Atmospheric Chemistry

Lecture 10
$h\nu + O_3 \rightarrow O_2 + O + k.e.$

Kinetic energy shared with other molecules by collision; leads to heating of stratosphere.
Photon Energetics

\[ E(\text{energy}) = h\nu = \frac{hc}{\lambda} \]

\[ hc = 6.6 \cdot 10^{-27} (\text{erg sec}) \cdot 3 \cdot 10^8 (\text{cm sec}^{-1}) = 1.98 \cdot 10^{-18} (\text{erg cm}) \]

\[ hc = \frac{1.98 \cdot 10^{-18} (\text{erg cm})}{1.6 \cdot 10^{-12} (\text{erg/eV})} = 1.24 \cdot 10^{-6} (\text{eV cm}) = 1240 (\text{eV nm}) \]

310 nm photon = \sim 4 \text{ eV energy}

1 eV = 23 \text{ kCal/mol}

1 eV = 96 \text{ kJ/mol}
Ozone Photodissociation vs Wavelength

Ozone Enthalpy of formation (bond strength) = 143 kJ/mol = ~1.5 eV/molecule

Needs wavelength of about 800nm (near IR) for photodissociation. Chappuis bands dissociate ozone in the visible, but are forbidden transitions with small cross section.
Heating vs Altitude

Figure 4. The solar heating contributed by each absorption band for ascent II.

- CH: Chappuis band
- HA: Hartley band 240–300 nm
- O1: Oxygen absorption 180–200 nm
- HB: Hartley band 200–240 nm
- O2: Oxygen absorption 200–240 nm
- HU: Huggins band 300–350 nm
- SR: Schumann Runge bands
- T: Total

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Maximum Heating Near 1 hPa; Well Above the Ozone Maximum

from Dütsch, Advances in Geophysics, 1971

Atmospheric Chemistry Lecture 10
Two-dimensional atmospheric temperature structure

- Warm summer stratopause
- Cold tropical tropopause
- Cold winter polar lower stratosphere
January Temperature Structure

**Warm Winter**

**Cold Winter**

Atmospheric Chemistry Lecture 10
July Temperature Structure

Warm Winter

Cold Winter

Latitude

Pressure (hPa)
Stratospheric Heat Balance Equation

\[ \frac{\partial T}{\partial t} + \text{Transport of heat} = \text{Heating}(O_3) - \text{Cooling}(CO_2) \]

*Cooling often approximated by linear response proportional to temperature*

\[ \text{Cooling} = aT + b \]

where \( a \) has units of inverse time with \( 1/a \) of the order of a few days to a week
Why does the troposphere warm while the stratosphere cools with the addition of CO$_2$ to the atmosphere?
Stratospheric Cooling: CO$_2$ IR Bands
Observed IR Spectrum at Top of Atmosphere

Fig. 3. Comparison of observed and theoretical radiances for a clear atmosphere near Guam at 15.1°N and 153.3°W on April 27, 1970.

Atmospheric Chemistry Lecture 10
Response of Outgoing Radiation to Increased CO$_2$

Outgoing radiation from troposphere has absorption feature from 15μ CO$_2$ band. In stratosphere, collisions repopulate the excited state (CO$_2$) bending mode, which can then radiate upward to space, leading to a decrease in the energy locally.

Fig. 16. Vertical distributions of temperature in radiative convective equilibrium for various values of CO$_2$ content.