Introduction to Photolysis

AOSC / CHEM 433 & AOSC / CHEM 633

Ross Salawitch

Class Web Sites:
http://www2.atmos.umd.edu/~rjs/class/spr2022
https://myelms.umd.edu/courses/137772

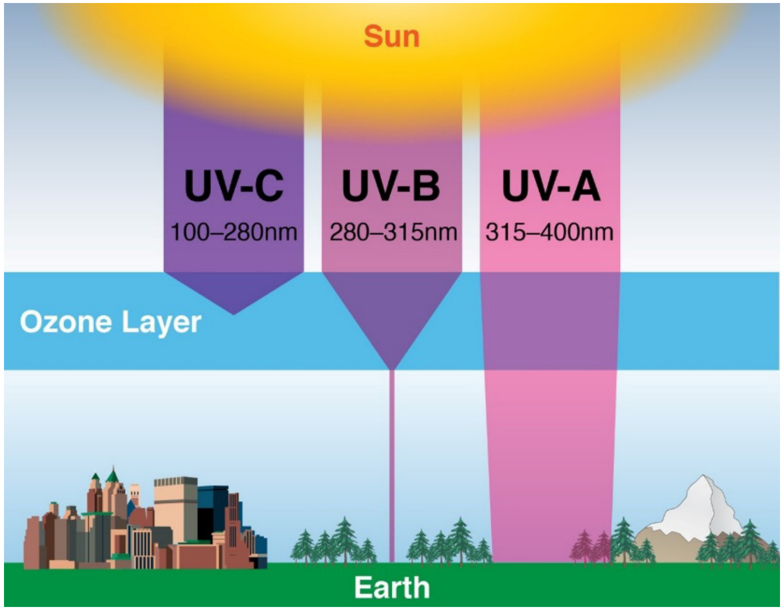

Figure 3.3.2, Wilmouth, Salawitch, and Canty, 2018
https://www2.atmos.umd.edu/~rjs/class/spr2022/readings/green_chemistry_chapter_3.3.pdf

Lecture 11

10 March 2022

Admission Ticket Lecture 11

According to Section 2.6 of Chemistry in Context:

a) what is the upper limit for photodissociation of O_2?

b) what is the classification of this type of radiation?

c) how damaging is this radiation and would it be a problem, for humans to be exposed to this type of radiation?

According to Section 2.6 of Chemistry in Context:

a) what is the upper limit for photodissociation of O_3?

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c) how damaging is this radiation and would it be a problem, for humans to be exposed to this type of radiation?

Figure 2.12 of the Warneck reading shows the photodissocation *frequency* of O_2 and O_3, termed J_{O2} and J_{O3}, as a function of altitude. An altitude of 15 km corresponds to Earth's upper troposphere. Also, the lifetime for loss by dissociation is given by the reciprocal of the photodissociation frequency.

Calculate the lifetimes for loss of O_2 and for loss of O_3 by photodissociation at 15 km, in units that you can easily conceptualize. Then, for each molecule, state whether you think the gas will be lost by photodissociation in Earth's upper troposphere.

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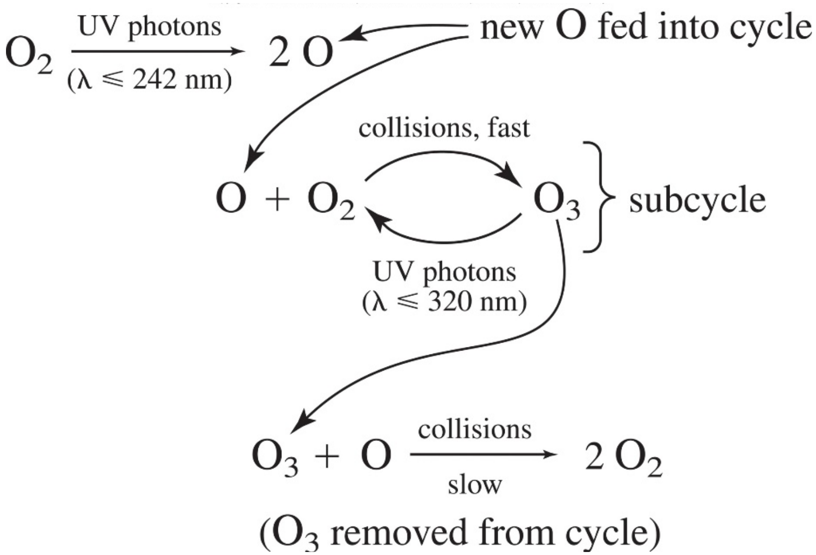


Figure 2.10, Chemistry in Context

$$O_2 \xrightarrow[(\lambda \leqslant 242\ \text{nm})]{\text{UV photons}} 2\,O$$

Equation 2.4, Chemistry in Context

$$O_3 \xrightarrow[\lambda \leq 320\ \text{nm}]{\text{UV photon}} O_2 + O$$

Equation 2.5, Chemistry in Context

According to Section 2.6 of Chemistry in Context:

a) what is the upper limit for photodissociation of O_2

b) what is the classification of this type of radiation?

c) how damaging is this radiation and would it be a problem, for humans to be exposed to this type of radiation?

O_2 protects us even more so than O_3

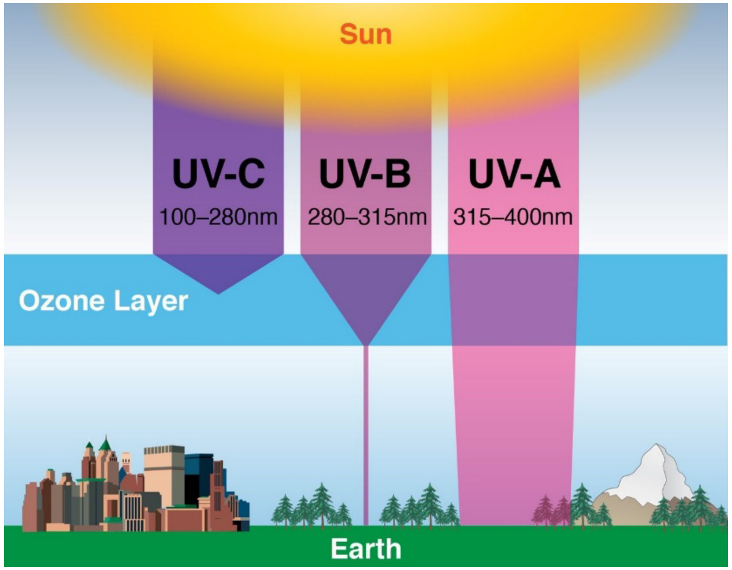
According to Section 2.6 of Chemistry in Context:

a) what is the upper limit for photodissociation of O_3

b) what is the classification of this type of radiation?

c) how damaging is this radiation and would it be a problem, for humans to be exposed to this type of radiation?

When we examine skin cancer and ozone depletion, it is all about UV-B radiation.

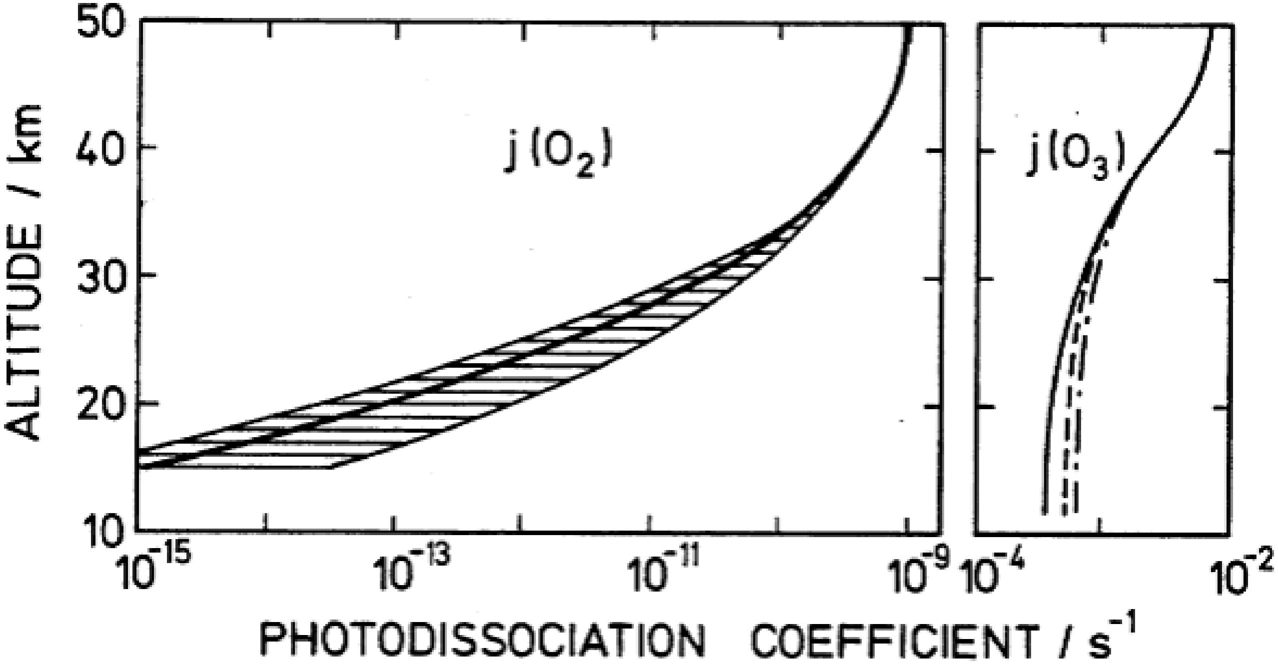


Wilmouth et al., 2018

Admission Ticket Lecture 11

Figure 2.12 of the Warneck reading shows the photodissocation *frequency* of O_2 and O_3, termed J_{O2} and J_{O3}, as a function of altitude. An altitude of 15 km corresponds to Earth's upper troposphere. And, the lifetime for loss by dissociation is given by the reciprocal of the photodissociation frequency.

Calculate the lifetimes for loss of O_2 and for loss of O_3 by photodissociation, for the upper troposphere, in units that you can easily conceptualize. Then, for each molecule, state whether you think the gas will be lost by photodissociation in Earth's upper troposphere.



Biological Effects of UV Radiation

Table 2.4 Types of UV Radiation

Type	Wavelength	Relative Energy	Comments
UV-A	320–400 nm	Lowest energy	Least damaging and reaches the Earth's surface in greatest amount
UV-B	280–320 nm	Higher energy than UV-A but less energetic than UV-C	More damaging than UV-A but less damaging than UV-C. Most UV-B is absorbed by O_3 in the stratosphere
UV-C	200–280 nm	Highest energy	Most damaging but not a problem because it is totally absorbed by O_2 and O_3 in the stratosphere

Chemistry in Context

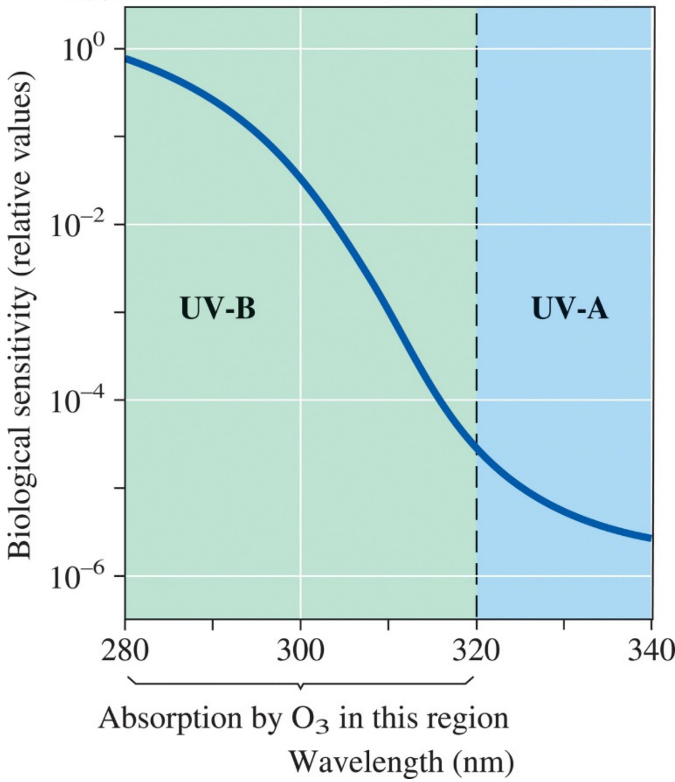


Figure 2.11, Chemistry in Context

Biological Effects of UV Radiation

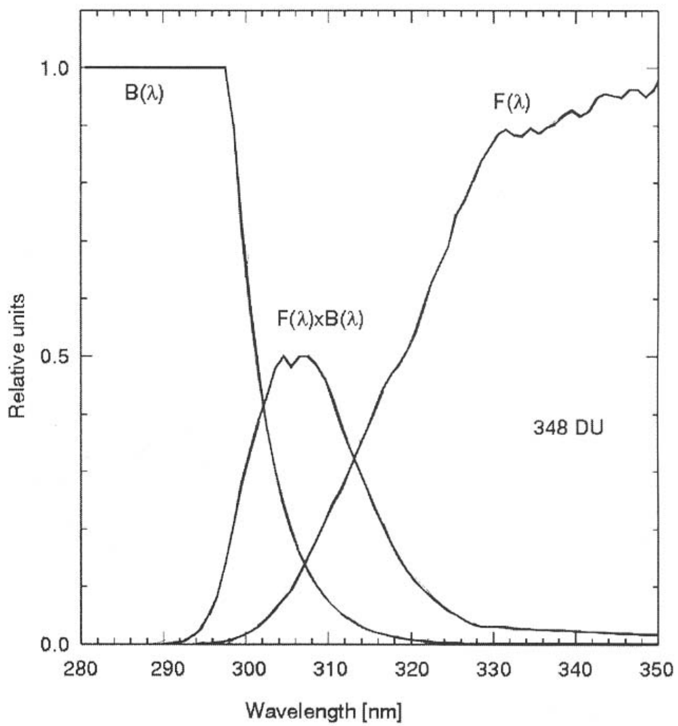


Fig. 1. Biologically active UV radiation. The overlap between the spectral irradiance $F(\lambda)$ and the erythemal action spectrum $B(\lambda)$ given by McKinlay and Diffey [6] shows the spectrum of biologically active radiation, $F(\lambda)B(\lambda)$. The area under the product function $F(\lambda)B(\lambda)$ 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)

http://www.who.int/uv/uv_and_health/en

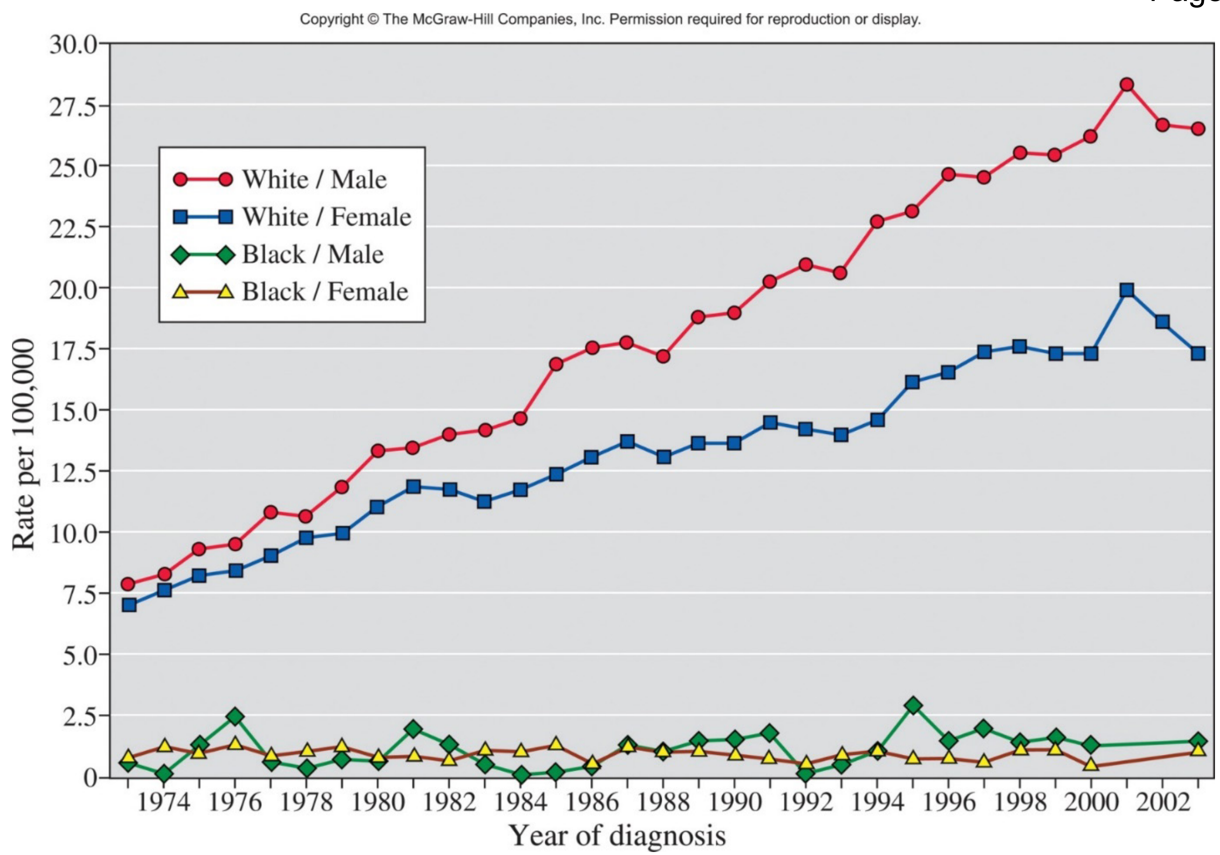
⇐ From Mandronich et al., *J. Photochemistry and Photobiology*, vol. 46, pg. 5, 1998

The "biologically active dose rate" maximizes in the UV-B region at ~305 nm

Skin Cancer versus Time

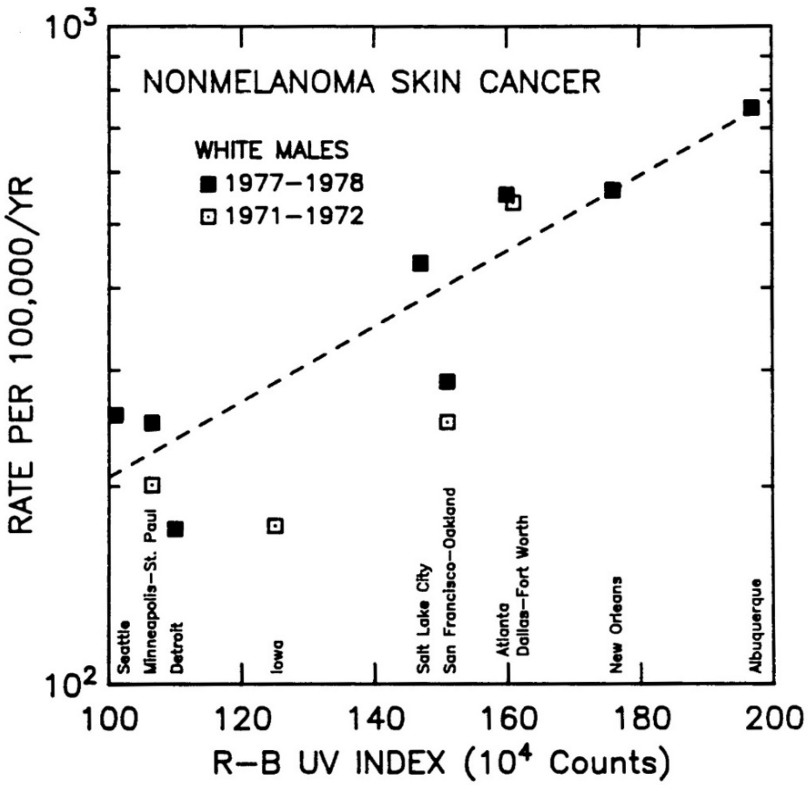
According to calculations, a given percent decrease in stratospheric ozone is expected to increase the biological damage done by UV radiation by twice that percentage. For example, from a 6% decrease in stratospheric ozone we predict a 12% rise in skin cancer, especially the more easily treated forms such as basal cell and squamous cell carcinomas <u>(non-melanoma)</u>

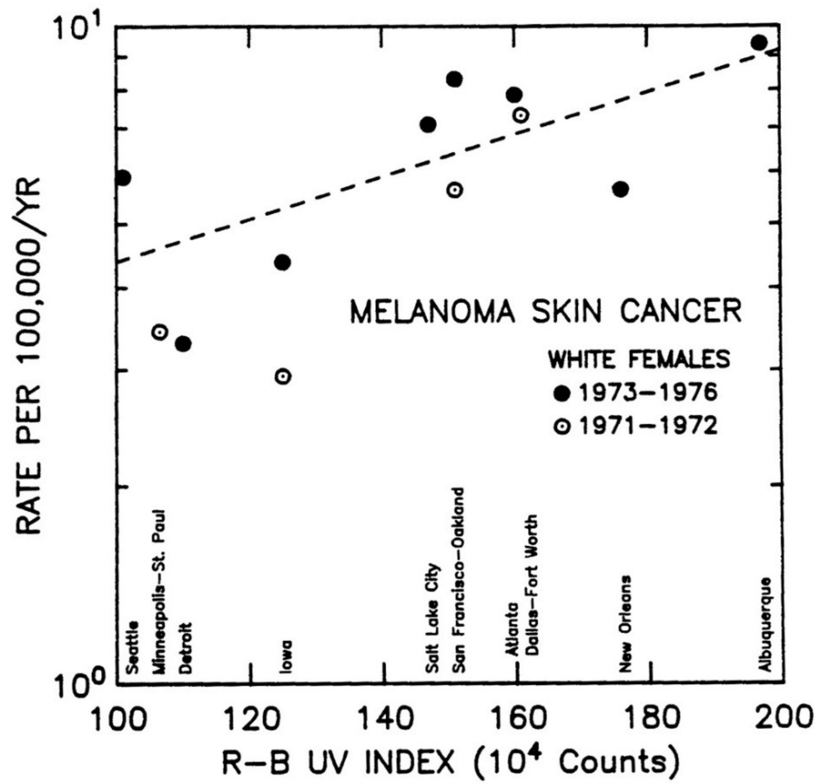
Page 83, Chemistry in Context



Increase in incidence of melanoma skin cancer in the U.S.
Figure 2.12, Chemistry in Context

Relationship Between Cancer and UV





Scotto and Fraumeni, *Cancer Epidemiology*, W. B. Saunders and Co, Philadelphia, 1982.

Factor of 2 rise in UV Index leads to factor of 4 rise in Non-Melanoma Skin Cancer:

i.e., *Non-Melanoma Skin Cancer* rises *about twice as fast* as incident solar ultraviolet (UV) radiation

Factor of 2 rise in UV Index leads to factor of 2 rise in Melanoma Skin Cancer:

i.e., *Melanoma Skin Cancer* rises at about the *same rate* as incident solar ultraviolet (UV) radiation

Melanoma Skin Cancer is more aggressive and dangerous than Non-Melanoma Skin Caner

https://www.premiersurgical.com/01/whats-the-difference-between-melanoma-and-non-melanoma-skin-cancer

Relationship Between UV and Column Ozone

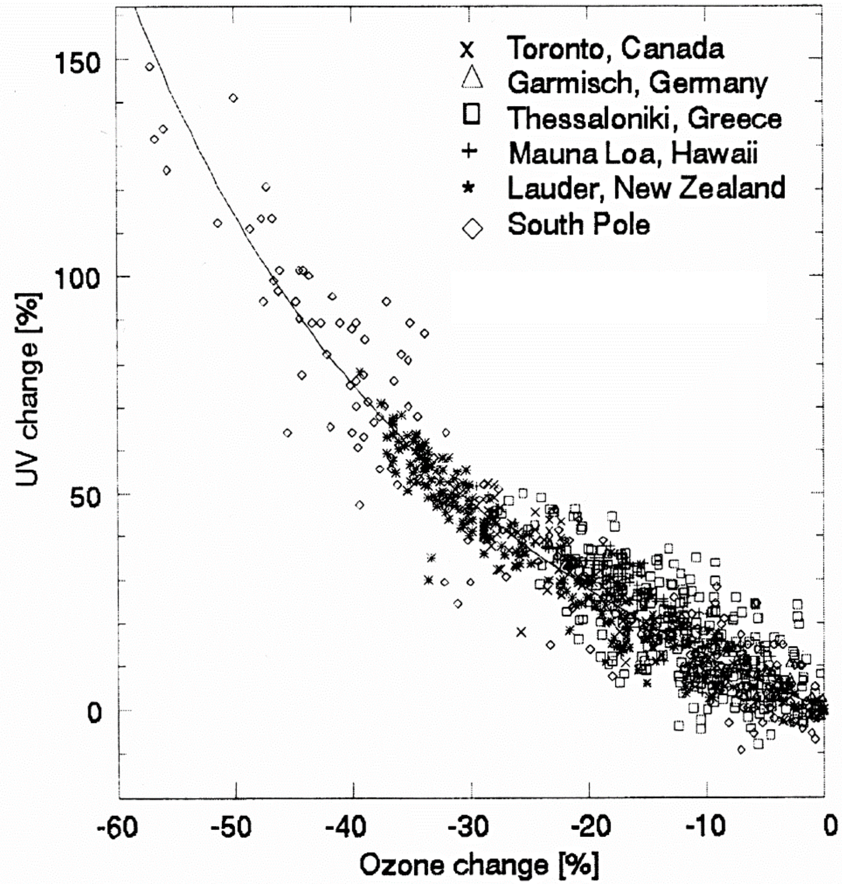


Fig. 2. Dependence of erythemal ultraviolet (UV) radiation at the Earth's surface on atmospheric ozone, measured on cloud-free days at various locations, at fixed solar zenith angles. Legend: South Pole [8]; Mauna Loa, Hawaii [9]; Lauder, New Zealand [10]; Thessaloniki, Greece (updated from Ref. [11]); Garmisch, Germany [12]; and Toronto, Canada (updated from Ref. [13]).

Madronich et al., *J. of Photochemistry and Photobiology B*, Vol. 46, 5–19, 1998.

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	$+\ h\nu$	$\rightarrow$	$O(^1D)$	$+\ O_2(^1\Delta_g)$	**ΔEnthalpy = 93.3 kcal/mole**

Photon Energy:

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

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

$$\lambda_{max} = \frac{hc}{\Delta \text{Enthalpy}} = \frac{2.85 \times 10^4 \text{ kcal/mole nm}}{\Delta \text{Enthalpy}} = \underline{\qquad\qquad\qquad} =$$

Energetics of Photodissociation

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

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

	(1s)^2	**(2s)^2**	**(2p)^4**		
ground state:	↑↓	↑↓	↑↓	↑	↑
			+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:

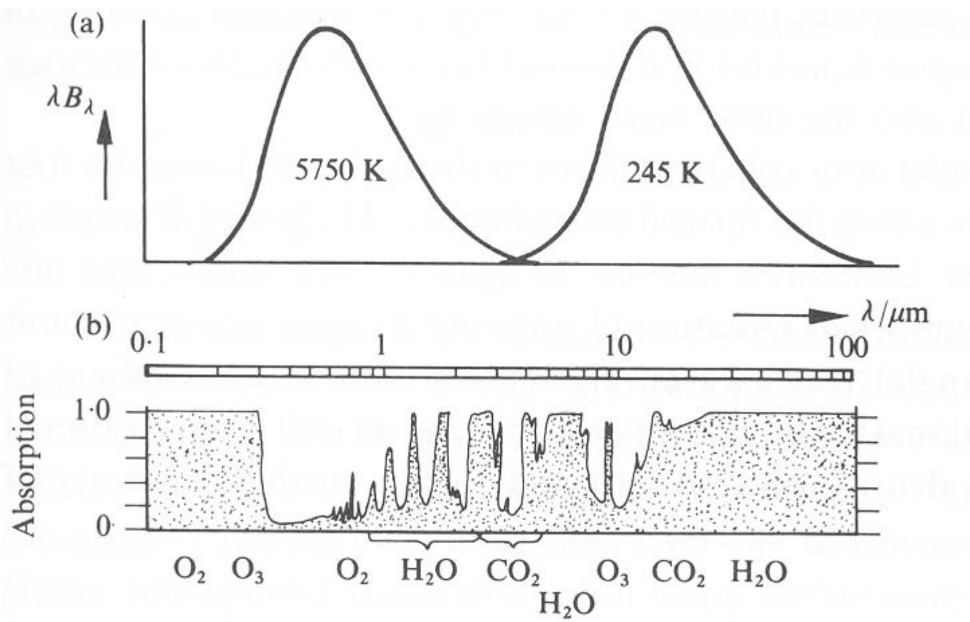
	(1s)^2	**(2s)^2**	**(2p)^4**		
excited state:	↑↓	↑↓	↑↓	↑↓	
			+1	0	-1

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

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.

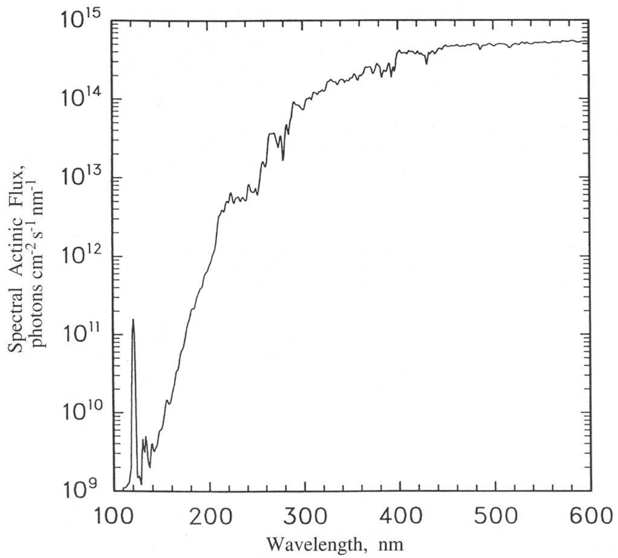
Panel (b): absorption by atmospheric gases for a clear vertical column of the atmosphere (1.0 represents complete absorption).

From Houghton, *Physics of Atmospheres*, 1991

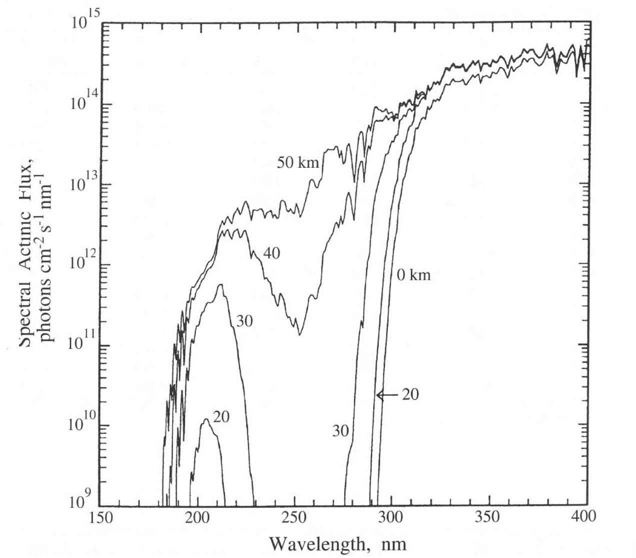
- Absorption and photodissociation in the UV occurs due to changes in the electronic state (orbital configuration) of molecules

• Motivation for Rest of Today's Lecture:

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



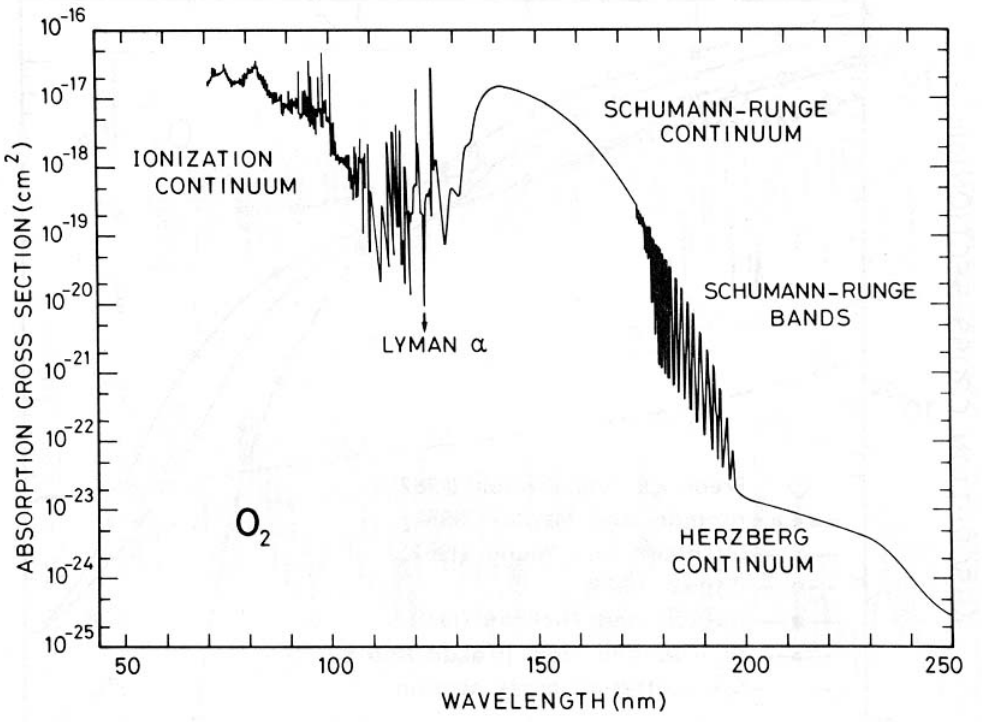
From DeMore et al., *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, Evaluation No. 11, 1994.



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

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 (cm^2/molecule)
C : concentration of absorbing gas (molecules/cm^3)
m : ratio of slant path to vertical path, equal to $1/\cos(\theta)$ for $\theta < \sim75°$
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:

$$\int_0^{\infty} [O_2]\, dz' \approx 4 \times 10^{24} \text{ molecules/cm}^2$$

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

Where Does Optical Depth = 1.0 for O_2 ?

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

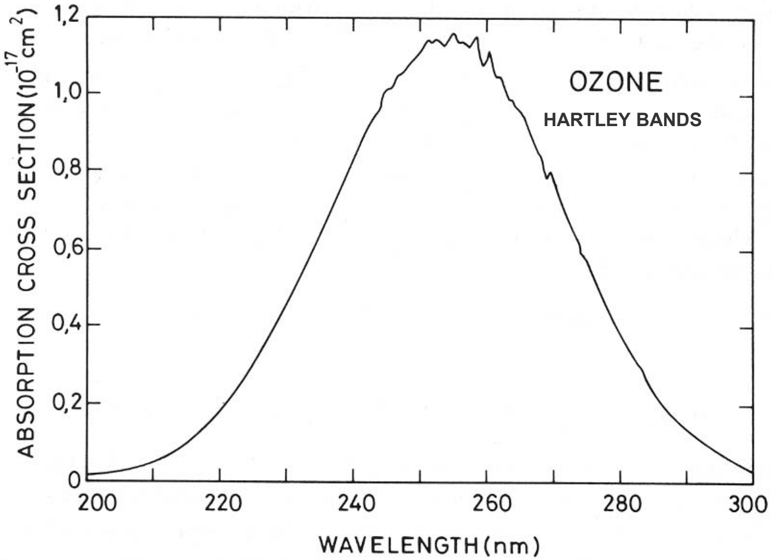
$$\approx \sigma_\lambda\, m\, 4 \times 10^{24}\, e^{-z/H}$$

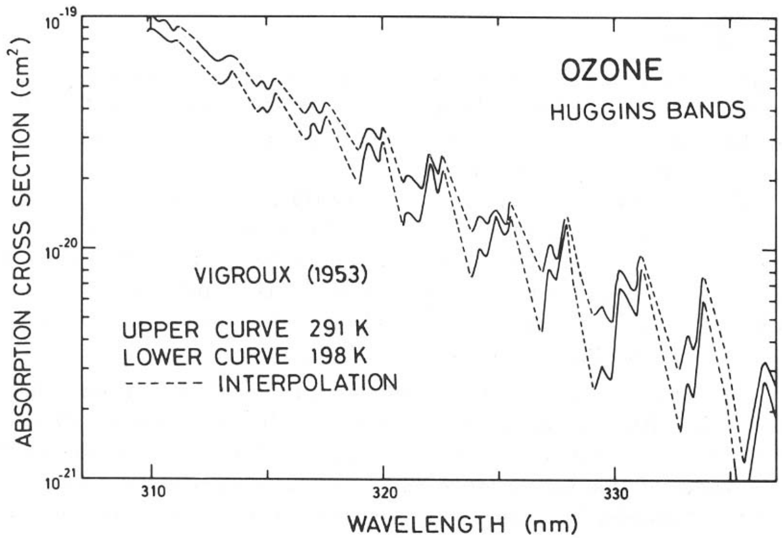
Setting $\tau = 1$ and re-arranging gives:

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

Altitude where $\tau = 1$ (for $\theta = 0°$)		
	σ_{max} (cm^2)	z (km)
Schumann-Runge Continuum	10^{-17}	140
Schumann-Runge Bands	10^{-20}	85
	3×10^{-23}	38
Herzberg Continuum	10^{-23}	29

Absorption Cross Section of O_3





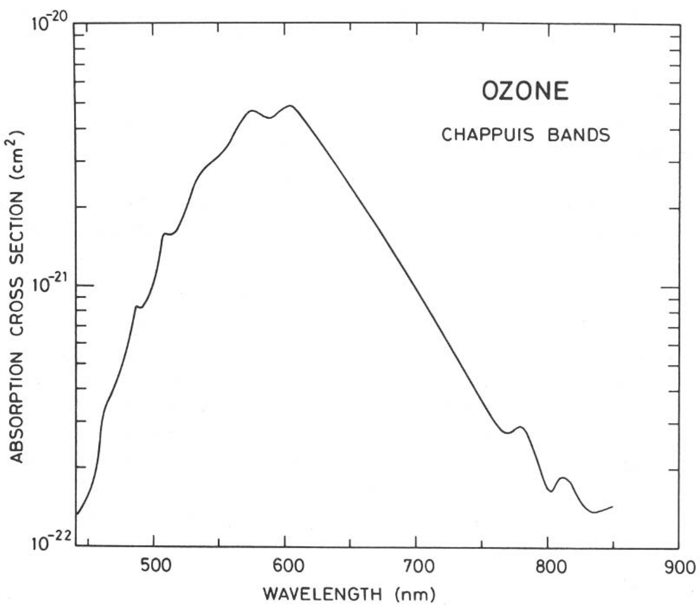


Table 4.6 Theoretical limits corresponding to different photolysis products (nm).

	$O_2(^3\Sigma_g)$	$O_2(^1\Delta_g)$	$O_2(^1\Sigma_g+)$	$O_2(^3\Sigma_u+)$	$O_2(^3\Sigma_u^-)$
$O(^3P)$	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):

$$1 \text{ DU} = 2.687 \times 10^{16} \text{ molecules/cm}^2; \quad 300 \text{ DU} = 8 \times 10^{18} \text{ molecules/cm}^2$$

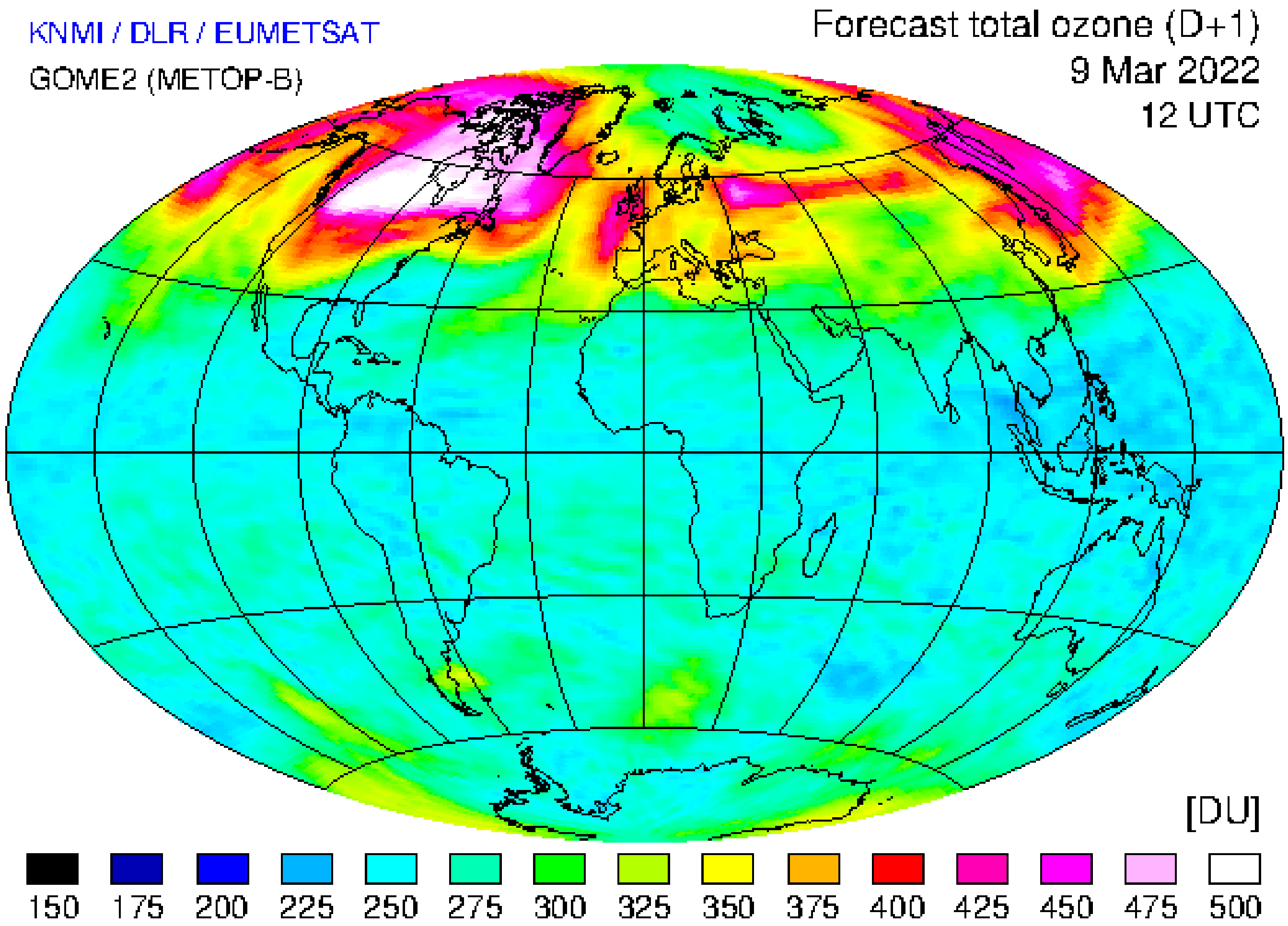
Aside:

$$\frac{\text{Column O}_3}{\text{Column Air}} = \frac{8\times10^{18}}{2\times10^{25}} = 0.4 \text{ parts per million} \Rightarrow \text{Ozone is a trace species!}$$

O_3 Optical Depth for $\theta = 0°$, z = 0 km				
	σ_{max} (cm^2)	τ (0 km)	$e^{-\tau\,(0\text{ km})}$	O_3 Column, $\tau = 1.0$
Hartley (~220 to 280 nm)	10^{-17}			
Huggins (~310 to 330 nm)				
Chappuis (~500 to 700 nm)				

Total Ozone, NASA Aura OMI

OMI: Ozone Monitoring Instrument, aboard NASA Aura satellite
KNMI: Royal Netherlands Meteorological Institute



http://www.temis.nl/protocols/O3global.html

Solar Spectral Actinic Flux

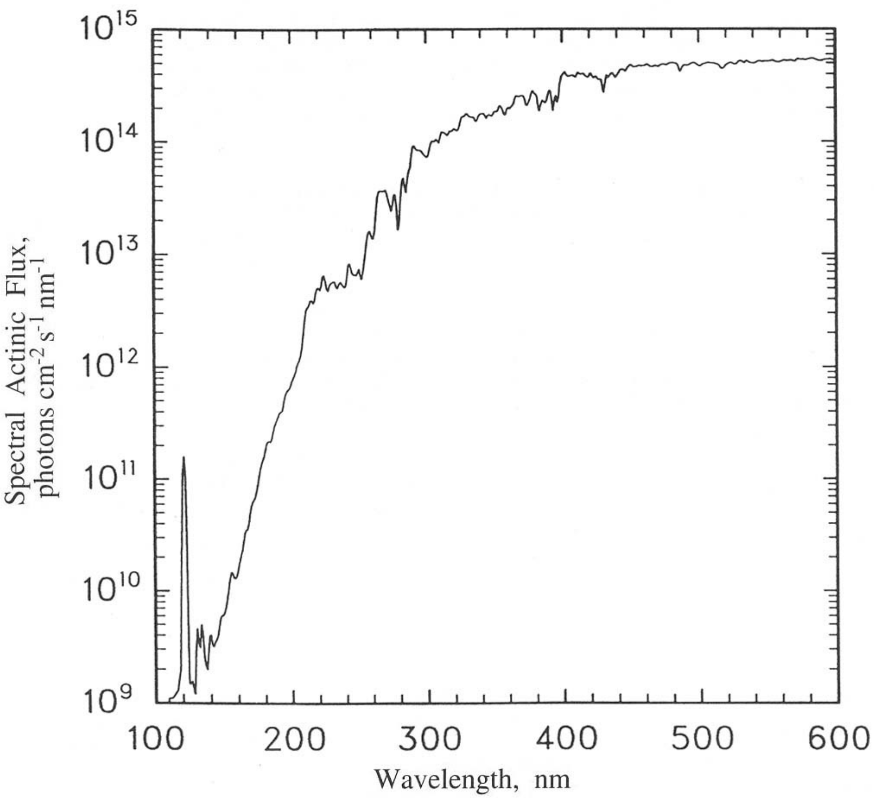
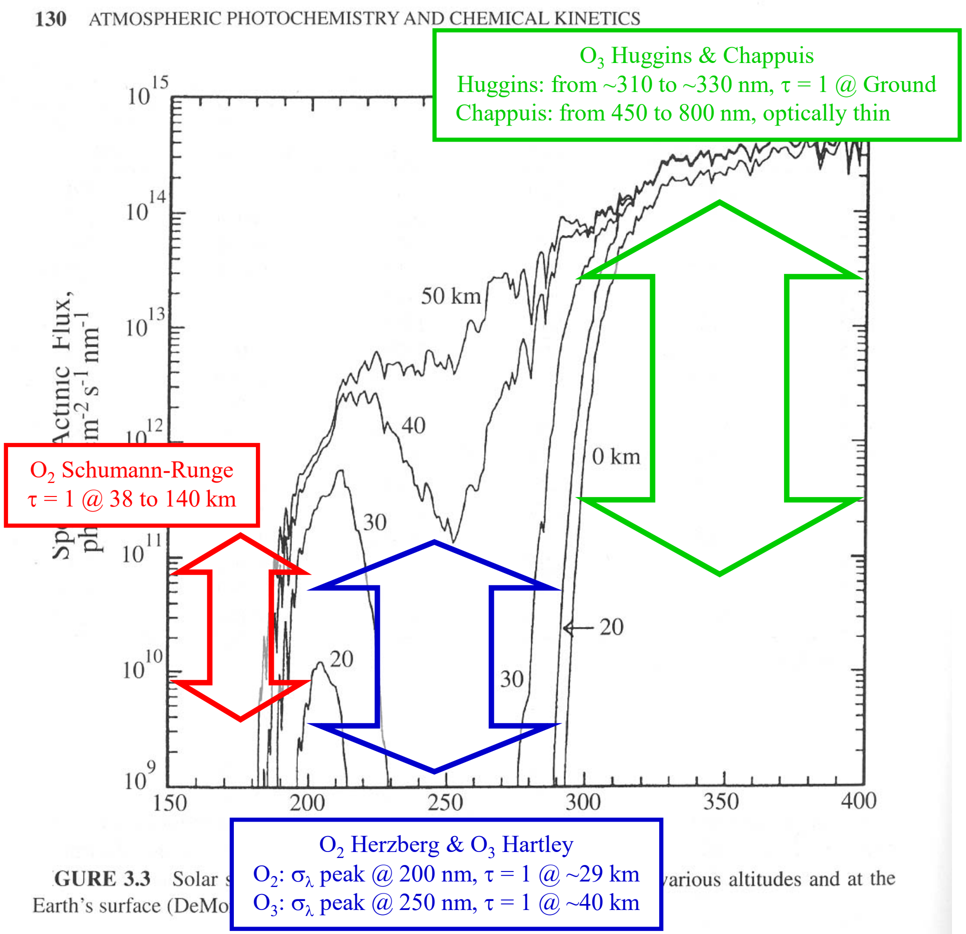


FIGURE 6. Solar spectral actinic flux (photons cm^{-2} s^{-1} nm^{-1}) at the top of Earth's atmosphere.



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:

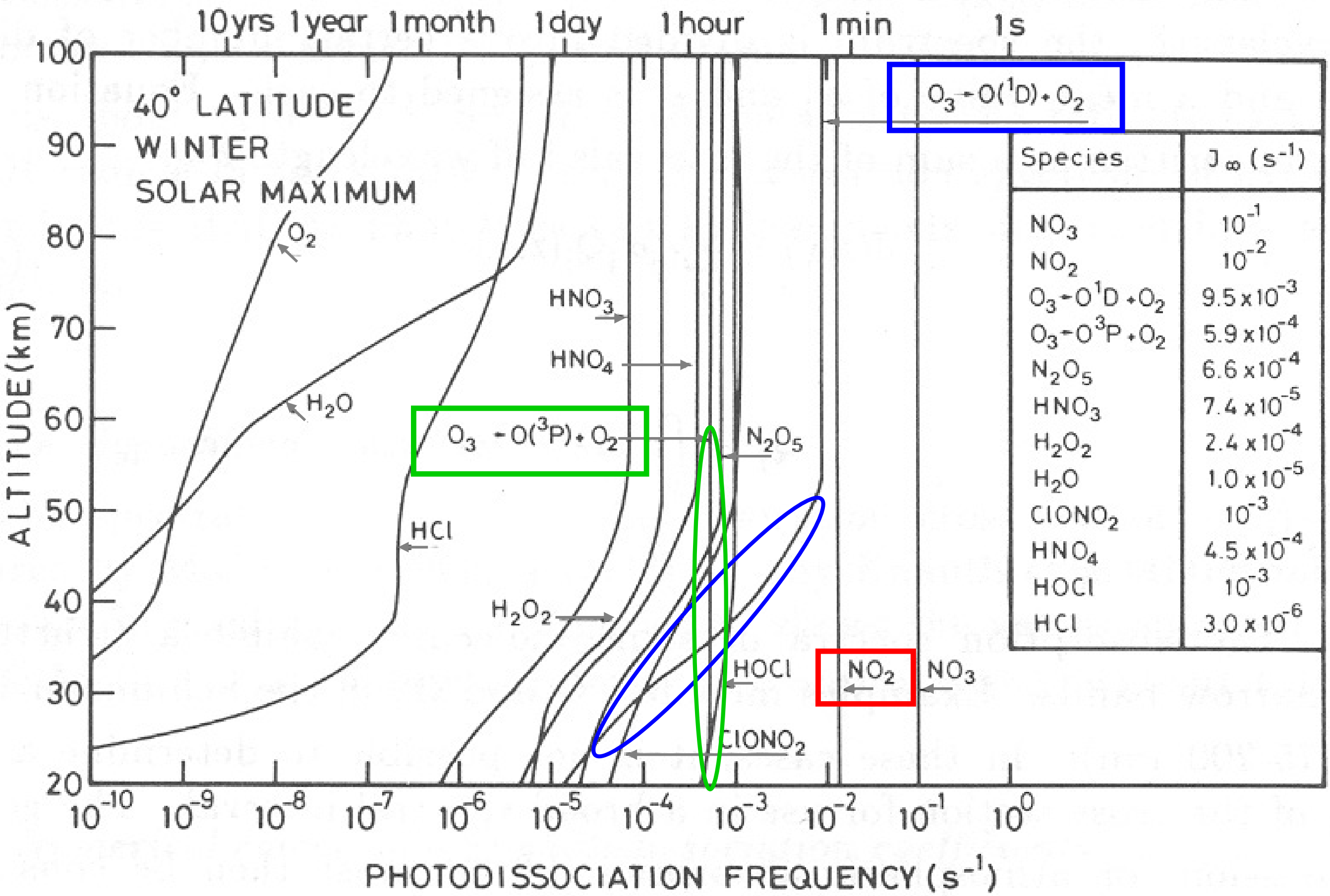
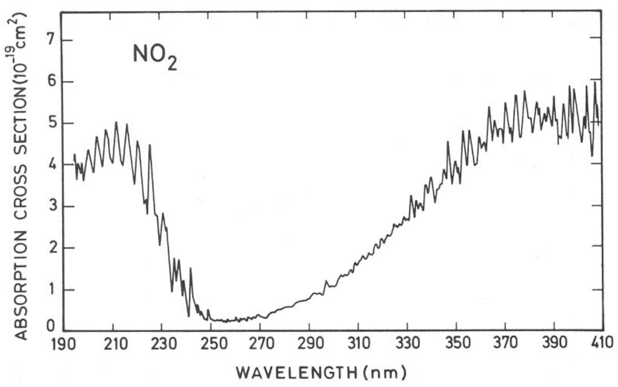


FIGURE 4.58 Photodissociation frequencies for numerous important atmospheric species.

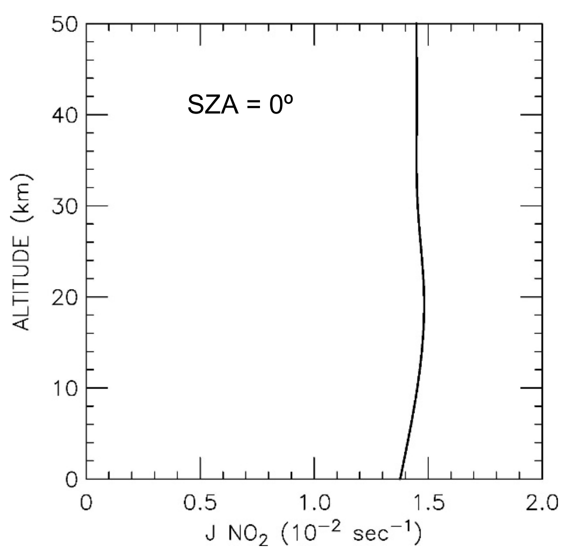
From Brasseur & Solomon, *Aeronomy of the Middle Atmosphere*, 1986

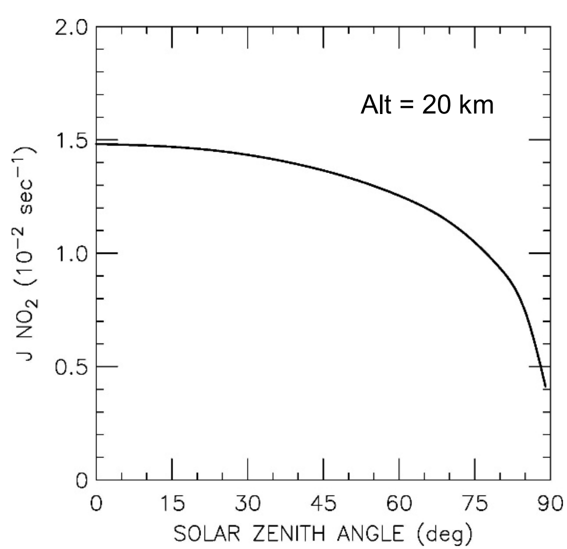
NO_2 Photolysis

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:

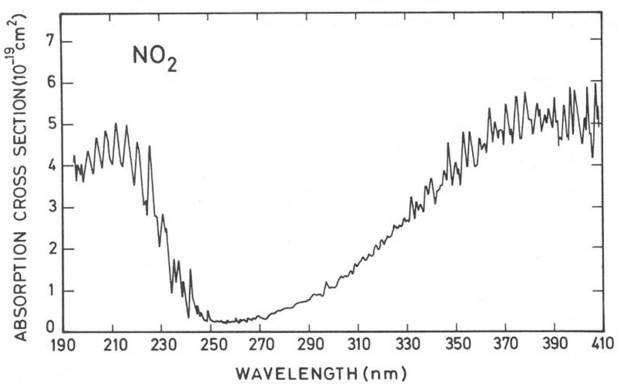


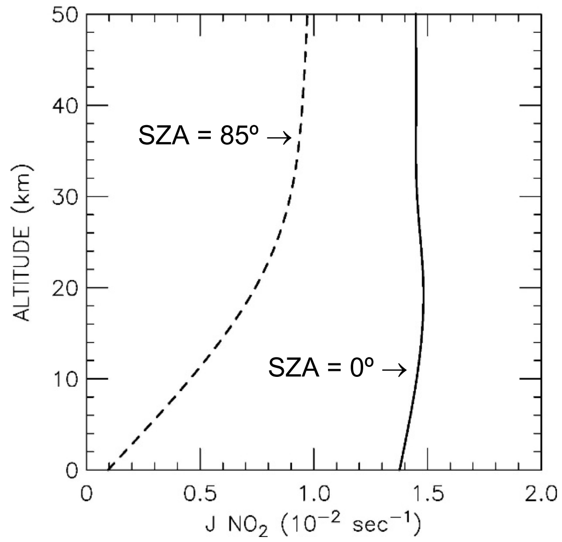
leading to a value for J_{NO2} that is nearly <u>independent</u> of height and SZA:

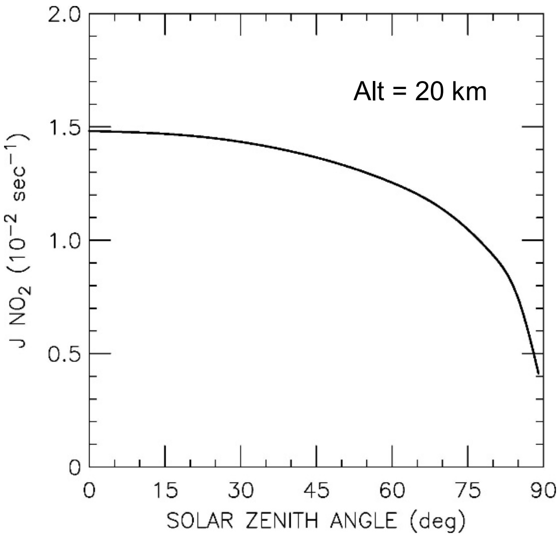


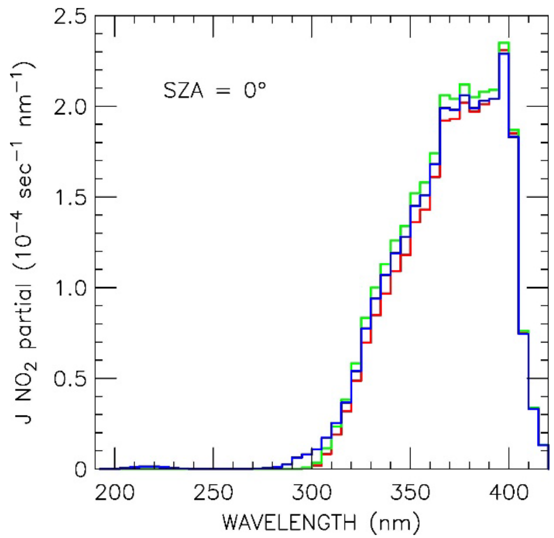


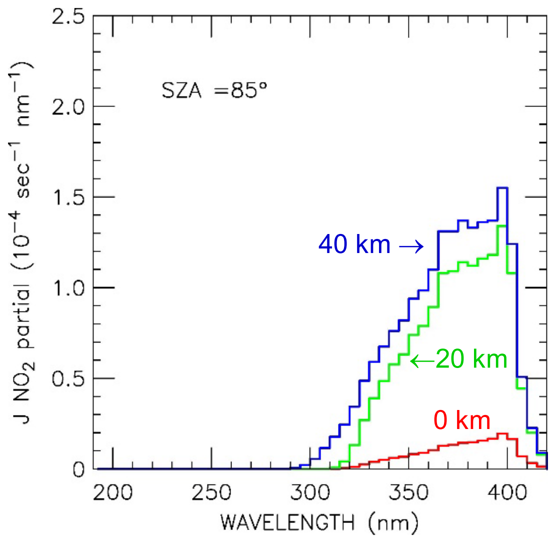
NO$_2$ Photolysis





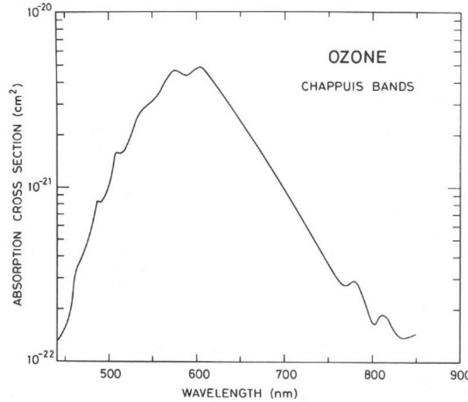




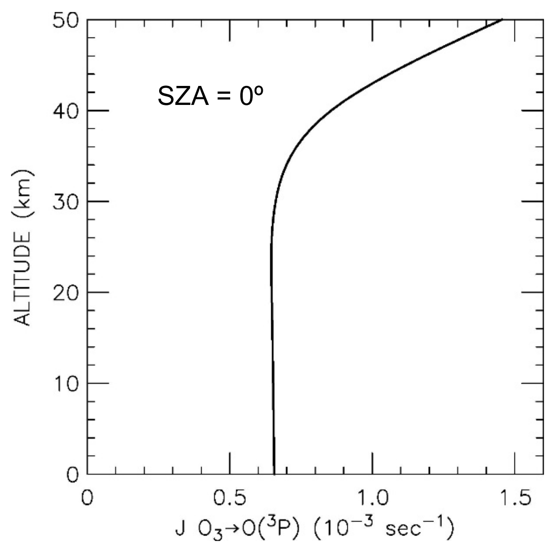


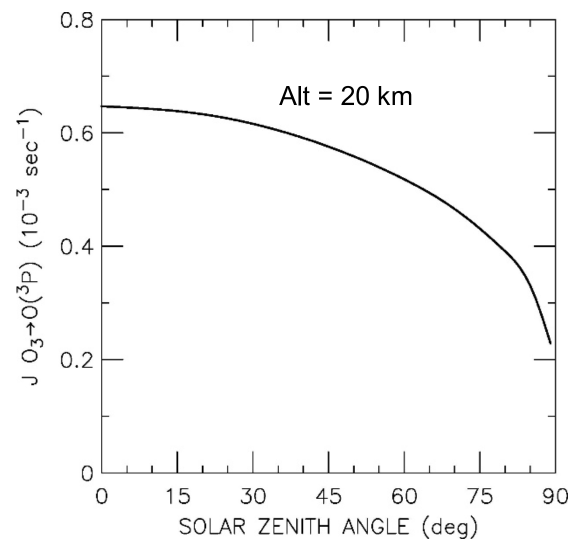
$O_3 \rightarrow O(^3P)$ Photolysis

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:

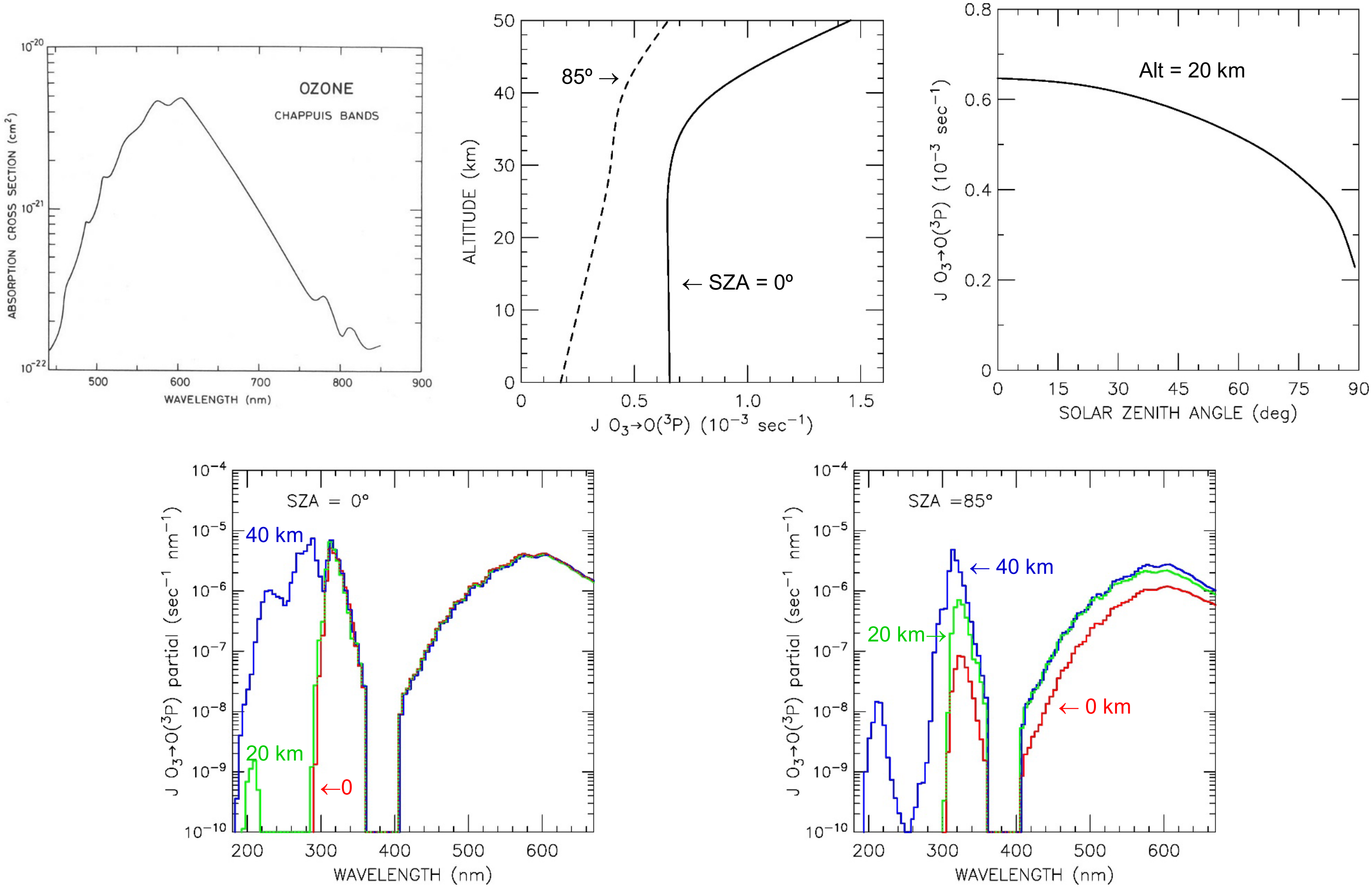


leading to a value for $J_{O3 \rightarrow O(3P)}$ that is essentially <u>independent</u> of height and SZA:



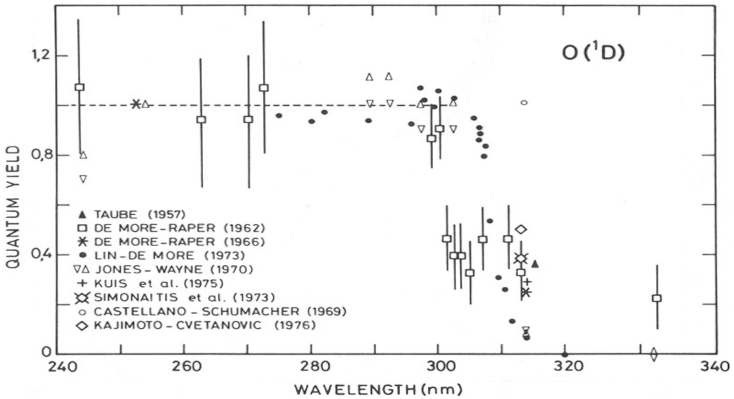


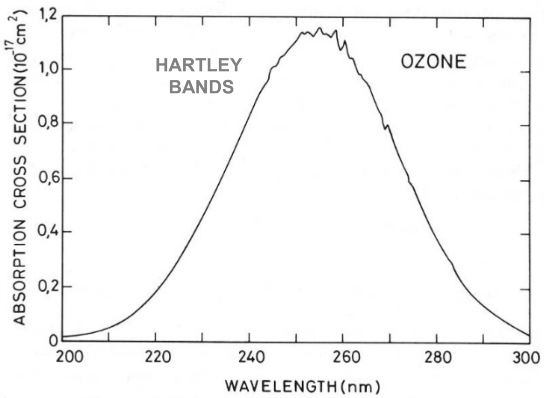
$O_3 \rightarrow O(^3P)$ Photolysis

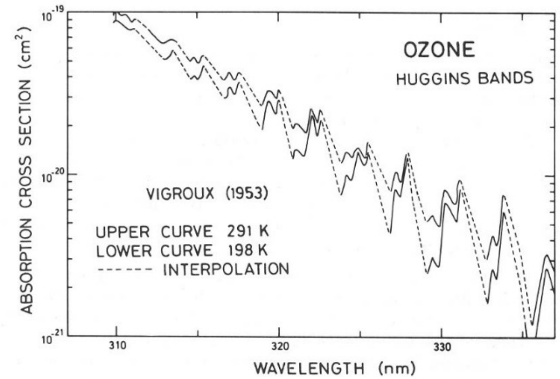


$O_3 \rightarrow O(^1D)$ Photolysis

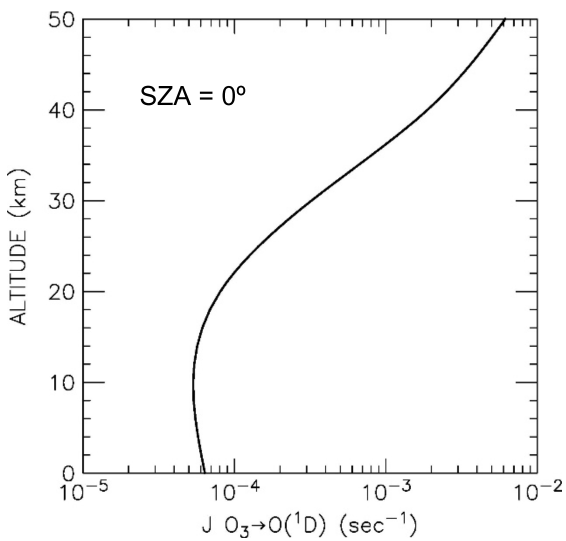
The production of $O(^1D)$ from photolysis of O_3 occurs shortward of 320 nm, where the atmosphere is basically optically thick with respect to absorption by O_3:

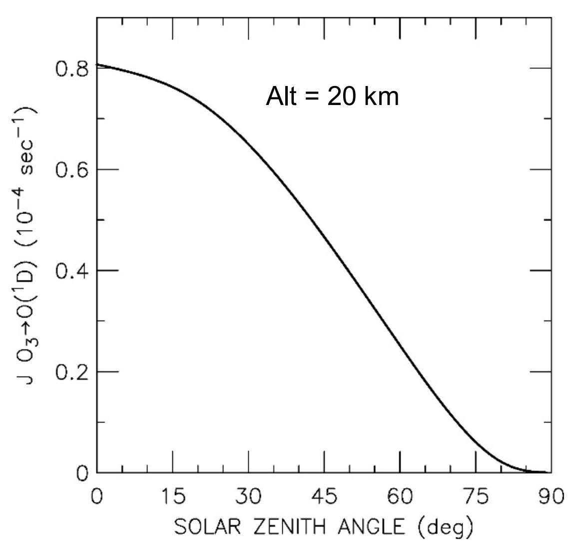




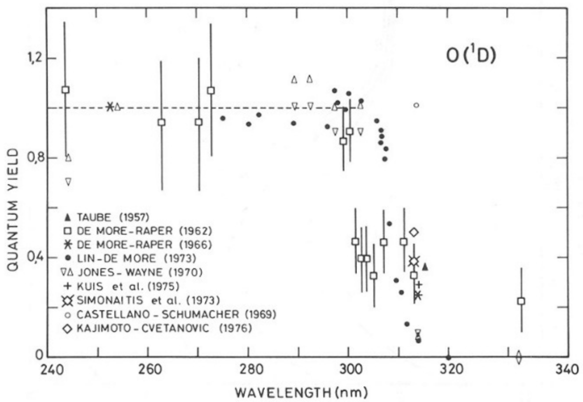


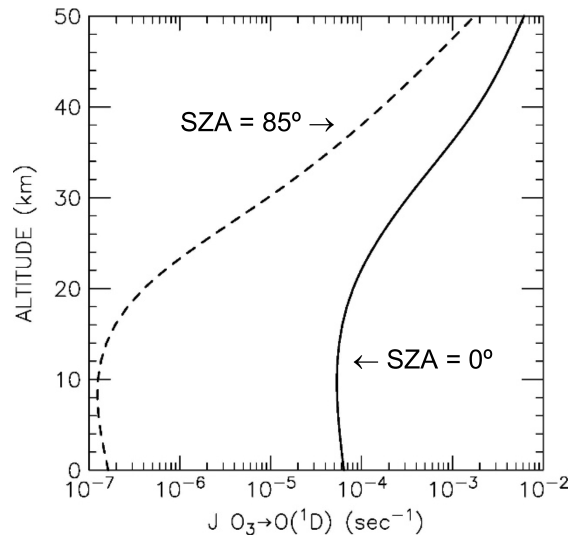
leading to a value for $J_{O3 \rightarrow O(1D)}$ that is dependent on height and SZA:

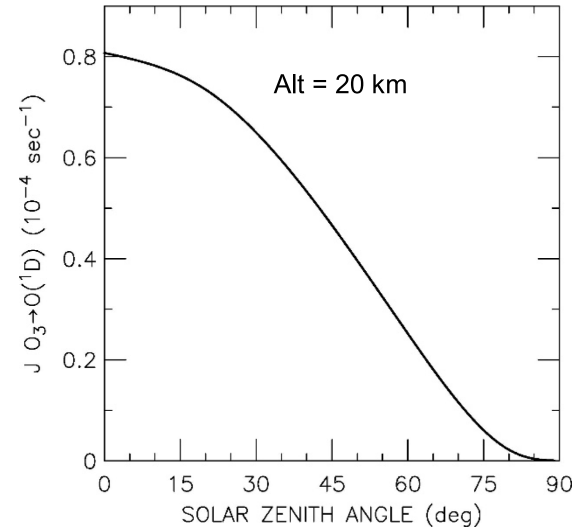


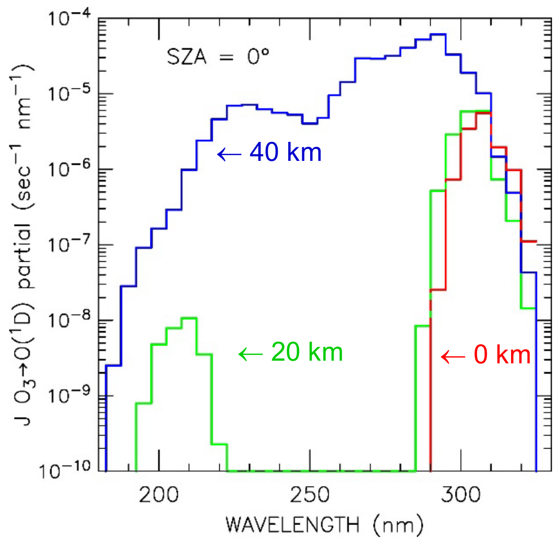


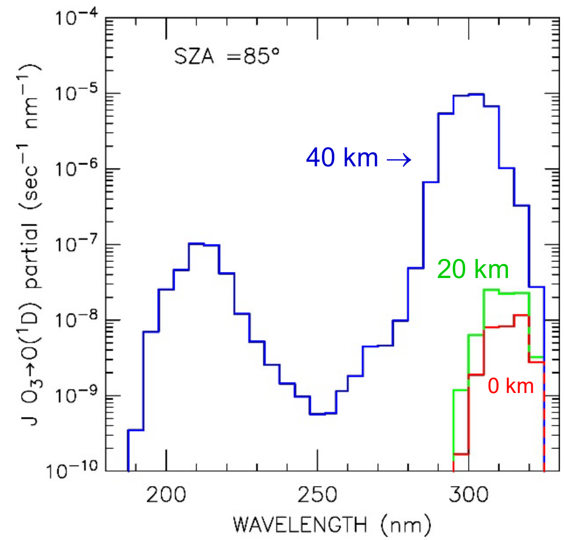
$O_3 \rightarrow O(^1D)$ Photolysis











Extra #1: Height and Abundance of 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

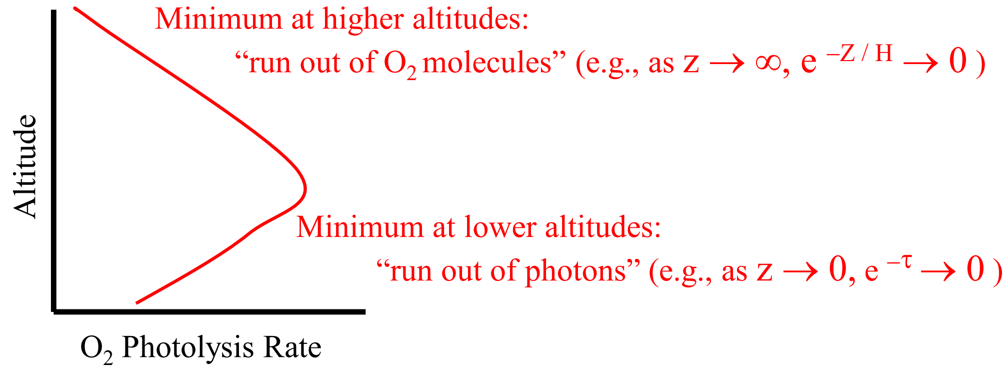
Extra #1: Height and Abundance of Ozone

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