Introduction to Photolysis
AOSC 433/633 & CHEM 433
Ross Salawitch

Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2015

Lecture 10
10 March 2015
Importance of Radicals

• With a few exceptions, the only reactions between molecules that proceed at appreciable rates are those involving at least one radical

• Radicals require significant energy to form: a bond must be broken

• Radical formation is tied to absorption of photons that “photodissociate” a compound, leading to radical formation

Initiation

\[ \text{O}_2 + \text{photon} \rightarrow \text{O} + \text{O} \]

Propagation

\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \]
\[ \text{O}_3 + \text{photon} \rightarrow \text{O}(^1\text{D}) + \text{O}_2 \]
\[ \text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH} \]
\[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \]
\[ \text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2 \]

Termination

\[ \text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \]
• Motivation for Today’s Lecture:

a) How does atmosphere go from this: 

\[ \text{Spectral Actinic Flux, photons cm}^{-2} \text{s}^{-1} \text{nm}^{-1} \]

\[ \begin{align*}
10^9 & \quad 10^{10} \\
10^{11} & \quad 10^{12} \\
10^{13} & \quad 10^{14} \\
10^{15} & \quad 100 \quad 200 \quad 300 \quad 400 \quad 500 \quad 600 \\
\text{Wavelength, nm} & \\
\end{align*} \]

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

b) Biological Effects of UV Radiation


Energetics of Photolysis

\[ \text{O}_3 + h\nu \rightarrow \text{O}^{(1D)} + \text{O}_2 \]

\( h\nu \) represents a photon with specific energy.

Let’s examine enthalpy of this reaction:

\[
\begin{array}{ccc}
33.9 \text{ kcal/mole} & 104.7 \text{ kcal/mole} & 22.5 \text{ kcal/mole} \\
\text{O}_3 + h\nu \rightarrow \text{O}^{(1D)} + \text{O}_2^{(1\Delta_g)} & \Delta \text{Enthalpy} = \\
\end{array}
\]

Photon Energy:

\[ \varepsilon = \frac{hc}{\lambda} \quad \Rightarrow \quad \lambda_{\text{max}} = \frac{hc}{\Delta \text{Enthalpy}} \]

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

\[ \lambda_{\text{max}} = \frac{hc}{\Delta \text{Enthalpy}} = \frac{2.85 \times 10^4 \text{ kcal/mole nm}}{\Delta \text{Enthalpy}} = \]
Energetics of Photodissociation

\[ \text{O}_3 + h\nu \rightarrow \text{O}^{(1D)} + \text{O}_2^{(\Delta_g)} \quad \Delta\text{Enthalpy} = \text{kcal/mole} \quad \lambda_{\text{max}} = \text{nm} \]

\[ \text{O}_3 + h\nu \rightarrow \text{O}^{(3P)} + \text{O}_2^{(3\Sigma_g)} \quad \Delta\text{Enthalpy} = 25.7 \text{ kcal/mole} \quad \lambda_{\text{max}} = \text{nm} \]

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 \(^3P\)*:

“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 \(2S+1 = 3 \iff \) spin angular momentum

\(P\) represents orbital angular momentum, found from an electron diagram of filled orbitals:

<table>
<thead>
<tr>
<th>ground state:</th>
<th>(1s)²</th>
<th>(2s)²</th>
<th>(2p)⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑↑↑↑</td>
</tr>
<tr>
<td>(\Lambda)</td>
<td>+1</td>
<td>0</td>
<td>-1</td>
</tr>
</tbody>
</table>

**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 \(2S+1 = 1 \iff \) spin angular momentum

\(D\) represents orbital angular momentum, found from an electron diagram of filled orbitals:

<table>
<thead>
<tr>
<th>excited state</th>
<th>(1s)²</th>
<th>(2s)²</th>
<th>(2p)⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑↓</td>
</tr>
<tr>
<td>(\Lambda)</td>
<td>+1</td>
<td>0</td>
<td>-1</td>
</tr>
</tbody>
</table>
Atmospheric Radiation

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

Panel (a): Curves of black-body energy versus wavelength for \(5750\) K (Sun’s approximate temperature) and for \(245\) 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).


- Absorption and photodissociation in the UV occurs due to changes in the electronic state (orbital configuration) of molecules
Absorption Cross Section of $O_2$

- $O_2$ can not dissociate longward of $\sim 250$ nm
- All absorption shown above is dissociative (e.g., leads to production of two $O$ atoms)
- Structure in the $O_2$ 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)

From Brasseur & Solomon, *Aeronomy of the Middle Atmosphere*, 1986
**Beer-Lambert Law**

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

where:

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

- **F**: solar irradiance (photons/cm^2/sec)
- **\( \sigma_{\lambda} \)**: absorption cross section
- **C**: concentration of absorbing gas (molecules/cm^3)
- **m**: ratio of slant path to vertical path, equal to \( 1/\cos(\theta) \) for \( \theta < \sim 75^\circ \)
- **\( \theta \)**: solar zenith angle

Governed 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:

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

Units: s$^{-1}$ 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:

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

Units: 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.

Rate of Reaction $= \frac{dO_3}{dt} = J \ [O_3]$; Units of $J$ are s$^{-1}$
Optical Depth of O₂ 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 \text{(\(\tau\): optical depth)} \]

Also:

\[ \int_{0}^{\infty} [O_{2}] \, dz' \approx 4 \times 10^{24} \text{ molecules/cm}^2 \]

<table>
<thead>
<tr>
<th>O₂ Optical Depth for (\theta = 0^\circ), (z = 0) km</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sigma_{\text{max}}) (cm²)</td>
</tr>
<tr>
<td>Schumann-Runge Continuum</td>
</tr>
<tr>
<td>Schumann-Runge Bands</td>
</tr>
<tr>
<td>Herzberg Continuum</td>
</tr>
</tbody>
</table>
Figure 4.31, Brasseur and Solomon
Where Does Optical Depth $= 1.0$ for O$_2$?

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

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

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

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

<table>
<thead>
<tr>
<th>Altitude where $\tau = 1$ (for $\theta = 0^\circ$)</th>
<th>$\sigma_{\text{max}}$ (cm$^2$)</th>
<th>$z$ (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schumann-Runge Continuum</td>
<td>$10^{-17}$</td>
<td></td>
</tr>
<tr>
<td>Schumann-Runge Bands</td>
<td>$10^{-20}$</td>
<td>$3 \times 10^{-23}$</td>
</tr>
<tr>
<td>Herzberg Continuum</td>
<td>$10^{-23}$</td>
<td></td>
</tr>
</tbody>
</table>
Absorption Cross Section of O$_3$

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

<table>
<thead>
<tr>
<th>Photolysis Product</th>
<th>1180</th>
<th>590</th>
<th>460</th>
<th>230</th>
<th>170</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$(3$\Sigma_g^-$)</td>
<td>O$_2$(1$\Delta_g$)</td>
<td>O$_2$(1$\Sigma_g^+$)</td>
<td>O$_2$(3$\Sigma_u^+$)</td>
<td>O$_2$(3$\Sigma_u^-$)</td>
<td></td>
</tr>
<tr>
<td>O(3P)</td>
<td>2240</td>
<td>196</td>
<td>179</td>
<td>129</td>
<td>108</td>
</tr>
<tr>
<td>O(1D)</td>
<td>210</td>
<td>170</td>
<td>150</td>
<td>108</td>
<td>108</td>
</tr>
<tr>
<td>O(1S)</td>
<td>180</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
</tbody>
</table>

From Brasseur & Solomon, *Aeronomy of the Middle Atmosphere*, 1986
Optical Depth of $O_3$ Absorption

A typical mid-latitude column abundance for $O_3$ 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:

$$\frac{\text{Column } O_3}{\text{Column Air}} = \frac{8 \times 10^{18}}{2 \times 10^{25}} = 0.4 \text{ parts per million} \Rightarrow \text{Ozone is a trace species!}$$

| $O_3$ Optical Depth for $\theta = 0^\circ$, $z = 0$ km |
|-------------------------------------------------|-------------------------------------------------|
| $\sigma_{\text{max}}$ (cm$^2$) | $\tau$ (0 km) | $e^{-\tau}$ (0 km) | $O_3$ Column, $\tau = 1.0$ |
| Hartley ($\sim$220 to 280 nm) |                          |                  |                                  |
| Huggins ($\sim$310 to 330 nm) |                          |                  |                                  |
| Chappuis ($\sim$500 to 700 nm) |                          |                  |                                  |
Solar Spectral Actinic Flux


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
NO$_2$ Photolysis

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

leading to a value for J$_{NO2}$ that is nearly independent of height and SZA:
NO₂ Photolysis

Absorption Cross Section (10² cm⁻¹)

Wavelength (nm)

NO₂ Photolysis

SZA = 0° → SZA = 85° → Alt = 20 km

J NO₂ (10⁻² sec⁻¹)

Wavelength (nm)

J NO₂ photolysis (10⁻⁴ sec⁻¹ cm⁻¹)

Wavelength (nm)
O$_3$ → O($^1$D) Photolysis

The production of O($^1$D) 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:
$\text{O}_3 \rightarrow \text{O}(^1\text{D})$ Photolysis

$\text{O}_3 \rightarrow \text{O}(^1\text{D})$ Photolysis

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$\text{O}_3 \rightarrow \text{O}(^1\text{D})$ Photolysis

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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:
$\text{O}_3 \rightarrow \text{O}^{(3P)} \text{ Photolysis}$
### Biological Effects of UV Radiation

#### Table 2.4: Types of UV Radiation

<table>
<thead>
<tr>
<th>Type</th>
<th>Wavelength</th>
<th>Relative Energy</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV-A</td>
<td>320–400 nm</td>
<td>Lowest energy</td>
<td>Least damaging and reaches the Earth's surface in greatest amount</td>
</tr>
<tr>
<td>UV-B</td>
<td>280–320 nm</td>
<td>Higher energy</td>
<td>More damaging than UV-A but less damaging than UV-C. Most UV-B is absorbed by $O_3$ in the stratosphere</td>
</tr>
<tr>
<td>UV-C</td>
<td>200–280 nm</td>
<td>Highest energy</td>
<td>Most damaging but not a problem because it is totally absorbed by $O_2$ and $O_3$ in the stratosphere</td>
</tr>
</tbody>
</table>

**Chemistry in Context**

#### Figure 2.11, Chemistry in Context

- **UV-B**
- **UV-A**

Absorption by $O_3$ in this region

Wavelength (nm)

**Increase in incidence of melanoma skin cancer, U.S.**

<table>
<thead>
<tr>
<th>Year of diagnosis</th>
<th>Rate per 100,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>1974</td>
<td>2.5</td>
</tr>
<tr>
<td>1976</td>
<td>3.0</td>
</tr>
<tr>
<td>1978</td>
<td>4.0</td>
</tr>
<tr>
<td>1980</td>
<td>5.0</td>
</tr>
<tr>
<td>1982</td>
<td>6.0</td>
</tr>
<tr>
<td>1984</td>
<td>7.0</td>
</tr>
<tr>
<td>1986</td>
<td>8.0</td>
</tr>
<tr>
<td>1988</td>
<td>9.0</td>
</tr>
<tr>
<td>1990</td>
<td>10.0</td>
</tr>
<tr>
<td>1992</td>
<td>11.0</td>
</tr>
<tr>
<td>1994</td>
<td>12.0</td>
</tr>
<tr>
<td>1996</td>
<td>13.0</td>
</tr>
<tr>
<td>1998</td>
<td>14.0</td>
</tr>
<tr>
<td>2000</td>
<td>15.0</td>
</tr>
<tr>
<td>2002</td>
<td>16.0</td>
</tr>
</tbody>
</table>
Biological Effects of UV Radiation

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)

The “biologically active dose rate” maximizes in the UV-B region at ~305 nm, where $\sigma_{O_3} = 3 \times 10^{-19} \text{ cm}^2 \Rightarrow \tau (0 \text{ km}) = 2.4$

(for $O_3$ column= 300 DU)

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

http://www.who.int/uv/uv_and_health/en