Emitting Diodes (Cambridge Univ. Press)
www.LightEmittingDiodes.org

Figure 2. Blackbody radiation emission spectra.

However, solar radiation is not a perfect blackbody emitter of radiation due to absorption by gases in the outer layers of the sun and its corona. Radiation absorption and scattering in the Earth's atmosphere affect the actinic flux reaching the boundary layer too. Figure 3 shows that the mixing ratio of ozone reaches a maximum in the stratosphere and Figure 4 shows that very relatively little highly energetic radiation makes it through the stratosphere. Figure 5 shows that the photolysis rate of molecular oxygen decreases at lower altitudes due to the ozone above while the rate of ozone formation from ground state oxygen atom decreases as altitude increases due to the pressure decrease. These two competing reaction rates reach an optimum in the mid-stratosphere so ozone reaches a maximum. Absorption of ultraviolet radiation warms the stratosphere making it stable with respect to mixing. Figure 6 shows the direct radiation, scattering and albedo effects on actinic flux. It can be measured by spectral radiometers that approximate an integration over a spherical volume of air as discussed in the next section.

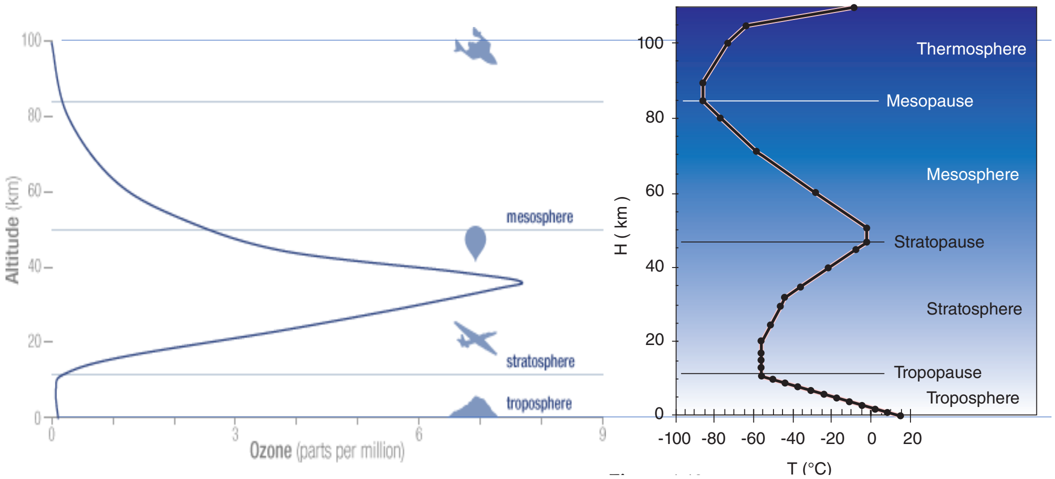


Figure 3. Atmospheric structure and ozone mixing ratios. Note how the ozone mixing ratio reaches a maximum in the stratosphere. The ozone mixing ratio plot is from https://ozonewatch.gsfc.nasa.gov/facts/SH.html and the atmospheric structure plot is from Practical Meteorology: An Algebra-based Survey of Atmospheric Science by Roland Stull.

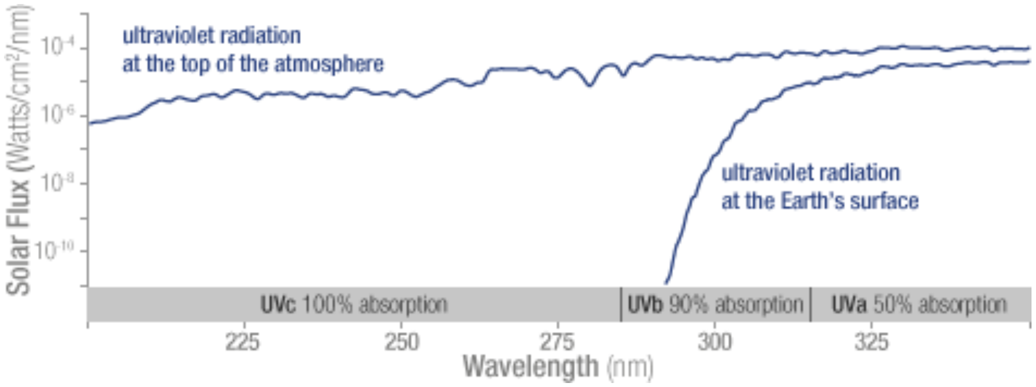


Figure 4. Very little of the extraterrestrial solar radiation flux with wavelengths less than 300 nm reaches the Earth's surface. The plot is from https://ozonewatch.gsfc.nasa.gov/facts/SH.html.

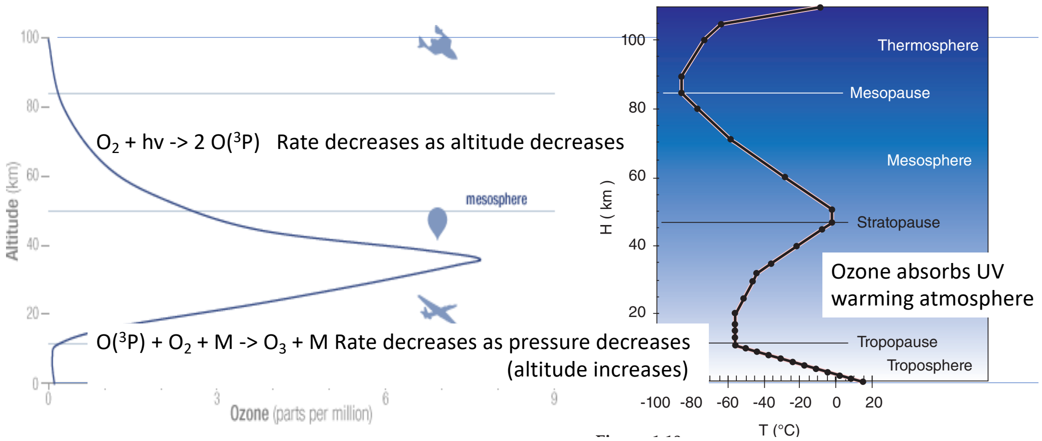


Figure 5. The photolysis rate of molecular oxygen decreases at lower altitudes due to the ozone above while the rate of ozone formation from ground state oxygen atom decreases as altitude increases due to the pressure decrease. These two competing reaction rates reach an optimum in the mid-stratosphere. Absorption of ultraviolet radiation warms the stratosphere making it stable with respect to mixing. The ozone mixing ratio plot is from https://ozonewatch.gsfc.nasa.gov/facts/SH.html and the atmospheric structure plot is from Practical Meteorology: An Algebra-based Survey of Atmospheric Science by Roland Stull.

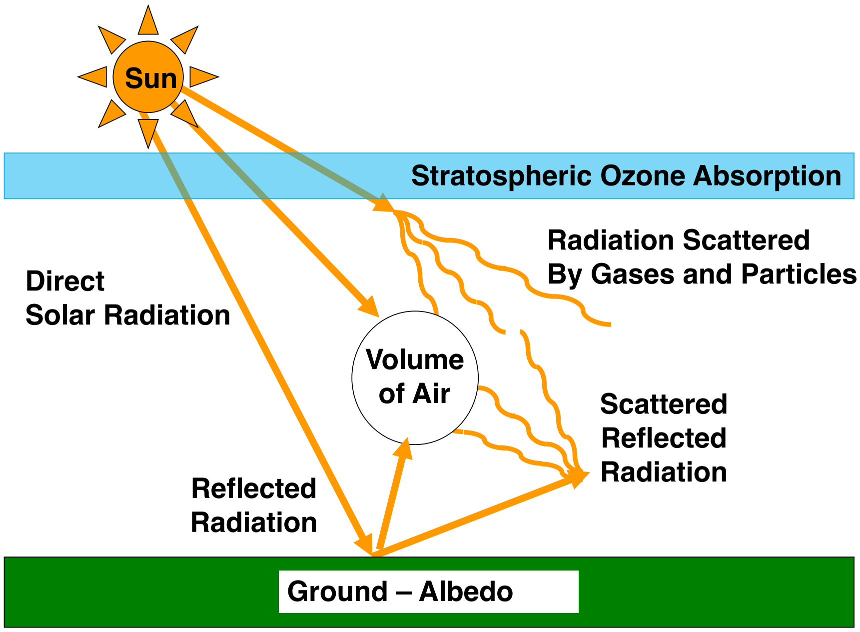


Figure 6. Solar radiation is absorbed by stratospheric ozone and other trace gases. Radiation is scattered by gases and particles. Clouds affect radiation by absorbing and scattering radiation.

Measurement

A quartz hemispherical collector may be used to collect solar radiation over one hemisphere (a solid angle of 2π). Therefore, to measure over a solid angle of 4π two collectors must be used, Figure 7.

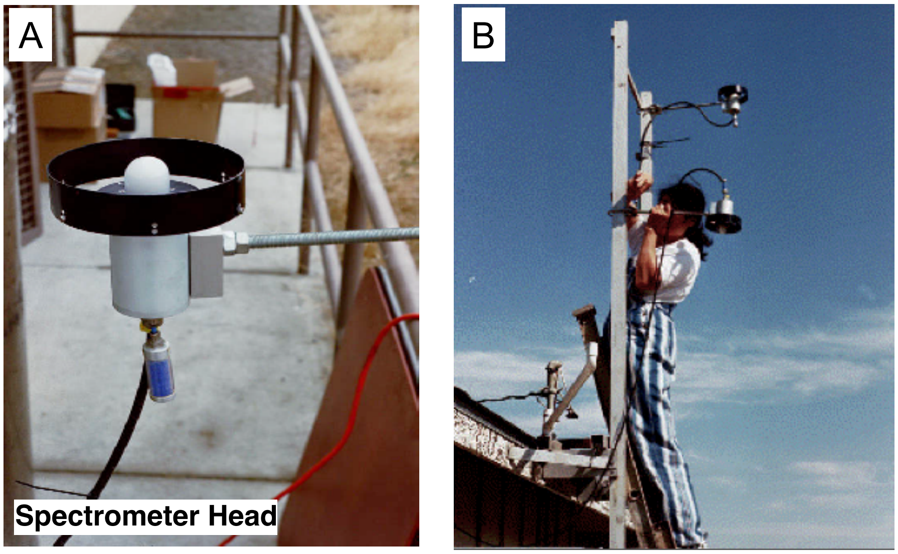


Figure 7. Panel A shows a quartz hemispherical collector (Spectrometer Head). The blackened ring shields from scattering from below, the black cable is an optical cable that conducts light to a spectrometer and the blue capsule contains a drying agent. Panel B shows two collectors being installed at a field research station at the University of California, Davis.

The optical cable conducts the collected solar radiation to a diode-array spectrometer where it is measured, Figure 8. This figure shows a schematic showing that radiation from the collector is conducted into a spectrometer. Next the radiation passes through a slit and onto a diffraction grating. The diffraction grating disperses the radiation. The grating is good enough to provide a typical resolution of 1 nm. The radiation is detected by an array of light sensitive diodes which may be scanned rapidly at rates of a 1 scan s^{-1} or with higher time resolution. There is a control computer for the spectrometer that stores the electrical signals from the diode array and controls the instrument.

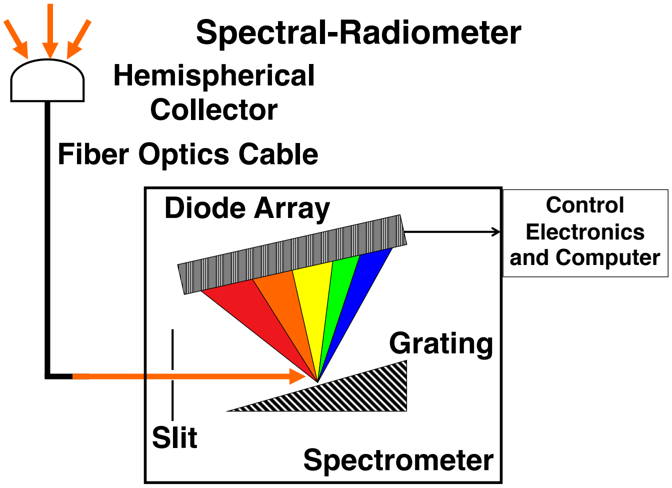


Figure 8. Radiation from the collector is conducted to a spectrometer. In the spectrometer the radiation passes through a slit and onto a diffraction grating where it is dispersed and detected by an array of light sensitive diodes. The electrical signals from the diode array are stored by the computer that controls the instrument.

The spectrometer is collaborated by using a standard lamp that should be tracible to a NIST standard. The results of an actinic flux measurement are shown in Figure 9.

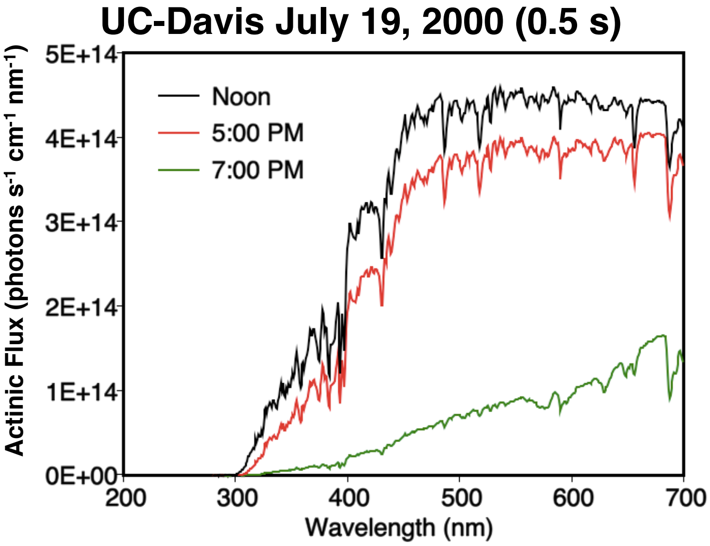


Figure 9. Actinic flux measurements made near the surface at the University of California, Davis.

The times are given for the local time at the measurement site.

Radiation absorption in the stratosphere, aerosol-scattering and other factors affect the overall shape of the actinic flux plots. The lines are due to absorption in the outer layers of the sun (Fraunhofer lines) and by gases in the Earth's atmosphere. Figure 10 shows a time series of actinic flux measured at the University of California, Davis on July 29, 2020 for a number of wavelengths. Note that the plots of the wavelengths in the range 305 and 316 nm show a sharper midday increase than those wavelengths in the range 340 and 351 nm.

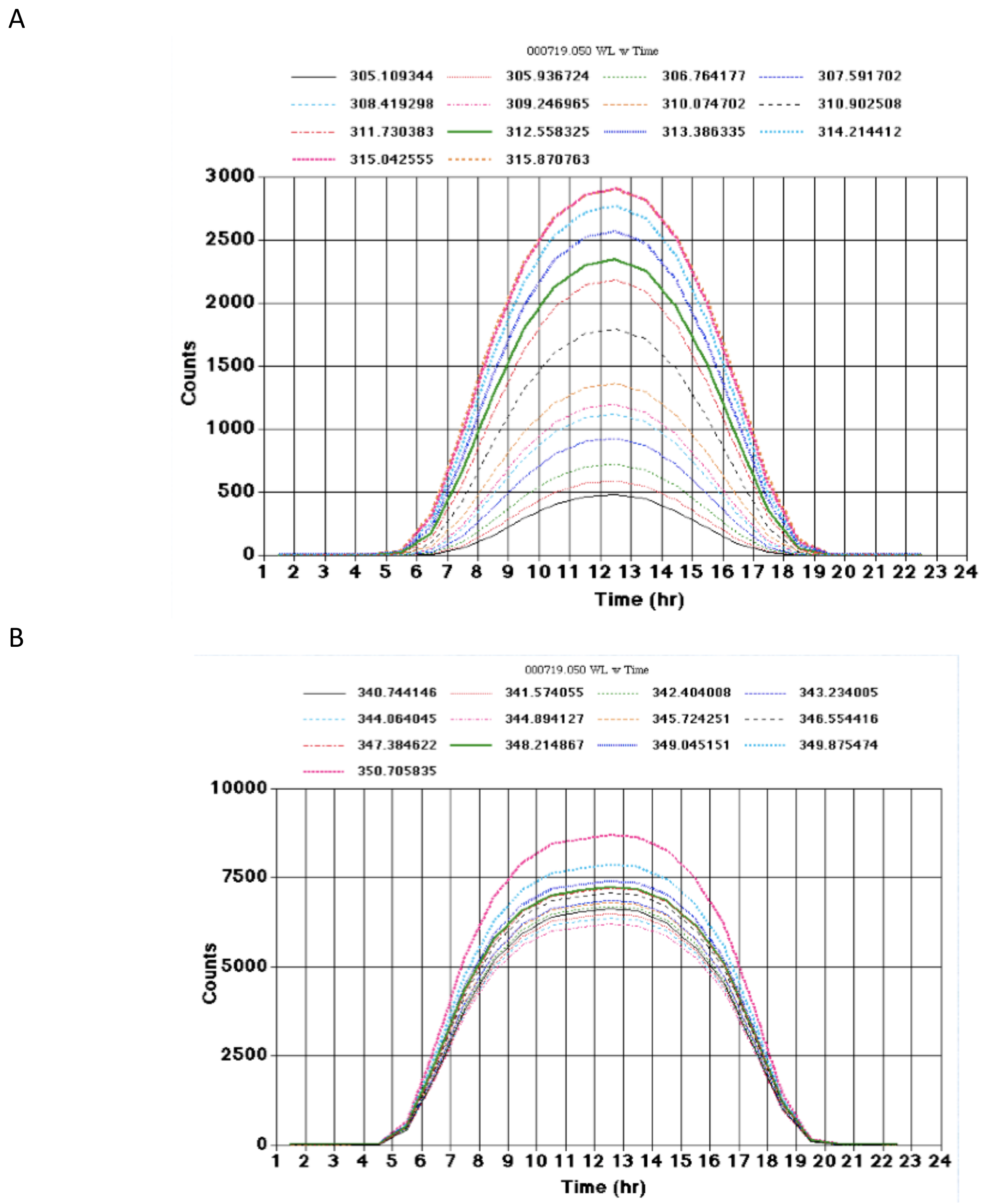


Figure 10. This figure shows actinic flux measured at the University of California, Davis on July 29, 2020. Panel A shows actinic flux between 305 and 316 nm. Panel B shows the measured actinic flux between 340 and 351 nm.

Absorption Cross Sections

Beer's law relates absorbance, absorption cross-sections and chemical concentrations to each other. Imagine a monochromatic radiation beam passing through a column filled with a gas composed of identical molecules, Figure 11. The initial intensity of the beam is I_o but successive increments of molecules, dn, absorb equal increments of the radiation, dI, across the length of the column, L. The total number of molecules across the beam is N.

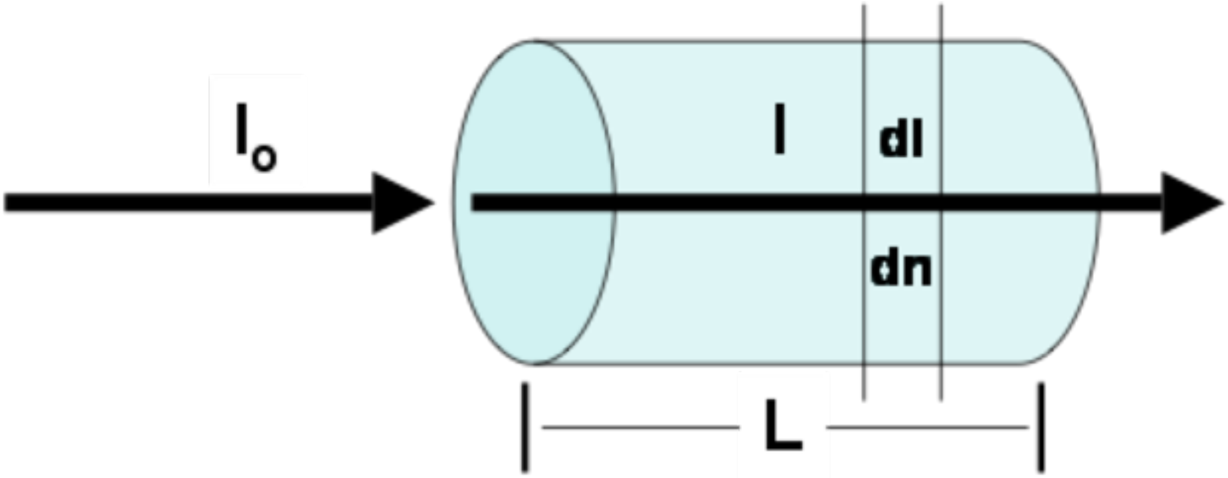


Figure 11. I_o is the initial intensity of a beam of monochromatic radiation, dn and dI are infinitesimally small increments in the number of molecules and radiation intensity, respectively and L is the length of the column.

The relationship between dI/dn and the radiation intensity for a monochromatic beam (single wavelength) is given by the following equation. The sign is negative because radiation is absorbed as dI/dn increases. The absorption cross-section, σ, is a proportionality constant and it is determined by the molecular properties a chemical substance.

$$\frac{dI}{dn} = -\sigma I$$

This equation may be rearranged and integrated between the initial and final conditions.

$$\int_{I_o}^{I} \frac{dI}{I} = -\sigma \int_{0}^{N} dn$$

The result is as follows.

$$\ln(I) - \ln(I_o) = -\sigma N$$

$$ln\left(\frac{I}{I_o}\right) = -\sigma N$$

Which may be rearranged to yield the following expression of Beer's law.

$$I = I_o \exp\,(-\sigma N)$$

If the absorbance is defined as the natural log of the ratio, I/Io then an alternative expression is Beer's law is obtained.

$$A = ln\left(\frac{I}{I_o}\right)$$

$$A = [C]\sigma L$$

If the concentration is expressed in units of molecules per cm_3 and L is in cm then the units of σ must be cm_2 which is area and therefore a cross-section. Cross-sections are determined by taking absorption spectra of known concentrations of gases. Figure 12, 13 and 14 show sample absorption spectra of nitrogen dioxide, ozone and formaldehyde, respectively.

Notice that the ozone absorption spectrum shows peak absorption cross-sections that are much greater than nitrogen dioxide and formaldehyde. The ozone cross-sections are high until near 300 nm, so given the high concentrations of stratospheric ozone there is not much radiation with wavelengths lower than 300 nm that reaches the PBL.

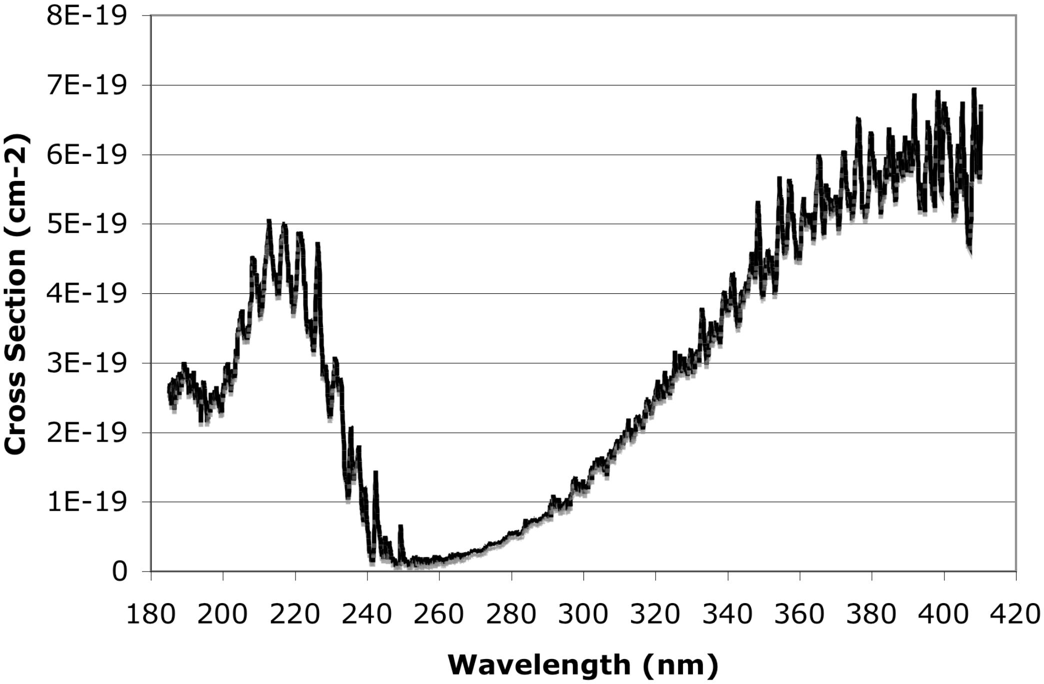


Figure 12. Absorbance spectrum of nitrogen dioxide, NO_2.

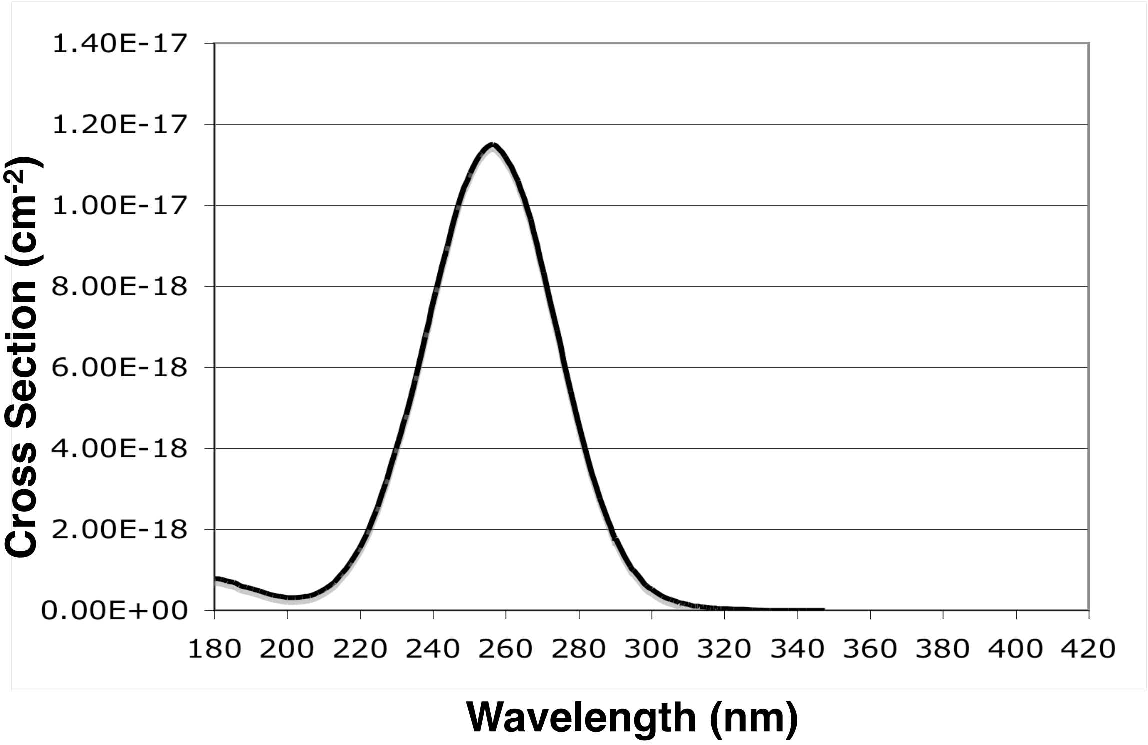


Figure 13. Absorbance spectrum of ozone, O_3.

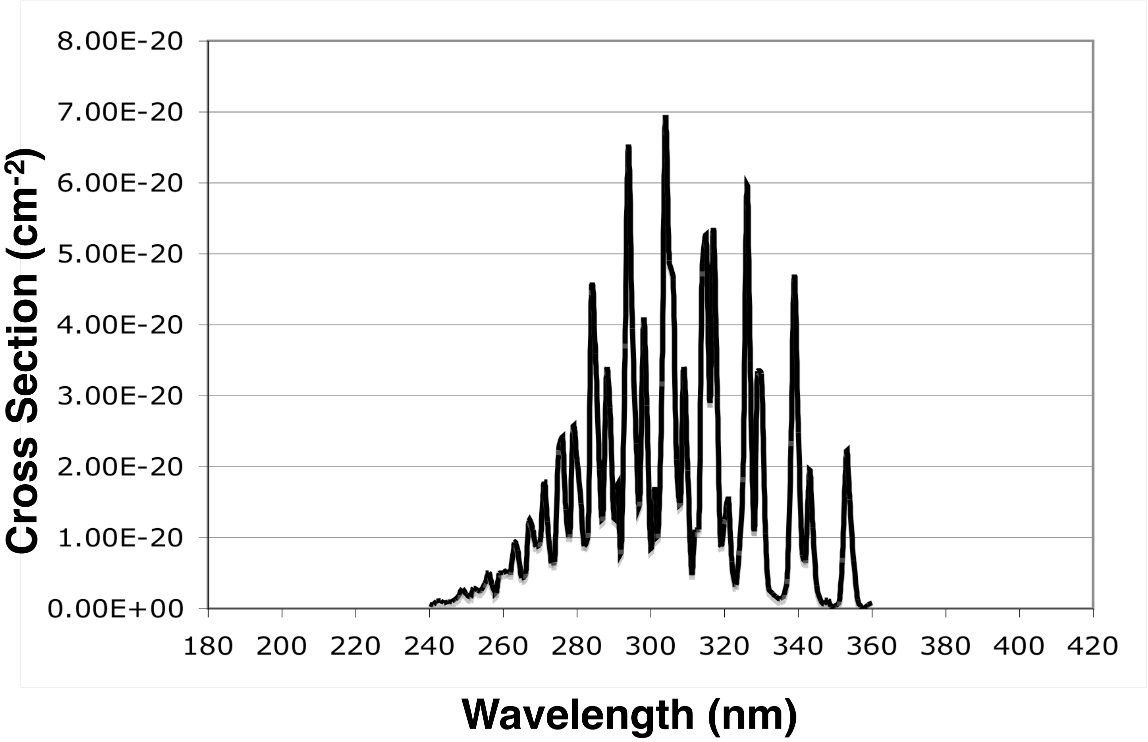


Figure 14. Absorbance spectrum of formaldehyde.

Quantum Yields

When a molecule absorbs a photon, the excited molecule may react by one or more pathways, reemit a photon or undergo other physical processes. The quantum yield for a given radiation-induced process, such as a photochemical reaction, is the fractional probability that the process will occur per photon absorbed. The sum of the quantum yields for all processes that the excited molecule may undergo must be equal to one. So the quantum yield for a given photochemical reaction is the probability that molecule will react following the absorption of a photon. Quantum yields depend on the energy of a photon and are therefore wavelength dependent. Figures 15, 16 and 17 show the quantum yields of nitrogen dioxide, ozone and formaldehyde, respectively.

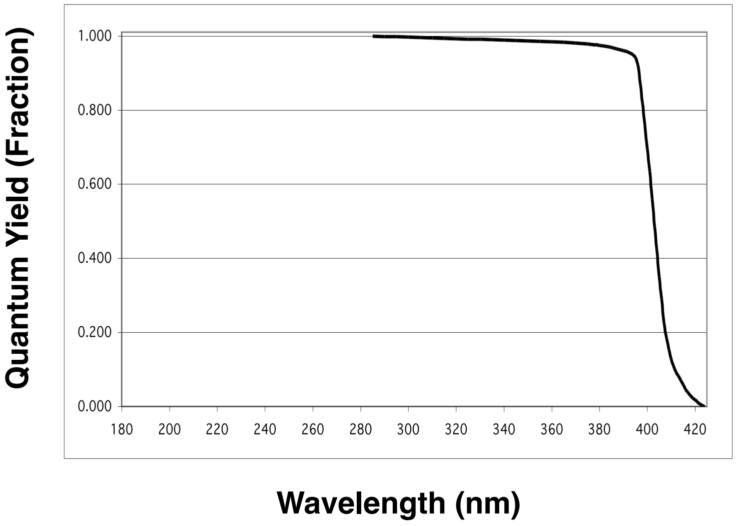


Figure 15. Quantum yield for the $NO_2 + h\nu \rightarrow O(^3P) + NO$ reaction.

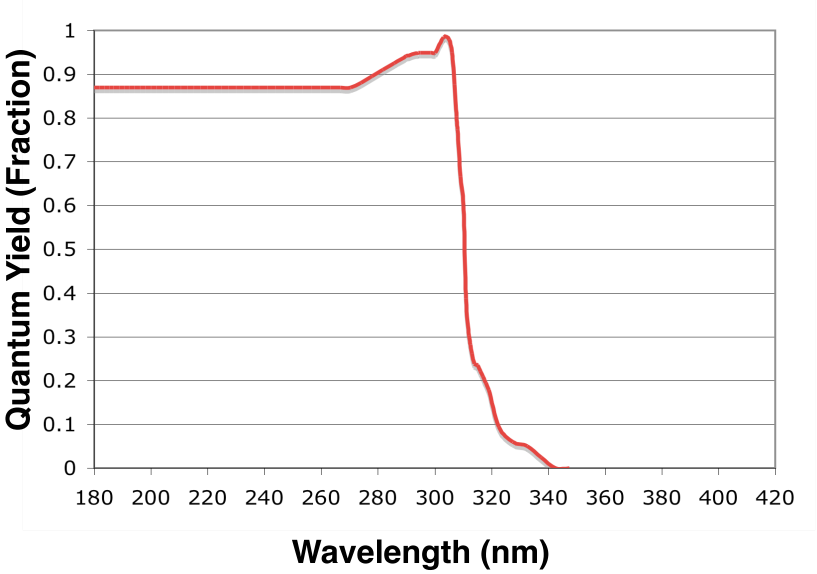


Figure 16. Quantum yield for the $O_3 + h\nu \rightarrow O(^1D) + O_2$ reaction.

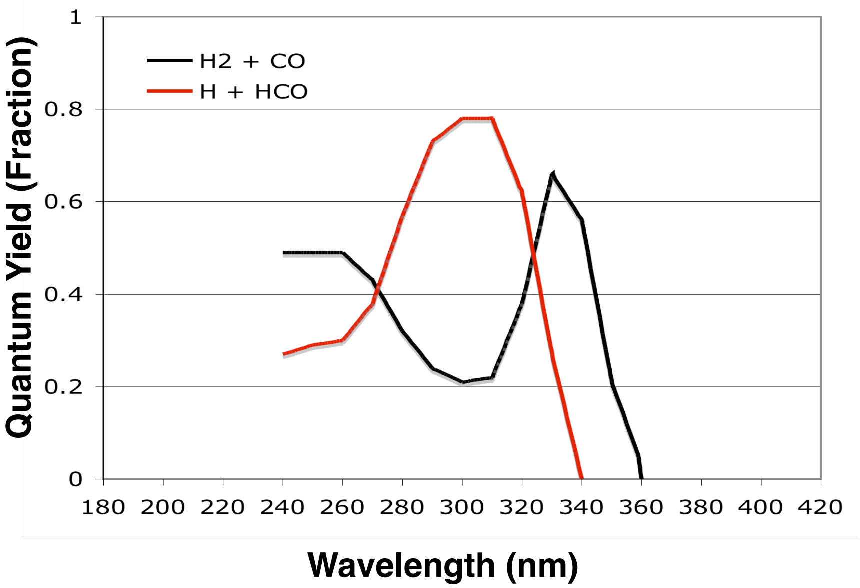


Figure 17. Quantum yield for the HCHO + h$\nu \rightarrow$ H + HCO and HCHO + h$\nu \rightarrow$ H_2 + CO reactions.

Note that the two formaldehyde reactions have different quantum yields, at some wavelengths the reaction that produces H + HCO is more important while at others the reaction that produces H_2 + CO is more important.

Exercise 1: NCAR Quick TUV Calculations of Photolysis Frequencies (J)
Go to Quick TUV http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/

The Latitude and Longitude (deg) of Beltsville is 39.0348° N, 76.9075° W. Make photolysis calculations for Latitude of Beltsville but use Longitude = 0 so that output time corresponds to local solar hour angle.

Part A: Variation of J with time.

Input	Value
Latitude and Longitude (deg)	39.0348° N, 76.9075° W
Date (Default)	Year 2015, Month 06, Day 30
Time (hh:mm:ss, GMT/UT)	Vary from 4:00 to 20:00 in 1 hr steps
Overhead ozone column (du):	300
Surface albedo (0-1):	0.1
Ground elevation (Location of surface, km asl):	0
Measurement altitude (Altitude for calculation km asl):	0
Clouds Optical Depth Base Top	 0.00 4.00 5.00
Aerosol Optical Depth S-S Albedo Alpha	 0.235 0.99 1.0
Use Output Option 1	Check the box: Molecular photolysis frequencies (s^{-1})
Radiation Transport Model	Pseudo-spherical discrete ordinate 4 streams (slower, more accurate) If time allows you may compare the Pseudo-spherical 2 streams model.
Output:	Save: solar zenith, times and Js for: $O_3 + h\nu \rightarrow O(^1D) + O_2$ $NO_2 + h\nu \rightarrow O(^3P) + NO$ $CH_2O + h\nu \rightarrow H + HCO$ $CH_2O + h\nu \rightarrow H_2 + CO$

Part B: Variation of J with altitude and through clouds.

Input	Value	
Latitude and Longitude (deg)	39.0348° N, 76.9075° W	
Date (Default)	Year 2015, Month 06, Day 30	
Time (hh:mm:ss, GMT/UT)	12:00	
Overhead ozone column (du):	300	
Surface albedo (0-1):	0.1	
Ground elevation (Location of surface, km asl):	0	
Measurement altitude (Altitude for calculation km asl):	Vary in steps of 0.5 km from 0 to 10 km	
Clouds Optical Depth Base Top	Clear Air 0.00 4.00 5.00	with Cloud 5.00 4.00 5.00
Aerosol Optical Depth Single Scattering Albedo Alpha	 0.235 0.99 1.0	
Use Output Option 1	Check the box: Molecular photolysis frequencies (s^{-1})	
Radiation Transport Model	Pseudo-spherical discrete ordinate 4 streams (slower, more accurate) If time allows you may compare the Pseudo-spherical 2 streams model.	
Output:	Save: solar zenith, times and Js for: $O_3 + h\nu \rightarrow O(^1D) + O_2$ $NO_2 + h\nu \rightarrow O(^3P) + NO$ $CH_2O + h\nu \rightarrow H + HCO$ $CH_2O + h\nu \rightarrow H_2 + CO$	

Plot your calculated Js from Part A as time series and your Js from Part B with respect to altitude. For the Part B plots it would be good to plot the clear air and cloud results for each J so you may compare them.

Exercise 2: Photostationary-State Ozone Calculations

In polluted regions near urban regions such as Beltsville the photolysis of nitrogen dioxide (NO_2) yields ozone.

$$NO_2 + h\nu \rightarrow O(^3P) + NO$$
$$O(^3P) + O_2 \rightarrow O_3 \text{ (Very fast due to high oxygen concentration)}$$

The rate of the ozone production from these two reactions is given by the following equation; were $J_{NO_2}$is the photolysis frequency of NO_2 and $[NO_2]$ is the concentration of NO_2.

$$R_{O_3\ Formation} = J_{NO_2}[NO_2]$$

The major loss reaction of ozone is with nitric oxide (NO).

$$O_3 + NO \rightarrow NO_2 + O_2$$

$$R_{O_3\ Loss} = k_{O_3+NO}\,[O_3][NO]$$

As a first approximation assume that $R_{O_3\ Formation} = R_{O_3\ Loss}$ then we have the following equation.

$$J_{NO_2}[NO_2] = k_{O_3+NO}\,[O_3][NO]$$

This equation can be rearranged to give an expression for the concentration of ozone, $[O_3]$.

$$[O_3] = \frac{J_{NO_2}}{k_{O_3+NO}} \times \frac{[NO_2]}{[NO]}$$

This shows that concentration of ozone, $[O_3]$, is directly proportional to J_{NO2} and the $[NO_2]/[NO]$ ratio to a first approximation. Use the J_{NO2} time series that you calculated Exercise 1A, assume a $[NO_2]/[NO]$ ratio equal to 30, temperature (T) = 298.15 K and k_{O_3+NO} $=1.8 \times 10^{-12} \times \exp(-1370/T)$ cm^3 $molecule^{-1}$ s^{-1}; to calculate a diurnal ozone concentration time series over a period of one day. Using this approach, $[O_3]$ will be in units of molecules cm^{-3}; convert $[O_3]$ to parts per billion by volume (ppbV) to make a second plot.

Converting between volume mixing ratio (ppb) and air concentration (molecules cm^{-3}).

First calculate the concentration of air.

Pressure = P
Volume = V take as 1.000 litter = 1000 cm^3
Temperature = T
Ideal Gas Constant = R = 8.20574×10^{-2} liter × atm / (mole K)
Avogadro's Number = 6.02214×10^{23} molecules/mole
n = number of moles

$$\frac{n}{V} = \frac{P\ (atm)}{8.20574 \times 10^{-2}\,\frac{liter \times atm}{mole\ \times K} \times T(K)}$$

$$\frac{n}{V} = 12.1866 \times \frac{P(atm)}{T(K)} \frac{mole}{liter}$$

$$\frac{molecules}{cm^3} = 12.1866 \times \frac{P(atm)}{T(K)} \frac{mole}{liter} \times 6.02214 \times 10^{23}\,\frac{molecules}{mole} \times \frac{1\ liter}{1000cm^3}$$

Air Concentration Expression:

$$\frac{molecules}{cm^3} = 7.33894 \times 10^{21} \times \frac{P(atm)}{T(K)} \frac{molecules}{cm^3}$$

Converting to Mixing ratio (ppbV)
There are 1×10^9 ppb in a cm^3 of air by definition.

$$1 \times 10^9 ppb = 7.33894 \times 10^{21} \times \frac{P(atm)}{T(K)} \frac{molecules}{cm^3}$$

$$1\ ppbV = 7.33894 \times 10^{12} \times \frac{P(atm)}{T(K)} \frac{molecules}{cm^3}$$

Example:

Assume:

Pressure = 1.000 atm
Temperature = 298.15 K

Using the assumed values

$$1\ ppbV = 7.33894 \times 10^{12} \times \frac{1\ atm}{298.15\ K} \frac{molecules}{cm^3}$$

$$1\ ppbV = 2.46149 \times 10^{10}\ \frac{molecules}{cm^3}$$

Note that the conversion is pressure and temperature dependent so a mixing ratio of 1 ppb at the surface is not the same concentration as a mixing ratio of 1 ppb at say 10 km.