

Lecture 7: Photochemistry of Important Atmospheric Species

Required Reading: FP Chapter 4

Atmospheric Chemistry
CHEM-5151 / ATOC-5151
Spring 2005
Prof. Jose-Luis Jimenez

Outline of Lecture

- General remarks
- O₂
- O₃
- Nitrogen species
- Aldehydes and ketones
- CFCs

- *We won't cover everything in class, read the rest in the book*
 - *Have to know how to find + interpret quickly*

Reminder from last time

- Sunlight drives chemistry of trop. & strat.
 - “Hot” photons break bonds and create free radicals
 - Radicals can react with many molecules
 - Obj: calculate rates of photolysis & product generation

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})

This lecture

- $\sigma_A(\lambda)$ – wavelength dependent cross section of A ($cm^2/molec$)
- $\phi_A(\lambda)$ – wavelength dependent quantum yield for photolysis
- $F(\lambda)$ – spectral actinic flux density ($\#/cm^2/s$) } Last lecture

General Remarks

Photodissociation is the most important class of photochemical process in the atmosphere:
 $AB + h\nu \rightarrow A + B$

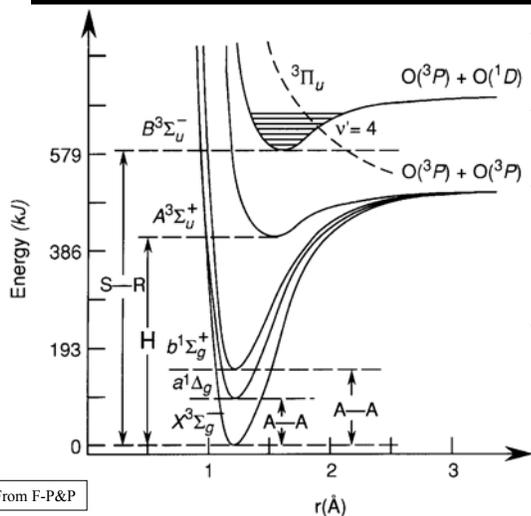
- In order to photodissociate a molecule it must be excited above its dissociation energy (D_0).
- In the lower troposphere, only molecules with D_0 corresponding to $\lambda > 290$ nm are photochemically active. Most common atmospheric molecules, including N_2 , CO , O_2 , CO_2 , CH_4 , NO , etc. are stable against photodissociation in the troposphere.
- In addition, the molecule should have bright electronic transitions above D_0 . For example, HNO_3 has a low dissociation energy ($D_0 = 2.15$ eV) but it needs UV for its photolysis because it does not have appropriate electronic transitions in the visible.
- In general, both the absorption cross sections and photodissociation quantum yields are wavelength dependent.
- Photoionization processes are generally not important in the lower atmosphere (ionization potentials for most regular molecules > 9 eV).

Table 2.4 Dissociation energies of selected molecules of atmospheric interest

Species	Dissociation energies (eV)	Equivalent wavelength (Å)
H ₂	4.52	2743
CH ₄	4.55	2722
C ₂ H ₆	4.36	2844
C ₂ H ₄	4.80	2583
C ₂ H ₂	5.76	2153
PH ₃	3.40	3650
NH ₃	4.70	2637
H ₂ S	3.96	3134
H ₂ O	5.17	2398
H ₂ O ₂	2.22	5582
O ₂	5.17	2400
O ₃	1.10	11222
CO	11.14	1113
CO ₂	5.52	2247
H ₂ CO	3.82	3244
N ₂	9.80	1265
N ₂ O	1.73	7152
NO	6.55	1893
NO ₂	3.18	3903
NO ₃	2.16	5731
N ₂ O ₅	0.99	12536
HNO ₃	2.15	5774
HO ₂ NO ₂	1.01	12320
HCl	4.47	2773
CFCl ₃	3.25	3811
CF ₂ Cl ₂	3.46	3582
ClONO ₂	1.16	10665
Cl ₂ O ₂	0.77	16057
SO	5.40	2296
SO ₂	5.72	2168
COS	3.20	3873
HCN	5.37	2309
HC ₃ N	6.34	1955
C ₂ N ₂	5.84	2123

From S. Nidkorodov

O₂ Electronic Transitions



From F-P&P

FIGURE 4.1 Potential energy curves for ground and first four excited states of O₂. S-R = Schumann-Runge system, H = Herzberg continuum, A-A = atmospheric bands (adapted from Gaydon, 1968).

- Always start in ground state $X^3\Sigma_g^-$
- Only transitions to triplet states are spin-allowed
- $X^3\Sigma_g^- \rightarrow A^3\Sigma_u^+$ forbidden because $- \rightarrow +$
 - Occurs weakly, "Herzberg continuum", 190-300 nm
- $X^3\Sigma_g^- \rightarrow B^3\Sigma_u^-$ is allowed
 - Schumann-Runge system, 175-200 nm, bands due to different vib-rot states
 - $B^3\Sigma_u^-$ crossed by $^3\Pi_u$ repulsive state, dissociates to $O(^3P)+O(^3P)$
- Later (< 175 nm) spectrum is continuum, dissociation of $B^3\Sigma_u^-$ to $O(^3P)+O(^1D)$

Oxygen Spectrum

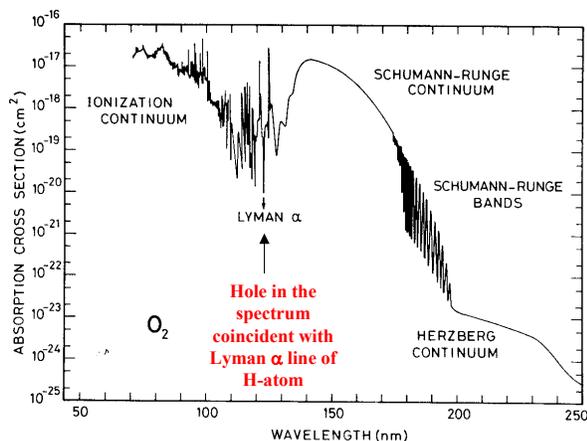


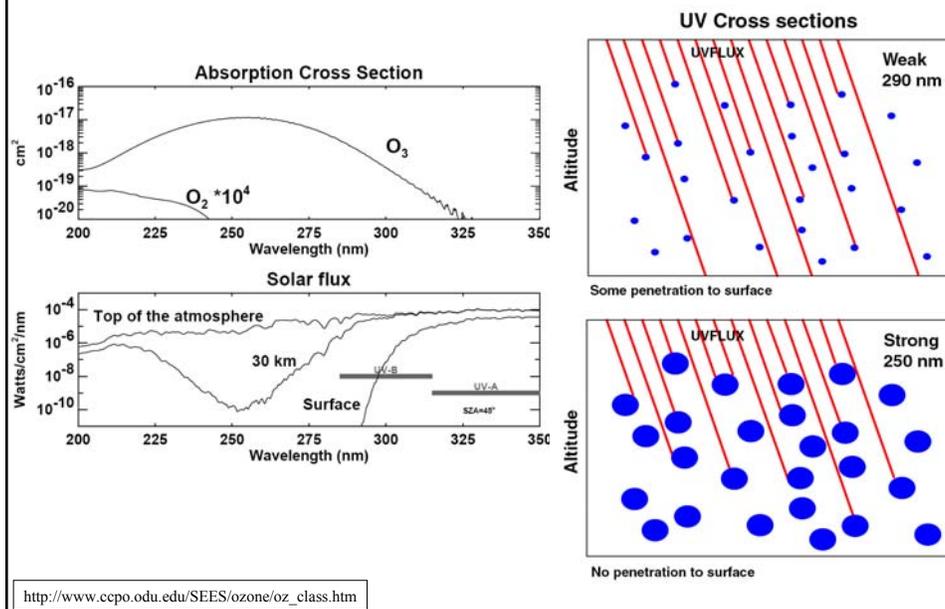
Fig. 4.26. Spectral distribution of the absorption cross section of molecular oxygen.

From Brasseur and Solomon

- O₂ photolysis in the 200-240 nm range is the major source of O₃ in the stratosphere
- O₂ can absorb nearly all radiation with $\lambda = 10$ -200 nm high up in the atmosphere

Solve in class: Estimate the length of air column at $P = 0.01$ Torr and $T = 200$ K (characteristic of 80 km altitude) required to reduce the radiation flux at 150 nm by 10 orders of magnitude. Neglect the fact that a substantial portion of oxygen is atomized at this altitude. (A: 230 m)

UV absorption by O₂ and O₃



O₂ Photochemistry

- Schumann continuum very efficient screening radiation below 200 nm
- Solar radiation more intense towards longer λ
- Dissociation of O₂ in Herzberg continuum (200-240 nm) is very important for O₃ in the stratosphere
 - $O_2 + h\nu \rightarrow O(^3P) + O(^3P)$
 - $O(^3P) + O_2 (+M) \rightarrow O_3$
- Troposphere $\lambda > 290$ nm
 - Not enough energy for O₂ dissociation
 - O₃ from NO₂ + h ν

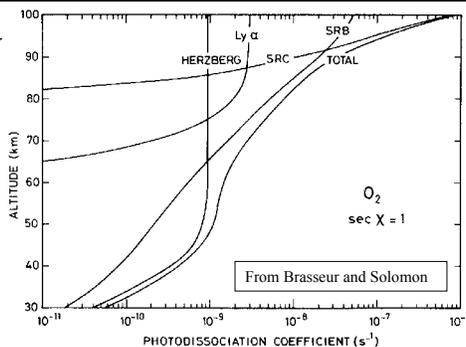


Fig. 4.31. Contribution of each spectral region to the photodissociation of molecular oxygen as a function of altitude.

TABLE 4.2 Threshold Wavelengths for the Production of Ground-State or Electronically Excited Oxygen Atoms from O₂ Photolysis^a

Electronic state of oxygen atoms ^b	Threshold wavelength (nm)
O(³ P) + O(³ P)	242.4
O(³ P) + O(¹ D)	175.0
O(³ P) + O(¹ S)	133.2

^a From Okabe (1978).

^b O(³P) is the ground-state species.

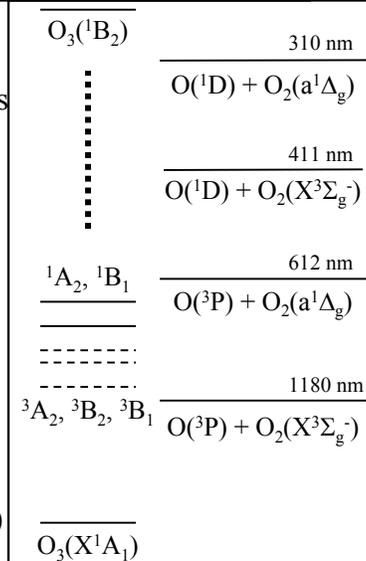
From F-P&P

Importance of O₃

- *Central role in atmospheric chemistry*
- Highly reactive
- Highly toxic => health effects in humans
- Crop degradation => billions of \$ in losses
- Absorbs UV
 - Shield surface from hard UV
 - Its photolysis produces O(¹D), which yields OH
 - OH is most important tropospheric oxidant
 - Photolysis to O(³P) regenerates O₃, not important!
- Absorbs IR
 - Greenhouse gas

Ozone: Electronic States

- Transitions into triplet states: extremely weak (forbidden)
- All (allowed) excited electronic transitions lead to O₃ above its lowest dissociation threshold!
- Multiple dissociation pathways are available for O₃:
 - $O_3 + h\nu \rightarrow O(^1D) + O_2(a^1\Delta_g)$
 - $O_3 + h\nu \rightarrow O(^1D) + O_2(X^3\Sigma_g^-)$
 - $O_3 + h\nu \rightarrow O(^3P) + O_2(a^1\Delta_g)$
 - $O_3 + h\nu \rightarrow O(^3P) + O_2(X^3\Sigma_g^-)$ – lowest
- Transition into the ¹B₂ state ~255 nm (Hartley band) is strongest. Weaker transitions into other singlet states at ~600 nm (Chappuis bands) and 330 nm (Huggins bands).



From S. Nidkorodov

O₃ Absorption Spectrum

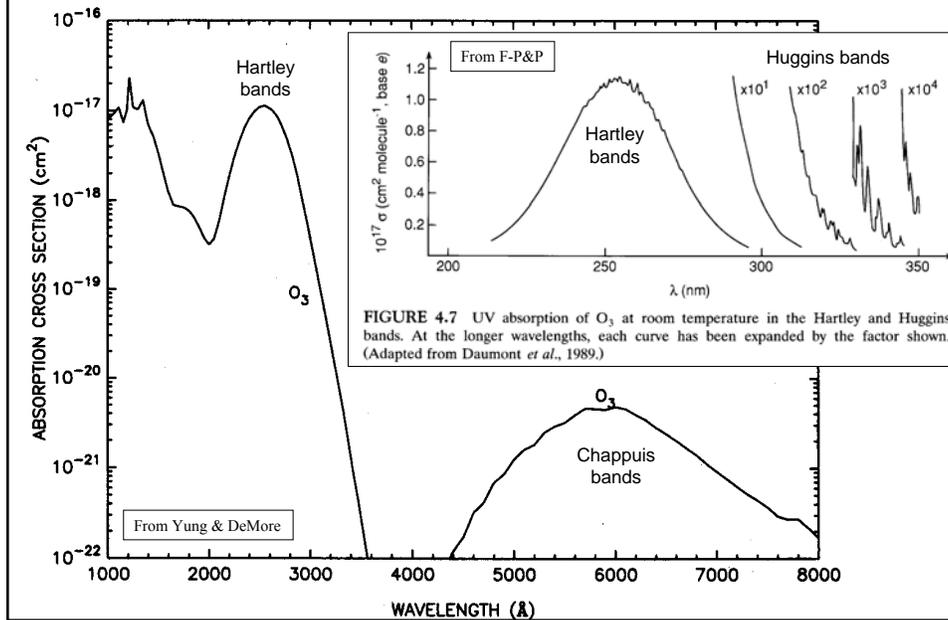


FIGURE 4.7 UV absorption of O₃ at room temperature in the Hartley and Huggins bands. At the longer wavelengths, each curve has been expanded by the factor shown. (Adapted from Daumont *et al.*, 1989.)

O₃ Photochemistry

- Most important aspect is production of O(¹D) (*and thus OH*)
 - $O_3 + hv \rightarrow O_2 + O(^1D)$ $\phi(^1D) \approx 90\%$ below 305 nm
 - $O_3 + hv \rightarrow O_2 + O(^3P)$ $\phi(^3P) \approx 10\%$ below 305 nm
 - $O(^1D) + H_2O \rightarrow 2 OH$ OH yield $\approx 10\%$ (at the surface)
 - $O(^1D) + M \rightarrow O(^3P)$ the rest of O(¹D) atoms are quenched

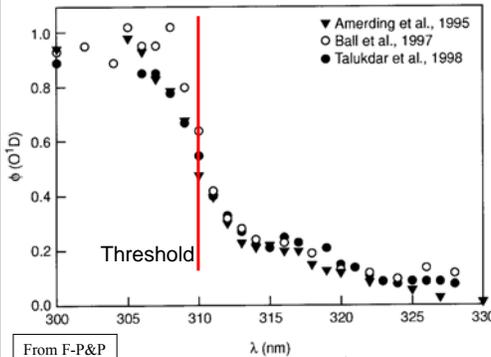
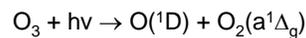


FIGURE 4.9 Some measurements of the quantum yields for production of O(¹D) in the photolysis of O₃ at 298 K.

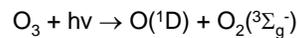
Dissociation threshold for



is at 310 nm. However, O(¹D) products are observed up to 330 nm because of:

a). dissociation of *internally excited* O₃, which requires less energy to break apart (responsible for 306 – 325 nm falloff). Drops as T ↓

b). spin-forbidden process



(sole contributor $\lambda > 325$ nm, $\neq f(T)$)

Photodissociation Thresholds in NO_2 and O_3

For NO_2 and O_3 , photodissociation quantum yields do not drop immediately to zero below the dissociation threshold. This effect is explained by channeling the internal energy of molecules into the dissociation process.

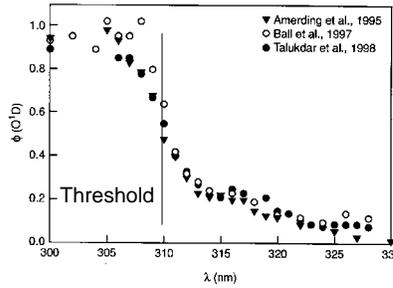
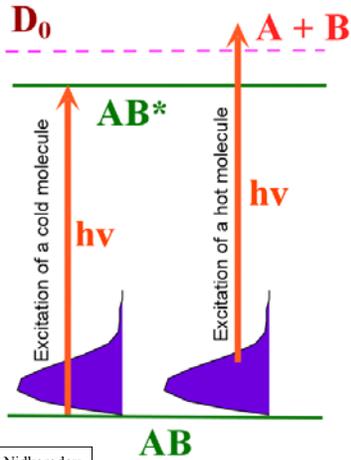


FIGURE 4.9 Some measurements of the quantum yields for production of $\text{O}(^1\text{D})$ in the photolysis of O_3 at 298 K.

From F-P&P

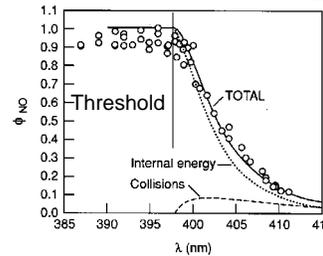


FIGURE 4.12 Quantum yields for NO production in the photolysis of NO_2 at 298 K. Calculated quantum yields due to internal energy (dotted line), the calculated dissociation due to collision (dashed line), and the sum of these two calculations (solid line) are also shown (adapted from Roehl *et al.*, 1994).

O_3 Photodissociation Channels

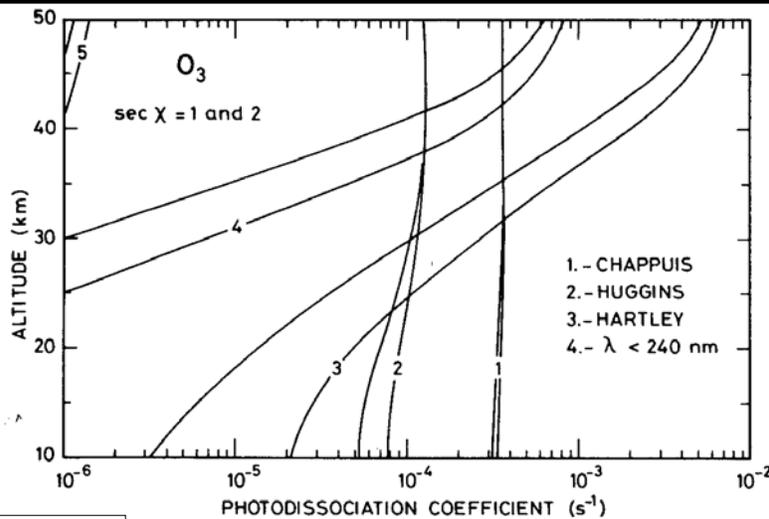
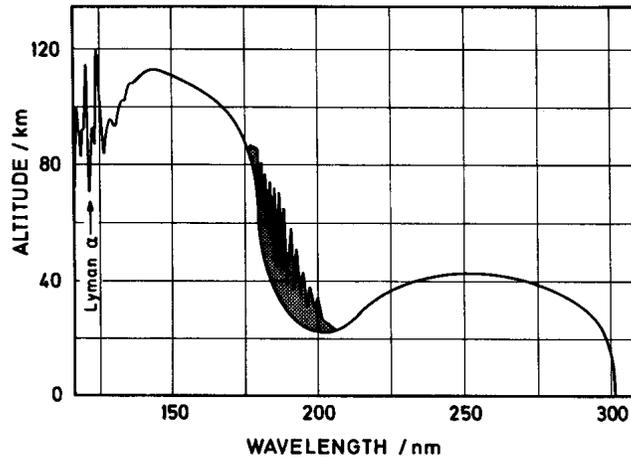


Fig. 4.35. Contribution of each spectral region to the total photodissociation of ozone as a function of altitude. From Nicolet (1980).

Combined UV Shielding by O₂ and O₃

O₂ takes care of 90% of deep UV radiation well above 80 km, i.e. in the mesosphere and thermosphere. O₃ important below 40 km. Window at 210 nm between O₂ and O₃ absorption of paramount importance for making O₃ in stratosphere via photolysis of O₂.



From Warneck
Fig. 2.9

Fig. 2.9 Elevation at which solar radiation is attenuated by O₂ and O₃ by one order of magnitude.

Table 4.1 Spectral regions of photochemical importance in the atmosphere

Wavelength	Atmospheric absorbers
121.6 nm	Solar Lyman α line, absorbed by O ₂ in the mesosphere; no absorption by O ₃
100 to 175 nm	O ₂ Schumann Runge continuum. Absorption by O ₂ in the thermosphere. Can be neglected in the mesosphere and stratosphere.
175 to 200 nm	O ₂ Schumann Runge bands. Absorption by O ₂ in the mesosphere and upper stratosphere. Effect of O ₃ can be neglected in the mesosphere, but is important in the stratosphere.
200 to 242 nm	O ₂ Herzberg continuum. Absorption by O ₂ in the stratosphere and weak absorption in the mesosphere. Absorption by the O ₃ Hartley band is also important; both must be considered.
242 to 310 nm	O ₃ Hartley band. Absorption by O ₃ in the stratosphere leading to the formation of O(¹ D).
310 to 400 nm	O ₃ Huggins bands. Absorption by O ₃ in the stratosphere and troposphere leads to the formation of O(³ P).
400 to 850 nm	O ₃ Chappuis bands. Absorption by O ₃ in the troposphere induces photodissociation even at the surface.

Summary
of O₂ & O₃
Photochem.

From Brasseur & Solomon

Photolysis Rates for O₂, NO₂, and O₃

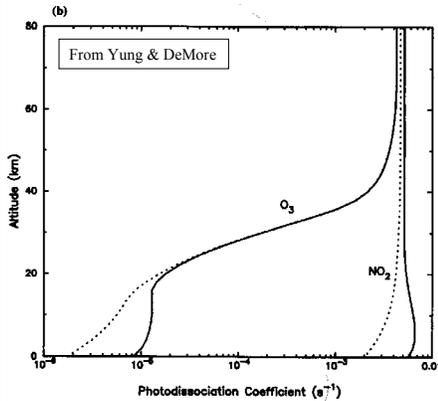
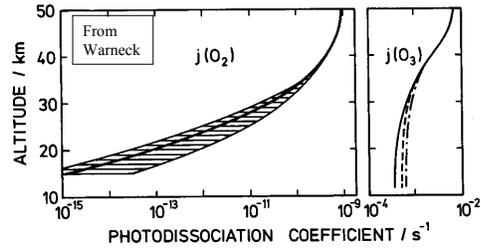


Figure 2.26 (b) Photodissociation coefficient for O₃ [O₃ + hν → O₂ + O(¹D)] and NO₂ (NO₂ + hν → NO + O) in Earth's atmosphere. The dotted line gives the contribution of the direct attenuated solar flux; the solid line gives the sum of the direct and diffuse fluxes. The calculations are diurnally averaged for a midlatitude atmosphere in spring with surface reflectivity of 0.25 and without aerosols. The total ozone column in the model is 341 DU (Dobson units). From the authors' Caltech/Jet Propulsion Lab model of Earth's atmosphere. See, for example, Michelangeli, D. V., Allen, M., and Yung, Y. L., 1989, "El Chichon Volcanic Aerosols: Impact of Radiative, Thermal and Chemical Perturbations." *J. Geophys. Res.* **94**, 18429.

Typical values for photodissociation coefficients, J , for O₃, O₂, & NO₂ as a function of altitude. Photolysis rate for O₂ is strongly altitude dependent because the lower you go the less UV radiation capable of breaking O₂ is available (self-shielding). Photolysis rate for O₃ becomes altitude dependent below 40 km for similar self-shielding reasons. On the contrary, visible NO₂ photolysis occurs with about the same rate throughout the atmosphere because there is not enough of it for self-shielding.



Solve in class: Based on the figures shown here, estimate the lifetime of NO₂, O₂ and O₃ against photodissociation at 20 km and 50 km.

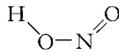
Structure of Important N-Species

Nitrogen Species

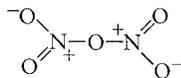
Molecular nitrogen
N₂



Nitrous acid
HONO



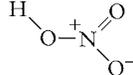
Dinitrogen pentoxide
N₂O₅



Nitric oxide
NO



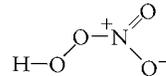
Nitric acid
HNO₃



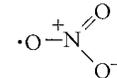
Nitrogen dioxide
NO₂



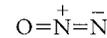
Peroxynitric acid
HO₂NO₂



Nitrate radical
NO₃

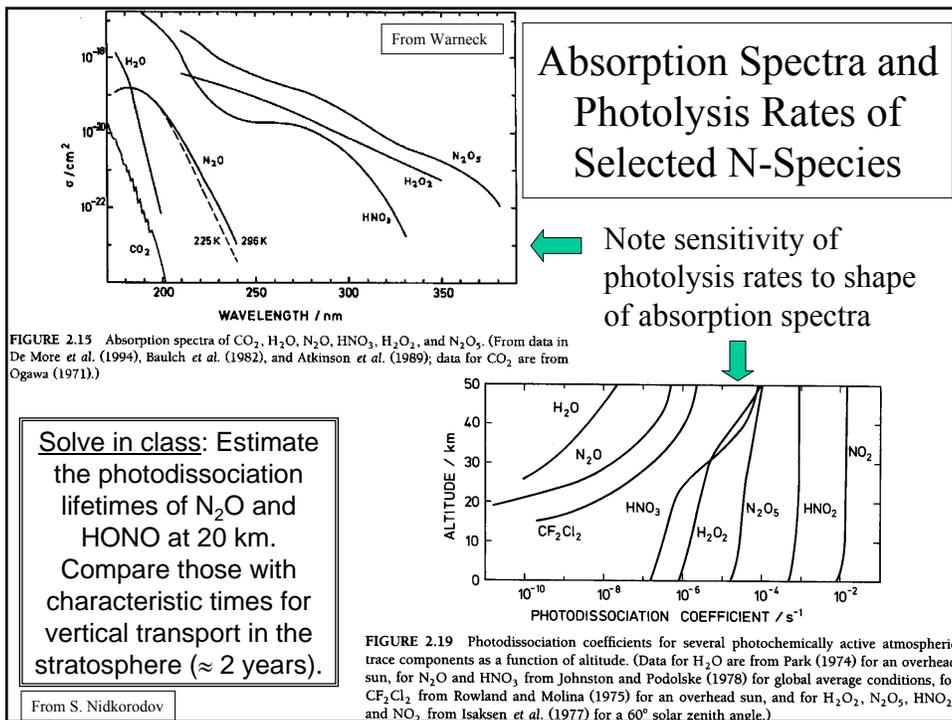
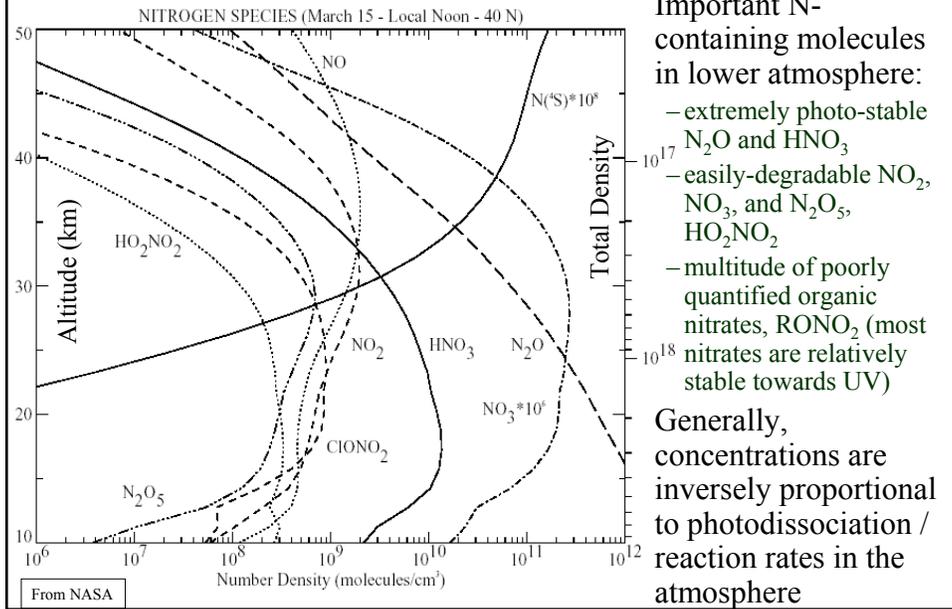


Nitrous oxide
N₂O



- From Jacobson (1999) Table B
 - posted on course web page
 - Many other species there, useful when you don't know detailed structure

Atm. Profiles of Important N-Species



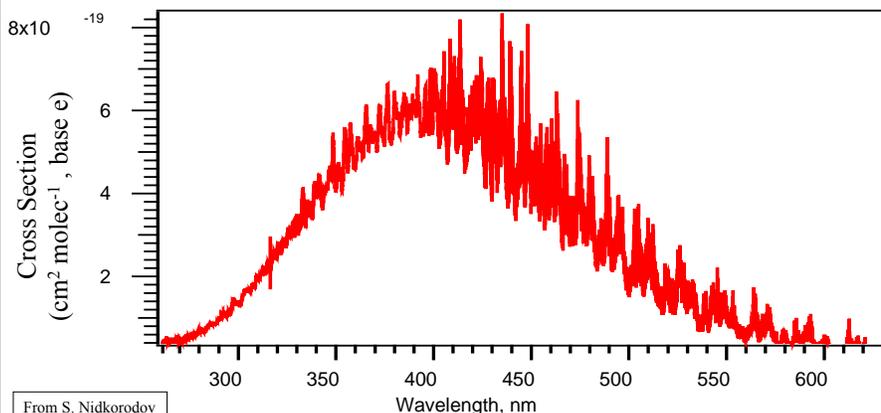
Solve in class: Estimate the photodissociation lifetimes of N₂O and HONO at 20 km. Compare those with characteristic times for vertical transport in the stratosphere (≈ 2 years).

Nitrogen Dioxide (NO₂)

- NO₂ is one of a very few atmospheric molecules that absorb & photolyze in the visible range
- Photolysis of NO₂ generates ozone in the troposphere:

$$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}({}^3\text{P})$$

$$\text{O}({}^3\text{P}) + \text{O}_2 + \text{M} \rightarrow \text{NO}_2$$
- Absorption cross sections are structured, and have a non-trivial dependence on T,P.
- NO₂ contributes to the brown color of air in very polluted cities (*but most due to aerosols!*).

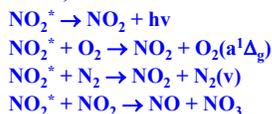


Photochemistry of NO₂

- Photolysis occurs with nearly 100% yield below 397.8 nm. O-atom immediately makes O₃:

$$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}({}^3\text{P})$$

$$\text{O}({}^3\text{P}) + \text{O}_2 (+ \text{M}) \rightarrow \text{O}_3$$
- Between 398 nm and 415 nm, room temperature NO₂ still partially photodissociates because of contributions of internal energy to the process, but the quantum yield declines rapidly with wavelength
- Above 410 nm, electronic excitation of NO₂ can result in the following processes:



- Fluorescence
- Electronic energy transfer
- Electronic-to-vibrational energy transfer
- Disproportionation (lab conditions only)

TABLE 4.10 Calculated Wavelengths (nm) for NO₂ Photolysis Below Which the Fragments Shown Can Be Produced^{a,b}

NO	Oxygen atoms		
	³ P	¹ D	¹ S
X ² Π	397.8	243.9	169.7
A ² Σ ⁺	144.2	117.4	97

^a From Okabe (1978).

^b Assuming no contribution from internal energy of the molecule.

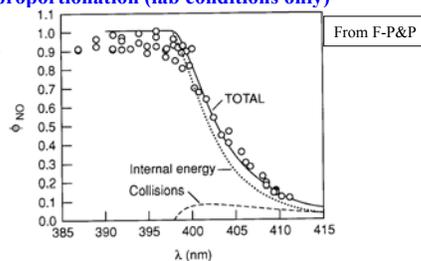
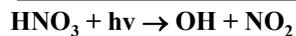


FIGURE 4.12 Quantum yields for NO production in the photolysis of NO₂ at 298 K. Calculated quantum yields due to internal energy (dotted line), the calculated dissociation due to collision (dashed line), and the sum of these two calculations (solid line) are also shown (adapted from Roehl *et al.*, 1994).

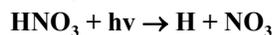
Nitric Acid (HNO₃)



$\phi \approx 1$ between 200 and 315 nm

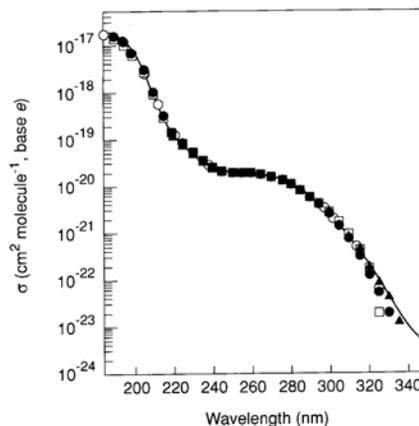


requires vacuum UV; ϕ is only 0.03 at 266 nm



requires vacuum UV; ϕ is only 0.002 at 266 nm

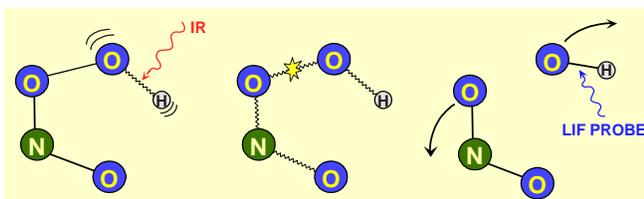
- Overall relatively long lifetime against photolysis



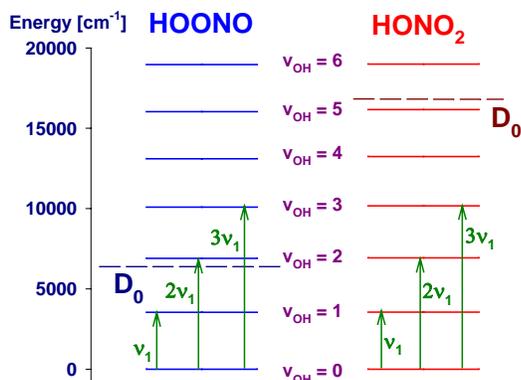
From F-P&P

FIGURE 4.13 Absorption spectrum of HNO₃ (solid line) at 298 K. Symbols represent data reported in previous studies from other laboratories. (Adapted from Burkholder *et al.*, 1993.)

Overtone Dissociation



If one supplies enough vibrational energy into a molecule (more than its dissociation energy $\equiv D_0$) the molecule may break.



From S. Nidkorodov

Ex. 1: Near-infrared excitation of $2v_1$ overtone in HOONO will break it into OH and NO₂

Ex. 2: Visible excitation of $6v_1$ in HNO₃ will also break it into OH and NO₂

Such **overtone dissociation** is a very indirect process involving highly inefficient intermolecular vibrational energy exchange between low and high frequency modes. Therefore it is slow (nanoseconds) and it competes with collisional stabilization.

Nitrous Acid (HONO)

- $\text{HONO} + h\nu \rightarrow \text{OH} + \text{NO}$ $\phi \approx 1$ below 400 nm
- HONO, like NO_2 , has strong absorption in visible and a highly structured spectrum. Its photochemical lifetime in the atmosphere is \sim a few minutes.
- Very important as source of OH radicals in the morning

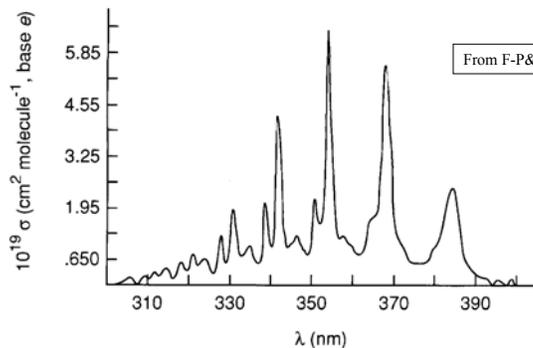
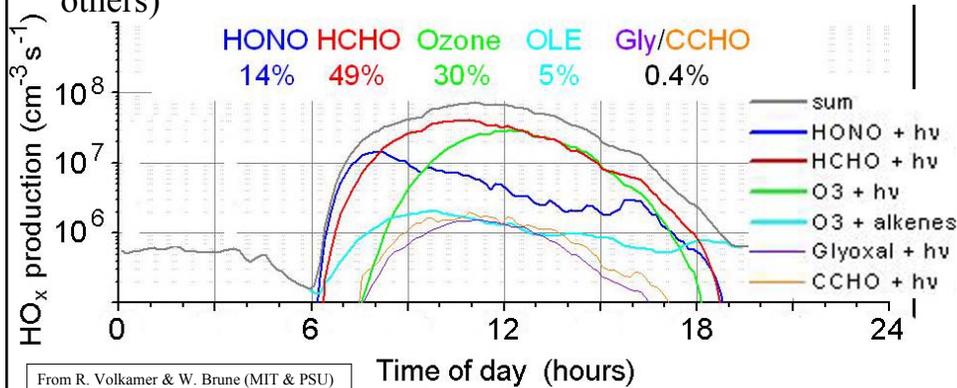


FIGURE 4.14 Absorption spectrum of HONO at 277 K (adapted from Bongartz *et al.*, 1991). Note that the absolute values of the cross sections shown here should be multiplied by 0.855 as recommended by Bongartz *et al.* (1994).

Sources of $\text{HO}_x = \text{OH} + \text{HO}_2$ in Mexico City

- HO_x drive smog and secondary aerosol chemistry
- HONO photolyzes at long λ , very important in early morning
- HCHO (formaldehyde) is dominant source
- O_3 source needs to wait for O_3 to be produced! (depends on others)



From R. Volkamer & W. Brune (MIT & PSU)

Pernitric Acid (HO₂NO₂)

- HO₂NO₂ + hv → HO₂ + NO₂ quantum yields uncertain; φ ~ 0.65 recommended
- HO₂NO₂ + hv → OH + NO₃ φ ≈ 0.35 at 248 nm; more measurements needed!
- Unique in that it *can be broken by near-infrared radiation*. This is important at large SZA, with orders of magnitude larger NIR vs. UV.

–HO₂NO₂ + hv (near-IR) → HO₂NO₂ (v₁=2) → HO₂ + NO₂ φ ≈ 0.25 (P & T dep.)

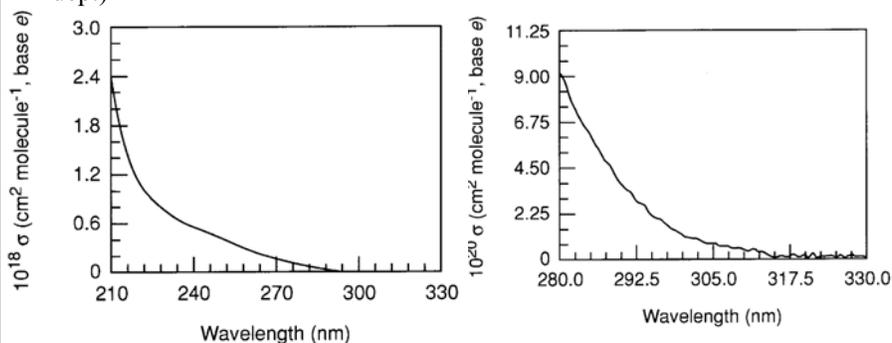


FIGURE 4.15 Absorption spectra of HO₂NO₂ at 298 K in the (a) 210- to 300-nm and (b) 280- to 330-nm regions (adapted from Singer *et al.*, 1989).

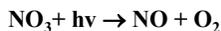
From F-P&P

Nitrate Radical (NO₃)

- NO₃ is important in nighttime chemistry. It has unusually large cross sections in the red ⇒ photodissociates in seconds in the morning.



φ is λ dependent; important towards the blue



φ is λ dependent; important in the red; competes with fluorescence; this process is nearly thermoneutral but it is inhibited by a tall energy barrier.

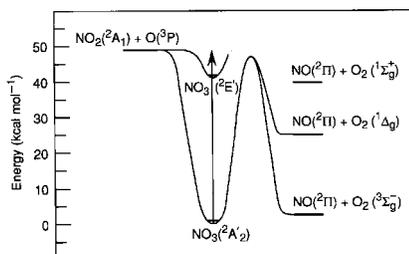


FIGURE 4.17 Energetics of NO₃ photodissociation (adapted from Davis *et al.*, 1993).

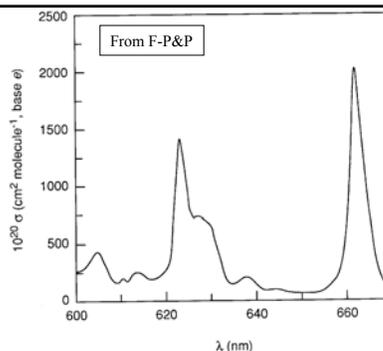


FIGURE 4.16 Absorption spectrum of NO₃ at 298 K [adapted from DeMore *et al.*, 1997 based on data from Ravishankara and Mauldin (1986), Sander (1986), and Canosa-Mas *et al.* (1987)].

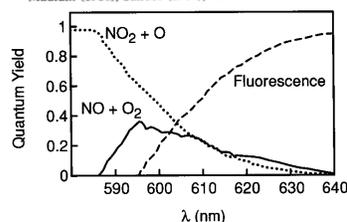
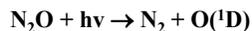


FIGURE 4.18 Quantum yields for NO₃ photolysis: dotted line, NO₃ → NO₂ + O; solid line, NO₃ → NO + O₂; dashed line, fluorescence quantum yields (adapted from Johnston *et al.*, 1996).

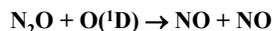
Nitrous Oxide (N₂O)

- N₂O is extremely long-lived because it is unreactive, and it does not absorb much above 200 nm. Below 200 nm:



- Note: this is a popular laboratory method of generating O(¹D); $\phi \approx 1$

- Subsequent reactions of O(¹D) with N₂O lead to production of other nitrogen oxides in the stratosphere:



major source of NO in the stratosphere



competing step

- Because of its stability, N₂O is used a "tracer". Concentrations of other molecules are often compared to that of N₂O to see if they are well mixed.

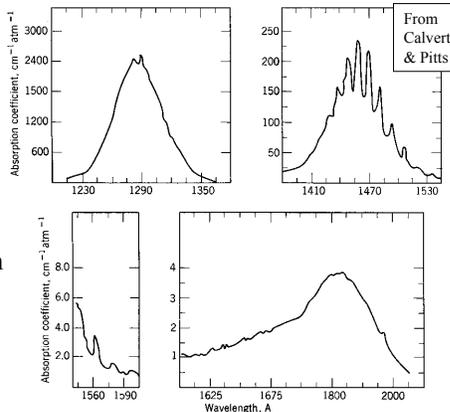
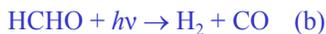
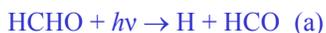


Fig. 3-43 The absorption spectrum of nitrous oxide, N₂O. From Zeilikoff, Watanabe, and Inn.¹⁴⁶

Solve in class: Find a conversion between absorption coefficient in cm⁻¹atm⁻¹ and cross sections in cm²/# at room temperature. Evaluate N₂O cross sections at 193 nm using the data shown here.

Formaldehyde (HCHO)

- Two competing photodissociation channels:



- Channel (a) leads to HO₂ radical production via:



- Sources of HO₂ are effectively sources of OH because:



Remember:
HCHO is dominant HO_x source in Mexico City

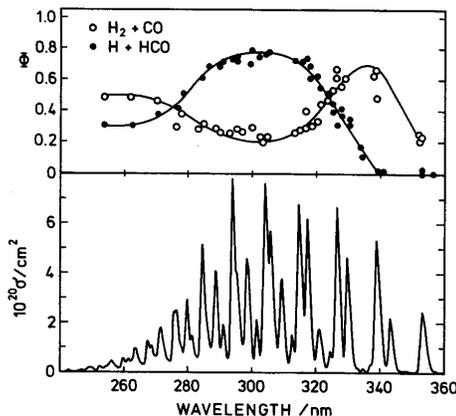


FIGURE 2.18 Absorption spectrum and quantum yields for the two photodecomposition channels of formaldehyde in air at atmospheric pressure. (From the data of Clark *et al.* (1978), Horowitz and Calvert (1978), Tang *et al.* (1979), and Moortgat *et al.* (1979, 1983).)

Acetaldehyde and higher aldehydes

- Four possible photodissociation channels:



- Can also be HO_x source
- Similarly for higher aldehydes

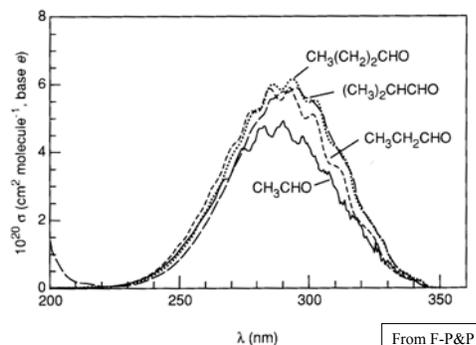


FIGURE 4.27 Absorption spectra for some simple aldehydes (adapted from Martinez *et al.*, 1992).

Process	Quantum yield	$\Delta H(298 \text{ K})$	Threshold	Note
a). $\text{CH}_3 + \text{HCO}$	0 – 0.5	$84.7 \pm 1.2 \text{ kcal/mol}$	$\approx 338 \text{ nm}$	-
b). $\text{CH}_4 + \text{CO}$	0 – 0.5; goes up in UV	- 4.6 kcal/mol	none	Large barrier
c). $\text{CH}_3\text{O} + \text{H}$	< 0.01 above 290 nm	$95.8 \pm 1.2 \text{ kcal/mol}$	$\approx 298 \text{ nm}$	-
d). $\text{CH}_2\text{CO} + \text{H}_2$	0	$28.7 \pm 3 \text{ kcal/mol}$	$\approx 1000 \text{ nm}$	Large barrier

Acetone ($\text{CH}_3\text{-CO-CH}_3$)

- Two main photodissociation channels:



- (a) more important near the earth surface. Photodissociation competes with collisional relaxation, ϕ P-dependent. Also a competition between photodissociation and reaction with OH:

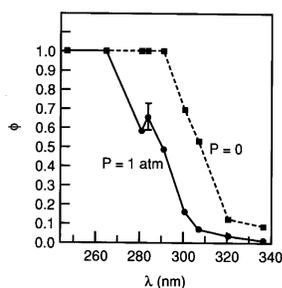


FIGURE 4.30 Measured quantum yields for acetone photodissociation as a function of wavelength at 1 atm total pressure and extrapolated to zero total pressure (adapted from Gierczak *et al.*, 1998).

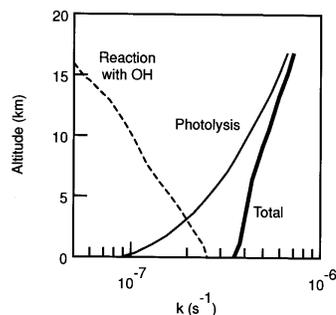


FIGURE 4.31 Calculated first-order rate constants for loss of CH_3COCH_3 due to reaction with OH (i.e., $k[\text{OH}]$) or photolysis (i.e., k_p) as a function of altitude (adapted from Gierczak *et al.*, 1998).

Chlorofluorocarbons (CFCs)

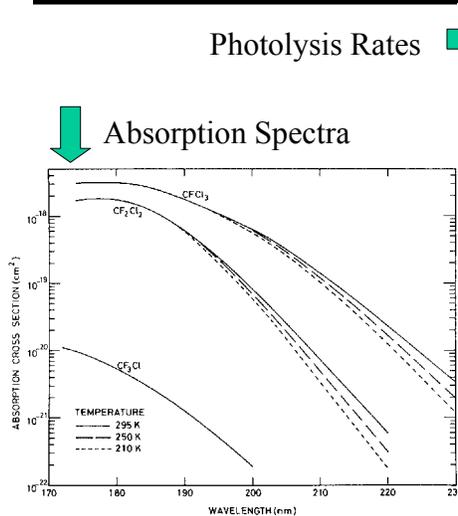


Fig. 4.53 Spectral distribution of the absorption cross sections of several halocarbons and their temperature dependence. From Vanlaethem-Meuree et al. (1978).

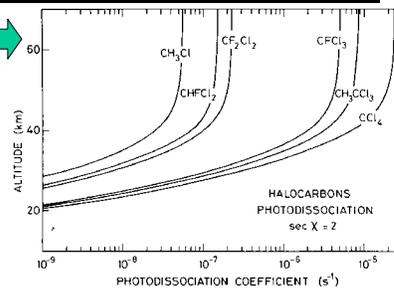


Fig. 4.54. Vertical distribution of the photolysis rate of several chlorocarbons.

- No other CFC sinks than photolysis
- Known that Cl would destroy O_3
- 1995 Nobel Prize (M&R) is the idea in this slide: CFCs will provide large source of Cl in stratosphere and lead to O_3 destruction

From Brasseur and Solomon