Introduction to Photolysis
AOSC 433/633 & CHEM 433/633

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Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2013

Lecture 10

5 March 2013

Importance of Radicals

- With a few exceptions, the only reactions between molecules that proceed at appreciable rates are those involving at least one radical
- Radicals require significant energy to form: a bond must be broken
- Radical formation is tied to absorption of photons that "photodissociate" a compound, leading to radical formation

Initiation

O_2 + photon $\rightarrow$ O + O

Propagation

$O + O_2 + M \rightarrow O_3 + M$

O_3 + photon $\rightarrow O(^1D) + O_2$

$O(^1D) + H_2O \rightarrow OH + OH$

$OH + O_3 \rightarrow HO_2 + O_2$

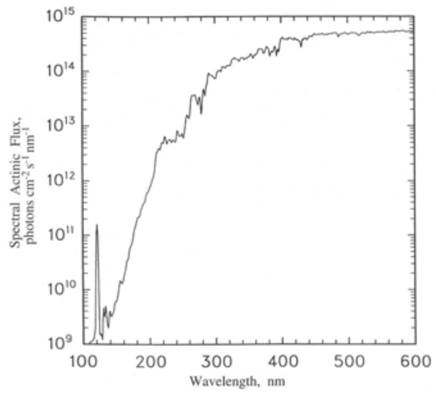
$HO_2 + O \rightarrow OH + O_2$

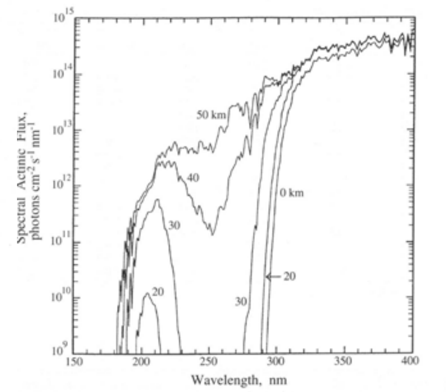
Termination

$OH + HO_2 \rightarrow H_2O + O_2$

• Motivation for Today's Lecture:

a) How does atmosphere go from this: **to this ?**





GURE 3.3 Solar spectral actinic flux (photons cm^{-2} s^{-1} nm^{-1}) at various altitudes and at the Earth's surface (DeMore et al., 1994).

From DeMore et al., *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, Evaluation No. 11, 1994.

From Seinfeld and Pandis, *Atmospheric Chemistry and Physics*, 1998.

b) Relation between ozone depletion and exposure to UV radiation

c) Why is the ozone layer at a height of ~29 km with a thickness of ~400 DU ?

Energetics of Photolysis

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

$h\nu$ represents a photon with specific energy.

Let's examine enthalpy of this reaction:

33.9 kcal/mole		104.7 kcal/mole	22.5 kcal/mole		
O_3 +	$h\nu$ →	$O(^1D)$ +	$O_2(^1\Delta_g)$		**ΔEnthalpy = 93.3 kcal/mole**

Photon Energy:

$$\varepsilon = \frac{hc}{\lambda} \Rightarrow \lambda_{max} = \frac{hc}{\Delta \text{Enthalpy}}$$

For O_3 photo-dissociating to $O(^1D)$:

$$\lambda_{max} = \frac{hc}{\Delta\text{Enthalpy}} = \frac{2.85\times10^4 \text{kcal/mole nm}}{\Delta\text{Enthalpy}} = \frac{2.85\times10^4 \text{ nm}}{93.3} = \mathbf{305\ nm}$$

Energetics of Photodissociation

$O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta_g)$ **ΔEnthalpy = 93.3 kcal/mole** λ_{max} = **305 nm**

$O_3 + h\nu \rightarrow O(^3P) + O_2(^3\Sigma_g)$ **ΔEnthalpy = 25.7 kcal/mole** λ_{max} = **1120 nm**

Atomic oxygen: **(Note: you will not be "responsible" for the material below on any exam ☺)**

Ground state – two unpaired electrons in the 2p orbitals: $(1s)^2(2s)^2(2p_1)^2(2p_2)^1(2p_3)^1$

Called ^{3}P:

"**3**" represents 2S+1, where S is spin of all of the unpaired electrons.

There are 2 unpaired electrons, each with spin of ½

Hence, S = 1 and 2S+1 = **3** ⇐ spin angular momentum

P represents orbital angular momentum, found from an electron diagram of filled orbitals:

ground state: $(1s)^2$ [↑↓] $(2s)^2$ [↑↓] $(2p)^4$ [↑↓][↑][↑] (+1 0 -1)

$\Lambda = +1+1+0-1 = 1$

Λ	0	1	2	3
Term	S	P	D	F

Excited state – one electron moves from $2p_3$ to $2p_2$: $(1s)^2(2s)^2(2p_1)^2(2p_2)^2$

Called ^{1}D:

"**1**" represents 2S+1, where S is spin of all of the unpaired electrons.

There are no unpaired electrons!

Hence, S = 0 and 2S+1 = **1** ⇐ spin angular momentum

D represents orbital angular momentum, found from an electron diagram of filled orbitals:

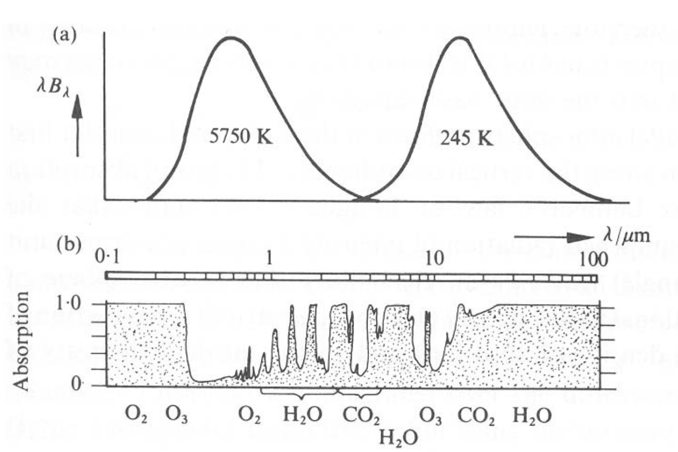
excited state: $(1s)^2$ [↑↓] $(2s)^2$ [↑↓] $(2p)^4$ [↑↓][↑↓][ ] (+1 0 -1)

$\Lambda = +1+1+0+0 = 2$

Λ	0	1	2	3
Term	S	P	D	F

Atmospheric Radiation

- Solar irradiance (downwelling) at top of atmosphere occurs at wavelengths between ~200 and 2000 nm (~5750 K "black body" temperature)



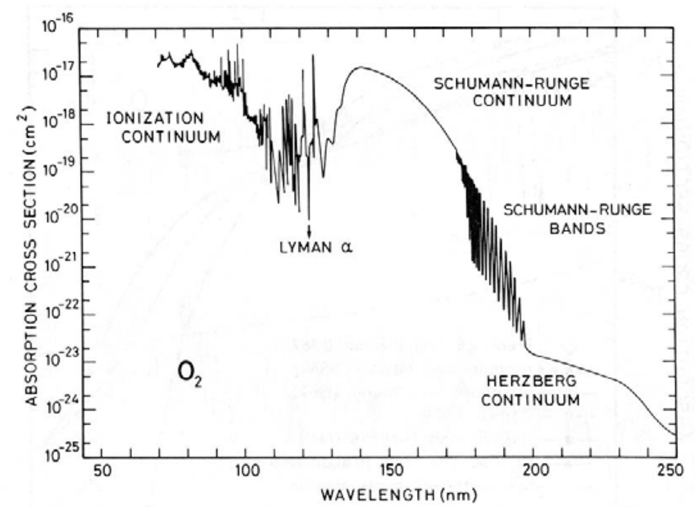
Panel (a) : Curves of black-body energy versus wavelength for 5750 K (Sun's approximate temperature) and for 245 K (Earth's mean temperature).
The curves are drawn with equal area since, integrated over the entire Earth at the top of the atmosphere, the solar (downwelling) and terrestrial (upwelling) fluxes must be equal.

Panel (b): absorption by atmospheric gases for a clear vertical column of the atmosphere (1.0 represents complete absorption).

From Houghton, *Physics of Atmospheres*, 1991

- Absorption and photodissociation in the UV occurs due to changes in the electronic state (orbital configuration) of molecules

Absorption Cross Section of O_2



From Brasseur & Solomon, *Aeronomy of the Middle Atmosphere*, 1986

- O_2 can not dissociate longward of ~250 nm
- All absorption shown above is dissociative (e.g., leads to production of two O atoms)
- Structure in the O_2 cross section is related to whether the initial transition involves an unbound electronic state (smooth) or involves a specific vibrational level of an electronic state (banded, due to requirement of specific quanta of energy)

Beer-Lambert Law

$$F(z,\lambda) = F_{TOA}(\lambda)\, e^{-\tau(z,\lambda)}$$ (TOA : Top of Atmosphere)

where:

$$\tau(z,\lambda) = m \int_z^{\infty} \sigma_\lambda\, [C]\, dz'$$ (τ: optical depth)

F : solar irradiance (photons/cm^2/sec)
σ_λ : absorption cross section
C : concentration of absorbing gas (molecules/cm^3)
m : ratio of slant path to vertical path, equal to $1/\cos(\theta)$ for $\theta <$ ~75°
θ : solar zenith angle

Governs basics of radiative transfer in the UV and near IR regions

Photolysis Frequency

For a specific spectral interval, the photolysis frequency (***partial J value***) of a gas is given by the product of its absorption cross section and the solar irradiance:

$$J_{gas}(z,\lambda) = \text{Quantum\_Yield}(\lambda)\ \sigma_{gas}(\lambda,T)\ F(z,\lambda)$$

Units: $s^{-1}\ nm^{-1}$

The total ***photolysis frequency*** (***J value***) is found by integrating $J_{gas}(z,\lambda)$ over all wavelengths for which the gas photodissociates:

$$J_{gas}(z) = \int_{\lambda_{min}}^{\lambda_{max}} J_{gas}(z,\lambda)\, d\lambda$$

Units: s^{-1}

$$\text{Rate of Reaction} = \frac{dO_3}{dt} = J\ [O_3]; \quad \text{Units of } J \text{ are } s^{-1}$$

More precisely, calculations of photolysis frequencies consider the "spectral actinic flux", which represents the amount of available photons integrated over all angles, rather than "solar irradiance". These two quantities differ because of scattering of solar radiation by gases and aerosols, and reflection of radiation by clouds and the surface.

Optical Depth of O_2 Absorption

Recall the *Beer-Lambert Law*:

$$F(z,\lambda) = F_{TOA}(\lambda)\ e^{-\tau(z,\lambda)}$$ (TOA : Top of Atmosphere)

where:

$$\tau(z,\lambda) = m \int_{z}^{\infty} \sigma_{\lambda}\, [C]\, dz'$$ (τ: optical depth)

Also:

$$\int_{0}^{\infty} [O_2]\, dz' \approx 4\times10^{24}\ \text{molecules/cm}^2$$

O_2 Optical Depth for $\theta = 0°$, $z = 0$ km			
	σ_{max} (cm^2)	τ (0 km)	$e^{-\tau\,(0\,km)}$
Schumann-Runge Continuum			
Schumann-Runge Bands			
Herzberg Continuum			

Photolysis Frequency of O_2

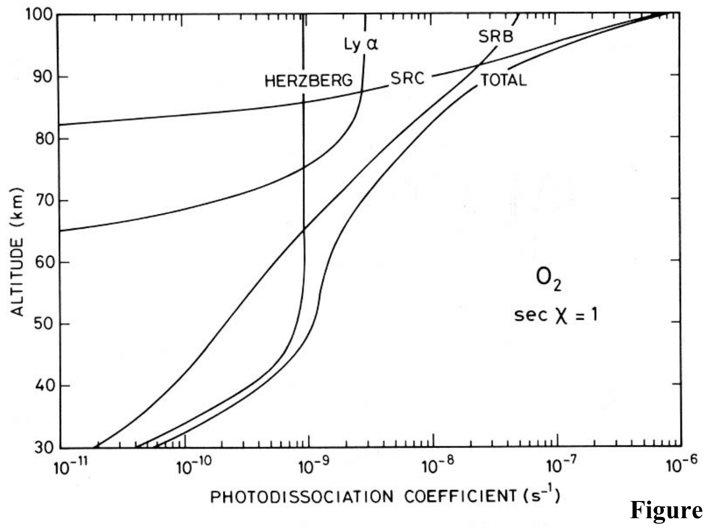


Figure 4.31, Brasseur and Solomon

Where Does Optical Depth = 1.0 for O_2 ?

$$\tau(z, \lambda) = m \int_z^{\infty} \sigma_\lambda [O_2] \, dz'$$

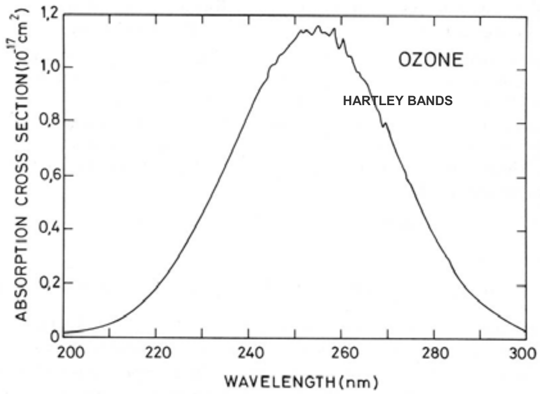
$$\approx \sigma_\lambda \, m \, 4 \times 10^{24} \, e^{-z/H}$$

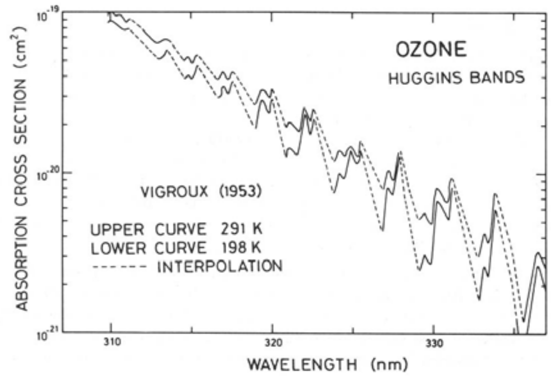
Setting $\tau = 1$ and re-arranging gives:

$$z = H \ln (\sigma_\lambda \cdot m \cdot 4 \times 10^{24})$$

Altitude where $\tau = 1$ (for $\theta = 0°$)		
	σ_{max} (cm^2)	z (km)
Schumann-Runge Continuum	10^{-17}	
Schumann-Runge Bands	10^{-20}	
	3×10^{-23}	
Herzberg Continuum	10^{-23}	

Absorption Cross Section of O_3





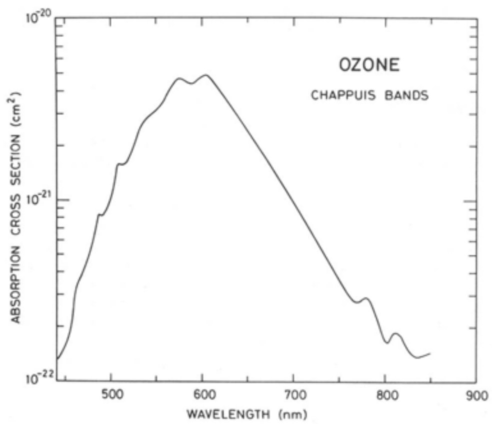


Table 4.6 Theoretical limits corresponding to different photolysis products (nm).

	$O_2(^3\Sigma_g)$	$O_2(^1\Delta_g)$	$O_2(^1\Sigma_g+)$	$O_2(^3\Sigma_u+)$	$O_2(^3\Sigma_u^-)$
$O(^3P)$	1180	590	460	230	170
$O(^1D)$	410	310	260	167	150
$O(^1S)$	234	196	179	129	108

From Brasseur & Solomon, *Aeronomy of the Middle Atmosphere*, 1986

Optical Depth of O_3 Absorption

A typical mid-latitude column abundance for O_3 is 300 Dobson units (DU):

1 DU = 2.687×10^{16} molecules/cm^2; 300 DU = 8×10^{18} molecules/cm^2

Aside:

$$\frac{\text{Column } O_3}{\text{Column Air}} = \frac{8\times10^{18}}{2\times10^{25}} = 0.4 \text{ parts per million } \Rightarrow \text{Ozone is a trace species!}$$

O_3 Optical Depth for $\theta = 0°$, $z = 0$ km

	σ_{max} (cm^2)	τ (0 km)	$e^{-\tau(0\,km)}$	O_3 Column, $\tau = 1.0$
Hartley (~220 to 280 nm)				
Huggins (~310 to 330 nm)				
Chappuis (~500 to 700 nm)				

Solar Spectral Actinic Flux

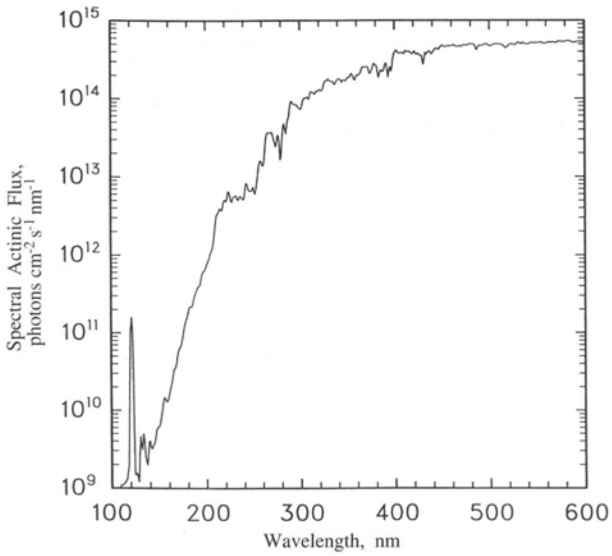
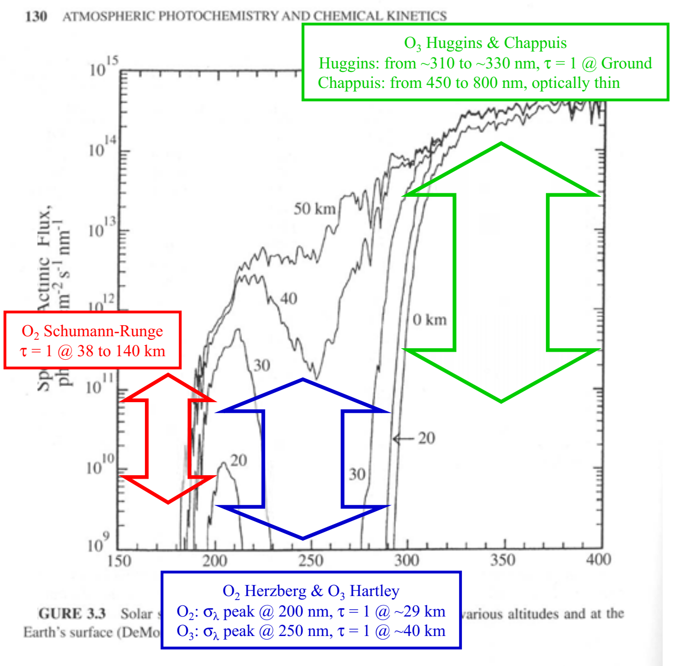


FIGURE 6. Solar spectral actinic flux (photons cm^{-2} s^{-1} nm^{-1}) at the top of Earth's atmosphere.



From DeMore et al., *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, Evaluation No. 11, 1994.

From Seinfeld and Pandis, *Atmospheric Chemistry and Physics*, 1998.

Photodissociation Frequencies

Next goal is to understand:

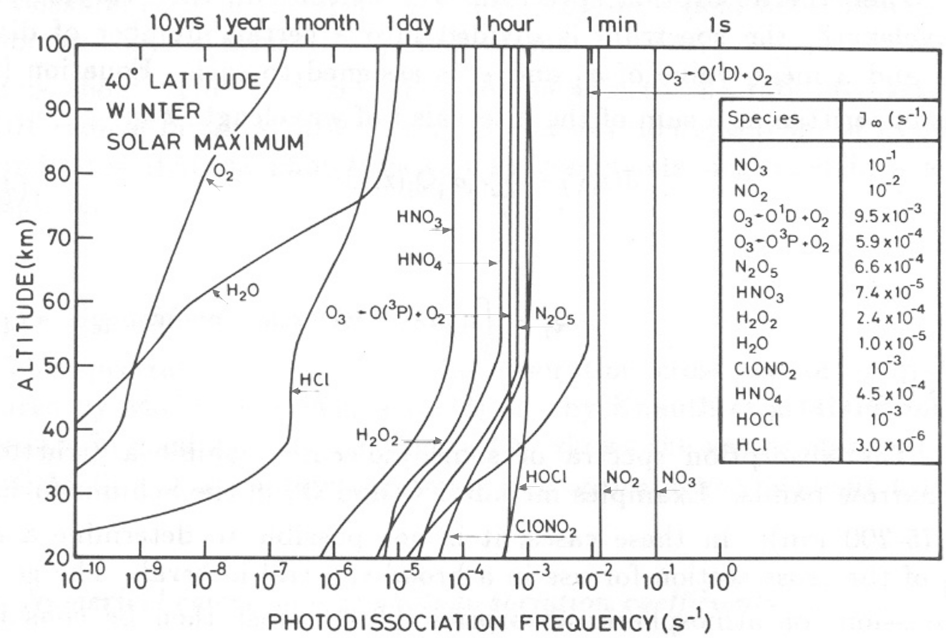
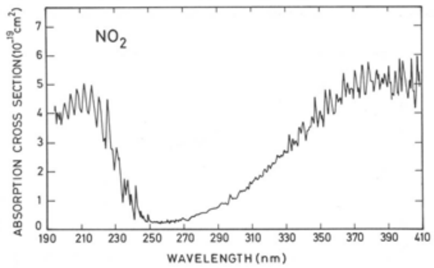


FIGURE 4.58 Photodissociation frequencies for numerous important atmospheric species.

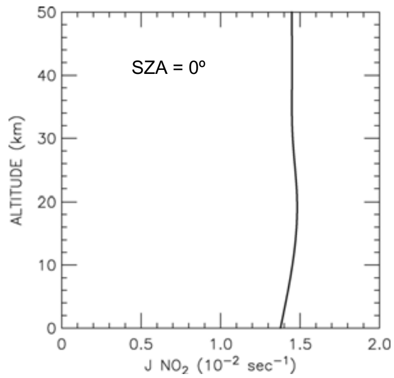
From Brasseur & Solomon, *Aeronomy of the Middle Atmosphere*, 1986

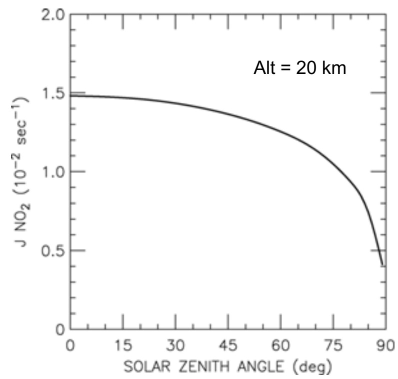
NO_2 Photolysis

The majority of NO_2 photolysis occurs longward of 300 nm, where the atmosphere is optically thin with respect to absorption by O_3 and O_2:

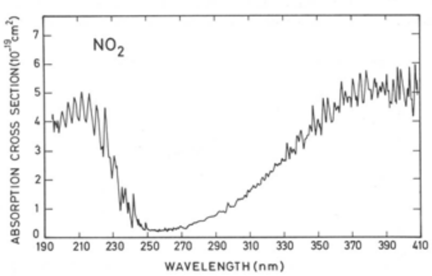


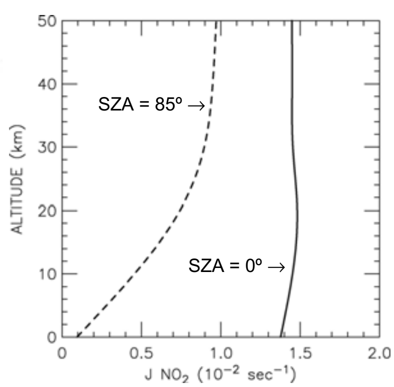
leading to a value for J_{NO2} that is nearly <u>independent</u> of height and SZA:

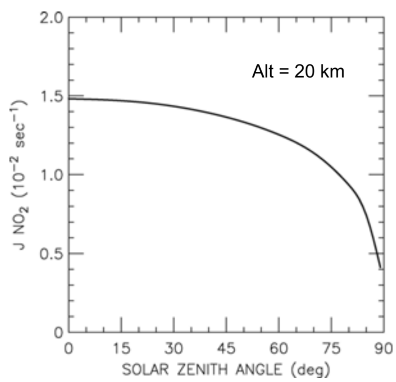


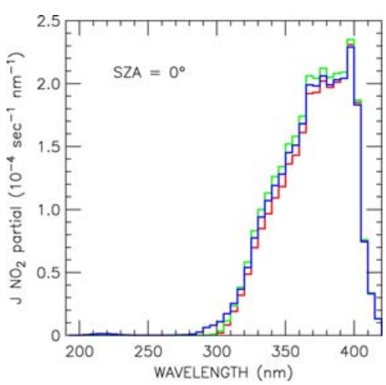


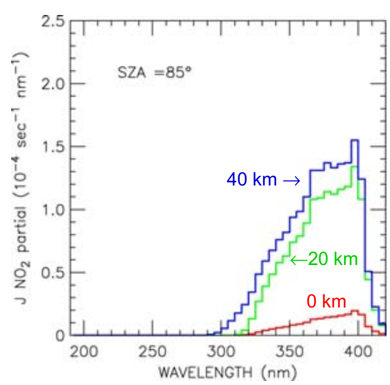
NO_2 Photolysis





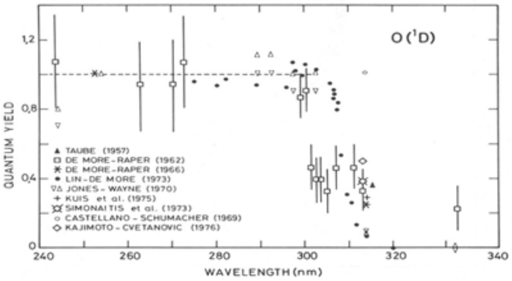


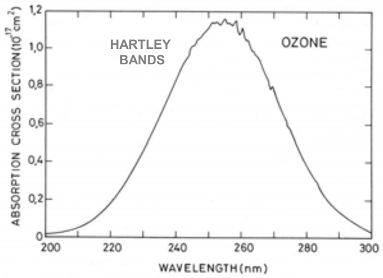


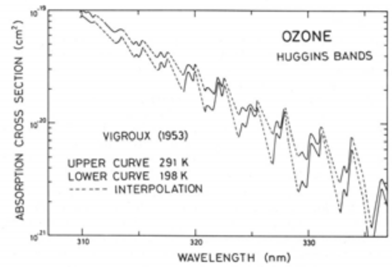


$O_3 \rightarrow O(^1D)$ Photolysis

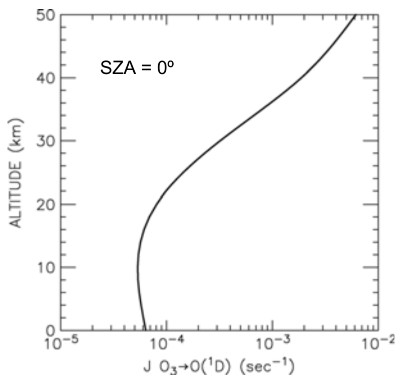
The production of $O(^1D)$ from photolysis of O_3 occurs shortward of 320 nm, where the atmosphere is basically optically thick with respect to absorption by O_3:

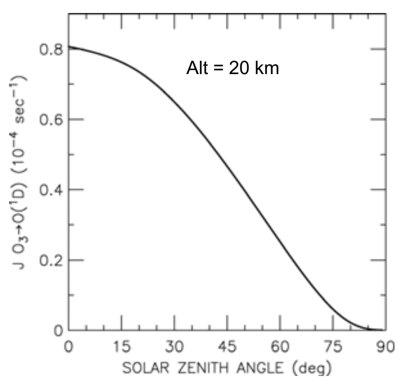




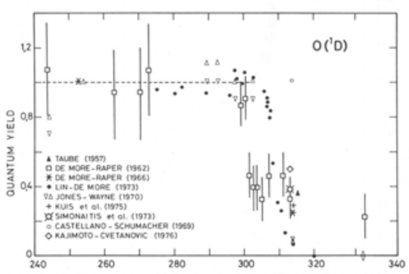


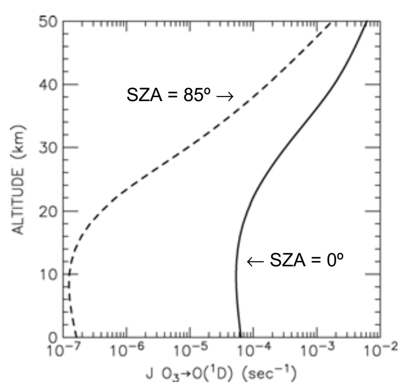
leading to a value for $J_{O3 \rightarrow O(1D)}$ that is <u>dependent</u> on height and SZA:

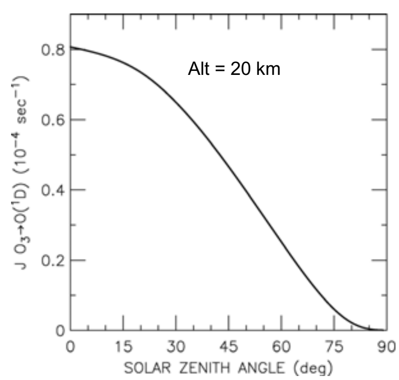


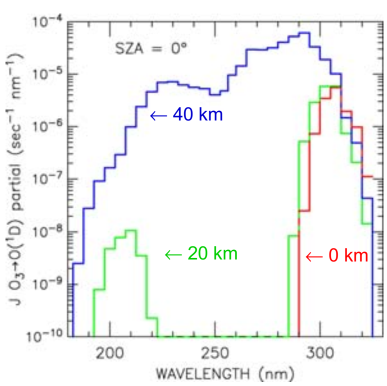


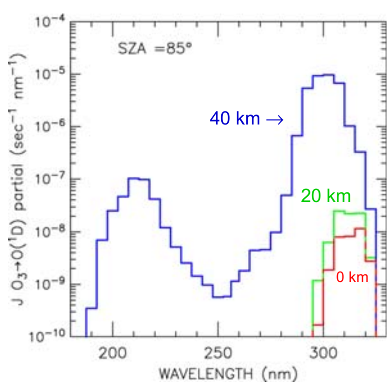
$O_3 \rightarrow O(^1D)$ Photolysis





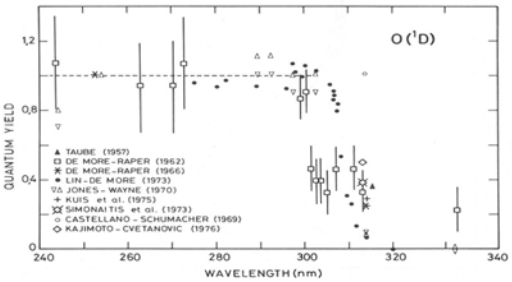


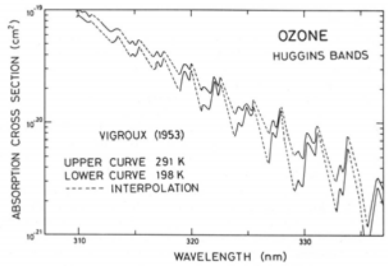


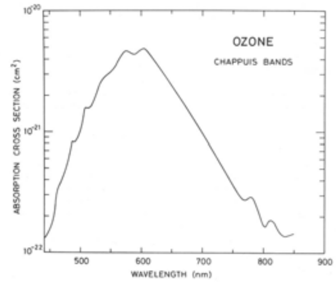


$O_3 \rightarrow O(^3P)$ Photolysis

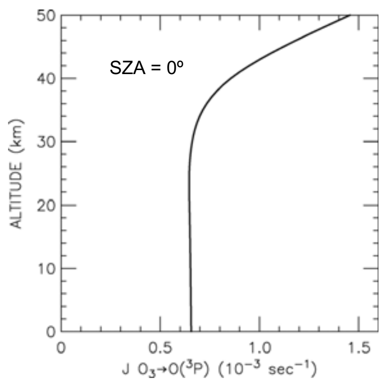
The production of $O(^3P)$ from photolysis of O_3 occurs mainly longward of 500 nm, where the atmosphere is optically thin with respect to absorption by O_3:

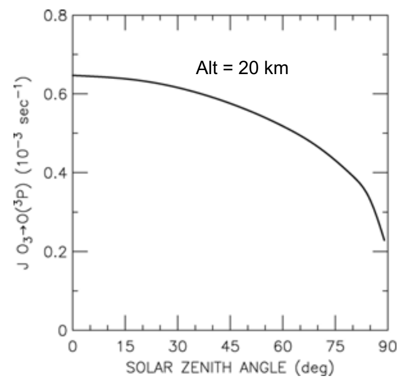




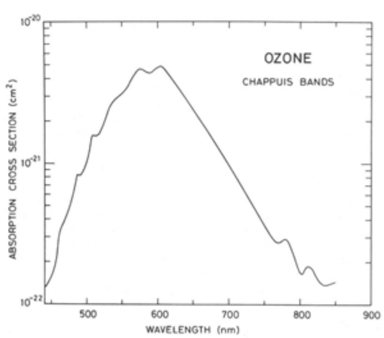


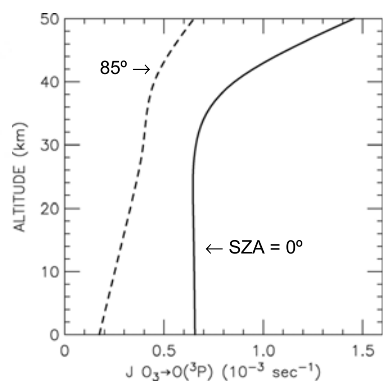
leading to a value for $J_{O3 \rightarrow O(3P)}$ that is essentially <u>independent</u> of height and SZA:

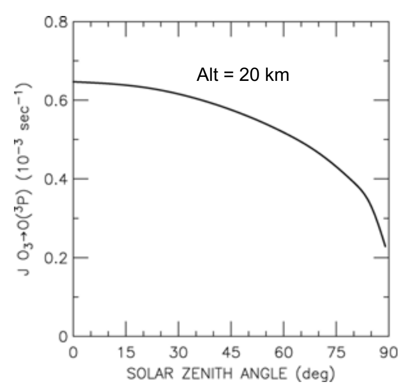


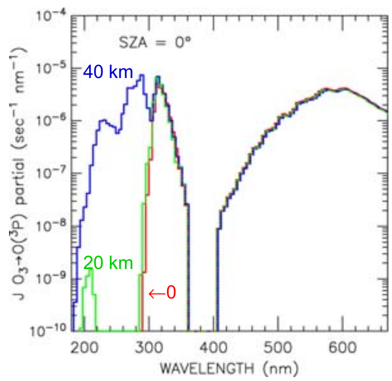


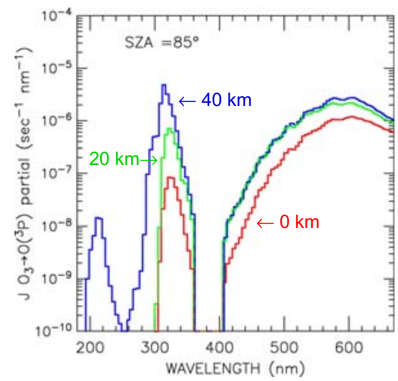
$O_3 \rightarrow O(^3P)$ Photolysis











Biological Effects of UV Radiation

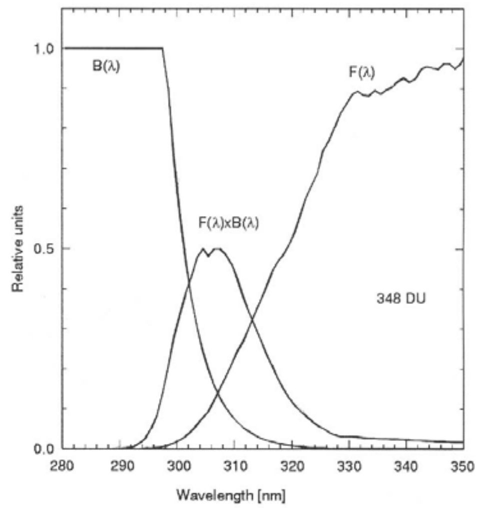


Fig. 1. Biologically active UV radiation. The overlap between the spectral irradiance $F(\lambda)$ and the erythemal action spectrum $B(\lambda)$ given by McKinlay and Diffey [6] shows the spectrum of biologically active radiation, $F(\lambda)B(\lambda)$. The area under the product function $F(\lambda)B(\lambda)$ is the biologically active dose rate. For a total ozone column of 348 DU.

Humans are:

- strongly affected by exposure to UV-C radiation (100 to 280 nm)
- moderately affected by exposure to UV-B radiation (280 to 315 nm)
- weakly affected by exposure to UV-A radiation (315 to 400 nm)

⇐ From Mandronich et al., *J. Photochemistry and Photobiology*, vol. 46, pg. 5, 1998

The "biologically active dose rate" maximizes in the UV-B region at ~305 nm, where $\sigma_{O3} = 3 \times 10^{-19}$ cm² ⇒ τ (0 km) = 2.4 (for O_3 column= 300 DU)

Returning to Stratospheric Ozone

Chapman expression for $[O_3]$:

$$[O_3] = \left(\frac{f_{O2}\, k_2}{J_3\, k_4} \right)^{\frac{1}{2}} \left(J_1[O_2] \right)^{\frac{1}{2}} [M]$$

The concentration of O_3 should peak at the altitude where the product of the square-root of the O_2 photolysis rate times the density of air is largest

$\left(J_1[O_2] \right)^{\frac{1}{2}}$ peaks at same altitude as $J_1[O_2]$: ~35 km

$\left(J_1[O_2] \right)^{\frac{1}{2}}$ [M] peaks about a scale height lower: ~28 km

Photolysis Rates

The total ***photolysis rate*** is the product of the concentration of a gas and the total photolysis frequency (***J value***):

Photolysis Rate Gas (z) = [Gas] × J_{gas} Units: molecules cm^{-3} sec^{-1}

$$= [\text{Gas}] \int_{\lambda_{min}}^{\lambda_{max}} J_{gas}(z,\lambda)\, d\lambda$$

$$\approx [\text{Gas}] \int_{\lambda_{min}}^{\lambda_{max}} \sigma_{gas}(z,T)\, F_{TOA}(\lambda) e^{-\tau(z,\lambda)}\, d\lambda$$

where:

$$\tau(z,\lambda) = m \int_z^{\infty} \sigma_{O2}(\lambda,T)\,[O_2(z)]\, dz' + m \int_z^{\infty} \sigma_{O3}(\lambda,T)\,[O_3(z)]\, dz'$$

Photolysis Rate of O_2

The total ***photolysis rate*** is the product of the concentration of a gas and the total photolysis frequency (***J value***):

$$\text{Photolysis Rate } O_2(z) \approx [O_2(z)] \int_{\lambda_{min}}^{\lambda_{max}} \sigma_{O2}(z,T)\, F_{TOA}(\lambda) e^{-\tau(z,\lambda)}\, d\lambda$$

Assume:

1. O_2 is the only absorber:

$$\tau(z,\lambda) = m \int_z^{\infty} \sigma_{O2}(\lambda,T)\,[O_2]\, dz'$$

2. σ_{O2} is independent of T:

$$\tau(z,\lambda) = m\, \sigma_{O2}(\lambda,T) \int_z^{\infty} [O_2]\, dz'$$

3. $[O_2]$ falls off exponentially with increasing height:

$$\tau(z,\lambda) = m\, \sigma_{O2}(\lambda,T)\, [O_2]_{ground}\, H\, e^{-z/H}$$

Photolysis Rate $O_2(z,\lambda) = J_{O2}\,[O_2]$

$$[O_2]_{ground}\, e^{-z/H}\, \sigma_{O2}\, F_{TOA} \exp\{-m\, \sigma_{O2}\, [O_2]_{ground}\, H\, e^{-z/H}\}$$

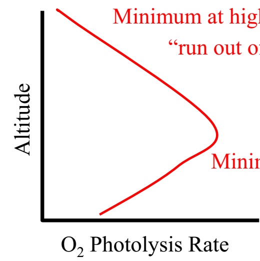
Photolysis Rate of O_2

Photolysis Rate $O_2(z,\lambda) = J_{O2}\,[O_2] =$

$$[O_2]_{ground}\, e^{-z/H}\, \sigma_{O2}\, F_{TOA} \exp\{-m\, \sigma_{O2}\, [O_2]_{ground}\, H\, e^{-z/H}\}$$

What does this function look like?

Informally-



Formally-

Can show:

$$\frac{d\,[\text{Photolysis Rate } O_2\,(z,\lambda)\,]}{dz} = 0$$

if $\mathbf{m\, \sigma_{O2}\, [O_2]_{ground}\, H\, e^{-z/H} = 1}$

Photolysis Rate of O_2

The *partial photolysis rate* of O_2 maximizes at the altitude where $\tau = 1$

This is true for any gas that is the primary absorber

At what altitude does $\tau = 1$?

$$z \approx H \log [\, \sigma_\lambda\, m\, 4\times 10^{24}\, (\text{molecules/cm}^2)\,]$$

What is the value of the partial photolysis rate of O_2 when $\tau = 1$?

$$\text{Photolysis Rate of } O_2 \approx 5\times10^{18}(\text{molecules/cm}^3)\, e^{-z/H}\, \sigma_{O2}\, F_{TOA}\, \frac{1}{e}$$

Let's examine the partial photolysis rate of O_2 in its three absorption regions

Assume H = 7 km (realistic for 240 K) & $\theta = 45°$

	σ_{max} (cm^2)	z (τ=1) (km)	F_{TOA} (#/cm^2/s)	J (sec^{-1})	Photolysis Rate (#/cm^3/sec)
Schumann-Runge Continuum	10^{-17}	125	1×10^{11}	3.7×10^{-7}	3.3×10^{4}
Schumann-Runge Bands	10^{-20}	77	8×10^{11}	2.9×10^{-9}	2.4×10^{5}
	3×10^{-23}	36	3×10^{12}	3.3×10^{-11}	9.6×10^{5}
Herzberg Continuum	10^{-23}	**29**	2×10^{14}	7.3×10^{-10}	$\mathbf{5.8 \times 10^{7}}$

Height and Abundance of Ozone

The height of the ozone layer (~30 km) and the thickness of the ozone layer (~400 DU) are determined by values of solar actinic flux (F_{TOA}) & O_2 absorption cross section (σ_{max})

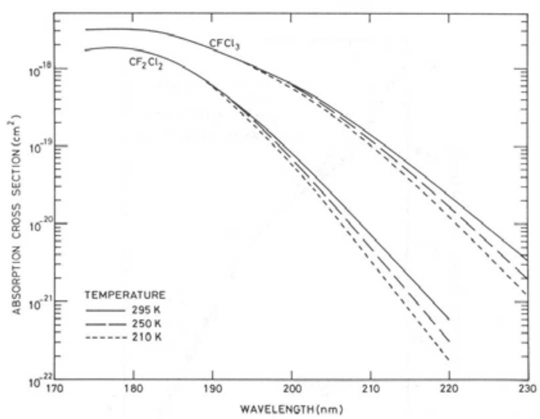
Suppose the Herzberg Continuum region dominated the photolysis rate of O_2, but the maximum cross section was different:

$$\sigma_{max} = 3 \times 10^{-22}\ cm^2 \quad \rightarrow \quad z_{\text{OZONE LAYER}} = 48\ km$$
$$\sigma_{max} = 3 \times 10^{-25}\ cm^2 \quad \rightarrow \quad z_{\text{OZONE LAYER}} = 2\ km$$

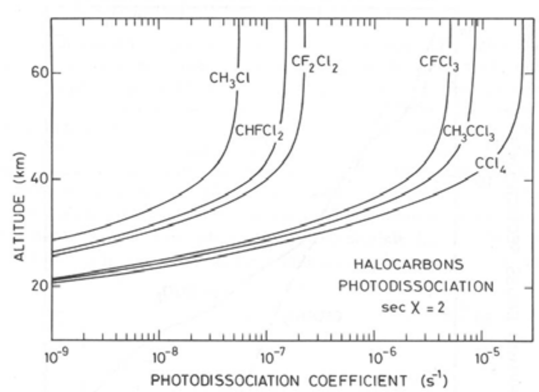
Suppose the Herzberg Continuum region dominated the photolysis rate of O_2, but the solar irradiance at these wavelengths was different:

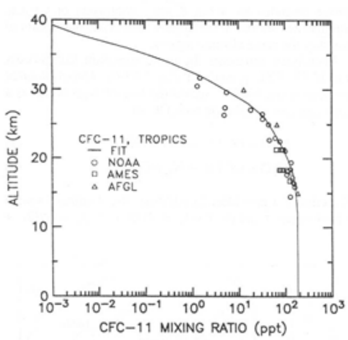
$$F_{TOA} = 2 \times 10^{15}\ \#/cm^2/s \quad \rightarrow \quad \text{Ozone Column} \approx 900\ DU$$
$$F_{TOA} = 2 \times 10^{13}\ \#/cm^2/s \quad \rightarrow \quad \text{Ozone Column} \approx 100\ DU$$

Extra #1: CFC Photolysis



Brasseur & Solomon, *Aeronomy of the Middle Atmosphere*, 1986





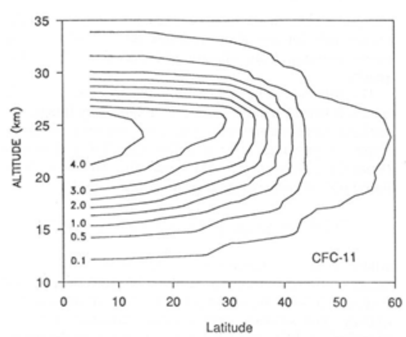


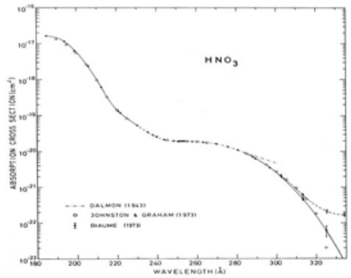
Fig. 12. Diurnally averaged loss rate for $CFCl_3$ (molecules cm^{-3} s^{-1}) as a function of altitude and latitude, calculated with the line-by-line model, for equinox. The loss rate was calculated assuming destruction of $CFCl_3$ by photolysis only.

	Inventory (kg)	Loss Rate (kg/yr)	Lifetime (years)
$CFCl_3$	3.1×10^9	7.2×10^7	44
CF_2Cl_2	3.5×10^9	3.0×10^7	116

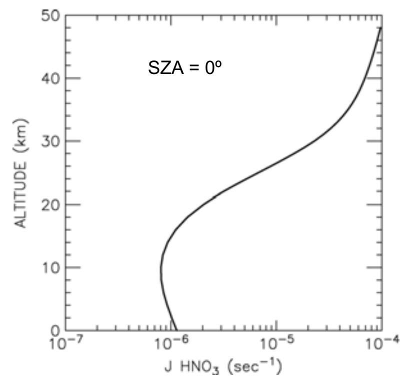
Minschwaner *et al., JGR, 98*, 10543, 1993

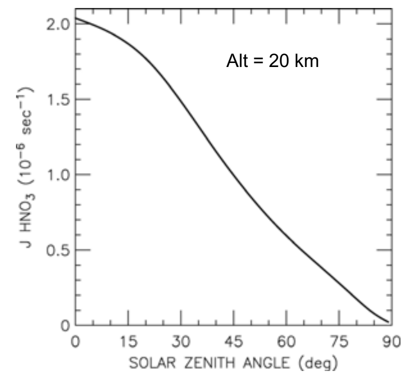
Extra #2: HNO_3 Photolysis

The majority of HNO_3 photolysis occurs shortward of 320 nm, where the atmosphere is optically thick with respect to absorption by O_3 and O_2:



leading to a value for J_{HNO3} that is strongly dependent on height and SZA:





Extra #3: HNO_3 Photolysis