

Lecture 6: Spectroscopy and Photochemistry II

Required Reading: FP Chapter 3

Suggested Reading: SP Chapter 3

Atmospheric Chemistry
CHEM-5151 / ATOC-5151
Spring 2005
Prof. Jose-Luis Jimenez

Outline of Lecture

- The Sun as a radiation source
- Attenuation from the atmosphere
 - Scattering by gases & aerosols
 - Absorption by gases
 - Beer-Lamber law
- Atmospheric photochemistry
 - Calculation of photolysis rates
 - Radiation fluxes
 - Radiation models

Reminder of EM Spectrum

TABLE 3.2 Typical Wavelengths, Frequencies, Wavenumbers, and Energies of Various Regions of the Electromagnetic Spectrum

Name	Typical wavelength or range of wavelengths (nm)	Typical range of frequencies ν (s^{-1})	Typical range of wavenumbers ω (cm^{-1})	Typical range of energies ($kJ\ einstein^{-1}$) ^a
Radiowave	$\sim 10^8$ – 10^{13}	$\sim 3 \times 10^4$ – 3×10^9	10^{-6} – 0.1	$\sim 10^{-3}$ – 10^{-8}
Microwave	$\sim 10^7$ – 10^8	$\sim 3 \times 10^9$ – 3×10^{10}	0.1 – 1	$\sim 10^{-2}$ – 10^{-3}
Far-infrared	$\sim 10^5$ – 10^7	$\sim 3 \times 10^{10}$ – 3×10^{12}	1 – 100	$\sim 10^{-2}$ – 1
Near-infrared	$\sim 10^3$ – 10^5	$\sim 3 \times 10^{12}$ – 3×10^{14}	10^2 – 10^4	~ 1 – 10^2
Visible				
Red	700	4.3×10^{14}	1.4×10^4	1.7×10^2
Orange	620	4.8×10^{14}	1.6×10^4	1.9×10^2
Yellow	580	5.2×10^{14}	1.7×10^4	2.1×10^2
Green	530	5.7×10^{14}	1.9×10^4	2.3×10^2
Blue	470	6.4×10^{14}	2.1×10^4	2.5×10^2
Violet	420	7.1×10^{14}	2.4×10^4	2.8×10^2
Near-ultraviolet	400–200	$(7.5$ – $15.0) \times 10^{14}$	$(2.5$ – $5) \times 10^4$	$(3.0$ – $6.0) \times 10^2$
Vacuum ultraviolet	~ 200 – 50	$(1.5$ – $6.0) \times 10^{15}$	$(5$ – $20) \times 10^4$	$\sim (6.0$ – $24) \times 10^2$
X-Ray	~ 50 – 0.1	$\sim (0.6$ – $300) \times 10^{16}$	$(0.2$ – $100) \times 10^6$	$\sim 10^3$ – 10^6
γ -Ray	≤ 0.1	$\sim 3 \times 10^{18}$	$\geq 10^8$	$> 10^6$

^a For kcal einstein⁻¹, divide by 4.184 (1 cal = 4.184 J).

Blackbody Radiation

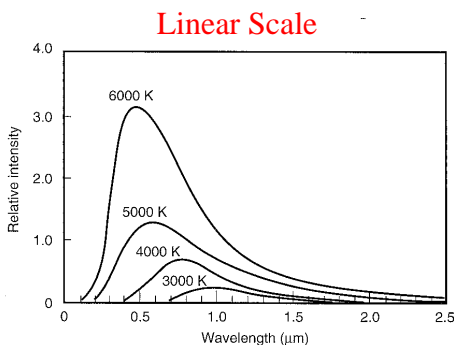


Figure 3.6 The blackbody, or Planckian, radiation spectrum. The intensity varies with wavelength in a smooth and relatively simple manner. The shape and position of the spectrum depend on the temperature. In general, the lower the temperature is, the greater the wavelength of the peak intensity and the lower the overall intensity of the radiation will be. For an object at a temperature of 6000 K, the intensity peaks at about 0.5 microns, similar to sunlight.

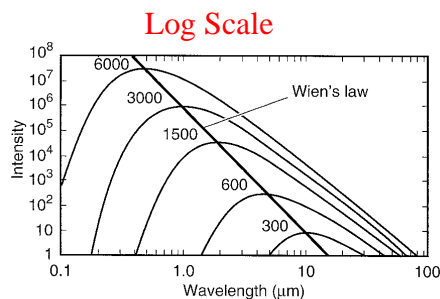
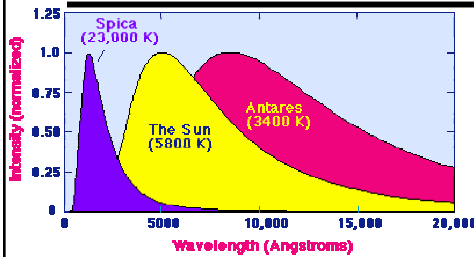


Figure 3.7 Blackbody radiation spectra as a function of temperature (kelvin), over the entire range of temperatures relevant to environmental studies. The values are displayed here on a log-log graph, so that both the wavelength and intensity scales are greatly compressed and cover many orders of magnitude. (From P. R. Gast, Air Force Cambridge Research Laboratory, McGraw Hill (1967). Appendix B of Revision of Chapter 22 of the *Handbook of Geophysics and Space Environments*, Air Force Survey in Geophysics #199, Office of Aerospace Research, USAF, Bedford, Mass. Template only.)

From R.P. Turco, *Earth Under Siege: From Air Pollution to Global Change*, Oxford UP, 2002.

Solar & Earth Radiation Spectra



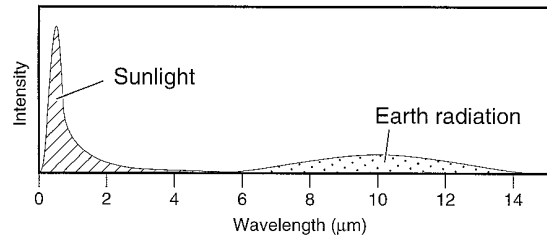
From S. Nidkorodov

- Sun is a radiation source with an effective blackbody temperature of about 5800 K
- Earth receives circa 1368 W/m² of energy from solar radiation

From Turco

Figure 3.8 The relative spectra of sunlight and Earth's blackbody radiation (referred to as terrestrial radiation or Earthglow). The spectral regions of the emissions are seen to be quite distinct, with little overlap of spectra.

- Question: are relative vertical scales ok in right plot? →



Solar Radiation Spectrum II

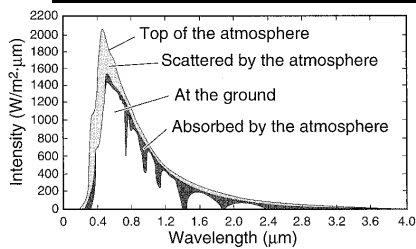


Figure 3.5 Details of the spectrum that reaches the top of the Earth's atmosphere and penetrates to the surface. The outer envelope is the full intensity of sunlight that one would encounter in space. The inner curve is lower because the Earth's atmosphere scatters some of the radiation back to space, particularly at short wavelengths. The shaded region below the inner curve indicates those regions of the spectrum where atmospheric water vapor, carbon dioxide, and ozone molecules absorb the sunlight, further reducing its penetration. The units of solar intensity are often expressed as watts per meter squared per micron of wavelength (w/m²·μm). (From J.N. Howard, J. I. F. King, and P. R. Gast, "Thermal Radiation," *Handbook of Geophysics*, [New York: Macmillan, 1960], Chapter 16, p. 15)

From Turco

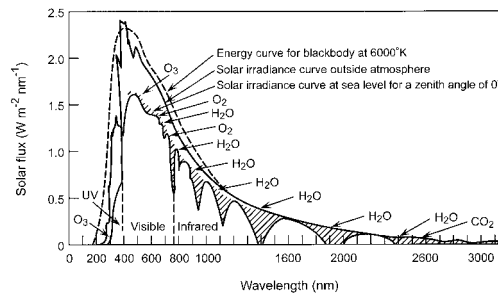


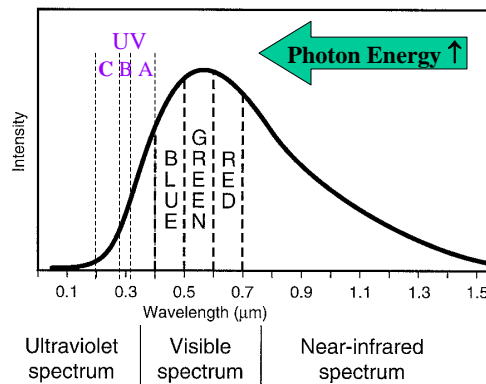
FIGURE 3.12 Solar flux outside the atmosphere and at sea level, respectively. The emission of a blackbody at 6000 K is also shown for comparison. The species responsible for light absorption in the various regions (O₃, H₂O, etc.) are also shown (from Howard *et al.*, 1960).

From F-P&P

- Solar spectrum is strongly modulated by atmospheric scattering and absorption

Solar Radiation Spectrum III

Figure 3.4 The basic spectrum of sunlight. The intensity of sunlight peaks in the visible part of the spectrum and decreases in the ultraviolet region, at shorter wavelengths, and in the infrared region, at longer wavelengths. Within the visible region, the spectrum can be further subdivided into the primary colors of light: blue, green, and red. The visible region actually contains a continuous spectrum of colors ranging from deep red at one end to violet at the blue end.



Solar Radiation Spectrum IV

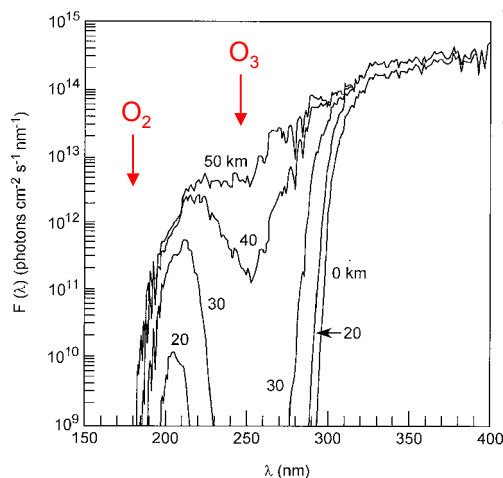


FIGURE 3.32 Calculated actinic fluxes as a function of altitude for a solar zenith angle of 30° and a surface albedo of 0.3. (From DeMore *et al.*, 1997.)

- Solar spectrum is strongly modulated by atmospheric absorptions
- Remember that UV photons have most energy
 - O_2 absorbs extreme UV in mesosphere; O_3 absorbs most UV in stratosphere
 - Chemistry of those regions partially driven by those absorptions
 - Only light with $\lambda > 290$ nm penetrates into the lower troposphere
 - Biomolecules have same bonds (e.g. C-H), bonds can break with UV absorption \Rightarrow damage to life
 - Importance of protection provided by O_3 layer

Solar Radiation Spectrum vs. altitude

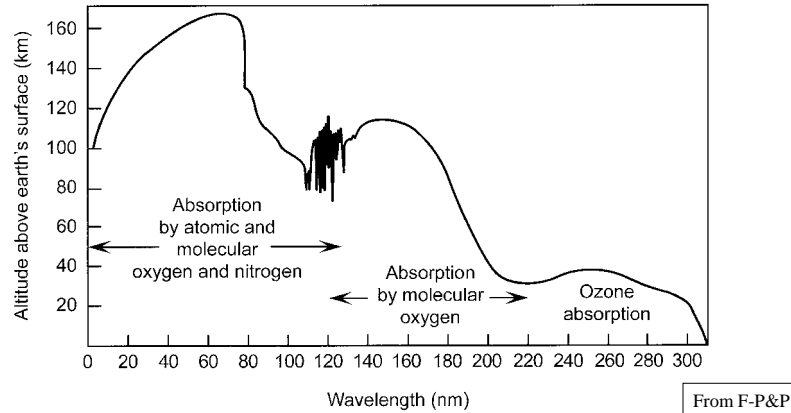


FIGURE 3.13 Approximate regions of maximum light absorption of solar radiation in the atmosphere by various atomic and molecular species as a function of altitude and wavelength with the sun overhead (from Friedman, 1960).

- Very high energy photons are depleted high up in the atmosphere
- Some photochemistry is possible in stratosphere but not in troposphere
 - Only $\lambda > 290$ nm in trop.

Solar Zenith Angle

- Aside from the altitude, the path length through the atmosphere critically depends on the time of day and geographical location.
- Path length can be calculated using the flat atmosphere approximation for zenith angles under 80° . Beyond that, Earth curvature and atmospheric refraction start to matter.

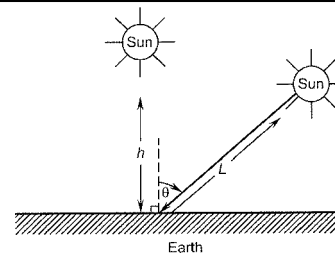


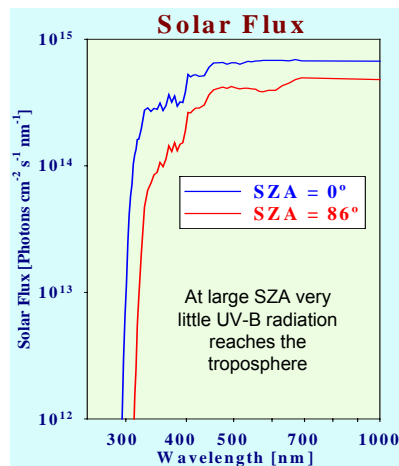
FIGURE 3.14 Definition of solar zenith angle θ at a point on the earth's surface.

$$\text{"Air Mass"} = m = \frac{\text{Actual pathlength}}{\text{Vertical pathlength}} \approx \frac{L}{h} = \sec \theta$$

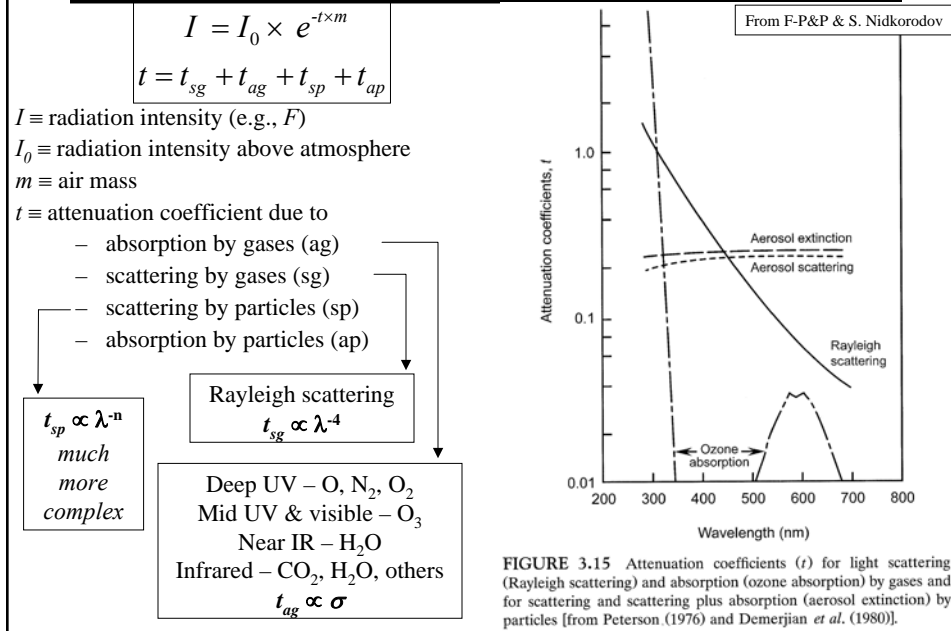
TABLE 3.5 Values of the Air Mass m at the Earth's Surface for Various Zenith Angles: (a) Calculated from $m = \sec \theta$ and (b) Corrected for Atmospheric Curvature and for Refraction

Zenith angle θ (deg)	$m = \sec \theta$	Air mass (m)
0	1.00	1.00
10	1.02	1.02
20	1.06	1.06
30	1.15	1.15
40	1.31	1.31
50	1.56	1.56
60	2.00	2.00
70	2.92	2.90
78	4.81	4.72
86	14.3	12.4

Source: Demerjian *et al.* (1980).



Direct Attenuation of Radiation



Scattering by Gases

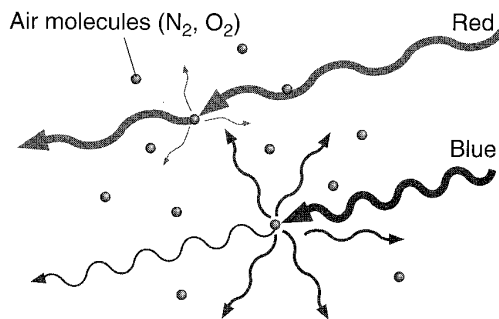


Figure 3.11 Light scattering by air molecules. According to the Rayleigh scattering law, blue light, which has shorter wavelengths than red light, is scattered more effectively by air molecules. Hence the clear sky illuminated by the sun takes on the blue color of the scattered light.

From Turco

- Purely physical process, not absorption
- Approximation:

$$t_{sg} = 1.044 \cdot 10^5 \cdot (n_{0\lambda} - 1)^2 / \lambda^4$$

- Strongly increases as λ decreases
- Reason why “sky is blue” during the day

Scattering & Absorption by Particles

- Particles can scatter and absorb radiation
- Scattering efficiency is very strong function of particle size
 - For a given wavelength
- Visible: $\lambda \sim 0.5 \mu\text{m}$
 - Particles 0.5-2 μm are most efficient scatterers!
- Will discuss in more detail in aerosol lectures

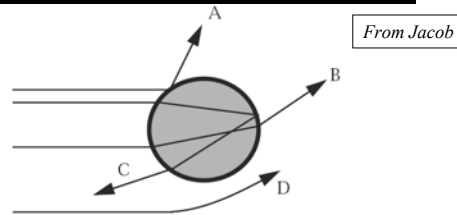


Figure 8-3 Scattering of a radiation beam: processes of reflection (A), refraction (B), refraction and internal reflection (C), and diffraction (D).

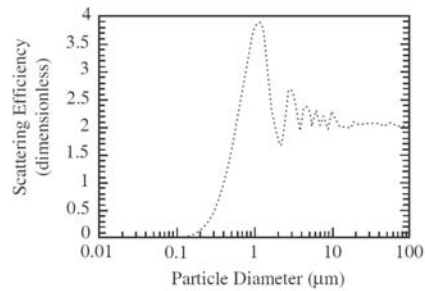


Figure 8-4 Scattering efficiency of green light ($\lambda = 0.5 \mu\text{m}$) by a liquid water sphere as a function of the diameter of the sphere. Scattering efficiencies can be larger than unity because of diffraction. Adapted from Jacobson, M.Z., *Fundamentals of Atmospheric Modeling*, Cambridge University Press, Cambridge, 1998.

Gas Absorption: Beer-Lambert Law I

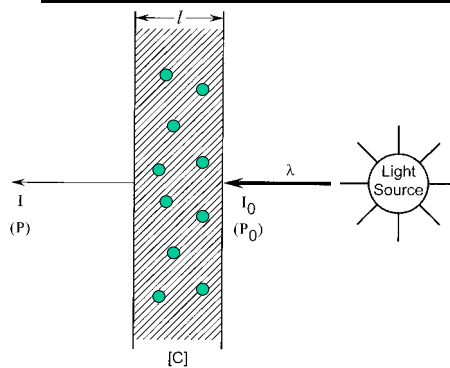


FIGURE 3.11 Schematic diagram of experimental approach to the Beer-Lambert law.

$$I = I_0 \exp(-\sigma \cdot L \cdot N)$$

- Allows the calculation of the decay in intensity of a light beam due to absorption by the molecules in a medium

Definitions:

- $A = \ln(I_0/I) = \text{Absorbance} = \sigma \cdot L \cdot N$ (also "optical depth")
- $\sigma \equiv$ absorption cross section [cm^2/molec]
- $L \equiv$ absorption path length [cm]
- $n \equiv$ density of the absorber [molec/cm^3]

Solve in class: Show that in the small absorption limit the relative change in light intensity is approximately equal to absorbance.

From F-P&P & S. Nidkorodov

Beer-Lambert Law II

Pitfalls:

- Other units are frequently used to express absorbance, for example:

$$A = \ln(I_0/I) = \varepsilon \times L \times C$$

$$A = \ln(I_0/I) = \alpha \times L \times P$$

ε \equiv extinction coefficient [$\text{L mol}^{-1} \text{cm}^{-1}$]

α \equiv absorption coefficient [$\text{atm}^{-1} \text{cm}^{-1}$]

C \equiv density of the absorber [mol L^{-1}]

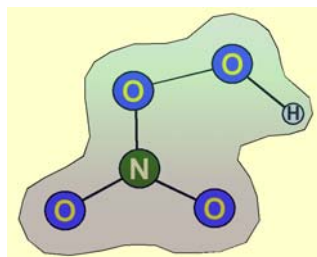
P \equiv partial pressure [atm]

- Base 10 is used in most commercial spectrometers instead of the natural base:

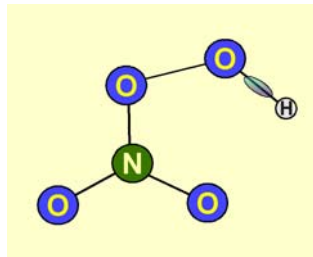
$$A_{\text{base 10}} = \log(I_0/I) = A_{\text{base e}} / \ln(10)$$

Physical interpretation of σ

- σ , absorption cross section ($\text{cm}^2 / \text{molecule}$)
 - Effective area of the molecule that photon needs to traverse in order to be absorbed.
 - The larger the absorption cross section, the easier it is to photoexcite the molecule.
 - E.g., pernitric acid HNO_4



Collisions
 $\sigma \approx 10^{-15} \text{ cm}^2/\text{molec}$

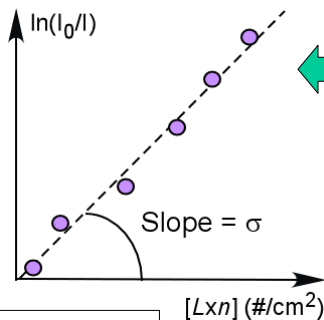
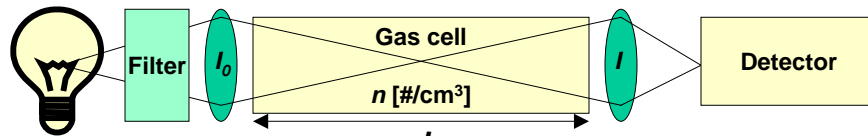


Light absorption
 $\sigma \approx 10^{-18} \text{ cm}^2/\text{molec}$

From S. Nidkorodov

Measurement of Absorption Cross Sections

Measurement of absorption cross sections is, in principle, trivial. We need a light source, such as a lamp (UV), a cell to contain the molecule of interest, a spectral filter (such as a monochromator) and a detector that is sensitive and responds linearly to the frequency of radiation of interest:



Measurements are repeated for a number of concentrations at each wavelength of interest.

Although seemingly trivial, in practice such measurements are difficult because of impurities, especially when it comes to very small cross sections ($< 10^{-20} \text{ cm}^2/\text{molec}$)

Solve in class: Sample contains 1 Torr of molecules of interest with $\sigma = 3 \times 10^{-21} \text{ cm}^2/\text{molec}$ and 1 mTorr of impurity with $\sigma = 2 \times 10^{-18} \text{ cm}^2/\text{molec}$. What is the total absorbance in a 50 cm cell?

Example: UV Attenuation by O_3 and O_2

Attenuation coefficient is dominated by O_3 absorption in the 200-300 nm window. Therefore, direct attenuation can be easily calculated from known absorption cross sections of O_3 . Similar formulas apply to attenuation by O_2 in 120-180 nm window.

$$I(\lambda) = I_0(\lambda) \times e^{-\sigma(\lambda) \times A \times m}$$

where $A \equiv$ column density

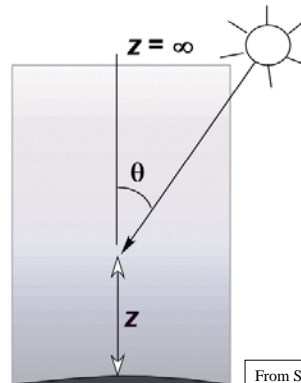
$$A = \int_z^{\infty} [\text{O}_3(z)] dz$$

Alternatively written :

$$I(\lambda) = I_0(\lambda) \times e^{-\tau(\lambda, z)}$$

where $\tau \equiv$ optical depth

$$\tau(\lambda, z) = \int_z^{\infty} \sigma(\lambda) \times m \times [\text{O}_3(z)] dz$$



From S. Nidkorodov

Solve in class: Using barometric law estimate column density of O_2 in the atmosphere. By how much does atmospheric O_2 attenuate solar radiation at around 170 nm ($\sigma \approx 10^{-17} \text{ cm}^2/\text{molec}$) at noon ($m = 1$)? Assume that O_2 fraction (21%) is independent of altitude and $T = 270 \text{ K}$.
 Ans: 4×10^{24} ; by $\exp(-10^7)$

Solar Radiation Intensity

To calculate solar spectral distribution in any given volume of air at any given time and location one must know the following:

- Solar spectral distribution outside the atmosphere
- Path length through the atmosphere
- Wavelength dependent attenuation by atmospheric molecules
- Amount of radiation indirectly scattered by the earth surface, clouds, aerosols, and other volumes of air

From F-P&P

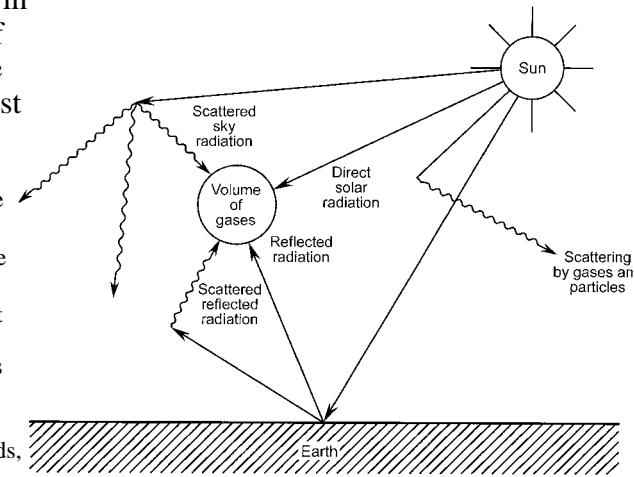


FIGURE 3.16 Different sources of radiation striking a volume of gas in the atmosphere. These sources are direction radiation from the sun, radiation scattered by gases and particles, and radiation reflected from the earth's surface.

Surface Albedo

$$Albedo(\lambda) = \frac{\text{Reflected Radiation}(\lambda)}{\text{Incident Radiation}(\lambda)}$$

- Wavelength dependent!
- Question: for the same incident UV solar flux, will you tan faster over snow or over a desert?

TABLE 3.6 Some Typical Albedos for Various Types of Surfaces

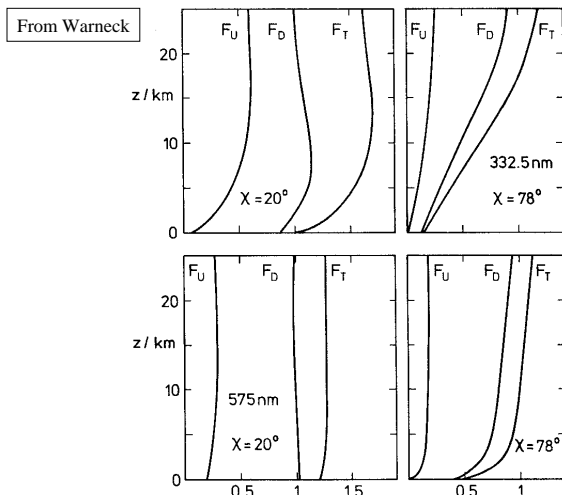
Type of surface	Albedo	Reference
Snow	0.69	Angle <i>et al.</i> , 1992
	0.93 ^b	Dickerson <i>et al.</i> , 1982
	0.9–1.0	Junkermann, 1994
Ocean	0.07 ^b	Dickerson <i>et al.</i> , 1982
	0.06–0.08 ^a	Eck <i>et al.</i> , 1987
Forests	0.06–0.18 ^b	Dickerson <i>et al.</i> , 1982
	0.02 ^a	Eck <i>et al.</i> , 1987
	0.17	Angle <i>et al.</i> , 1992
Fields and meadows	0.03–0.04 ^a	Eck <i>et al.</i> , 1987
Desert	0.06–0.09 ^a	Eck <i>et al.</i> , 1987
Salt flats	0.57–0.65 ^a	Eck <i>et al.</i> , 1987

^a Minimum reflectivities at 370 nm.

^b Measured with respect to NO₂ photolysis.

From F-P&P

Total vs. Downwelling Radiation



- If atmosphere was completely transparent and surface completely absorbing (albedo = 0)
 - $F_U = 0$
 - $F_D = F_T = 1$
- Due to gas + aerosol scattering and surface reflection
 - F_U can be large
 - $F_T > \text{solar flux!}$

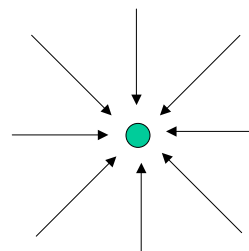
FIGURE 2.10 Upward directed flux F_U , downward directed flux F_D , and total actinic flux F_T as a function of altitude in the lower atmosphere. Values are given relative to a solar constant of unity for two wavelengths, 332.5 and 575 nm, and for two zenith angles, 20° and 78°. The calculations of Peterson (1976) included Rayleigh scattering, absorption by ozone, and scattering and absorption by aerosol particles.

Calculation of Photolysis Rates I

Generic reaction: $A + h\nu \rightarrow B + C$

$$\frac{d[A]}{dt} = -J_A[A]$$

- A “first-order process”
- *What does J_A depend on?*
- J_A depends on
 - Light intensity from all directions
 - “Actinic flux”
 - Absorption cross section (σ)
 - Quantum yield for photodissociation (ϕ)
 - All are functions of wavelength



Calculation of Photolysis Rates II

Generic reaction: $A + h\nu \rightarrow B + C$

$$\frac{d[A]}{dt} = -J_A[A] = -\int \sigma_A(\lambda)\phi_A(\lambda)F(\lambda)d\lambda \times [A]$$

J_A – first order photolysis rate of A (s^{-1})

$\sigma_A(\lambda)$ – wavelength dependent cross section of A ($cm^2/\#$)

$\phi_A(\lambda)$ – wavelength dependent quantum yield for photolysis

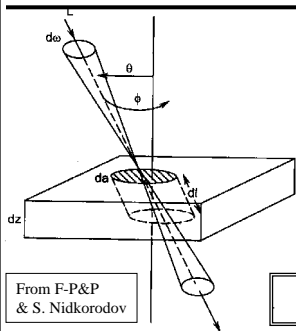
$F(\lambda)$ – spectral *actinic flux* density ($\#/cm^2/s$)

So, what are the smallest cross sections that matter?

The solar actinic flux (photons $cm^{-2} s^{-1} nm^{-1}$) is of order 10^{14} . In many cases, we need to know whether the photolytic lifetime of a molecule is 10 days ($J=10^{-6} s^{-1}$), or 100 days ($J=10^{-7} s^{-1}$). This means that cross sections as small as $10^{-20} cm^2$ or even smaller are potentially interesting. Such small cross sections are very challenging to measure with sufficient accuracy.

Radiation Fluxes Definitions

Quantity	Description	Units
F	Actinic flux density: energy crossing a unit area per unit time without consideration of direction (we do not care where photons come from)	$J m^{-2} s^{-1}$
$F(\lambda)$	Spectral actinic flux density: same as flux but per unit wavelength	$J m^{-2} s^{-1} nm^{-1}$
E	Irradiance: same as flux but for a unit area with a <u>fixed orientation</u>	$J m^{-2} s^{-1}$
$E(\lambda)$	Spectral irradiance: same as radiance but per unit wavelength range	$J m^{-2} s^{-1} nm^{-1}$
$L(\theta, \varphi)$	Radiance: radiant flux density per unit solid angle	$J m^{-2} s^{-1} sr^{-1}$
$L(\theta, \varphi, \lambda)$	Spectral radiance: same as radiance but per unit wavelength range	$J m^{-2} s^{-1} nm^{-1} sr^{-1}$



$$E = \int_{\omega} L(\theta, \varphi) \cos \theta d\omega = \int_0^{2\pi} \int_0^{\pi} L(\theta, \varphi) \cos \theta \sin \theta d\theta d\varphi$$

$$F = \int_{\omega} L(\theta, \varphi) d\omega = \int_0^{2\pi} \int_0^{\pi} L(\theta, \varphi) \sin \theta d\theta d\varphi$$

Radiance as a function of direction gives a complete description of the radiation field. When L is independent of direction, the field is called *isotropic*, in which case $E = \pi L$ and $F = 2\pi L$.

From F-P&P
& S. Nidkorodov

Solve in class: There are 10^9 photons flying into a 0.01 cm diameter opening every second. What is F with respect to this opening in units of $\#/cm^2/s$?

Radiation Measurements

Flat Plate → Irradiance

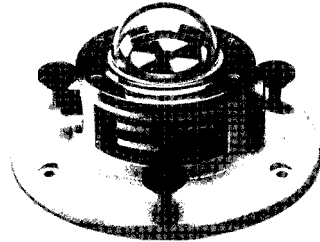


FIGURE 3.17 Typical device (Eppley Laboratories Model 8-48) used to measure solar irradiance. The detector consists of a differential thermopile with the hot junction receivers blackened with flat black coating and the cold junction receivers whitened with BaSO₄ (photo supplied courtesy of G. L. Kirk, Eppley Laboratories).

2π → ½ of Actinic Flux

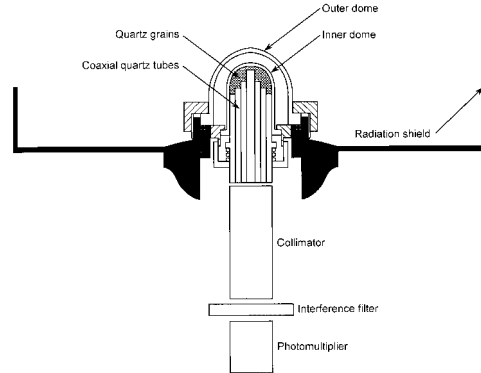


FIGURE 3.20 Schematic diagram of a 2π radiometer used to measure actinic fluxes (adapted from Junkermann *et al.*, 1989).

- Radiation does not just come directly from the sun
 - scattered radiation is just as important
 - Measure total or spectrally-resolved flux
 - Use models

From F-P&P

Radiation Models

- Predict radiation intensity
 - As f(time, altitude, latitude, λ)
 - Results of Madronich (1998) described in text
 - Will use extensively in homeworks & exams
 - Typical model results:

From F-P&P

TABLE 3.7 Actinic Flux Values $F(\lambda)$ at the Earth's Surface as a Function of Wavelength Interval and Solar Zenith Angle within Specific Wavelength Intervals for Best Estimate Surface Albedo Calculated by Madronich (1998)^a

Wavelength interval (nm)	Exponent ^b	Solar zenith angle (deg)									
		0	10	20	30	40	50	60	70	78	86
Actinic fluxes (photons cm ⁻² s ⁻¹)											
290–292	14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
292–294	14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
294–296	14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
296–298	14	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
298–300	14	0.03	0.03	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.00
300–302	14	0.07	0.07	0.06	0.04	0.03	0.01	0.00	0.00	0.00	0.00
302–304	14	0.18	0.18	0.15	0.12	0.08	0.04	0.01	0.00	0.00	0.00
304–306	14	0.33	0.32	0.29	0.23	0.16	0.09	0.04	0.01	0.00	0.00
306–308	14	0.51	0.49	0.45	0.37	0.28	0.17	0.08	0.02	0.00	0.00
308–310	14	0.66	0.65	0.60	0.51	0.40	0.27	0.14	0.04	0.01	0.00
310–312	14	0.99	0.97	0.90	0.79	0.64	0.45	0.25	0.09	0.02	0.00
312–314	14	1.22	1.19	1.12	1.00	0.82	0.61	0.36	0.14	0.04	0.00

Example model results

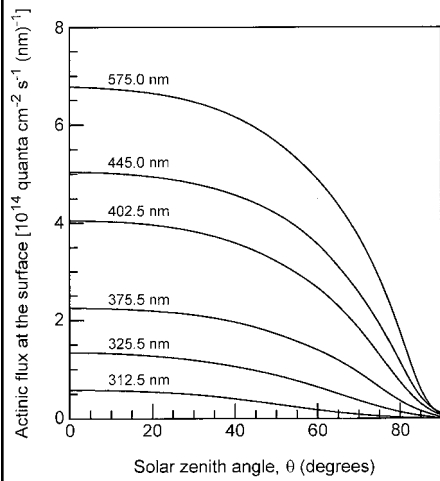


FIGURE 3.21 Calculated actinic flux centered on the indicated wavelengths at the earth's surface using best estimate albedos as a function of solar zenith angle (from Madronich, 1998).

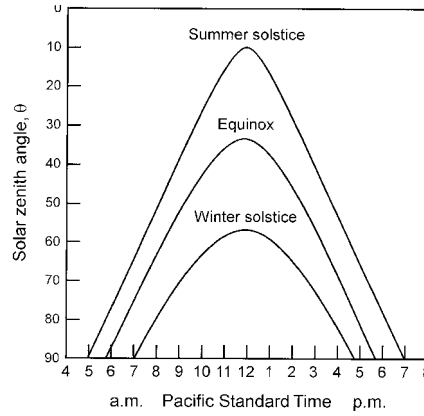


FIGURE 3.23 Relation between solar zenith angle and time of day at Los Angeles, California (from Leighton, 1961).

From F-P&P

Q: summer/winter solstices intensity at 445 nm: @ 8 am? @ noon?

Examples of Photolysis Rates

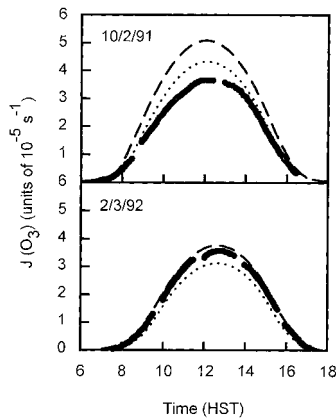


FIGURE 3.29 Measured rates of O_3 photolysis, $J(O_3)$, shown as heavy solid line, at Mauna Loa Observatory on two days (October 2, 1991, and February 3, 1992) compared to model calculations using two different assumptions (shown by the lighter dotted and dashed lines, respectively) for the quantum yield for O_3 photolysis at $\lambda > 310$ nm. (Adapted from Shetter *et al.*, 1996.)

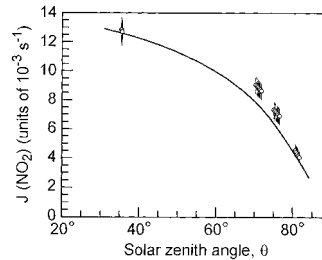


FIGURE 3.30 Values of $J(NO_2)$ at 7- to 7.5-km altitude as a function of solar zenith angle (θ) measured using 2π radiometers (circles) compared to a model calculated photolysis rate (solid line). (Adapted from Volz-Thomas *et al.*, 1996.)

From F-P&P

Example: Photolysis of CH₃CHO

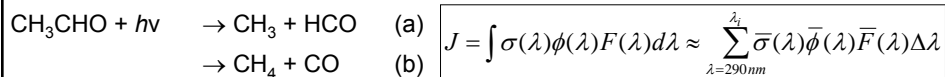


TABLE 3.19 Calculated Photolysis Rate Constants for CH₃CHO Photolysis at 30°N Latitude Six Hours after Noon on July 1

Wavelength interval, Δλ (nm)	Actinic flux, F _{av} (λ) (10 ¹⁴ photons cm ⁻² s ⁻¹)	Absorption cross section, σ _{av} (λ) (10 ⁻²⁰ cm ² molecule ⁻¹)	Quantum yield for reactions (9a) and (9b)		φ _{av} ^{9a} σ _{av} DF _{av} (10 ⁻⁶ s ⁻¹) ^a	φ _{av} ^{9b} σ _{av} DF _{av} (10 ⁻⁶ s ⁻¹) ^a
			φ _{av} ^{9a} (λ)	φ _{av} ^{9b} (λ)		
290-292	0	4.78	0.52	0.01	0	0
292-294	0	4.51	0.50	0	0	0
294-296	0	4.27	0.48	0	0	0
296-298	0	4.33	0.46	0	0	0
298-300	0	4.29	0.44	0	0	0
300-302	0	4.01	0.42	0	0	0
302-304	0	3.67	0.40	0	0	0
304-306	0	3.42	0.37	0	0	0
306-308	0	3.38	0.33	0	0	0
308-310	0.01	3.13	0.27	0	0.008	0
310-312	0.02	2.73	0.25	0	0.013	0
312-314	0.04	2.49	0.21	0	0.020	0
314-316	0.06	2.20	0.17	0	0.022	0
316-318	0.10	2.01	0.14	0	0.027	0
318-320	0.13	1.85	0.11	0	0.026	0
320-325	0.52	1.43	0.07	0	0.050	0
325-330	0.96	0.914	0.02	0	0.017	0

Totals^a: Σ φ_{av}^{9a}σ_{av}DF_{av} = 0.183 × 10⁻⁶ s⁻¹ = k_p^{9a} Σ φ_{av}^{9b}σ_{av}DF_{av} = 0 s⁻¹ = k_p^{9b}

^a D = earth-sun correction distance of 0.966.

From F-P&P