Atmos. Chem. Lecture 5, 9/18/13: Light and photochemistry

- Photodissociation
- Absorption spectra of O_2 and O_3
- Absorption & Beer's Law
- Photolysis rate constants
- Atmospheric radiation

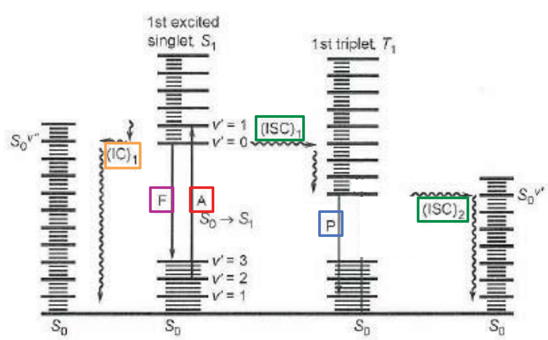
Problem Set 1 due Wednesday 9/25

Fate of electronically excited species

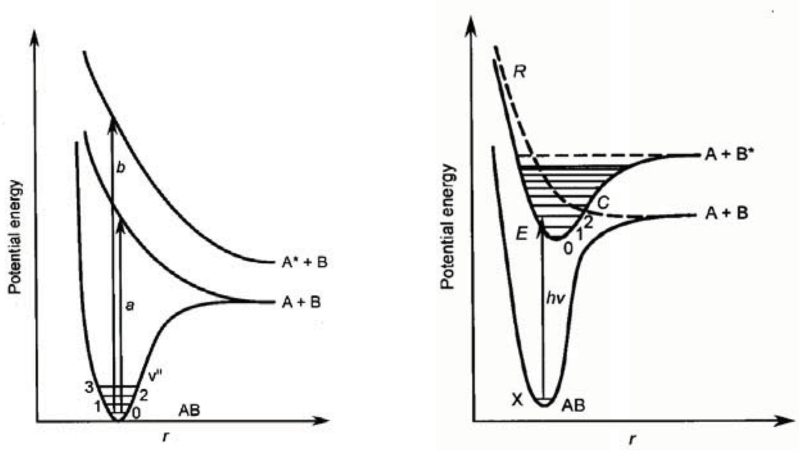
"Jablonski Diagram" (FP&P)

vertical: absorption (**A**), emission of light (**F**, **P**); collisional relaxation (⌇)

horizontal: intersystem crossing (**ISC**), internal conversion (**IC**)



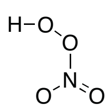
Photodissociation: direct vs. predissociation

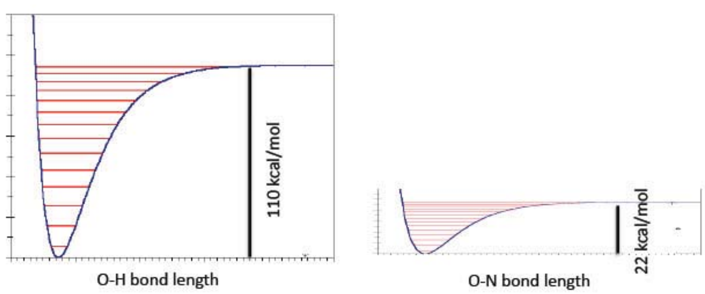


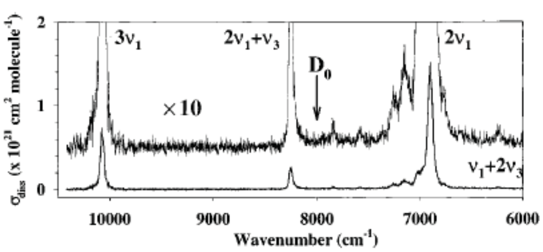
FP&P

Overtone photodissociation

Pernitric acid:

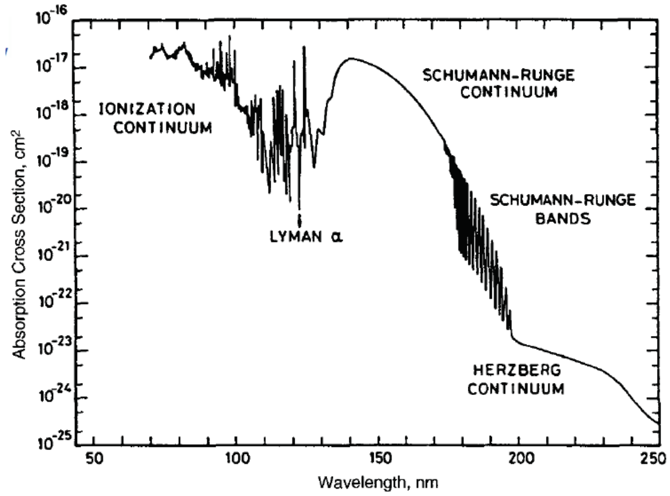






Roehl et al. *J. Phys. Chem. A, 106:3766 (2002)*

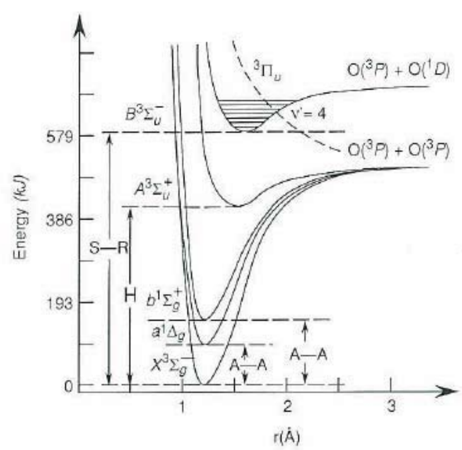
Light absorption by oxygen (O_2)



S&P

see G. Brasseur and S. Solomon, *Aeronomy of the Middle Atmosphere,* 3rd rev., Springer, 2005

Potential energy curves of O_2

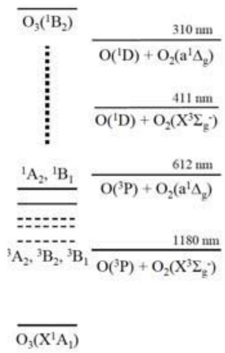


175 nm

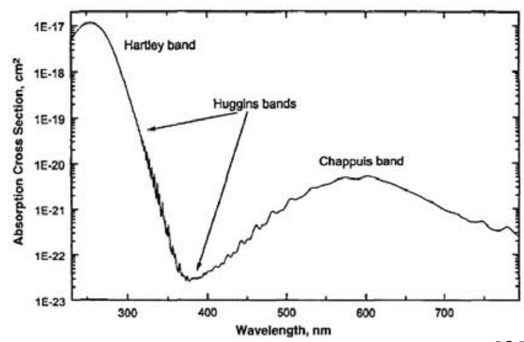
242.4 nm

FP&P

Light absorption by ozone (O_3)



S. Nizkorodov, UCI



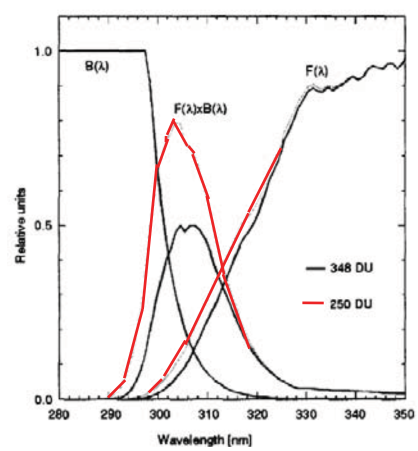
S&P

see G. Brasseur and S. Solomon, *Aeronomy of the Middle Atmosphere*, 3rd ed., Springer, 2005

Absorption of light by molecules

Beer-Lambert Law $I(\lambda) = I\ (\lambda)\ e^{-\sigma(\lambda)\, C\, L}$

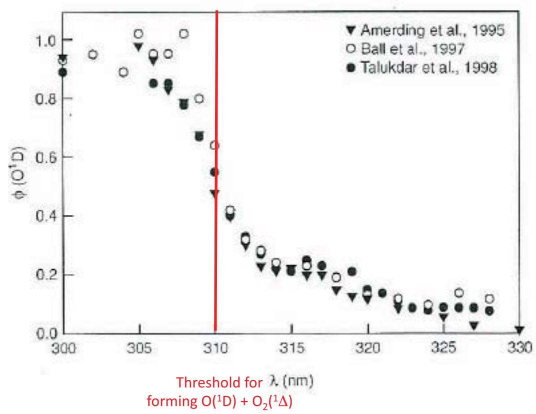
[Note: Additional material is discussed here during lecture.]



Madronich et al., *J. Photochem Photobiol B*, 46:5 (1999)

$O(^1D)$ production by O_3 photolysis

$O_3 + h\nu \rightarrow O(^3P) + O_2$
$\rightarrow O(^1D) + O_2$



FP&P

Photochemical reaction rates

Unimolecular reaction: $A + h\nu \rightarrow B + C \quad \Phi_1$
$\rightarrow X \quad \Phi_2$

Rate of loss of A depends on…
- How well A absorbs light
- Chance that a reaction will occur after absorption
- How much light there is
- Concentration of A

One wavelength:

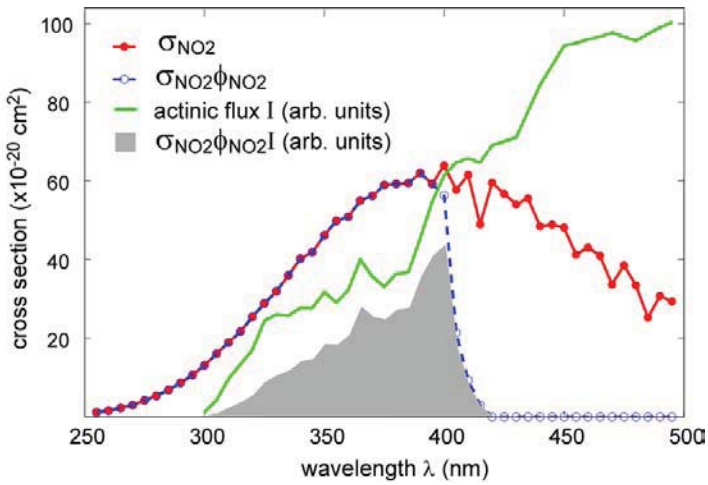
$$-\frac{d[A]}{dt} = J(\lambda)[A] = \phi_{Total}(\lambda)\ \sigma_A(\lambda)\ I(\lambda)\ [A]$$

Example 1: NO_2 photolysis

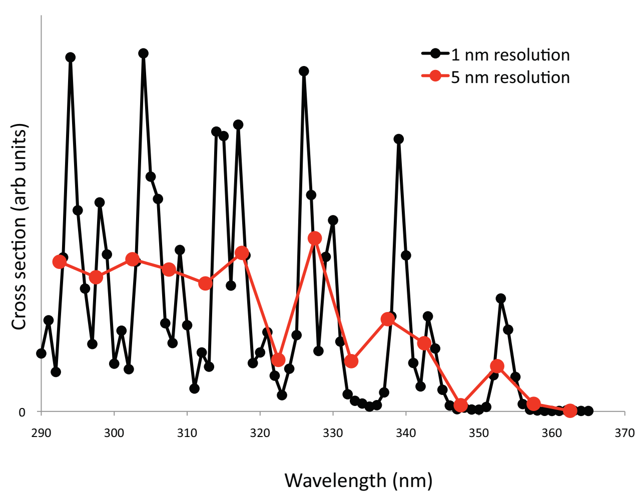
$NO_2 + h\nu \rightarrow NO + O(^3P)$

ΔH = 301 kJ/mol

$\lambda_{threshold}$ = 398 nm

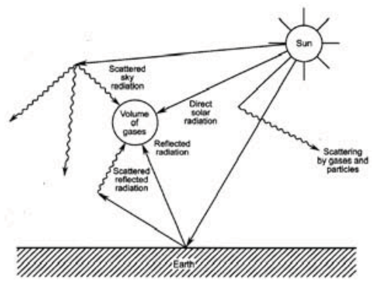


Example 2: CH_2O photolysis



Actinic flux I(λ)

Symbol	Quantity	units
L(λ)	**(Spectral) Radiance**: Energy flux coming from a specific (solid) angle, per unit wavelength	J m^{-2} s^{-1} nm^{-1} sr^{-1}
E(λ)	**(Spectral) Irradiance**: Energy flux through a flat plane (measured by instruments), per unit wavelength	J m^{-2} s^{-1} nm^{-1}
F(λ)	**(Spectral) Radiant Flux Density**: Energy flux through a point (relevant to molecules), per unit wavelength	J m^{-2} s^{-1} nm^{-1}
I(λ)	**(Spectral) Actinic Flux**: Photon flux through a point (relevant to molecules), per unit wavelength	photons cm^{-2} s^{-1} nm^{-1}
I(λ)	**Actinic Flux**: Total photon flux through a point (relevant to molecules), spanning a range of wavelengths	photons cm^{-2} s^{-1}



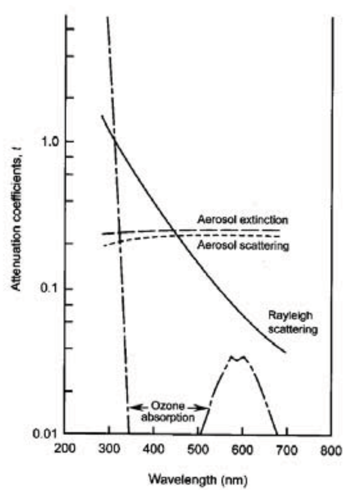
FP&P

Calculated Actinic Fluxes (FP&P)

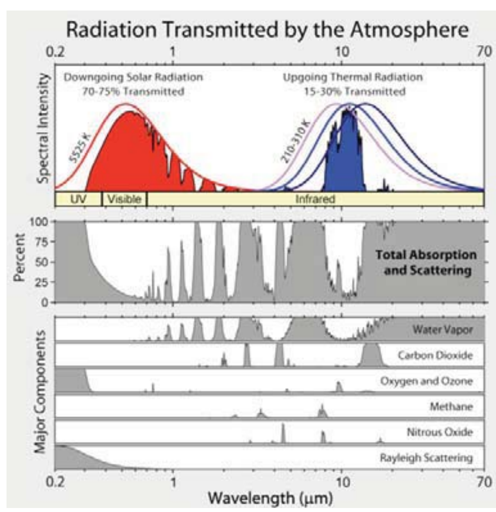
Images removed due to copyright restrictions. See Table 3.15 in Finlayson-Pitts and Pitts, *Chemistry of the Upper and Lower Atmosphere*. Academic Press, 2000.

Calculated Actinic Fluxes (FP&P)

Main absorbers/scatterers



FP&P



http://en.wikipedia.org/wiki/File:Atmospheric_Transmission.png

1.84J / 10.817J / 12.807J Atmospheric Chemistry
Fall 2013