AQ Modeling Fundamentals: photochemistry

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WMO GURME Training Course on
Air Quality Modeling for Latin American Cities Project
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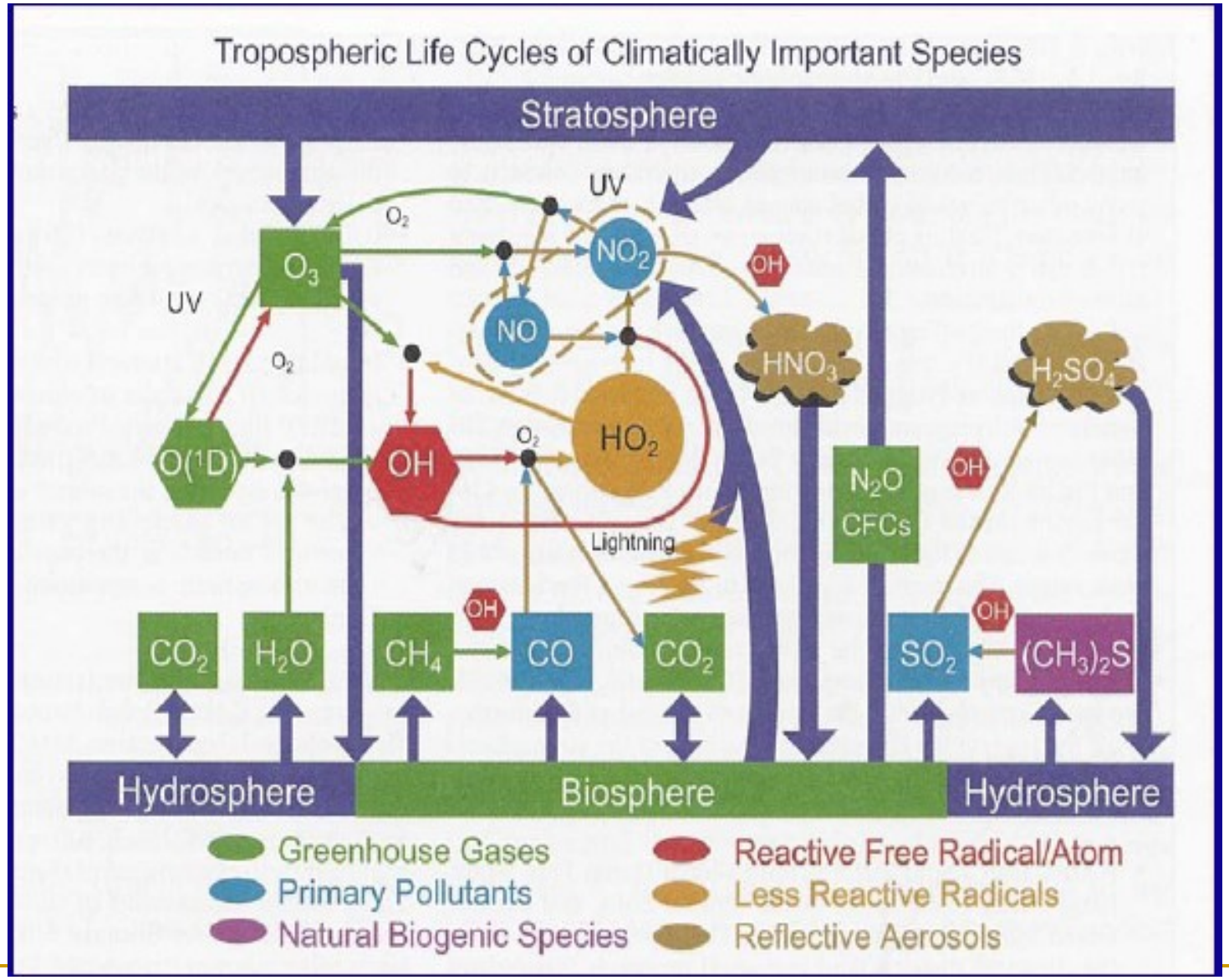
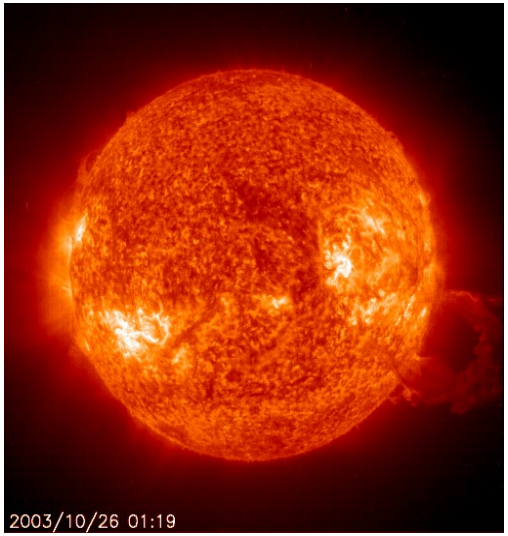
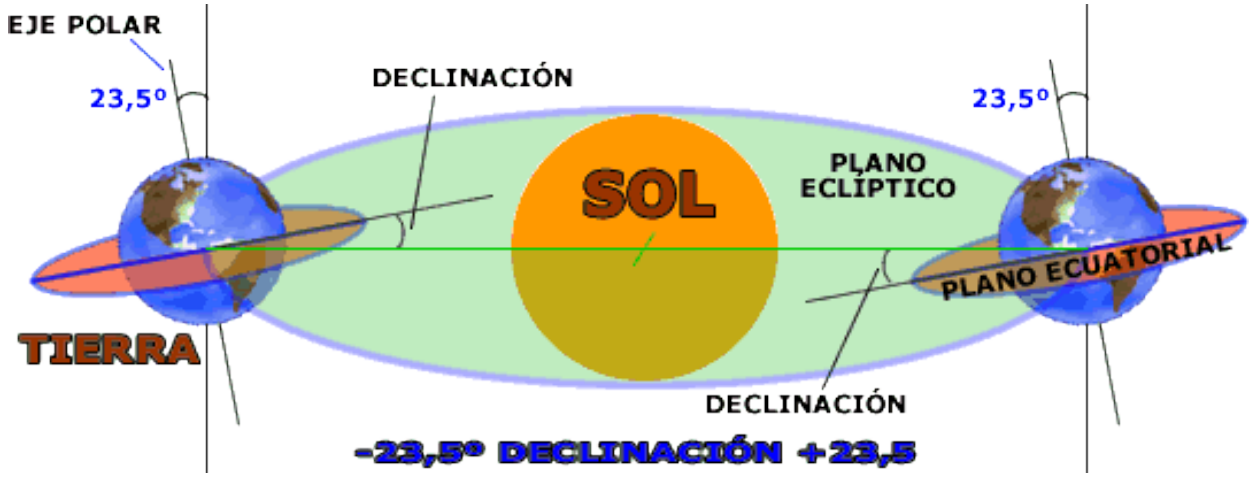

Tropospheric Life Cycles of Climatically Important Species
Stratosphere
UV
O_2
O_3
NO_2
OH
UV
NO
HNO_3
H_2SO_4
O_2
$O(^1D)$
OH
O_2
HO_2
N_2O
CFCs
OH
Lightning
OH
OH
CO_2
H_2O
CH_4
CO
CO_2
SO_2
$(CH_3)_2S$
Hydrosphere
Biosphere
Hydrosphere
Greenhouse Gases
Primary Pollutants
Natural Biogenic Species
Reactive Free Radical/Atom
Less Reactive Radicals
Reflective Aerosols

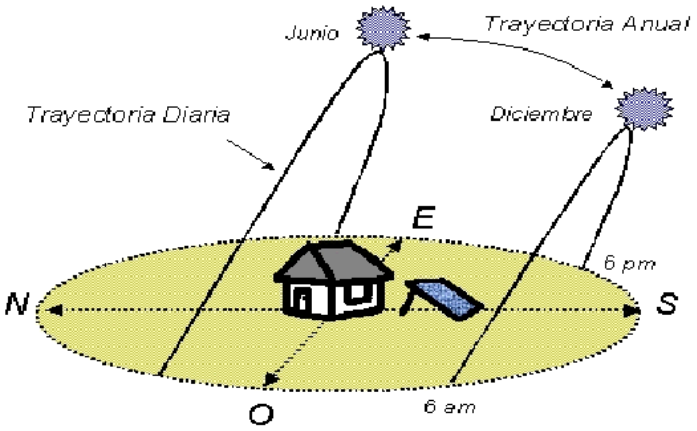
Solar radiation: energy source for the Earth



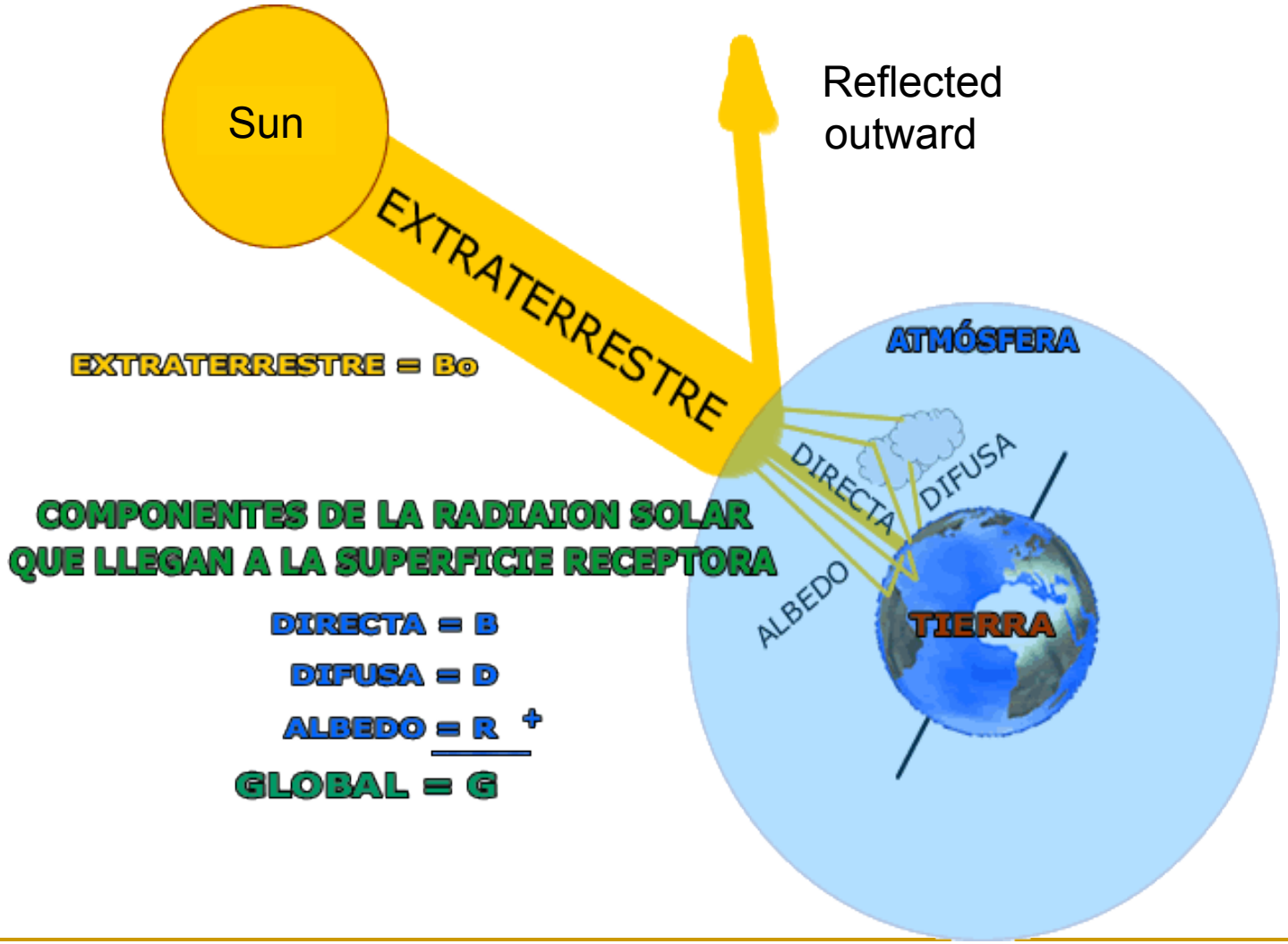
- Matter-to-energy conversion 4 Tg/s in the core
- Sun´s average temperature 5783 K
- Energy's Sun fraction entering to the Earth 4.5×10^{-15}
- Solar constant 1370 W/m^2 (solar energy flux) at the top of the Earth's atmosphere

Geometrical dependence of solar radiation

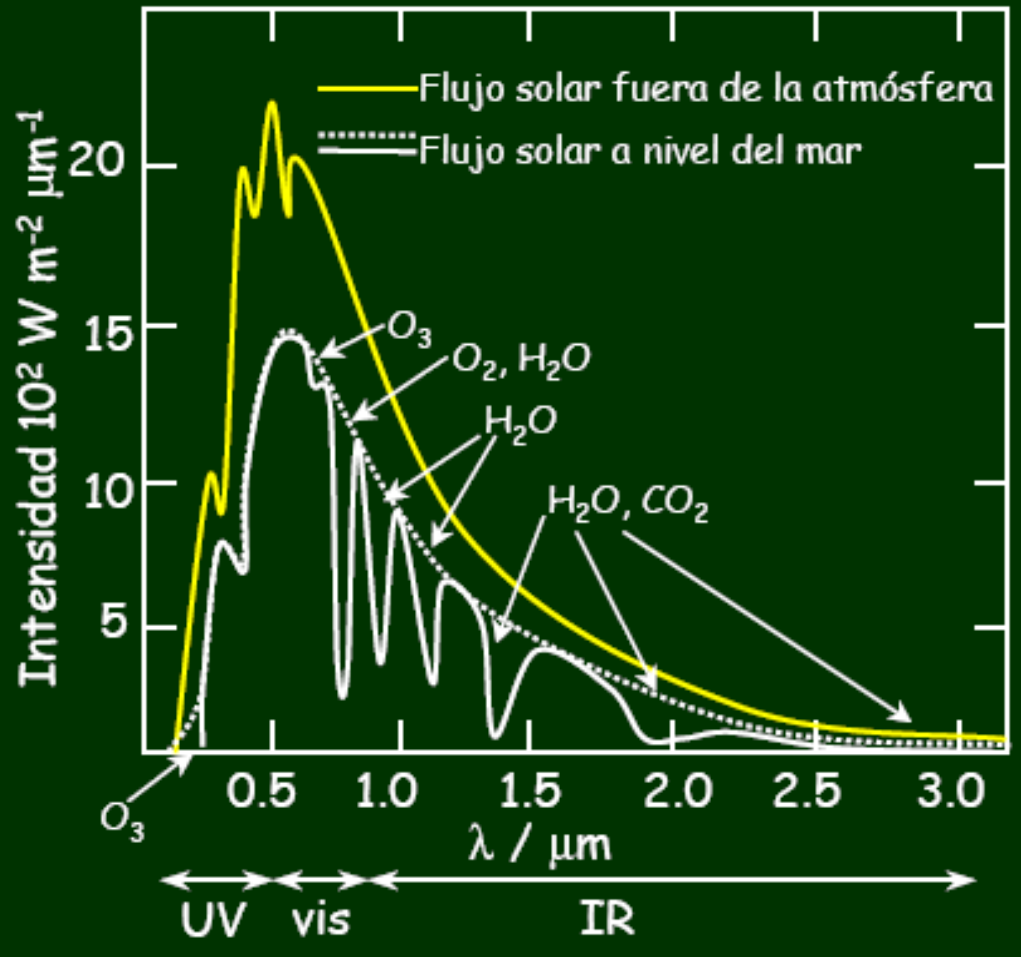


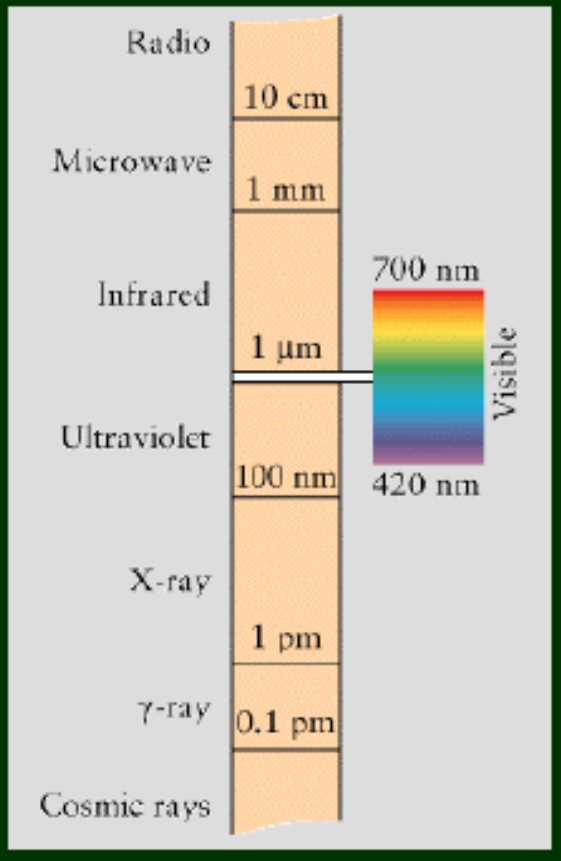


Radiative flux in the Atmosphere



Flujo solar actínico





Photochemical reactions in the Atmosphere

1. Available light

3. Quantum yield

$AB + h\nu \xrightarrow{j} A + B$

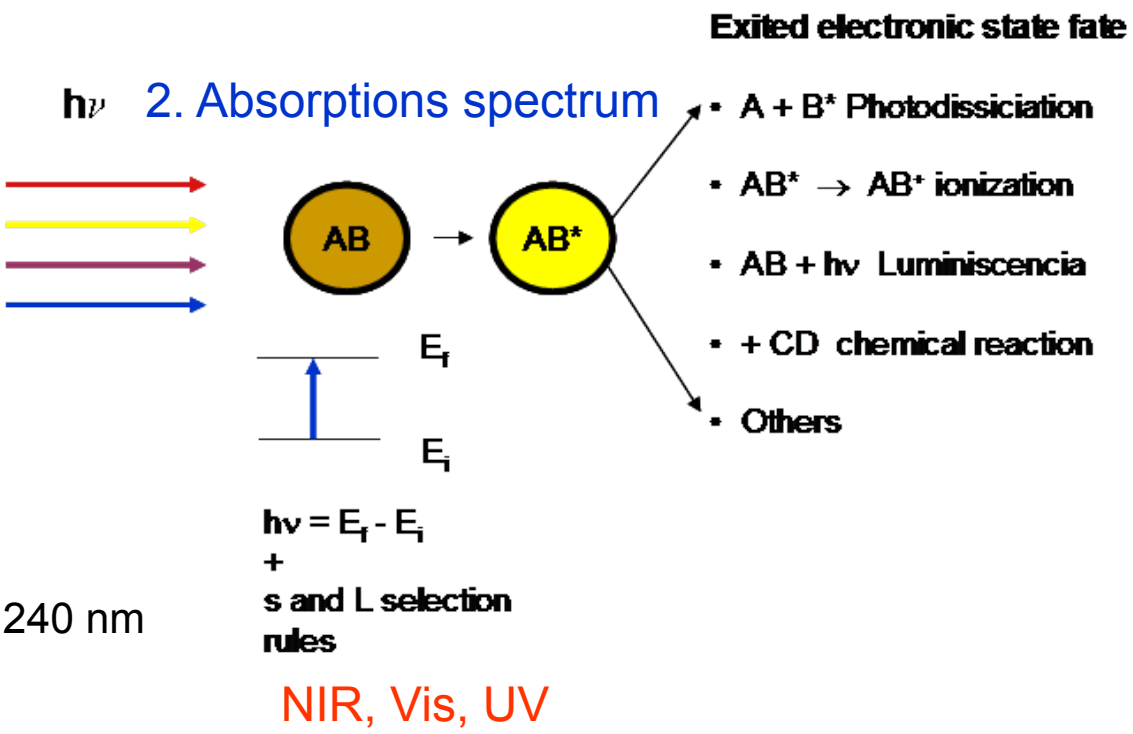
$h\nu = hc/\lambda$

ν light frequency
λ light wavelength
j photolysis rate

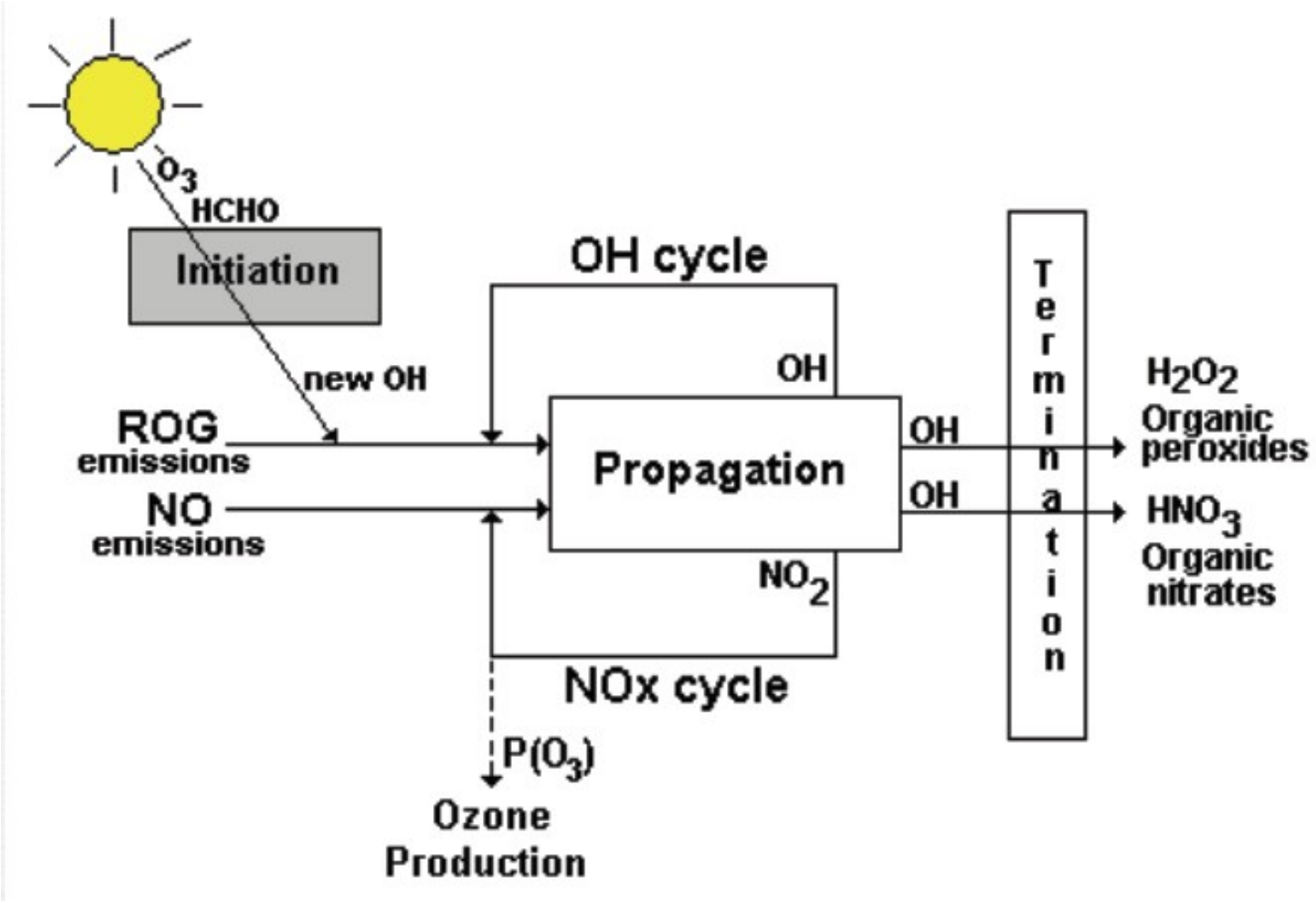
Examples:

Strong bond
O-O (O_2) 119 Kcal/mol; λ= 240 nm

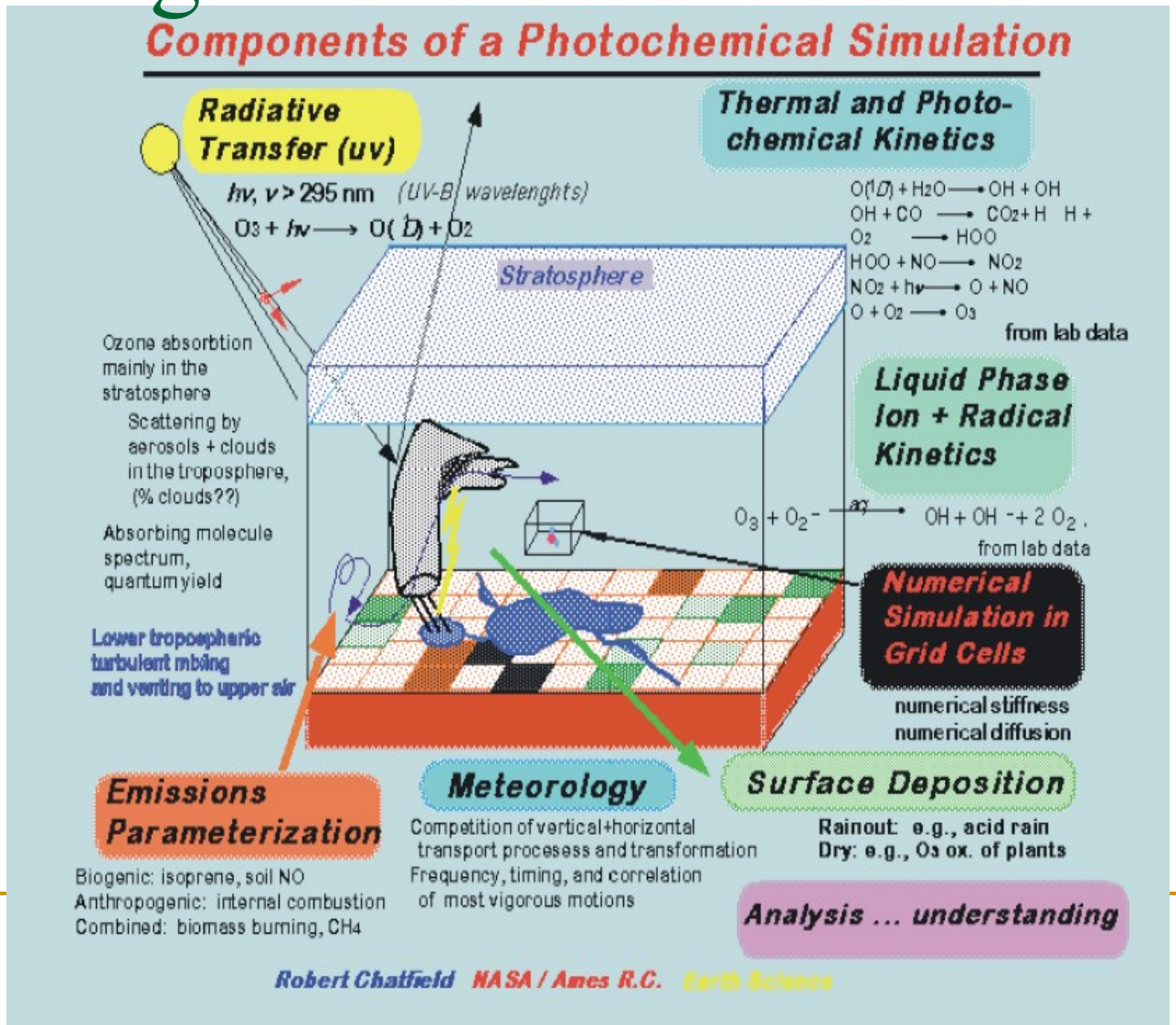
Weak bond
O-O_2 (O_3) 25 Kcal/mol; λ=1122 nm



Ozone formation mechanism



Tropospheric photochemistry modeling



Model's Formulation

$$\frac{\delta c_i}{\delta t} = -\left(\frac{\delta(uc_i)}{\delta x} + \frac{\delta(vc_i)}{\delta y} + \frac{\delta(wc_i)}{\delta z} \right)$$

Change in Concentration = Advection by Winds

$$+ \frac{\delta}{\delta x}\left(K_H \frac{\delta c_i}{\delta x} \right) + \frac{\delta}{\delta y}\left(K_H \frac{\delta c_i}{\delta y} \right) + \frac{\delta}{\delta z}\left(K_V \frac{\delta c_i}{\delta z} \right)$$

Turbulent Diffusion

$+$ Ri $+$ Si $+$ Li

Ri: Chemical Reaction

Si: Emissions

Li: Surface Removal/Deposition

Chemical Mechanism (SAPRC 99)

Reaction Number	Reactants	Products	K_{298} (ppm–n min–1)
1	NO2	NO + O	Photolysis
2	O + O2 + M	O3 + M	2.105E-05
3	O + O3	2O2	1.175E+01
4			3.676E-03
5			1.435E+04
6			2.690E+03
7			2.682E+01
8			5.202E-02
9			3.849E+04
10	NO + NO + O2	2NO2	7.104E-10
11	NO2 + NO3	N2O5	2.268E+03

SPRC99 Lumped Mechanism

217 chemical reactions

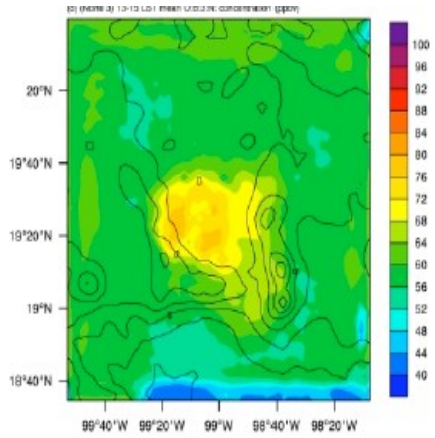
76 species (explicit and lumped)

Gas and aerosol phases

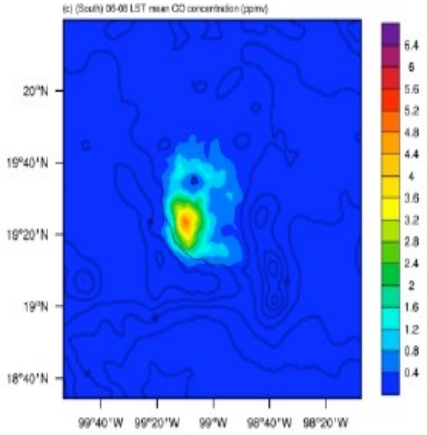
Air Quality Inputs

- Initial Conditions (ICs)
  - model spinup
  - role of ambient measurements
- Boundary Conditions (BCs)
  - Lateral boundaries (time, space varying)
  - Concentrations aloft (time, space invariant)
  - Based on clean air background, observations+clean air, and/or continental model simulations

Outputs from an Air quality Model



O_3



CO