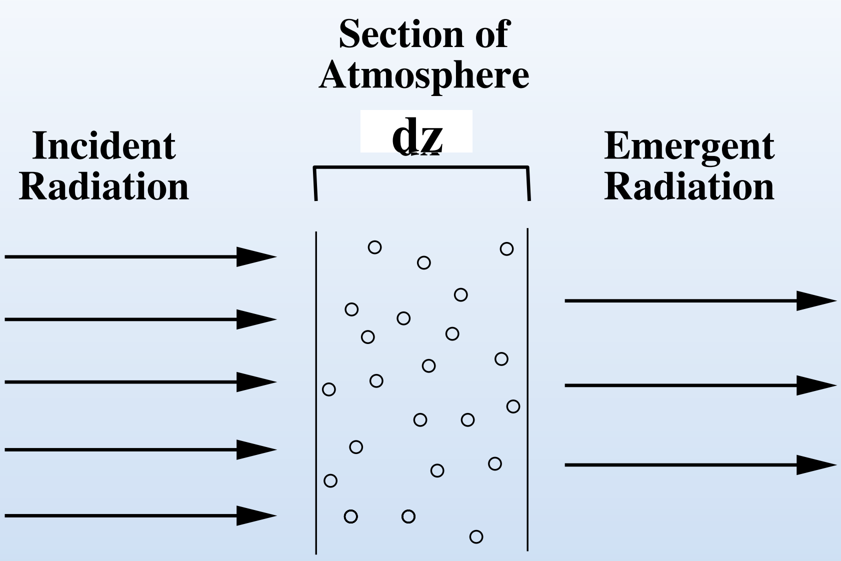
Atmospheric Chemistry

Fall 2014

Lecture 3

Absorption of Solar Radiation



Beer's Law Absorption:

reduction of incident intensity is proportional to the incident intensity, the density of scatterers and the thickness of the slab of atmosphere

$$dI = -\sigma \cdot n \cdot I \cdot dz$$

The proportionality constant is the "cross section", σ, with the units of cm²

Rearrange and integrate over z (from z to infinity)

$$\int \frac{dI}{I} = -\sigma \int n \cdot dz$$

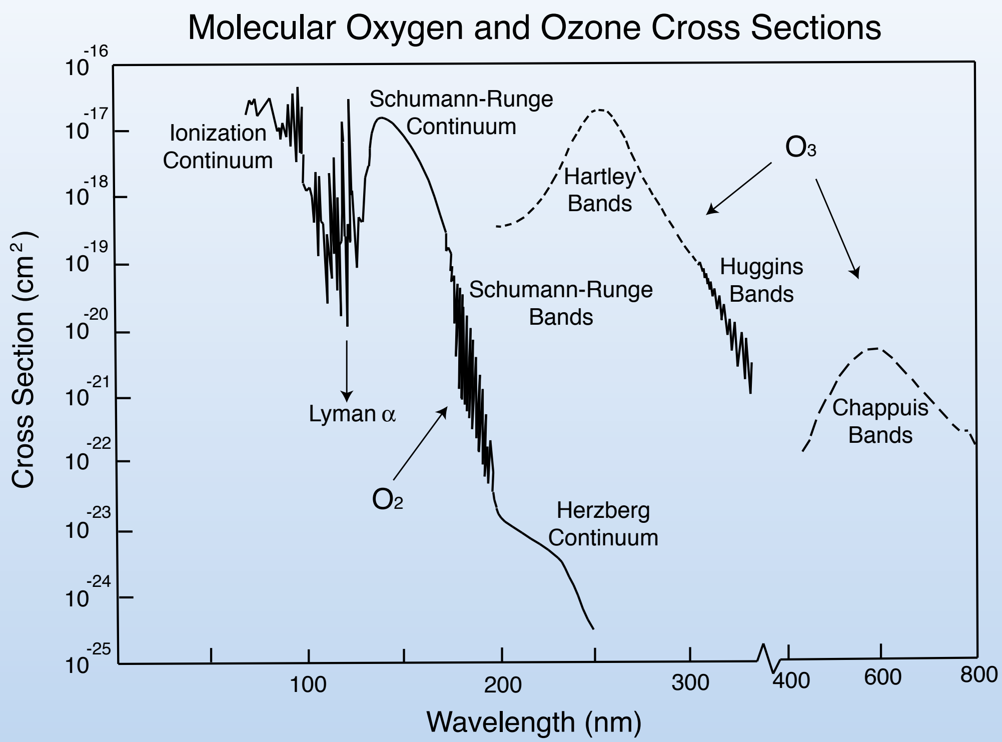
Solve for Intensity as a function of z (at a single wavelength)

$$I(z, \lambda) = I_o(\lambda) \cdot e^{-N(z) \cdot \sigma(\lambda)}$$

where N is the column density of absorbers above the altitude z

$$N(z) = \int_z^{\infty} n(z) dz$$

Oxygen and Ozone Cross Sections



What does a cross section of 10^{-17} cm^2 mean? Intensity of radiation will be reduced to 1/e when column density above altitude = 10^{17} cm^{-2}.

$$I(z,\lambda) = I_o(\lambda)\cdot e^{-N(z)\cdot\sigma(\lambda)}$$

$$O_2(z) = O_{2o}e^{-(z-z_o)/H}$$

$$N_{O2}(z_0) = \int_{z_0}^{\infty} n_{O20}\cdot e^{-(z-z_0)/H}dz$$

$$N_{O2}(z_0) = n_{O20}\cdot H$$

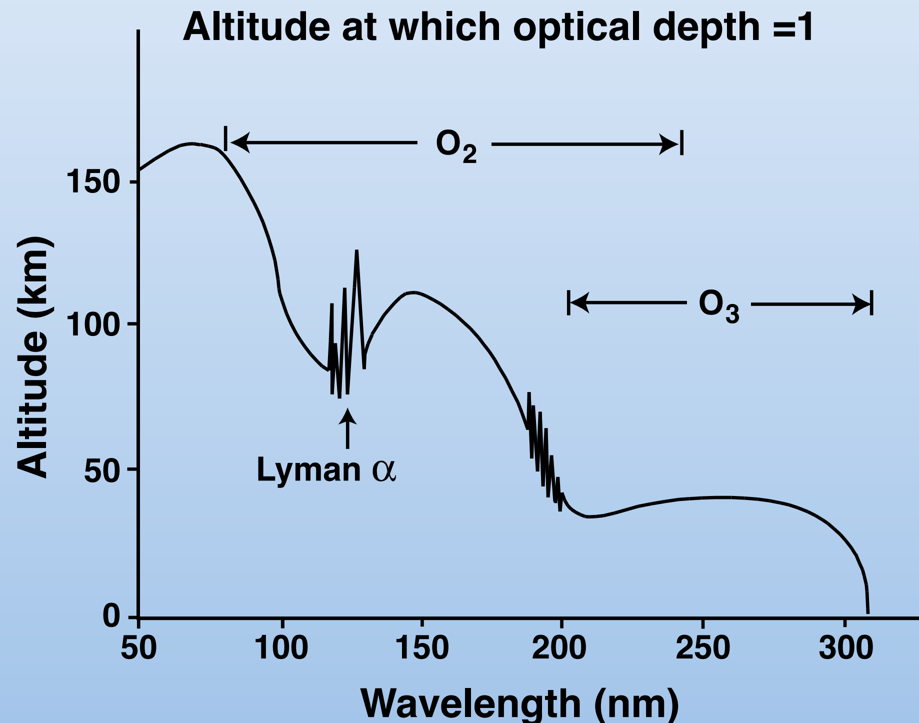
Column density of O_2 is 10^{17} when density is 10^{17}/H or about 1.4x10^{11} cm^{-3}.

O_2 density at surface is about 5x10^{18}. Thus 1/e absorption is at pressure of about .003 hPa – well above stratosphere

Penetration of Solar Radiation

$$I(z,\lambda) = I_o(\lambda) \cdot e^{-N(z)\cdot\sigma(\lambda)}$$

$$\tau = N \cdot \sigma \qquad Optical Depth$$



Photolysis of O_2 and O_3

$$O_2 + photon \rightarrow O + O$$
$$O_3 + photon \rightarrow O_2 + O$$

$$\frac{dn}{dt} = -J \cdot n$$

J has units of sec^{-1}

J is the rate of photon absorptions per second that lead to photolysis.

$$J(z) = \int \sigma(\lambda) \cdot I(\lambda, z) d\lambda$$

Chapman Mechanism for Formation of the Ozone Layer

$$h\nu + O_2 \rightarrow O + O$$ *Initiation*

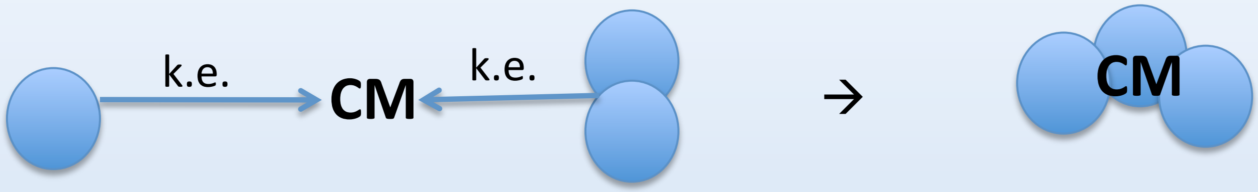
$$O + O_2 + M \rightarrow O_3 + M$$
$$h\nu + O_3 \rightarrow O_2 + O$$
Propagation

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

Put forward by Sydney Chapman in 1930

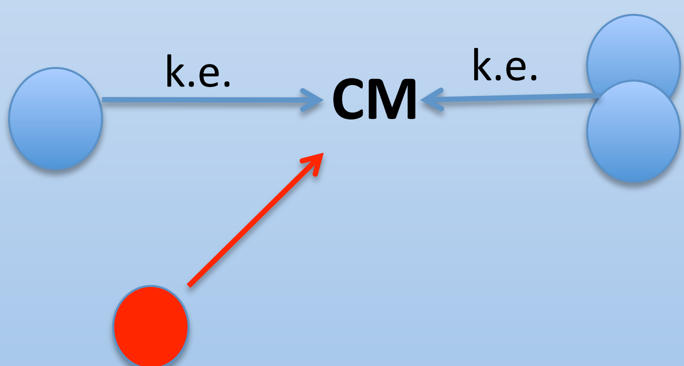
Three-body reactions

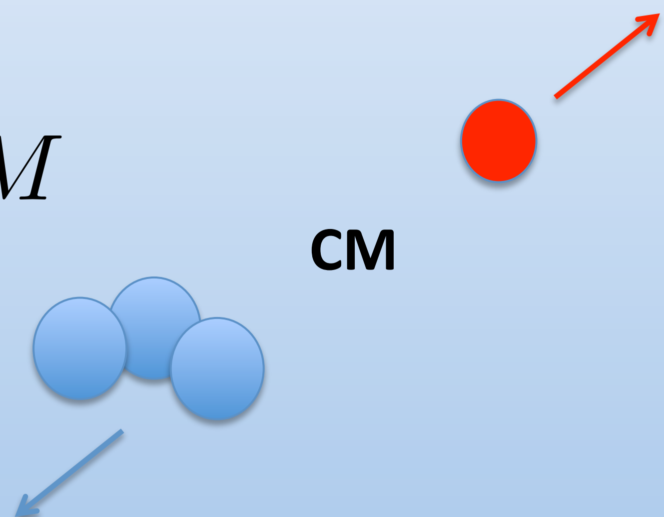
$$O + O_2 \rightarrow O_3$$



kinetic energy must be absorbed by O_3 molecule into an excited state because CM is at rest

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





excess kinetic energy goes into relative velocities of particles away from CM

Time Constants

$$\tau = \frac{1}{J} \qquad photolysis$$

$$\tau = \frac{1}{k \cdot [n]} \qquad two - body$$

$$\tau = \frac{1}{k \cdot [n] \cdot [M]} \qquad three - body$$

Photodissociation Coefficients versus Altitude

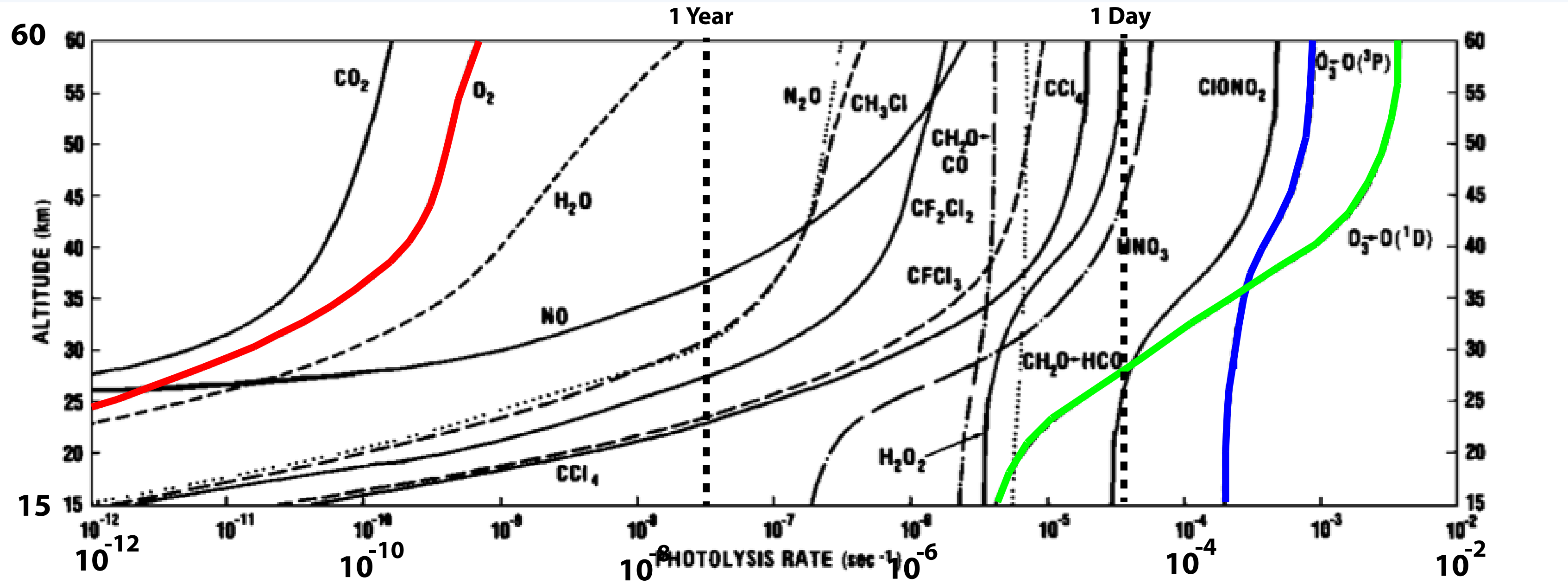


Fig. 1. Calculated 24-hour average J coefficients as a function of altitude. For $h\nu + NO_2 \rightarrow NO + O$, $h\nu + NO_3 \rightarrow NO_2 + O$, and $h\nu + NO_3 \rightarrow NO + O_2$, constant J coefficients were used. The values were 0.005, 0.05, and 0.02 s^{-1}, respectively. The dissociation of NO is discussed in the text.

$$h\nu(\lambda < 242nm) + O_2 \rightarrow O + O$$

$$h\nu(\lambda < 308nm) + O_3 \rightarrow O_2 + O(^1D)$$

$$h\nu(\lambda < 1\mu) + O_3 \rightarrow O_2 + O(^3P)$$

Chapman Mechanism Equations

		Time Scale at ~40 km
$h\nu + O_2 \rightarrow O + O$	J_1	
$O + O_2 + M \rightarrow O_3 + M$	k_2	***< 1 sec***
$h\nu + O_3 \rightarrow O_2 + O$	J_3	***few hundred seconds***
$O + O_3 \rightarrow O_2 + O_2$	k_4	***few days***

$$[O_x] = [O] + [O_3] \qquad OddOxygen$$

$$\frac{d[O_x]}{dt} = 2 \cdot J_1 \cdot [O_2] - 2 \cdot k_4 \cdot \left(\frac{[O]}{[O_3]}\right) \cdot [O_3]^2$$

$$\frac{[O]}{[O_3]} = \frac{J_3}{k_2 \cdot [O_2] \cdot [M]}$$

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

Reference Atmosphere

Altitude(km)	Temperature (K)	Air Density (cm^{-3})	Ozone (cm^{-3})
0	288	2.55×10^{19}	7.6×10^{11}
2	275	2.09×10^{19}	6.8×10^{11}
4	262	1.70×10^{19}	5.8×10^{11}
6	249	1.37×10^{19}	5.7×10^{11}
8	236	1.09×10^{19}	6.5×10^{11}
10	223	8.60×10^{18}	1.13×10^{12}
12	217	6.49×10^{18}	2.02×10^{12}
14	217	4.74×10^{18}	2.35×10^{12}
16	217	3.46×10^{18}	2.95×10^{12}
18	217	2.53×10^{18}	4.04×10^{12}
20	217	1.85×10^{18}	4.77×10^{12}
22	219	1.34×10^{18}	4.86×10^{12}
24	221	9.76×10^{17}	4.54×10^{12}
26	223	7.12×10^{17}	4.03×10^{12}
28	225	5.21×10^{17}	3.24×10^{12}
30	227	3.83×10^{17}	2.52×10^{12}
32	228	2.82×10^{17}	2.03×10^{12}
34	233	2.06×10^{17}	1.58×10^{12}
36	239	1.51×10^{17}	1.22×10^{12}
38	245	1.12×10^{17}	8.73×10^{11}
40	250	8.31×10^{16}	6.07×10^{11}
42	256	6.23×10^{16}	3.98×10^{11}
44	261	4.70×10^{16}	2.74×10^{11}
46	267	3.56×10^{16}	1.69×10^{11}
48	271	2.74×10^{16}	1.03×10^{11}
50	271	2.14×10^{16}	6.64×10^{10}
52	269	1.68×10^{16}	3.84×10^{10}
54	264	1.33×10^{16}	2.55×10^{10}
56	258	1.05×10^{16}	1.61×10^{10}
58	253	8.24×10^{15}	1.12×10^{10}
60	247	6.44×10^{15}	7.33×10^{9}

Some Important 2-Body Reaction Rate Coefficients

$$k(T) = A \cdot e^{-\frac{E}{R}/T}$$

Reaction	A-Factor	E/R	k(298K)
$O + O_3 \rightarrow O_2 + O_2$	8.0×10^{-12}	2060	8.0×10^{-15}
$O + NO_2 \rightarrow NO + O_2$	6.5×10^{-12}	-120	9.7×10^{-12}
$O_3 + NO \rightarrow NO_2 + O_2$	2.0×10^{-12}	1400	1.8×10^{-14}
$O + HO_2 \rightarrow OH + O_2$	3.0×10^{-11}	-200	5.9×10^{-11}
$O + OH \rightarrow H + O_2$	2.2×10^{-11}	-120	3.3×10^{-11}
$O_3 + HO_2 \rightarrow OH + O_2 + O_2$	1.1×10^{-14}	500	2.0×10^{-15}
$O_3 + OH \rightarrow HO_2 + O_2$	1.6×10^{-12}	940	6.8×10^{-14}
$Cl + O_3 \rightarrow ClO + O_2$	2.9×10^{-11}	260	1.2×10^{-11}
$ClO + O \rightarrow Cl + O_2$	3.0×10^{-11}	-70	3.8×10^{-11}
$Br + O_3 \rightarrow BrO + O_2$	1.7×10^{-11}	800	1.2×10^{-12}
$BrO + ClO \rightarrow Br + Cl + O_2$	2.9×10^{-12}	-220	6.1×10^{-12}
$BrO + BrO \rightarrow Br + Br + O_2$	1.4×10^{-12}	-150	2.3×10^{-12}
$Cl + CH_4 \rightarrow HCl + CH_3$	1.1×10^{-11}	1400	1.0×10^{-13}
$OH + HCl \rightarrow H_2O + Cl$	2.6×10^{-12}	350	8.0×10^{-13}

Some Important 3-Body Reaction Rate Coefficients

$$LowPressureLimit \qquad k_o(T) = k_o^{300} \cdot \left(\frac{T}{300}\right)^{-n}$$

$$HighPressureLimit \qquad k_\infty(T) = k_\infty^{300} \cdot \left(\frac{T}{300}\right)^{-m}$$

Reaction	k_o^{300}	n	k_∞^{300}	m
$O + O_2 + M \rightarrow O_3 + M$	6.0×10^{-34}	2.3	-	-
$OH + NO_2 + M \rightarrow HNO_3 + M$	2.6×10^{-30}	3.2	2.4×10^{-11}	1.3
$H + O_2 + M \rightarrow HO_2 + M$	5.7×10^{-32}	1.6	7.5×10^{-11}	0
$ClO + NO_2 + M \rightarrow ClONO_2 + M$	1.8×10^{-31}	3.4	1.5×10^{-11}	1.9