Basic Photochemistry of the Middle Atmosphere

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Photochemistry of the Middle Atmosphere

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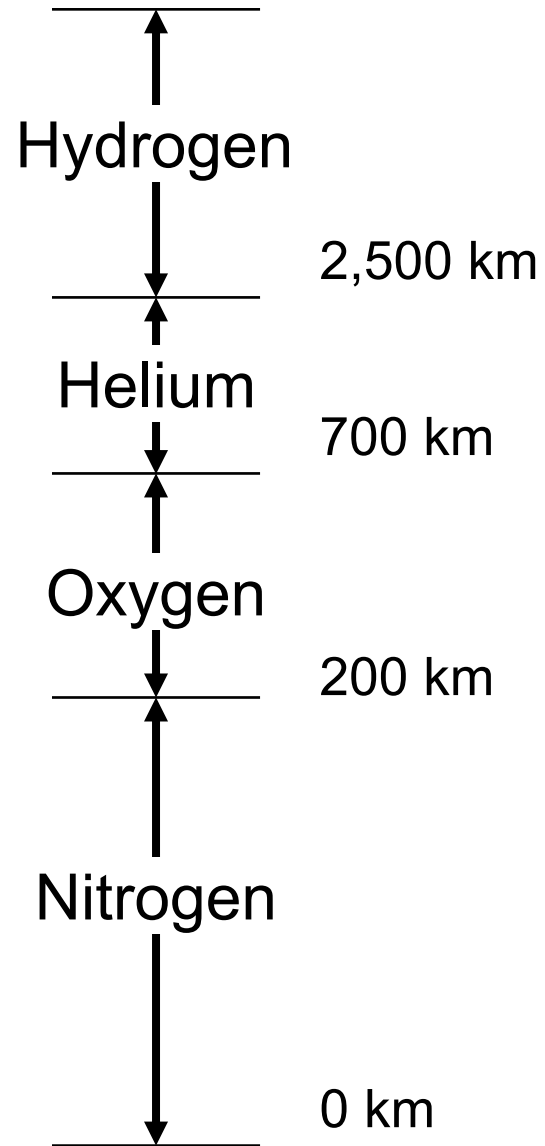## 8:30-10:30

Dan Marsh

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Boulder, USA

Overview

- Composition
  - Primary constituents
  - Continuity equation
  - Minor constituents - ozone, HOx, NOx
  - Catalytic cycles
- Energetics
  - Thermal structure
  - Energy deposition
  - Heating and cooling

Composition

Primary constituent

Hydrogen

2,500 km

Helium

700 km

Oxygen

200 km

Nitrogen

0 km

Total density height variation

$$p = nkT \quad \text{Ideal gas law}$$

$$\Delta p = -\rho g \Delta z \quad \text{Hydrostatic balance}$$

$$\frac{\Delta p}{p} = -\frac{\rho}{n}\frac{g}{kT}\Delta z = -\frac{1}{H}\Delta z \quad \text{where} \quad H = \frac{kT}{mg}$$

$$p(z) = p_0 \, exp\left(-\int_0^z \frac{dz}{H}\right)$$

$$n(z) = n_0 \frac{T_0}{T} exp\left(-\int_0^z \frac{dz}{H}\right)$$

Which leads to:

$$\frac{\partial n}{\partial z} = -\left(\frac{1}{T}\frac{\partial T}{\partial z} + \frac{1}{H}\right) n$$

In the "homosphere," where eddy diffusion tends to mix the atmosphere, the mean molecular weight is almost constant (m ~ 28.96 amu), and the density will decrease with a mean scale height of ~ 7km.

Above about 90km, constituents tend to diffuse with their own scale height ($H_i = kT/m_i g$) as the mean free path becomes longer. This is the "heterosphere." The ith constituent (assuming no significant sources or sinks) will have the following gradient:

$$\frac{\partial n_i}{\partial z} = -\left(\frac{1}{T}\frac{\partial T}{\partial z} + \frac{1}{H_i}\right) n_i$$

Constituents with low mass will fall off less rapidly with height, leading to diffusive separation.
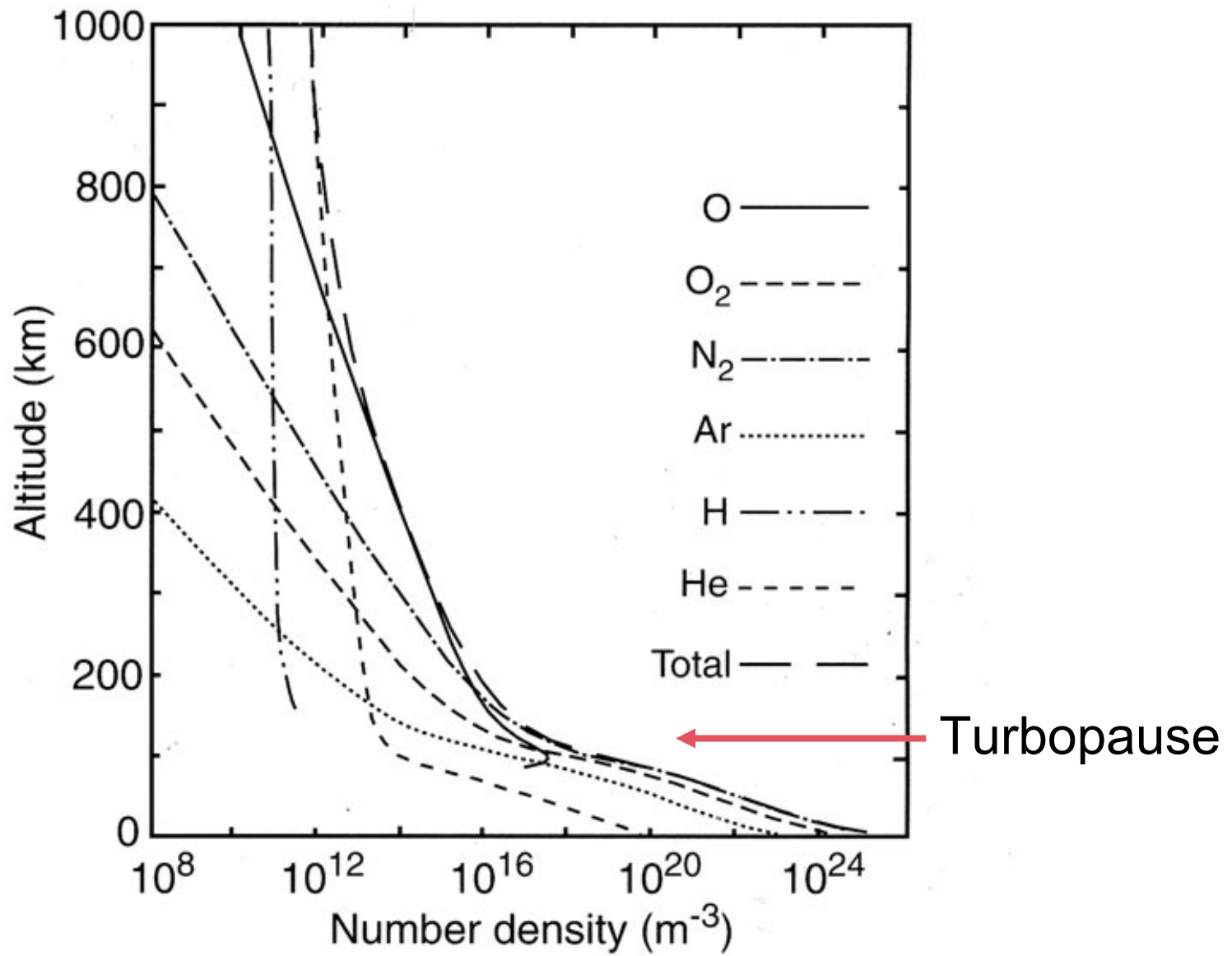
From Richmond [1983]

To recap…

- Above the turbopause (~105km), molecular diffusion causes constituents to drop off according to their mass.

- Below, the atmosphere is fully mixed:

- 78%N_2, 21%O_2, <1% Ar, <0.1% CO_2

- Density decreases with a mean scale height: H = kT/mg ~7km

- The lower thermosphere is also the transition from a molecular to atomic atmosphere.
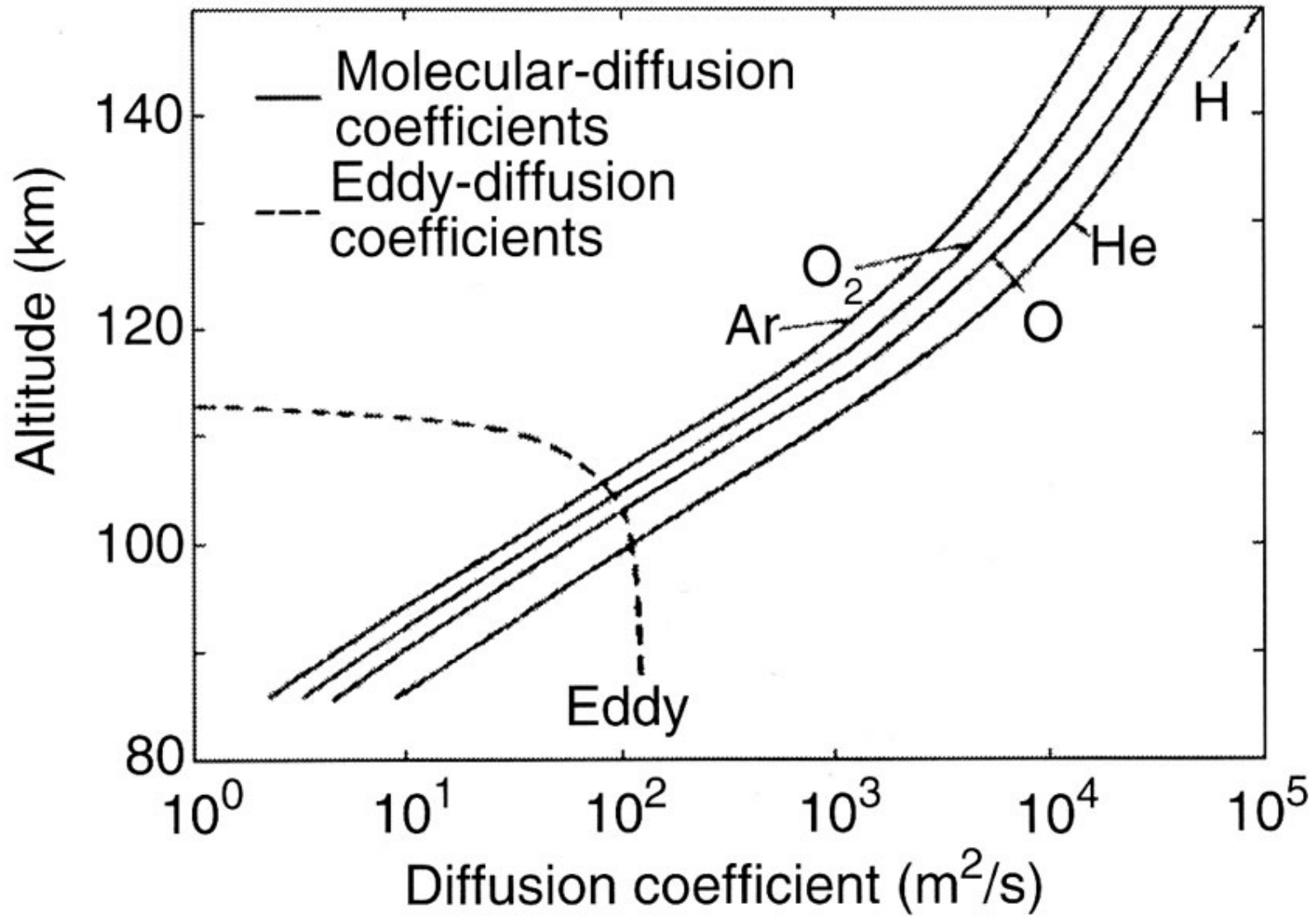
What about chemistry?

Recall:
$$\frac{\partial n_i}{\partial z} = -\left(\frac{1}{T}\frac{\partial T}{\partial z} + \frac{1}{H_i}\right)n_i$$

If there's chemical production or loss of a minor constituent then this equality will not hold and a diffusive flux occurs. The flux is proportional to the amount of the inequality. Above the turbopause this will be:

$$\phi_i = w_d n_i = -D_i\left(\frac{\partial n_i}{\partial z} + \left((1+\alpha_T)\frac{1}{T}\frac{\partial T}{\partial z} + \frac{1}{H_i}\right)n_i\right)$$

Where D_i is the diffusion coefficient:

$$D_i = \frac{3}{8n\sigma_i^2}\left\{\frac{kT(m+m_i)}{2\pi m m_i}\right\}^{1/2}$$
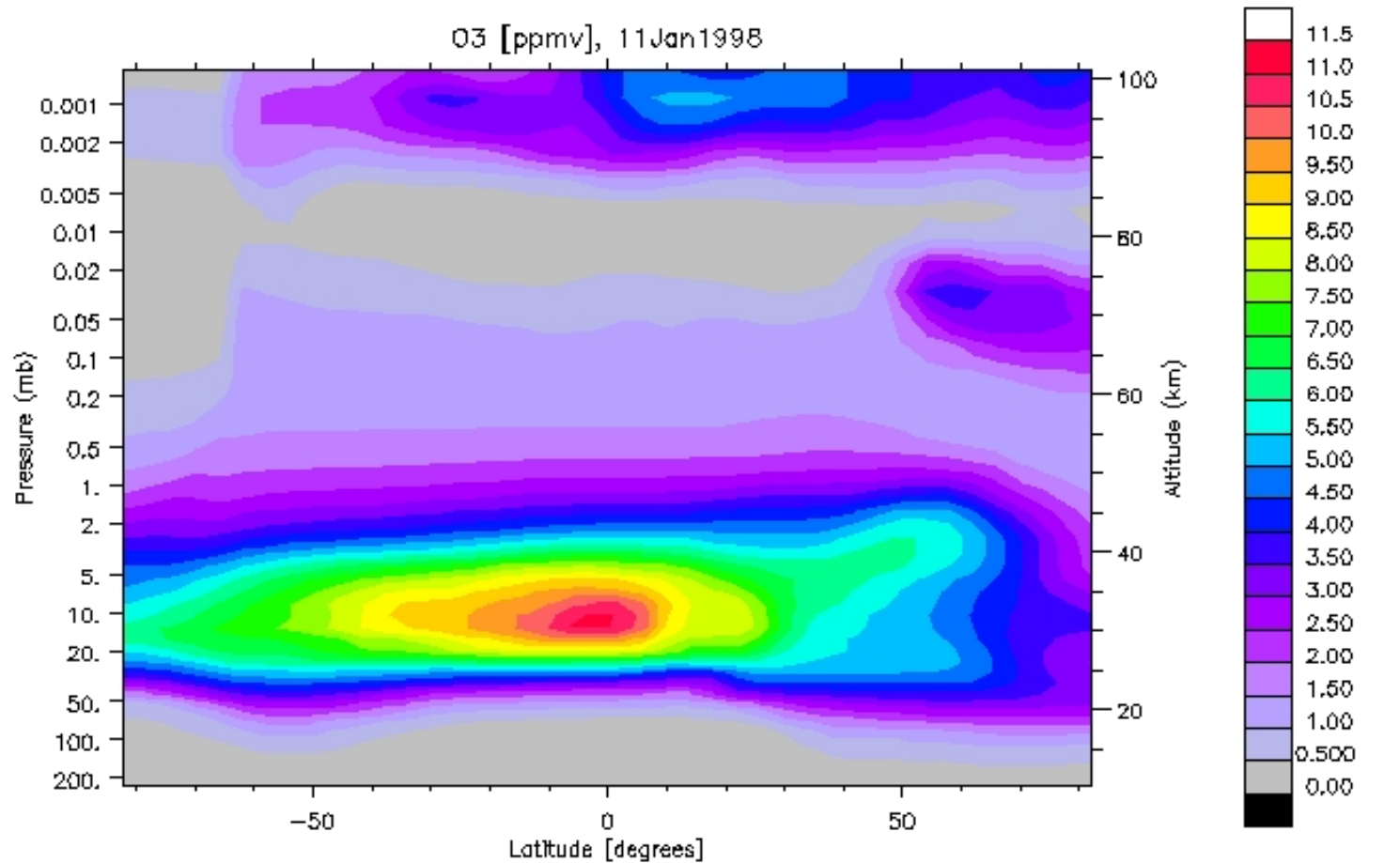
From Richmond [1983]

Continuity equation

The total diffusive flux will include both molecular and eddy diffusion terms:

$$\phi_i = -K\left\{\frac{\partial n_i}{\partial z} + \left(\frac{1}{T}\frac{\partial T}{\partial z} + \frac{1}{\bar{H}}\right)n_i\right\} - D_i\left\{\frac{\partial n_i}{\partial z} + \left((1+\alpha_T)\frac{1}{T}\frac{\partial T}{\partial z} + \frac{1}{H_i}\right)n_i\right\}$$

So, neglecting resolved transport, we now have a continuity equation for the ith minor constituent:

$$\frac{\partial n_i}{\partial t} = P_i - L_i n_i - \frac{\partial \phi_i}{\partial z}$$

The distribution of ozone

Zonal mean volume mixing ratio for January

Chapman chemistry
(Pure oxygen system)

		O	O_3
J_2:	$O_2 + h\nu \rightarrow O + O$	P	-
k_2:	$O + O_2 + M \rightarrow O_3 + M$	L	P
J_3:	$O_3 + h\nu \rightarrow O_2 + O$	P	L
k_1:	$O + O + M \rightarrow O_2 + M$	L	-
k_3:	$O + O_3 \rightarrow 2O_2$	L	L

Chapman, 1930

J_i: photolysis rate
k_i: bimolecular/termolecular rxn rate

Continuity equation for O, O_3

$$\frac{\partial(O)}{\partial t} = J_3(O_3) + 2J_2(O_2)$$
$$- k_3(O)(O_3) - k_2(M)(O_2)(O) - 2k_1(M)(O)^2$$

$$\frac{\partial(O_3)}{\partial t} = k_2(M)(O_2)(O) - J_3(O_3) - k_3(O)(O_3)$$

Define Ox = { O, O_3 } "odd-oxygen"

$$\frac{\partial(Ox)}{\partial t} = 2J_2(O_2) - 2k_3(O)(O_3) - 2k_1(M)(O)^2$$

Calculation of photolysis rates (J)

$$J_A(\lambda, z, \chi) = \int \epsilon_A(\lambda)\sigma_A(\lambda)q(\lambda, z, \chi)d\lambda$$

'Transmission' factors

e.g. $J_{O_2}(\lambda, z, \chi) = \int \sigma_{O_2}(\lambda)q_\infty(\lambda)T_{O_2}(\lambda, z, \chi)T_{O_3}(\lambda, z, \chi)d\lambda$

1/J lifetime

Note: ozone photolysis produces mostly excited atomic oxygen ($O(^1D)$)

Species	J_∞ (s^{-1})
NO_3	2×10^{-1}
NO_2	1×10^{-2}
$O_3 \rightarrow O^1D$	7.8×10^{-3}
$O_3 \rightarrow O^3P$	9.9×10^{-4}
N_2O_5	6×10^{-4}
HNO_3	1.6×10^{-4}
H_2O_2	9.5×10^{-5}
H_2O	4.7×10^{-6}
$ClONO_2$	7.1×10^{-4}
HNO_4	4×10^{-4}
$HOCl$	6×10^{-4}
HCl	4.3×10^{-6}

4096.4.48
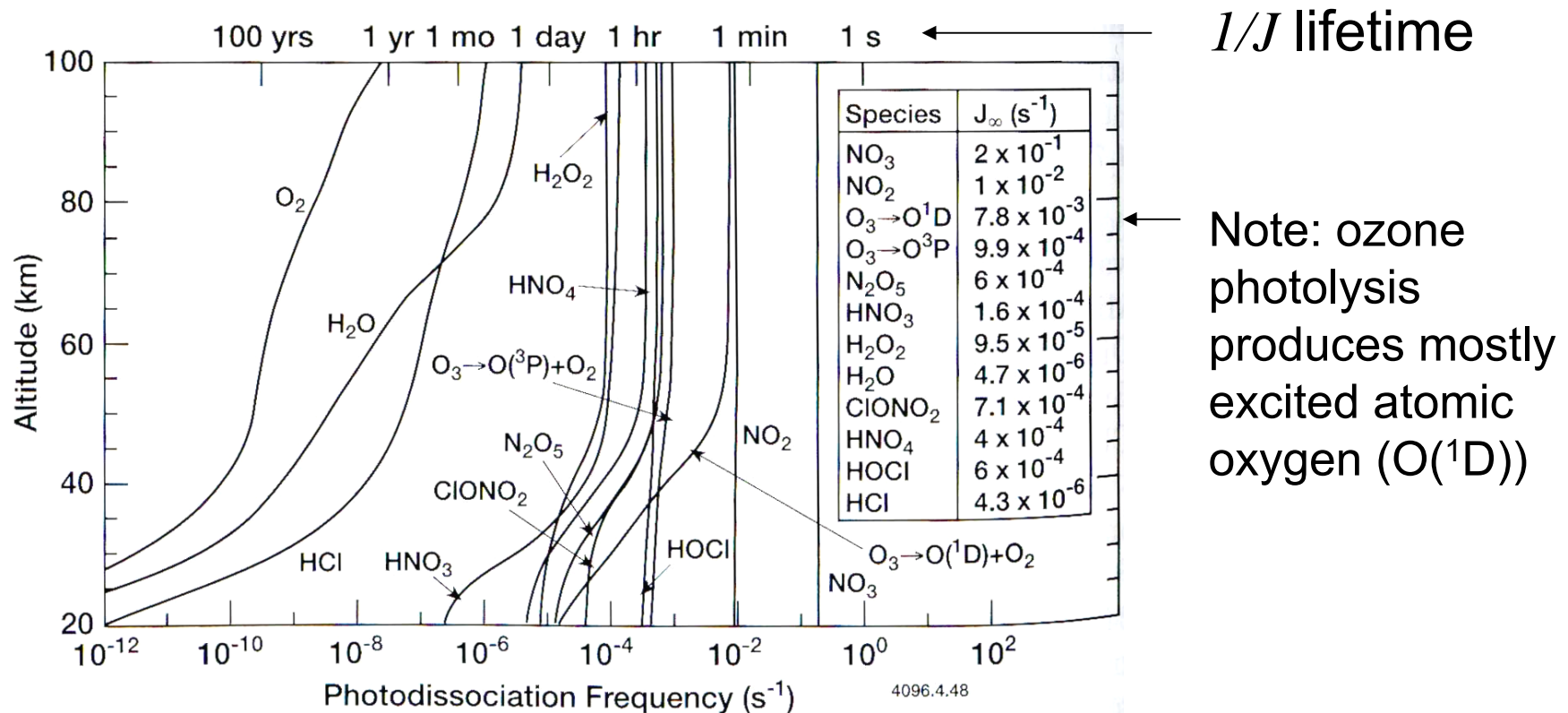
Photochemical lifetimes

$$\tau = \frac{n_i}{L_i} \qquad \tau_{O_3} = \frac{(O_3)}{J_3(O_3) - k_3(O)(O_3)} = \{J_3 - k_3(O)\}^{-1}$$

Q: why is the lifetime for atomic oxygen so long in the thermosphere?
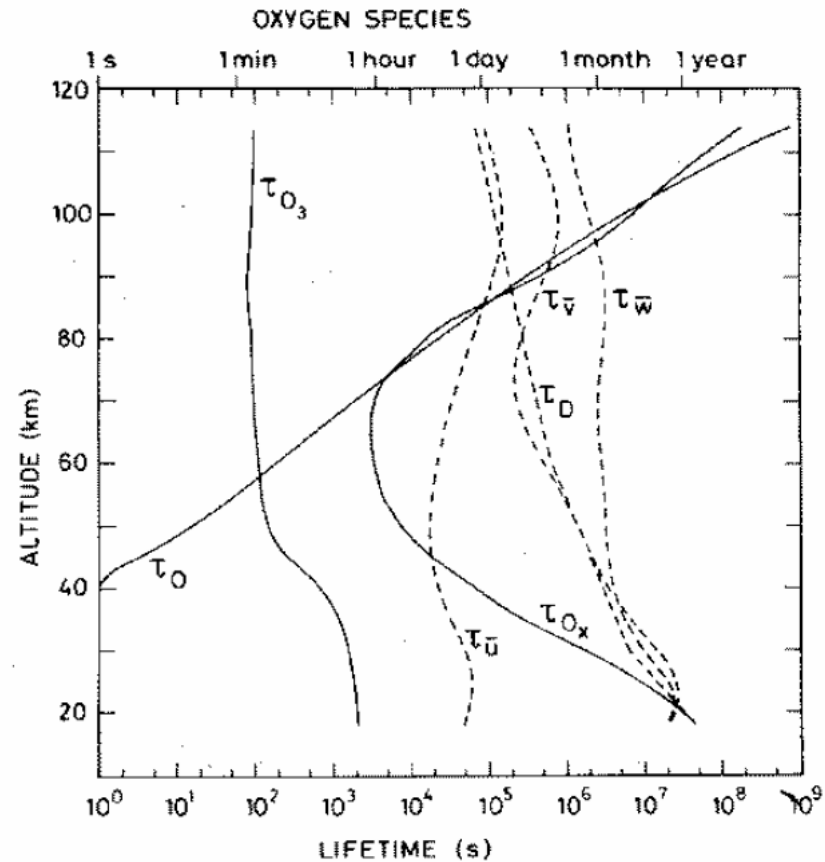
Brasseur & Solomon, 2006

Chemical/dynamical control
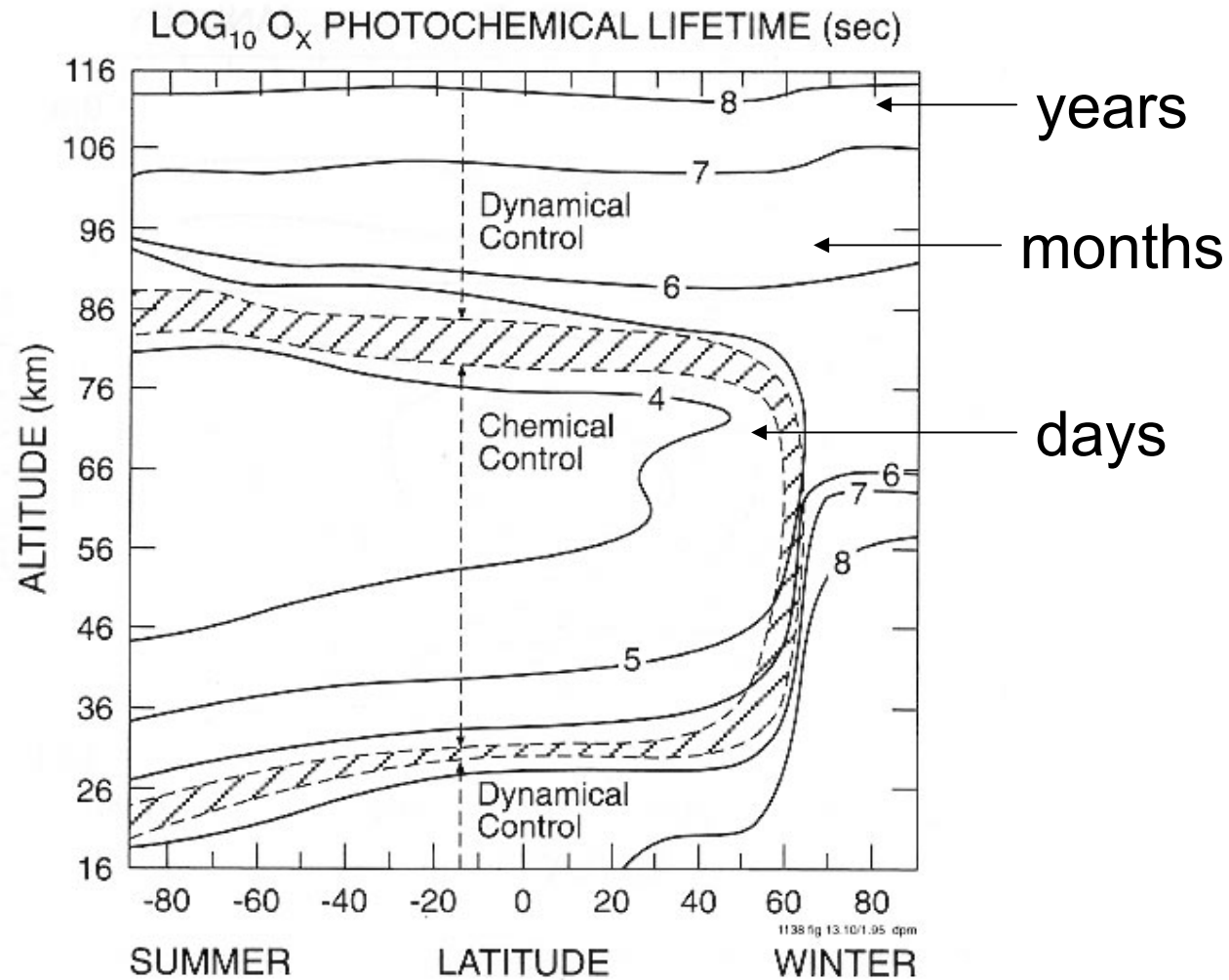
Ox Partitioning

Below ~80km τ_O is small and we can assume $dO/dt \sim 0$ and that oxygen is in *photochemical equilibrium*. So equating P to L:

$$(O) \approx \frac{J_3(O_3) + 2J_2(O_2)}{k_2(M)(O_2) + k_3(O_3)} \approx \frac{J_3(O_3)}{k_2(M)(O_2)}$$

$$\frac{(O)}{(O_3)} \approx \frac{J_3}{k_2(M)(O_2)}$$

So O/O_3 in the daytime is determined by the ratio of photolysis to recombination

Q: why do day/night differences increase with height? (<2x @ 60 km vs. 10x @ 70km)

Rapid recombination at sunset
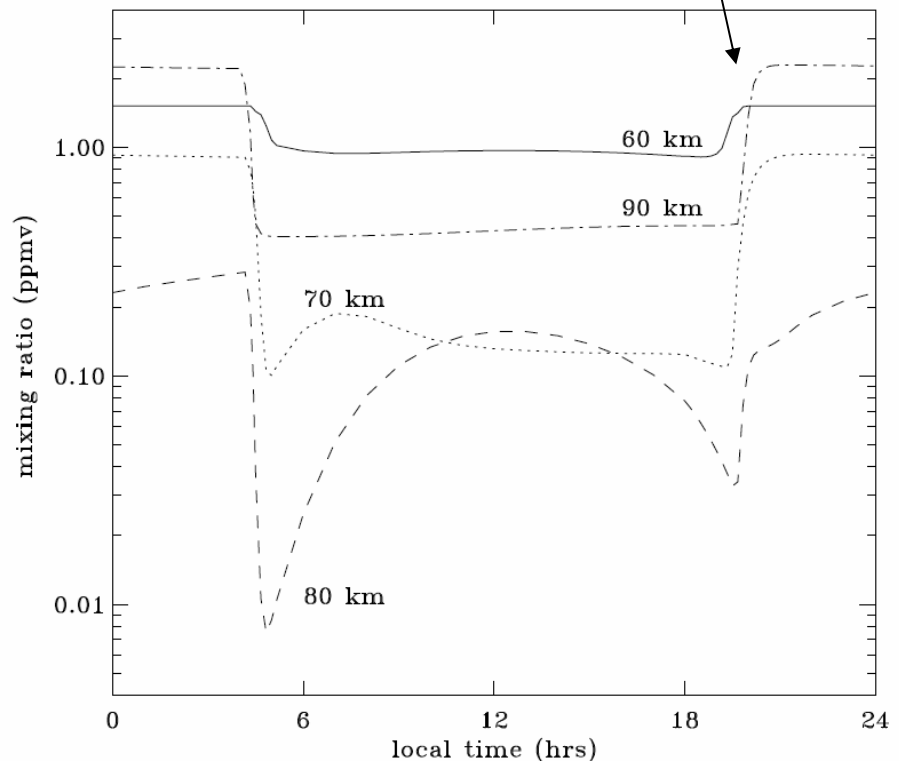
MLT Hydrogen chemistry
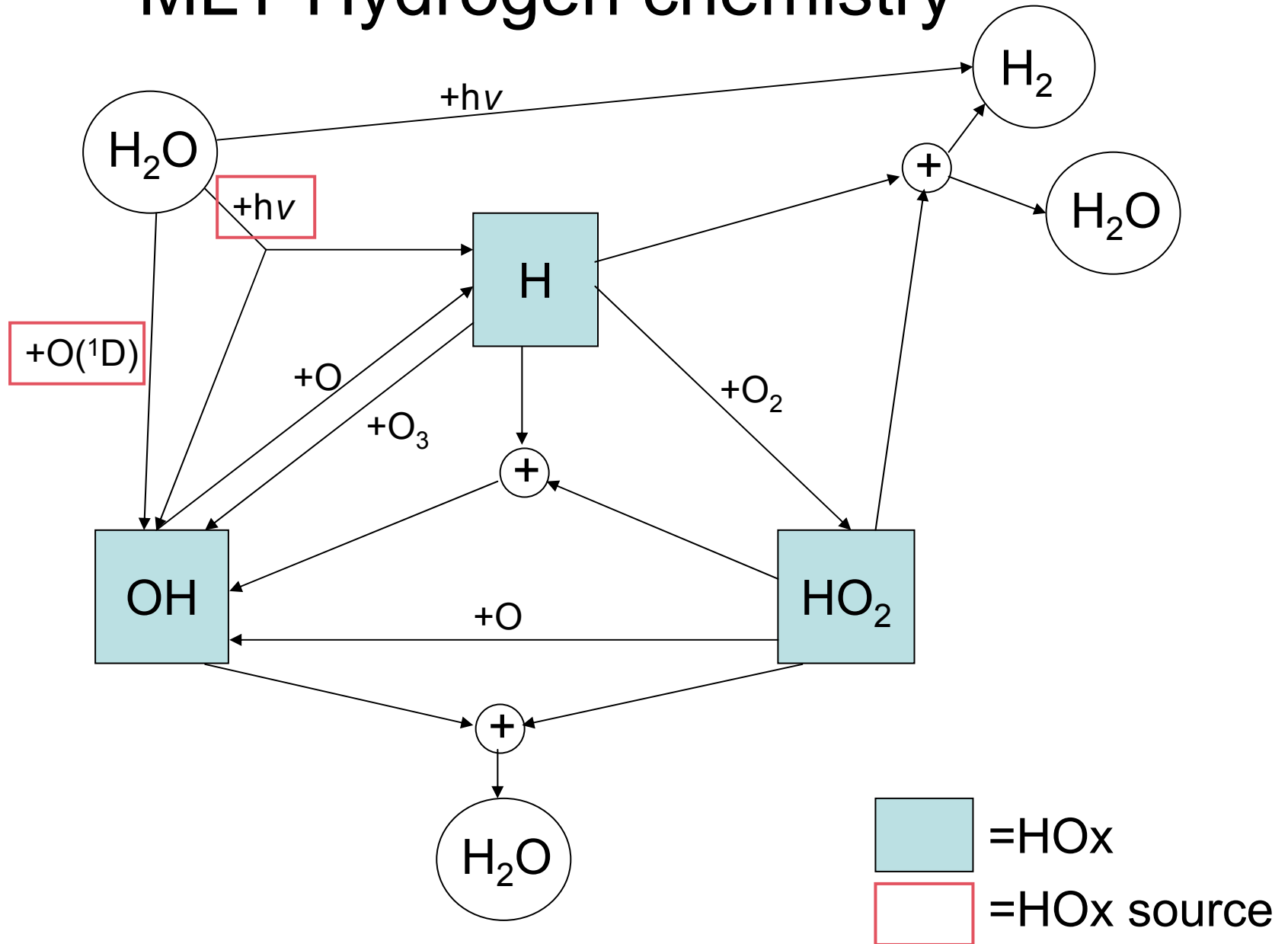
Catalytic cycles in the mesosphere

Mesosphere

$O + OH \rightarrow O_2 + H$

$H + O_2 + M \rightarrow HO_2 + M$

$O + HO_2 \rightarrow O_2 + OH$

$\langle net : 2O \rightarrow O_2 \rangle$

$O + OH \rightarrow O_2 + H$

$H + O_3 \rightarrow O_2 + OH$

$\langle net : O + O_3 \rightarrow 2O_2 \rangle$
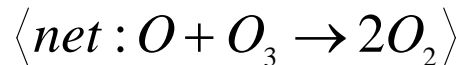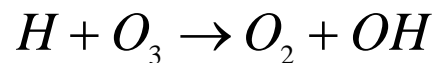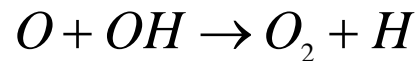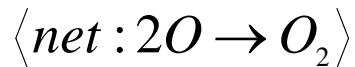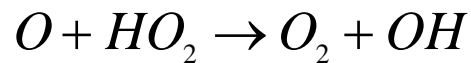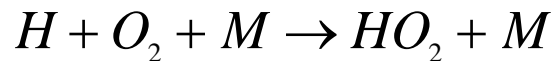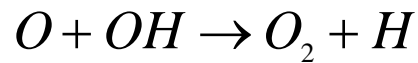
Zonal mean Ox loss rates 2.5ºN
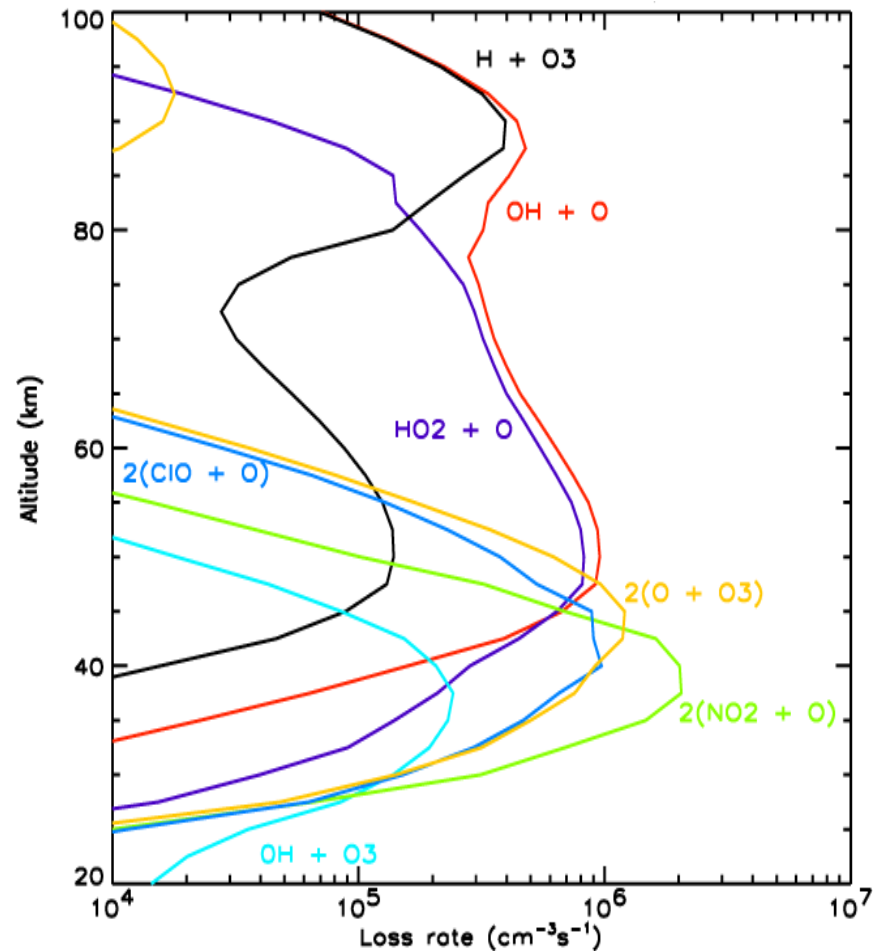
Revised Ox continuity eqn.

With some algebra:

$$(O_3)_{80km} \propto \frac{[J_{O_2}(O_2)]^2}{J_{H_2O}(H_2O)\left(J_{O_3} + a\frac{J_{O_2}}{(M)}\right)}$$

$$(O_3)_{70km} \propto \frac{J_{O_2}(M)(O_2)^2}{J_{O_3}[J_{H_2O}(H_2O)]^{1/2}}$$

$$(O_3)_{50km} \propto \left(\frac{J_{O_2}(M)}{J_{O_3}}\right)^{2/3} \left(\frac{(N_2)}{J_{O_3}^*(H_2O)}\right)^{1/3} (O_2)^{4/3}$$

See Allen, 1984

Q: why does water vapor dependency increase with height? Hint: what are the sources of HOx?

Even these formulae are simplifications. Ozone is usually calculated using a time-dependent model, that does not assume photochemical equilibrium. The response of ozone to water vapor changes with height and time of day:
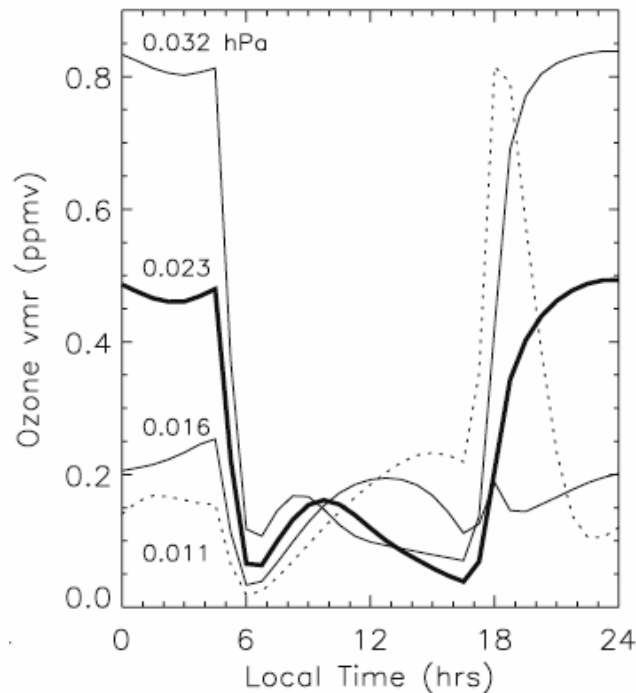
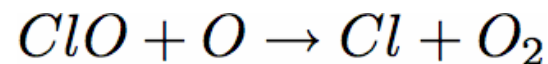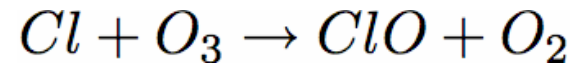Ozone $\%\Delta O_3$ for $10\%\Delta H_2O$
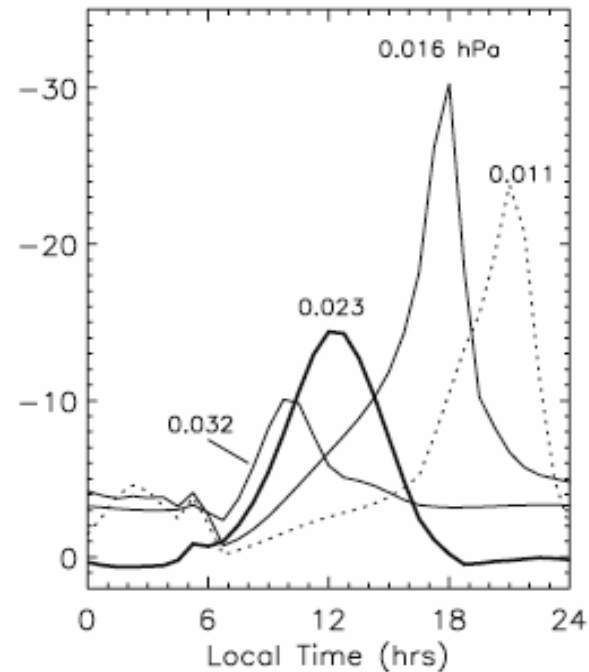
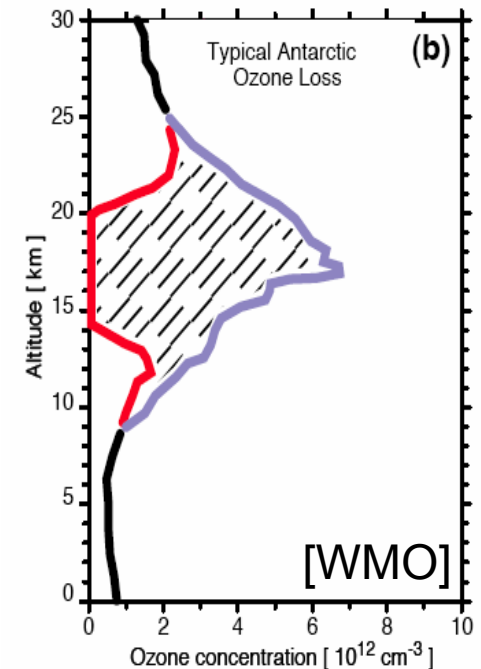# Catalytic cycles in the stratosphere: ClOx

Total ozone column

September 24, 2001
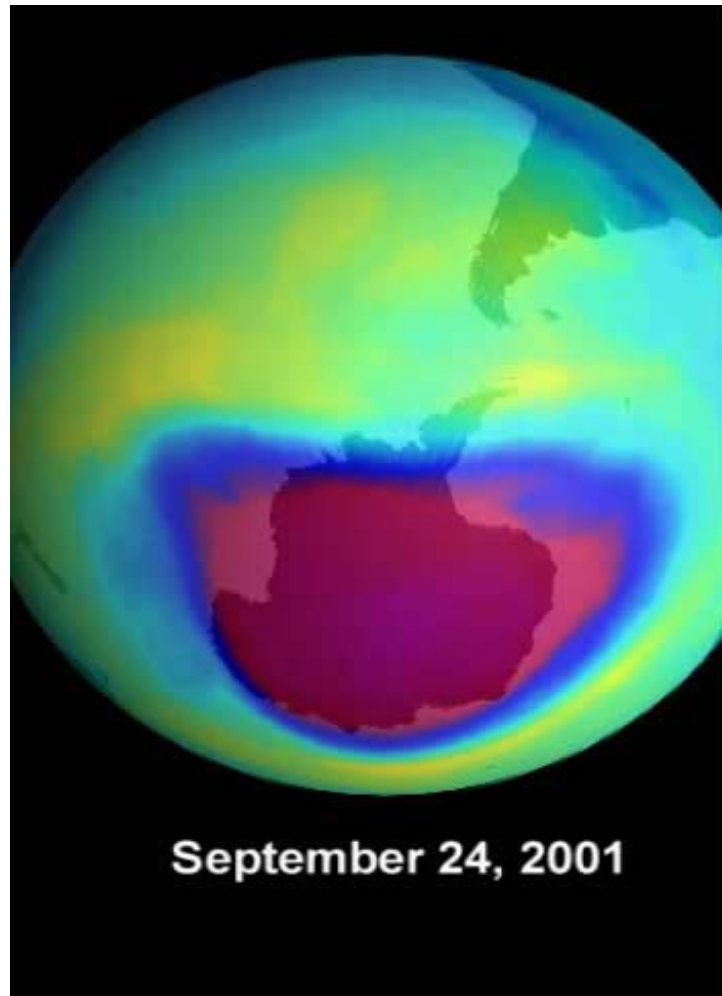
[GSFC, NASA]

40-50 km & Antarctic lower stratosphere

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

$$net : O_3 + O \rightarrow 2O_2$$
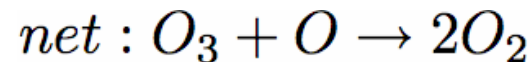
ClOx = Cl + ClO has a large source from chlorofluorocarbons (CFCs) - this lead to the creation of the Antarctic ozone hole. In the mid-1990s approximately 75-85% of stratospheric chlorine was of anthropogenic origin.


Typical Antarctic Ozone Loss (b)

Altitude [km]

Ozone concentration [10^{12} cm^{-3}]

[WMO]

Catalytic cycles in the stratosphere: NOx

35-45 km:

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + O \rightarrow NO + O_2$$

$$net : O_3 + O \rightarrow 2O_2$$
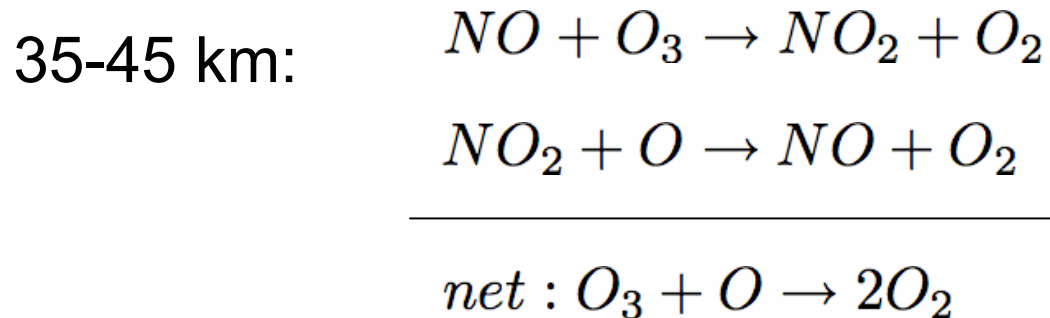
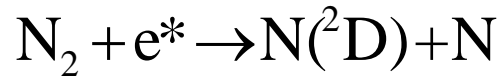Sources of stratospheric NOx = NO + NO$_2$:
- Oxidation of N_2O produced in the troposphere
- Ionization of N_2 by GCR & solar energetic particles
- Stratospheric aircraft
- NOx transported from the mesosphere/thermosphere

EUV/x-ray ionization rates

Solid: F107=210; Dotted: F107=70
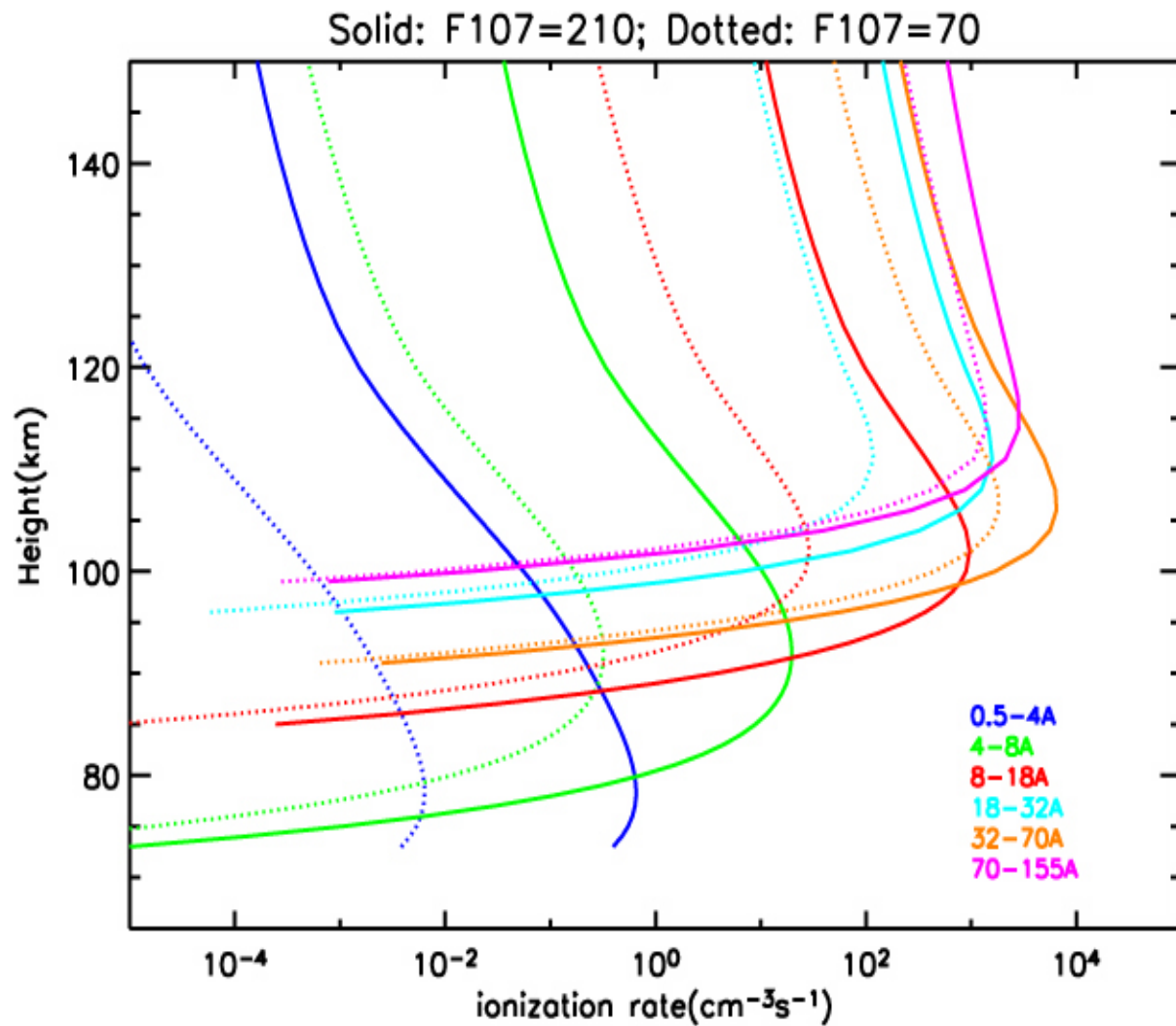
Ionization leads to N(^{2}D) production

electron impact

$$N_2 + e^* \rightarrow N(^2D) + N$$

(e* secondary/photoelectron

Produced by (1-10 keV) precipitating electrons and solar soft X-rays (2-7 nm)

dissociative recombination
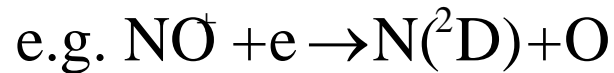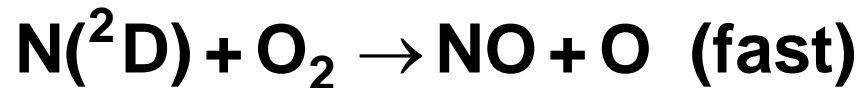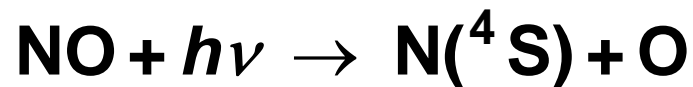
e.g. $NO^+ + e \rightarrow N(^2D) + O$
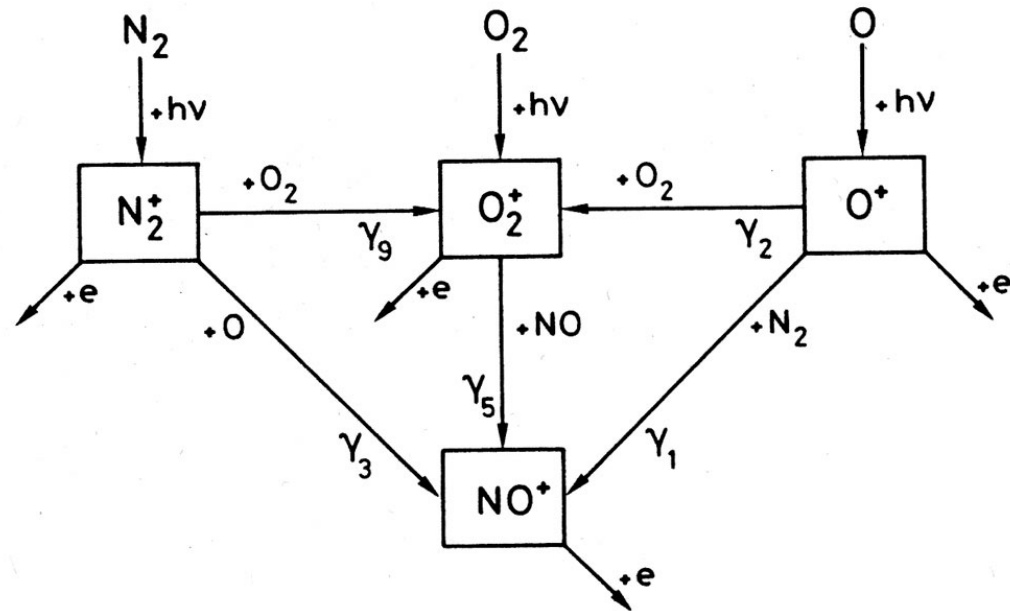
Fig. 6.12. Schematic diagram of E-region ion chemistry.

Nitric Oxide in the lower-thermosphere

Production:

$$N(^2D) + O_2 \rightarrow NO + O \quad \text{(fast)}$$

$$N(^4S) + O_2 \rightarrow NO + O \quad \text{(slow)}$$

Loss:

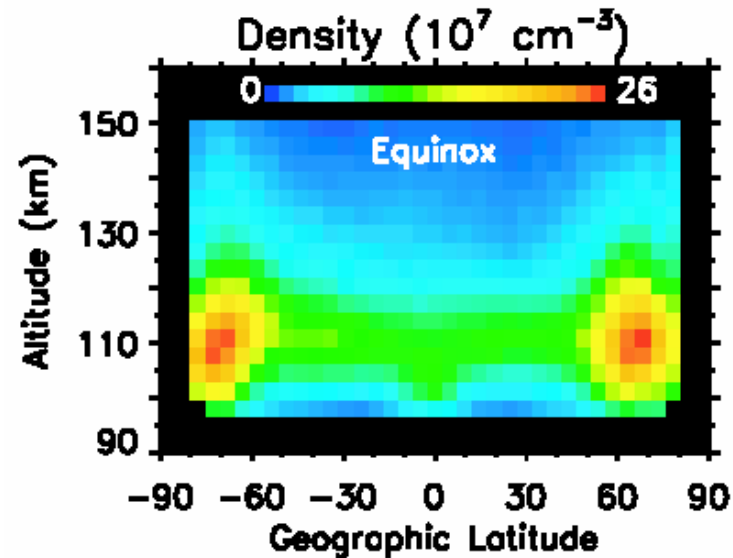$$NO + h\nu \rightarrow N(^4S) + O$$
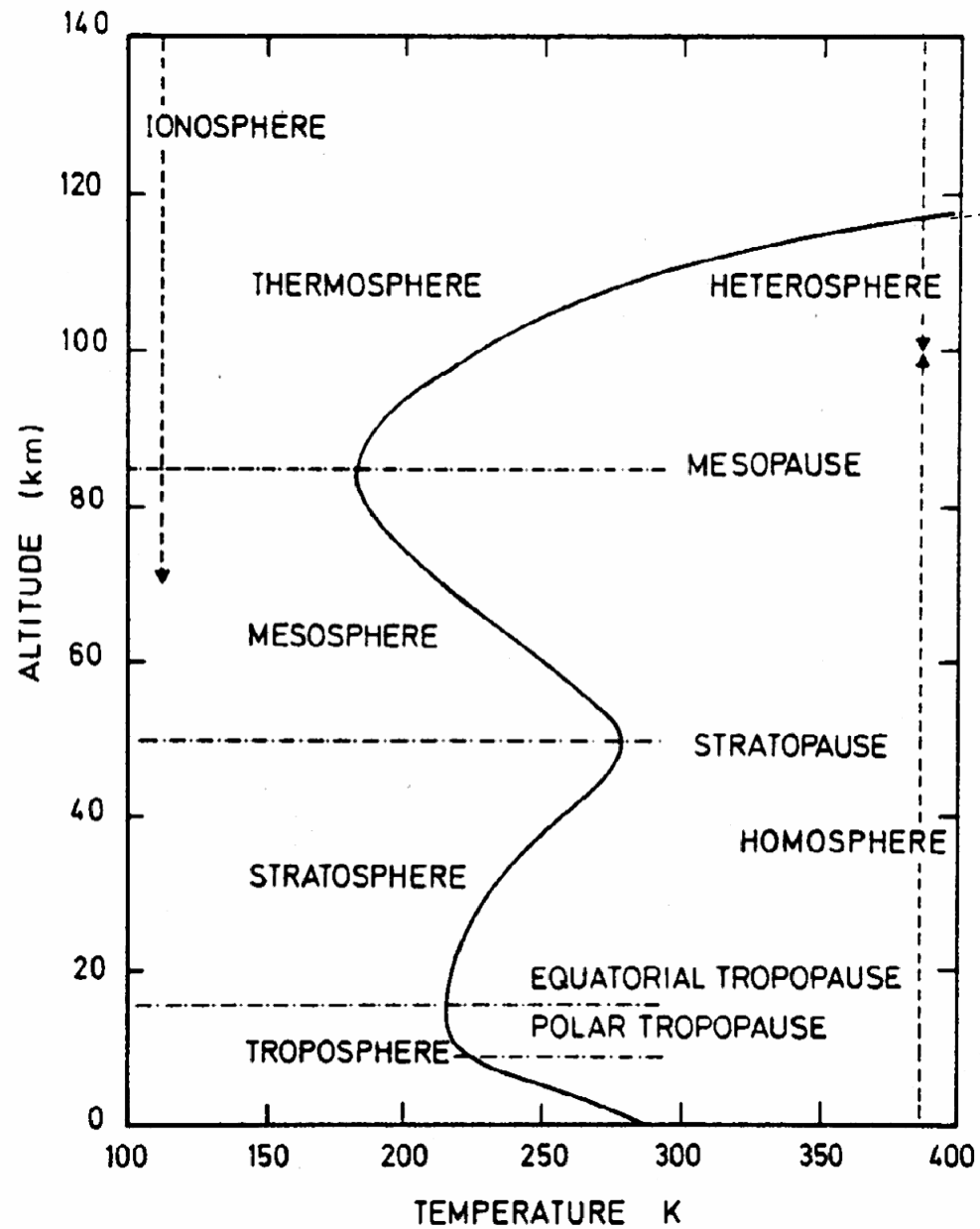
$$N(^4S) + NO \rightarrow N_2 + O$$

[a "canabalistic" reaction]
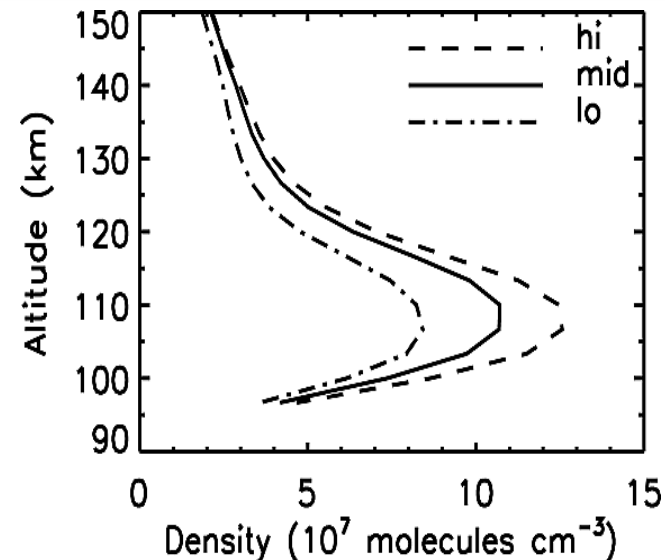
(*Barth et al.*, 2003)

Energetics

Thermal structure

Thermodynamic equation

$$\frac{\partial T}{\partial t} = -(\Gamma_d + \frac{\partial T}{\partial z})w - \mathbf{v} \cdot \nabla T + \frac{Q}{c_p} \quad + \ldots$$

Heat advection
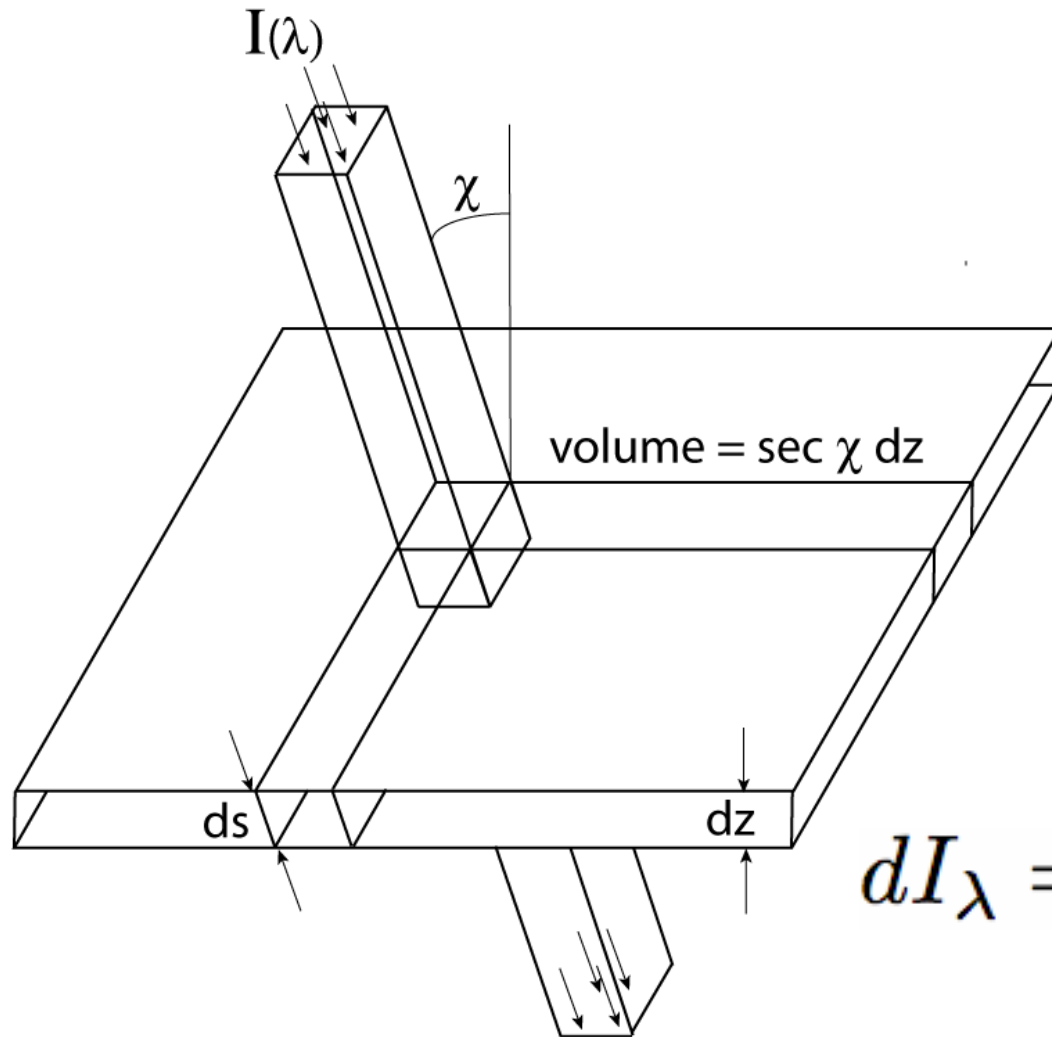
Adiabatic heating

Diabatic heating/cooling

Sources of diabatic heating/cooling

- Absorption of solar radiation and energetic particles (e.g. ozone)
- Chemical heating through exothermic reactions (A + B -> AB + Energy)
- Collisions between ions and neutrals (Joule heating)
- IR cooling (e.g. CO_2 and NO)
- Airglow

Absorption of solar radiation

$I(\lambda)$

χ

volume = sec χ dz

ds

dz

Beer-Lambert Law:

$$dI_\lambda = -I_\lambda \sigma_a(\lambda) n_a ds$$

For a plane-parallel atmosphere:

$$ds = dz\, sec\chi$$

Integrating:

$$I(z) = I_0 exp\left(-sec\chi \int_z^\infty \sigma_a n(z')dz'\right)$$

The optical depth is defined as:

$$\tau_a(\lambda, z) = sec\chi \int_z^\infty \sigma_a n(z')dz'$$

Recall: $n(z) = n_0 \dfrac{T_0}{T} exp \left(- \displaystyle\int_0^z \dfrac{dz}{H} \right)$

const. T: $n(z) = n_0 e^{-(z-z_0)/H}$

Under the assumption we have one absorbing species, with fixed scale height:
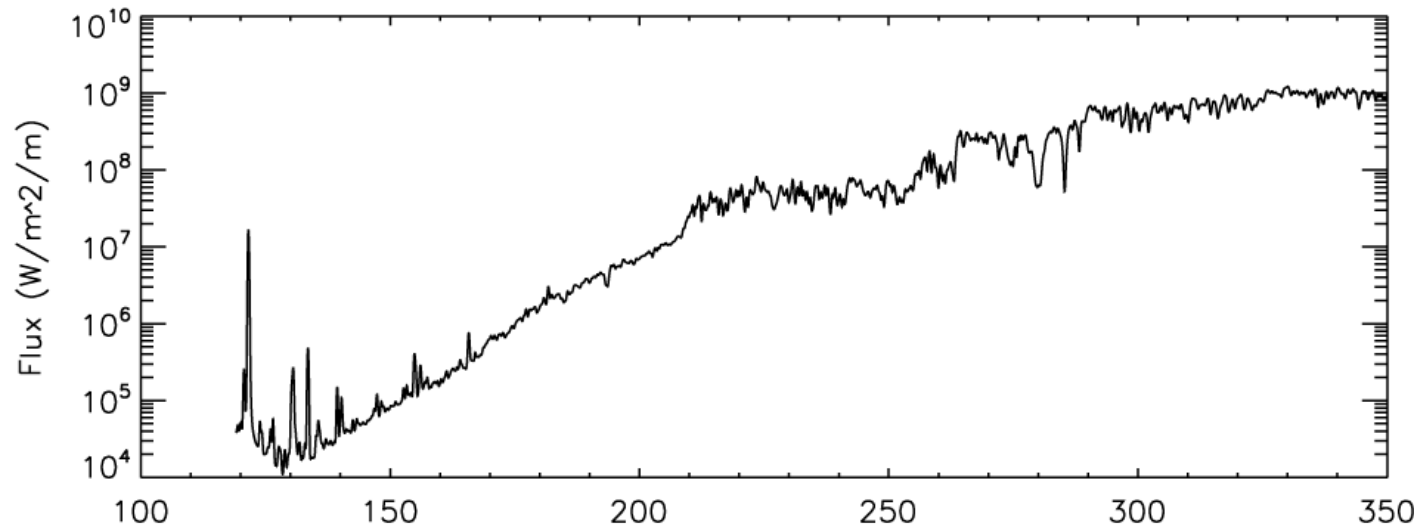
$$\tau = sec\chi \int_z^\infty \sigma_a n_0 e^{-z'/H} dz'$$

$$\tau = sec\chi \sigma_a n(z) H$$
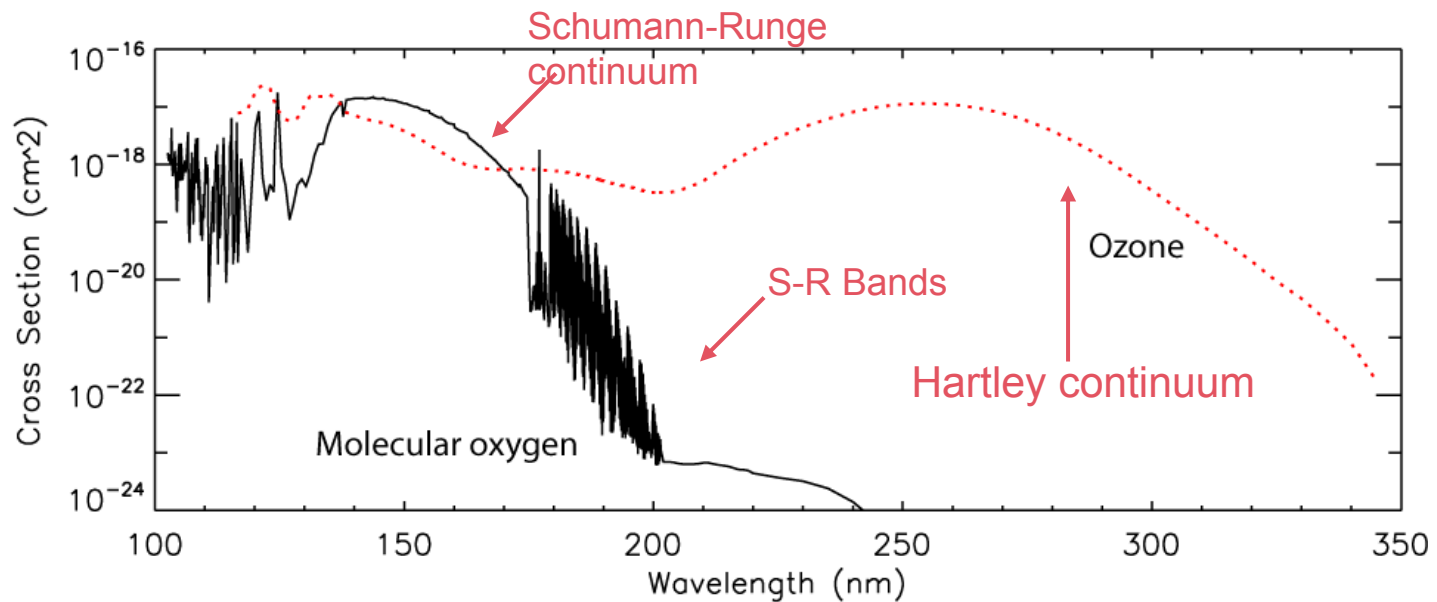
$$I(z) = I_\infty e^{-sec\chi \sigma_a n(z) H}$$

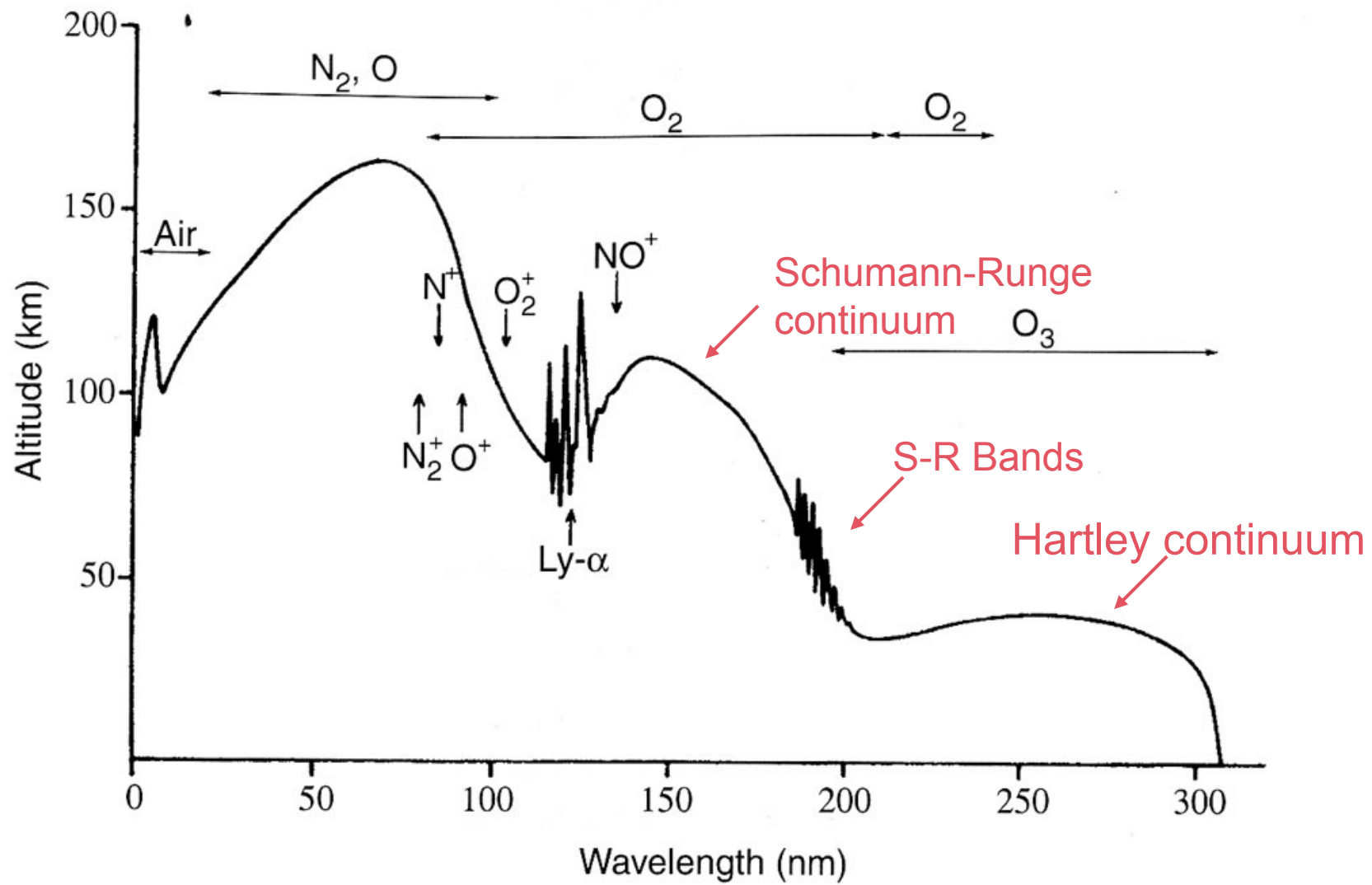Note: the height at which the exoatmospheric flux decrease by a factor of 1/e corresponds to $\tau(z)=1$

In practice there are multiple (overlapping) absorbers:

I_λ

$\sigma_{O2/O3}$

PRACTICUM: calculate $\tau=1$ height vs. λ

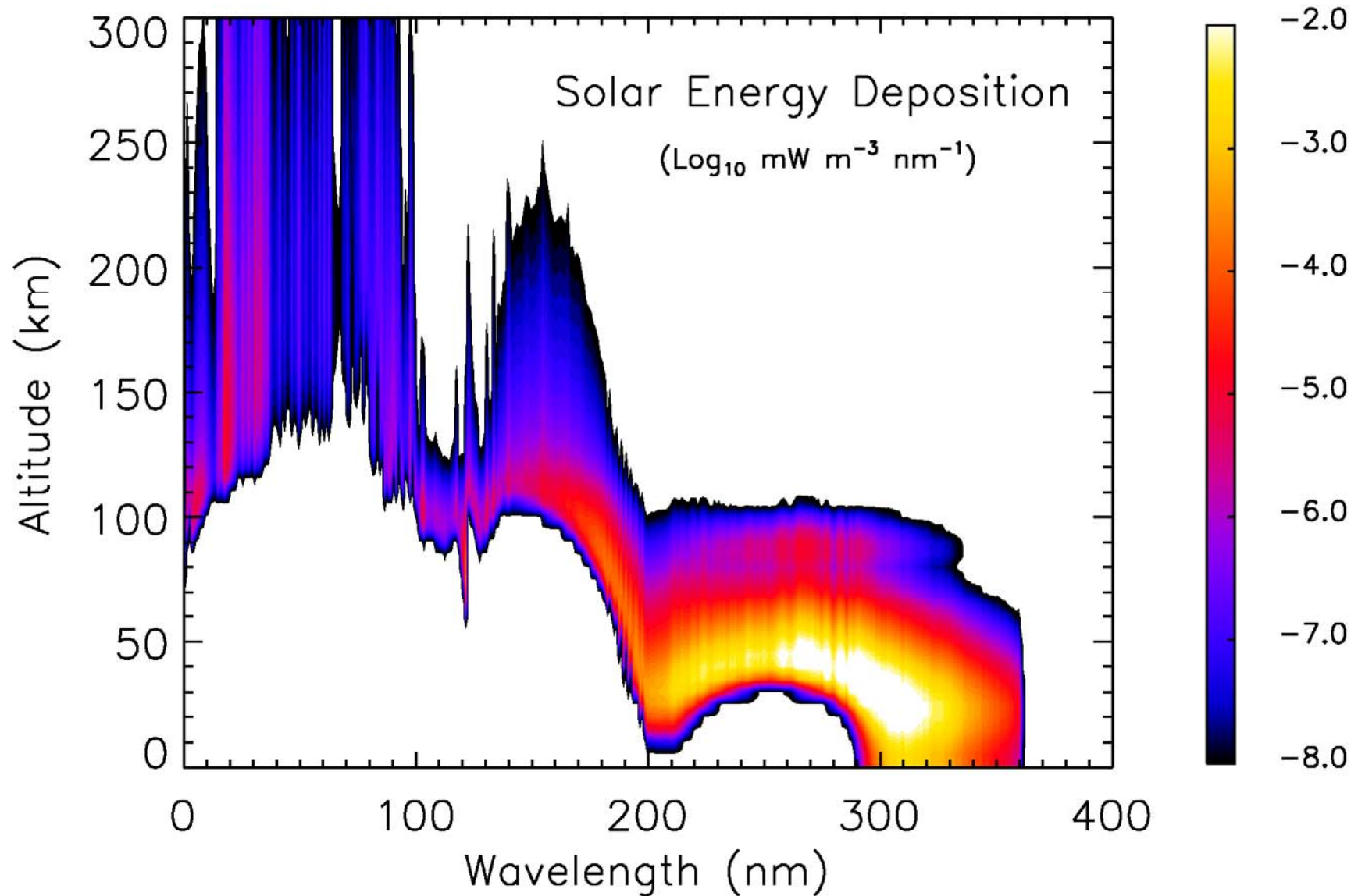# Energy deposition rate due to solar absorption

If we assume all absorbed radiation is thermalized at the location it is absorbed, then the energy deposition rate is the divergence of the vertical component of the total flux (spectral flux integrated over all wavelengths):

$$Q = \frac{\partial F}{\partial z}$$
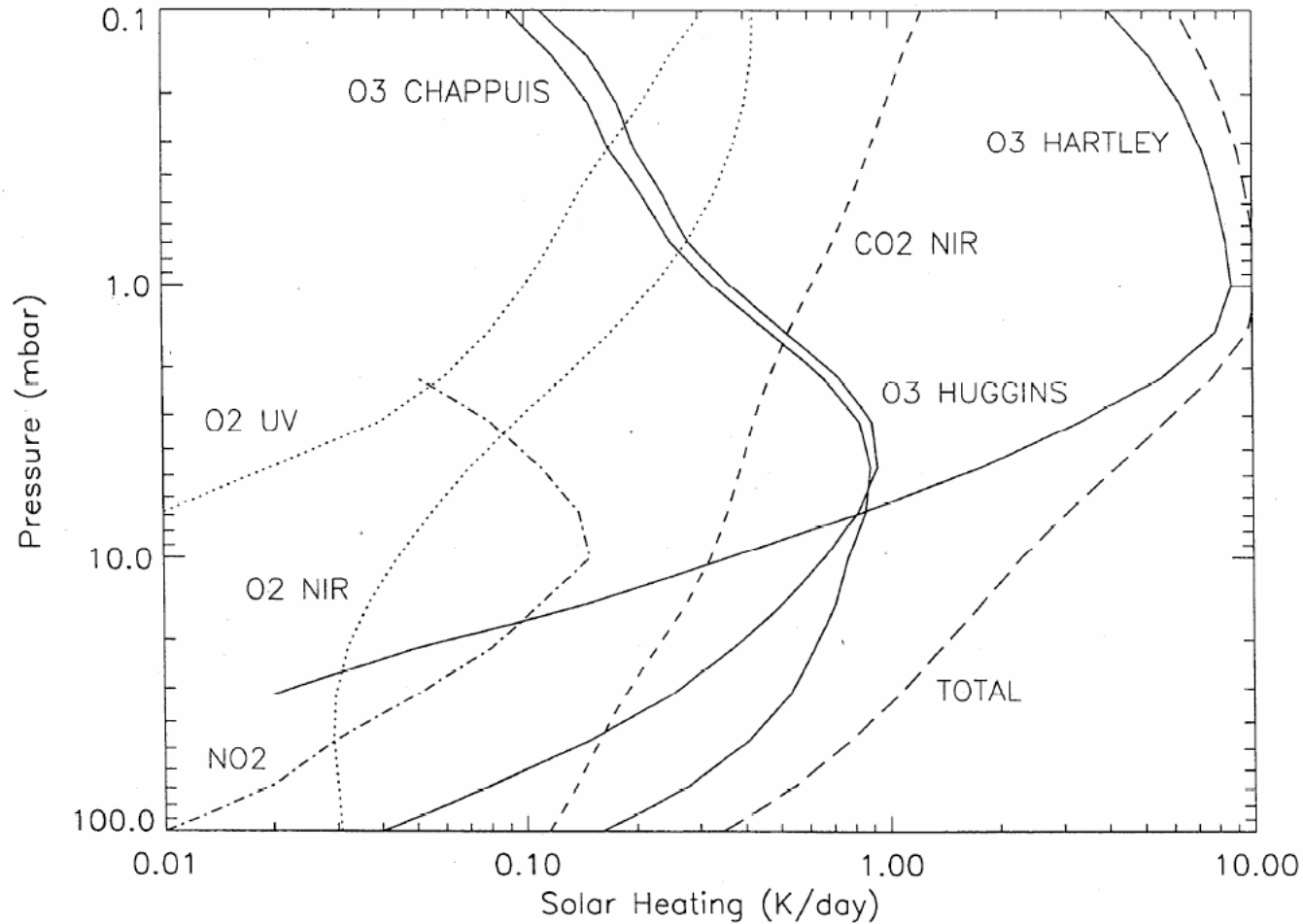
The heating rate is then:

$$\frac{\partial T}{\partial t} = \frac{1}{\rho c_p} \frac{\partial F}{\partial z}$$

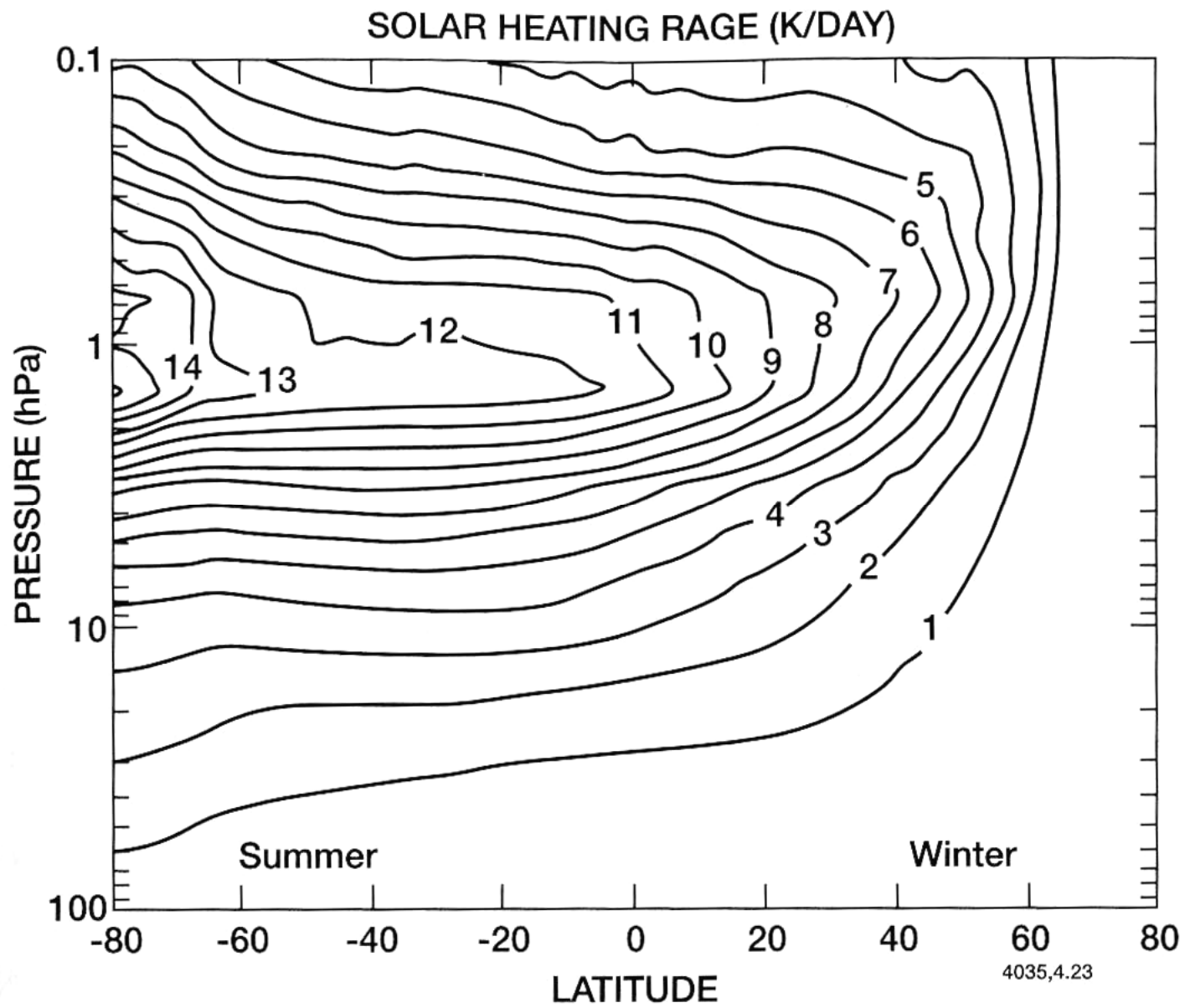# Solar UV Energy Deposition

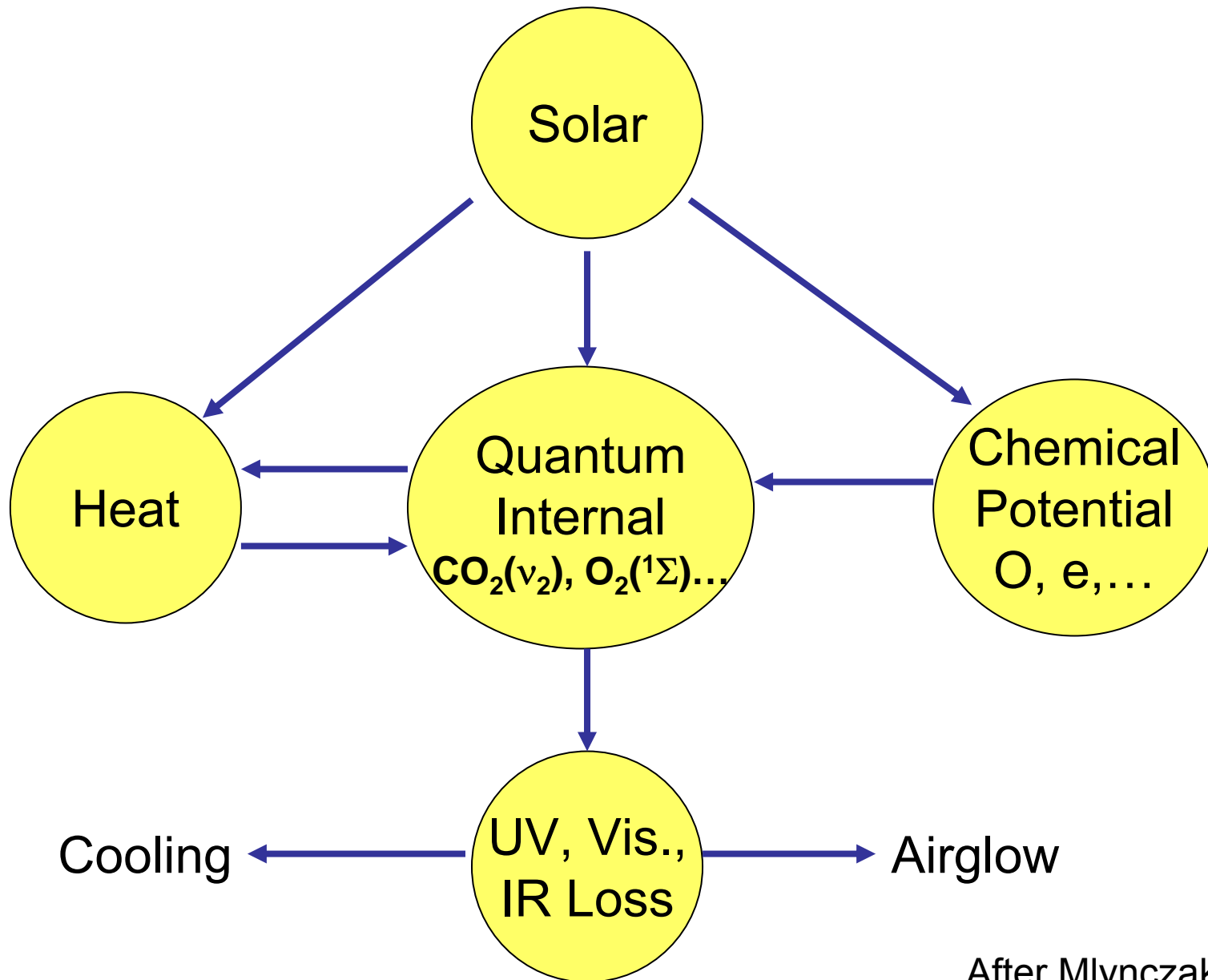Courtesy Stan Solomon

Stratospheric heating

Mertens et al., 1999
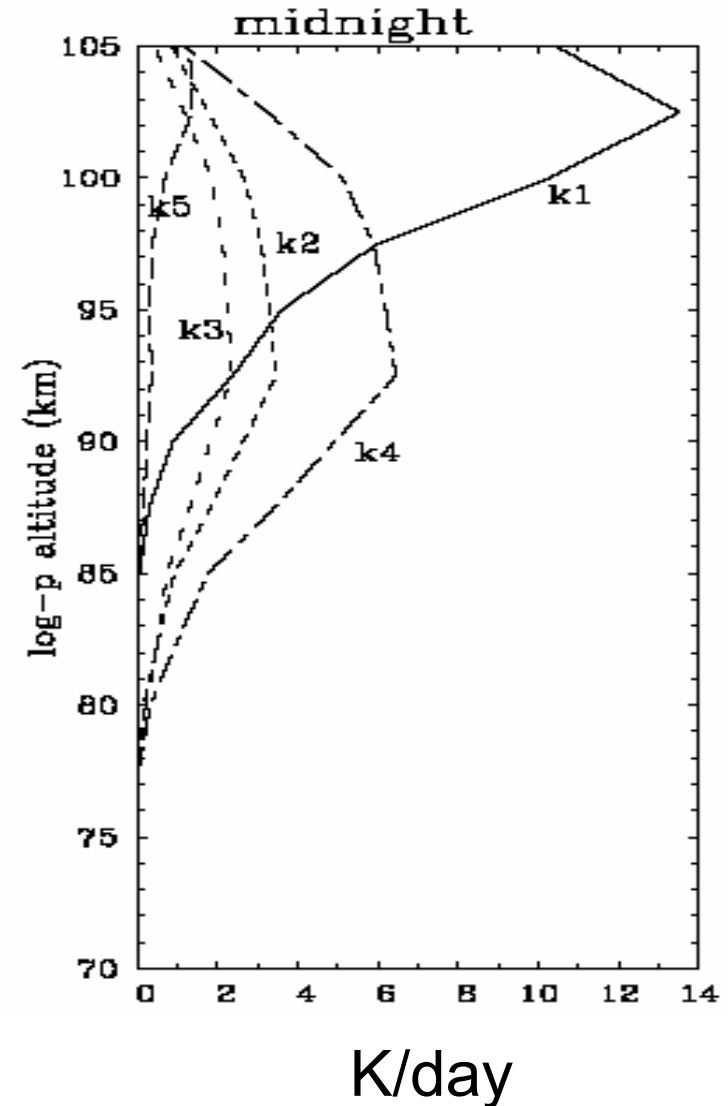
Absorbed energy is thermalized locally

SOLAR HEATING RAGE (K/DAY)

Not all absorbed radiation is directly thermalized

After Mlynczak et al.

Chemical heating through exothermic reactions

$H + O_3 \rightarrow OH + O_2$ (k4)
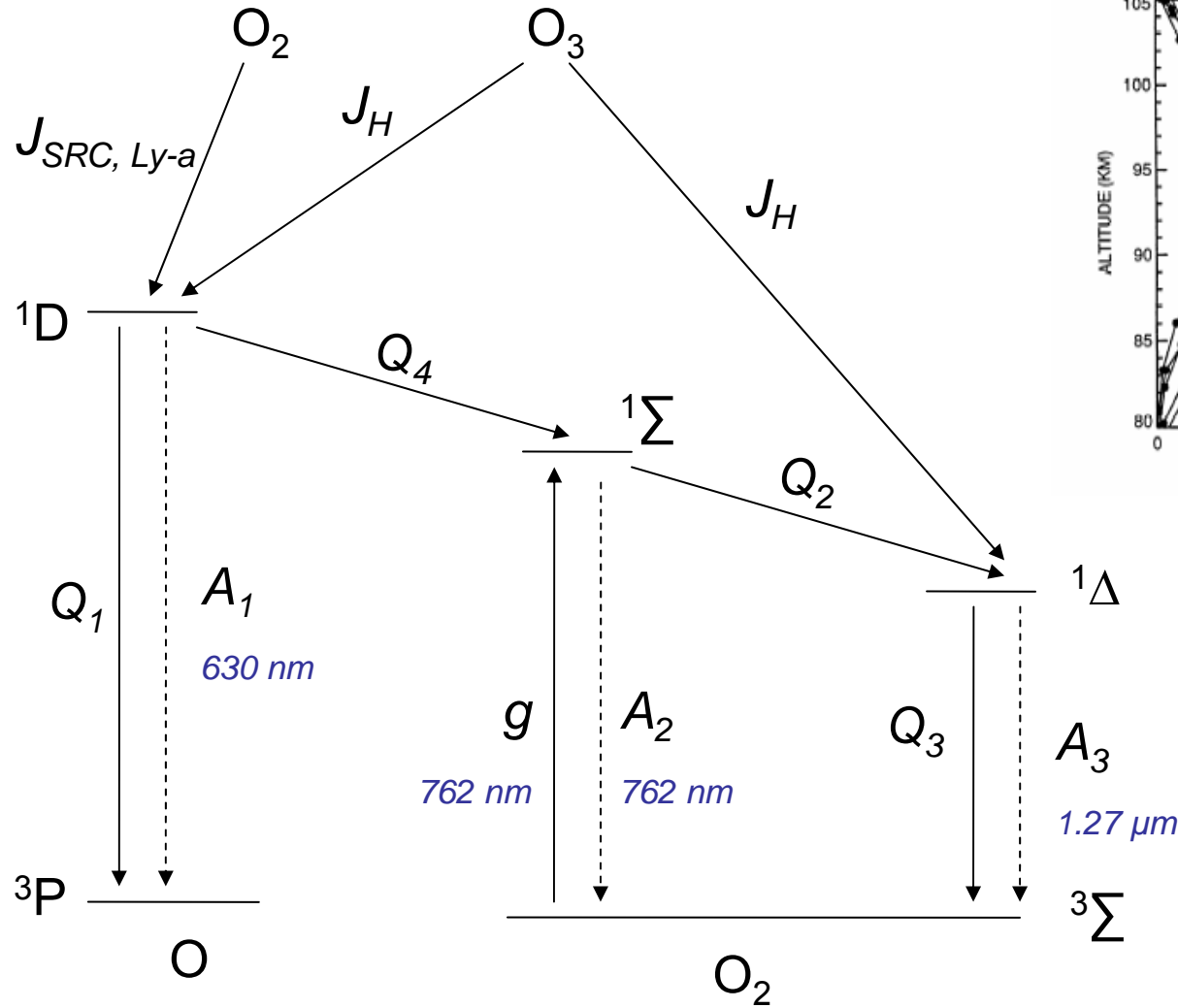
$O + O_2 + M \rightarrow O_3 + M$ (k2)

$O + O + M \rightarrow O_2 + M$ (k1)

$O + O_3 + \rightarrow O_2 + O_2$ (k3)

$OH + O \rightarrow H + O_2$ (k5)

$HO_2 + O \rightarrow OH + O_2$ (k6)

$H + O_2 + M \rightarrow HO_2 + M$ (k7)

midnight

K/day

Global mean chemical heating rates
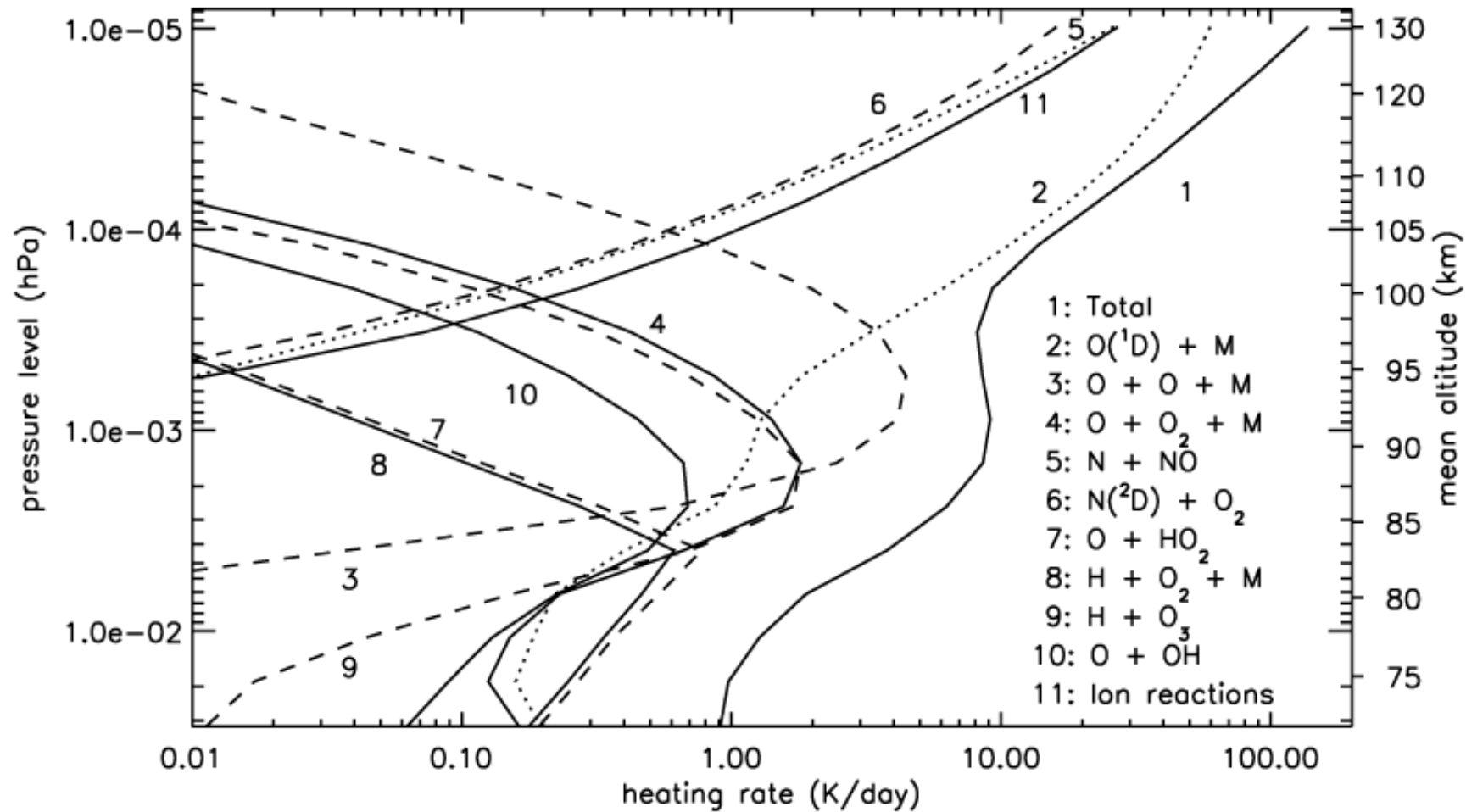
MLT Global average heating rates
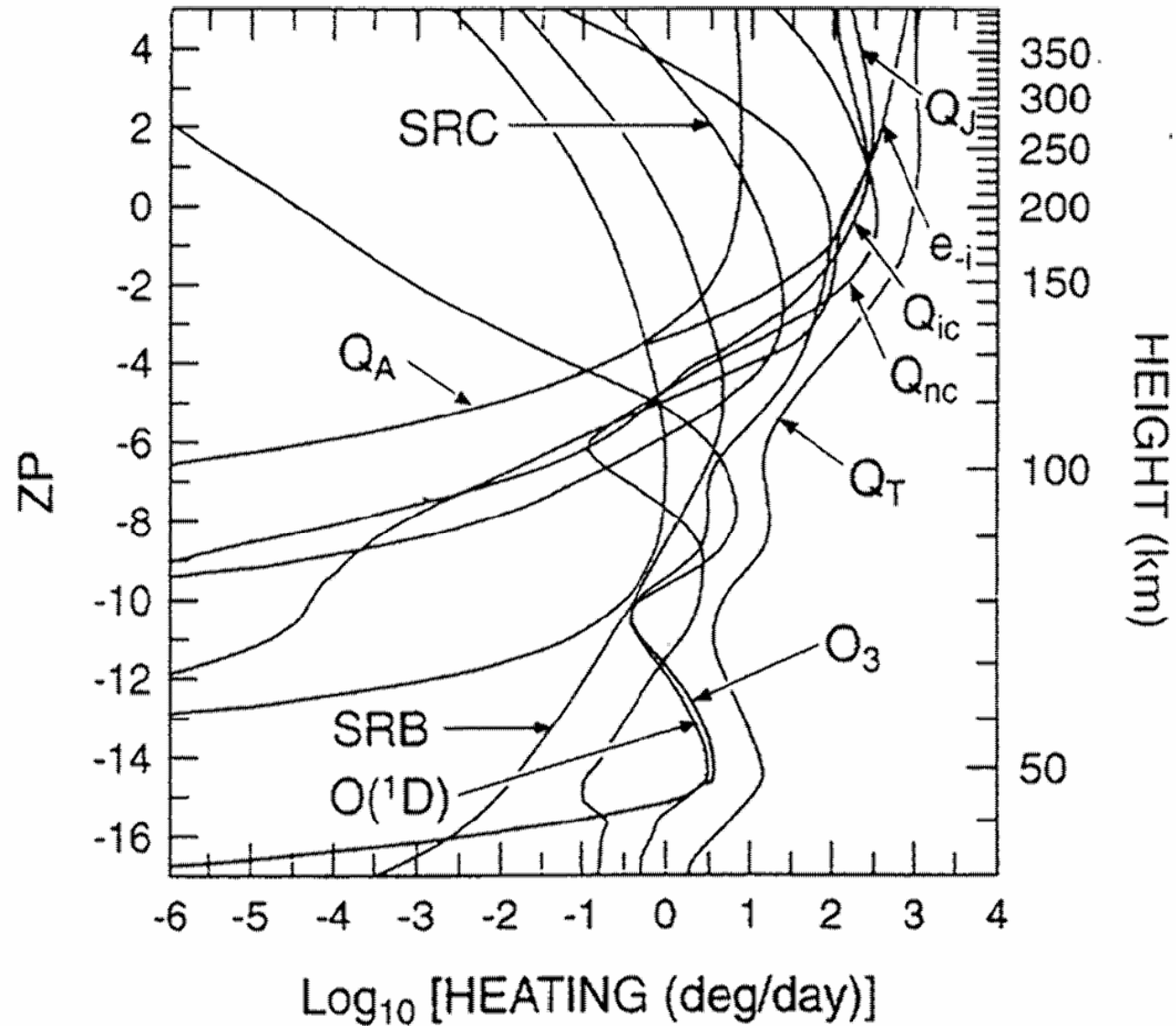
From [Roble, 1995]

Airglow

O_2 ($^1\Sigma$) emission

Burrage et al. [1994]

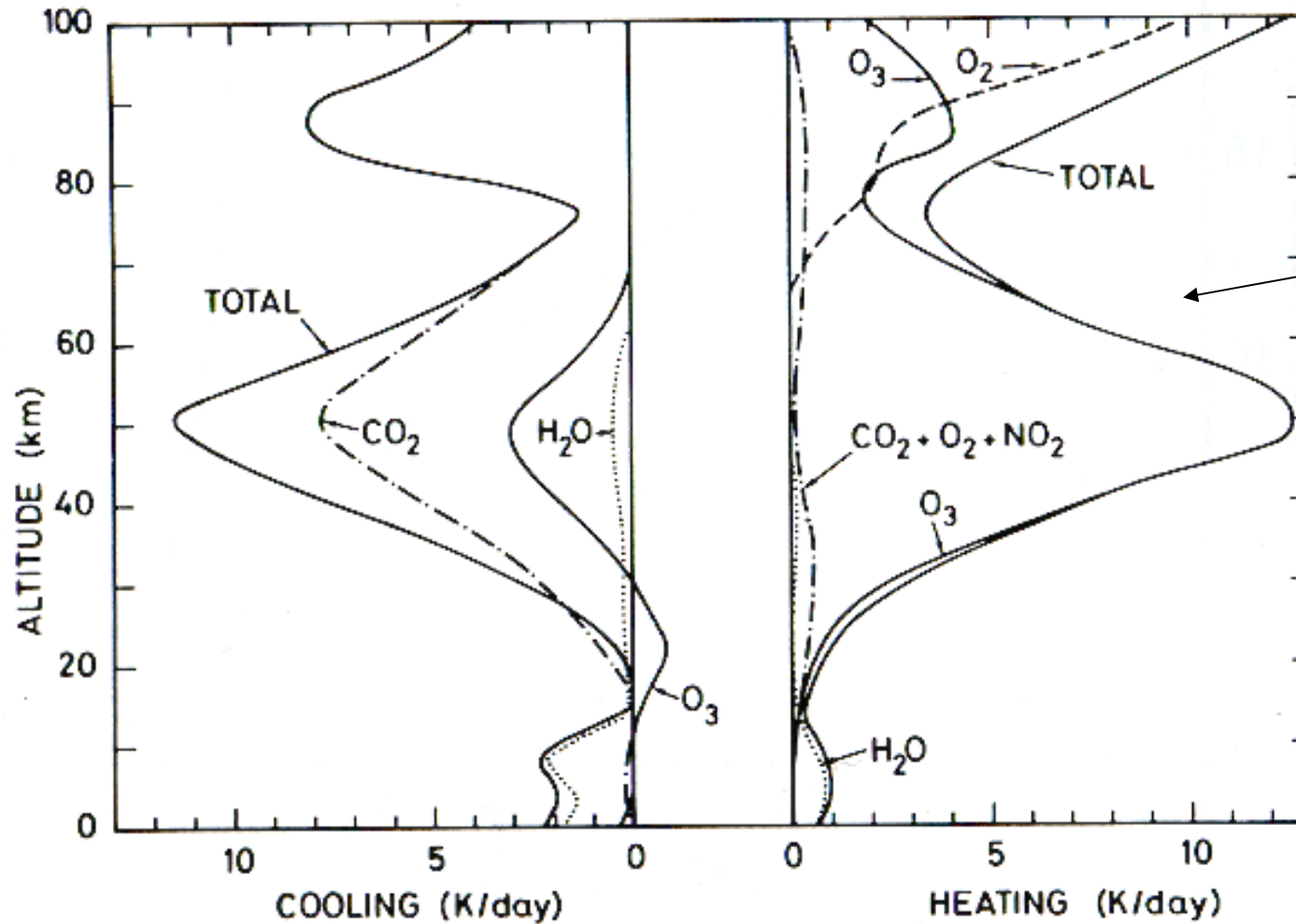After Mlynczak et al. [1993]
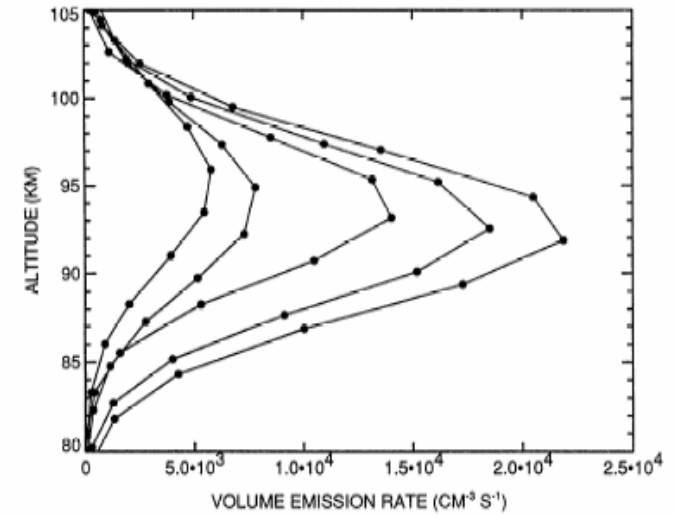
Joule Heating (K/day) due to ion/neutral collisions
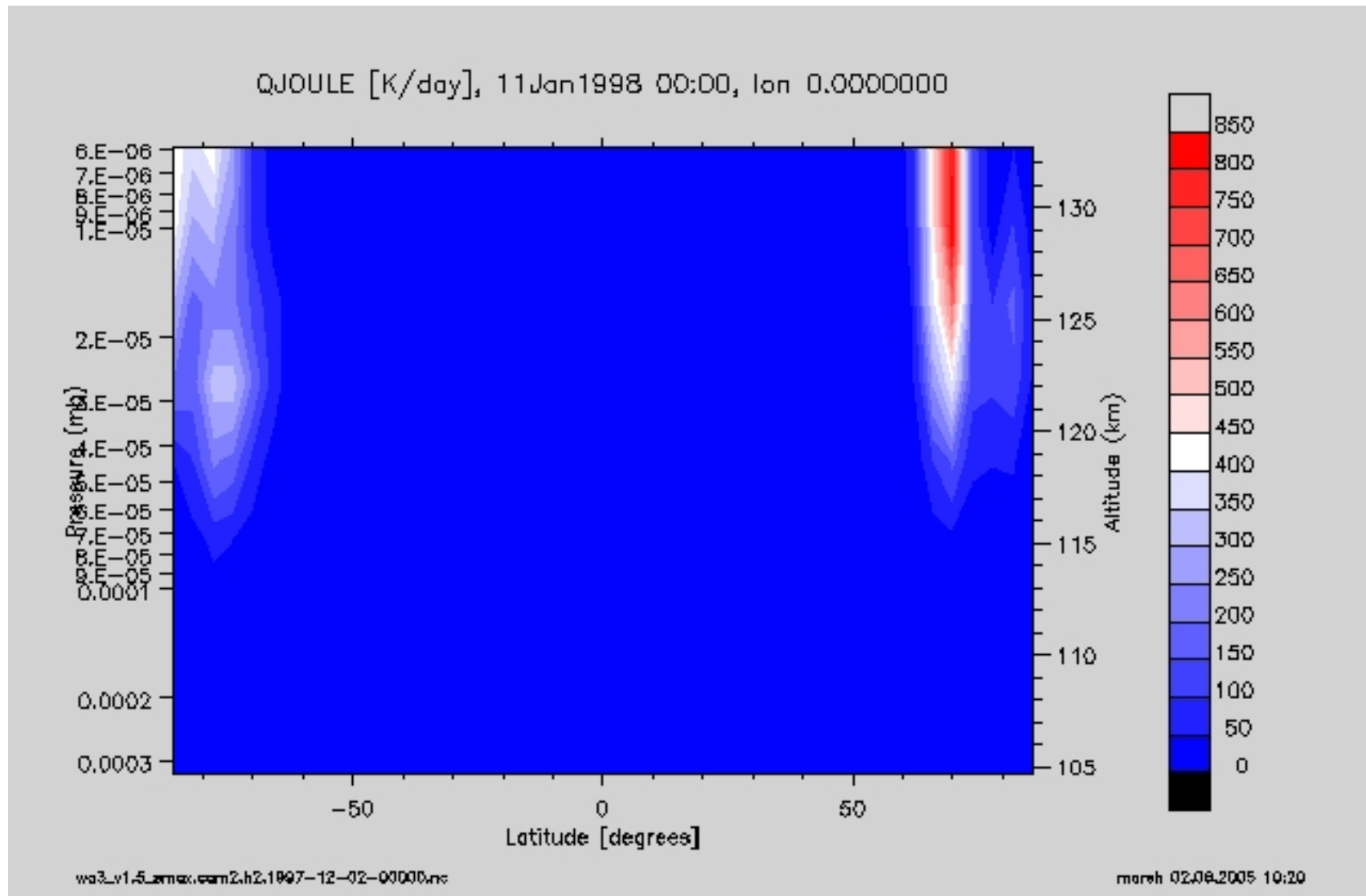
Heating from collisions between ions and neutrals

Heating in the middle atmosphere must be balanced by cooling
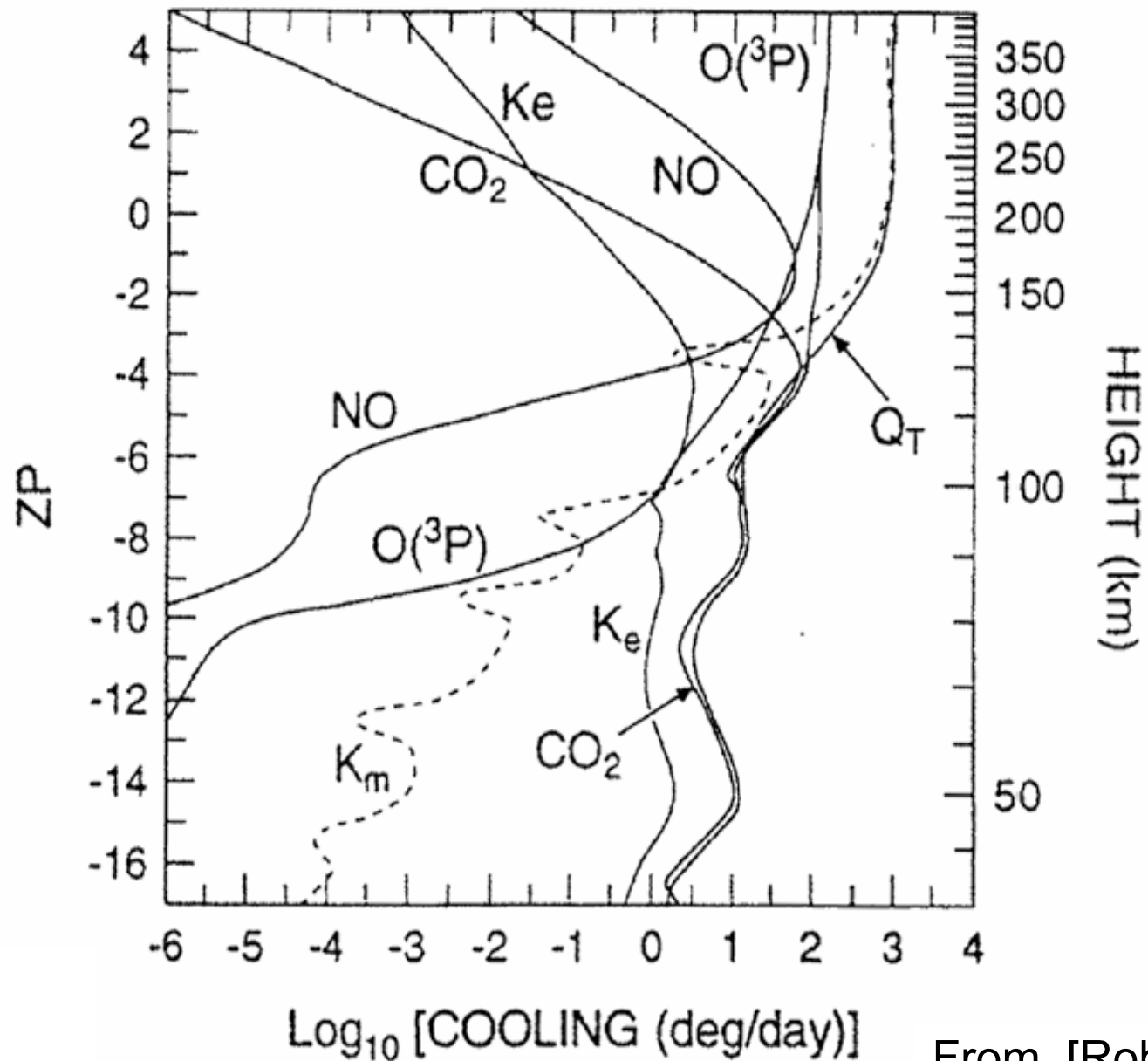

Practicum: calculate this curve

London (1980)

Radiative cooling

- IR atomic oxygen emission (63 µm) in the upper thermosphere

- Non-LTE IR emission of NO (5.3 µm) 120 to 200 km

- CO_2 15 µm (LTE and non-LTE) important below 120km

- IR emission by ozone and water vapor in the middle atmosphere

Global average cooling rates

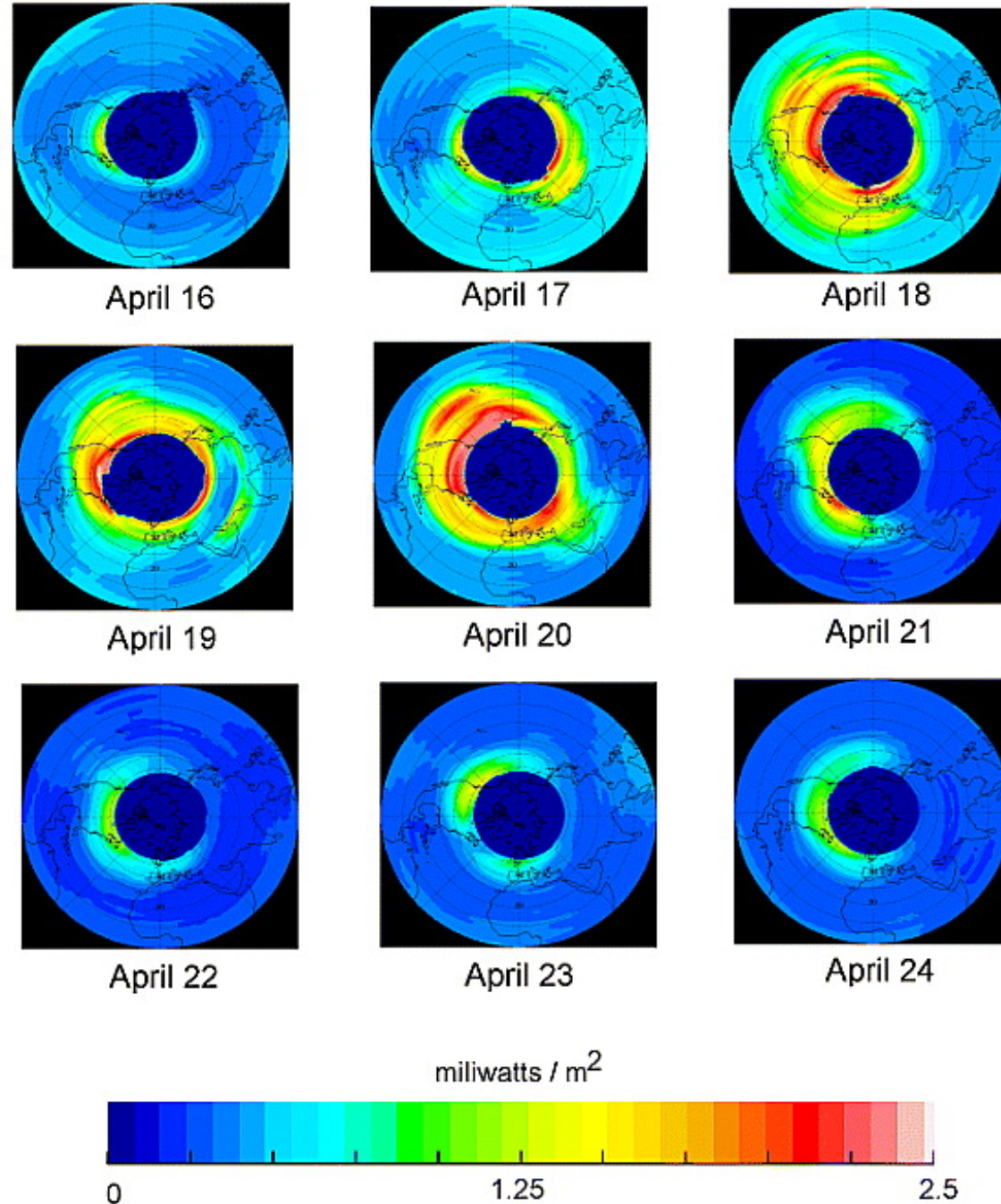From [Roble, 1995]

TIMED/SABER observations of NO cooling

## Response to the solar storm during April, 2002

NO 5.3 μm Radiated Flux (Northern Hemisphere)

April 16 · April 17 · April 18 · April 19 · April 20 · April 21 · April 22 · April 23 · April 24

miliwatts / m²

0   1.25   2.5

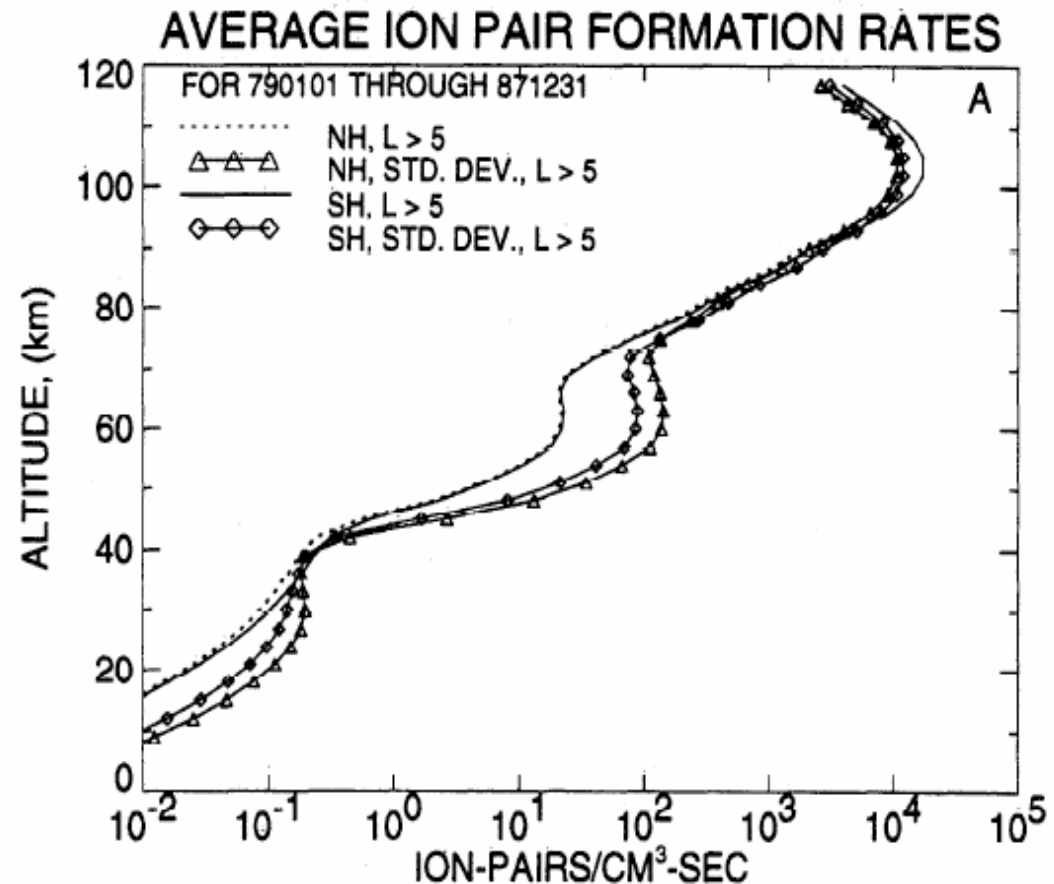# Additional forcing of the neutral atmosphere

- **Energetic particle precipitation**
  - Solar proton events (SPEs)
  - Medium energy electrons
  - Highly-relativistic electrons (HREs) >1MeV
- **Galactic cosmic rays**
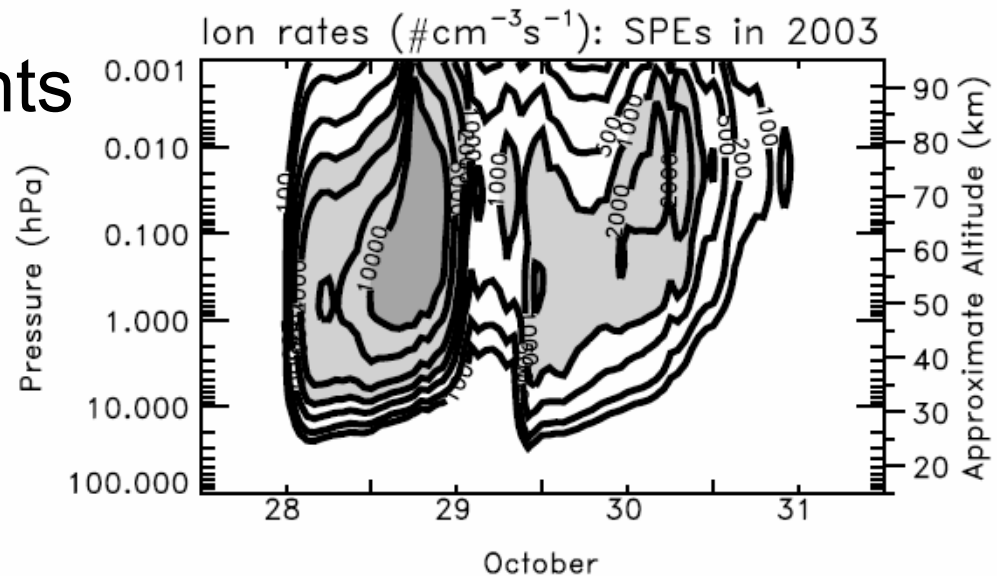
Jackman et al., 2005

Energetic Electron Precipitation

- **Thermosphere**
  - <30 keV
- **Mesosphere**
  - 30-300 keV
- **Stratosphere**
  - >300 keV

AVERAGE ION PAIR FORMATION RATES

Callis et al., 1998

The End