

# 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>

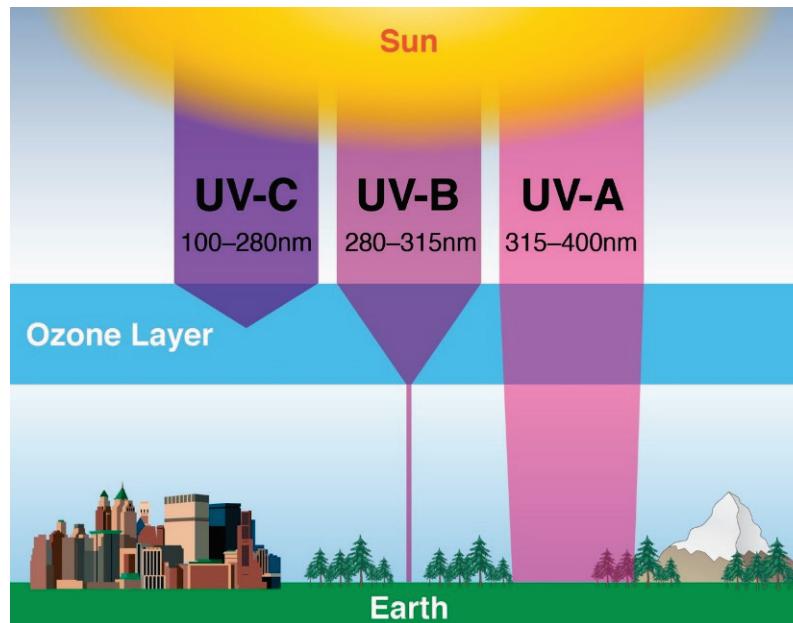


Figure 3.3.2, Wilmouth, Salawitch, and Carty, 2018

[https://www2.atmos.umd.edu/~rjs/class/spr2020/readings/green\\_chemistry\\_chapter\\_3.3.pdf](https://www2.atmos.umd.edu/~rjs/class/spr2020/readings/green_chemistry_chapter_3.3.pdf)

## Lecture 11 20 October 2020

# 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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Figure 2.12 of the Warneck reading shows the photodissocation *frequency* of  $O_2$  and  $O_3$ , termed  $J_{O_2}$  and  $J_{O_3}$ , 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.

# Admission Ticket Lecture 11

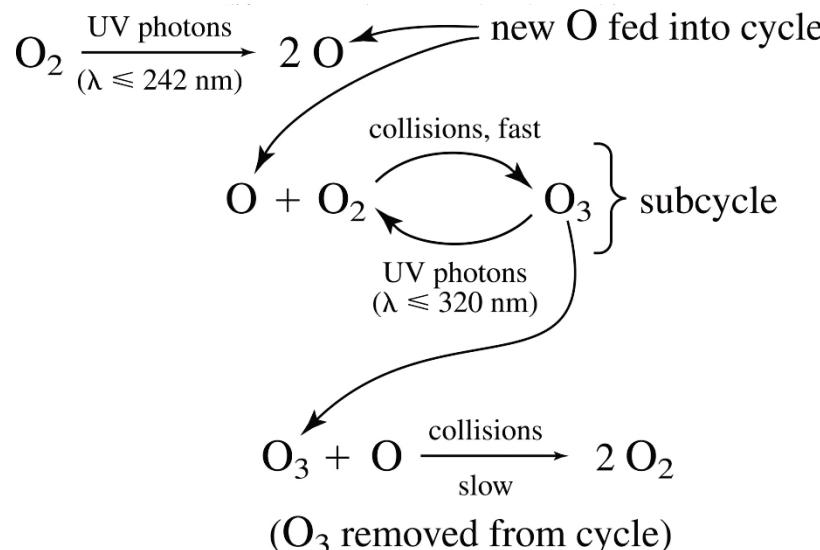
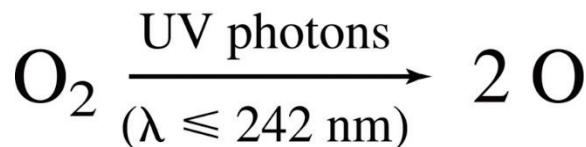


Figure 2.10, Chemistry in Context



Equation 2.4, Chemistry in Context

# Admission Ticket Lecture 11

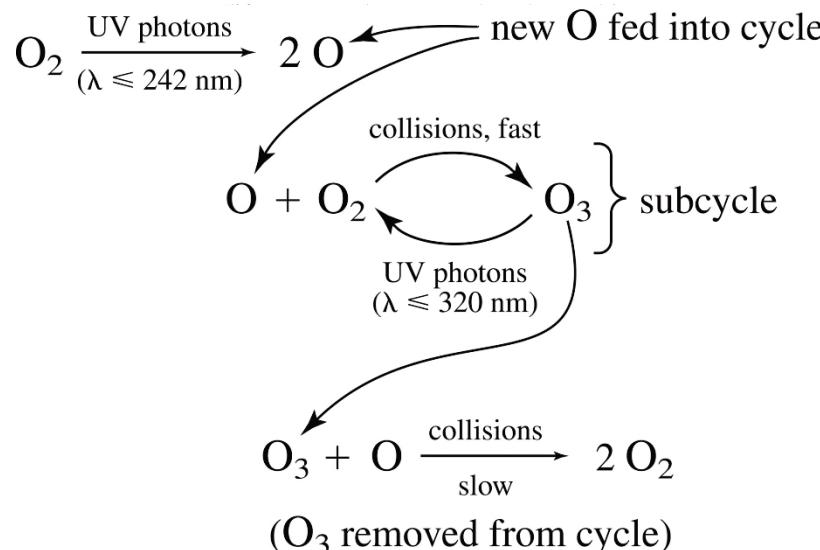
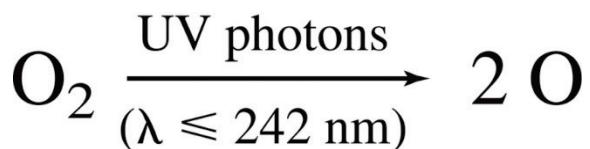
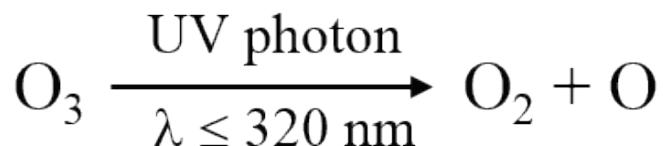


Figure 2.10, Chemistry in Context



Equation 2.4, Chemistry in Context



Equation 2.5, Chemistry in Context

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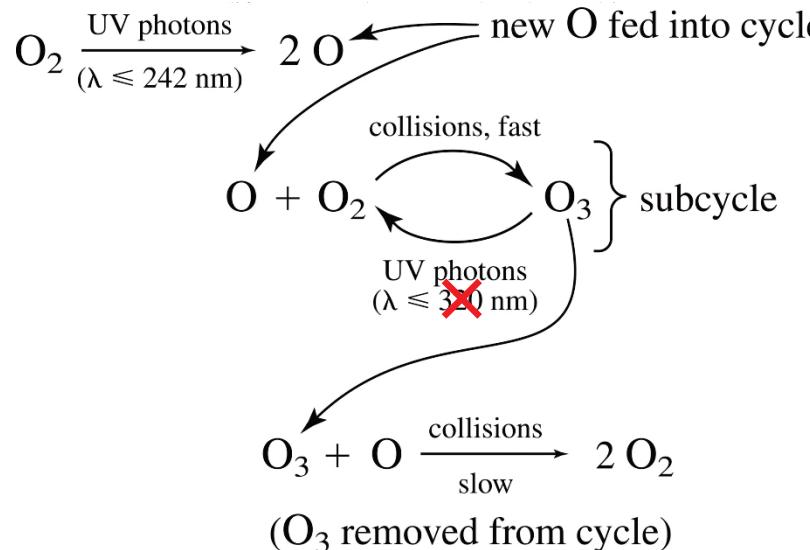
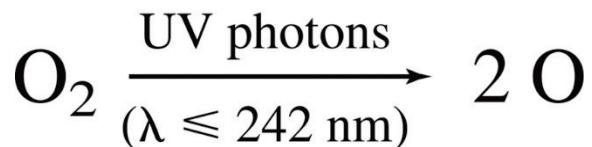
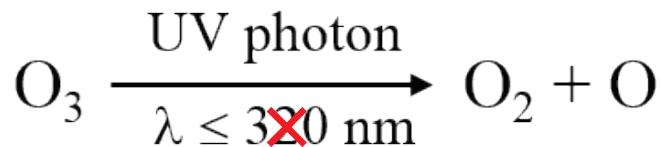


Figure 2.10, Chemistry in Context



Equation 2.4, Chemistry in Context



Equation 2.5, Chemistry in Context

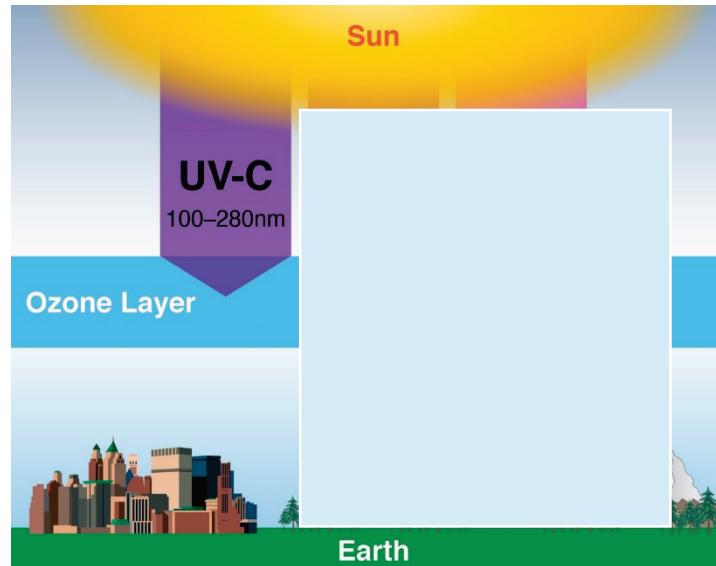
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### O<sub>2</sub> protects us even more so than O<sub>3</sub>

According to Section 2.6 of Chemistry in Context:

- what is the upper limit for photodissociation of O<sub>3</sub>
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Wilmouth et al., 2018

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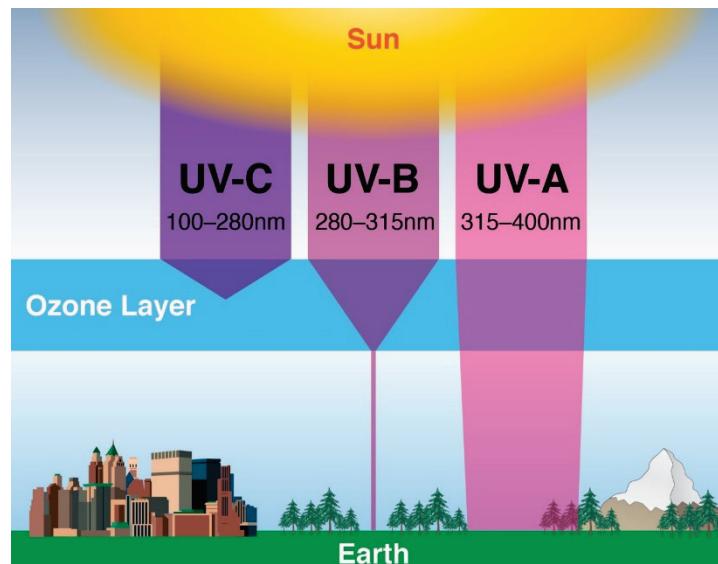
- what is the upper limit for photodissociation of O<sub>2</sub>
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According to Section 2.6 of Chemistry in Context:

- what is the upper limit for photodissociation of O<sub>3</sub>
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**When we examine skin cancer and ozone depletion, it is all about UV-B radiation.**

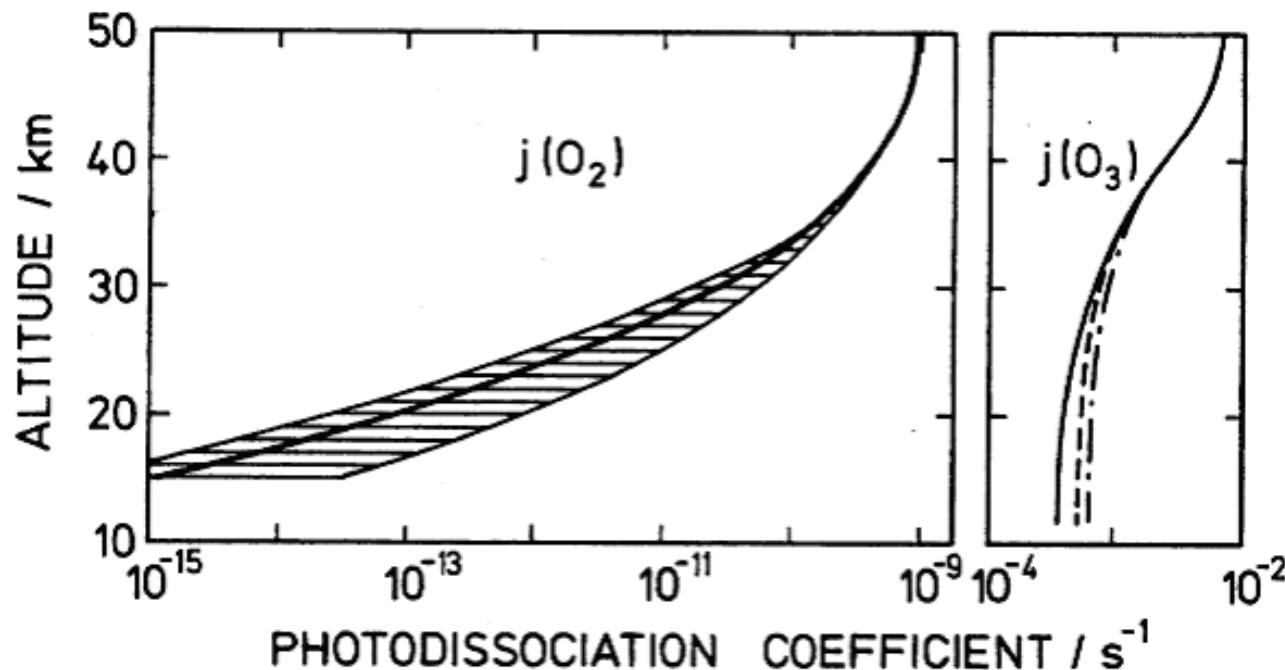


Wilmouth et al., 2018

# Admission Ticket Lecture 11

Figure 2.12 of the Warneck reading shows the photodissociation frequency of  $O_2$  and  $O_3$ , termed  $J_{O_2}$  and  $J_{O_3}$ , 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.

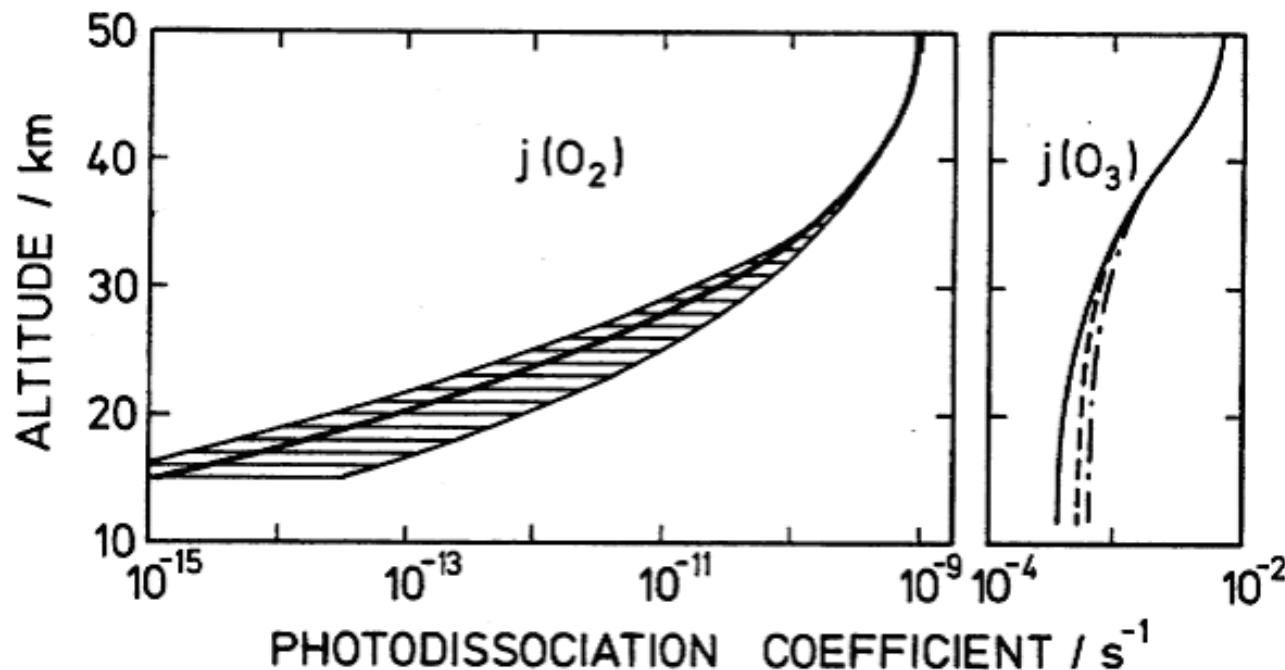
Calculate the lifetimes for loss of  $O_2$  and for loss of  $O_3$  by photodissociation, for the upper troposphere, in units that you can easily conceptualize. Then, for each molecule, state whether you think the gas will be lost by photodissociation in Earth's upper troposphere.



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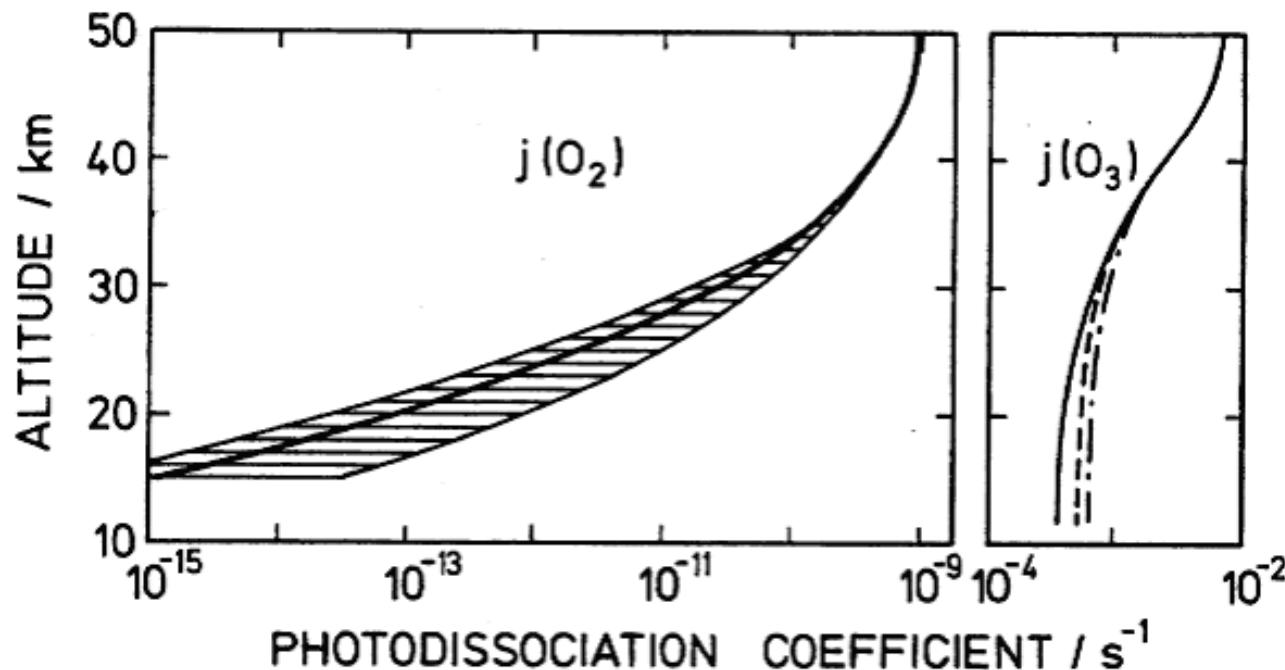
$$\text{Lifetime } O_2 \text{ at 15 km} = \text{Amount of } O_2 / \text{Loss Rate of } O_2$$

$$\text{Lifetime } O_3 \text{ at 15 km} = \text{Amount of } O_3 / \text{Loss Rate of } O_3$$

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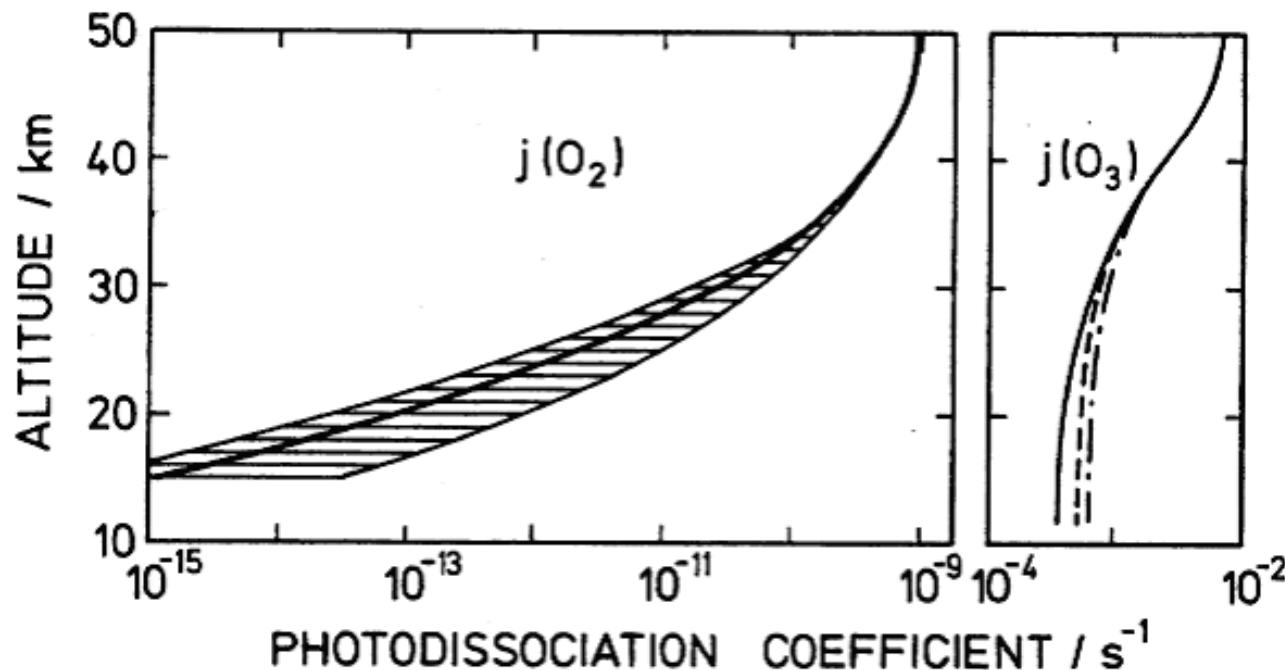
$$\text{Lifetime } O_2 \text{ at } 15 \text{ km} = [O_2] / (J_{O_2} [O_2])$$

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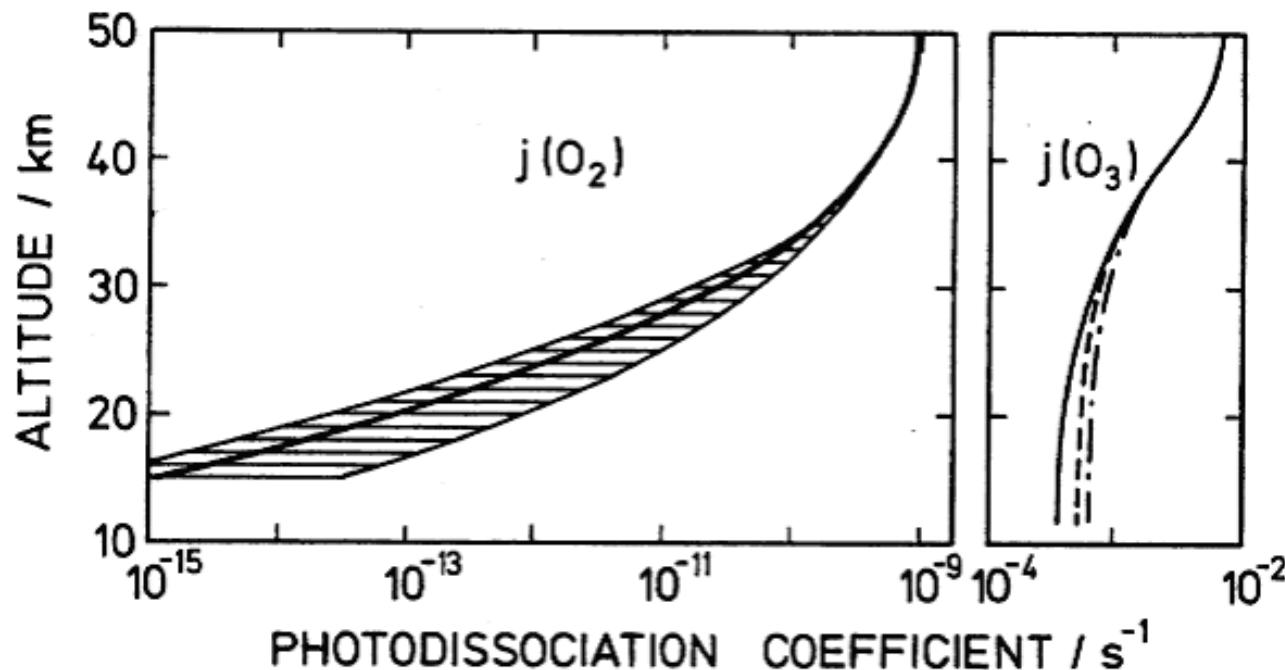
$$\text{Lifetime } O_2 \text{ at } 15 \text{ km} = [O_2] / (J_{O_2} [O_2]) = 1/J_{O_2}$$

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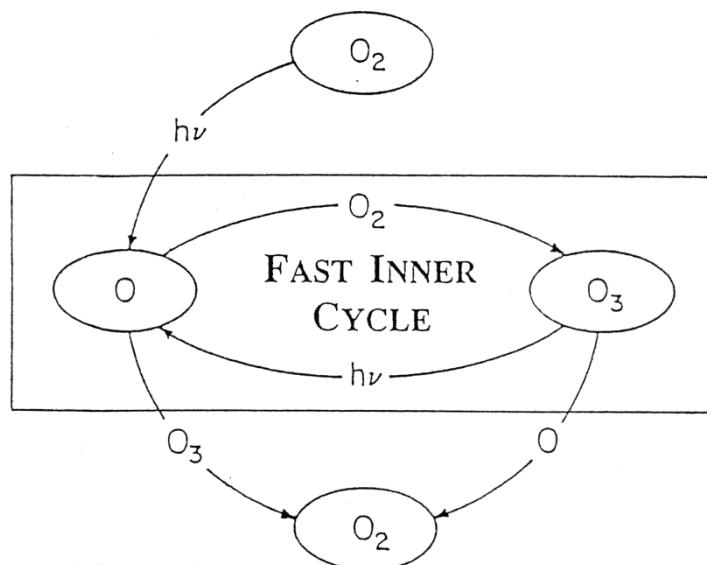


Lifetime  $O_2$  at 15 km =  $[O_2] / (J_{O_2} [O_2]) = 1/J_{O_2} = 1/(10^{-15} \text{ sec}^{-1}) = 10^{15} \text{ sec or 31 million years!}$   
Lifetime  $O_3$  at 15 km =  $[O_3] / (J_{O_3} [O_3]) = 1/J_{O_3} = 1/(5 \times 10^{-4} \text{ sec}^{-1}) = 2000 \text{ sec or 0.5 hour}$

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Figure 2.12 of the Warneck reading shows the photodissociation frequency of  $O_2$  and  $O_3$ , termed  $J_{O_2}$  and  $J_{O_3}$ , 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.

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$$\text{Lifetime } O_2 \text{ at 15 km} = [O_2] / (J_{O_2} [O_2]) = 1/J_{O_2} = 1/(10^{-15} \text{ sec}^{-1}) = 10^{15} \text{ sec or 31 million years!}$$
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# Biological Effects of UV Radiation

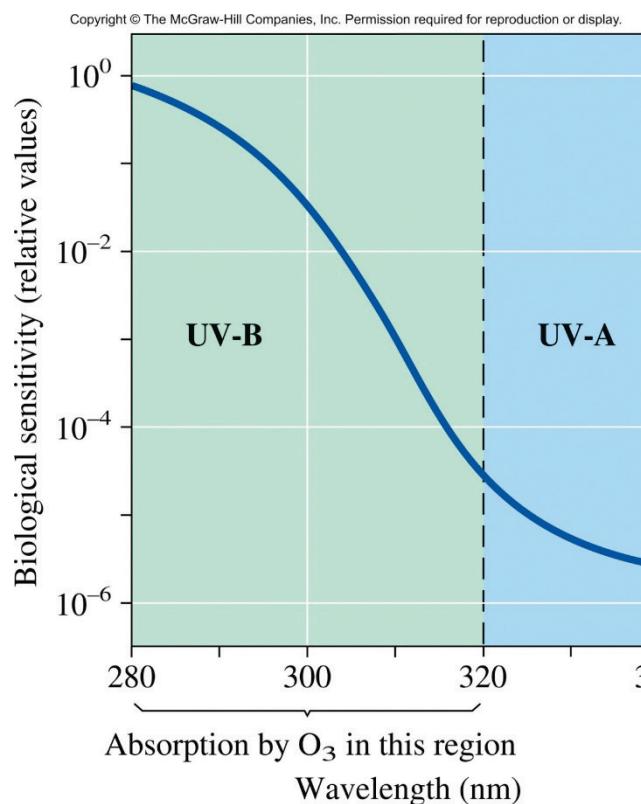
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**Table 2.4**

## 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 <sub>3</sub> in the stratosphere
UV-C	200–280 nm	Highest energy	Most damaging but not a problem because it is totally absorbed by O <sub>2</sub> and O <sub>3</sub> in the stratosphere

## Chemistry in Context



**Figure 2.11, Chemistry in Context**

# Biological Effects of UV Radiation

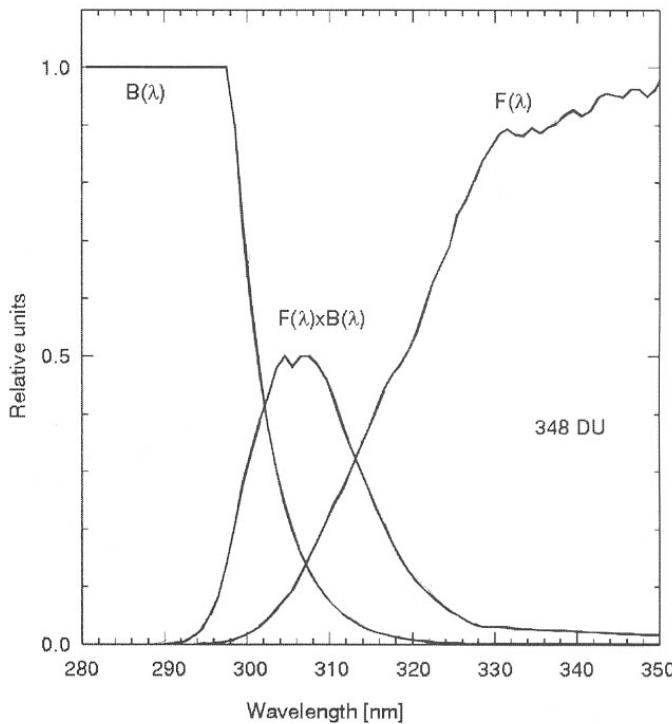


Fig. 1. Biologically active UV radiation. The overlap between the spectral irradiance  $F(\lambda)$  and the erythemal action spectrum  $B(\lambda)$  given by McKinlay and Diffey [6] shows the spectrum of biologically active radiation,  $F(\lambda)B(\lambda)$ . The area under the product function  $F(\lambda)B(\lambda)$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

Humans are:

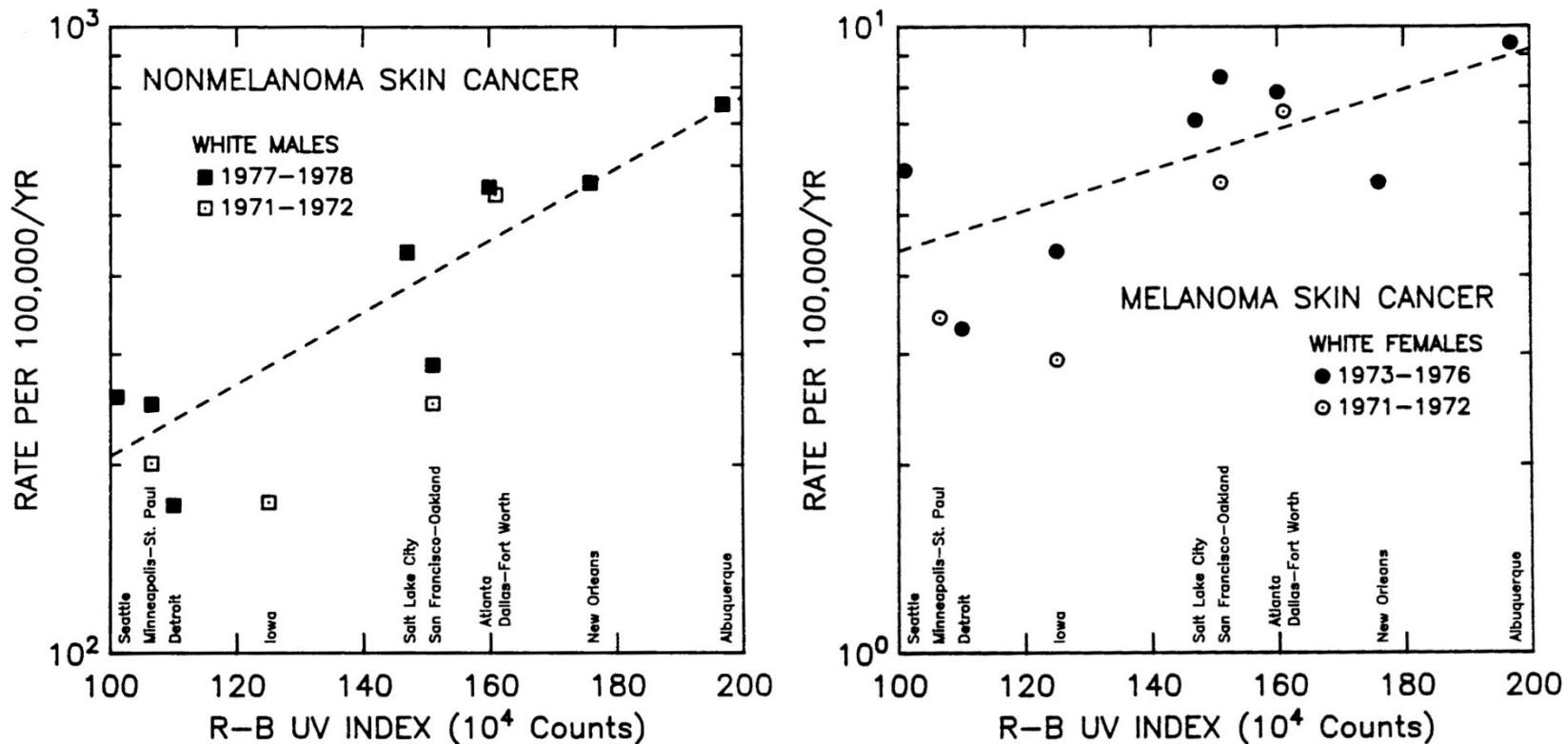
- strongly affected by exposure to UV-C radiation  
(100 to 280 nm)
- moderately affected by exposure to UV-B radiation  
(280 to 315 nm)
- weakly affected by exposure to UV-A radiation  
(315 to 400 nm)

[http://www.who.int/uv/uv\\_and\\_health/en](http://www.who.int/uv/uv_and_health/en)

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

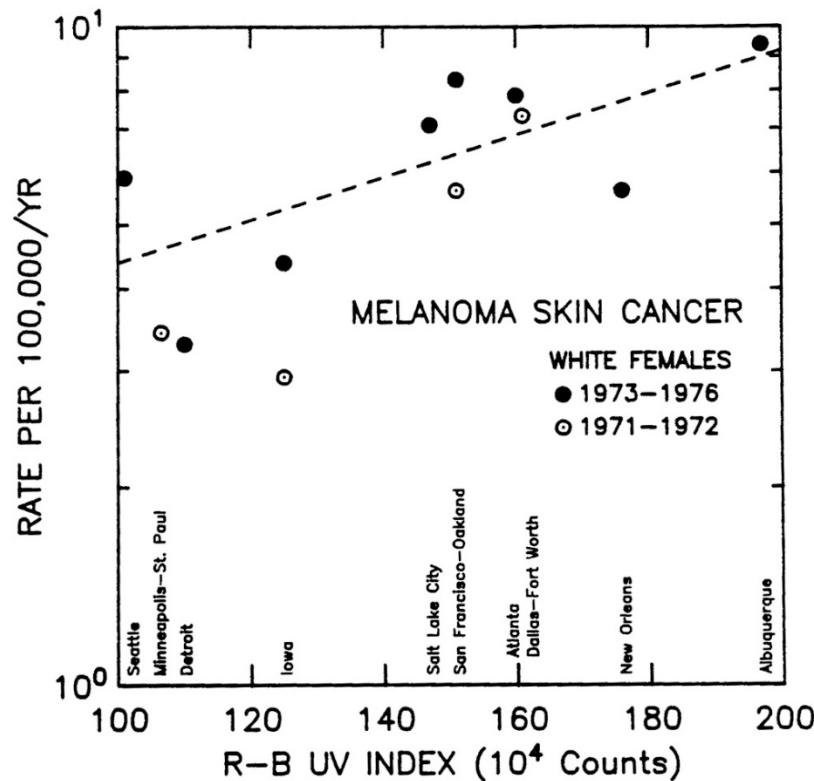
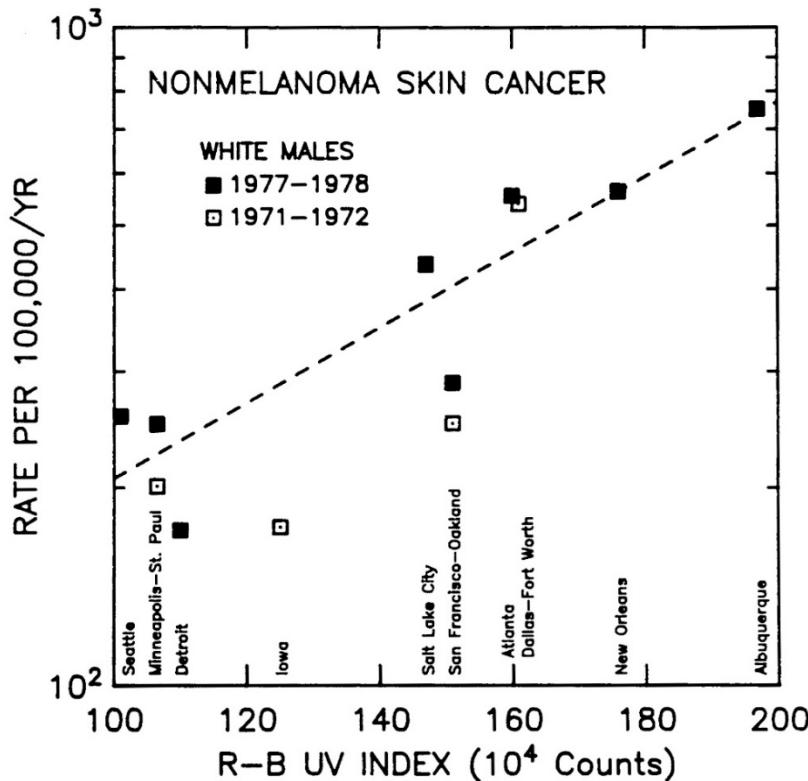
**The “biologically active dose rate” maximizes in the UV-B region at ~305 nm**

# Relationship Between Cancer and UV



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

# 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

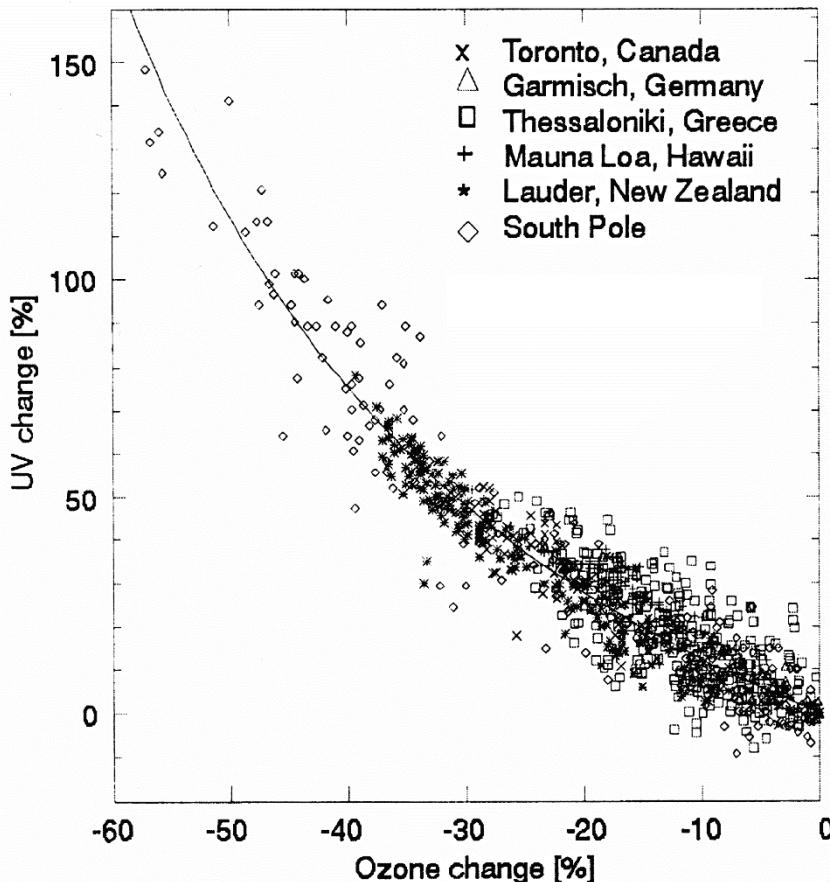


Fig. 2. Dependence of erythemal ultraviolet (UV) radiation at the Earth's surface on atmospheric ozone, measured on cloud-free days at various locations, at fixed solar zenith angles. Legend: South Pole [8]; Mauna Loa, Hawaii [9]; Lauder, New Zealand [10]; Thessaloniki, Greece (updated from Ref. [11]);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

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

# Relationship Between UV and Column Ozone

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

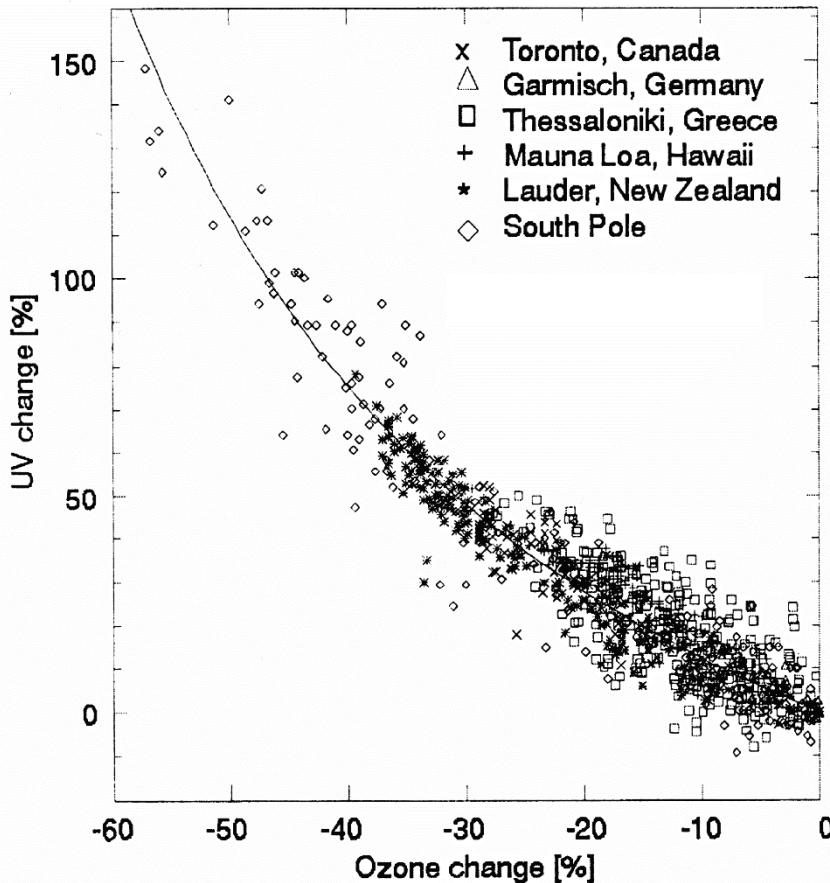


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50% drop in  $O_3$  leads to 100% rise in UV  
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Therefore, Melanoma Skin Cancer  
should rise by 2 % for every  
1 % drop in  $O_3$

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

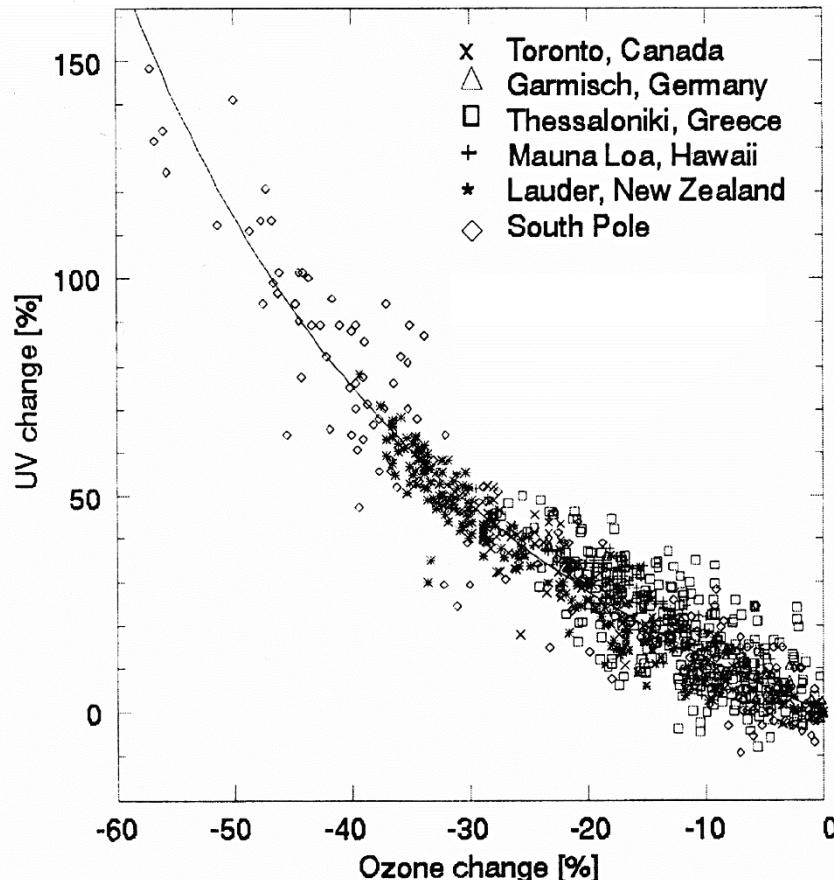
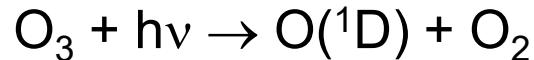


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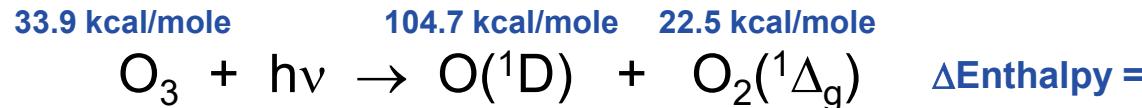
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# Energetics of Photolysis



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

Let's examine enthalpy of this reaction:



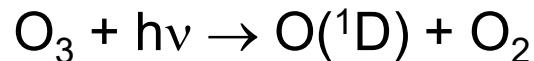
Photon Energy:

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

For  $\text{O}_3$  photo-dissociating to  $\text{O}({}^1\text{D})$ :

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

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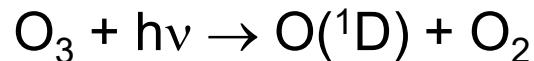
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# Energetics of Photodissociation



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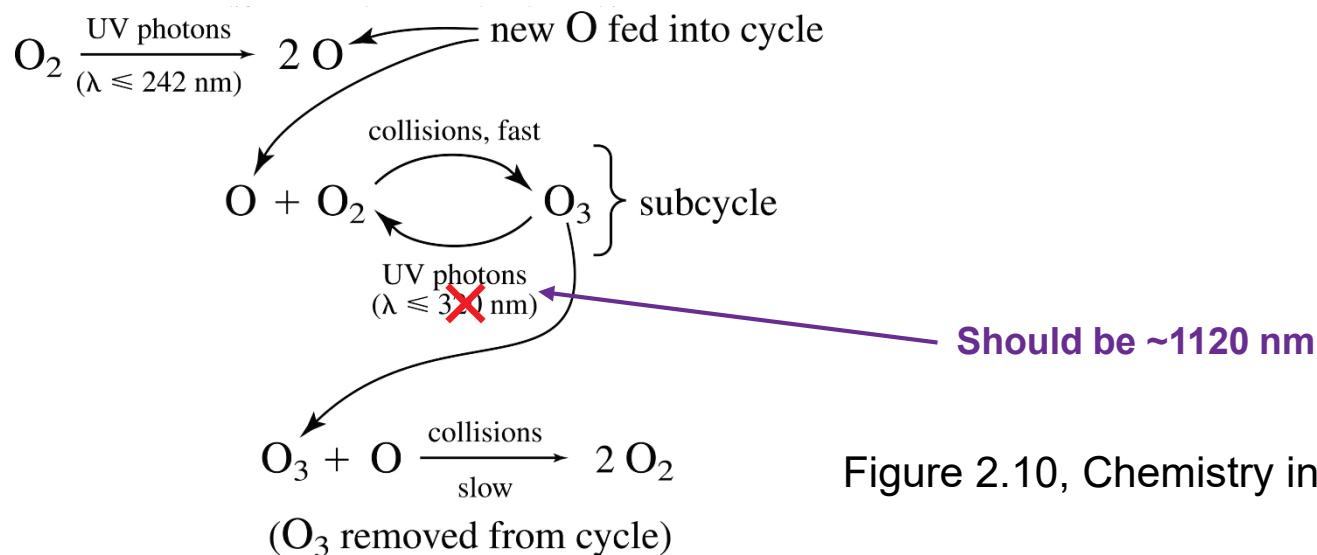


Figure 2.10, Chemistry in Context

# Energetics of Photodissociation



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

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

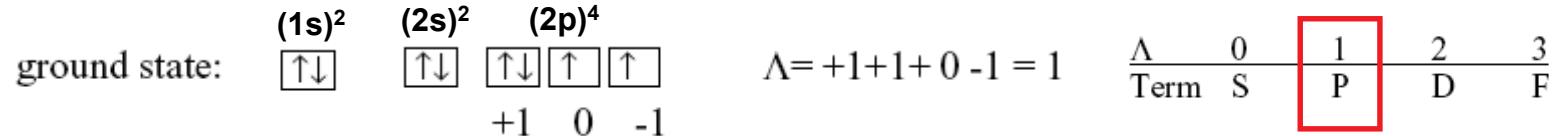
Called  ${}^3\text{P}$ :

“3” represents  $2S+1$ , where S is spin of all of the unpaired electrons.

There are 2 unpaired electrons, each with spin of  $\frac{1}{2}$

Hence,  $S = 1$  and  $2S+1 = 3 \Leftarrow$  spin angular momentum

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



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

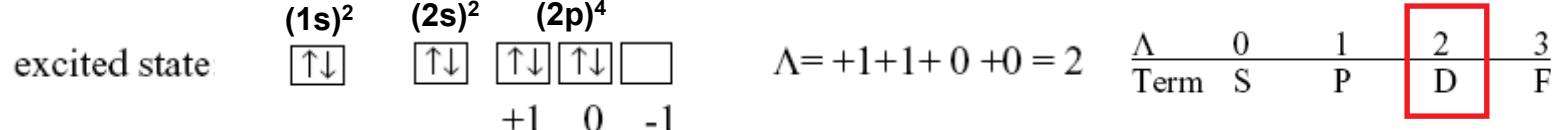
Called  ${}^1\text{D}$ :

“1” represents  $2S+1$ , where S is spin of all of the unpaired electrons.

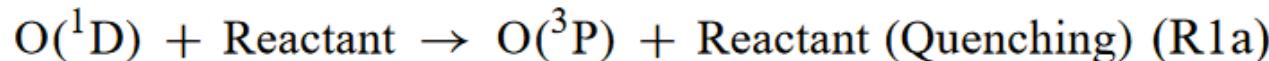
There are no unpaired electrons!

Hence,  $S = 0$  and  $2S+1 = 1 \Leftarrow$  spin angular momentum

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



# Energetics of Photodissociation



Baasandorj *et al.*, ACP, 2012

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

Called **1D**:

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

There are no unpaired electrons!

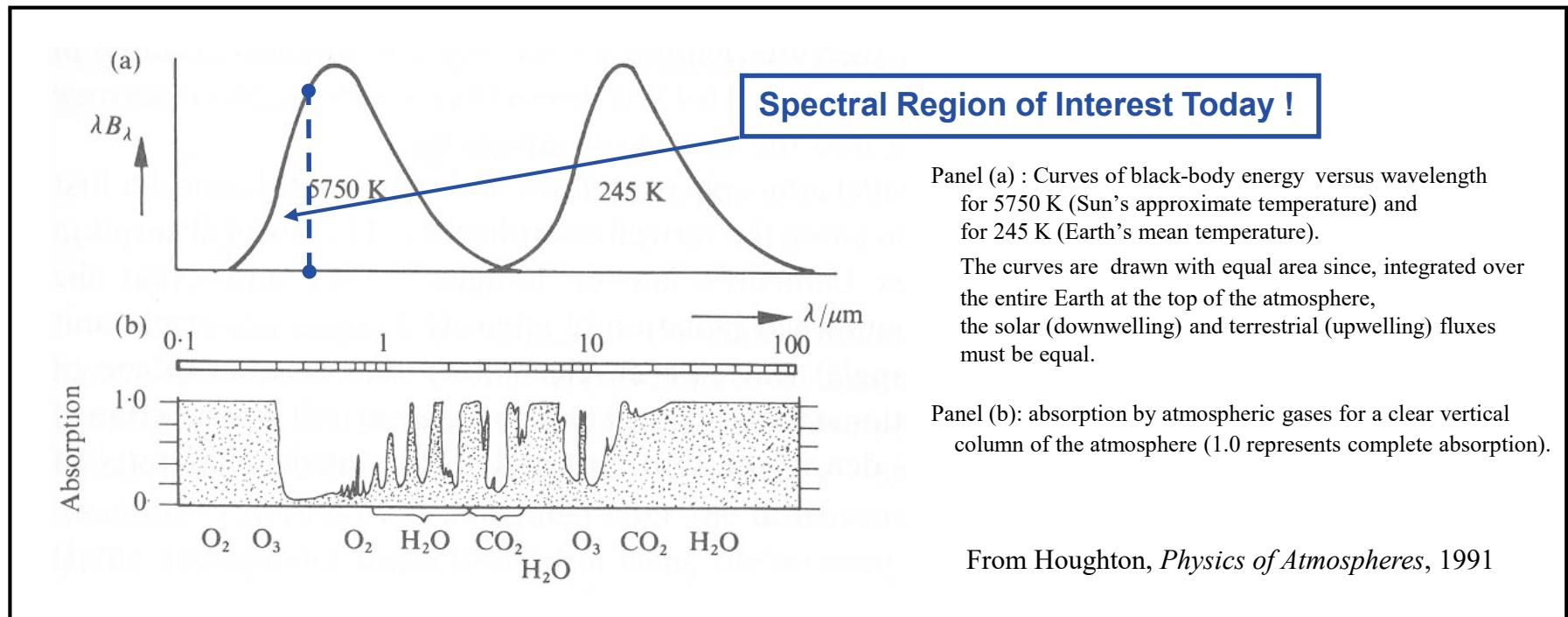
Hence,  $S = 0$  and  $2S+1 = 1 \Leftarrow$  spin angular momentum

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

	$(1s)^2$	$(2s)^2$	$(2p)^4$		$\Lambda = +1 + 1 + 0 + 0 = 2$	$\frac{\Lambda}{\text{Term}}$	0	1	2	3
excited state						S	P	D	F	
				$+1 \quad 0 \quad -1$						

# Atmospheric Radiation

- Solar irradiance (downwelling) at top of atmosphere occurs at wavelengths between  $\sim 200$  and  $2000$  nm ( $\sim 5750$  K “black body” temperature)

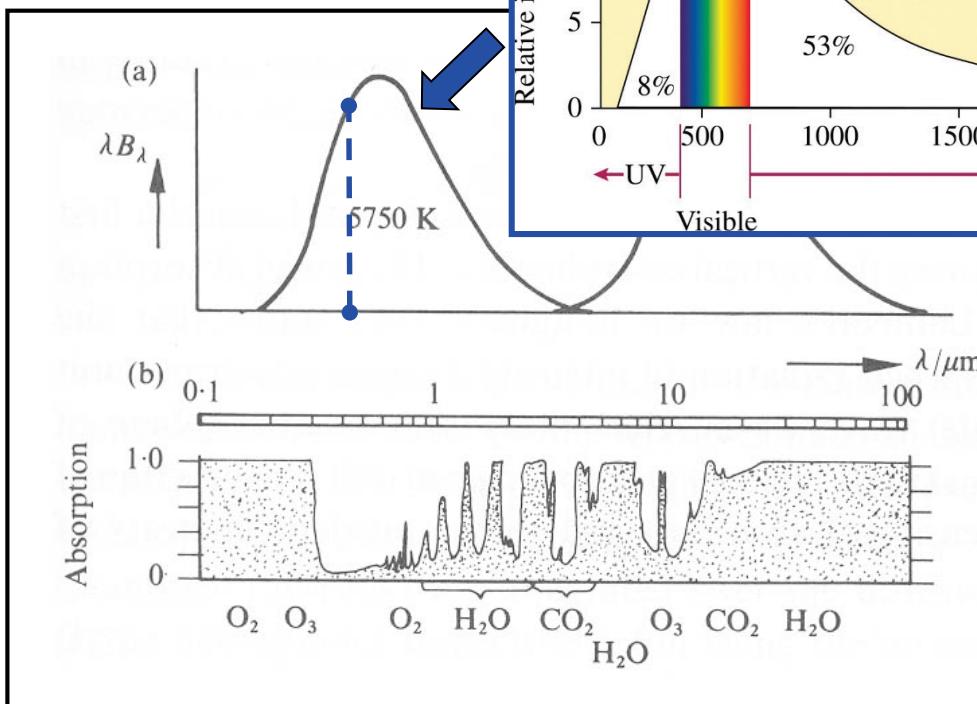


- Absorption and photodissociation in the UV occurs due to changes in the electronic state (orbital configuration) of molecules

Figure 2.8, Chemistry in Context

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- Solar irradiance (downwelling radiation) between  $\sim 200$  and  $2000\text{ nm}$



for  $5750\text{ K}$  (Sun's approximate temperature), and  
for  $245\text{ K}$  (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:

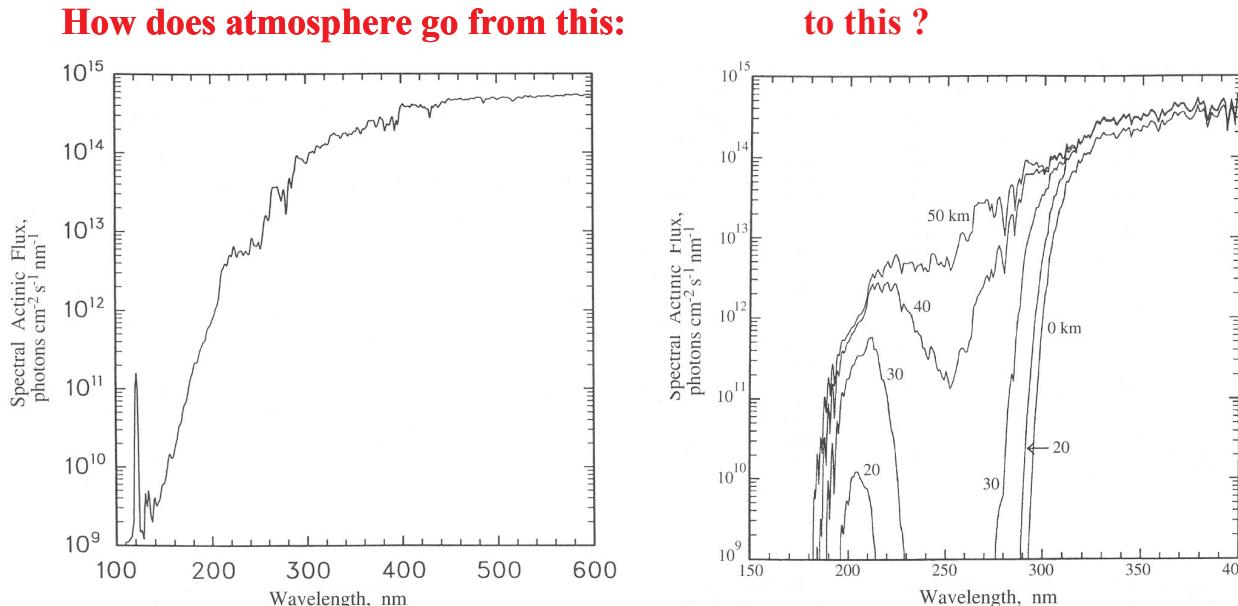
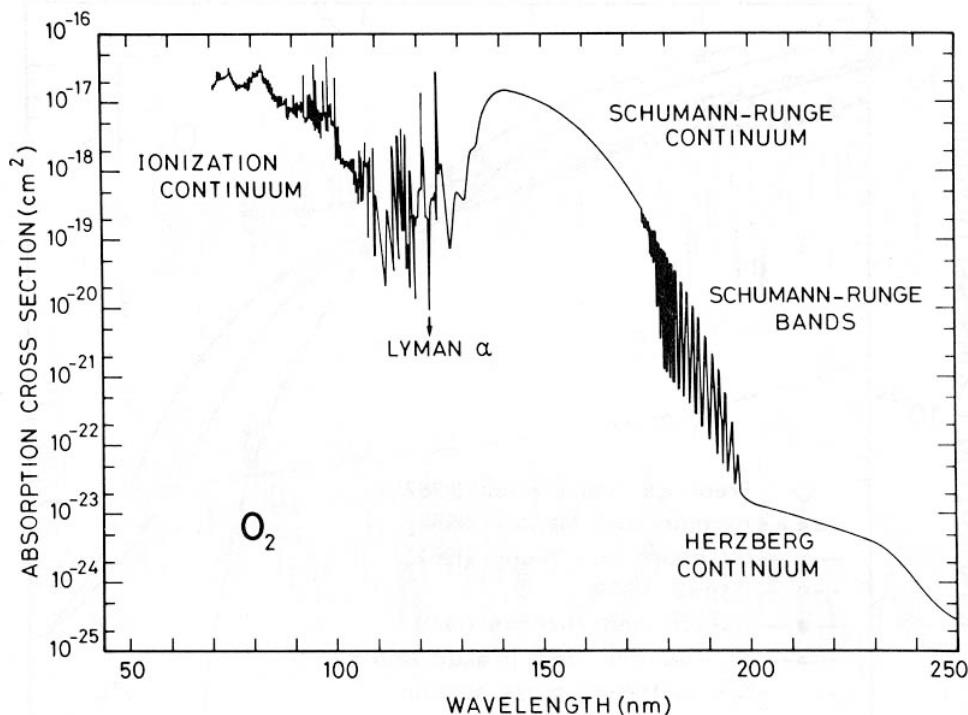


FIGURE 3.3 Solar spectral actinic flux ( $\text{photons cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$ ) at various altitudes and at the Earth's surface (DeMore et al., 1994).

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.

# Absorption Cross Section of O<sub>2</sub>



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

- O<sub>2</sub> 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<sub>2</sub> 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

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

where:

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

$F$  : solar irradiance (photons/cm<sup>2</sup>/sec)

$\sigma_{\lambda}$  : absorption cross section (cm<sup>2</sup>/molecule)

$C$  : concentration of absorbing gas (molecules/cm<sup>3</sup>)

$m$  : ratio of slant path to vertical path, equal to  $1/\cos(\theta)$  for  $\theta < \sim 75^\circ$

$\theta$  : 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:

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

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

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

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

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

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

*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<sub>2</sub> Absorption

Recall the *Beer-Lambert Law*:

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

where:

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

Also:

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

O <sub>2</sub> Optical Depth for $\theta = 0^\circ$ , $z = 0 \text{ km}$		
$\sigma_{\text{max}} (\text{cm}^2)$	$\tau (0 \text{ km})$	$e^{-\tau (0 \text{ km})}$
Schumann-Runge Continuum		
Schumann-Runge Bands		
Herzberg Continuum		

# Optical Depth of O<sub>2</sub> Absorption

Recall the *Beer-Lambert Law*:

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	$\sigma_{\text{max}} (\text{cm}^2)$	$\tau (0 \text{ km})$
Schumann-Runge Continuum	$10^{-17}$	$e^{-\tau (0 \text{ km})}$
Schumann-Runge Bands		
Herzberg Continuum		

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O <sub>2</sub> Optical Depth for $\theta = 0^\circ$ , $z = 0 \text{ km}$			
	$\sigma_{\text{max}} (\text{cm}^2)$	$\tau (0 \text{ km})$	$e^{-\tau (0 \text{ km})}$
Schumann-Runge Continuum	$10^{-17}$	$4 \times 10^7$	0.
Schumann-Runge Bands			
Herzberg Continuum			

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O <sub>2</sub> Optical Depth for $\theta = 0^\circ$ , $z = 0 \text{ km}$			
	$\sigma_{\text{max}} (\text{cm}^2)$	$\tau (0 \text{ km})$	$e^{-\tau (0 \text{ km})}$
Schumann-Runge Continuum	$10^{-17}$	$4 \times 10^7$	0.
Schumann-Runge Bands	$10^{-20}$		
		$3 \times 10^{-23}$	
Herzberg Continuum			

# Optical Depth of O<sub>2</sub> Absorption

Recall the *Beer-Lambert Law*:

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O <sub>2</sub> Optical Depth for $\theta = 0^\circ$ , $z = 0 \text{ km}$			
	$\sigma_{\text{max}} (\text{cm}^2)$	$\tau (0 \text{ km})$	$e^{-\tau (0 \text{ km})}$
Schumann-Runge Continuum	$10^{-17}$	$4 \times 10^7$	0.
Schumann-Runge Bands	$10^{-20}$	$4 \times 10^4$	0.
	$3 \times 10^{-23}$	120	$7.6 \times 10^{-53}$
Herzberg Continuum			

# Optical Depth of O<sub>2</sub> Absorption

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Herzberg Continuum	$10^{-23}$	40	$4.2 \times 10^{-18}$

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Also:

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

**Optically Thick !**

O <sub>2</sub> Optical Depth for $\theta = 0^\circ$ , $z = 0 \text{ km}$			
	$\sigma_{\max} (\text{cm}^2)$	$\tau (0 \text{ km})$	$e^{-\tau (0 \text{ km})}$
Schumann-Runge Continuum	$10^{-17}$	$4 \times 10^7$	0.
Schumann-Runge Bands	$10^{-20}$	$4 \times 10^4$	0.
	$3 \times 10^{-23}$	120	$7.6 \times 10^{-53}$
Herzberg Continuum	$10^{-23}$	40	$4.2 \times 10^{-18}$



# Photolysis Frequency of O<sub>2</sub>

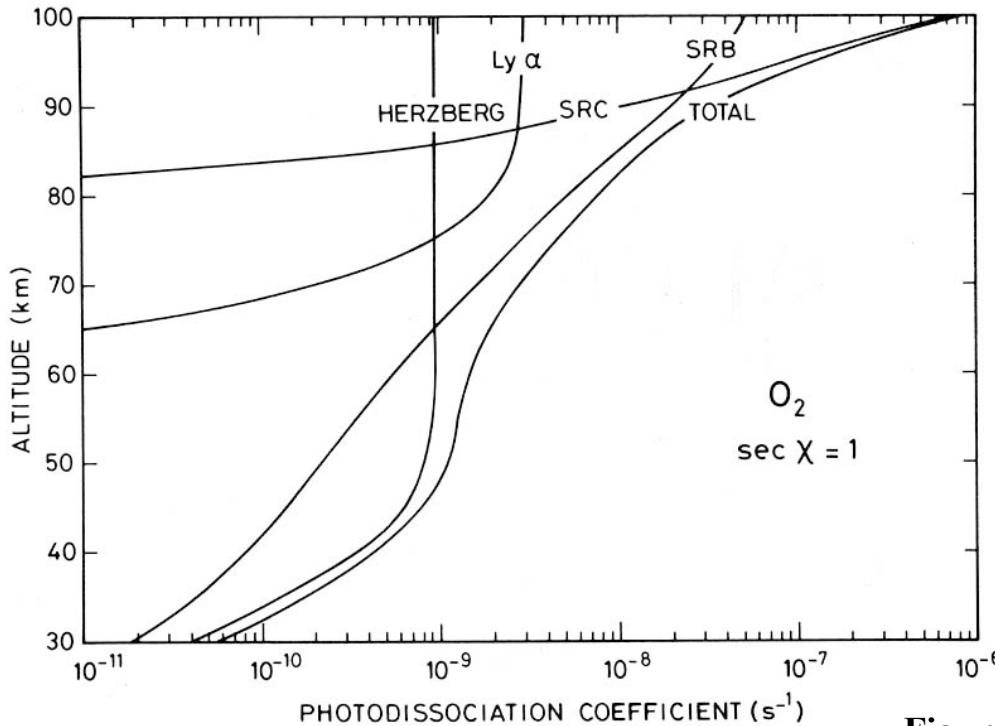


Figure 4.31, Brasseur and Solomon

O <sub>2</sub> Optical Depth for $\theta = 0^\circ$ , $z = 0$ km			
	$\sigma_{\max}$ (cm <sup>2</sup> )	$\tau$ (0 km)	$e^{-\tau}$ (0 km)
Schumann-Runge Continuum	$10^{-17}$	$4 \times 10^7$	0.
Schumann-Runge Bands	$10^{-20}$	$4 \times 10^4$	0.
	$3 \times 10^{-23}$	120	$7.6 \times 10^{-53}$
Herzberg Continuum	$10^{-23}$	40	$4.2 \times 10^{-18}$

# Where Does Optical Depth = 1.0 for O<sub>2</sub> ?

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

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

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

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

Altitude where $\tau = 1$ (for $\theta = 0^\circ$ )	
	$\sigma_{\max} (\text{cm}^2)$
Schumann-Runge Continuum	$10^{-17}$
Schumann-Runge Bands	$10^{-20}$
	$3 \times 10^{-23}$
Herzberg Continuum	$10^{-23}$

# Where Does Optical Depth = 1.0 for O<sub>2</sub> ?

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

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

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

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

# Absorption Cross Section of O<sub>3</sub>

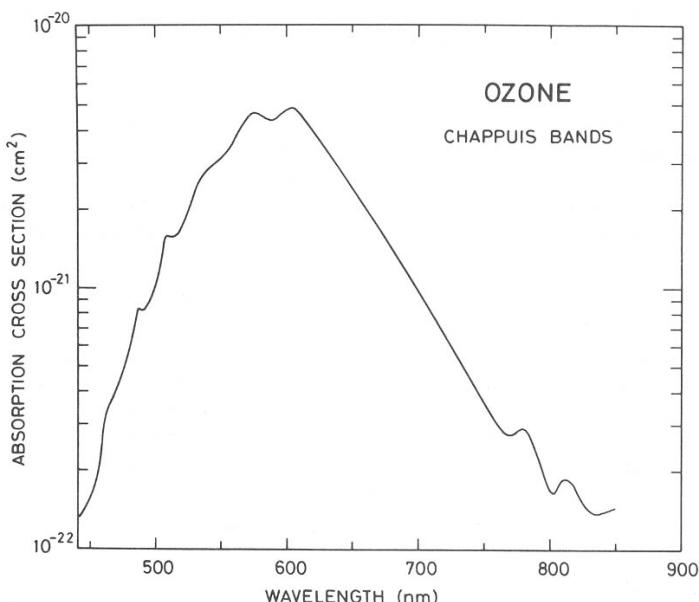
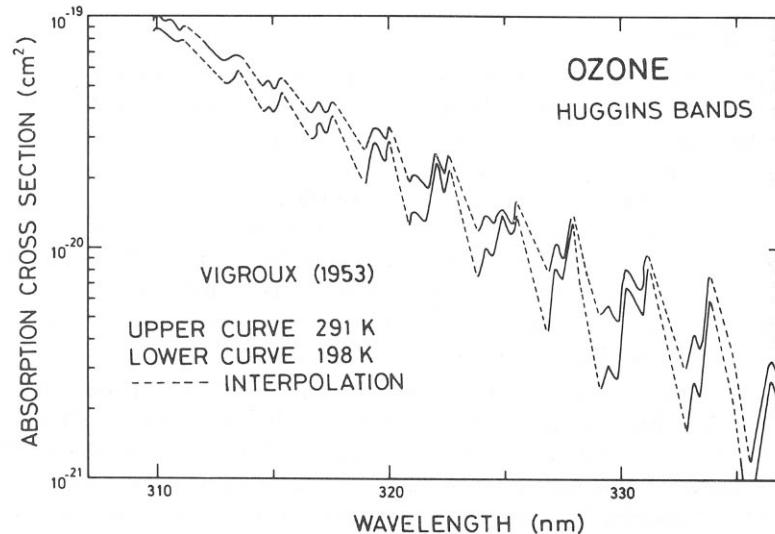
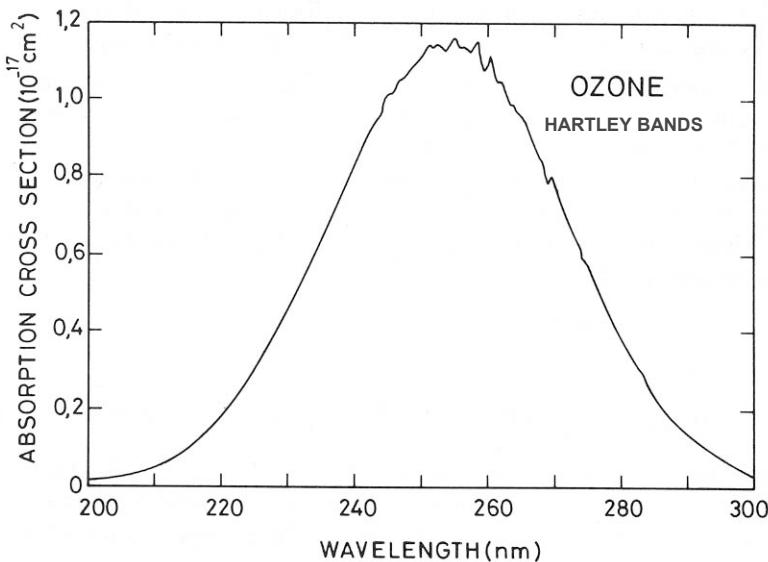
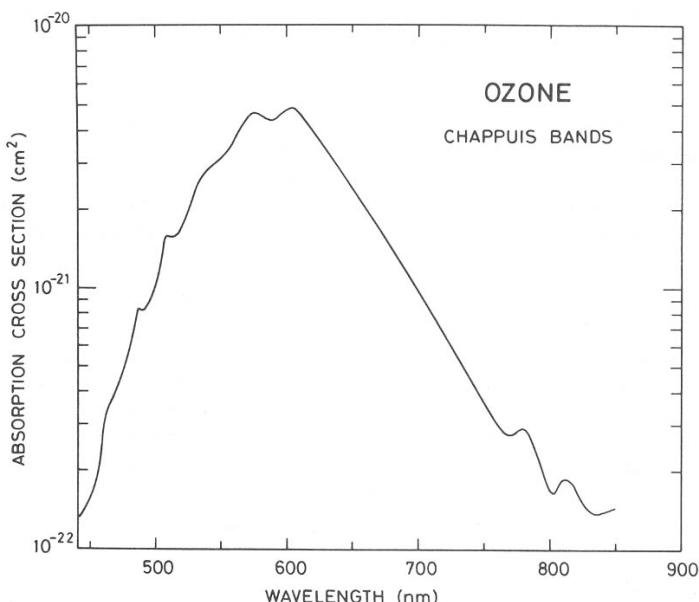
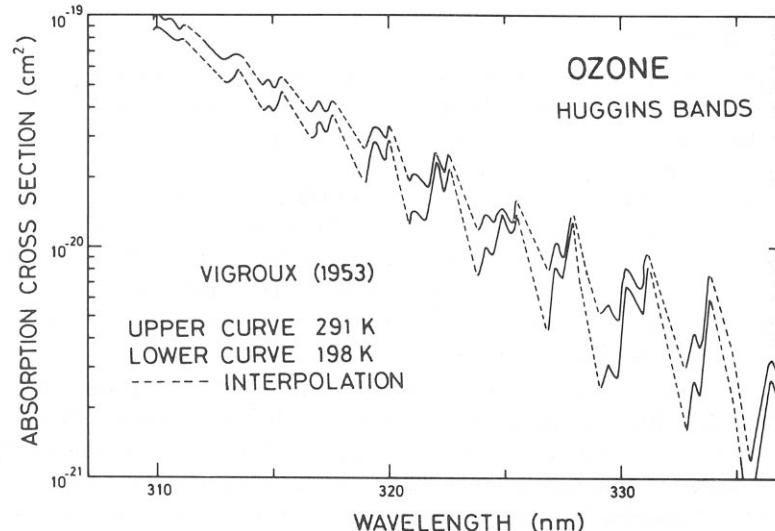
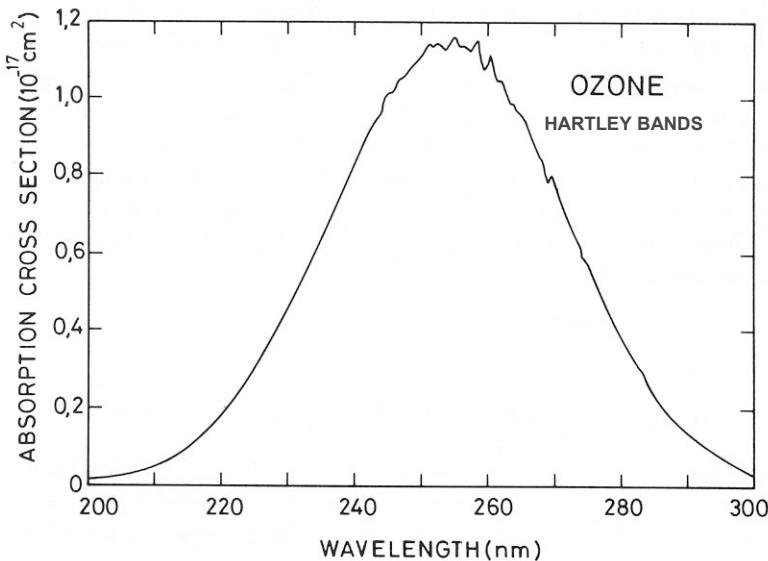


Table 4.6 Theoretical limits corresponding to different photolysis products (nm).

	O <sub>2</sub> ( $^3\Sigma_g$ )	O <sub>2</sub> ( $^1\Delta_g$ )	O <sub>2</sub> ( $^1\Sigma_g +$ )	O <sub>2</sub> ( $^3\Sigma_u +$ )	O <sub>2</sub> ( $^3\Sigma_u^-$ )
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

# Absorption Cross Section of O<sub>3</sub>



## Quantum Mechanically Allowed Transitions

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

	O <sub>2</sub> ( <sup>3</sup> $\Sigma_g$ )	O <sub>2</sub> ( <sup>1</sup> $\Delta_g$ )	O <sub>2</sub> ( <sup>1</sup> $\Sigma_g +$ )	O <sub>2</sub> ( <sup>3</sup> $\Sigma_u +$ )	O <sub>2</sub> ( <sup>3</sup> $\Sigma_u^-$ )
O( <sup>3</sup> P)	1180				
O( <sup>1</sup> D)	410	590		230	170
O( <sup>1</sup> S)	234	310	179	167	150
		196		129	108

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

# Optical Depth of O<sub>3</sub> Absorption

A typical mid-latitude column abundance for O<sub>3</sub> 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:

$$\frac{\text{Column O}_3}{\text{Column Air}} = \frac{8 \times 10^{18}}{2 \times 10^{25}} = 0.4 \text{ parts per million} \Rightarrow \text{Ozone is a trace species!}$$

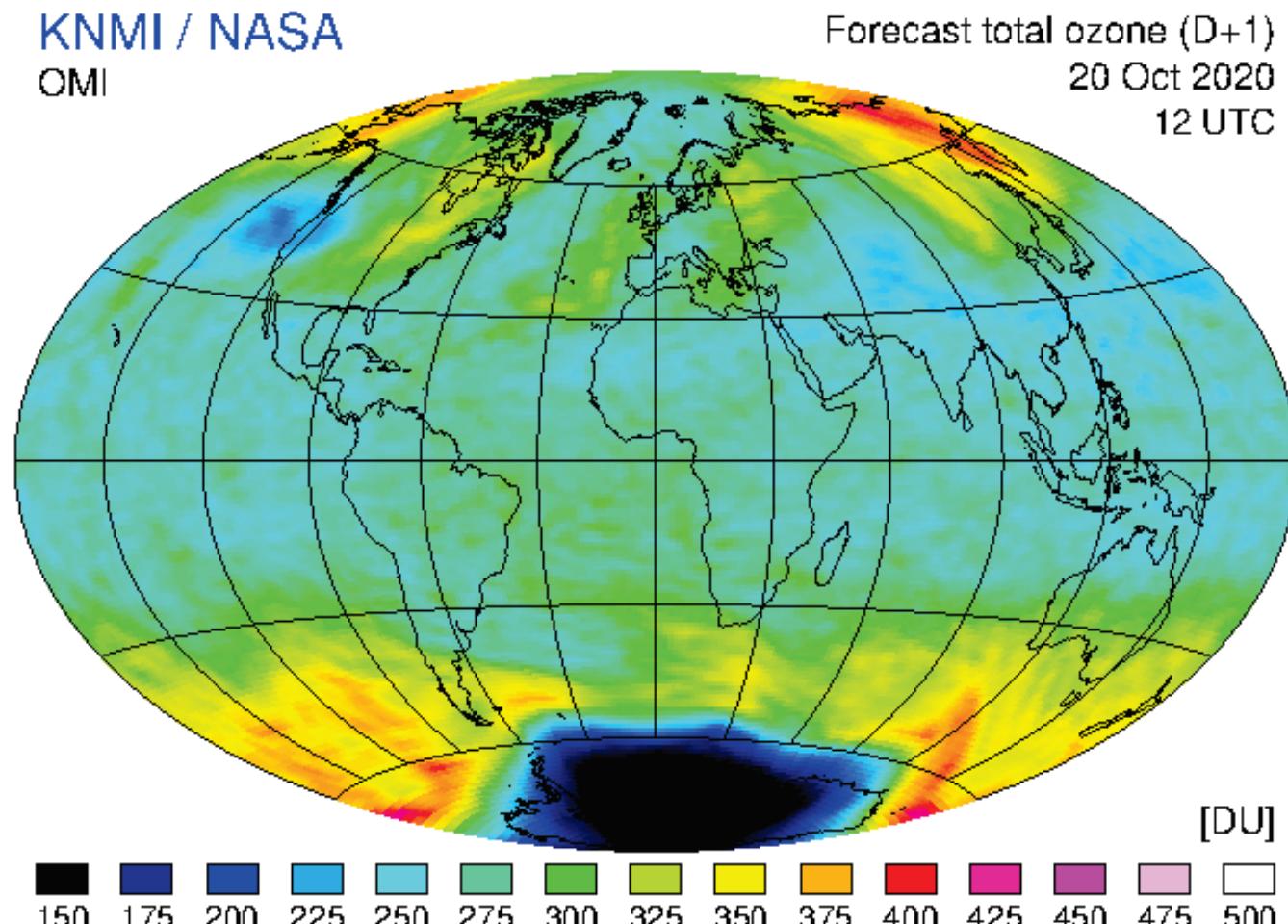
## O<sub>3</sub> Optical Depth for $\theta = 0^\circ$ , $z = 0 \text{ km}$

	$\sigma_{\max} (\text{cm}^2)$	$\tau (0 \text{ km})$	$e^{-\tau (0 \text{ km})}$	O <sub>3</sub> 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>

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Hartley (~220 to 280 nm)	$10^{-17}$	80	$1.8 \times 10^{-35}$	3.7 DU
Huggins (~310 to 330 nm)				
Chappuis (~500 to 700 nm)				

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O <sub>3</sub> Optical Depth for $\theta = 0^\circ$ , z = 0 km				
	$\sigma_{\max} (\text{cm}^2)$	$\tau (0 \text{ km})$	$e^{-\tau (0 \text{ km})}$	O <sub>3</sub> Column, $\tau = 1.0$
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Huggins (~310 to 330 nm)	$10^{-19}$	0.8	0.45	372 DU
Chappuis (~500 to 700 nm)	$3 \times 10^{-21}$	0.024	$\sim 1.0$	12,400 DU

# Optical Depth of O<sub>3</sub> Absorption

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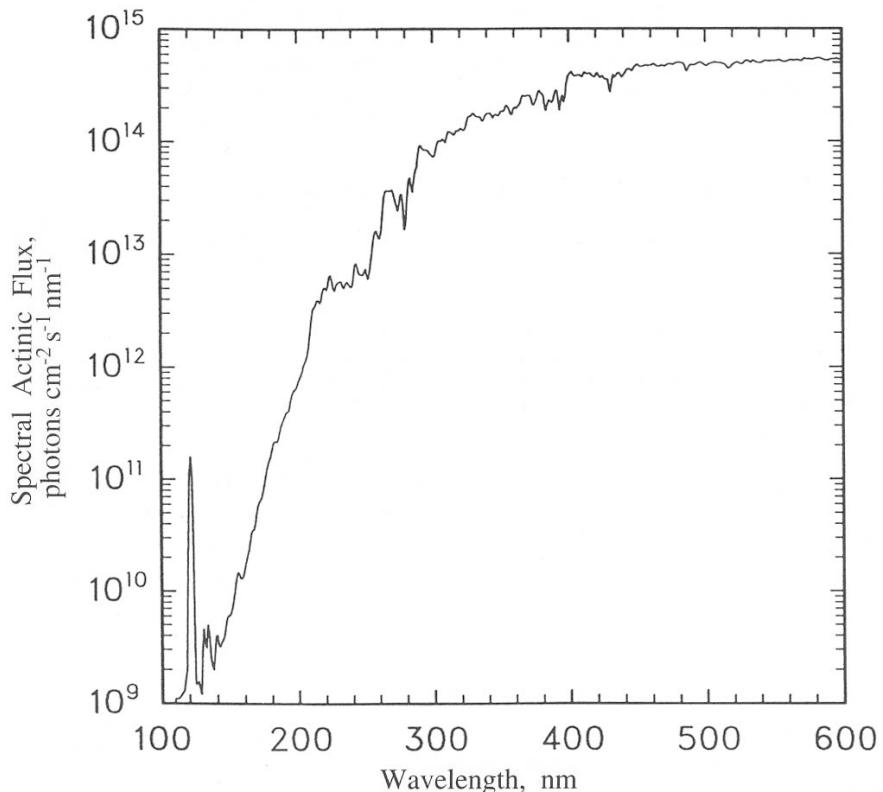
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Chappuis (~500 to 700 nm)	$3 \times 10^{-21}$	0.024	~1.0	12,400 DU

Optically Thin!

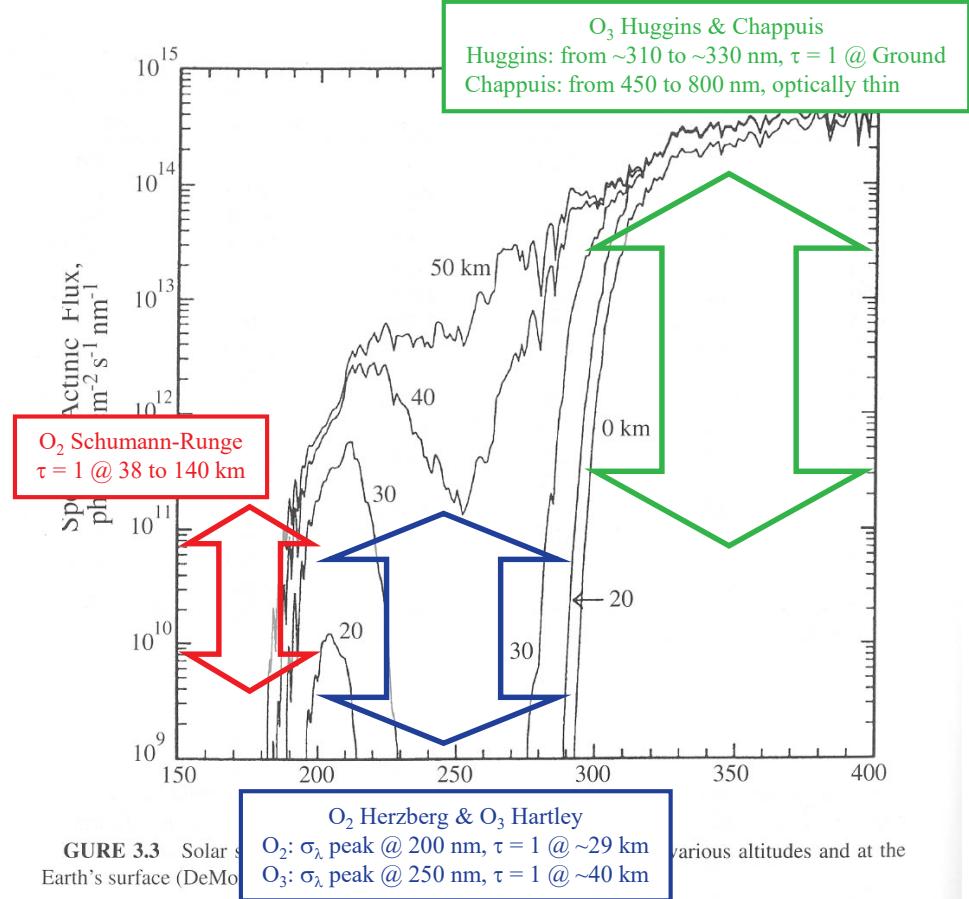
# Solar Spectral Actinic Flux

130 ATMOSPHERIC PHOTOCHEMISTRY AND CHEMICAL KINETICS



**FIGURE 6.** Solar spectral actinic flux ( $\text{photons cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$ ) 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.

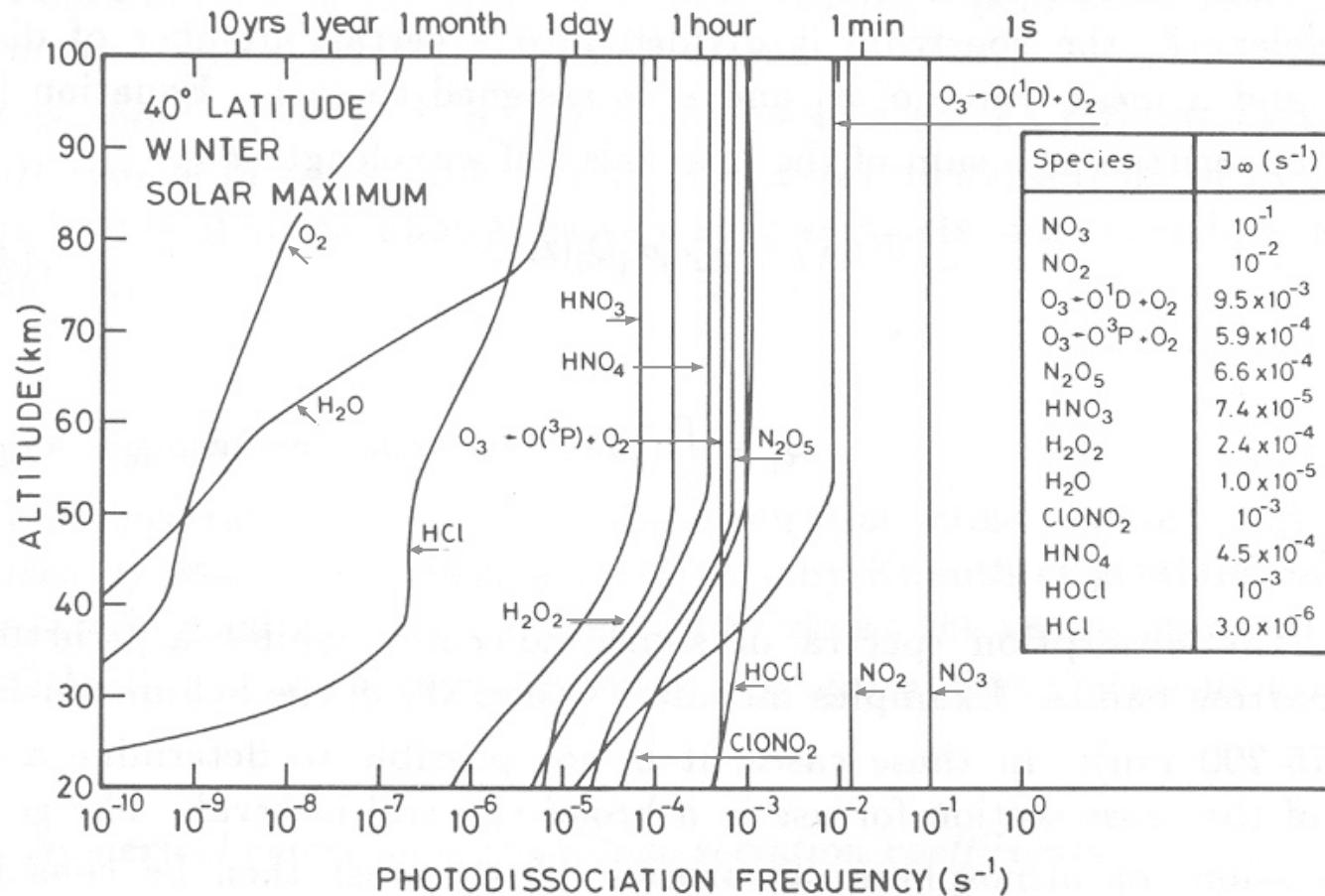


**FIGURE 3.3** Solar spectral actinic flux ( $\text{photons cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$ ) at various altitudes and at the Earth's surface (DeMore et al., 1994).

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

# Photodissociation Frequencies

Next goal is to understand:

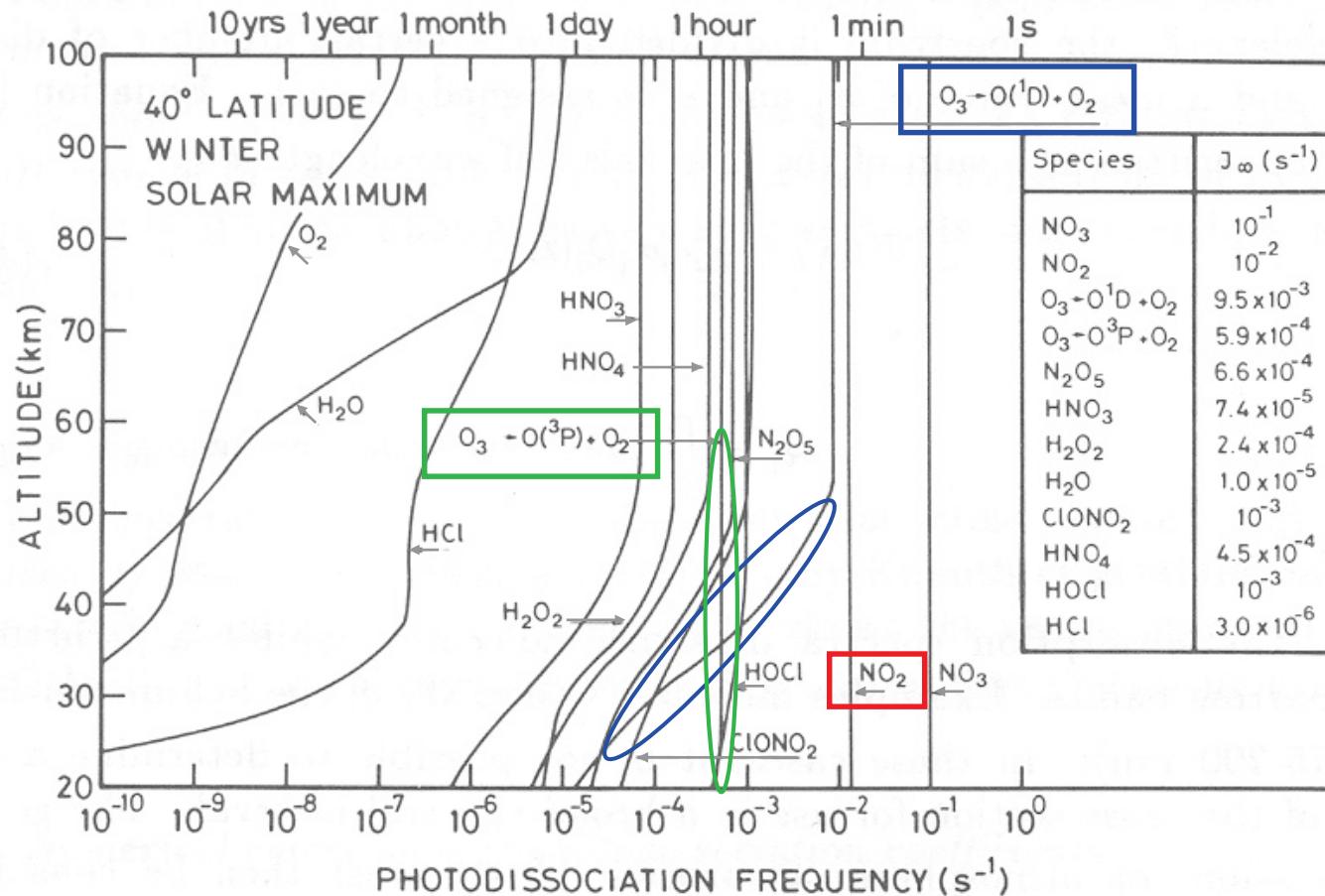


**FIGURE 4.58** Photodissociation frequencies for numerous important atmospheric species.

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

# Photodissociation Frequencies

Next goal is to understand:

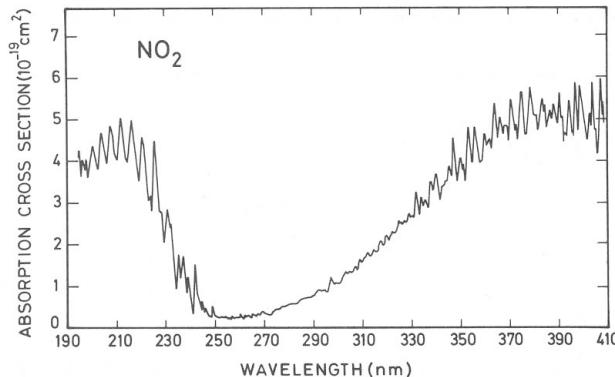


**FIGURE 4.58** Photodissociation frequencies for numerous important atmospheric species.

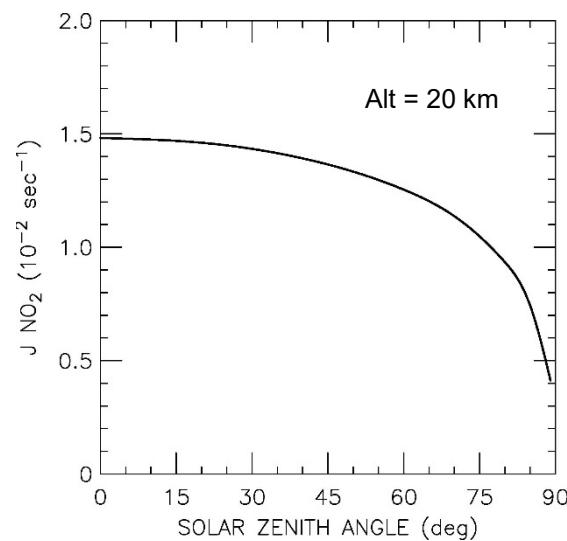
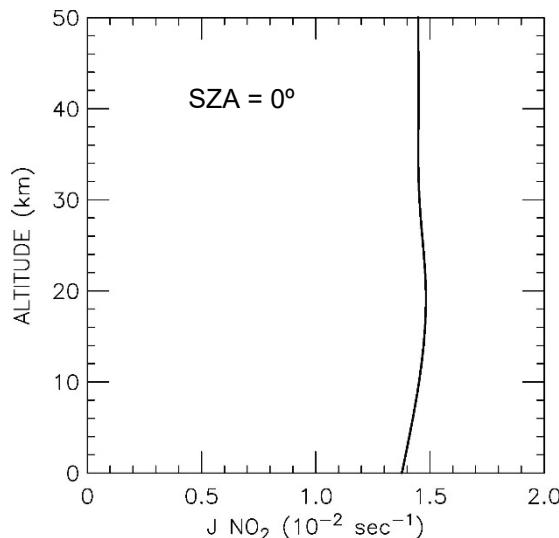
From Brasseur & Solomon, *Aeronomy of the Middle Atmosphere*, 1986

# $\text{NO}_2$ Photolysis

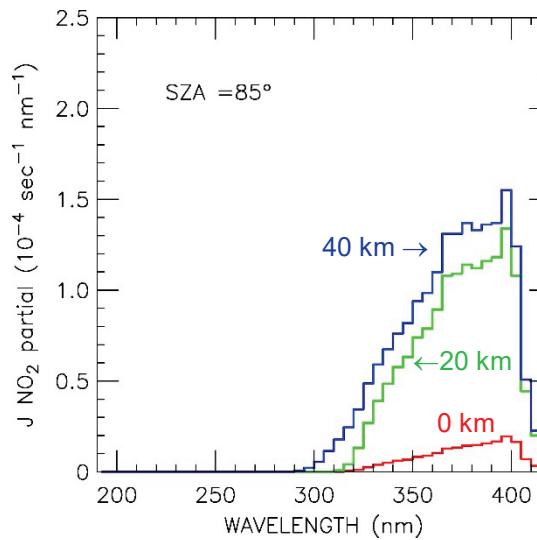
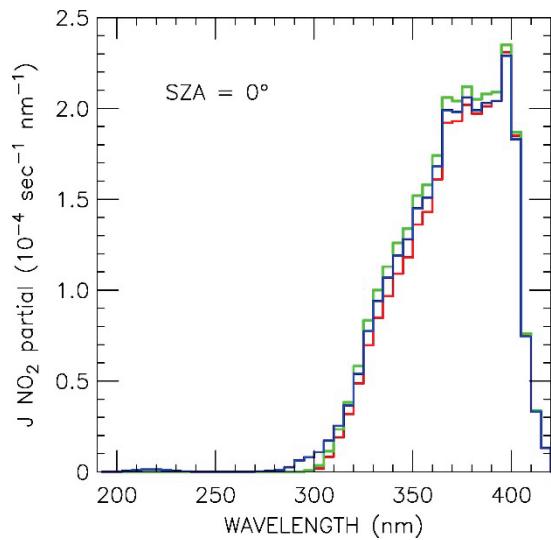
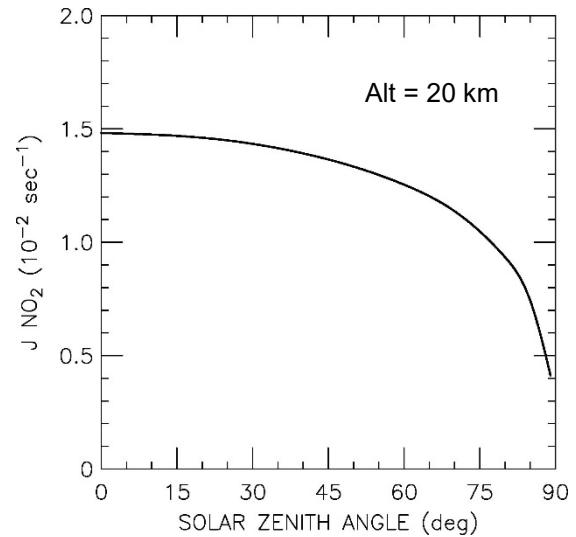
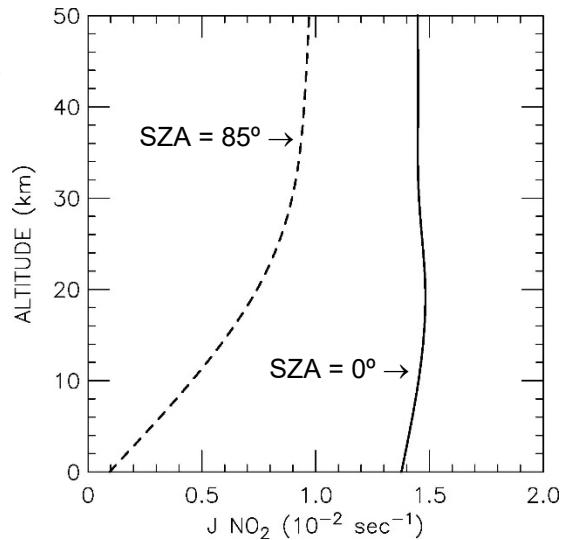
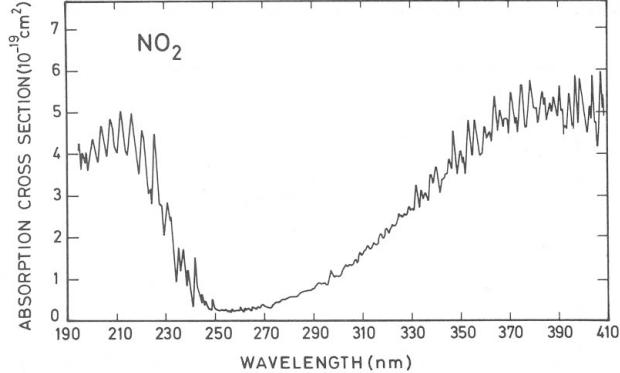
The majority of  $\text{NO}_2$  photolysis occurs longward of 300 nm, where the atmosphere is optically thin with respect to absorption by  $\text{O}_3$  and  $\text{O}_2$ :



leading to a value for  $J_{\text{NO}_2}$  that is nearly independent of height and SZA:

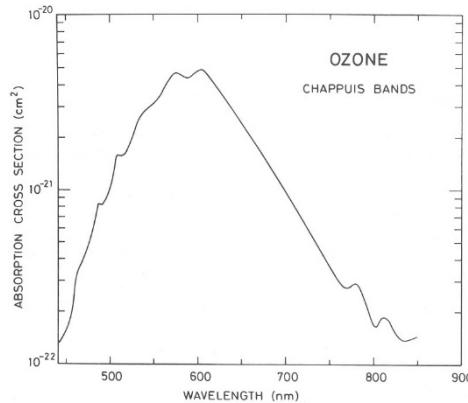


# NO<sub>2</sub> Photolysis

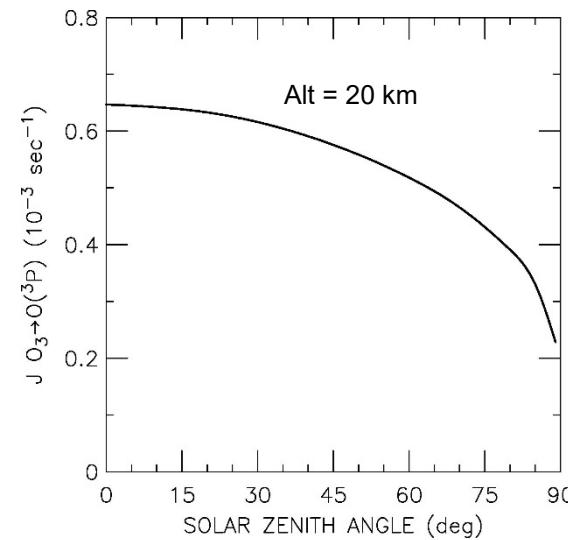
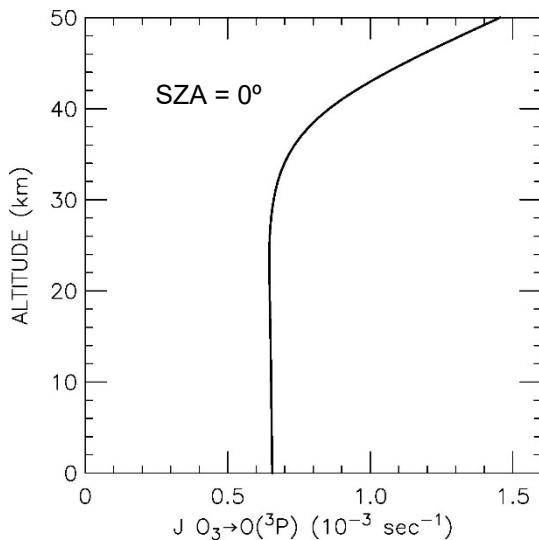


# $O_3 \rightarrow O(^3P)$ Photolysis

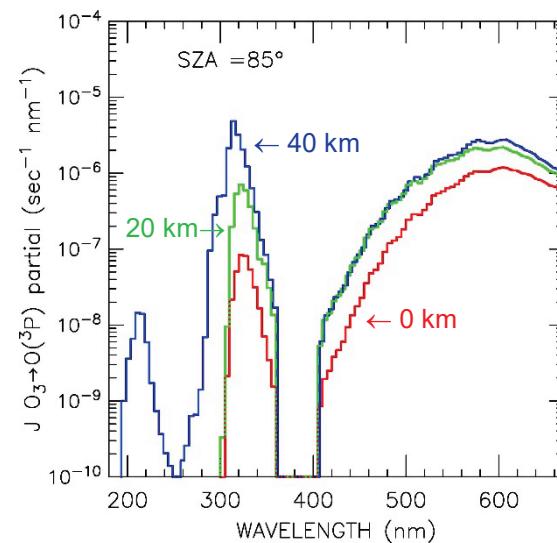
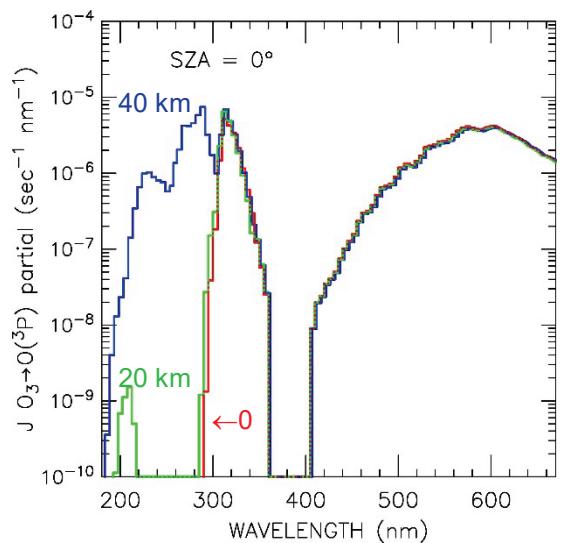
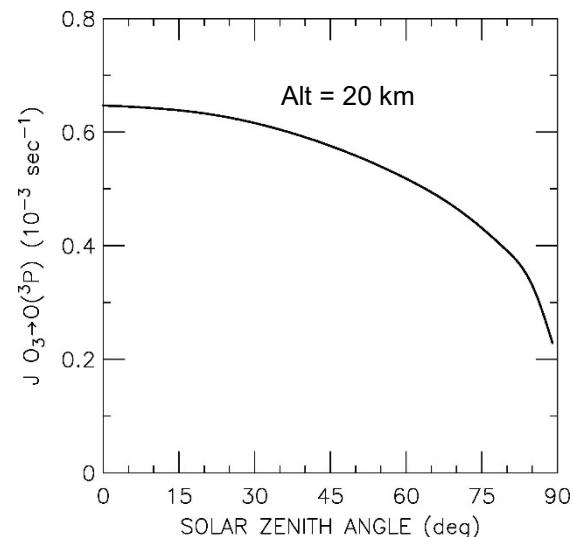
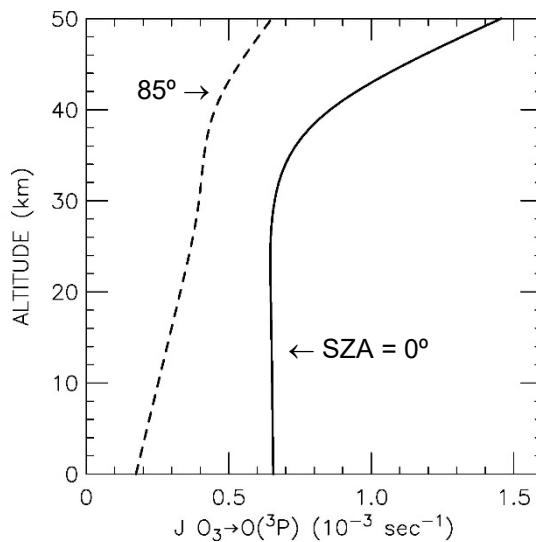
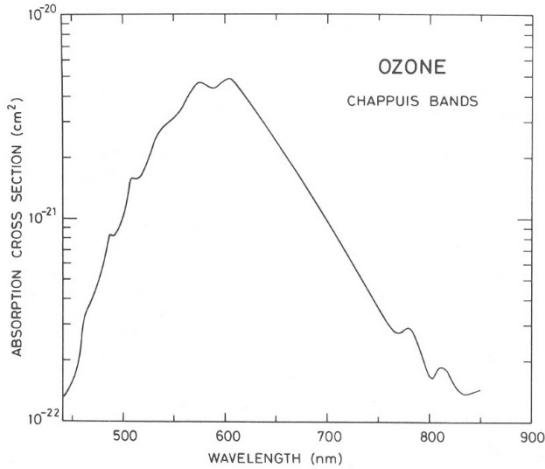
The production of  $O(^3P)$  from photolysis of  $O_3$  occurs mainly longward of 500 nm, where the atmosphere is optically thin with respect to absorption by  $O_3$ :



leading to a value for  $J_{O_3 \rightarrow O(^3P)}$  that is essentially independent of height and SZA:

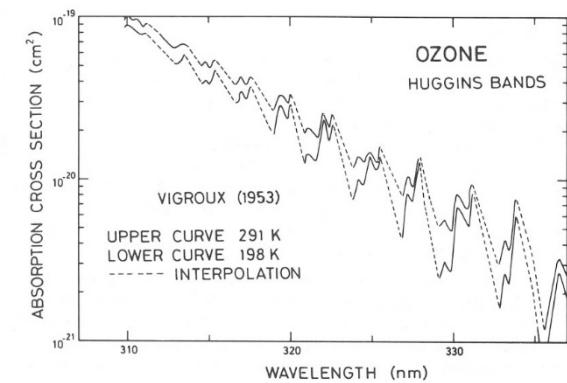
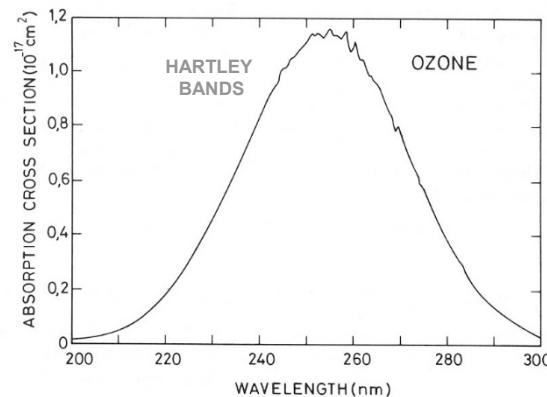
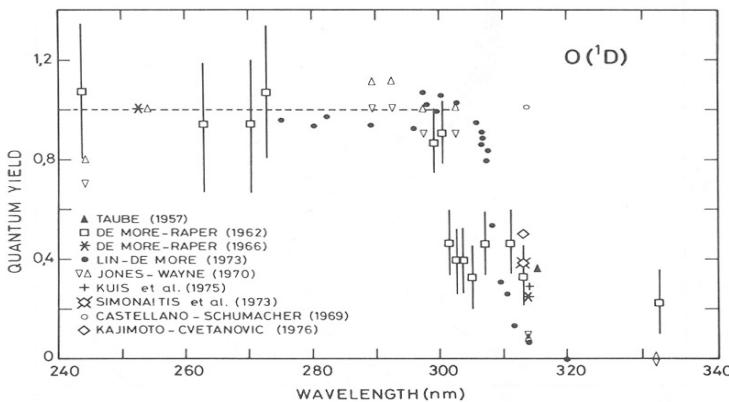


# $O_3 \rightarrow O(^3P)$ Photolysis

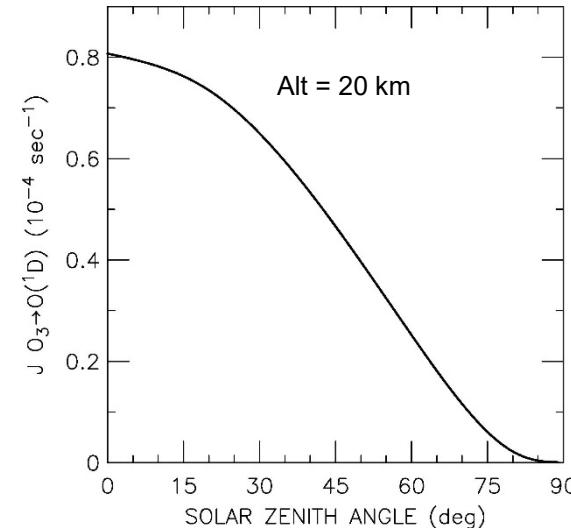
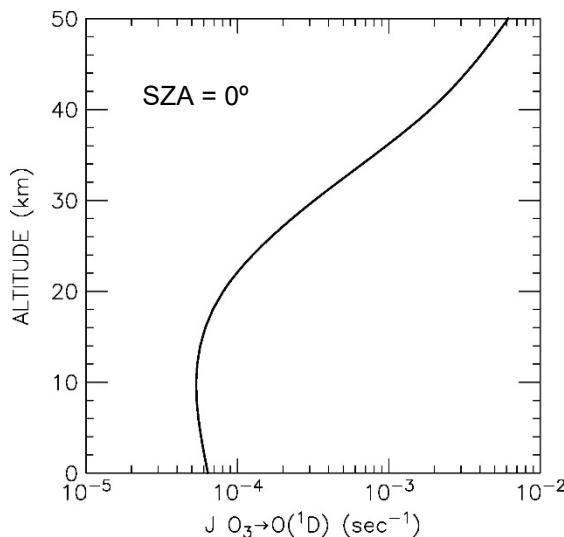


# $O_3 \rightarrow O(^1D)$ Photolysis

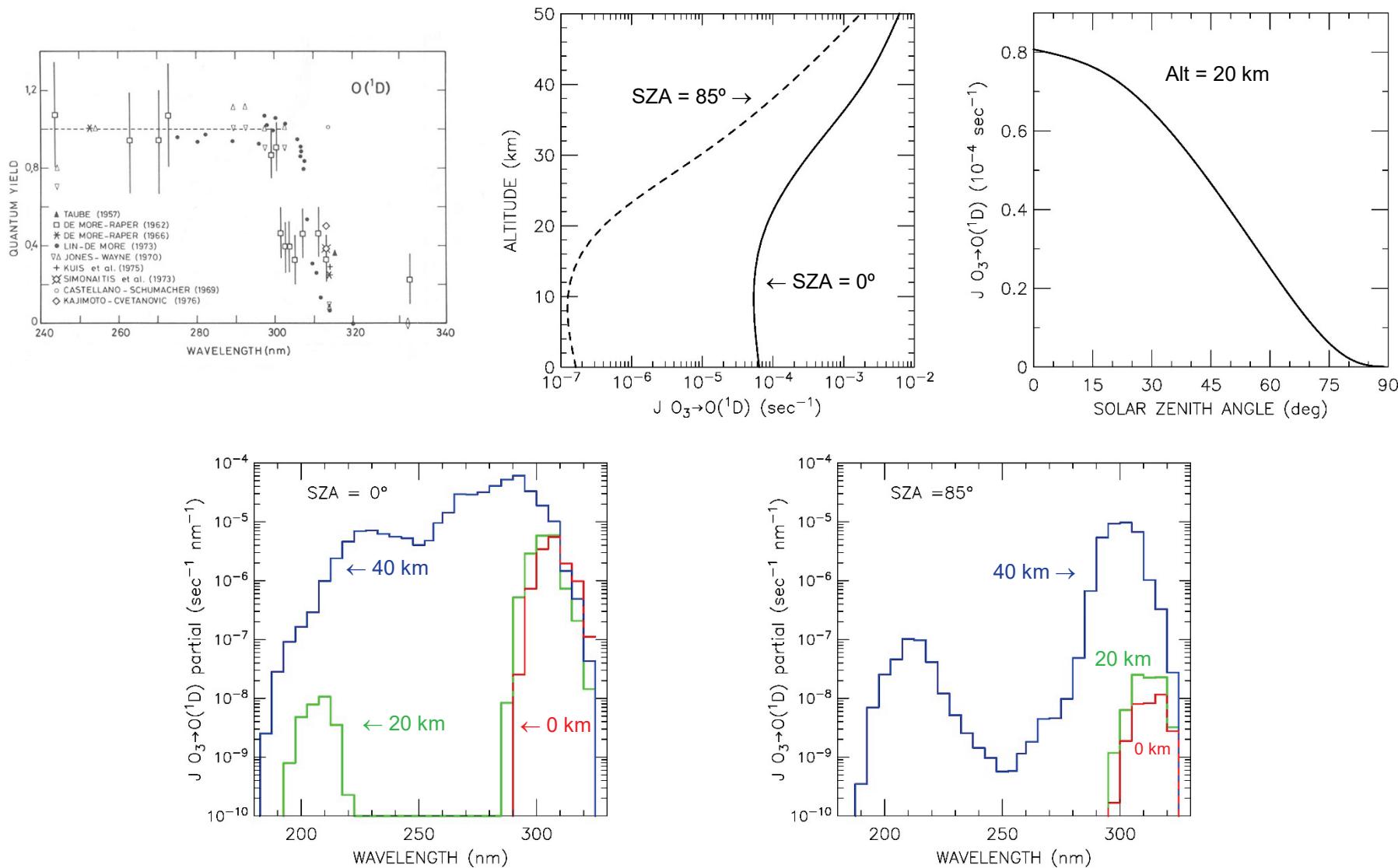
The production of  $O(^1D)$  from photolysis of  $O_3$  occurs shortward of 320 nm, where the atmosphere is basically optically thick with respect to absorption by  $O_3$ :



leading to a value for  $J_{O_3 \rightarrow O(^1D)}$  that is dependent on height and SZA:



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



## Extra #1: Height and Abundance of Ozone

Chapman expression for  $[O_3]$  :

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

*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  $J_1 [O_2]$  :  $\sim 35$  km

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

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

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

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

where:

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

# 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**):

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

Assume:

1.  $O_2$  is the only absorber:

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

2.  $\sigma_{O_2}$  is independent of T:

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

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

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

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

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

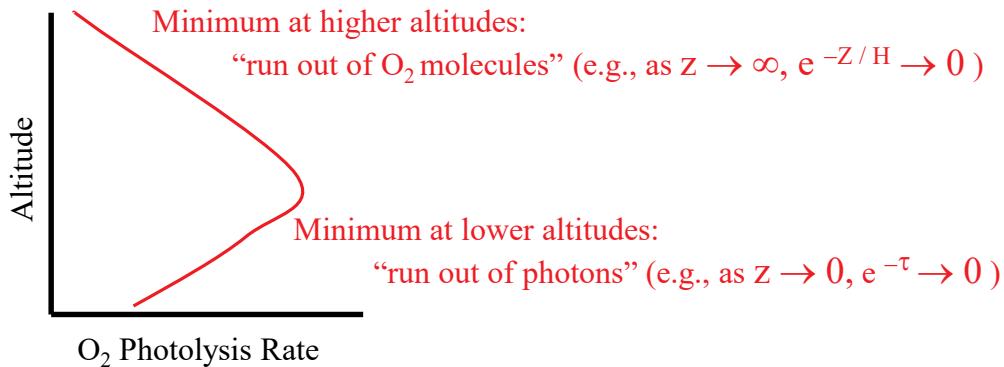
# Extra #1: Height and Abundance of Ozone

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

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

What does this function look like?

*Informally-*



*Formally-*

Can show:

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

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

# Extra #1: Height and Abundance of Ozone

The *partial photolysis rate* of O<sub>2</sub> 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<sub>2</sub> when  $\tau = 1$ ?

$$\text{Photolysis Rate of O}_2 \approx 5 \times 10^{18} (\text{molecules/cm}^3) e^{-z/H} \sigma_{O_2} F_{TOA} \frac{1}{e}$$

Let's examine the partial photolysis rate of O<sub>2</sub> in its three absorption regions

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

	$\sigma_{\max}$ (cm <sup>2</sup> )	z ( $\tau=1$ ) (km)	F <sub>TOA</sub> (#/cm <sup>2</sup> /s)	J (sec <sup>-1</sup> )	Photolysis Rate (#/cm <sup>3</sup> /sec)
Schumann-Runge Continuum	$10^{-17}$	125	$1 \times 10^{11}$	$3.7 \times 10^{-7}$	$3.3 \times 10^4$
Schumann-Runge Bands	$10^{-20}$	77	$8 \times 10^{11}$	$2.9 \times 10^{-9}$	$2.4 \times 10^5$
	$3 \times 10^{-23}$	36	$3 \times 10^{12}$	$3.3 \times 10^{-11}$	$9.6 \times 10^5$
Herzberg Continuum	$10^{-23}$	<b>29</b>	$2 \times 10^{14}$	$7.3 \times 10^{-10}$	<b><math>5.8 \times 10^7</math></b>

# 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 ( $\sigma_{max}$ )**

Altitude of largest  
 $O_2$  photolysis rate

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

	$\sigma_{max}$ (cm <sup>2</sup> )	$Z$ ( $\tau=1$ ) (km)	$F_{TOA}$ (#/cm <sup>2</sup> /s)	$J$ (sec <sup>-1</sup> )	Photolysis Rate (#/cm <sup>3</sup> /sec)
Schumann-Runge Continuum	$10^{-17}$	125	$1 \times 10^{11}$	$3.7 \times 10^{-7}$	$3.3 \times 10^4$
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	$3 \times 10^{-23}$	36	$3 \times 10^{12}$	$3.3 \times 10^{-11}$	$9.6 \times 10^5$
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## Extra #1: Height and Abundance of Ozone

The height of the ozone layer (~30 km) and  
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**solar actinic flux ( $F_{TOA}$ ) &  $O_2$  absorption cross section ( $\sigma_{max}$ )**

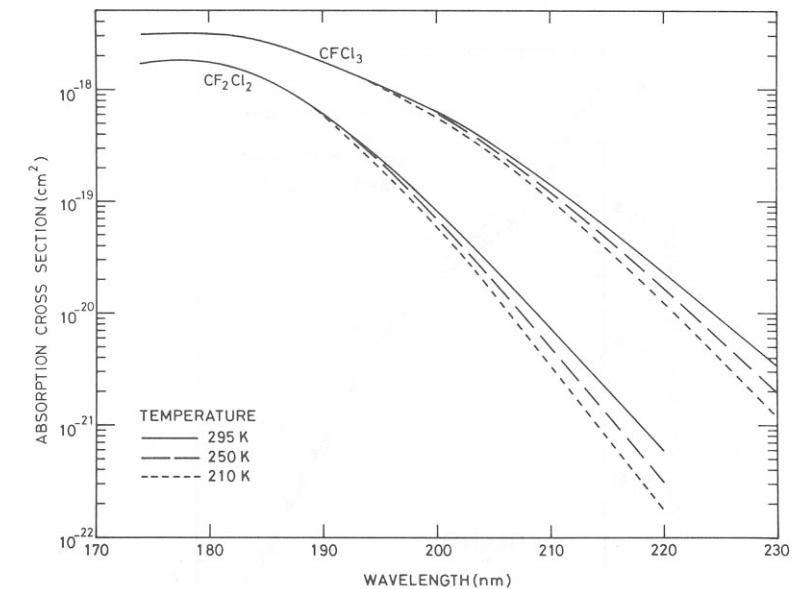
Suppose the Herzberg Continuum region dominated the photolysis rate of  $O_2$ ,  
but the maximum cross section was different:

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

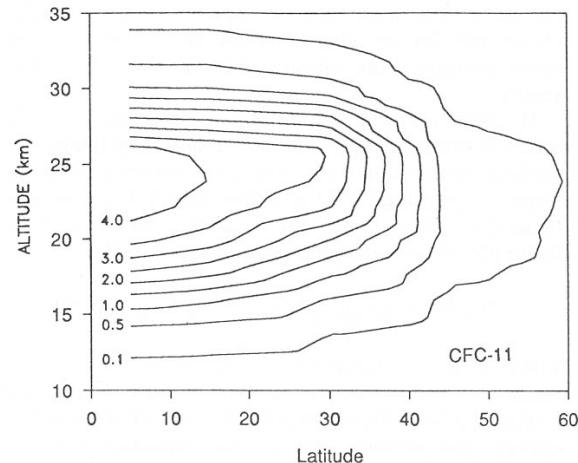
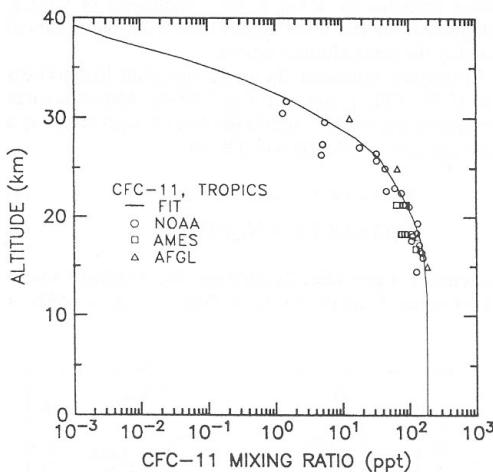
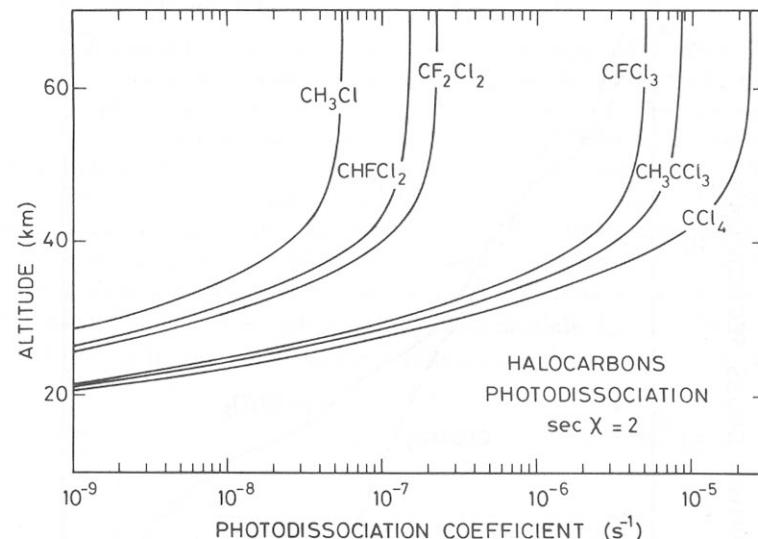
Suppose the Herzberg Continuum region dominated the photolysis rate of  $O_2$ ,  
but the solar irradiance at these wavelengths was different:

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

# Extra #2: CFC Photolysis



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



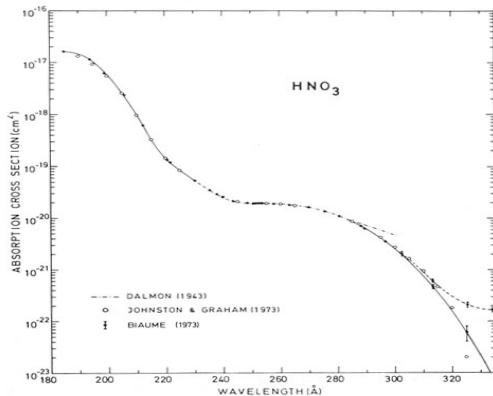
	Inventory (kg)	Loss Rate (kg/yr)	Lifetime (years)
CFCl <sub>3</sub>	$3.1 \times 10^9$	$7.2 \times 10^7$	44
CF <sub>2</sub> Cl <sub>2</sub>	$3.5 \times 10^9$	$3.0 \times 10^7$	116

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

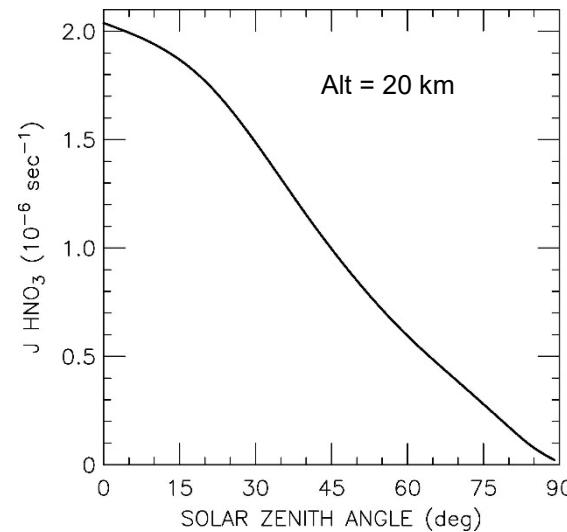
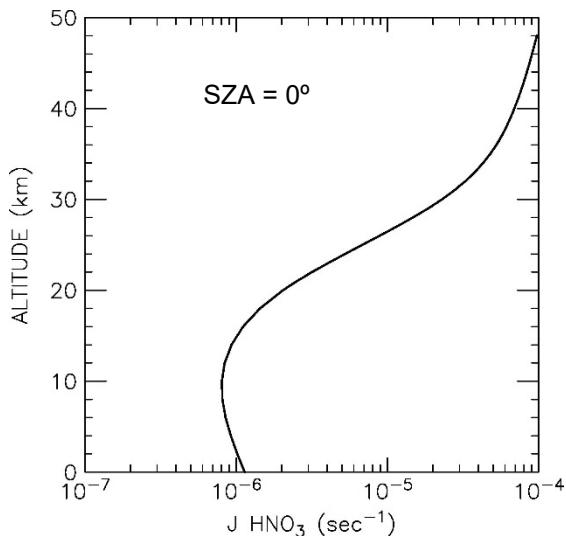
Fig. 12. Diurnally averaged loss rate for CFCl<sub>3</sub> (molecules cm<sup>-3</sup> s<sup>-1</sup>) as a function of altitude and latitude, calculated with the line-by-line model, for equinox. The loss rate was calculated assuming destruction of CFCl<sub>3</sub> by photolysis only.

## Extra #3: $\text{HNO}_3$ Photolysis

The majority of  $\text{HNO}_3$  photolysis occurs shortward of 320 nm, where the atmosphere is optically thick with respect to absorption by  $\text{O}_3$  and  $\text{O}_2$ :



leading to a value for  $J_{\text{HNO}_3}$  that is strongly dependent on height and SZA:



# Extra #3: $\text{HNO}_3$ Photolysis

