Recap

• Oxygen is a *bi-radical*

• strongest absorption in the UV-C
  – photolysis as the main result
  – absorption “tails” due to T→S transitions

• no solar radiation in the UV-C penetrates the atmosphere (absorbed by molecular oxygen)

• oxygen photolysis dominantly forms a ground state and an exited state oxygen atom
  (can you give the electron configurations of these?)
Add complexity: Ozone

• 3-atom molecule
  – angled (instead of linear)
  – thermodynamically unstable
    • chemically highly reactive, but …
    • … relatively stable in atmosphere
    • why?

can MO-theory give an answer?
1) Name these orbitals
2) Fill with electrons
Ozone MOs

$\sigma_s, \sigma_z$
4 electrons

$b$

$\pi_{b}$
2

$\pi_{nb}$
2

$\pi^*$
0 electrons

bonding order: \((4+2+0-0)/2 / 2 = 1 \frac{1}{2}\)
Figure 2.8: Absorption spectrum of ozone in the wavelength region 115-350 nm, with cross sections given in cm$^2$ molecule$^{-1}$. Data assembled from Lin and Tanka (1953), Tanka et al. (1963), and Criegee (1968).

WAVELLENGTH / nm

Hartley bands

Hugonis bands

O$_3$ absorption spectrum
Figure 2.14: Threshold behavior of the O(D) quantum yield for the photodissociation of ozone at 298 K and 203 K.

Wave length in nm

0
0.5
1.0

$O_3$ absorption in the troposphere
Important Definitions

• **Photolysis Frequency, \( J \)**

\[
J = \int_{\lambda} I(\lambda) \times \Phi(\lambda) \times \sigma(\lambda) \, d\lambda \approx \sum I(\lambda) \times \Phi(\lambda) \times \sigma(\lambda) \times \Delta\lambda
\]

- \( I(\lambda) \): incident radiation in photons cm\(^{-2}\) s\(^{-1}\)
- \( \Phi(\lambda) \): quantum efficiency = number of photons absorbed that lead to photolysis / total number of photons absorbed
- \( \sigma(\lambda) \): absorptivity (spectrum)

• **Molecular density**

Number of particles per cubic centimeter at stp

\[ \rightarrow 2.46 \times 10^{19} \text{ molecules cm}^{-3} \text{ (use ideal gas law to derive!)} \]
NO$_2$ MO energy diagram

- NO$_2$ is a radical
  $\rightarrow$ paramagnetic
- small energy gap between highest pot. energy orbitals
- light absorption in the UV-A
  $\rightarrow$ brown color of smog