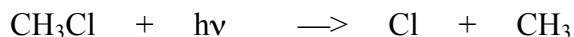


1. Use the mean *bond dissociation enthalpy* (a.k.a. bond energy – from the handout in class) for the bond broken in the reaction below to calculate the longest wavelength that has sufficient energy to “drive” it (i.e. the *threshold wavelength*, λ_{THRESH}).



2. More on the Chapman Cycle – photochemical considerations

a) Using the O_2 bond dissociation energy from the handout in class, calculate λ_{THRESH} for O_2 . Do most or all of the wavelengths absorbed by O_2 (in the UV) cause photo-dissociation?

b) O_2 absorbs strongly below 200nm, and somewhat weakly between 200-240nm (see handout from class). How would you expect J_1 , and in turn τ , to vary with altitude through the stratosphere? How would J_1 & τ in the troposphere compare to that in the stratosphere? This process is the primary source of O atoms (the sole Ox source in the stratosphere). So, among the three following regions (i) high in the stratosphere, ii) low in the stratosphere, iii) or in the troposphere, in which would you expect the mixing ratio of O to be the highest? In which would it be the lowest?

c) Some authors will add an additional step in the cycle: $\text{O} + \text{O} + \text{M} \longrightarrow \text{O}_2 + \text{M}$, but this reaction is not significant for two reasons, one being that reactions that need an M are often slow because they require three things to collide (simultaneously) instead of just two. Why else might this reaction be slow – except for at very high altitudes?

d) How does the Chapman cycle allow us to rationalize an ozone layer (or “region”)? (see i and ii)

- i) Provide a conceptual rationale, on the basis of factors that affect the rates of the reactions that result in the net production of Ox and/or O_3 .
- ii) Provide a quantitative rationale, based on the equation below (which is derived in the textbook and should be 100% consistent with your rationale in “i”). (Note Ox production rate constants are on top of the big fraction – and loss rate constants are on the bottom!)

$$X_{\text{O}_3}^{alt} \sim \frac{[\text{O}_3]}{[\text{O}_2]} = \left(\frac{J_1 k_2 [\text{M}]}{J_3 k_4} \right)^{1/2}$$

e) How does the amount of stratospheric ozone predicted by the Chapman mechanism compare to what’s observed? What are the specific differences?

3. “Differential” light penetration: Because of absorption of UV light by ozone (O_3) and oxygen (O_2), we separated UV light into three different wavelength regions (or “bins”) that penetrate to different altitudes in the atmosphere.

- i) Which wavelengths are available for photochemistry at only very high altitudes (above the stratosphere)?
- ii) Which wavelengths are absorbed by O_3 (and O_2 to some extent) and are filtered in the stratosphere – rendering them available high in the stratosphere, and only slightly in the lower stratosphere – but are absent in the troposphere?
- iii) Radiation beyond what wavelength penetrates to the troposphere/surface?

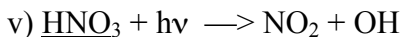
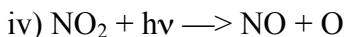
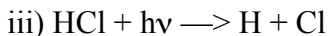
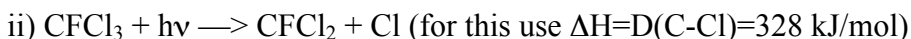
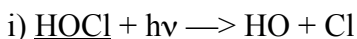
4. In this problem, we (a.k.a. *you*) will assess the photo-reactivity of each molecule listed as a reactant in the “photolysis” reactions below. (i-v). For each substance, examine the absorption spectra (displayed on the next page), use the ΔH_f values listed below to calculate ΔH_{rxn} , and in turn, λ_{THRESH} , and consider what altitudes the key wavelengths would penetrate to. Then, provide a brief assessment of each molecule’s overall photo-reactivity, either:

A) Unreactive except at very high altitudes,

B) Moderately photo-reactive in the stratosphere – not in the troposphere, or

C) Photo-reactive at all altitudes, even in the troposphere

(There may be a couple of borderline cases...this distinction can be subtle and I am trying to simplify as much as possible - I will elaborate in the key.)



You'll need the following data - ΔH_f values (in kJ/mole) – for all reactions except “ii”.

H: 218.0; Cl: 121.3; HO: 39.0; NO: 90.3; NO₂: 33.1;
HOCl: -74.5; HCl: -92.3; O: 249.2; HNO₃: -134.3;

Spectra for problem #4 – Note that 10\AA is equivalent to 1 nm – i.e. 2000\AA means 200 nm , etc. If the wavelengths are plotted in terms of \AA – just cross out a zero. Note that the HCl spectrum is plotted backwards.

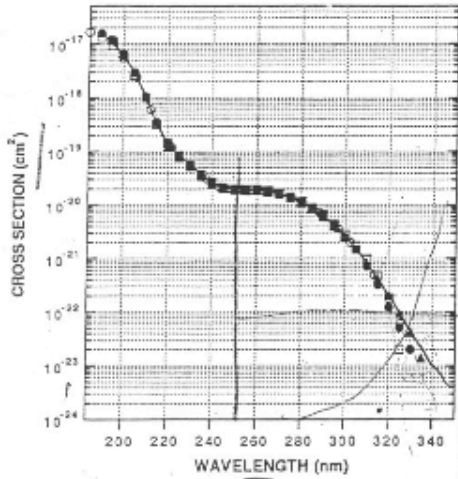
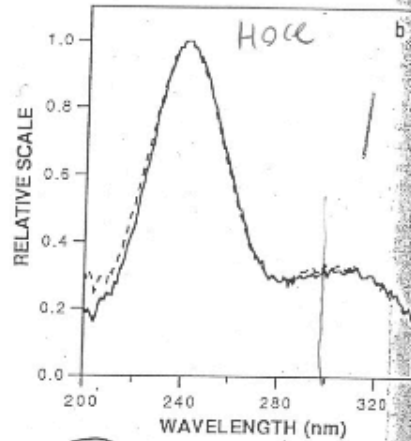


Fig. 2. Absorption spectrum of HNO_3 at 298 K measured in this work (solid curve) and in previous studies: Rattige et al. [1992a,b,c] (solid triangles), Molina and Molina [1981] (solid circles), Johnston and Graham [1973] (open squares), and Simons [1973/1974] (open circles).



3. (a) HCl UV absorption spectra obtained by [1] and [2] from equilibrium spectrum and [3] [4].

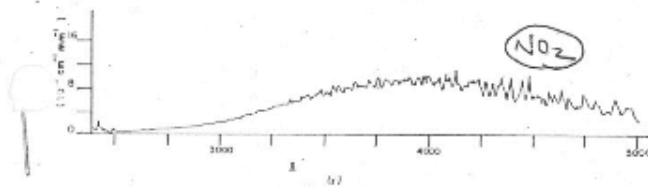


Fig. VI-B. (cont.)

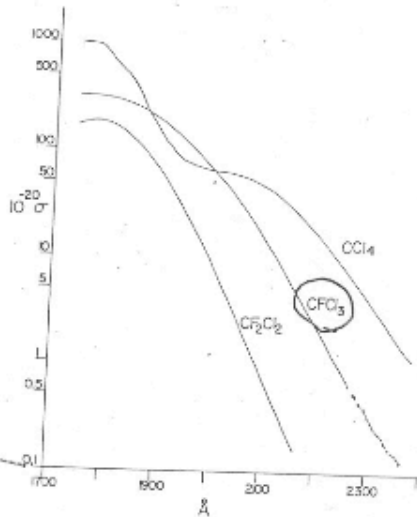
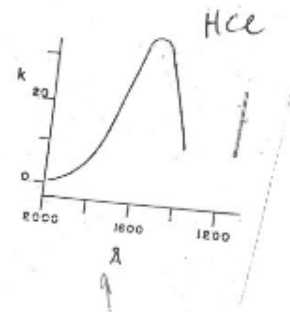


Fig. VII-16. Absorption cross sections of CF_2Cl_2 , CFC_3 , and CCl_4 in the ultraviolet region. σ is given in units of $\text{cm}^2\text{ molec}^{-1}$, base e, room temperature. From Rowland and Molina (843) and Robbins et al. (836), reprinted by permission of the authors. Copyright by the American Geophysical Union.



NOTE $10\text{\AA} = 1\text{ nm}$

SO: $2000\text{\AA} = 200\text{ nm}$
etc.