Basics of Photochemistry: Photolysis Calculations

CHEM-5152
Advanced Atmospheric Chemistry

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Calculation of Photolysis Rates

Generic reaction: A + $h\nu \rightarrow$ B + C

$$\frac{d[A]}{dt} = -J_A[A] = -\int \sigma_A(\lambda)\phi_A(\lambda)F(\lambda)d\lambda \times [A]$$

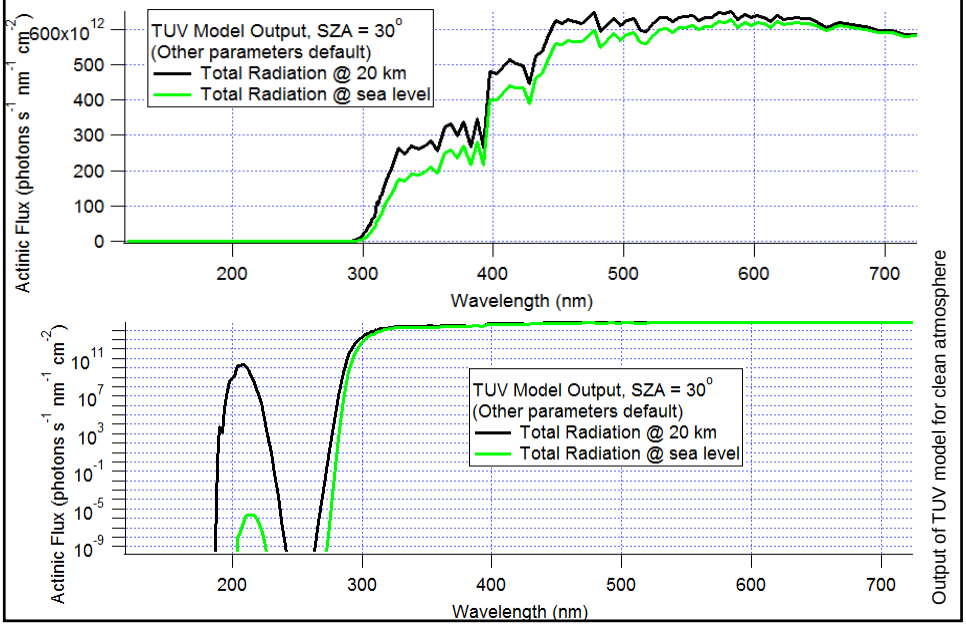
J_A – first order photolysis rate of A (s^{-1})

$\sigma_A(\lambda)$ – wavelength dependent cross section of A (cm^2/molec.)

$\phi_A(\lambda)$ – wavelength dependent quantum yield for photolysis

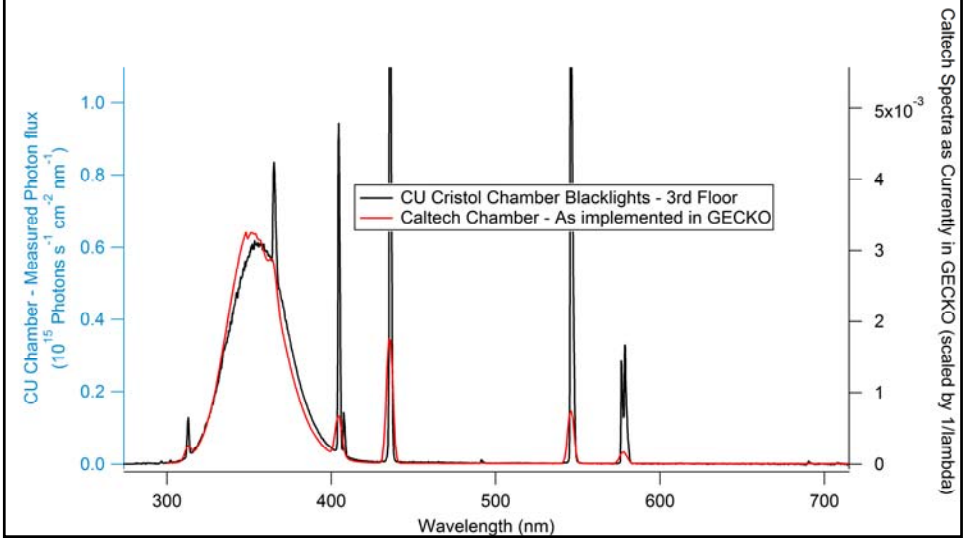
$F(\lambda)$ – spectral ***actinic flux*** density (photons /cm^2/s)

Actinic Flux @ surface & 20 km

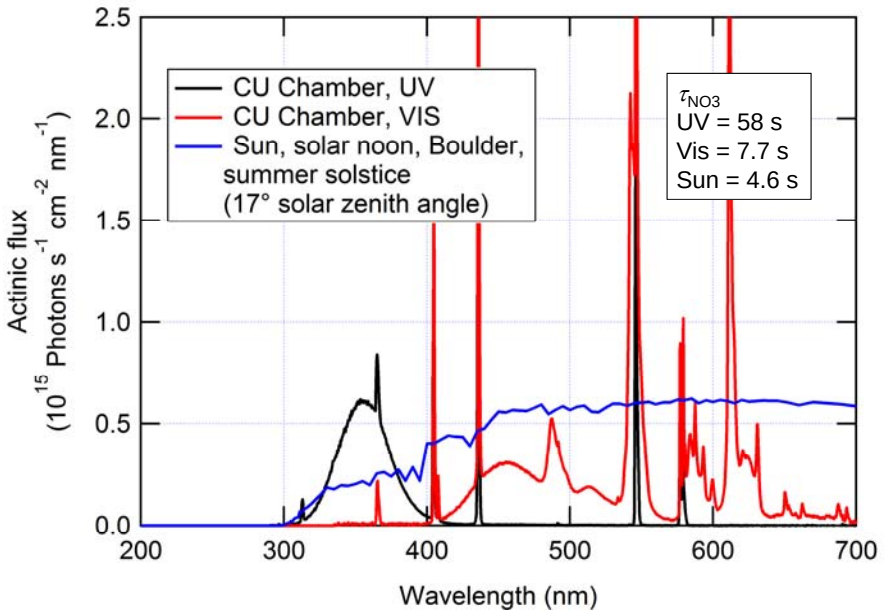


Blacklight Spectra

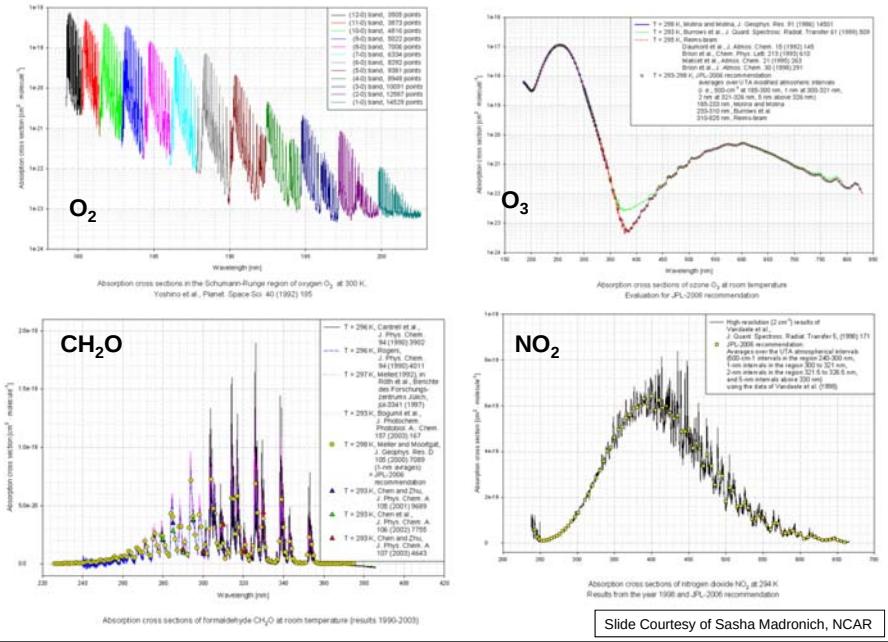
- Similar but not identical, likely Caltech spectrometer has lower resolution, lamps might also be different



Photolysis spectra: CU Chamber vs Sun



Absorption cross sections $\sigma(\lambda, T)$



Slide Courtesy of Sasha Madronich, NCAR

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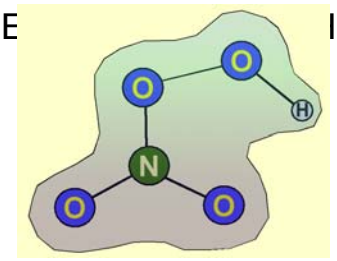
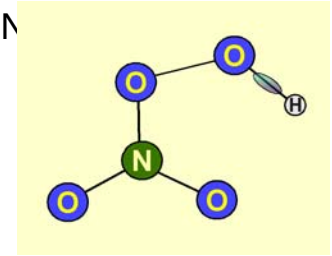
Physical interpretation of σ

- σ, absorption cross section (cm^2 / molecule)
  - Effective area of the molecule that photon needs to traverse in order to be absorbed.
  - The larger the absorption cross section, the easier it is to photoexcite the molecule.
  - E IN



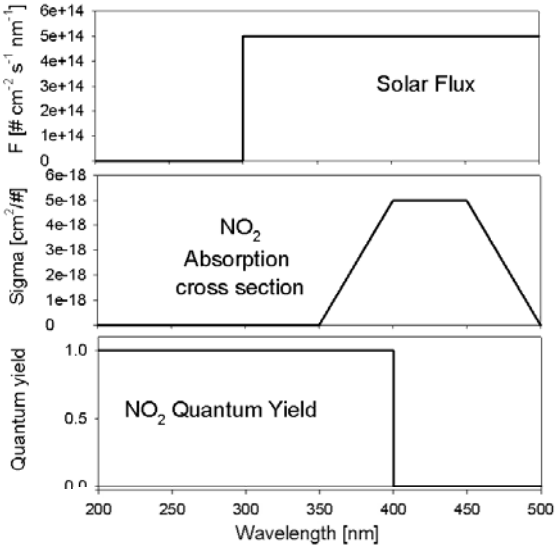
Collisions
$\sigma \approx 10^{-15}$ cm^2/molec



Light absorption
$\sigma \approx 10^{-18}$ cm^2/molec

From S. Nidkorodov

Group Problem



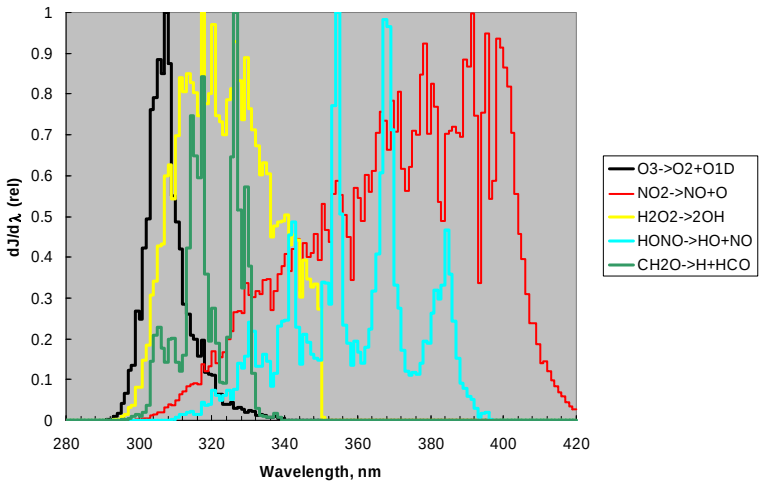
The graphs below show the approximate solar flux at the Earth surface, absorption cross section of NO_2 molecule, and photodissociation quantum yield of NO_2. What is the photodissociation lifetime of NO_2 (τ_{NO2})?

A. 16 s
B. 6 s^{-1}
C. 6000 s
D. 116 s^{-1}
E. I don't know

Part of 2005 Final exam

Corollary: What are the smallest cross sections that matter in the atmosphere?

Spectral Region For Tropospheric Photochemistry



surface, overhead sun

Slide Courtesy of Sasha Madronich, NCAR

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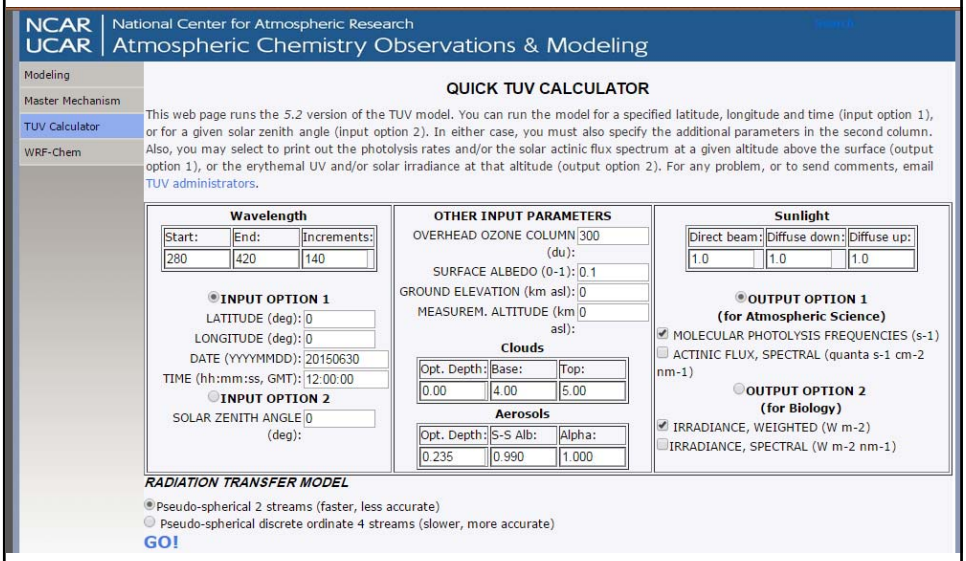
TUV Model from NCAR

(as run for previous slides)



http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/

Solar Zenith Angle

- Aside form the altitude, the path length through the atmosphere critically depends on the time of day and geographical location.
- Path length can be calculated using the flat atmosphere approximation for zenith angles under 80º. Beyond that, Earth curvature and atmospheric refraction start to matter.

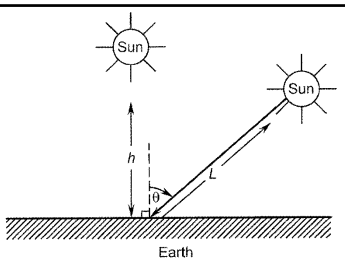


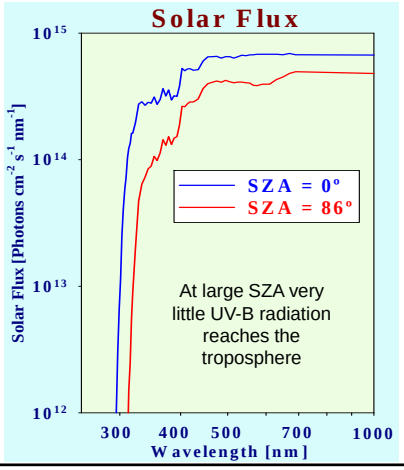
FIGURE 3.14 Definition of solar zenith angle θ at a point on the earth's surface.

$$\text{"Air Mass"} = m = \frac{\text{Actual pathlength}}{\text{Vertical pathlength}} \approx \frac{L}{h} = \sec\theta$$

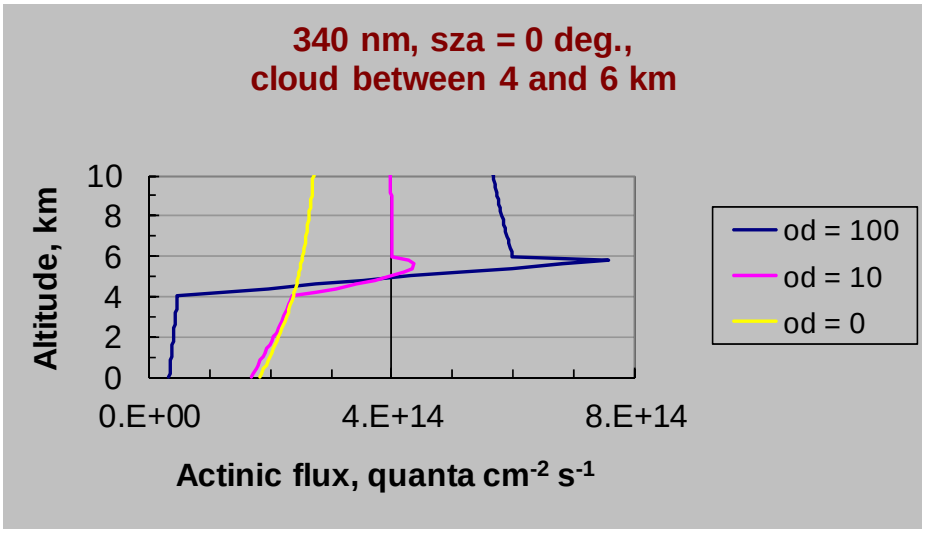
TABLE 3.5 Values of the Air Mass m at the Earth's Surface for Various Zenith Angles: (a) Calculated from $m = \sec\theta$ and (b) Corrected for Atmospheric Curvature and for Refraction

Zenith angle θ (deg)	$m = \sec\theta$	Air mass (m)
0	1.00	1.00
10	1.02	1.02
20	1.06	1.06
30	1.15	1.15
40	1.31	1.31
50	1.56	1.56
60	2.00	2.00
70	2.92	2.90
78	4.81	4.72
86	14.3	12.4

Source: Demerjian *et al.* (1980).



Effect of Uniform Clouds on Actinic Flux



In liquid spheres, multiply by ~ 1.6

Slide Courtesy of Sasha Madronich, NCAR

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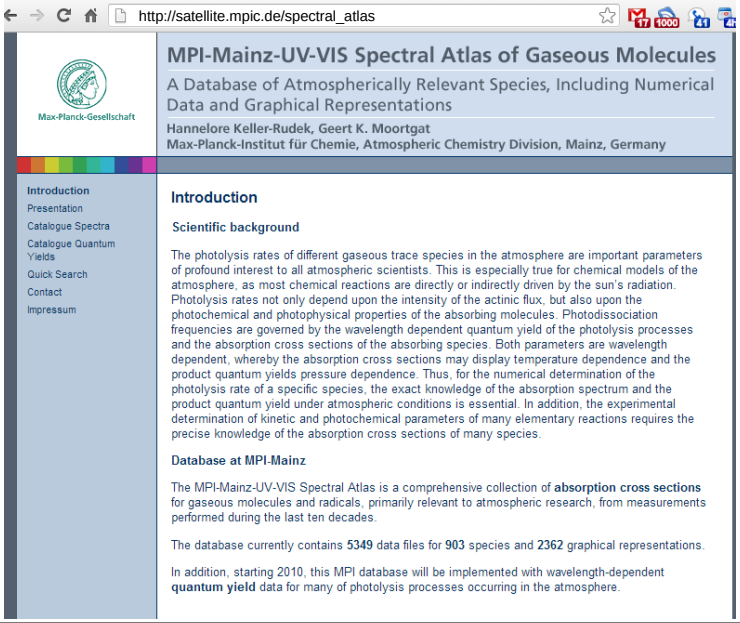
Database of Absorption Spectra



http://satellite.mpic.de/spectral_atlas

Limitations of Available Information

Spectra in database:

Categories

Alcohols
Alkali compounds
Alkanes+alkyl radicals
Alkanes+radicals with O
Alkenes,dienes+radicals
Alkynes,polyynes+radicals
Aromatic compounds
Boron compounds
Carbon-oxides
Ethers+alkyl radicals
Halogen oxides
Halogenated N-compounds(inorg)
Halogeno-alkanes, -alkyl radicals
Halogeno-alkenes+radicals
Halogeno-alkynes+radicals
Halogens+mixed halogens
Hydrogen halides
Hydrogen+water
Hypohalides
Nitrogen acids
Nitrogen oxides
Nitrogen+N-H compounds
Organics (acids)
Organics (carbonyls)
Organics (N-compounds)
Oxygen
Ozone
Peroxides
Peroxy radicals
Phosphor compounds
Silicon compounds
Sulfur compounds
Terpenes
X-others

Quantum yields in database:

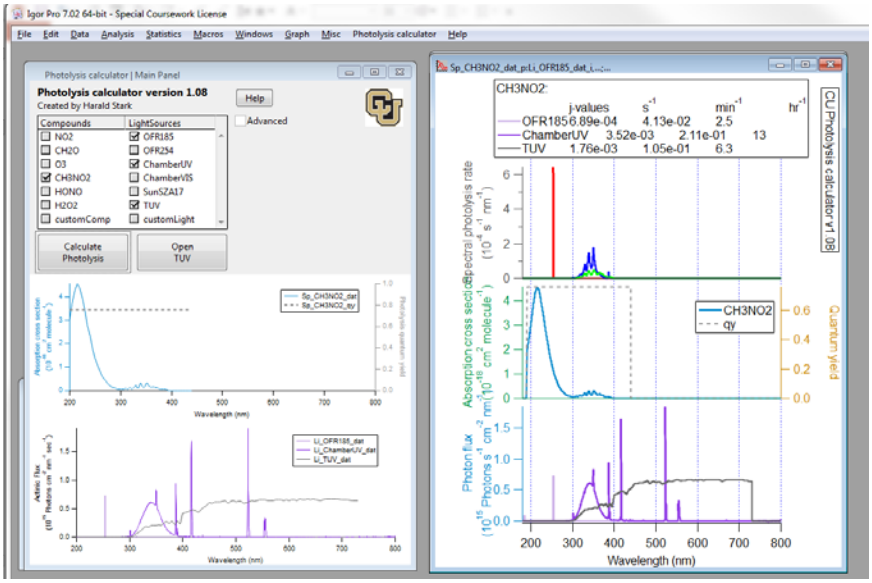
Catalogue Quantum Yields

Quantum Yields

Halogen oxides
Nitrogen oxides
Organics (carbonyls)
Ozone

Much less data for quantum yields, much harder to measure than absorption spectra. (Why?)

J-Grp Photolysis Calculator



http://tinyurl.com/photcalc-help

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Pathways for Loss of e⁻ Excitation

- Photophysical processes
  - Lead to emission of radiation
  - Energy converted to heat
- Photochemical processes
  - Dissociation, ionization, reaction, isomerization

From Wayne

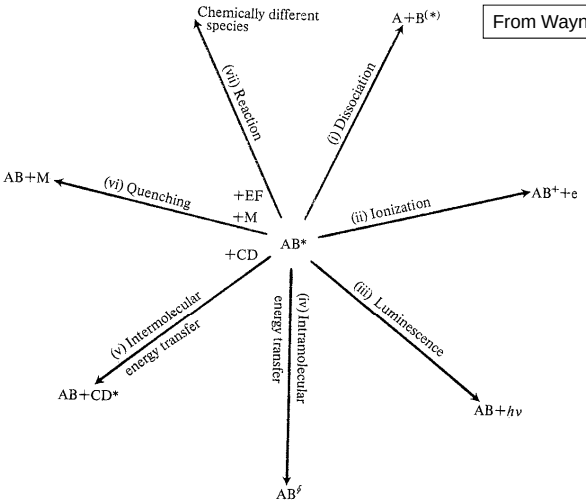


Fig. 3.1. Pathways for loss of electronic excitation that are of importance in atmospheric chemistry. The use of the symbols * and § illustrates the presence of electronic excitation: the products of any of the processes may be excited. With the exception of pathways (i) and (iv), excited atoms can participate as well as excited molecules.

Quantum Yields II

From F-P&P

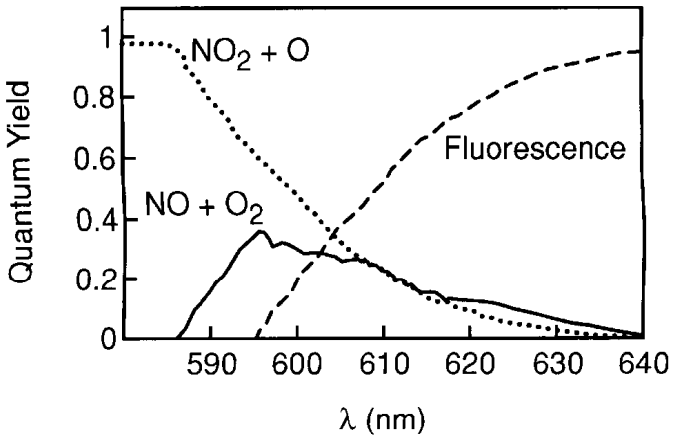
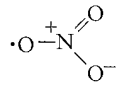
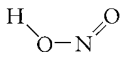
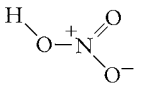
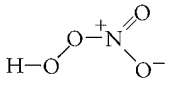
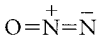
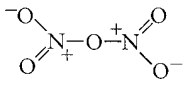


FIGURE 4.18 Quantum yields for NO_3 photolysis: dotted line, $NO_3 \rightarrow NO_2 + O$; solid line, $NO_3 \rightarrow NO + O_2$; dashed line, fluorescence quantum yields (adapted from Johnston *et al.*, 1996).

Structure of Important N-Species

Nitrogen Species

Molecular nitrogen N_2	Nitric oxide NO	Nitrogen dioxide NO_2	Nitrate radical NO_3
$N \equiv N$	$\dot{N}{=}O$		
Nitrous acid HONO	**Nitric acid HNO_3**	**Peroxynitric acid HO_2NO_2**	**Nitrous oxide N_2O**
			
Dinitrogen pentoxide N_2O_5			
			

- From Jacobson (1999) Table B
  - http://cires.colorado.edu/jimenez/AtmChem/Jacobson_Table_B.pdf
  - Many other species there, useful when you don't know detailed