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

<table>
<thead>
<tr>
<th>Name</th>
<th>Typical wavelength or range of wavelengths (nm)</th>
<th>Typical range of frequencies ν (s⁻¹)</th>
<th>Typical range of wavenumbers νν (cm⁻¹)</th>
<th>Typical range of energies (kJ einstein⁻¹)注</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiowave</td>
<td>~10⁸–10¹³</td>
<td>~3 × 10¹⁰–3×10³</td>
<td>10⁻⁶–0.1</td>
<td>~10⁻³–10⁻⁴</td>
</tr>
<tr>
<td>Microwave</td>
<td>~10⁷–10⁸</td>
<td>~3 × 10⁶–3×10²</td>
<td>0.1–1</td>
<td>~10⁻³–10⁻²</td>
</tr>
<tr>
<td>Far-infrared</td>
<td>~10⁶–10⁷</td>
<td>~3 × 10⁴–3×10²</td>
<td>1–100</td>
<td>~10⁻²–1</td>
</tr>
<tr>
<td>Near-infrared</td>
<td>~10⁵–10⁶</td>
<td>~3 × 10²–3×10⁴</td>
<td>10⁻³–10³</td>
<td>~1–10³</td>
</tr>
<tr>
<td>Visible</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Red</td>
<td>700</td>
<td>4.3 × 10¹⁴</td>
<td>1.4 × 10⁴</td>
<td>1.7 × 10¹</td>
</tr>
<tr>
<td>Orange</td>
<td>620</td>
<td>4.8 × 10¹⁴</td>
<td>1.6 × 10⁴</td>
<td>1.9 × 10¹</td>
</tr>
<tr>
<td>Yellow</td>
<td>580</td>
<td>5.2 × 10¹⁴</td>
<td>1.7 × 10⁴</td>
<td>2.1 × 10¹</td>
</tr>
<tr>
<td>Green</td>
<td>530</td>
<td>5.7 × 10¹⁴</td>
<td>1.9 × 10⁴</td>
<td>2.3 × 10¹</td>
</tr>
<tr>
<td>Blue</td>
<td>470</td>
<td>6.4 × 10¹⁴</td>
<td>2.1 × 10⁴</td>
<td>2.5 × 10¹</td>
</tr>
<tr>
<td>Violet</td>
<td>430</td>
<td>7.1 × 10¹⁴</td>
<td>2.4 × 10⁴</td>
<td>2.8 × 10¹</td>
</tr>
<tr>
<td>Near-ultraviolet</td>
<td>400–200</td>
<td>(7.5–15.0)×10¹⁴</td>
<td>(2.5–5)×10⁴</td>
<td>(3.0–6.0)×10²</td>
</tr>
<tr>
<td>Vacuum ultraviolet</td>
<td>~700–50</td>
<td>(1.5–6.0)×10⁷</td>
<td>(5–20)×10⁴</td>
<td>~6.0–240×10²</td>
</tr>
<tr>
<td>X-Ray</td>
<td>~50–0.1</td>
<td>~0.6–300×10⁶</td>
<td>(0.2–100)×10⁹</td>
<td>~10⁷–10⁹</td>
</tr>
<tr>
<td>γ-Ray</td>
<td>≤0.1</td>
<td>~3×10⁹</td>
<td>≥10⁹</td>
<td>&gt;10⁹</td>
</tr>
</tbody>
</table>

* For kcal einstein⁻¹, divide by 4,184 (1 cal = 4,184 J).

Blackbody Radiation

Linear Scale ~ Log Scale

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 0.15 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 Handbokk of Geophysics and Space Environments, Air Force Survey in Geophysics #199, Office of Aerospace Research, USAF, Bedford, Mass. Template only.)

Solar & Earth Radiation Spectra

- 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 okay in right plot?

Solar Radiation Spectrum II

- Solar spectrum is strongly modulated by atmospheric scattering and absorption

From F-P&P

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, 1959; Chapter 16, p. 19)
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

- Solar spectrum is strongly modulated by atmospheric absorptions
- Remember that UV photons have most energy
  - O₂ absorbs extreme UV in mesosphere; O₃ absorbs most UV in stratosphere
  - Chemistry of those regions partially driven by those absorptions
  - Only light with λ>290 nm penetrates into the lower troposphere
- Biomolecules have same bonds (e.g. C-H), bonds can break with UV absorption => damage to life
- Importance of protection provided by O₃ layer

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 Radiation Spectrum vs. altitude

- 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 80º. Beyond that, Earth curvature and atmospheric refraction start to matter.

**TABLE 3.5** Values of the Air Mass $m$ at the Earth’s Surface for Various Zenith Angles $(\theta)$, Calculated from $m = \sec \theta$ and $h$ Corrected for Atmospheric Curvature and for Refraction

<table>
<thead>
<tr>
<th>Zenith angle $\theta$ (deg)</th>
<th>$m = \sec \theta$</th>
<th>Air mass $(m)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>10</td>
<td>1.02</td>
<td>1.02</td>
</tr>
<tr>
<td>20</td>
<td>1.06</td>
<td>1.06</td>
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<tr>
<td>30</td>
<td>1.13</td>
<td>1.15</td>
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<tr>
<td>40</td>
<td>1.21</td>
<td>1.21</td>
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<tr>
<td>50</td>
<td>1.56</td>
<td>1.56</td>
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<tr>
<td>60</td>
<td>2.00</td>
<td>2.00</td>
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<tr>
<td>70</td>
<td>2.52</td>
<td>2.54</td>
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<tr>
<td>80</td>
<td>4.81</td>
<td>4.72</td>
</tr>
<tr>
<td>90</td>
<td>14.3</td>
<td>12.4</td>
</tr>
</tbody>
</table>

Source: Demerjian et al. (1980).
Direct Attenuation of Radiation

\[ I = I_0 \times e^{-t \cdot m} \]

\[ I = t_{sg} + t_{ag} + t_{sp} + t_{ap} \]

- \( I \) = radiation intensity (e.g., \( F \))
- \( I_0 \) = radiation intensity above atmosphere
- \( m \) = air mass
- \( t \) = attenuation coefficient due to
  - absorption by gases (ag)
  - scattering by gases (sg)
  - scattering by particles (sp)
  - absorption by particles (ap)

\[ t_{sp} \propto \lambda^{-n} \]

\[ t_{sg} \propto \lambda^{-4} \]

Deeper UV – O, N₂, O₂
Mid UV & visible – O₃
Near IR – H₂O
Infrared – CO₂, H₂O, others

\[ t_{ag} \propto \sigma \]

\[ t_{ap} \propto \lambda^{-n} \] much more complex

FIGURE 3.15 Attenuation coefficients \( t \) for light scattering (Rayleigh scattering) and absorption (ozone absorption) by gases and for scattering and absorption plus absorption (aerosol extinction) by particles (from Penrose (1970) and Donahue et al. (1996)).

Scattering by Gases

- Purely physical process, not absorption
- Approximation:

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

- Strongly increases as \( \lambda \) decreases
- Reason why “sky is blue” during the day

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.
Scattering & Absorption by Particles

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

Gas Absorption: Beer-Lambert Law I

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

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

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

\textbf{Solve in class:} Show that in the small absorption limit the relative change in light intensity is approximately equal to absorbance.
Beer-Lambert Law II

**Pitfalls:**

- Other units are frequently used to express absorbance, for example:
  \[ A = \ln(I_0/I) = \varepsilon \times L \times C \]  
  \[ A = \ln(I_0/I) = \alpha \times L \times P \]
  
  - \( \varepsilon \equiv \) extinction coefficient \([\text{L mol}^{-1} \text{ cm}^{-1}]\)
  - \( \alpha \equiv \) absorption coefficient \([\text{atm}^{-1} \text{ cm}^{-1}]\)
  - \( C \equiv \) density of the absorber \([\text{mol L}^{-1}]\)
  - \( P \equiv \) partial pressure \([\text{atm}]\)

- 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 \( \sigma \)**

- \( \sigma \), 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 \( \text{HNO}_4 \)

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:

\[ \ln(I/I_0) = n \sigma \]

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 (< \(10^{-20}\) cm²/molec).

Solve in class: Sample contains 1 Torr of molecules of interest with \(\sigma = 3 \times 10^{-21}\) cm²/molec and 1 mTorr of impurity with \(\sigma = 2 \times 10^{-18}\) cm²/molec. What is the total absorbance in a 50 cm cell?

Example: UV Attenuation by O₃ and O₂

Attenuation coefficient is dominated by O₃ absorption in the 200-300 nm window. Therefore, direct attenuation can be easily calculated from known absorption cross sections of O₃. Similar formulas apply to attenuation by O₂ in 120-180 nm window.

\[ I(\lambda) = I_0(\lambda) \times e^{-\sigma(\lambda) \tau A} \]

where \(A\) ≡ column density

\[ A = \int_0^\infty [O_3(z)] dz \]

Alternatively written:

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

where \(\tau\) ≡ optical depth

\[ \tau(\lambda, z) = \int z [\sigma(\lambda) \times m \times [O_3(z)] dz \]

Solve in class: Using barometric law estimate column density of O₂ in the atmosphere. By how much does atmospheric O₂ attenuate solar radiation at around 170 nm (\(\sigma \approx 10^{-17}\) cm²/molec) at noon \(m = 1\)? Assume that O₂ fraction (21%) is independent of altitude and \(T = 270\) K. 

Ans: \(4 \times 10^{24}\); 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

Surface Albedo

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

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

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

\(^a\) Minimum reflectivities at 370 nm.
\(^b\) Measured with respect to NO\(_2\) photolysis.
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
- \( F_T > \) solar flux!

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 (\( \sigma \))
  - Quantum yield for photodissociation (\( \phi \))
  - 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 \((J=10^{-6} \text{ s}^{-1})\), or 100 days \((J=10^{-7} \text{ s}^{-1})\). 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.

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

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 \(F = 2\pi L\).

**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

2\pi \rightarrow \frac{1}{2} \text{ of Actinic Flux}

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

Radiation Models

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

<table>
<thead>
<tr>
<th>Wavelength interval (nm)</th>
<th>Exponent</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>78</th>
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<td>290–292</td>
<td>14</td>
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<td>0.00</td>
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<td>0.00</td>
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<td>292–296</td>
<td>14</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>294–296</td>
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<td>0.00</td>
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<td>296–300</td>
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<td>0.01</td>
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<td>0.02</td>
<td>0.03</td>
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<td>0.02</td>
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<td>0.07</td>
<td>0.07</td>
<td>0.06</td>
<td>0.04</td>
<td>0.03</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
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<td>0.18</td>
<td>0.19</td>
<td>0.15</td>
<td>0.12</td>
<td>0.08</td>
<td>0.04</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>0.35</td>
<td>0.32</td>
<td>0.29</td>
<td>0.23</td>
<td>0.16</td>
<td>0.09</td>
<td>0.04</td>
<td>0.01</td>
<td>0.00</td>
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<td>0.49</td>
<td>0.45</td>
<td>0.37</td>
<td>0.28</td>
<td>0.17</td>
<td>0.08</td>
<td>0.04</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>310–312</td>
<td>14</td>
<td>0.70</td>
<td>0.69</td>
<td>0.60</td>
<td>0.51</td>
<td>0.40</td>
<td>0.27</td>
<td>0.14</td>
<td>0.04</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>312–314</td>
<td>14</td>
<td>0.99</td>
<td>0.97</td>
<td>0.90</td>
<td>0.79</td>
<td>0.64</td>
<td>0.45</td>
<td>0.25</td>
<td>0.09</td>
<td>0.02</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Example model results

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

Examples of Photolysis Rates

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 Madermacher, 1998).

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

FIGURE 3.29 Measured rates of O₃ photolysis, ḟ(O₃), 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 O₃ photolysis at λ > 310 nm. (Adapted from Shetter et al., 1996.)

FIGURE 3.30 Values of ḟ(NO₂) at 7- to 7.5-km altitude as a function of solar zenith angle (×) measured using 3sr radiometers (circles) compared to a model calculated photolysis rate (solid line). (Adapted from Volz-Thomas et al., 1996.)
Example: Photolysis of CH$_3$CHO

\[ \text{CH}_3\text{CHO} + h\nu \rightarrow \text{CH}_3 + \text{HCO} \quad (a) \]

\[ \rightarrow \text{CH}_4 + \text{CO} \quad (b) \]

\[ J = \int \sigma(\lambda)\phi(\lambda) F(\lambda) d\lambda \approx \int \sigma(\lambda) d\lambda \int \phi(\lambda) F(\lambda) d\lambda \]

TABLE 3.19 Calculated Photolysis Rate Constants for CH$_3$CHO Photolysis at 30°N Latitude

<table>
<thead>
<tr>
<th>Wavelength interval, ( \Delta \lambda ) (nm)</th>
<th>Actinic flux, ( F_{\lambda}(\lambda) ) (photons cm$^{-2}$ s$^{-1}$)</th>
<th>Absorption cross section, ( \sigma_{\lambda}(\lambda) ) ( \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1} )</th>
<th>Quantum yield for reactions (9a) and (9b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>290–292</td>
<td>0</td>
<td>4.79</td>
<td>( \phi_{\lambda}(\lambda) ) 0.52 0.01 0 0</td>
</tr>
<tr>
<td>293–294</td>
<td>0</td>
<td>4.51</td>
<td>( \phi_{\lambda}(\lambda) ) 0.50 0 0 0</td>
</tr>
<tr>
<td>294–296</td>
<td>0</td>
<td>4.27</td>
<td>( \phi_{\lambda}(\lambda) ) 0.48 0 0 0</td>
</tr>
<tr>
<td>296–298</td>
<td>0</td>
<td>4.33</td>
<td>( \phi_{\lambda}(\lambda) ) 0.46 0 0 0</td>
</tr>
<tr>
<td>298–300</td>
<td>0</td>
<td>4.29</td>
<td>( \phi_{\lambda}(\lambda) ) 0.44 0 0 0</td>
</tr>
<tr>
<td>300–302</td>
<td>0</td>
<td>4.01</td>
<td>( \phi_{\lambda}(\lambda) ) 0.42 0 0 0</td>
</tr>
<tr>
<td>302–304</td>
<td>0</td>
<td>3.67</td>
<td>( \phi_{\lambda}(\lambda) ) 0.40 0 0 0</td>
</tr>
<tr>
<td>304–306</td>
<td>0</td>
<td>3.42</td>
<td>( \phi_{\lambda}(\lambda) ) 0.37 0 0 0</td>
</tr>
<tr>
<td>306–308</td>
<td>0</td>
<td>3.38</td>
<td>( \phi_{\lambda}(\lambda) ) 0.33 0 0 0</td>
</tr>
<tr>
<td>308–310</td>
<td>0.01</td>
<td>3.13</td>
<td>( \phi_{\lambda}(\lambda) ) 0.27 0 0.008 0</td>
</tr>
<tr>
<td>310–312</td>
<td>0.02</td>
<td>2.73</td>
<td>( \phi_{\lambda}(\lambda) ) 0.25 0 0.013 0</td>
</tr>
<tr>
<td>312–314</td>
<td>0.04</td>
<td>2.49</td>
<td>( \phi_{\lambda}(\lambda) ) 0.21 0 0.030 0</td>
</tr>
<tr>
<td>314–316</td>
<td>0.06</td>
<td>2.20</td>
<td>( \phi_{\lambda}(\lambda) ) 0.17 0 0.022 0</td>
</tr>
<tr>
<td>316–318</td>
<td>0.10</td>
<td>2.08</td>
<td>( \phi_{\lambda}(\lambda) ) 0.14 0 0.017 0</td>
</tr>
<tr>
<td>318–320</td>
<td>0.13</td>
<td>1.85</td>
<td>( \phi_{\lambda}(\lambda) ) 0.11 0 0.006 0</td>
</tr>
<tr>
<td>320–322</td>
<td>0.15</td>
<td>1.63</td>
<td>( \phi_{\lambda}(\lambda) ) 0.07 0 0.050 0</td>
</tr>
<tr>
<td>322–325</td>
<td>0.52</td>
<td>0.94</td>
<td>( \phi_{\lambda}(\lambda) ) 0.02 0 0.017 0</td>
</tr>
<tr>
<td>325–330</td>
<td>0.96</td>
<td>0.914</td>
<td>( \phi_{\lambda}(\lambda) ) 0.05 0 0.014 0</td>
</tr>
</tbody>
</table>

\[ \Delta \lambda = 2 \mu \text{m} \]

\[ \int \sigma(\lambda) \phi(\lambda) F(\lambda) d\lambda \approx \int \sigma(\lambda) d\lambda \int \phi(\lambda) F(\lambda) d\lambda \]

\[ \phi(\lambda) = \phi_{\lambda}(\lambda) \]

\[ F(\lambda) = F_{\lambda}(\lambda) \]

\[ \sigma(\lambda) \]

\[ \lambda \]

\[ \Delta \lambda \]

\[ \Delta \lambda = 2 \mu \text{m} \]

\[ \phi(\lambda) = \phi_{\lambda}(\lambda) \]

\[ F(\lambda) = F_{\lambda}(\lambda) \]

\[ \sigma(\lambda) \]

\[ \lambda \]

\[ \Delta \lambda \]

\[ \phi(\lambda) = \phi_{\lambda}(\lambda) \]

\[ F(\lambda) = F_{\lambda}(\lambda) \]

\[ \sigma(\lambda) \]

\[ \lambda \]

\[ \Delta \lambda \]

\[ \phi(\lambda) = \phi_{\lambda}(\lambda) \]

\[ F(\lambda) = F_{\lambda}(\lambda) \]

\[ \sigma(\lambda) \]

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\[ \Delta \lambda \]

\[ \phi(\lambda) = \phi_{\lambda}(\lambda) \]

\[ F(\lambda) = F_{\lambda}(\lambda) \]

\[ \sigma(\lambda) \]

\[ \lambda \]

\[ \Delta \lambda \]

\[ \phi(\lambda) = \phi_{\lambda}(\lambda) \]

\[ F(\lambda) = F_{\lambda}(\lambda) \]

\[ \sigma(\lambda) \]

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\[ \Delta \lambda \]

\[ \phi(\lambda) = \phi_{\lambda}(\lambda) \]

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\[ \phi(\lambda) = \phi_{\lambda}(\lambda) \]

\[ F(\lambda) = F_{\lambda}(\lambda) \]

\[ \sigma(\lambda) \]

\[ \lambda \]