Atmos. Chem. Lecture 5, 9/18/13:
Light and photochemistry

- Photodissociation
- Absorption spectra of O₂ and O₃
- Absorption & Beer’s Law
- Photolysis rate constants
- Atmospheric radiation

Problem Set 1 due Wednesday 9/25

Fate of electronically excited species

“Jablonski Diagram” (FP&P)
vertical: absorption (A), emission of light (F, P); collisional relaxation (ζ)
horizontal: intersystem crossing (ISC), internal conversion (IC)
Photodissociation: direct vs. predissociation

Overtone photodissociation

Light absorption by oxygen (O₂)

Potential energy curves of O₂
Light absorption by ozone (O₃)

Absorption of light by molecules

Beer-Lambert Law

\[ I(\lambda) = I(\lambda_o) e^{-\int \alpha(\chi) d\chi} \]

[Note: Additional material is discussed here during lecture.]
**O(1D) production by O₃ photolysis**

\[
\begin{align*}
O_3 + h\nu &\rightarrow O(\text{1P}) + O_2 \\
&\rightarrow O(\text{1D}) + O_2 
\end{align*}
\]

**Photochemical reaction rates**

Unimolecular reaction: \[ A + h\nu \rightarrow B + C \quad \Phi_1 \]

\[ \rightarrow X \quad \Phi_2 \]

*Rate of loss of A depends on...*

- How well A absorbs light
- Chance that a reaction will occur after absorption
- How much light there is
- Concentration of A

*One wavelength:*

\[
- \frac{d[A]}{dt} = J(\lambda)[A] = \Phi_{\text{int}}(\lambda) \sigma_{\text{a}}(\lambda) I(\lambda) [A]
\]
Example 1: NO₂ photolysis

\[
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}^{1}\text{P)}
\]

\[\Delta H = 301 \text{ kJ/mol} \]
\[\lambda_{	ext{excit}} = 318 \text{ nm} \]

Example 2: CH₂O photolysis

\[\text{Cross section (arb. units)} \]
\[\text{Wavelength (nm)} \]

1 nm resolution
5 nm resolution
Actinic flux $I(\lambda)$

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Quantity</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I(\lambda)$</td>
<td>(Spectral) Radiance: Energy flux coming from a specific (solid) angle, per unit wavelength</td>
<td>$J \text{ m}^{-2} \text{ s}^{-1} \text{ nm}^{-1} \text{ sr}^{-1}$</td>
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<td>$E(\lambda)$</td>
<td>(Spectral) Irradiance: Energy flux through a flat plane (measured by instruments), per unit wavelength</td>
<td>$J \text{ m}^{-2} \text{ s}^{-1} \text{ nm}^{-1}$</td>
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<tr>
<td>$F(\lambda)$</td>
<td>(Spectral) Radiant Flux Density: Energy flux through a point (relevant to molecules), per unit wavelength</td>
<td>$J \text{ m}^{-2} \text{ s}^{-1} \text{ nm}^{-1}$</td>
</tr>
<tr>
<td>$I(\lambda)$</td>
<td>(Spectral) Actinic Flux: Photon flux through a point (relevant to molecules), per unit wavelength</td>
<td>photons cm$^{-2} \text{ s}^{-1} \text{ nm}^{-1}$</td>
</tr>
<tr>
<td>$I(\lambda)$</td>
<td>Actinic Flux: Total photon flux through a point (relevant to molecules), spanning a range of wavelengths</td>
<td>photons cm$^{-2} \text{ s}^{-1}$</td>
</tr>
</tbody>
</table>

Calculated Actinic Fluxes (FP&P)

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Main absorbers/scatterers

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