Atmospheric Chemistry

Lecture 5

Rate Determining Step for NO_x Catalysis of Ozone Loss

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O \rightarrow NO + O_2$$
$$NO_2 + h\nu \rightarrow NO + O$$

Rapid reactions set relationship between NO and NO_2 in the stratosphere

NO continuity equation

$$\frac{dNO}{dt} = -k_{NO,O_3} \cdot [O_3] \cdot [NO] + k_{O,NO_2} \cdot [O] \cdot [NO_2] + J_{NO_2} \cdot [NO_2]$$

$$\frac{NO}{NO_2} = \frac{J_{NO_2} + k_{O,NO_2} \cdot [O]}{k_{O_3,NO} \cdot [O_3]}$$

Solve for NO to NO_2 ratio

Substitute into Ozone Continuity Equation

O_3 continuity equation for NO_x reactions

$$\left.\frac{dO_x}{dt}\right|_{NO_x} = -k_{O_3,NO} \cdot [O_3] \cdot [NO] - k_{O,NO_2} \cdot [O] \cdot [NO_2] + J(NO_2) \cdot [NO_2]$$

NO continuity equation

$$0 = -k_{NO,O_3} \cdot [O_3] \cdot [NO] + k_{O,NO_2} \cdot [O] \cdot [NO_2] + J_{NO_2} \cdot [NO_2]$$

Subtract to obtain:

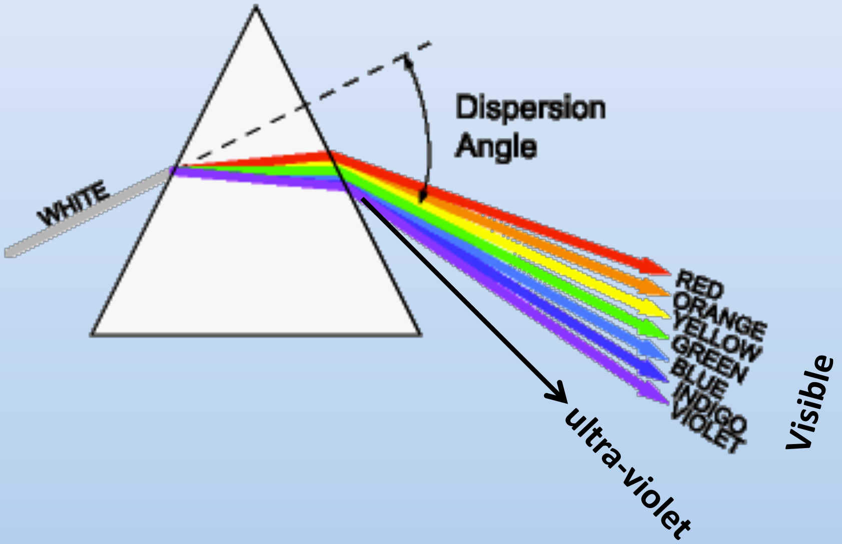
$$\left.\frac{dO_x}{dt}\right|_{NO_x} = -2 \cdot k_{O,NO_2} \cdot [O] \cdot [NO_2]$$

When added to the pure oxygen continuity equation:

$$\frac{dO_x}{dt} = 2 \cdot J(O_2) \cdot [O_2] - 2 \cdot k_{O,O_3} \cdot [O] \cdot [O_3] - 2 \cdot k_{O,NO_2} \cdot [O] \cdot [NO_2]$$

The Discovery of UV

- Johann Wilhelm Ritter uses a prism in 1801 to discover UV radiation
- Radiation beyond the violet darkened silver chloride!



- One year earlier Herschel had discovered infrared radiation

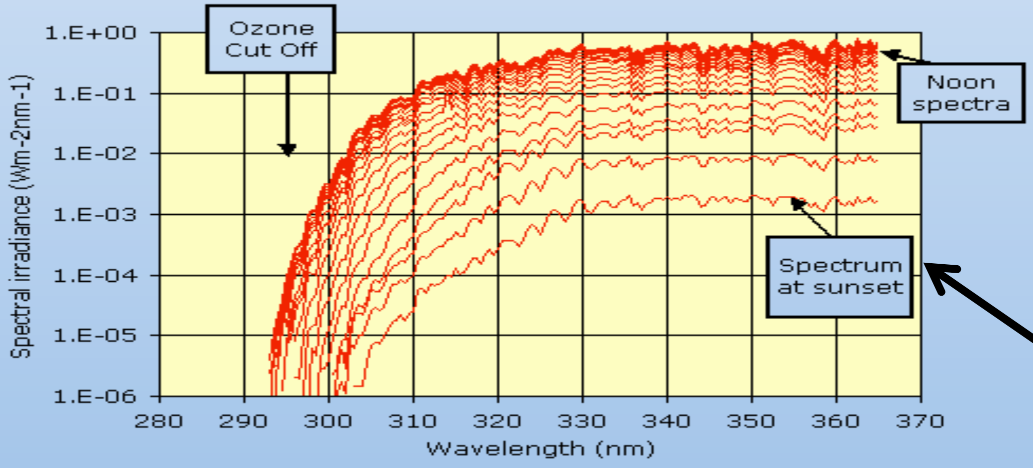
Ritter

Cutoff of the solar UV spectrum and the discovery of atmospheric ozone

1879: Marie Alfred Cornú used newly-developed techniques for ultraviolet spectroscopy to measure the sun's spectrum.

To his surprise, the intensity of the sun's radiation dropped off rapidly at wavelengths below ~300 nm.

Cornú

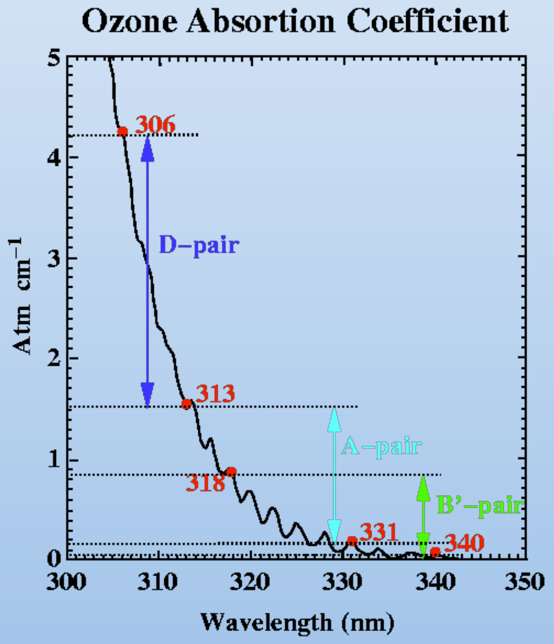


Modern spectral measurements

Hartley and the Identification of Atmospheric Ozone

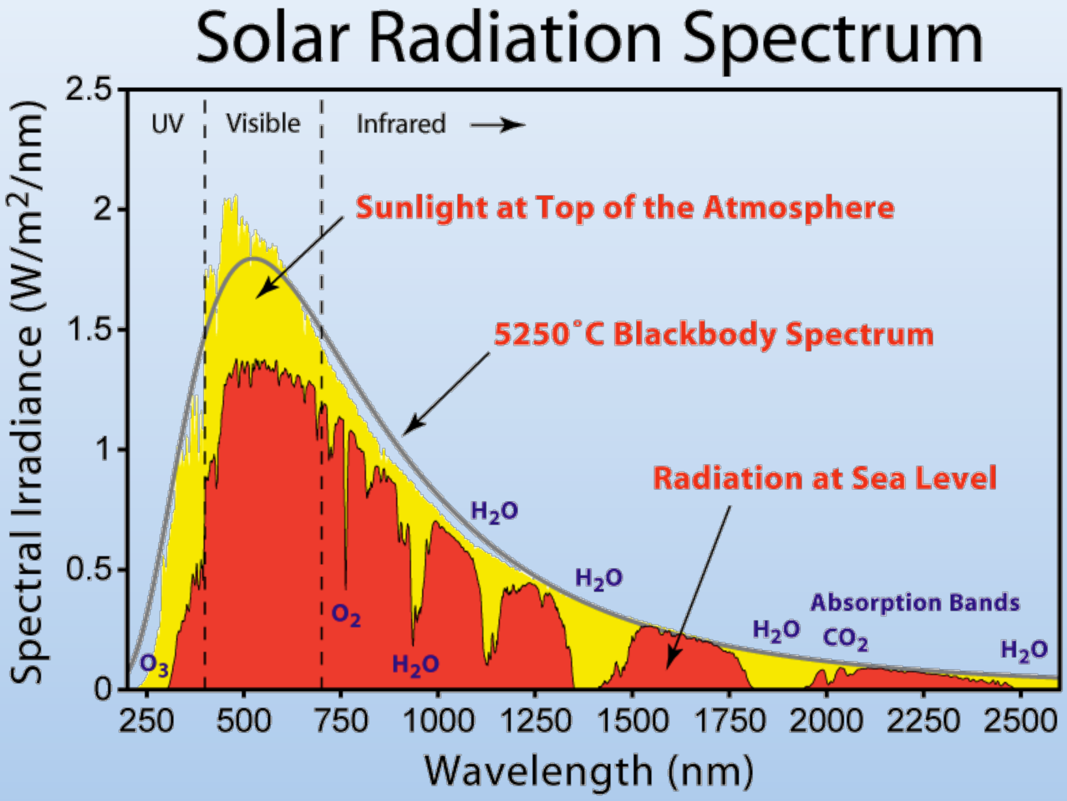
- **1883: Hartley identified ozone as the substance absorbing uv from the sun at wavelengths less than 290 nanometers**

Hartley's Spectrometer (note prism)

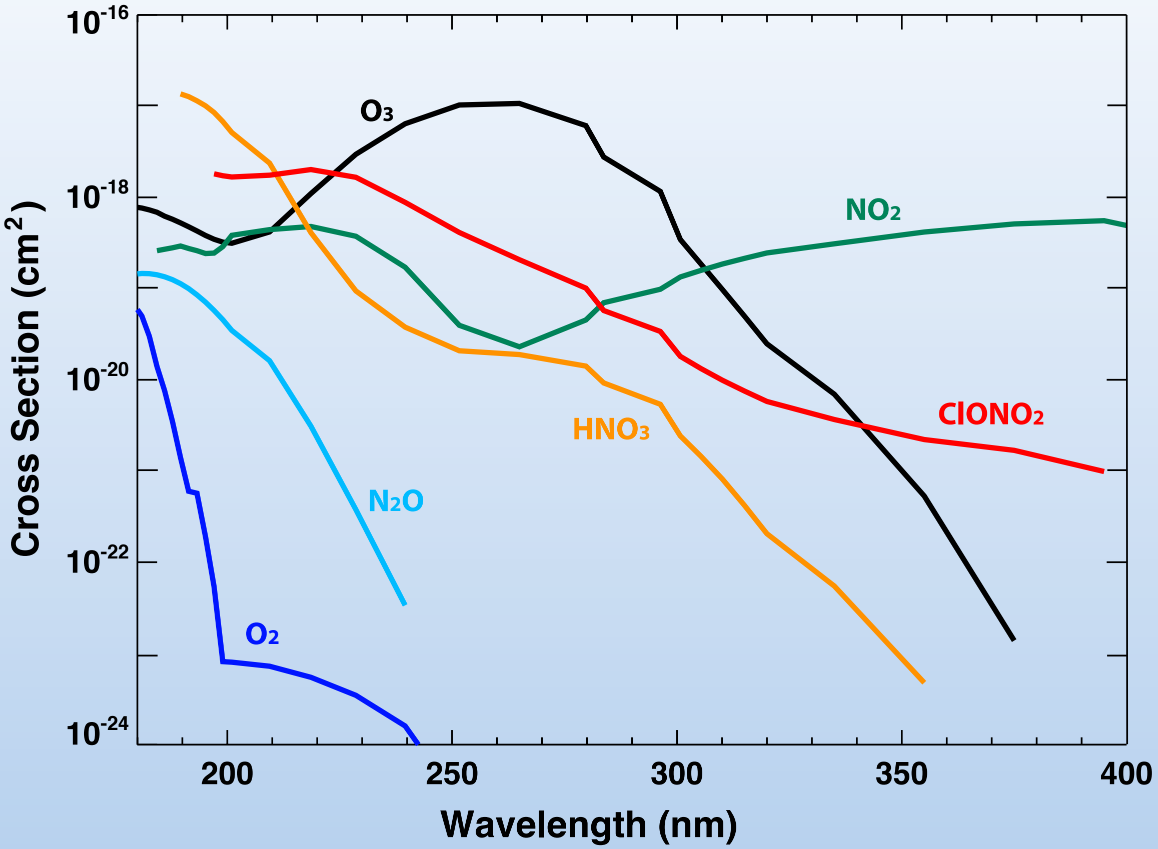


Sir Walter Noel Hartley

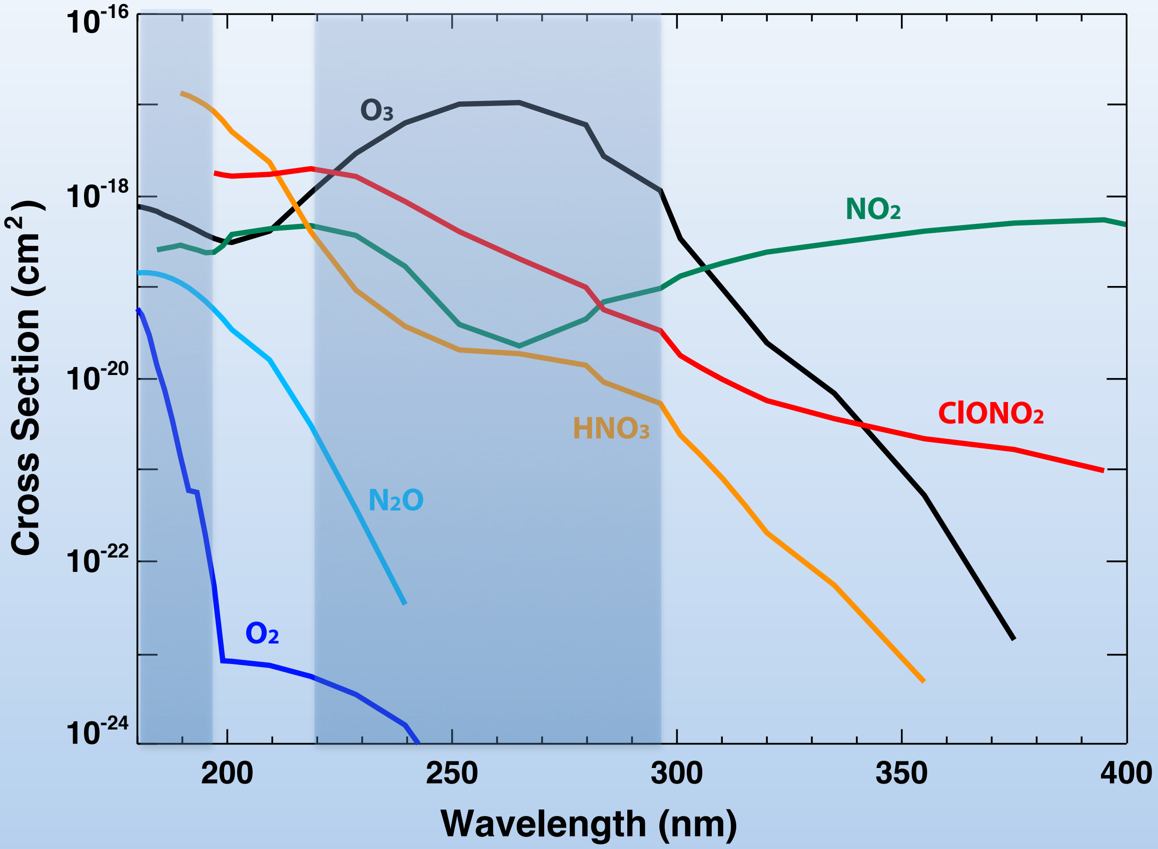
Back to Solar UV Radiation



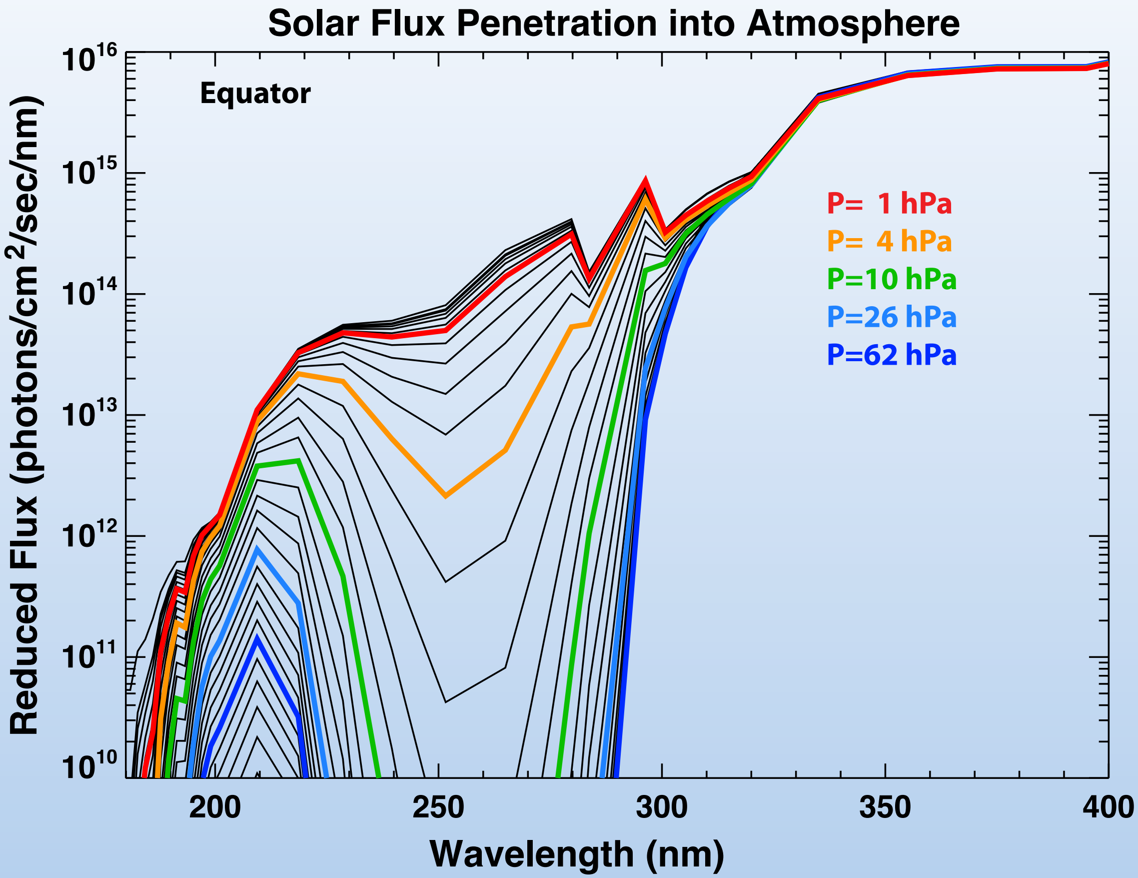
Cross Sections for Photolysis



Cross Sections for Photolysis



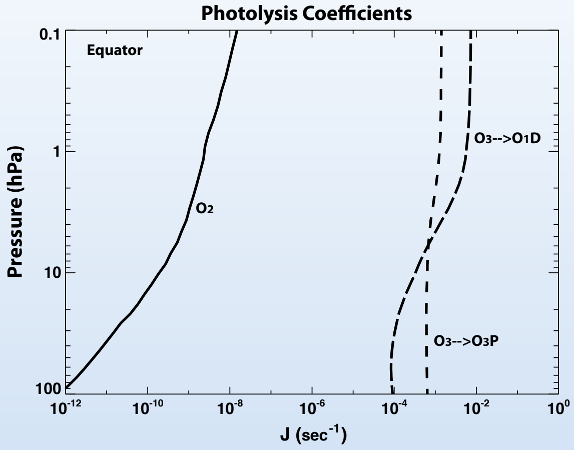
Reduced Solar Flux vs Altitude



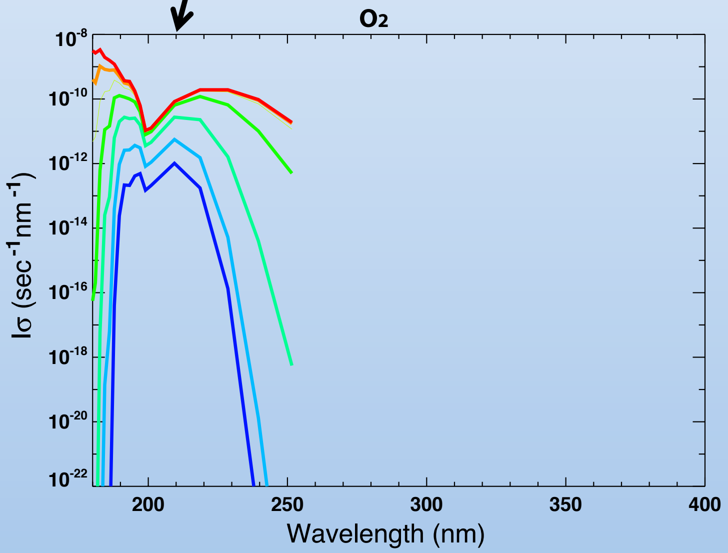
$$I(\lambda, z) = I_0(\lambda) \cdot e^{-N_{O_2}(z)\cdot\sigma_{O_2}(\lambda) - N_{O_3}(z)\cdot\sigma_{O_3}(\lambda)}$$

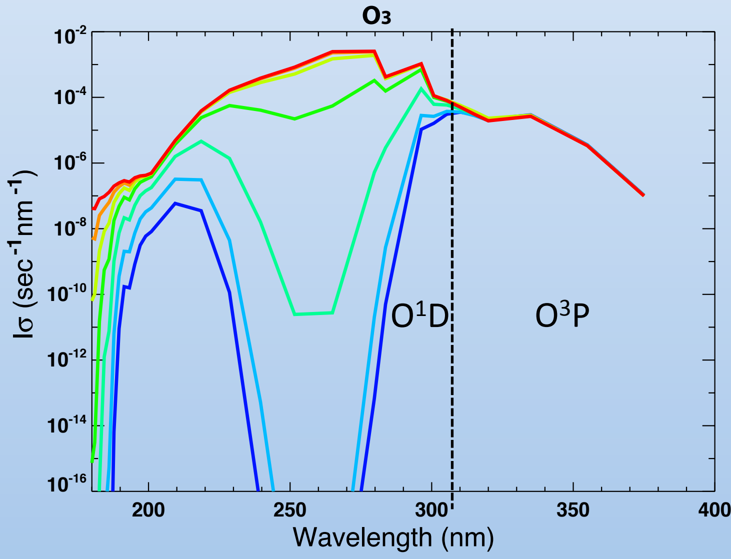
Photolysis Rates vs Wavelength

$$J_x(z) = \int \sigma_x(\lambda) \cdot I(\lambda, z) d\lambda$$

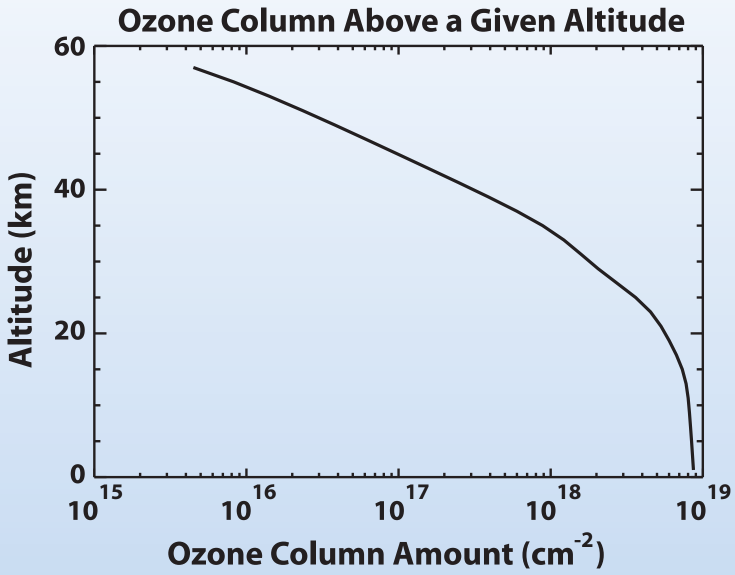


O_2 photolysis occurs mainly in the “window” near 200 nm





“Self-Healing”



Ozone Production

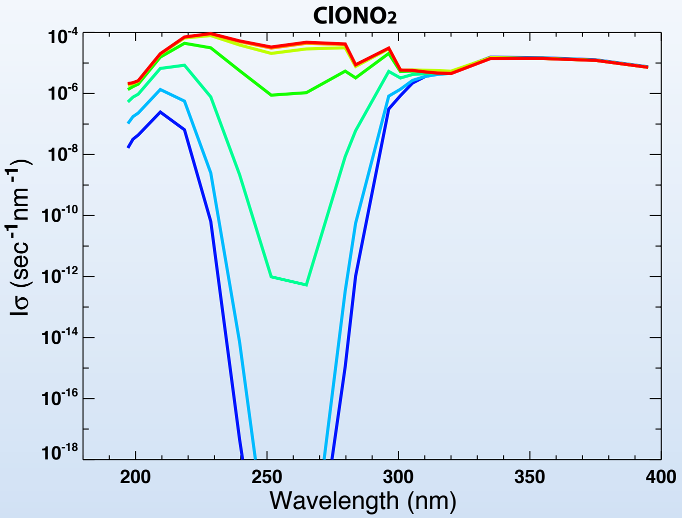
$$P_{O_3} = 2 \cdot J_{O_2} \cdot [O_2]$$

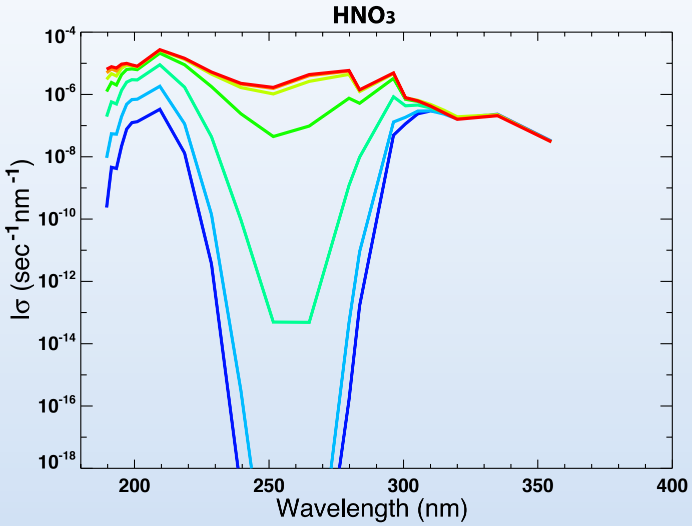
Decrease of ozone above altitude, z, results in decrease of radiative flux that leads to ozone production.

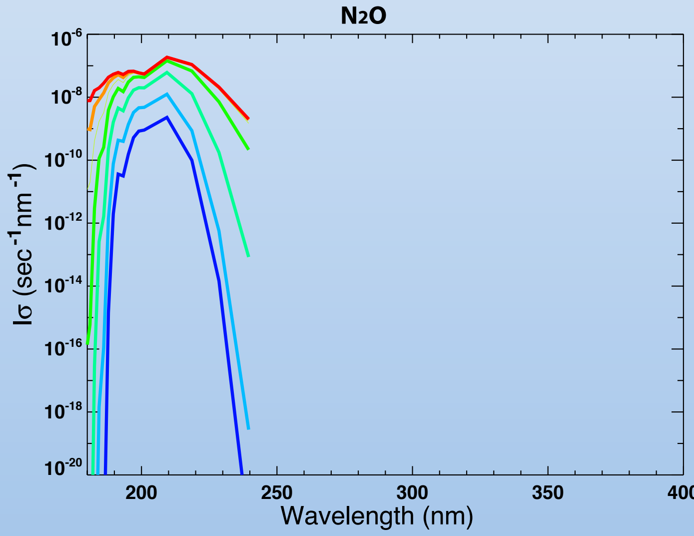
$$J_{O_2}(z) = \int \sigma_{O_2}(\lambda) \cdot I_0 e^{-[N_{O_2}(z)\cdot\sigma_{O_2}(\lambda)+N_{O_3}(z)\cdot\sigma_{O_3}(\lambda)]} d\lambda$$

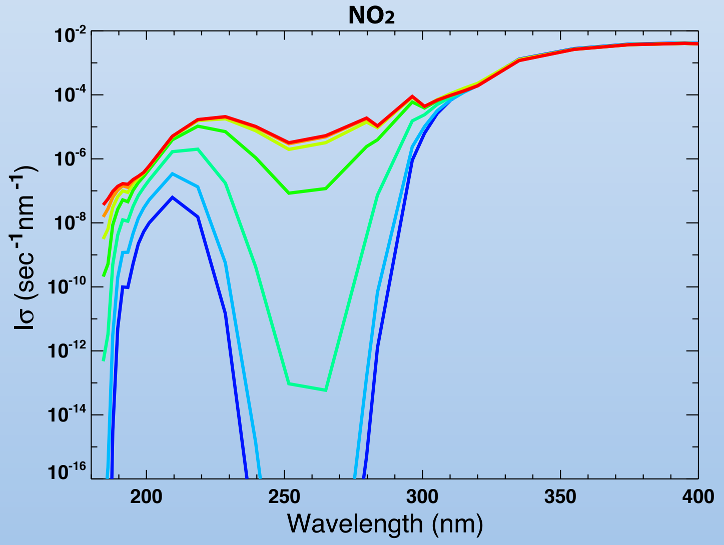
Result is that a decrease in ozone above a given altitude leads to an increase in ozone at that altitude; a sort of “self-healing”.

Photolysis Rates vs Wavelength

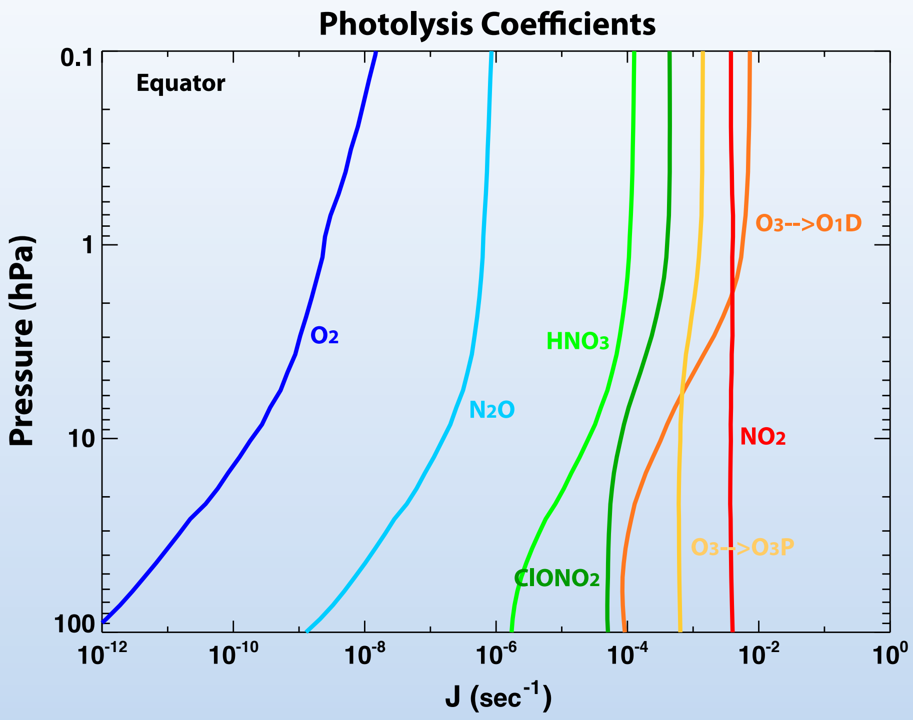








Photolysis Coefficients vs Altitude



- Molecules that absorb in the near UV and visible have significant photolysis rates in the troposphere
- Molecules that absorb only below 300 nm have no significant photolysis in the troposphere
- Molecules that absorb only in the 200 nm window have long lifetimes unless they have chemical reactions that limit their lifetime