CHM 5423 – Atmospheric Chemistry
Problem Set 2 - Due date: Tuesday, February 16th (by 11:59pm). Please turn in your homework by sending it to me at my FIU email address joensj@fiu.edu Indicate in your email that you are sending me your Homework 2 solutions.

NOTE: Exam 1 will be a take home exam. I will pass out the exam on Thursday, February 18th, and it will be due by 11:59pm on Tuesday, February 23rd. Note this is a change from the original date given in the syllabus.

Do the following problems. Show your work.

1) Beer's law, as derived in class, can be written as

$$\ln(I_\ell/I_0) = - \sigma N \ell \qquad (1.1)$$

where I_0 is the initial intensity of light (at a specific wavelength λ), I_ℓ is the intensity after the light has traveled a distance ℓ (in cm), σ is the absorption cross-section for the absorbing molecule (in cm^2/molecule), and N is the number density of absorbing molecules (in molecule/cm^3). Beer's law is a common method for monitoring concentrations of absorbing molecules both in the laboratory and in in the atmosphere.

The absorption cross section for ozone (O_3) at T = 295. K and λ = 310.0 nm is $\sigma = 10.2 \times 10^{-20}$ cm^2/molecule at λ = 300. nm.

a) In a sample of air at T = 295. K the value for I_ℓ/I_0 was found to be 0.762 The pathlength used in the measurement was ℓ = 600. m. Assuming that the only light absorbing molecule in the air sample is ozone, find N, the number density of ozone molecules in the air sample. Give your final answer in units of molecules/cm^3.

b) The total pressure of the air sample is p = 0.968 atm. Based on this value for total pressure and the information and your answer in part a, find the concentration of ozone in the air sample in units of ppm (parts per million).

2) Consider monochromatic light at a wavelength λ = 500. nm. Find the following:

a) The energy of one photon of light in units of J and in units of cm^{-1}.

b) The energy of one mole of photons, in units of kJ/mol.

3) Find the value for θ (zenith angle) and f_s (Earth-sun correction factor) for the following conditions:

a) 1600 hours, latitude = 30 °N, date = April 1st

b) 1100 hours, latitude = 20 °S, date = December 1st

c) 1200 hours, latitude = 25 °N, date = February 15th

4) The molecule acetaldehyde (CH_3CHO) is a trace constituent in the troposphere. In this problem we explore the photochemistry of acetaldehyde.

a) Find the threshold wavelength for photodissociation of acetaldehyde to form the following sets of products:

process 1 $CH_3CHO + h\nu \rightarrow CH_3 + HCO$

process 2 $CH_3CHO + h\nu \rightarrow CH_3CO + H$

process 3 $CH_3CHO + h\nu \rightarrow CH_4 + CO$

Note: Use the thermochemical data in Chapter 7 of the most recent JPL review (JPL 19-5) to do this part of the problem.

b) Find the rate constant for photodissociation of acetaldehyde for the following conditions: Sea level, cloudless conditions, "best estimate" albedo, latitude = 30.0 °N, time of day = 1000 hours, time of year = May 1. Use the photon flux values given in the Chapter 2 handout to do your calculation. Absorption cross-section data and photodissociation quantum yields are given in Chapter 4 of the most recent JPL review (JPL 19-5). There are two tables you will need to use from this review – one with the absorption cross-section data for acetaldehyde (Table 4D-3-1), and one with the primary quantum yield for the process

$$CH_3CHO + h\nu \rightarrow CH_3 + HCO$$

(Table 4D-3-2), which is the only photodissociation process observed for acetaldehyde photodissociation in the troposphere.

c) Based on your answer in b, find $t_{1/2}$, the half-life for acetaldehyde with respect to photodissociation for the conditions in part b of this problem. Give your final answer in units of days.