Introduction to Photolysis

AOSC / CHEM 433 & AOSC / CHEM 633

Ross Salawitch

Class Web Sites:
http://www2.atmos.umd.edu/~rjs/class/fall2020
https://myelms.umd.edu/courses/1291919

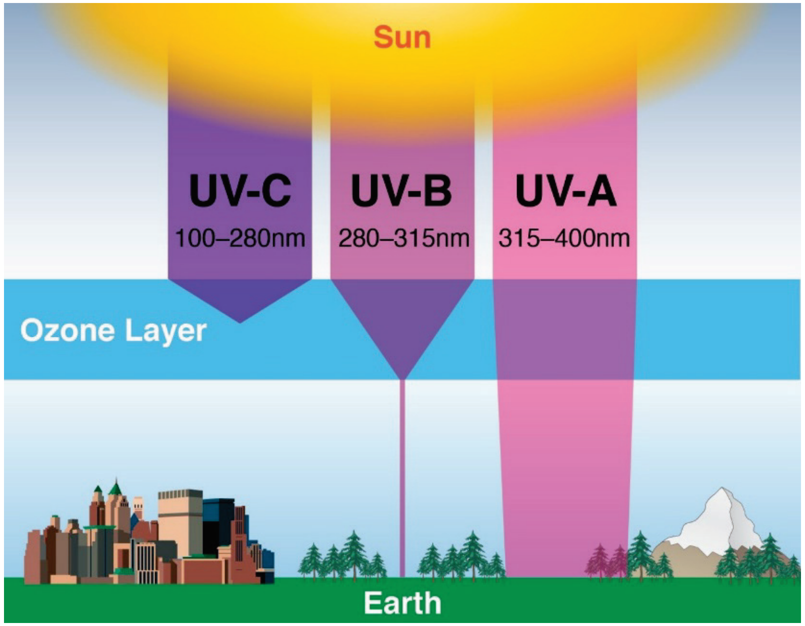


Figure 3.3.2, Wilmouth, Salawitch, and Canty, 2018
https://www2.atmos.umd.edu/~rjs/class/spr2020/readings/green_chemistry_chapter_3.3.pdf

Lecture 11 Catch-Up

21 October 2020

Biological Effects of UV Radiation

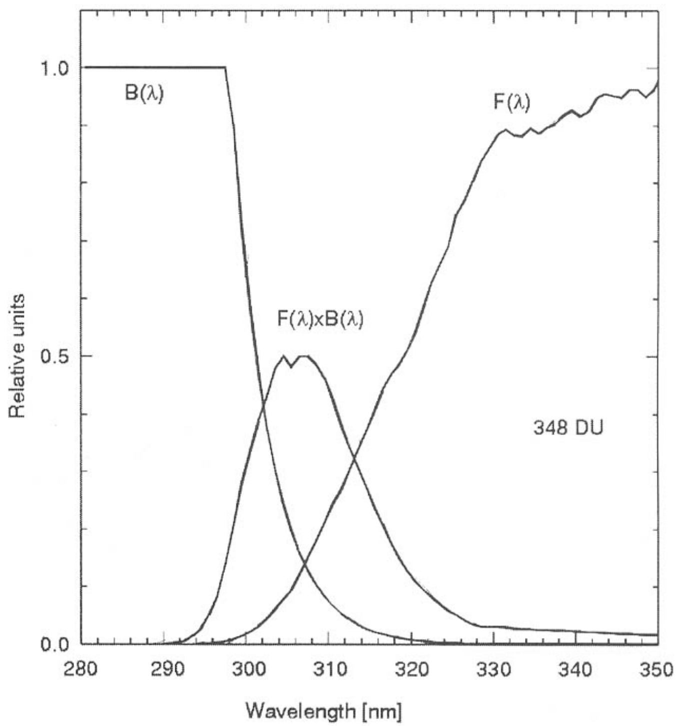


Fig. 1. Biologically active UV radiation. The overlap between the spectral irradiance $F(\lambda)$ and the erythemal action spectrum $B(\lambda)$ given by McKinlay and Diffey [6] shows the spectrum of biologically active radiation, $F(\lambda)B(\lambda)$. The area under the product function $F(\lambda)B(\lambda)$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

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

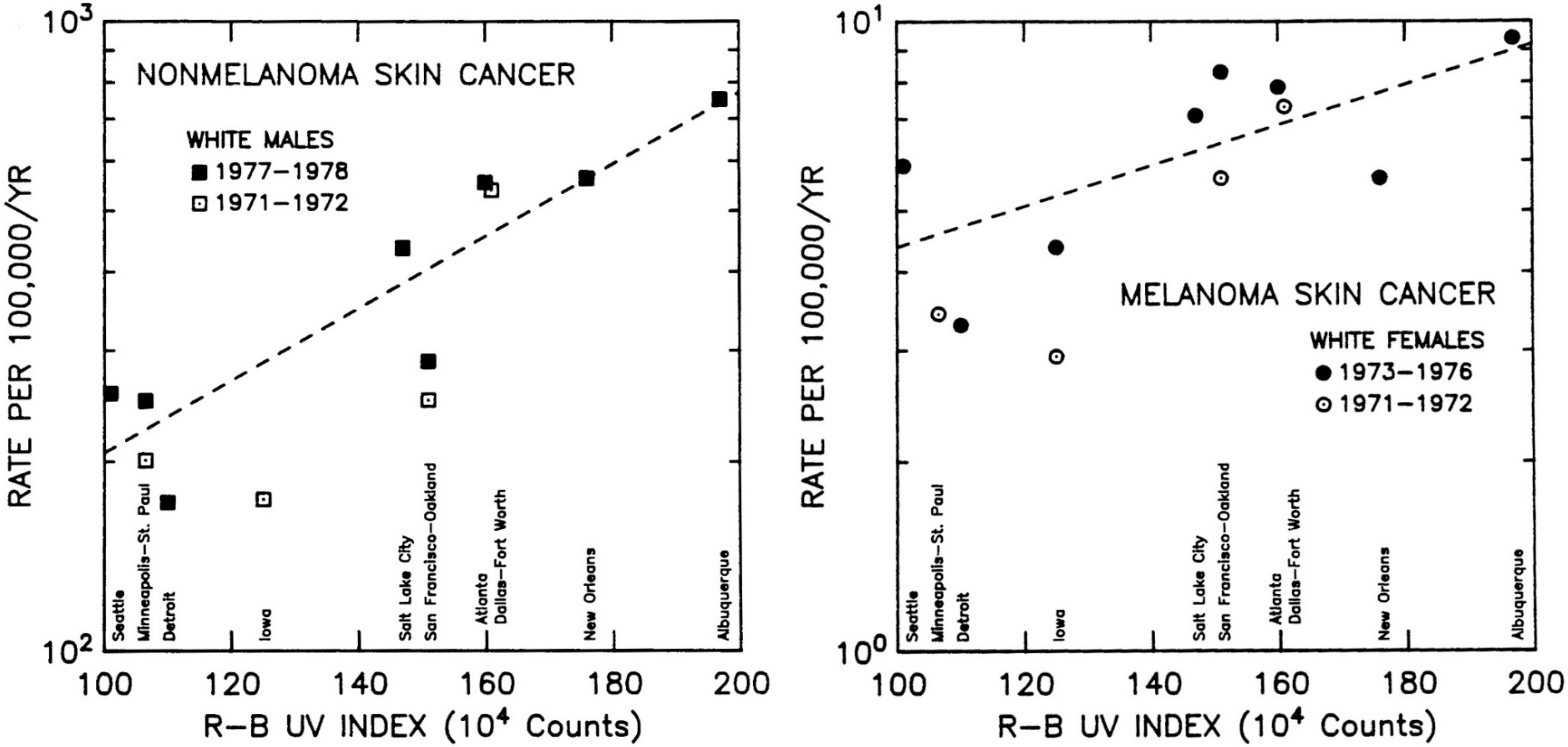
Humans are:

- 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

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

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

Relationship Between UV and Column Ozone

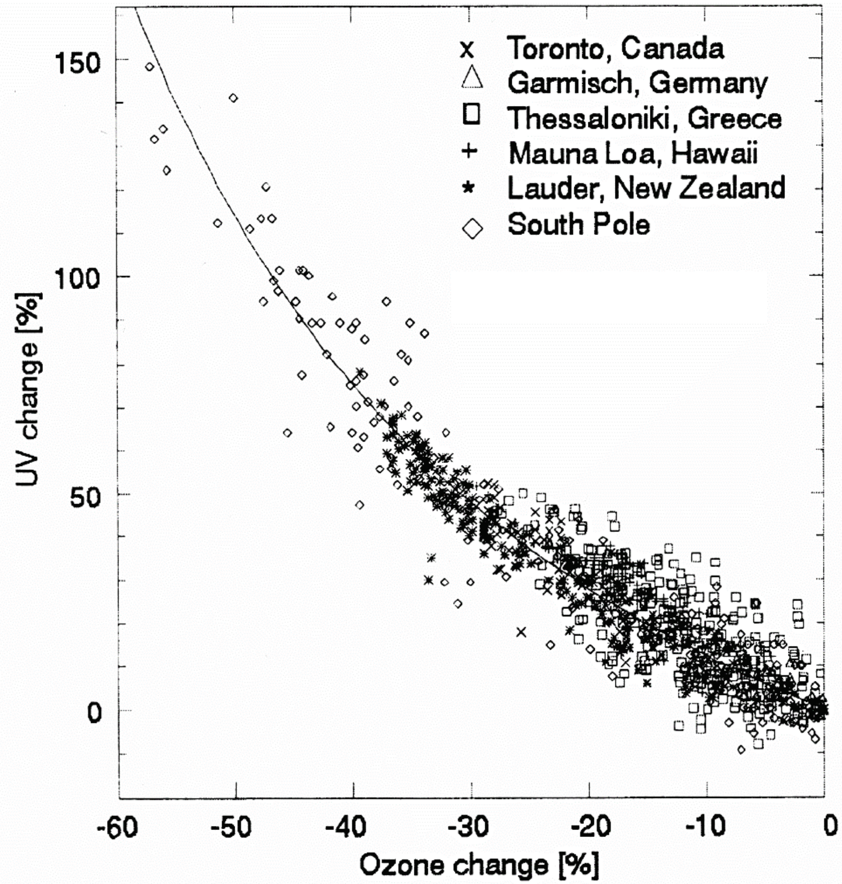


Fig. 2. Dependence of erythemal ultraviolet (UV) radiation at the Earth's surface on atmospheric ozone, measured on cloud-free days at various locations, at fixed solar zenith angles. Legend: South Pole [8]; Mauna Loa, Hawaii [9]; Lauder, New Zealand [10]; Thessaloniki, Greece (updated from Ref. [11]);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

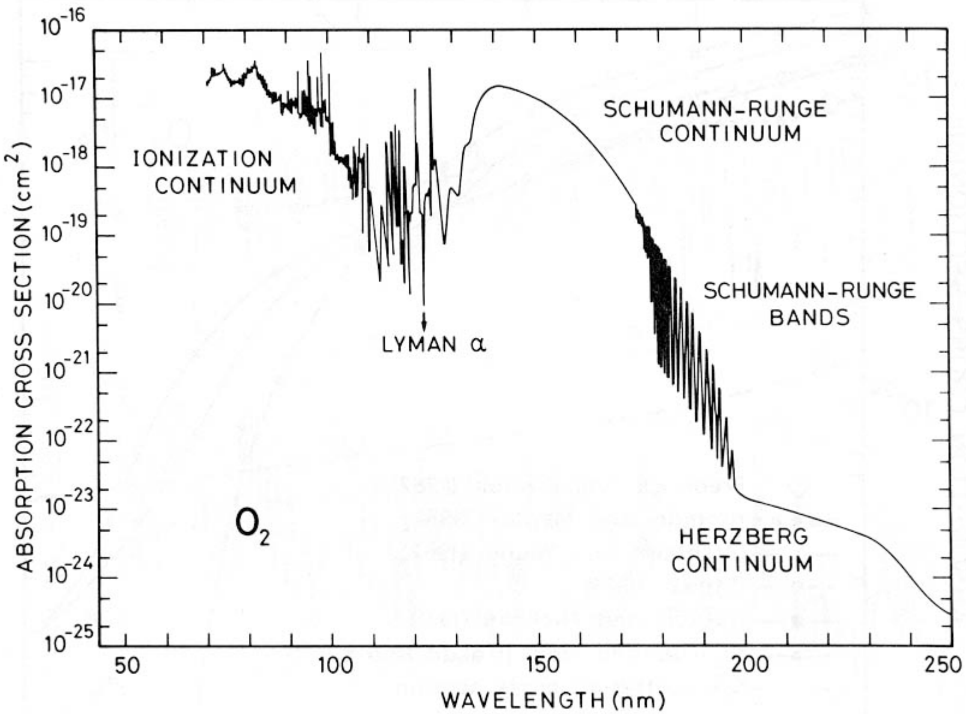
50% drop in O_3 leads to 100% rise in UV
i.e., UV rises about twice as fast as O_3 declines

Therefore, Melanoma Skin Cancer should rise by 2 % for every 1 % drop in O_3

and Non-Melanoma Skin Cancer should rise by 4 % for every 1 % drop in O_3

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

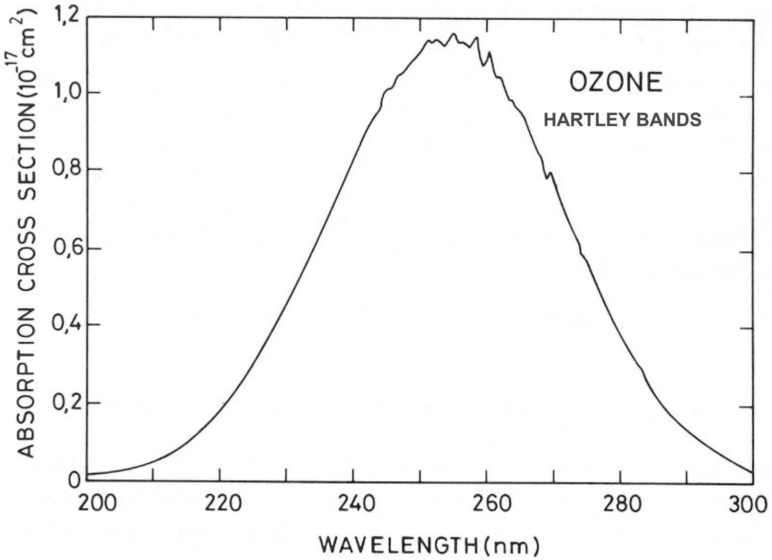
Absorption Cross Section of O_2

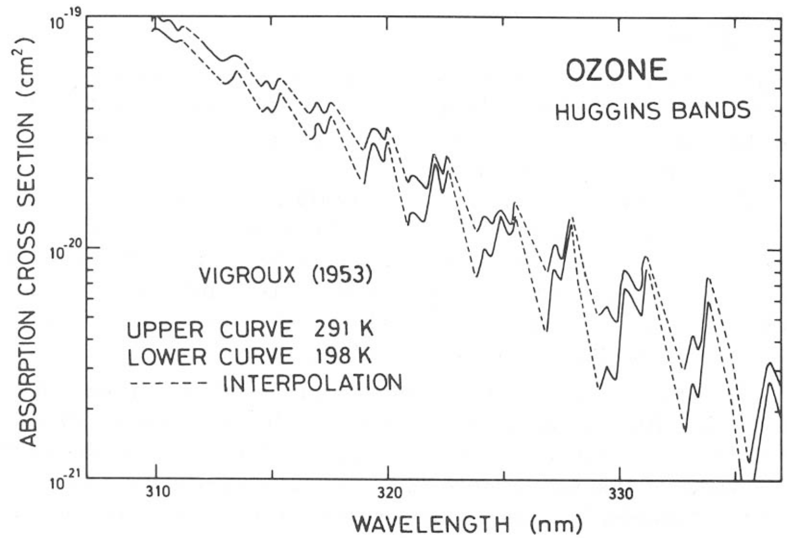


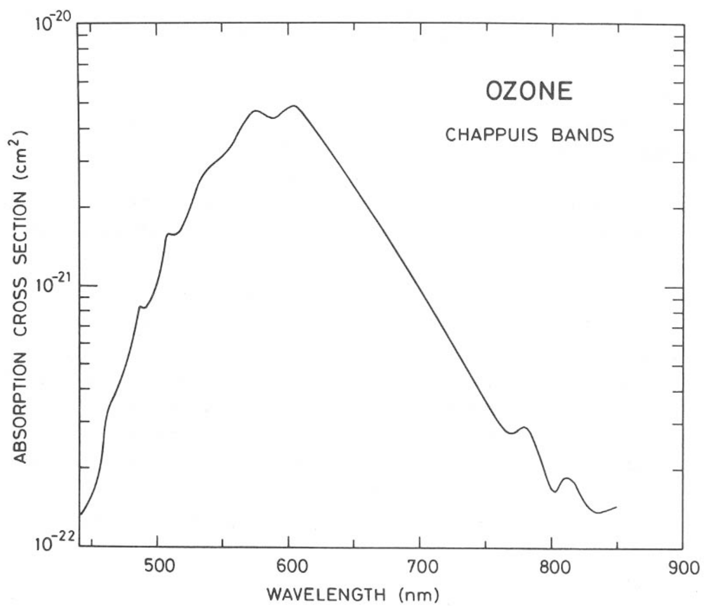
From Brasseur & Solomon, *Aeronomy of the Middle Atmosphere*, 1986

- 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)

Absorption Cross Section of O_3







Quantum Mechanically Allowed Transitions

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

Solar Spectral Actinic Flux

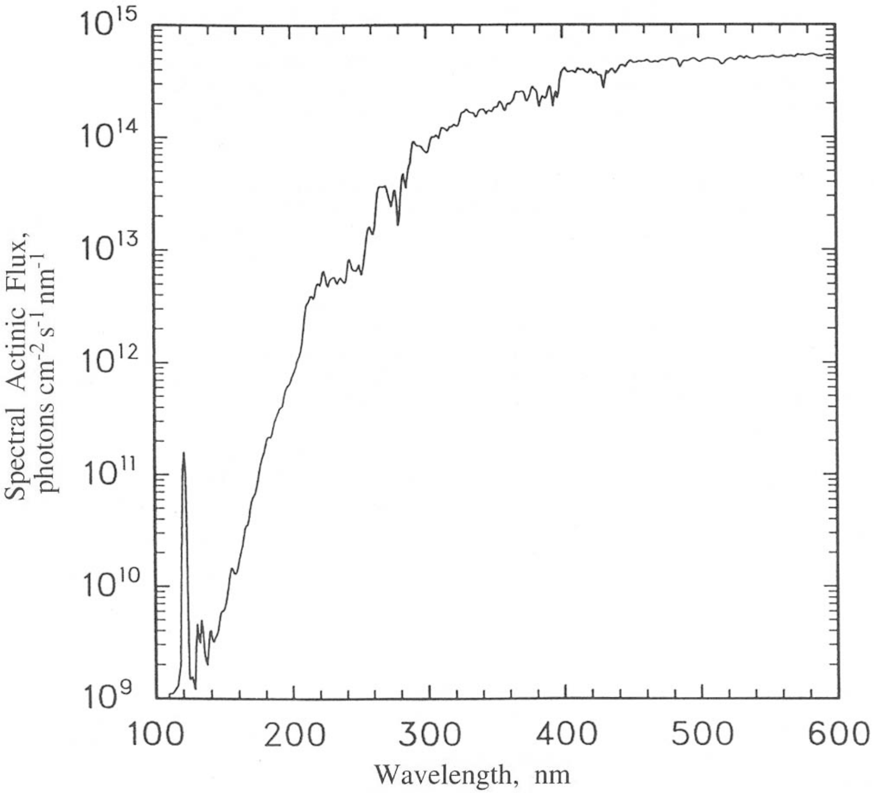
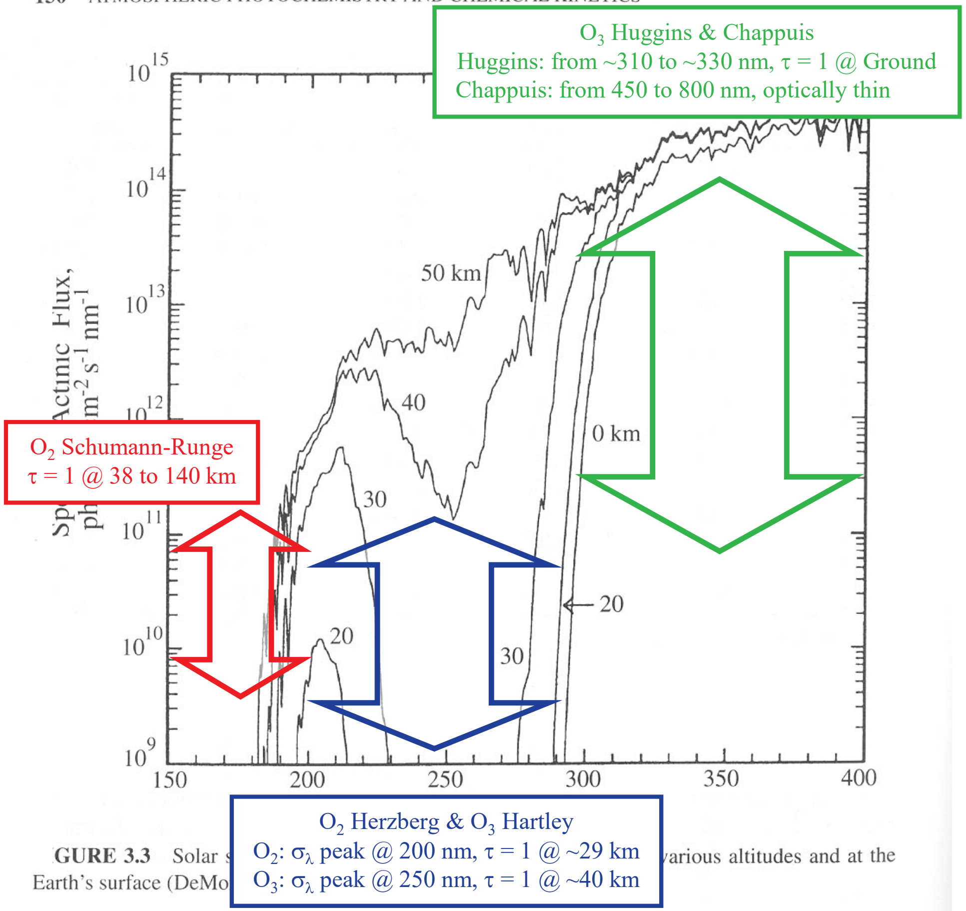


FIGURE 6. Solar spectral actinic flux (photons cm^{-2} s^{-1} nm^{-1}) at the top of Earth's atmosphere.

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

130 ATMOSPHERIC PHOTOCHEMISTRY AND CHEMICAL KINETICS



GURE 3.3 Solar s… various altitudes and at the Earth's surface (DeMo…

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

Photodissociation Frequencies

Next goal is to understand:

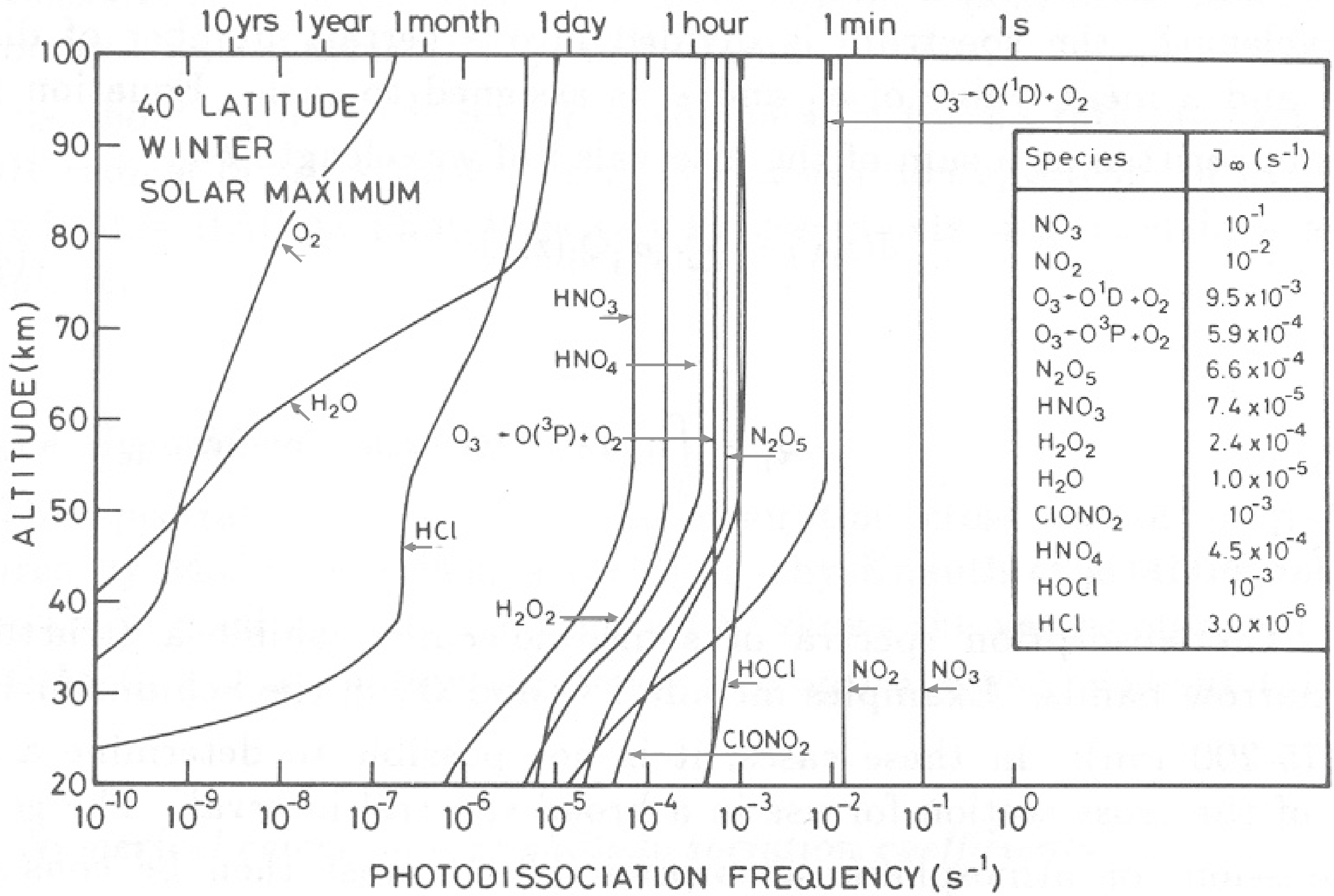


FIGURE 4.58 Photodissociation frequencies for numerous important atmospheric species.

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

Photodissociation Frequencies

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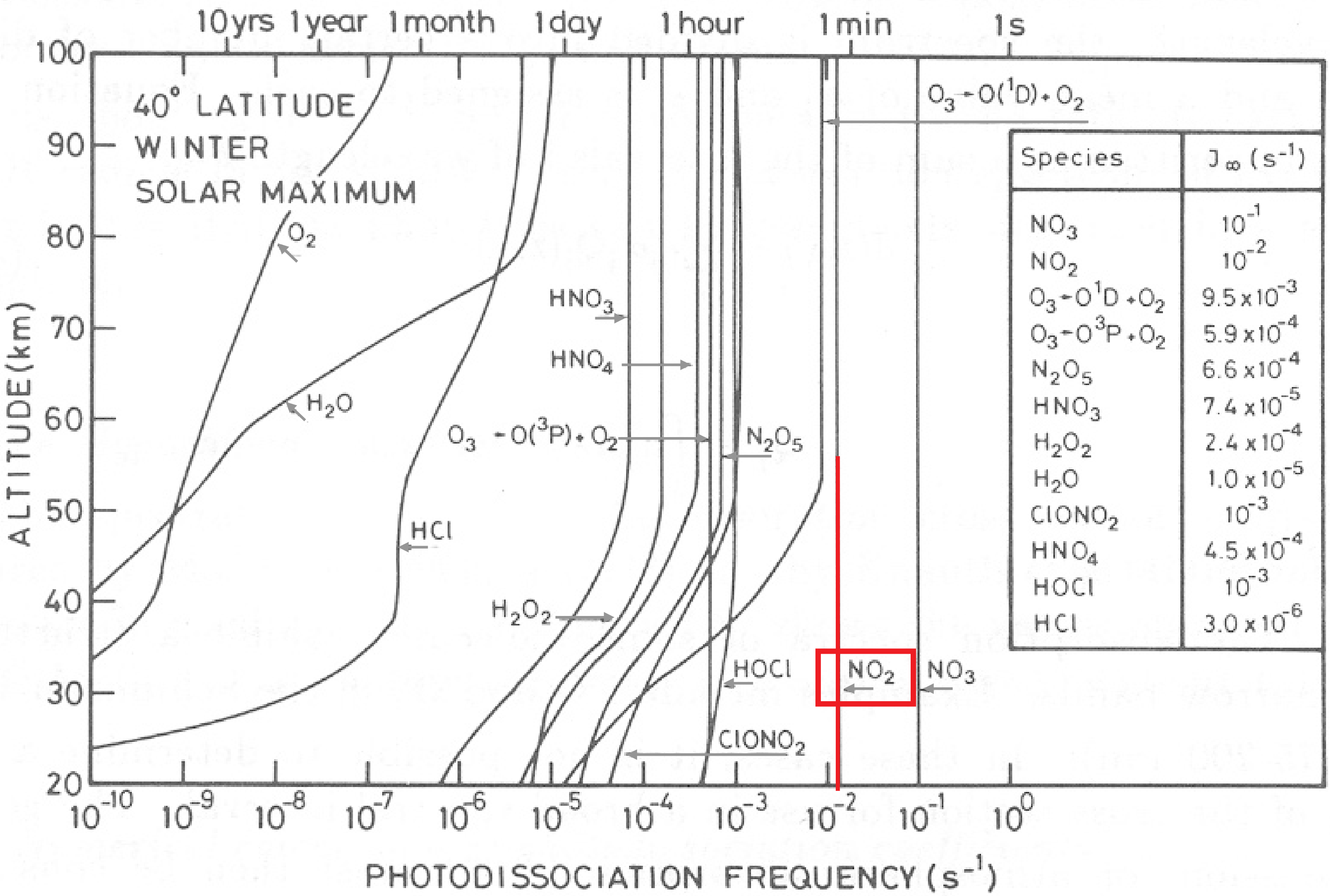

Species	J_∞ (s^{-1})
NO_3	10^{-1}
NO_2	10^{-2}
$O_3 \rightarrow O^1D + O_2$	9.5×10^{-3}
$O_3 \rightarrow O^3P + O_2$	5.9×10^{-4}
N_2O_5	6.6×10^{-4}
HNO_3	7.4×10^{-5}
H_2O_2	2.4×10^{-4}
H_2O	1.0×10^{-5}
$ClONO_2$	10^{-3}
HNO_4	4.5×10^{-4}
$HOCl$	10^{-3}
HCl	3.0×10^{-6}

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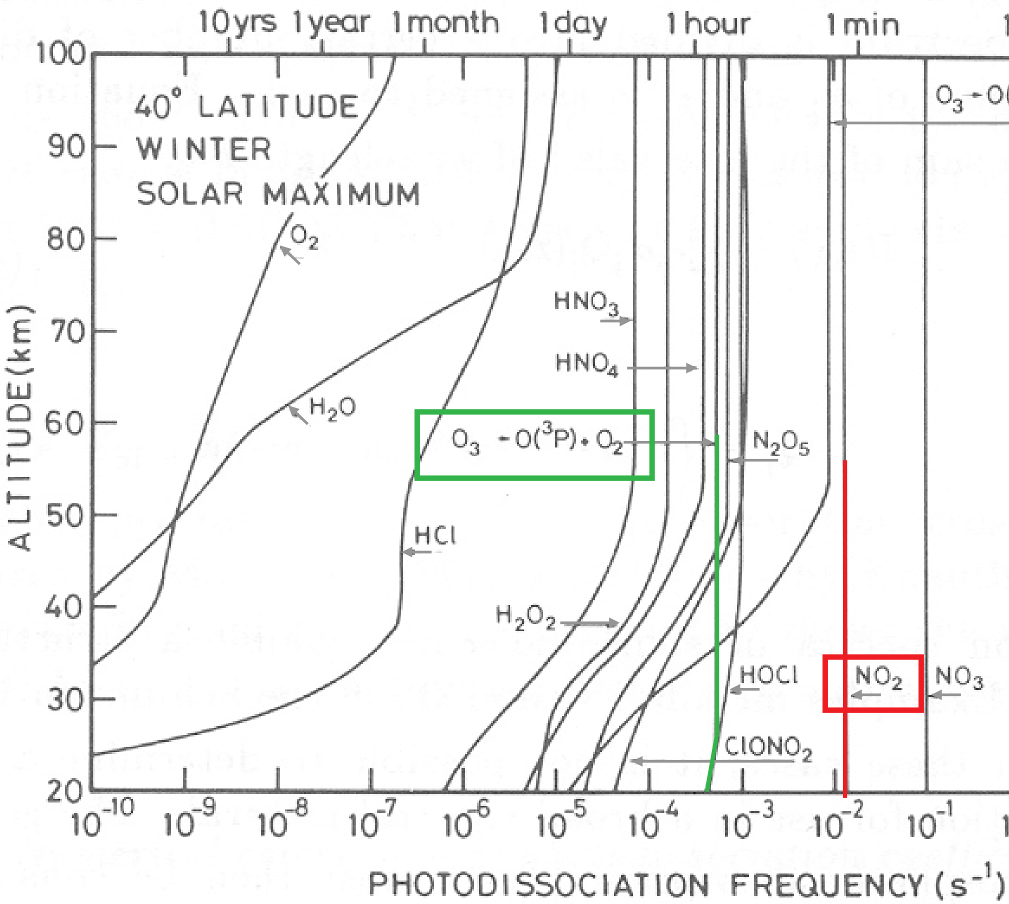

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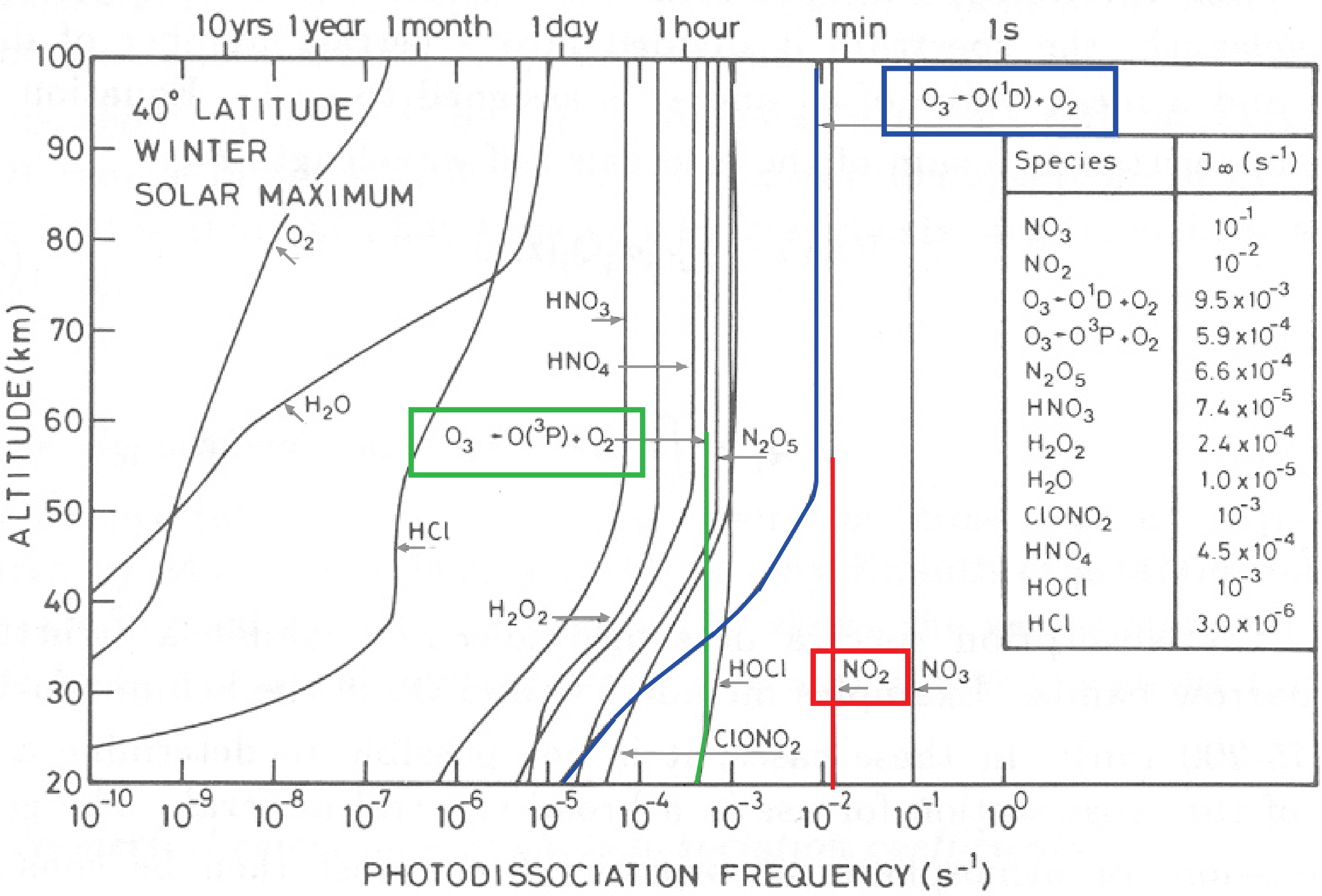
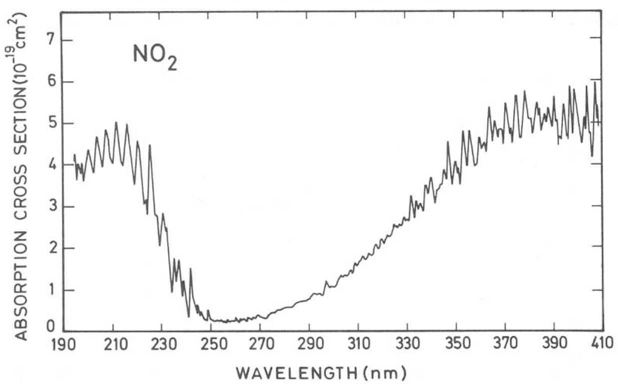


FIGURE 4.58 Photodissociation frequencies for numerous important atmospheric species.

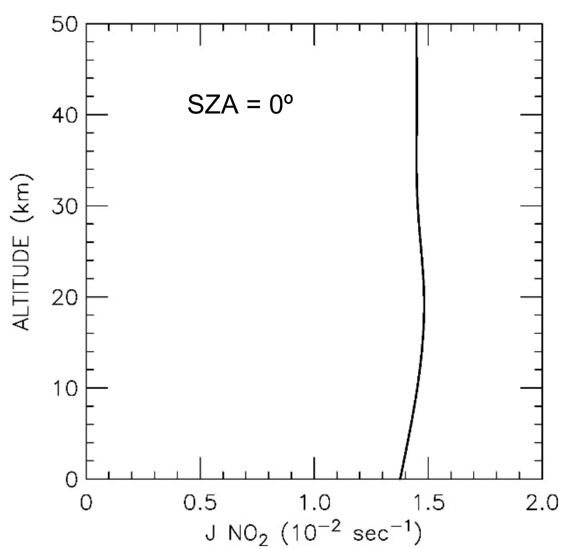
From Brasseur & Solomon, *Aeronomy of the Middle Atmosphere*, 1986

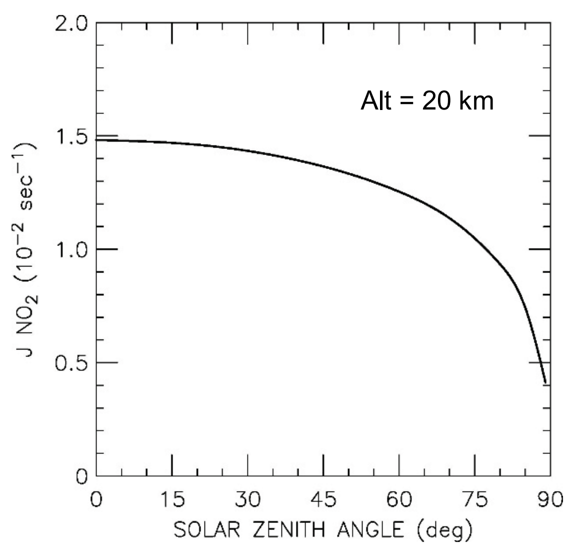
NO_2 Photolysis

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:

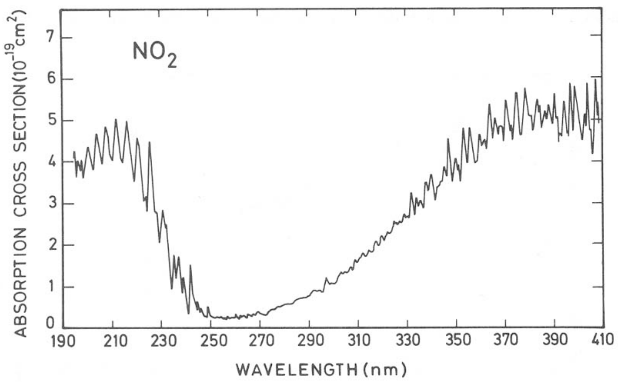


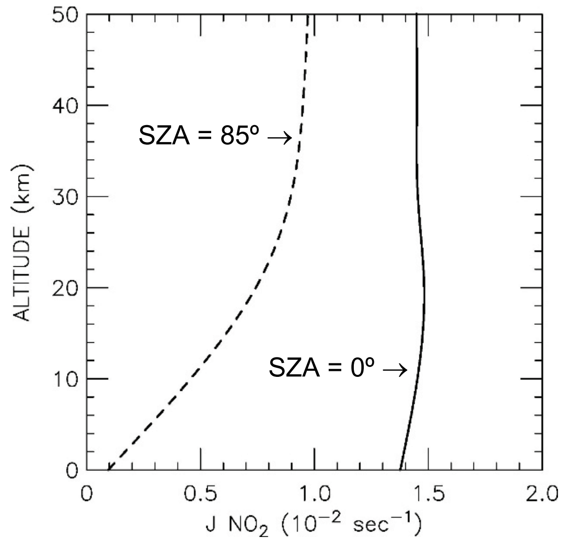
leading to a value for J_{NO2} that is nearly <u>independent</u> of height and SZA:

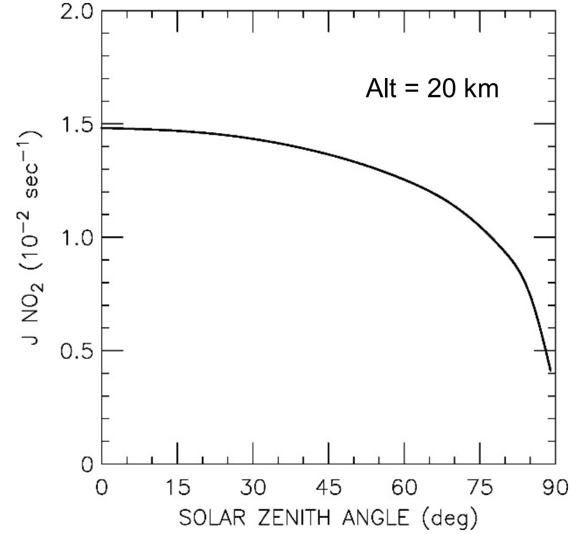


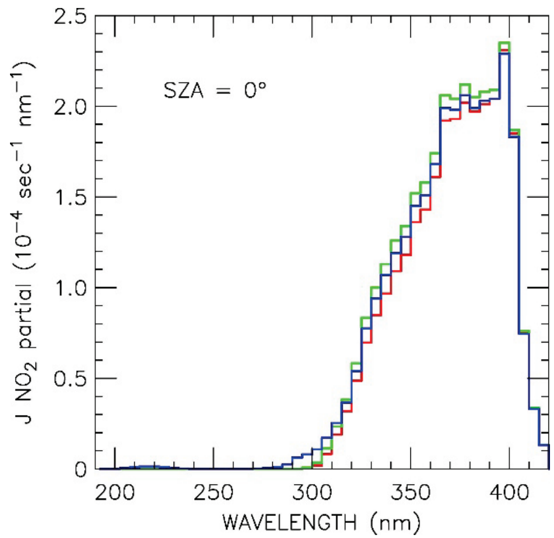


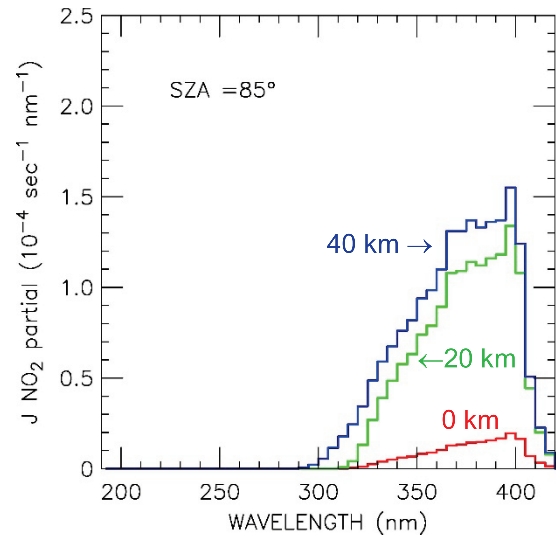
NO_2 Photolysis





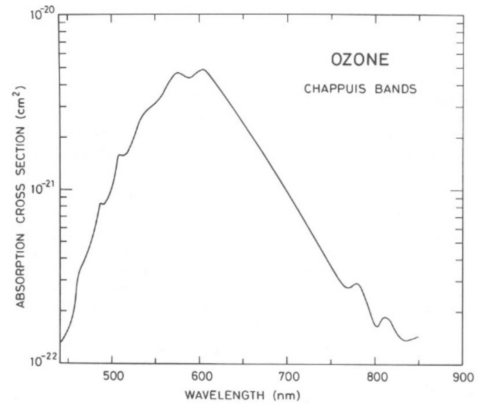




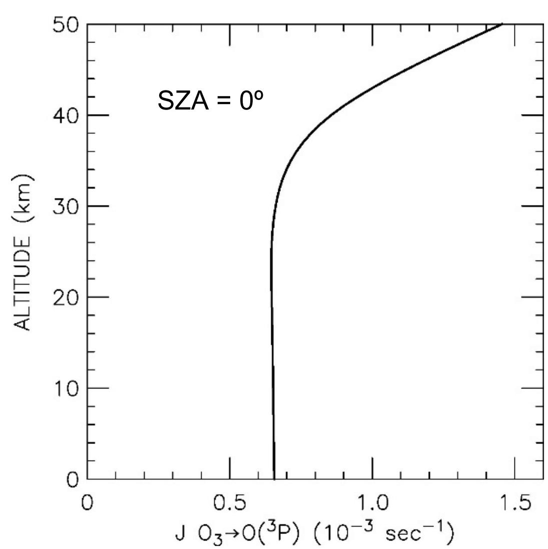


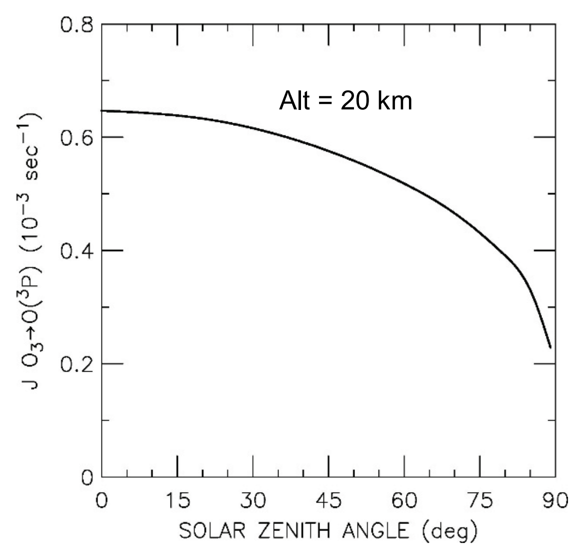
$O_3 \rightarrow O(^3P)$ Photolysis

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:

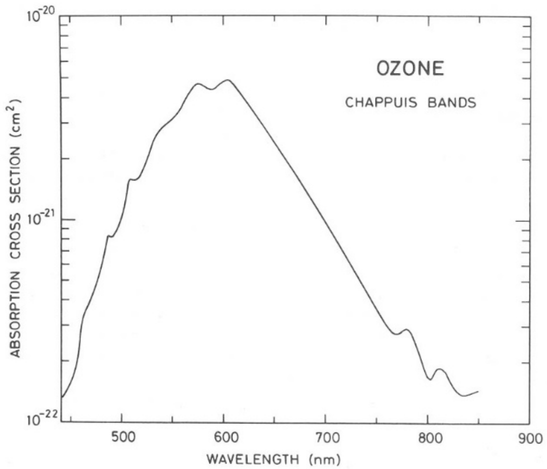


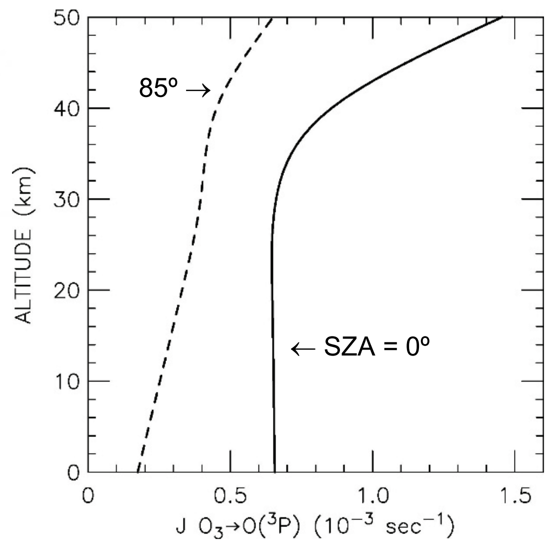
leading to a value for $J_{O3 \rightarrow O(3P)}$ that is essentially <u>independent</u> of height and SZA:

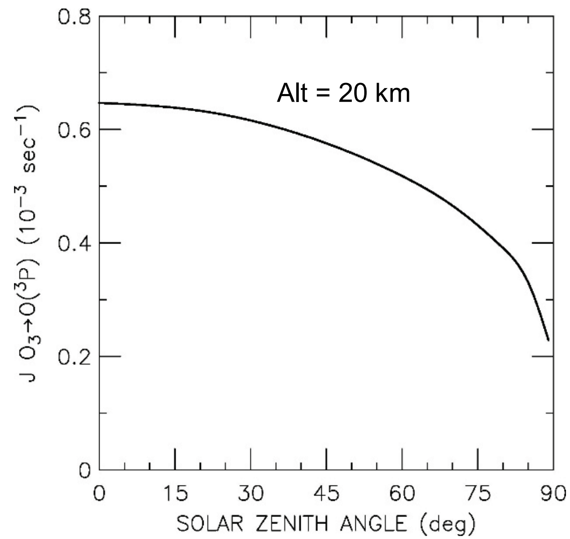


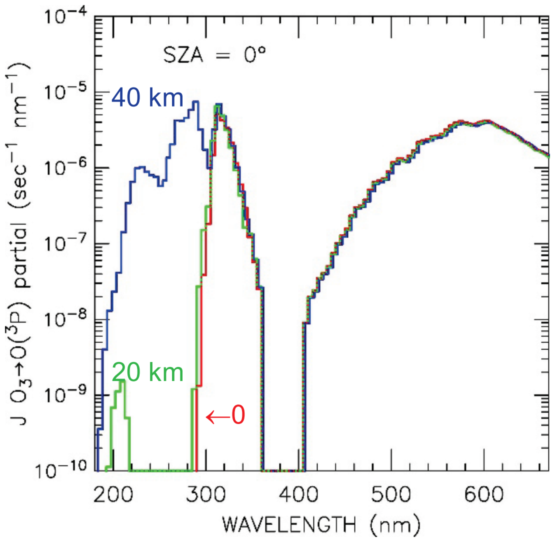


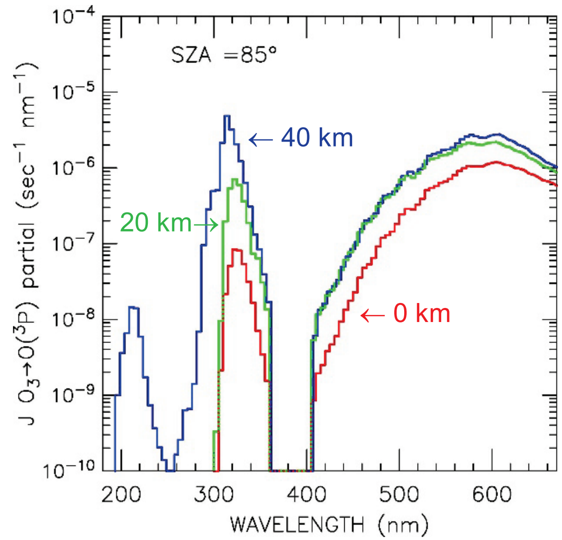
$O_3 \rightarrow O(^3P)$ Photolysis





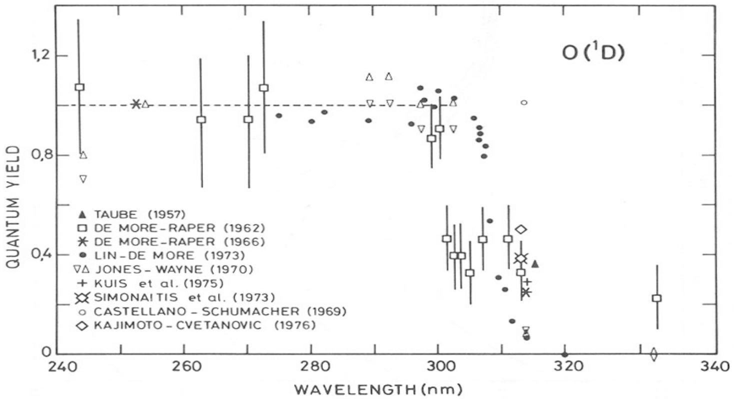


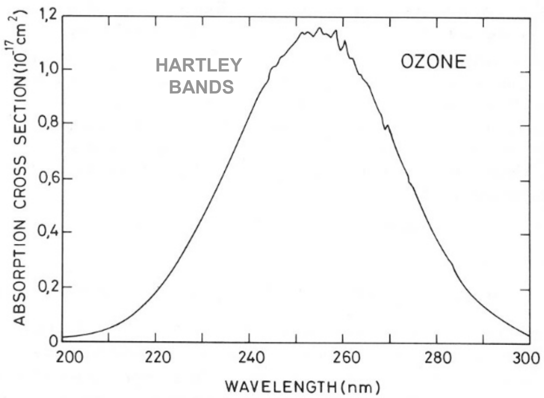


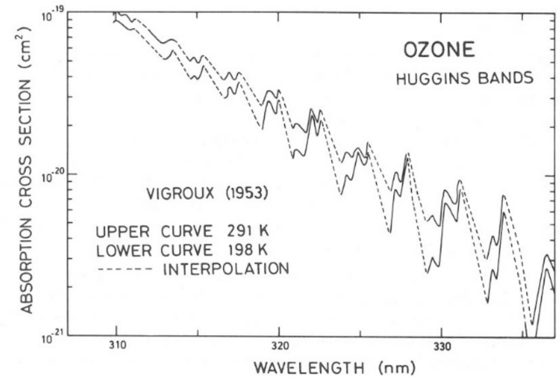


$O_3 \rightarrow O(^1D)$ Photolysis

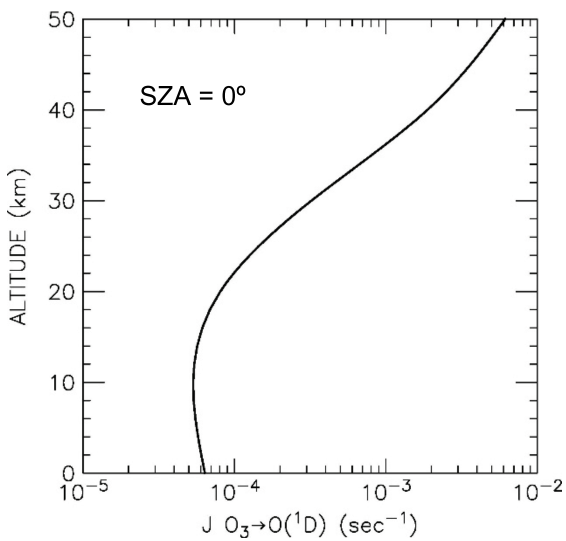
The production of $O(^1D)$ from photolysis of O_3 occurs shortward of 320 nm, where the atmosphere is basically optically thick with respect to absorption by O_3:

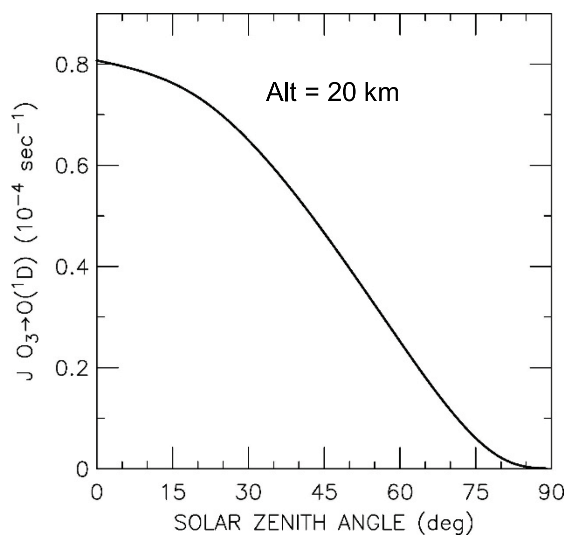




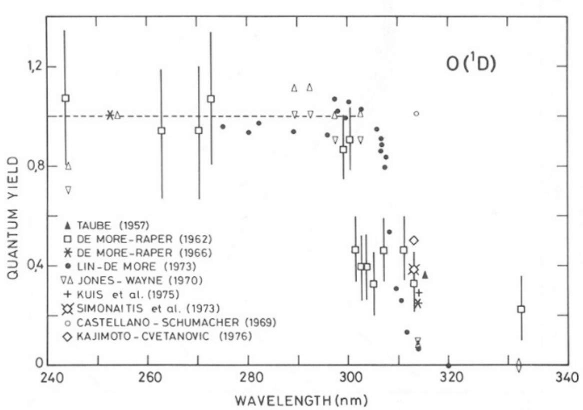


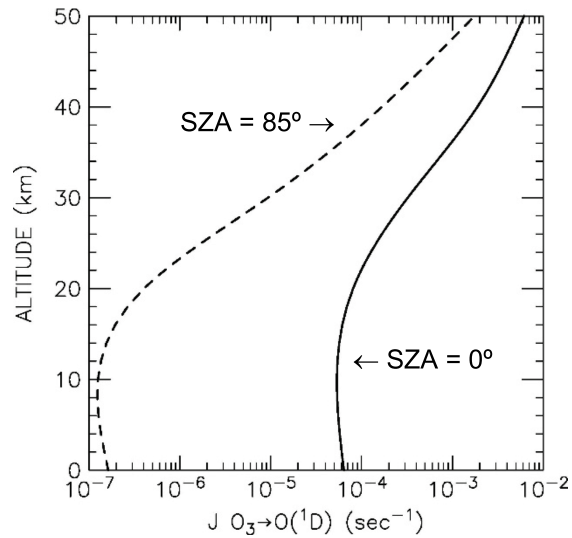
leading to a value for $J_{O3 \rightarrow O(1D)}$ that is <u>dependent</u> on height and SZA:

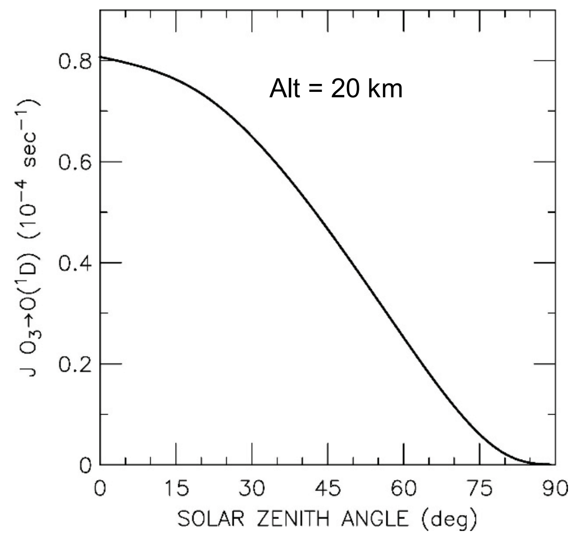


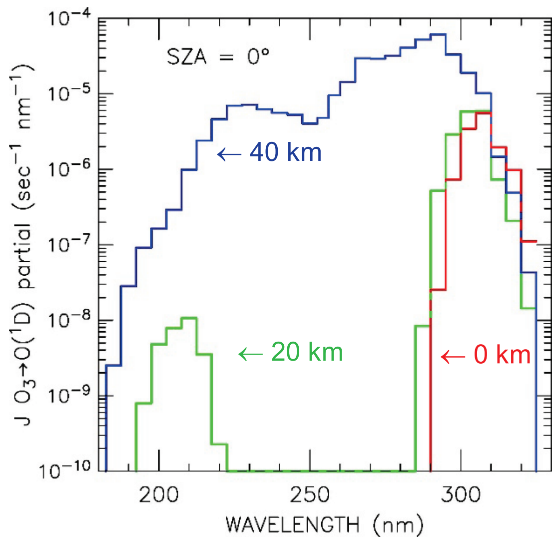


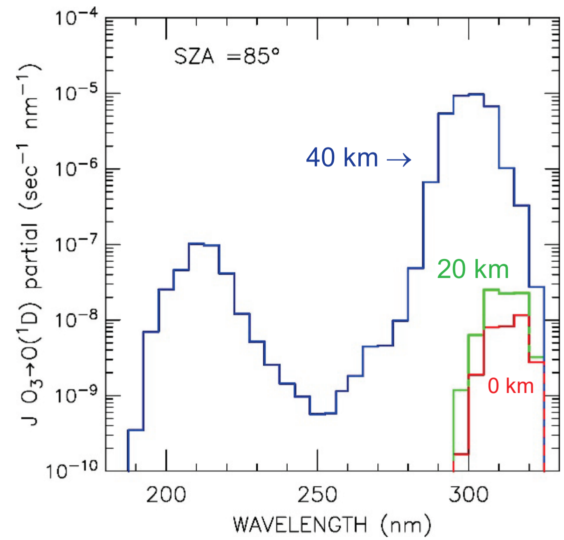
$O_3 \rightarrow O(^1D)$ Photolysis











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

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

$$\text{Photolysis Rate Gas (z)} = [\text{Gas}] \times J_{gas} \qquad \text{Units: molecules cm}^{-3}\ \text{sec}^{-1}$$

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

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

where:

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

Extra #1: Height and Abundance of Ozone

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:

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

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

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

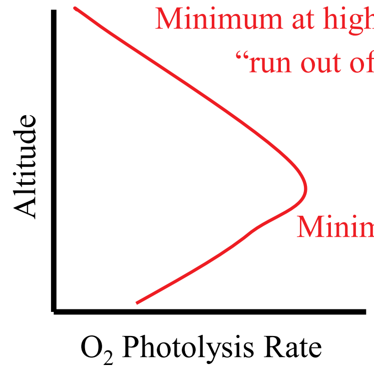
Extra #1: Height and Abundance of Ozone

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

Extra #1: Height and Abundance of Ozone

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}	**5.8×10^{7}**

Extra #1: 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})

Altitude of largest O_2 photolysis rate

Value of O_2 photolysis rate, $J_1[O_2]$ in Chapman expression at peak altitude

	σ_{max} (cm^2)	z (τ=1) (km)	F_{TOA} ($\#/cm^2/s$)	J (sec^{-1})	Photolysis Rate ($\#/cm^3/sec$)
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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:

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

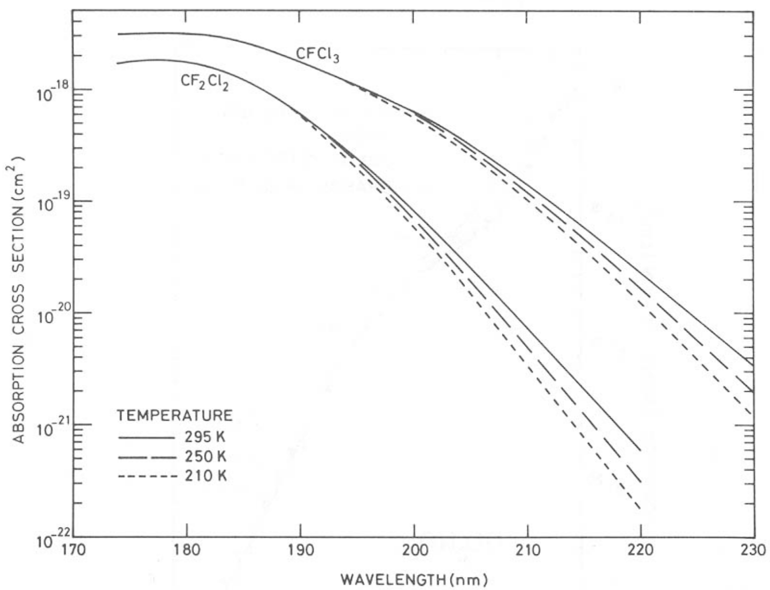
$$\sigma_{max} = 3 \times 10^{-25}\ \text{cm}^2 \rightarrow z_{\text{OZONE LAYER}} = 2\ \text{km}$$

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

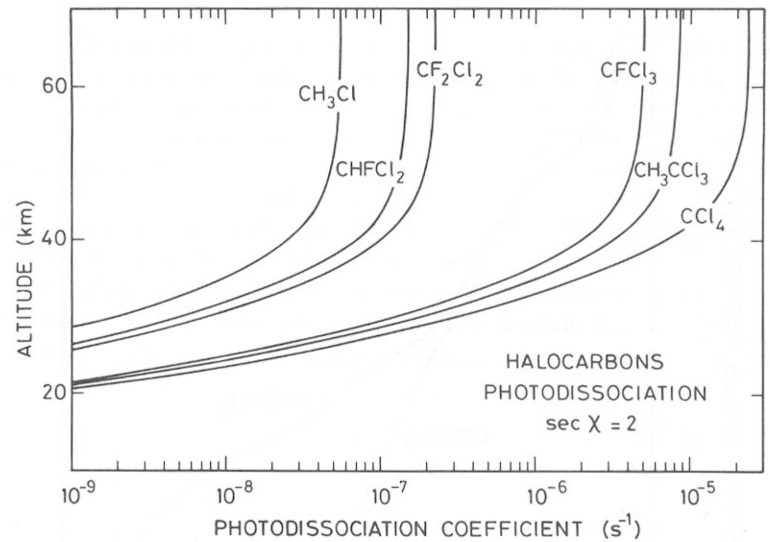
$$F_{TOA} = 2 \times 10^{15}\ \text{\#/cm}^2\text{/s} \rightarrow \text{Ozone Column} \approx 900\ \text{DU}$$

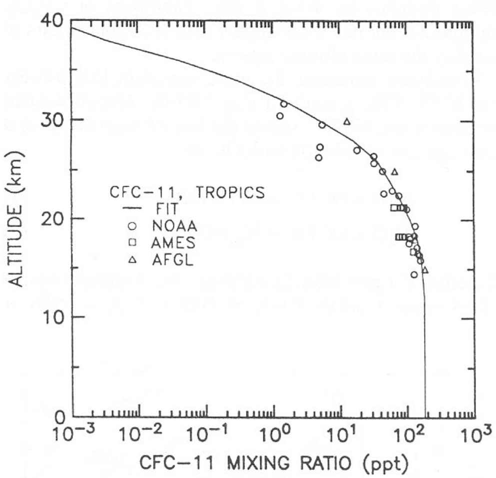
$$F_{TOA} = 2 \times 10^{13}\ \text{\#/cm}^2\text{/s} \rightarrow \text{Ozone Column} \approx 100\ \text{DU}$$

Extra #2: CFC Photolysis



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





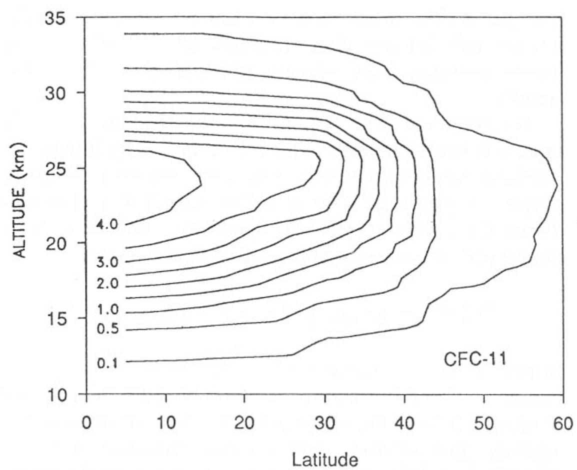


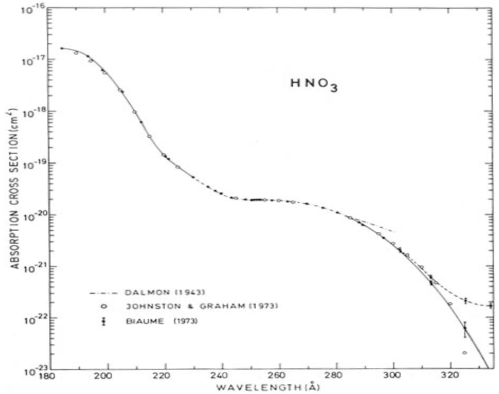
Fig. 12. Diurnally averaged loss rate for $CFCl_3$ (molecules cm^{-3} s^{-1}) as a function of altitude and latitude, calculated with the line-by-line model, for equinox. The loss rate was calculated assuming destruction of $CFCl_3$ by photolysis only.

	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

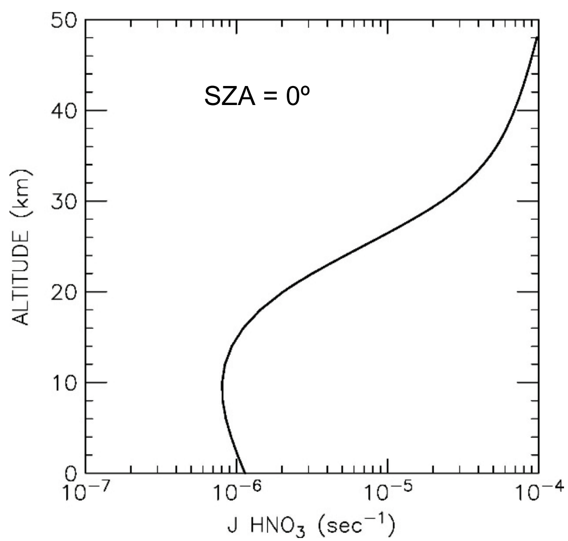
Minschwaner *et al., JGR, 98*, 10543, 1993

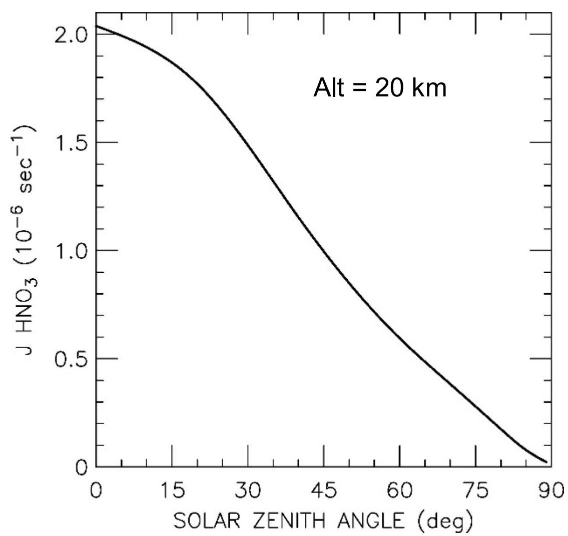
Extra #3: HNO_3 Photolysis

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