

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})

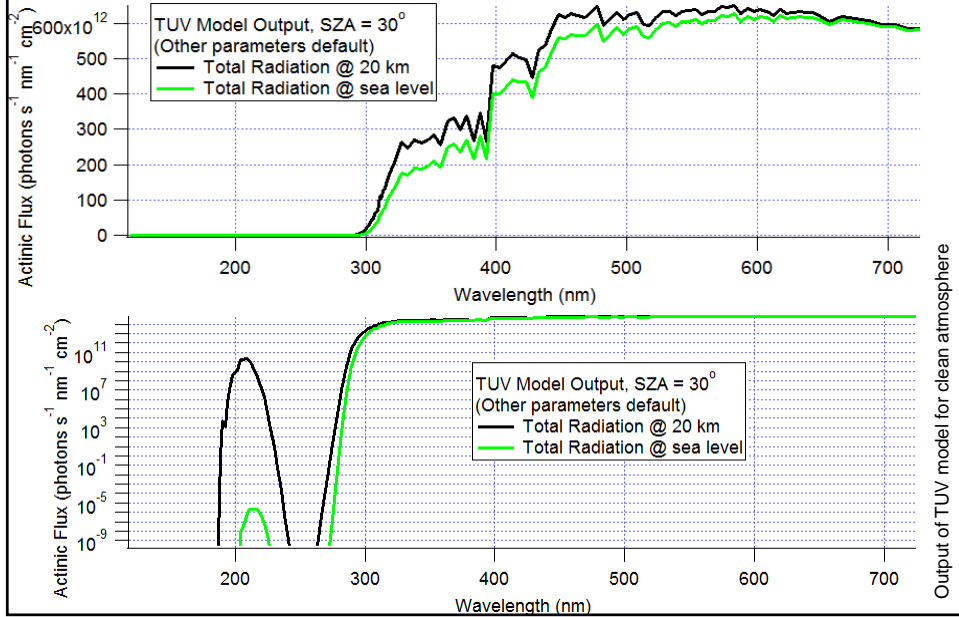
$\sigma_A(\lambda)$ – wavelength dependent cross section of A ($cm^2/molec.$)

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

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

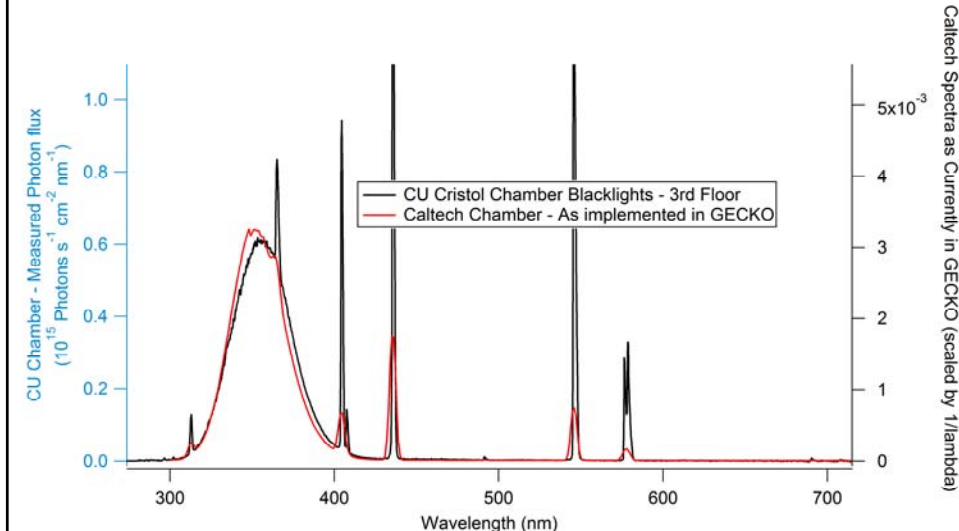


Actinic Flux @ surface & 20 km

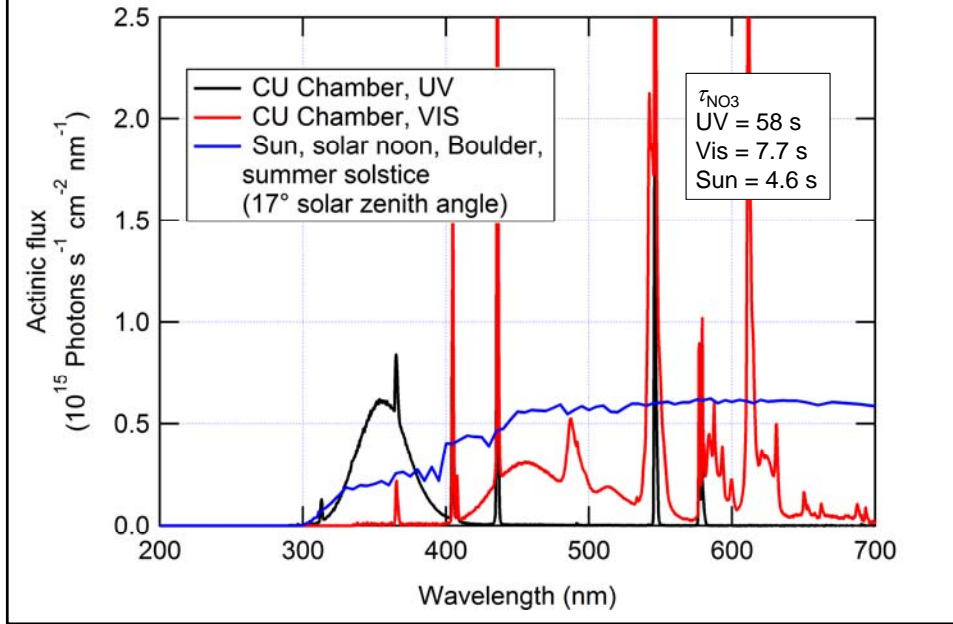


Blacklight Spectra

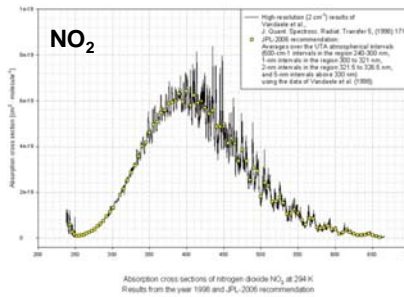
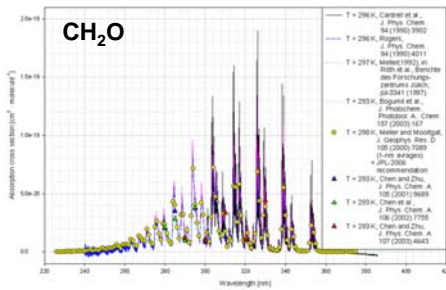
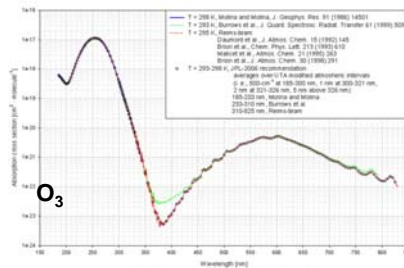
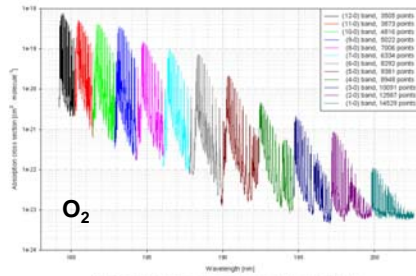
- Similar but not identical, likely Caltech spectrometer has lower resolution, lamps might also be different



Photolysis spectra: CU Chamber vs Sun



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

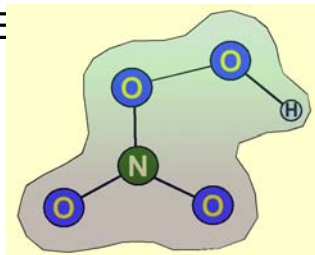


Slide Courtesy of Sasha Madronich, NCAR

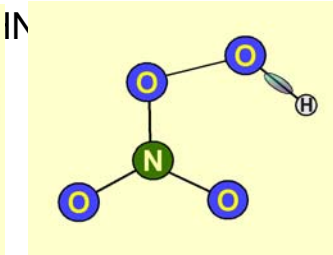
Physical interpretation of σ

- σ , absorption cross section ($\text{cm}^2 / \text{molecule}$)
 - 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



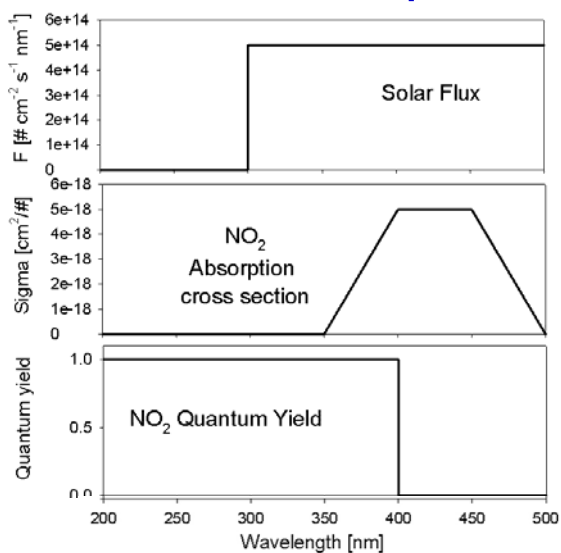
Collisions
 $\sigma \approx 10^{-15} \text{ cm}^2/\text{molec}$



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

From S. Nidkorodov

Group Problem



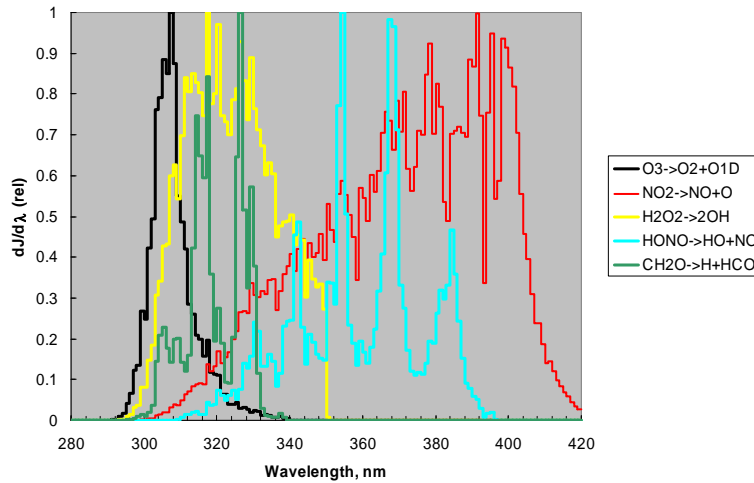
The graphs below show the approximate solar flux at the Earth surface, absorption cross section of NO_2 molecule, and photodissociation quantum yield of NO_2 . What is the **photodissociation lifetime** of NO_2 (τ_{NO_2})?

- 16 s
- 6 s^{-1}
- 6000 s
- 116 s^{-1}
- 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)

NCAR UCAR National Center for Atmospheric Research
 Atmospheric Chemistry Observations & Modeling

QUICK TUV CALCULATOR

This web page runs the 5.2 version of the TUV model. You can run the model for a specified latitude, longitude and time (input option 1), or for a given solar zenith angle (input option 2). In either case, you must also specify the additional parameters in the second column. Also, you may select to print out the photolysis rates and/or the solar actinic flux spectrum at a given altitude above the surface (output option 1), or the erythemal UV and/or solar irradiance at that altitude (output option 2). For any problem, or to send comments, email TUV administrators.

Wavelength	OTHER INPUT PARAMETERS	Sunlight												
<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td>Start:</td> <td>End:</td> <td>Increments:</td> </tr> <tr> <td>280</td> <td>420</td> <td>140</td> </tr> </table>	Start:	End:	Increments:	280	420	140	OVERHEAD OZONE COLUMN: 300 (du) SURFACE ALBEDO (0-1): 0.1 GROUND ELEVATION (km asl): 0 MEASUREMENT ALTITUDE (km asl): 0	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td>Direct beam:</td> <td>Diffuse down:</td> <td>Diffuse up:</td> </tr> <tr> <td>1.0</td> <td>1.0</td> <td>1.0</td> </tr> </table>	Direct beam:	Diffuse down:	Diffuse up:	1.0	1.0	1.0
Start:	End:	Increments:												
280	420	140												
Direct beam:	Diffuse down:	Diffuse up:												
1.0	1.0	1.0												
INPUT OPTION 1 LATITUDE (deg): 0 LONGITUDE (deg): 0 DATE (YYYYMMDD): 20150630 TIME (hh:mm:ss, GMT): 12:00:00 INPUT OPTION 2 SOLAR ZENITH ANGLE (deg): 0	Clouds <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td>Opt. Depth:</td> <td>Base:</td> <td>Top:</td> </tr> <tr> <td>0.00</td> <td>4.00</td> <td>5.00</td> </tr> </table> Aerosols <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td>Opt. Depth:</td> <td>S-S Alb:</td> <td>Alpha:</td> </tr> <tr> <td>0.235</td> <td>0.990</td> <td>1.000</td> </tr> </table>	Opt. Depth:	Base:	Top:	0.00	4.00	5.00	Opt. Depth:	S-S Alb:	Alpha:	0.235	0.990	1.000	OUTPUT OPTION 1 (for Atmospheric Science) <input checked="" type="checkbox"/> MOLECULAR PHOTOLYSIS FREQUENCIES (s ⁻¹) <input type="checkbox"/> ACTINIC FLUX, SPECTRAL (quanta s ⁻¹ cm ⁻² nm ⁻¹) OUTPUT OPTION 2 (for Biology) <input checked="" type="checkbox"/> IRRADIANCE, WEIGHTED (W m ⁻²) <input type="checkbox"/> IRRADIANCE, SPECTRAL (W m ⁻² nm ⁻¹)
Opt. Depth:	Base:	Top:												
0.00	4.00	5.00												
Opt. Depth:	S-S Alb:	Alpha:												
0.235	0.990	1.000												

RADIATION TRANSFER MODEL

Pseudo-spherical 2 streams (faster, less accurate)
 Pseudo-spherical discrete ordinate 4 streams (slower, more accurate)

GO!

http://cpm.aom.ucar.edu/Models/TUV/Interactive_TUV/

Solar Zenith Angle

- Aside from 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 80°. Beyond that, Earth curvature and atmospheric refraction start to matter.

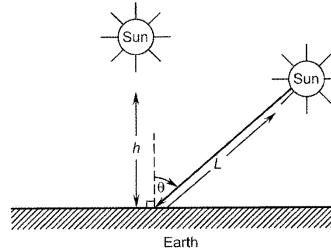


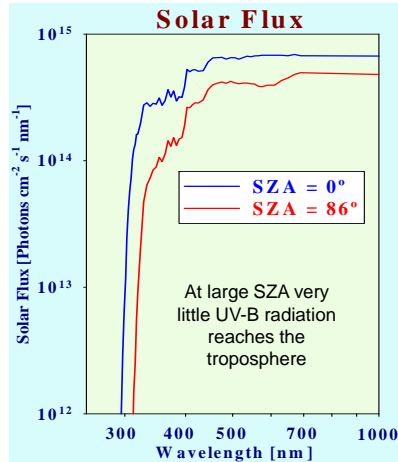
FIGURE 3.14 Definition of solar zenith angle θ at a point on the earth's surface.

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

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

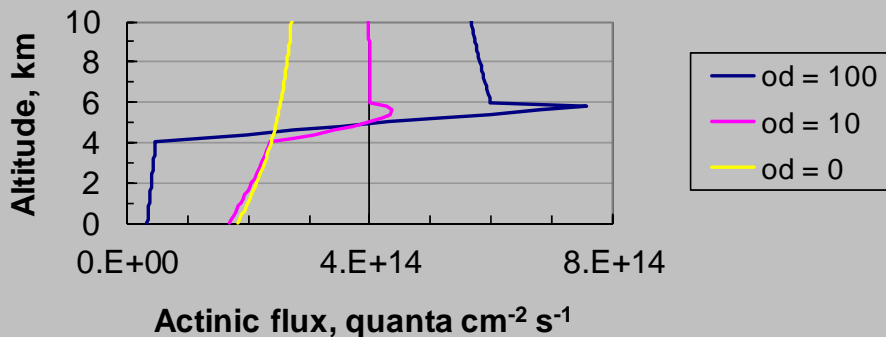
Zenith angle θ (deg)	$m = \sec \theta$	Air mass (m)
0	1.00	1.00
10	1.02	1.02
20	1.06	1.06
30	1.15	1.15
40	1.31	1.31
50	1.56	1.56
60	2.00	2.00
70	2.92	2.90
78	4.81	4.72
86	14.3	12.4

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



Effect of Uniform Clouds on Actinic Flux

340 nm, sza = 0 deg.,
cloud between 4 and 6 km




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 ☆ 📧 📄 📱 📡



Max-Planck-Gesellschaft

MPI-Mainz-UV-VIS Spectral Atlas of Gaseous Molecules

A Database of Atmospherically Relevant Species, Including Numerical Data and Graphical Representations

Hannelore Keller-Rudek, Geert K. Moortgat
Max-Planck-Institut für Chemie, Atmospheric Chemistry Division, Mainz, Germany

Introduction
Presentation
Catalogue Spectra
Catalogue Quantum Yields
Quick Search
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Impressum

Introduction

Scientific background

The photolysis rates of different gaseous trace species in the atmosphere are important parameters of profound interest to all atmospheric scientists. This is especially true for chemical models of the atmosphere, as most chemical reactions are directly or indirectly driven by the sun's radiation. Photolysis rates not only depend upon the intensity of the actinic flux, but also upon the photochemical and photophysical properties of the absorbing molecules. Photodissociation frequencies are governed by the wavelength dependent quantum yield of the photolysis processes and the absorption cross sections of the absorbing species. Both parameters are wavelength dependent, whereby the absorption cross sections may display temperature dependence and the product quantum yields pressure dependence. Thus, for the numerical determination of the photolysis rate of a specific species, the exact knowledge of the absorption spectrum and the product quantum yield under atmospheric conditions is essential. In addition, the experimental determination of kinetic and photochemical parameters of many elementary reactions requires the precise knowledge of the absorption cross sections of many species.

Database at MPI-Mainz

The MPI-Mainz-UV-VIS Spectral Atlas is a comprehensive collection of **absorption cross sections** for gaseous molecules and radicals, primarily relevant to atmospheric research, from measurements performed during the last ten decades.

The database currently contains **5349** data files for **903** species and **2362** graphical representations.

In addition, starting 2010, this MPI database will be implemented with wavelength-dependent **quantum yield** data for many of photolysis processes occurring in the atmosphere.

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](#)
[Halogeno-alkynes+radicals](#)
[Halogeno-alkynes+radicals](#)
[Halogeno-alkynes+radicals](#)
[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:

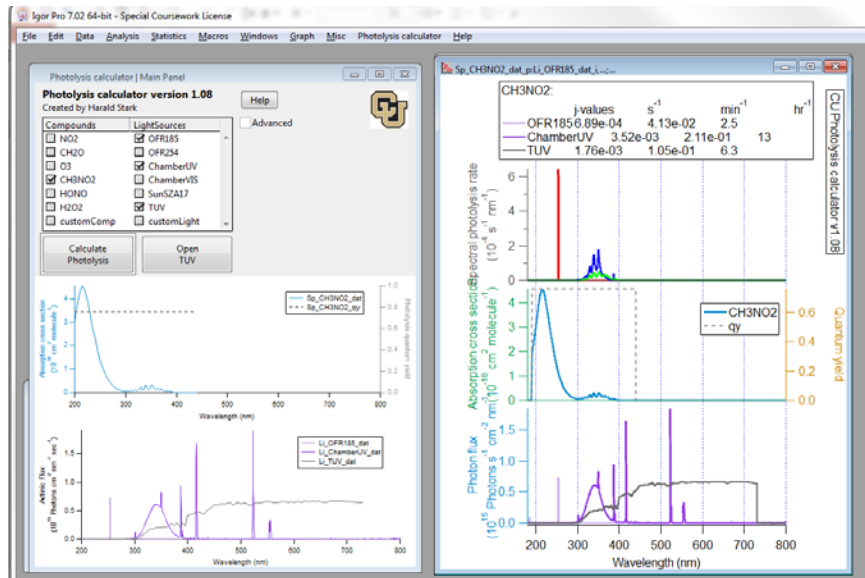
Catalogue Quantum Yields

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

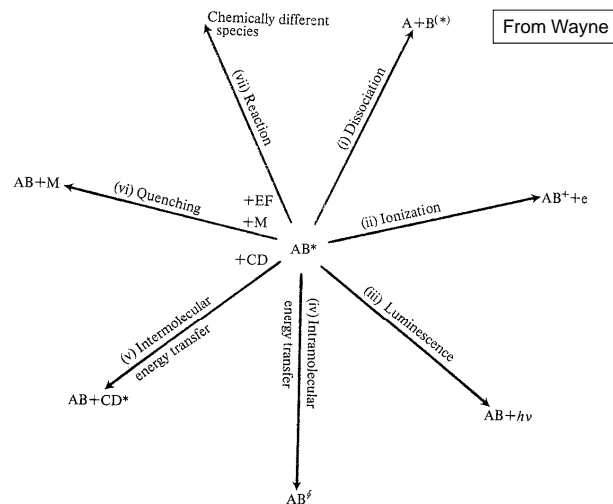


Fig. 3.1. Pathways for loss of electronic excitation that are of importance in atmospheric chemistry. The use of the symbols * and § illustrates the presence of electronic excitation: the products of any of the processes may be excited. With the exception of pathways (i) and (iv), excited atoms can participate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

Quantum Yields II

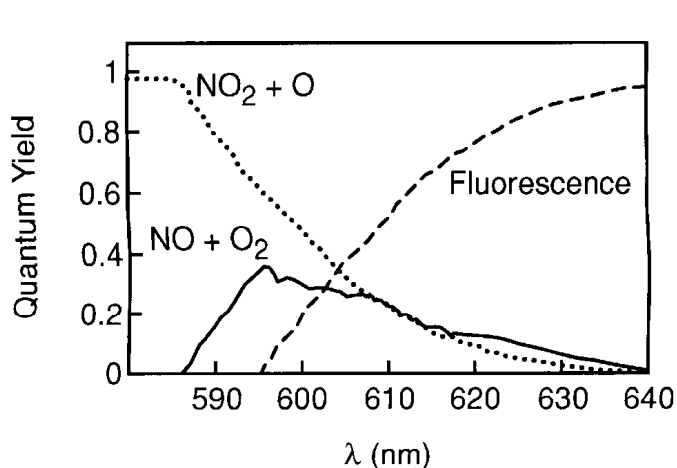


FIGURE 4.18 Quantum yields for NO_3 photolysis: dotted line, $\text{NO}_3 \rightarrow \text{NO}_2 + \text{O}$; solid line, $\text{NO}_3 \rightarrow \text{NO} + \text{O}_2$; dashed line, fluorescence quantum yields (adapted from Johnston *et al.*, 1996).

Structure of Important N-Species

Nitrogen Species

Molecular nitrogen
 N_2



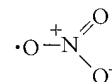
Nitric oxide
 NO



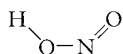
Nitrogen dioxide
 NO_2



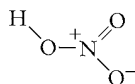
Nitrate radical
 NO_3



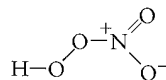
Nitrous acid
 HONO



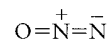
Nitric acid
 HNO_3



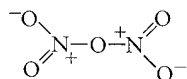
Peroxynitric acid
 HO_2NO_2



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