Photolysis

Sasha Madronich
National Center for Atmospheric Research
Boulder, Colorado USA

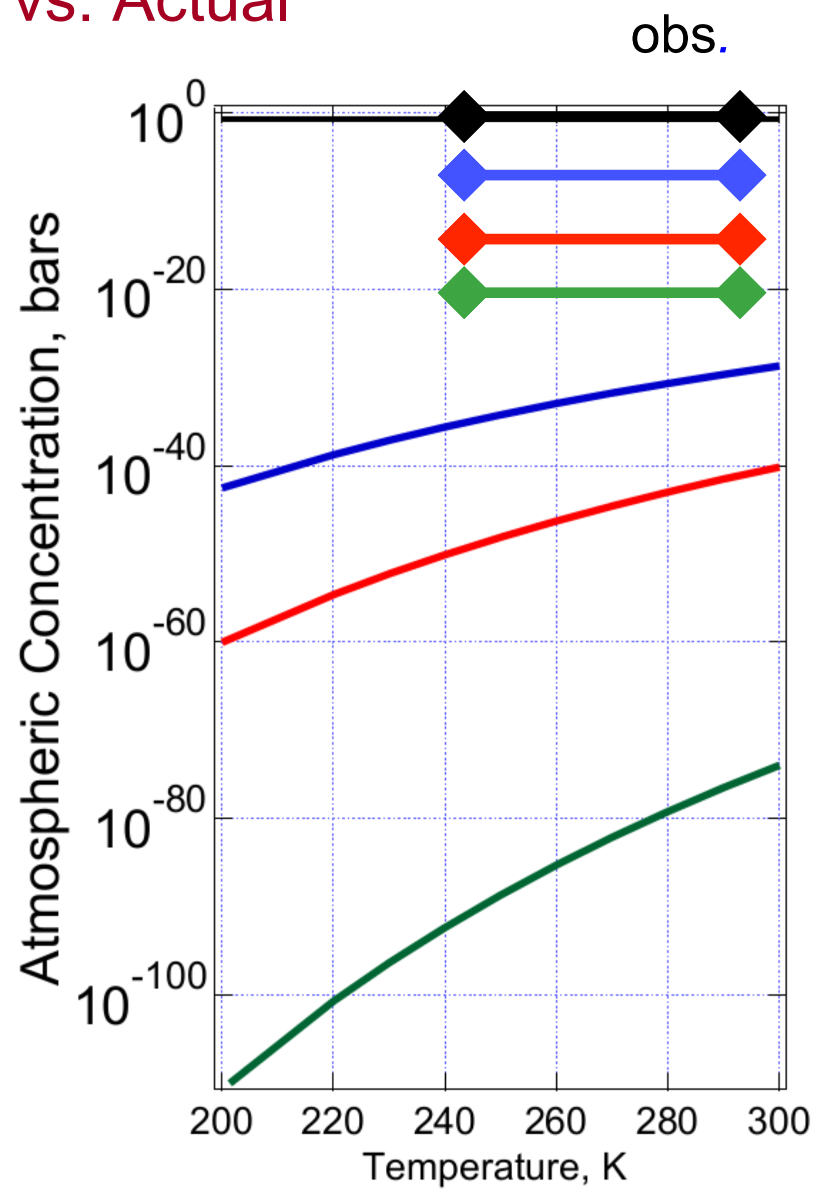
3 August 2015

NCAR

Atmospheric Oxygen Species

Thermodynamic vs. Actual

	ΔH_f kcal mol^{-1}
Normal O_2 molecules	0
Ozone, O_3	34.1
Ground state atoms, O	59.6
Excited atoms, O*	104.9



Photochemistry

Energy input from sunlight, e.g.

$O_2 + h\nu\ (\lambda < 242\ \text{nm}) \rightarrow O + O$

$O + O_2 \rightarrow O_3$ (ozone formation)

$O_3 + h\nu\ (\lambda < 330\ \text{nm}) \rightarrow O_2 + O^*$

$O^* + H_2O \rightarrow OH + OH$ (hydroxyl radical formation)

Some Important Photolysis Reactions

$O_2 + h\nu\ (\lambda < 240\ nm) \rightarrow O + O$	source of O_3 in stratosphere
$O_3 + h\nu\ (\lambda < 340\ nm) \rightarrow O_2 + O(^1D)$	source of OH in troposphere
$NO_2 + h\nu\ (\lambda < 420\ nm) \rightarrow NO + O(^3P)$	source of O_3 in troposphere
$CH_2O + h\nu\ (\lambda < 330\ nm) \rightarrow H + HCO$	source of HOx, everywhere
$H_2O_2 + h\nu\ (\lambda < 360\ nm) \rightarrow OH + OH$	source of OH in remote atm.
$HONO + h\nu\ (\lambda < 400\ nm) \rightarrow OH + NO$	source of radicals in urban atm.

Quantifying Photolysis Processes

Photolysis reaction: $AB + h\nu \rightarrow A + B$

Photolysis rates:

$$\left.\frac{d[AB]}{dt}\right|_{h\nu} = -J[AB]$$

$$\left.\frac{d[A]}{dt}\right|_{h\nu} = \left.\frac{d[B]}{dt}\right|_{h\nu} = +J[AB]$$

Photolysis frequency (s^{-1}) $J = \int_{\lambda} F(\lambda)\, \sigma(\lambda)\, \phi(\lambda)\, d\lambda$

(other names: photo-dissociation rate coefficient, J-value)

CALCULATION OF PHOTOLYSIS COEFFICIENTS

$$J\ (s^{-1}) = \int_\lambda F(\lambda)\,\sigma(\lambda)\,\phi(\lambda)\,d\lambda$$

$F(\lambda)$ = spectral actinic flux, quanta $cm^{-2}\ s^{-1}\ nm^{-1}$

$\propto$ probability of photon near molecule.

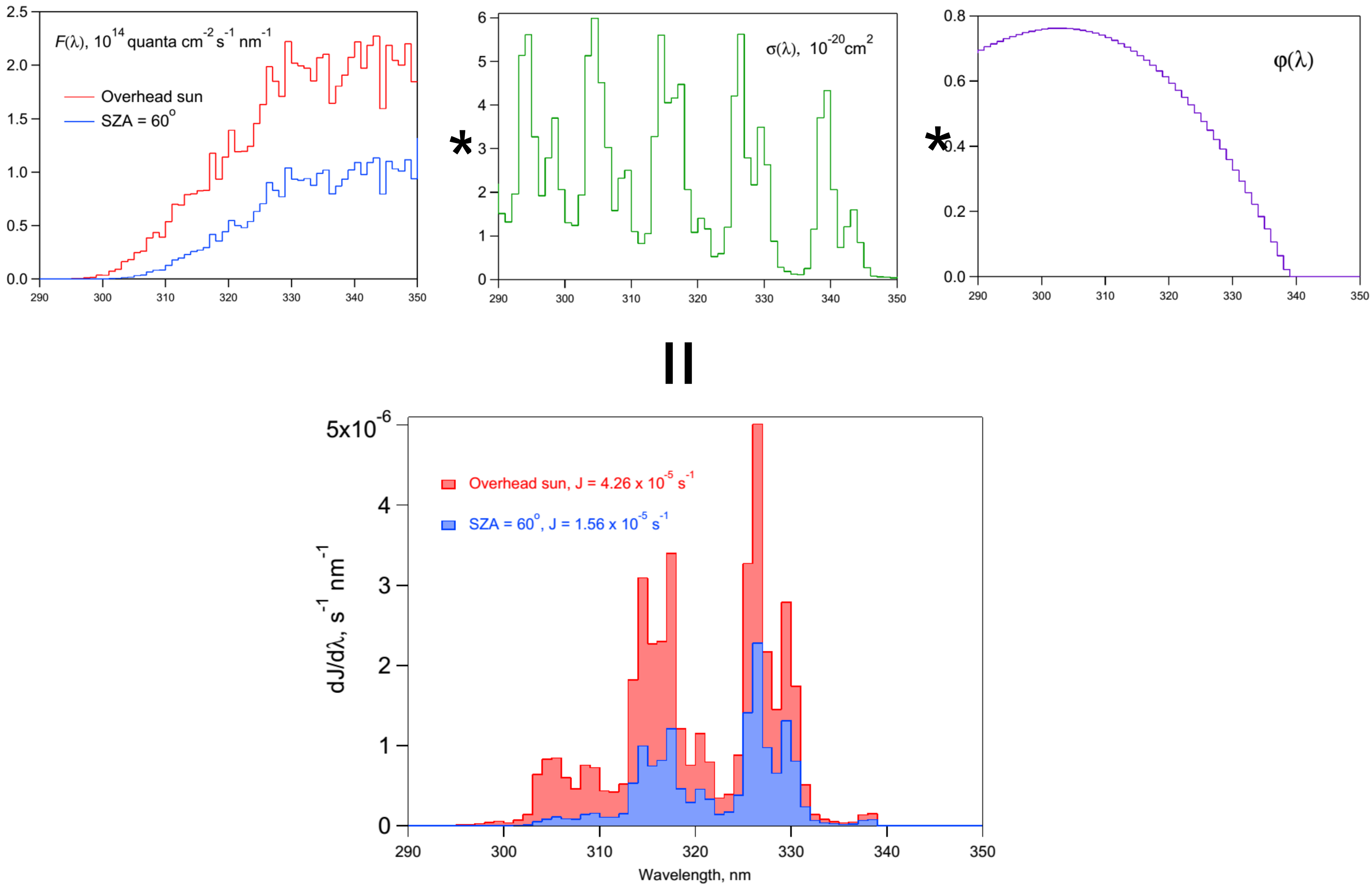
$\sigma(\lambda)$ = absorption cross section, $cm^2\ molec^{-1}$

$\propto$ probability that photon is absorbed.

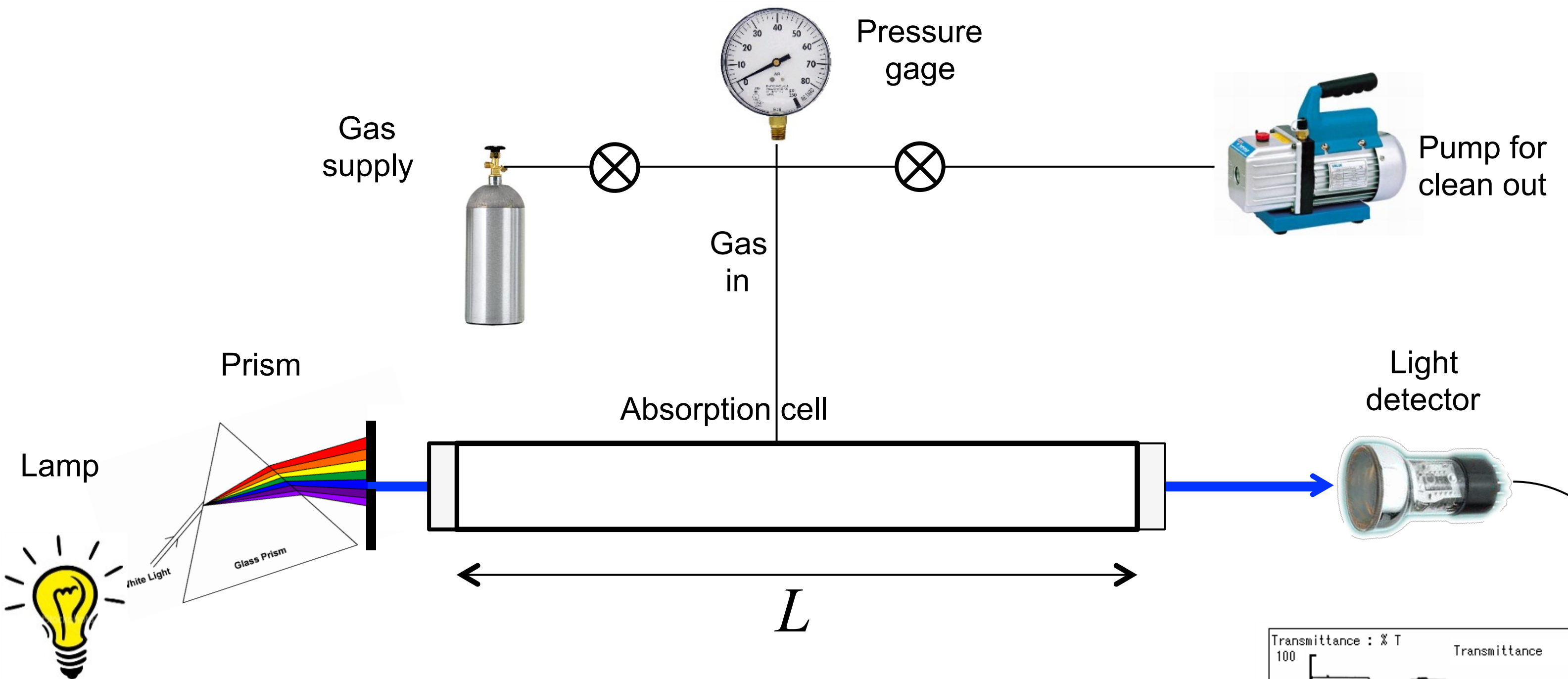
$\phi(\lambda)$ = photodissociation quantum yield, molec $quanta^{-1}$

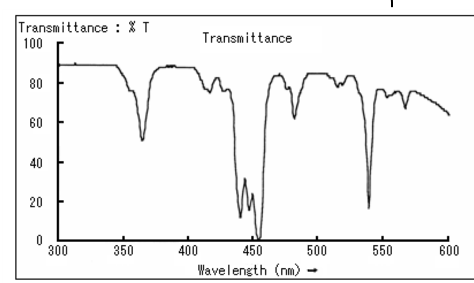
$\propto$ probability that absorbed photon causes dissociation.

Calculation of J for $CH_2O + h\nu \rightarrow CHO + H$



Measurement of Absorption Cross Section $\sigma(\lambda)$



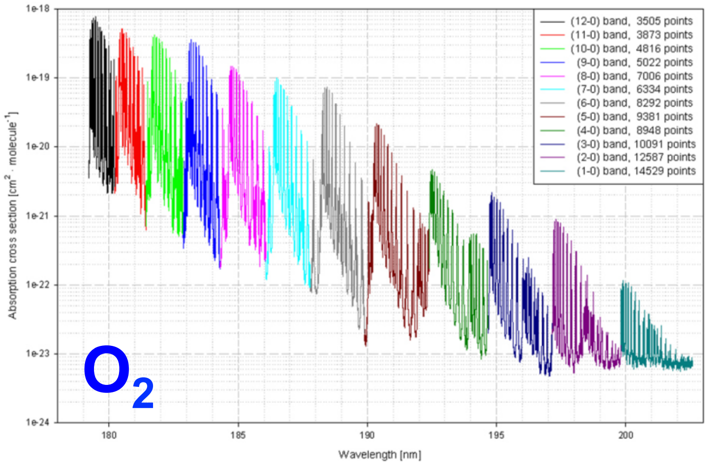


Transmittance = $I / I_o = \exp(-\sigma\, n\, L)$

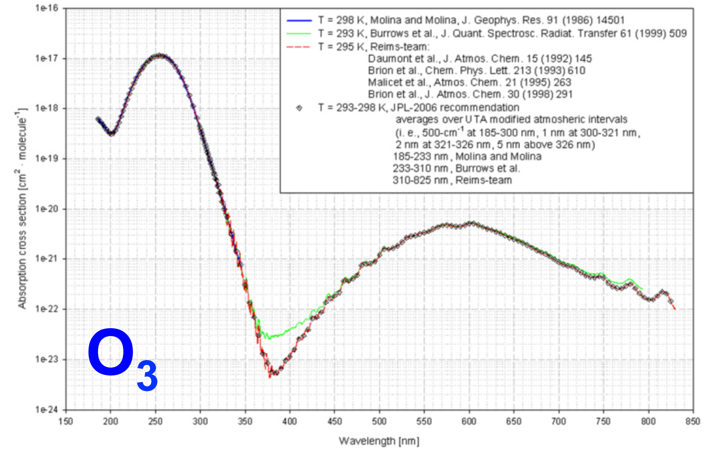
$\sigma = -1/(nL) \ln(I / I_o)$

Easy: measure pressure ($n = P/RT$), and relative change in light: I / I_o

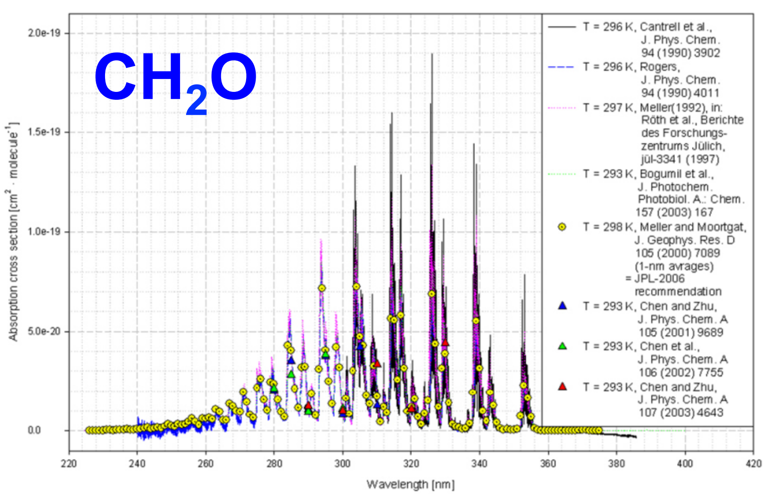
Absorption cross sections $\sigma(\lambda, T)$



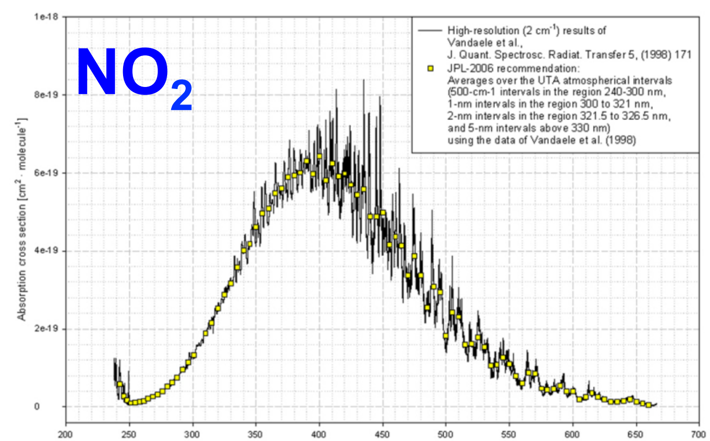
Absorption cross sections in the Schumann-Runge region of oxygen O_2 at 300 K,
Yoshino et al., Planet. Space Sci. 40 (1992) 185



Absorption cross sections of ozone O_3 at room temperature
Evaluation for JPL-2006 recommendation

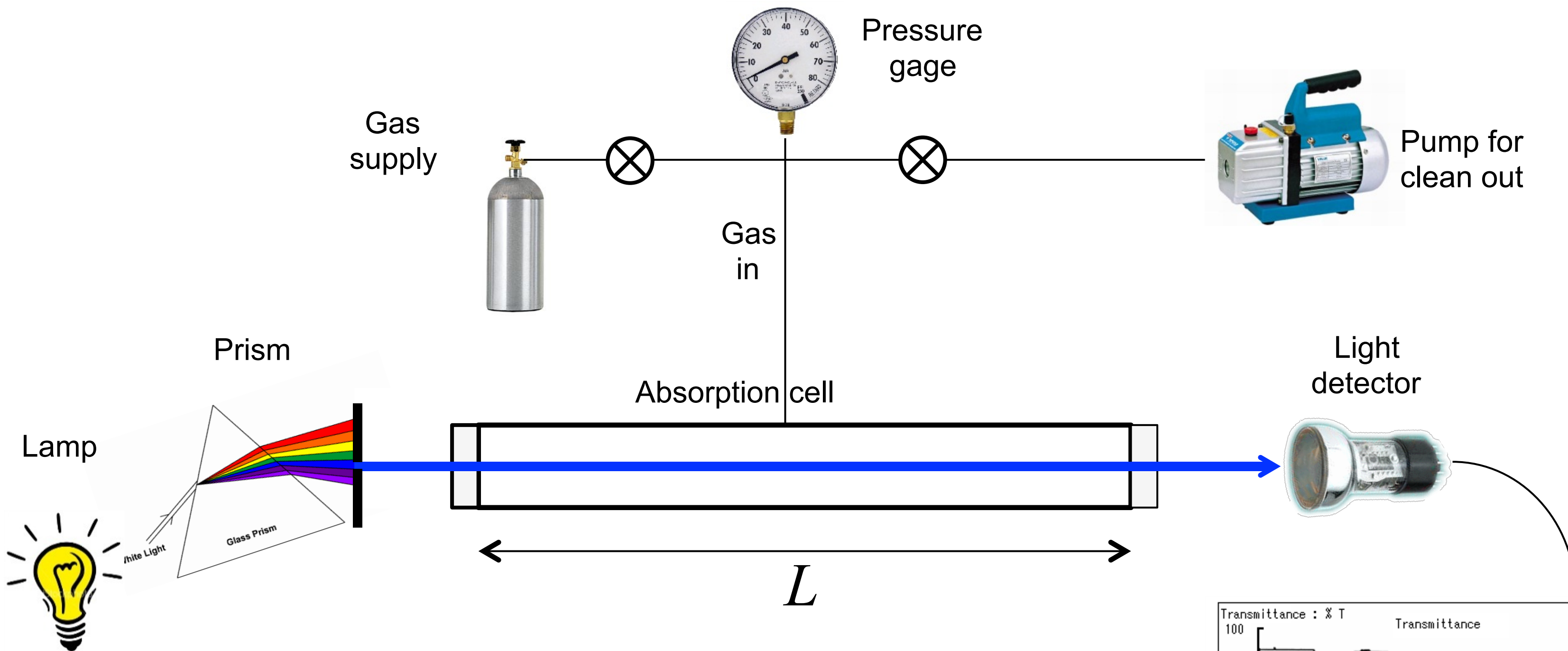


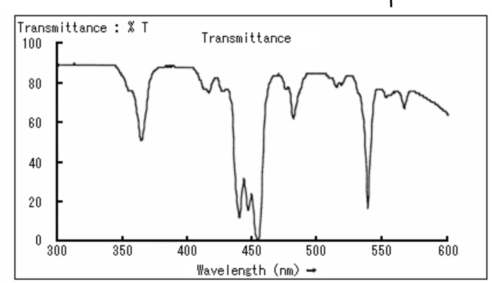
Absorption cross sections of formaldehyde CH_2O at room temperature (results 1990-2003)



Absorption cross sections of nitrogen dioxide NO_2 at 294 K
Results from the year 1998 and JPL-2006 recommendation

Measurement of Quantum Yields $\phi(\lambda)$





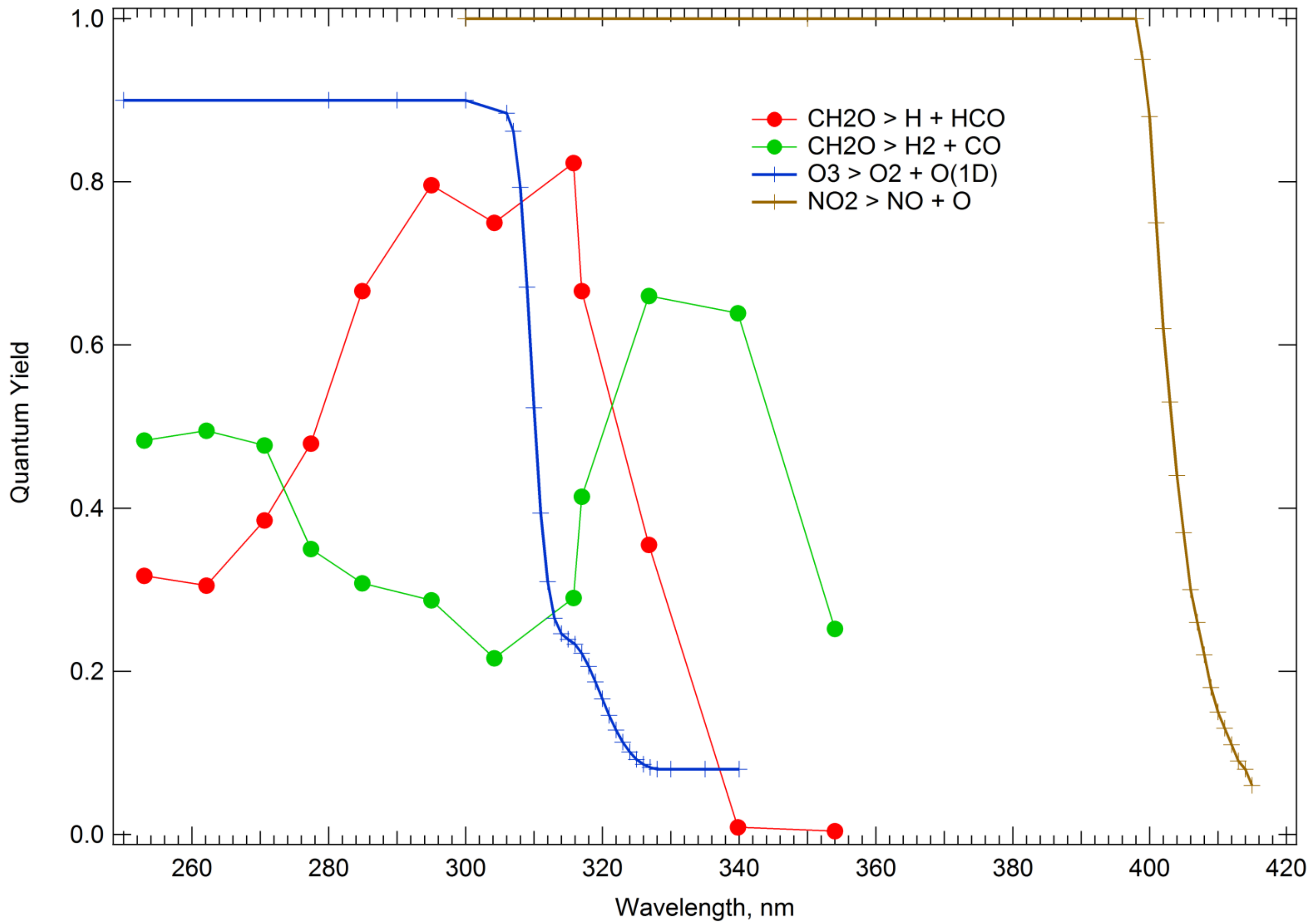
Transmittance = I / I_o = $\exp(-\sigma\, n\, L)$

Quantum Yield = number of breaks per photon absorbed

$$\phi = \Delta n / \Delta I$$

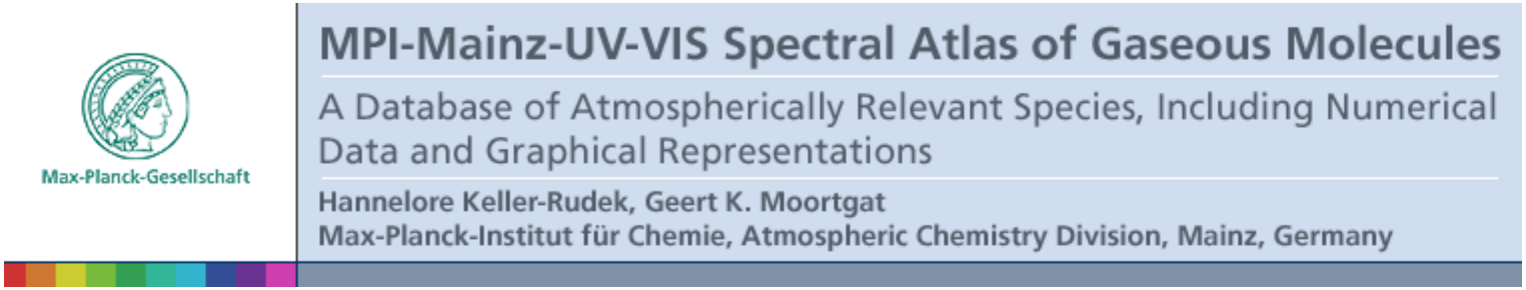
Difficult: must measure absolute change in n (products) and I (photons absorbed)

Photo-dissociation Quantum Yields $\phi(\lambda, T, P)$

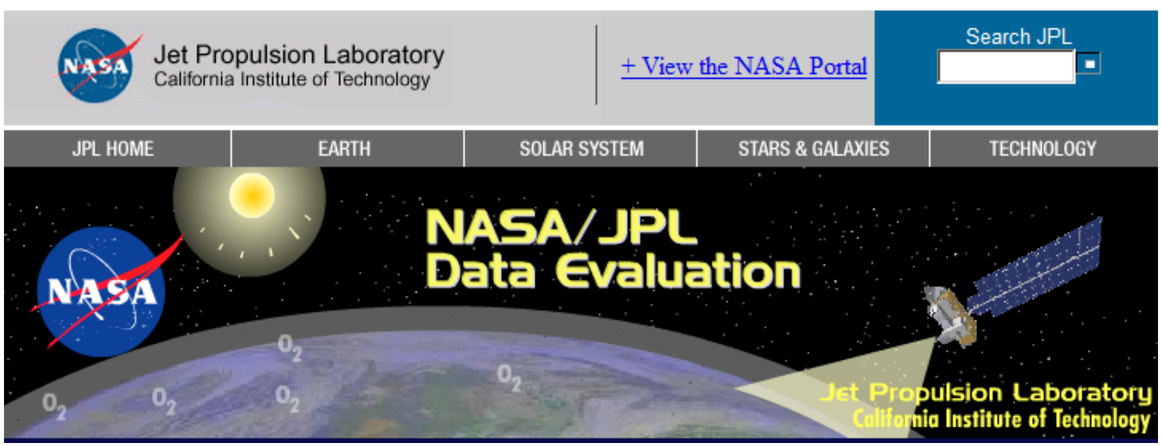


Compilations of Cross Sections & Quantum Yields

http://www.atmosphere.mpg.de/enid/2295

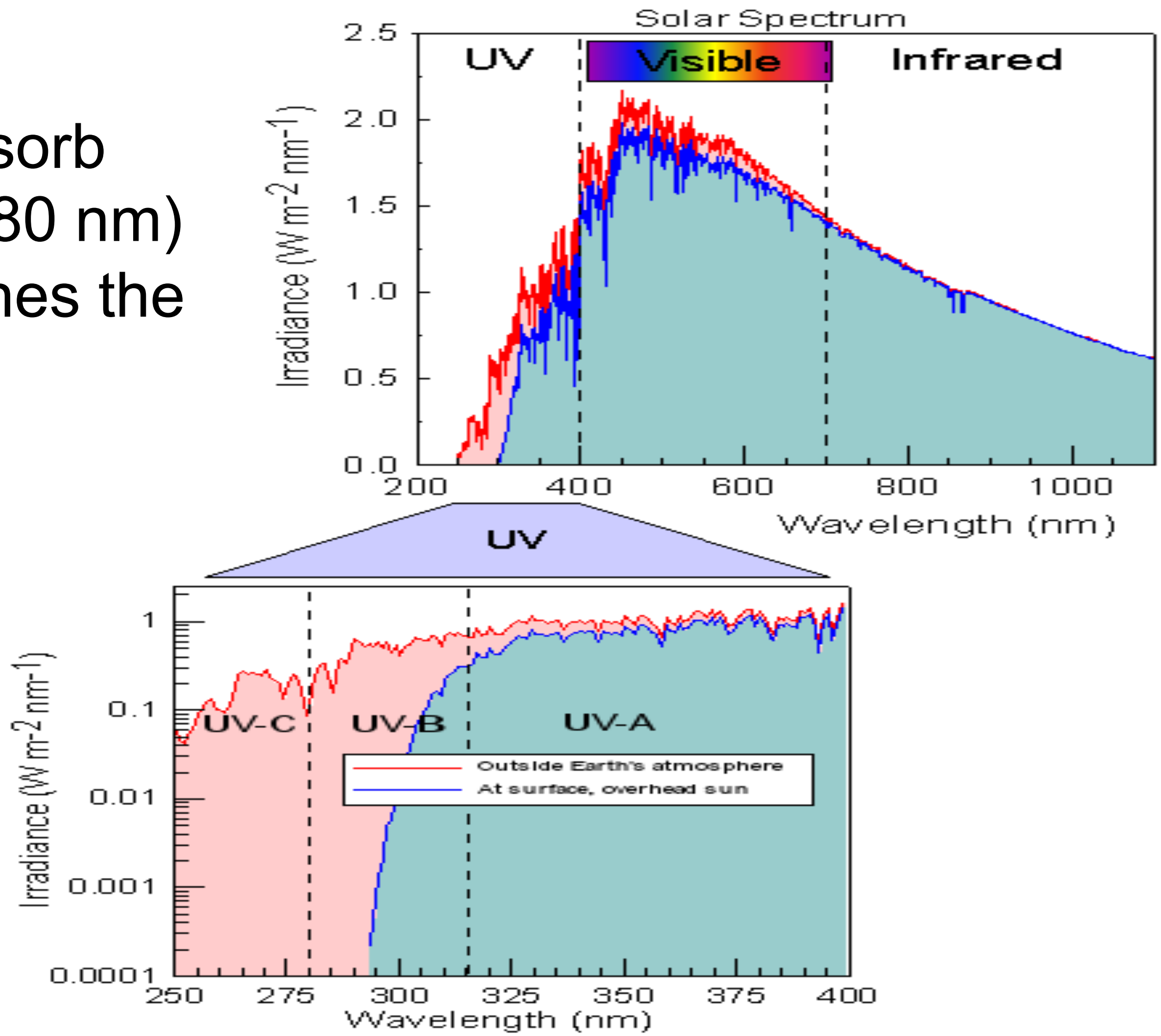


http://jpldataeval.jpl.nasa.gov/



Solar Spectrum

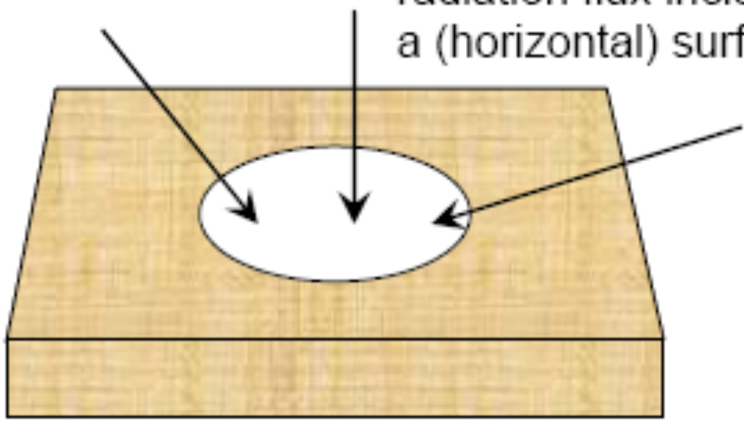
O_2 and O_3 absorb all UV-C (λ<280 nm) before it reaches the troposphere



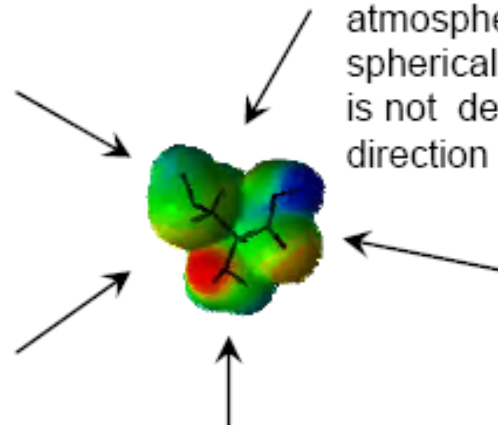
UNEP, 2002

INTEGRALS OVER INCIDENT DIRECTIONS

Irradiance: The radiation flux incident on a (horizontal) surface.



Actinic flux: The photochemically active radiation flux in the earth's atmosphere. This flux is spherically integrated and is not dependent the direction of the radiation.



$$E = \int_0^{2\pi}\int_0^{\frac{\pi}{2}} I(\theta,\varphi)\cos\theta\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi$$

Watts m^{-2}

$$F = \int_0^{\pi}\int_0^{2\pi} I(\theta,\varphi)\sin\theta\,\mathrm{d}\varphi\,\mathrm{d}\theta$$

Watts m^{-2} or quanta s^{-1} cm^{-2}

Optical Depth

n = particles per unit volume
σ = cross sectional area of each particle

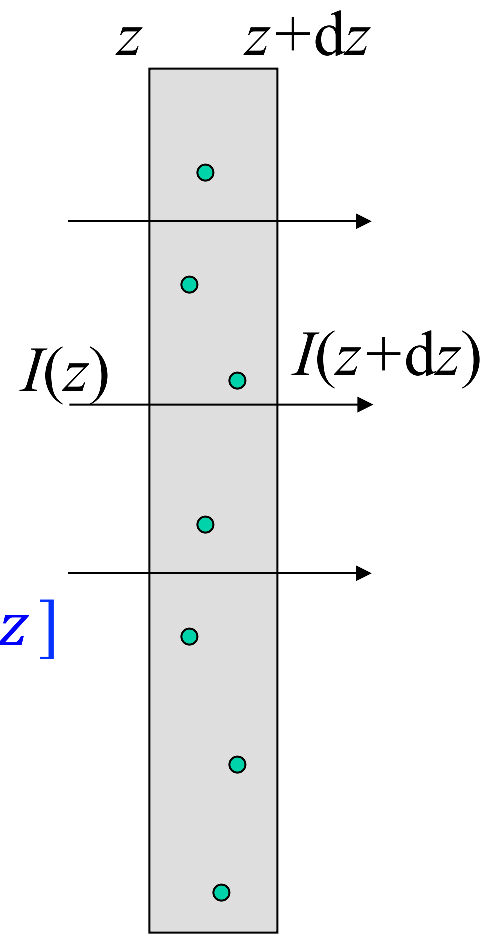
Beer-Lambert law
differential form $\mathrm{d}I/I = -\sigma n\, \mathrm{d}z$

integral form

$I(z_2) = I(z_1)$ exp [-∫z↓1 ↑z↓2 ▒s n dz]

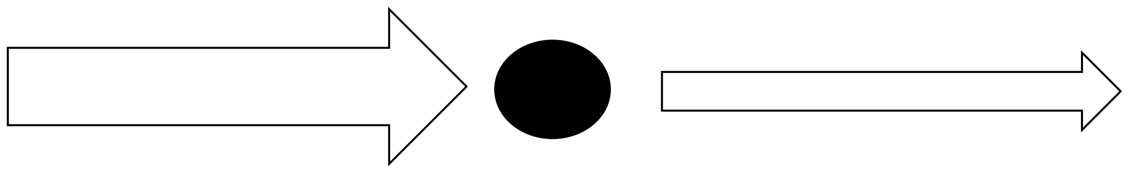
Optical Depth:

$$\tau = \int_{z1}^{z2} \sigma(z) n(z)\, \mathrm{d}z$$

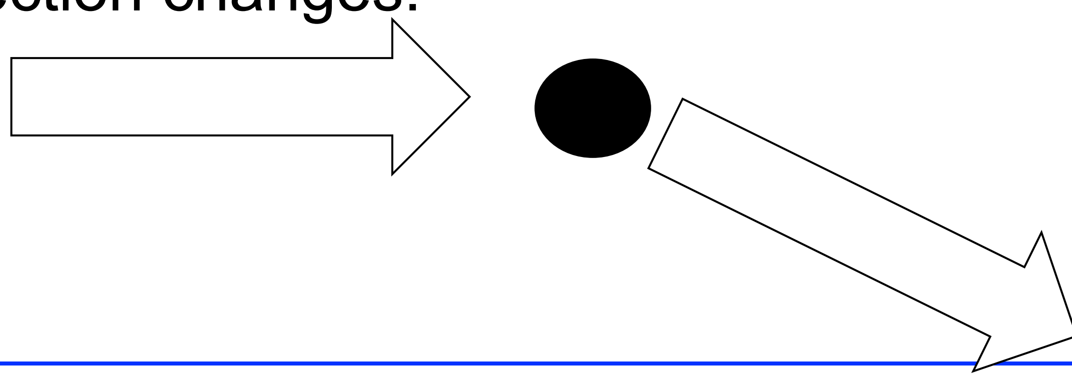


Absorption and Scattering

- Absorption – inelastic, loss of radiant energy:

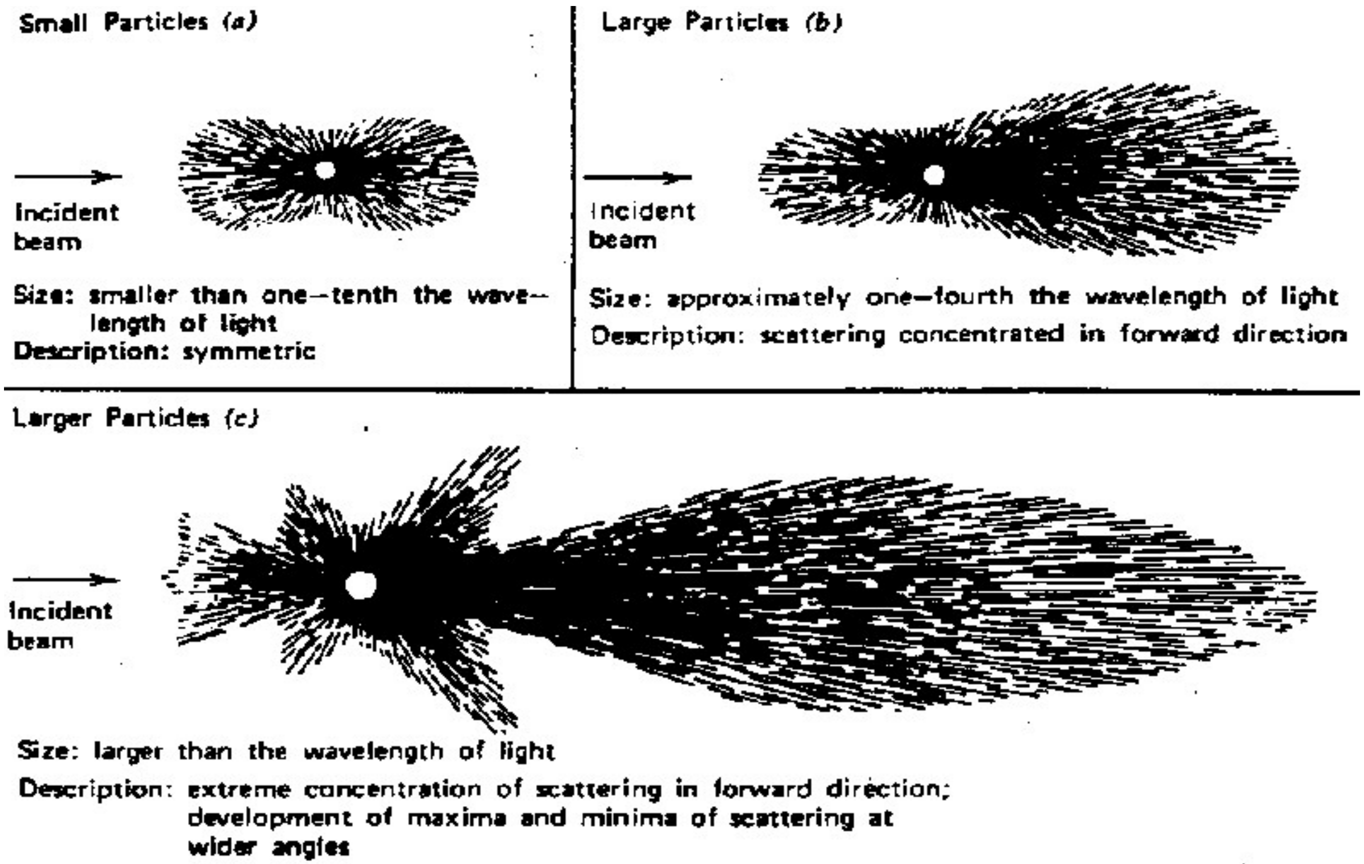


- Scattering – elastic, radiant energy is conserved, direction changes:



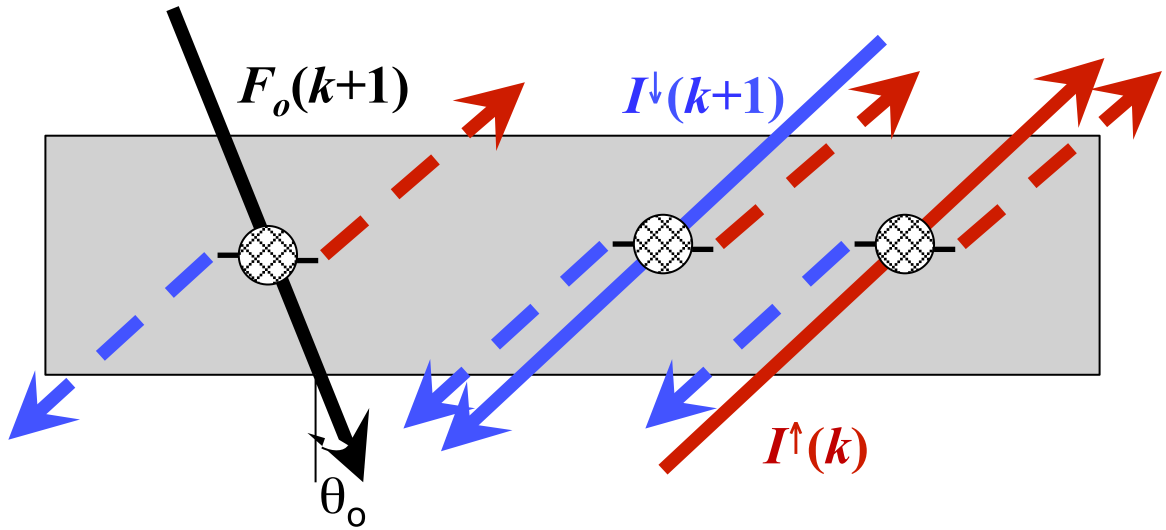
SCATTERING PHASE FUNCTIONS

$$P(\theta, \phi; \theta', \phi')$$



Multiple Atmospheric Layers
Each Assumed to be Homogeneous

In:
$F_o(k+1)$
$I^{\downarrow}(k+1)$
$I^{\uparrow}(k)$



Out:
$F_o(k)$
$I^{\downarrow}(k)$
$I^{\uparrow}(k+1)$

Each layer described by 3 parameters:

Optical depth, $\Delta\tau$

Single scattering albedo, ω_o = scatt./(scatt.+abs.)

Asymmetry factor, g: forward fraction ~ $(1+g)/2$

Typical Values

	Optical Depth	Single Scattering Albedo	Asymmetry Factor
Molecular scattering (Rayleigh)	0.5 – 2.0 λ^{-4}	1	0
Molecular absorption O_2, O_3, NO_2, SO_2,	0 – 30 spectra	0	na
Aerosols	0.01 – 5 $\lambda^{-\alpha}$, α = 0.5 – 2.0 (Angstrom exponent)	0.99 sulfate 0.6 soot	0.6 – 0.8
Clouds	1 – 1000 white, α = 0	0.9999	0.7 – 0.9

Radiative Transfer Equation

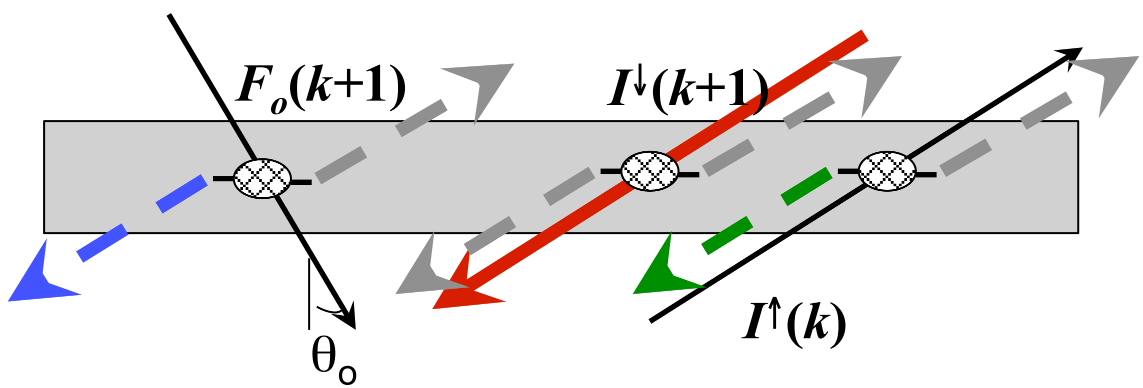
$\boxed{\text{Propagation derivative}}$ | Beer-Lambert attenuation | Scattering from direct solar beam

$$\cos\theta \frac{dI(\tau,\theta,\phi)}{d\tau} = -I(\tau,\theta,\phi) + \frac{\omega_o}{4\pi} F_\infty e^{-\tau/\cos\theta_o} P(\theta,\phi;\theta_o,\phi_o) + \frac{\omega_o}{4\pi}\int_0^{2\pi}\int_{-1}^{+1} I(\tau,\theta',\phi')P(\theta,\phi;\theta',\phi')\,d\cos\theta'\,d\phi'$$

Scattering from diffuse light (multiple scattering)

Equivalent coordinates: optical or geometric

$d\tau = \sigma n\, dz$



NUMERICAL SOLUTIONS TO RADIATIVE TRANSFER EQUATION

- Discrete ordinates

  n-streams (n = even), angular distribution

  exact as $n \rightarrow \infty$ but speed $\propto 1/n^2$

- Two-stream family

  delta-Eddington, many others

  very fast but not exact

- Monte Carlo

  slow, but ideal for 3D problems

- Others

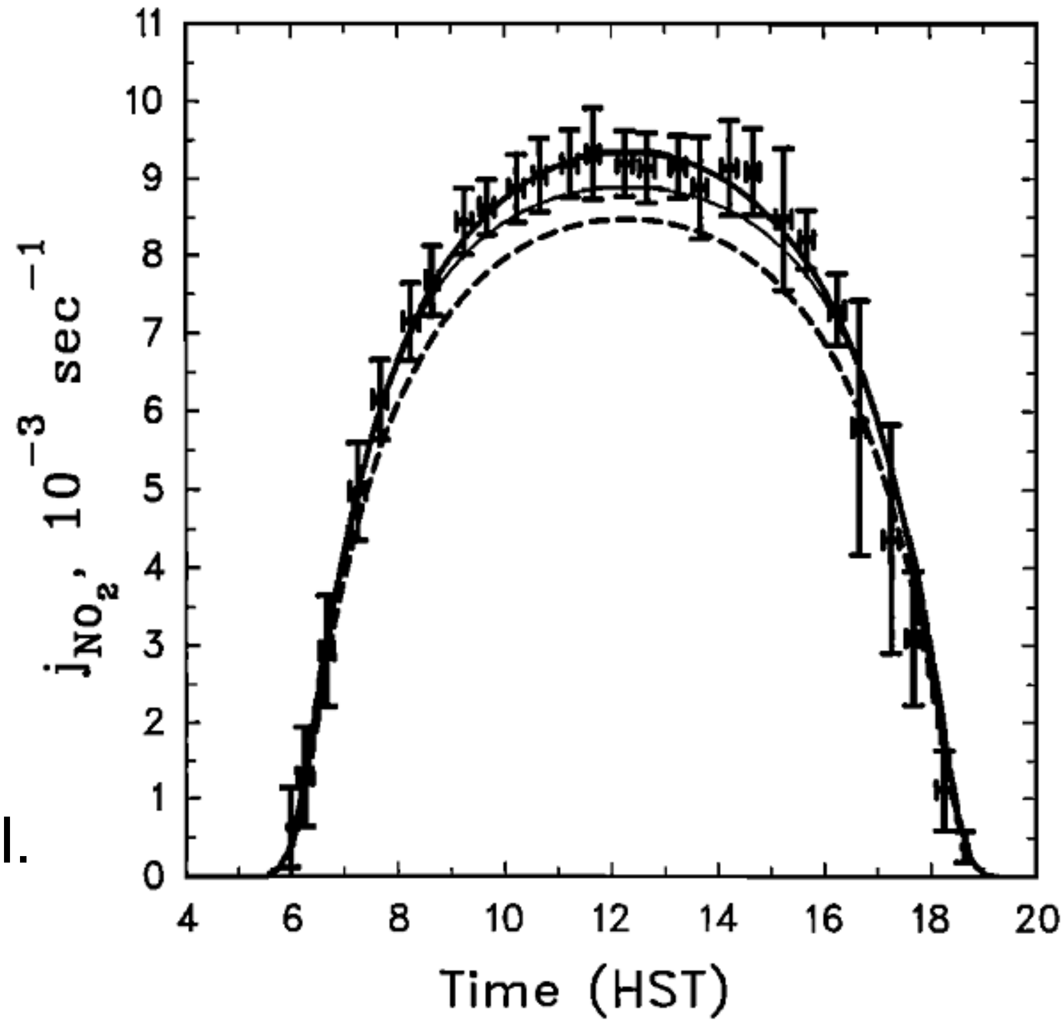
  matrix operator, Feautrier, adding-doubling, successive orders, etc.

J for $NO_2 \rightarrow NO + O$

Direct measurement with chemical actinometers

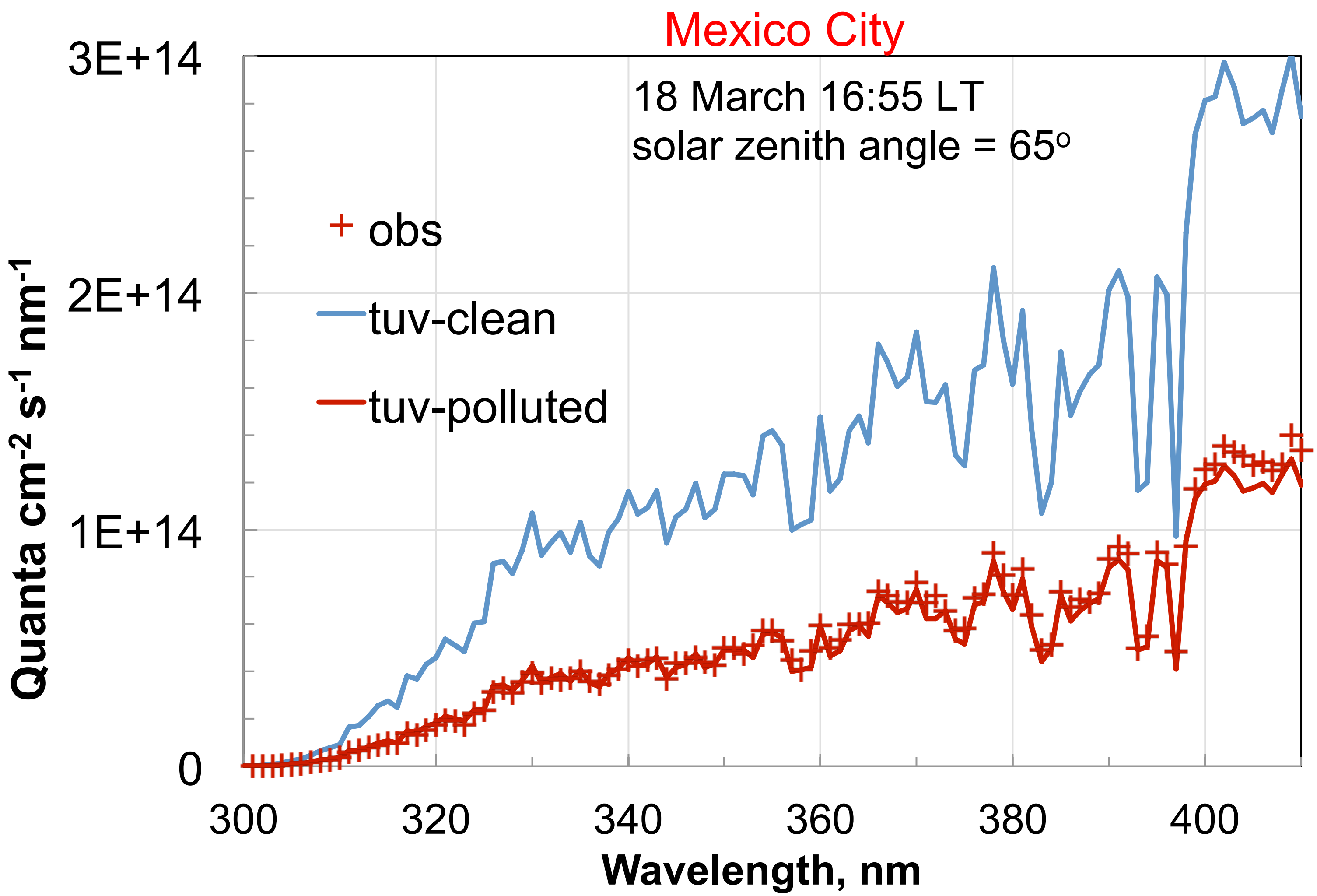
Good agreement with model for pristine conditions

e.g.,
Mauna Loa, Hawaii
3.4 km elevation a.s.l.



Lantz et al. 1996

Aerosols Can Attenuate Urban Actinic Flux → Slower Photochemistry



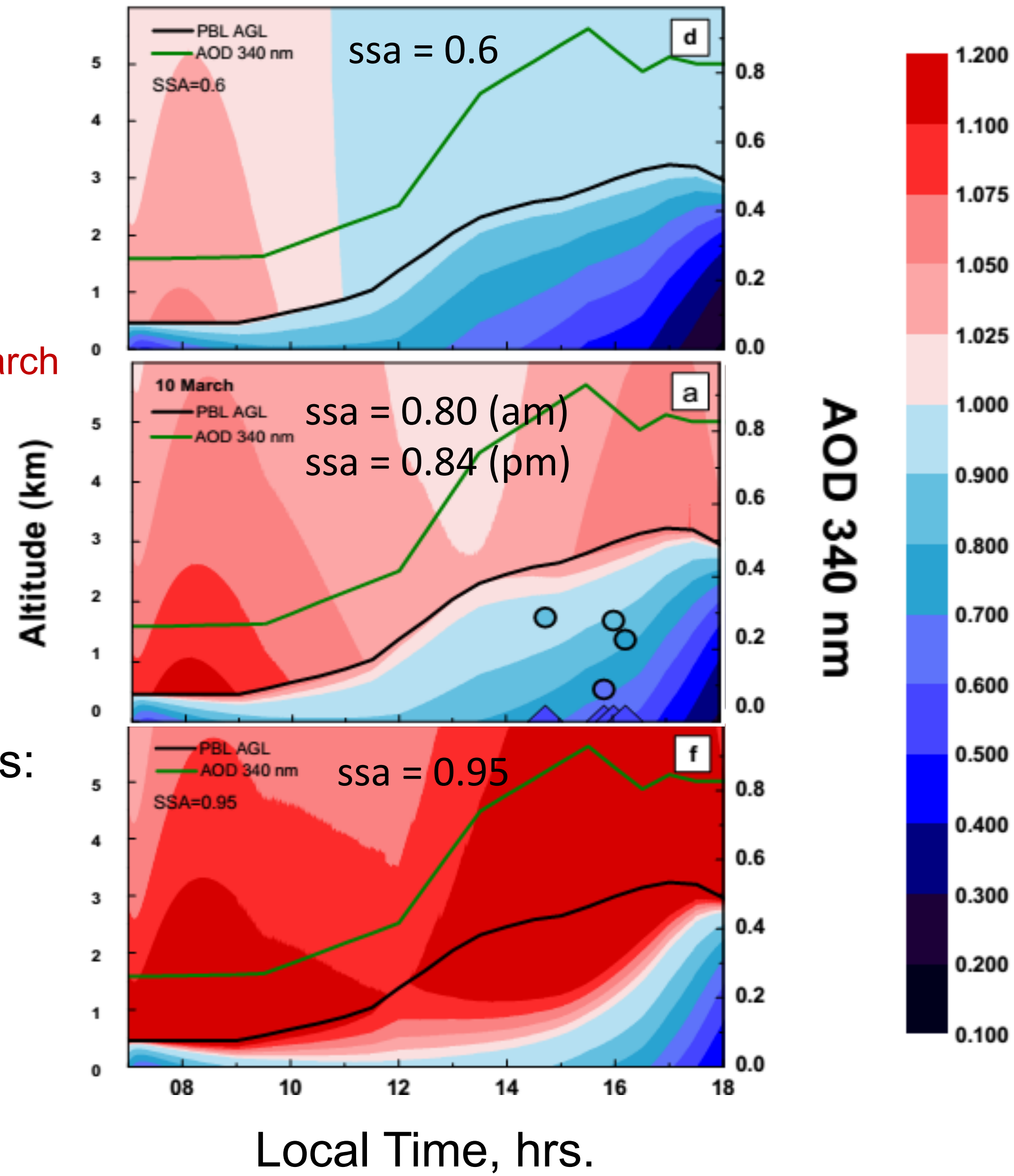
Madronich, Shetter, Halls, Lefer, AGU'07

Vertical Profile Is Sensitive to Single Scattering Albedo

Mexico City suburbs (T1) March 2006

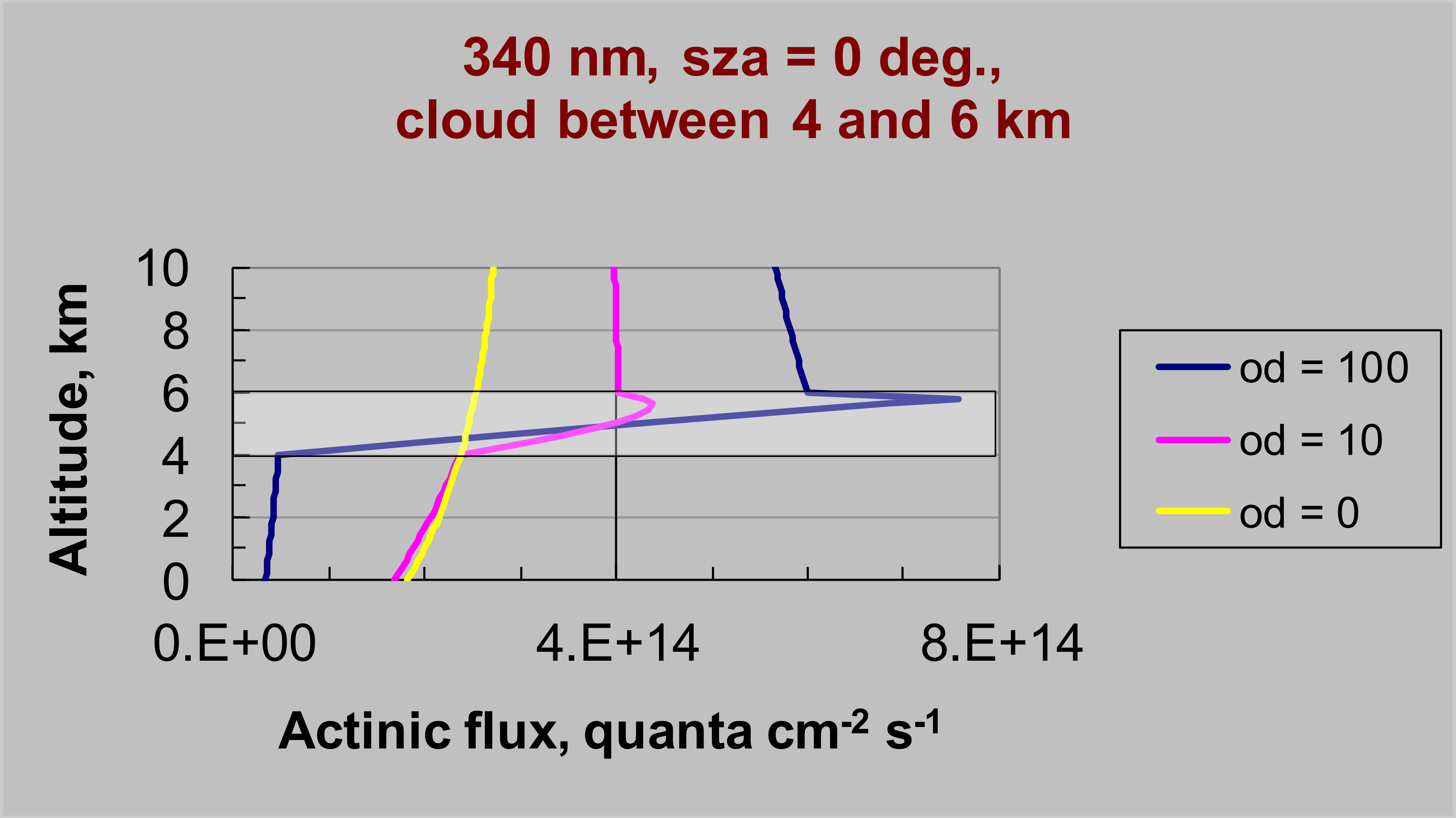
Central panel:
Model with observed ssa, and obs.

Upper and lower panels:
Sensitivity to ssa

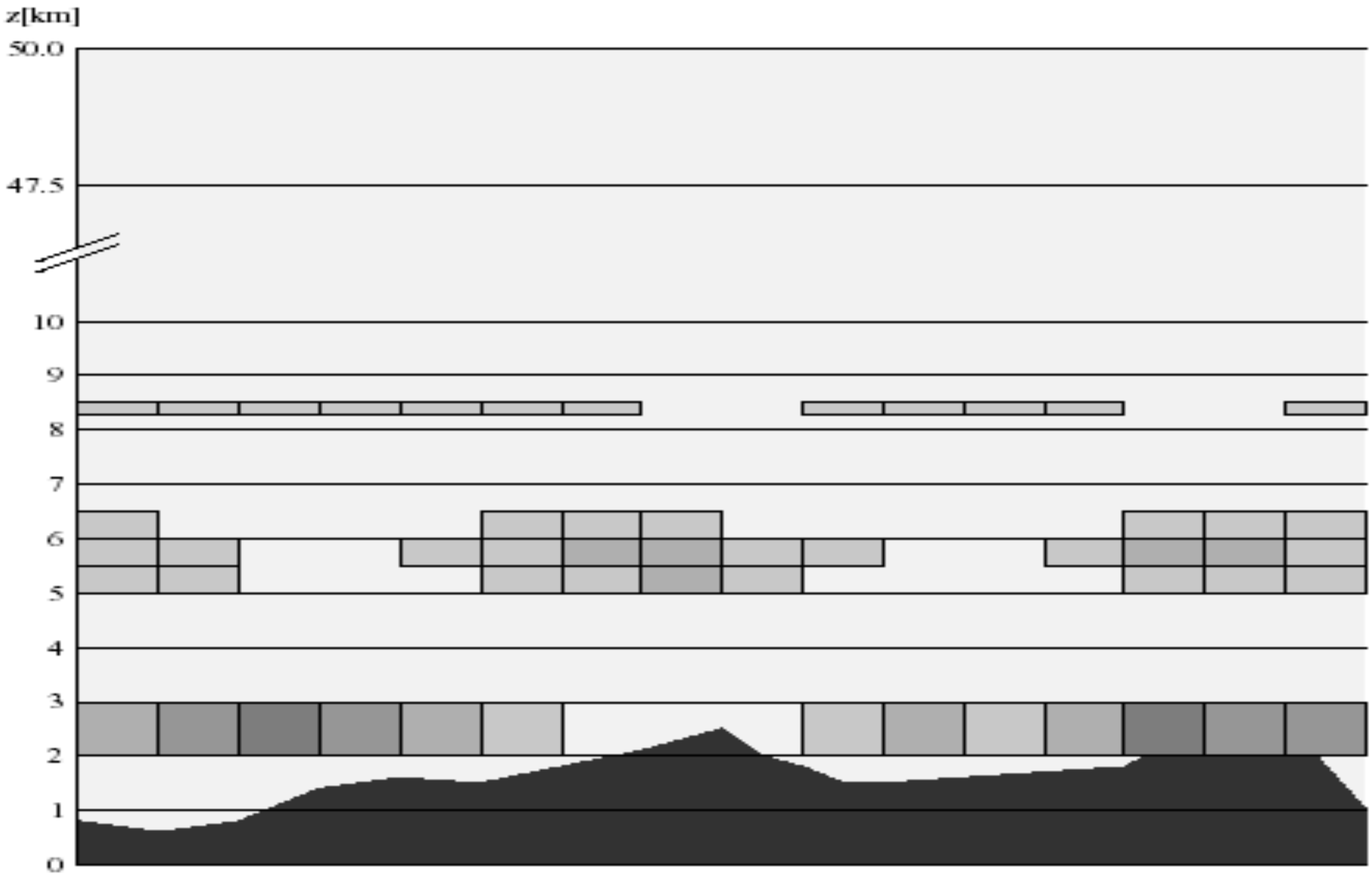


Palancar et al., 2013

EFFECT OF UNIFORM CLOUDS ON ACTINIC FLUX

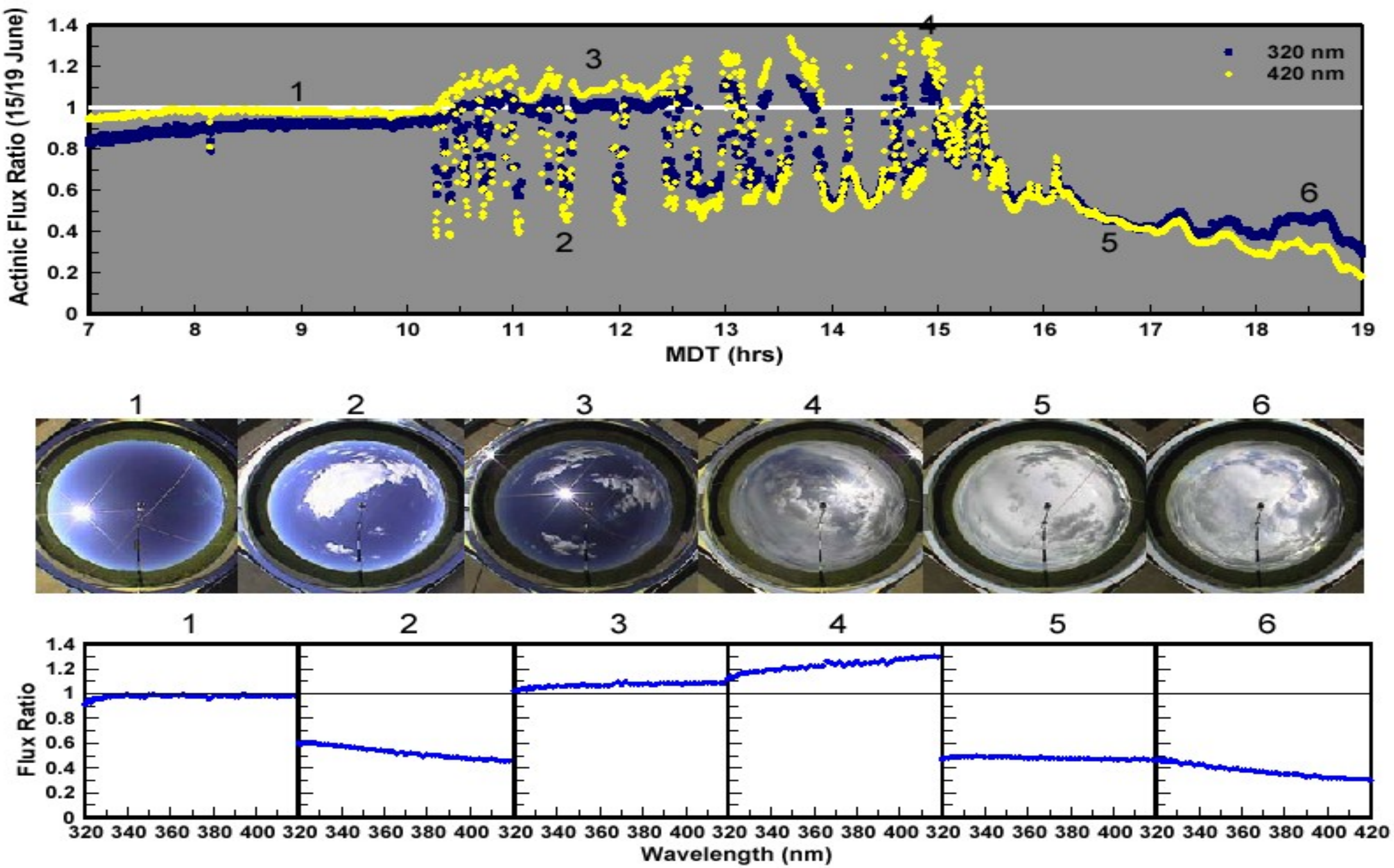


Broken Clouds



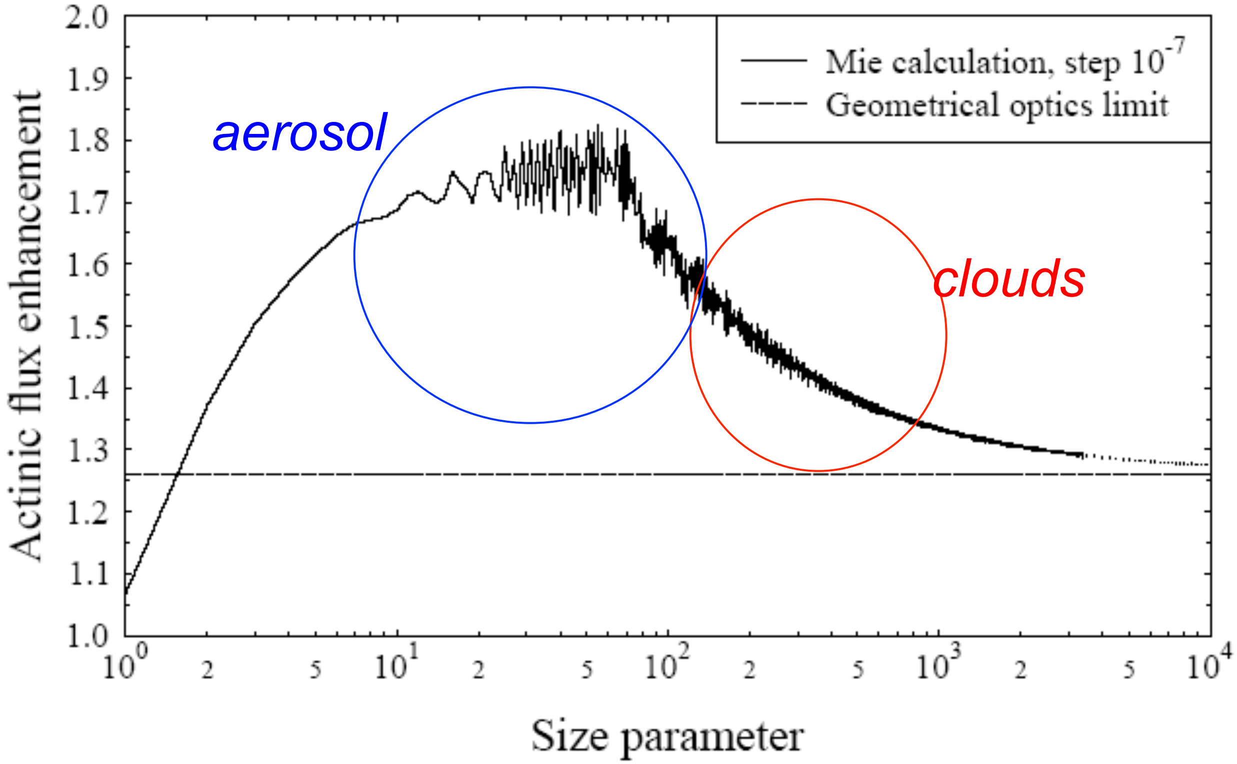
PARTIAL CLOUD COVER

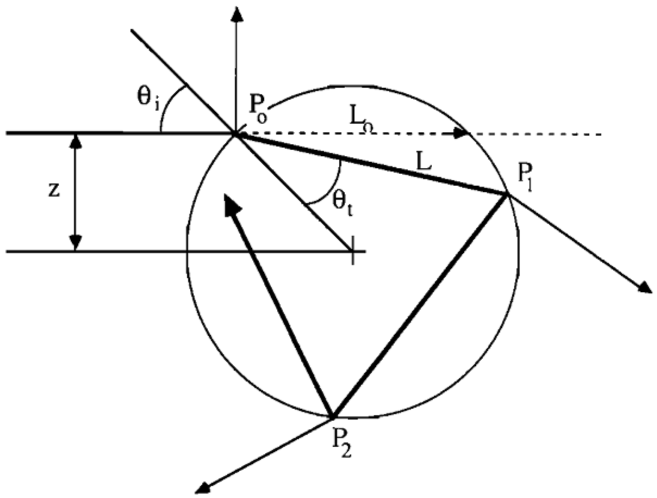
enhancements and reductions



Crafword et al., 2003

Photochemistry Inside Liquid Particles





Actinic flux enhancements due to refraction/diffraction

Mayer and Madronich, 2004

Photolysis in WRF-Chem

- Several radiative transfer options:

  TUV (delta-Eddington, 140 λ's) – major update soon

  Fast-J (8-str Feautrier, 17 λ's)

  Fast-TUV (delta-Eddington, 17 λ's, correction table)

  Other? – faster, more accurate

- Sub-grid cloud overlap schemes

  Max overlap if vertically contiguous, random otherwise

  Effects of overlap schemes on vertical distribution of actinic flux

  Need evaluation of WRF-Chem in the presence of clouds

- Aerosols:

  Mixing rules for index of refraction

  Mie scattering integrated over size distributions

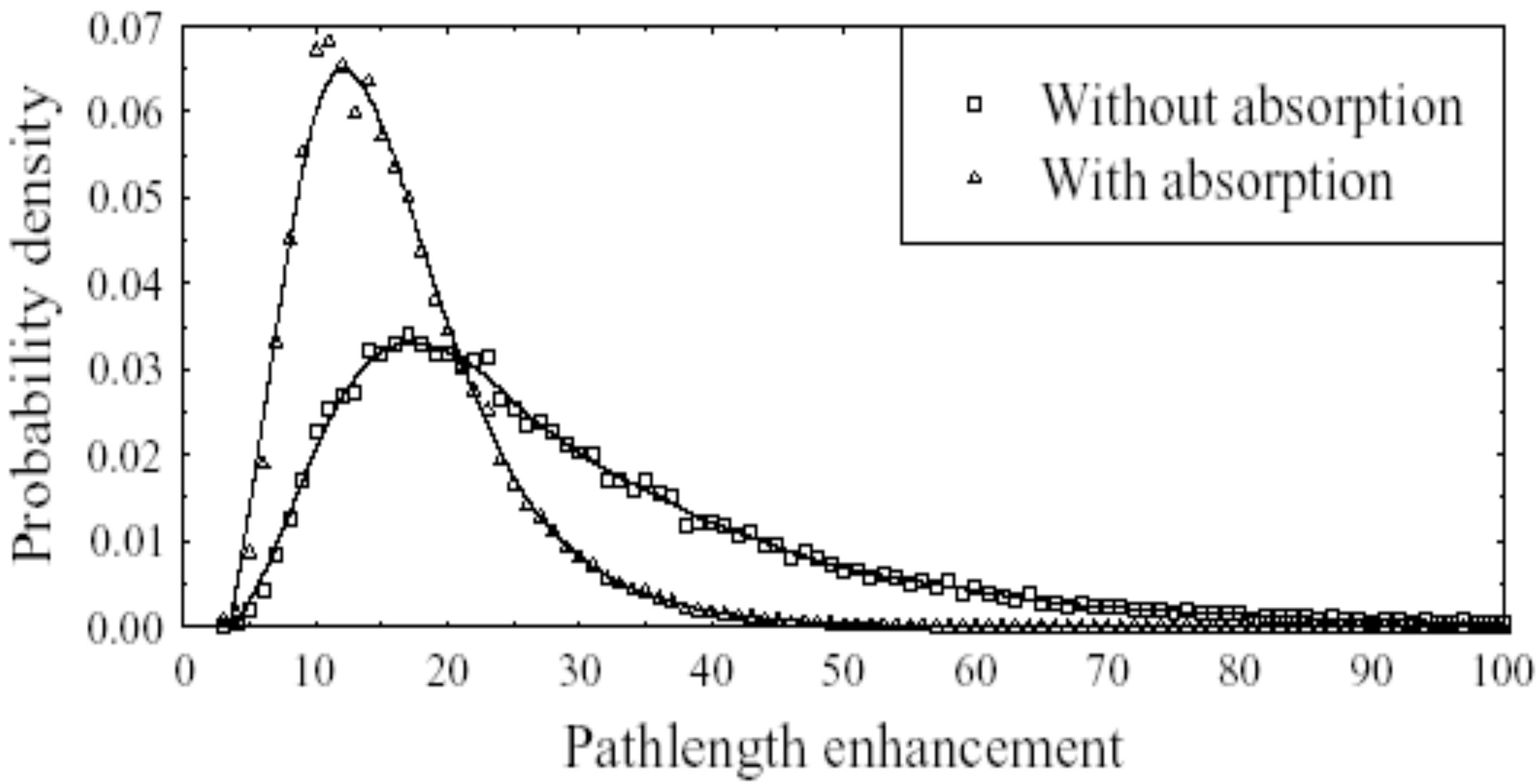
  Different core-shell options

OUTLINE

- role of photolysis
- j vals
- xsects & qys
- radiation
- aerosols
- clouds
- wrf-chem

INSIDE CLOUDS:
Photon Path Enhancements

Cumulonimbus, od=400

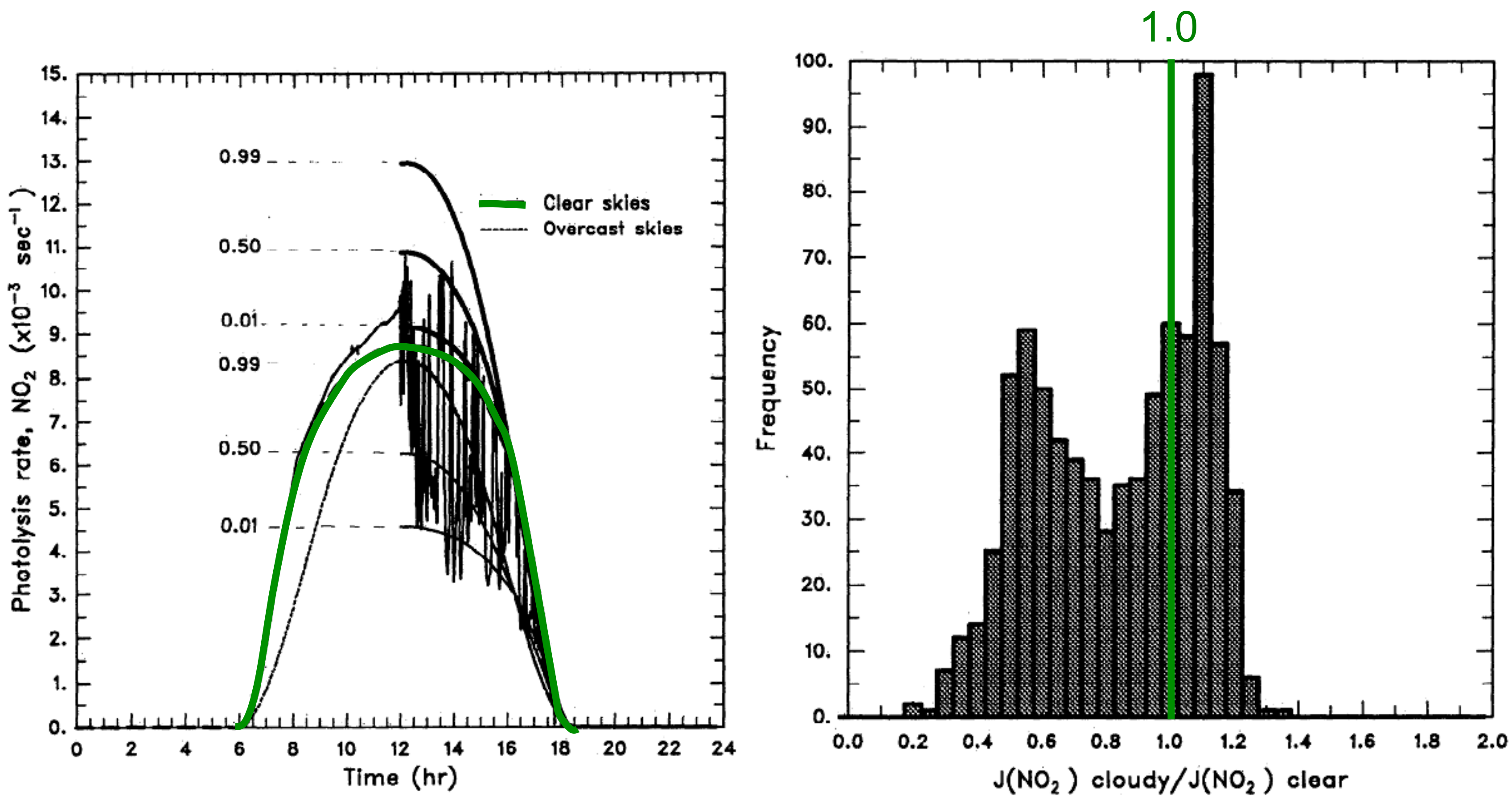


Mayer et al., 1998

Photochemistry in clouds can be stronger than outside clouds

Enhancements Possible with Broken Clouds

bimodal distribution



Lantz et al. 1996

SPECTRALLY INTEGRATED RADIATION

- Radiometry

  Signal (W m^{-2}) = $\int_{\lambda} E(\lambda)\, R(\lambda)\, \mathrm{d}\lambda$

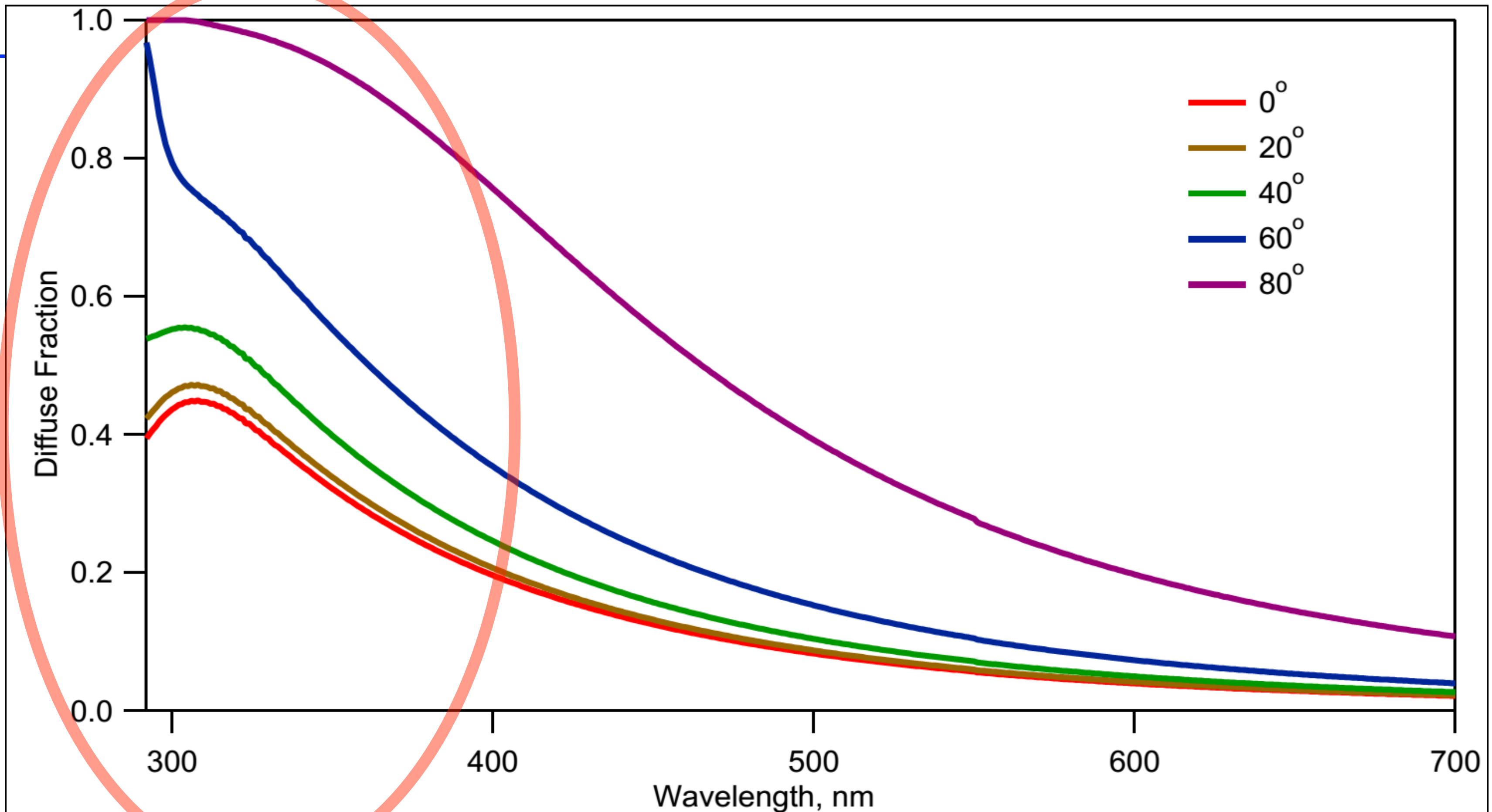
- Biological effects

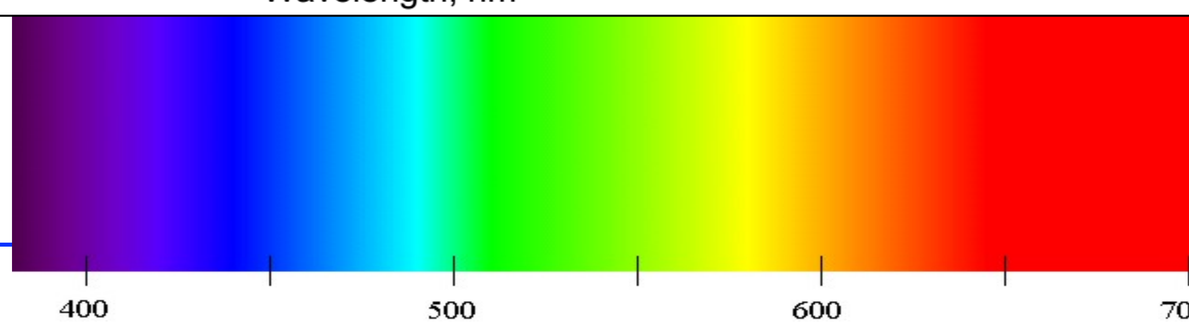
  Dose rate (W m^{-2}) = $\int_{\lambda} E(\lambda)\, B(\lambda)\, \mathrm{d}\lambda$

- Photo-dissociation of atmospheric chemicals

  Photolysis frequency (s^{-1}) = $\int_{\lambda} F(\lambda)\, \sigma(\lambda)\, \phi(\lambda)\, \mathrm{d}\lambda$

Diffuse Skylight vs. Direct Solar Beam (at sea level)





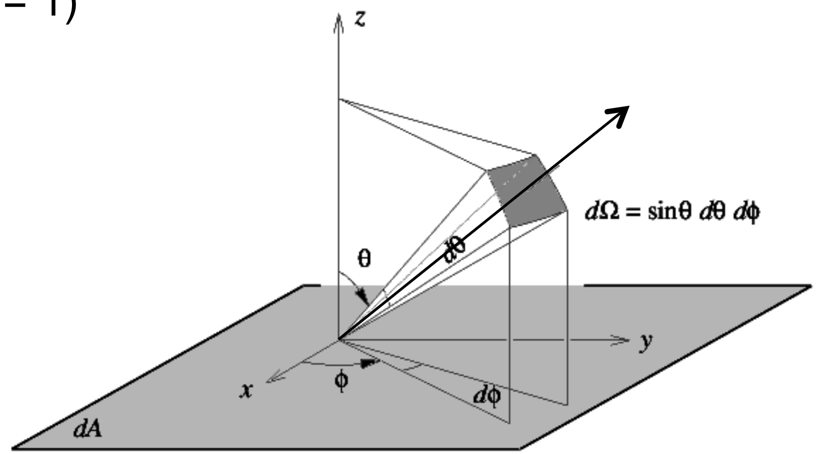
Scattering is important in UV

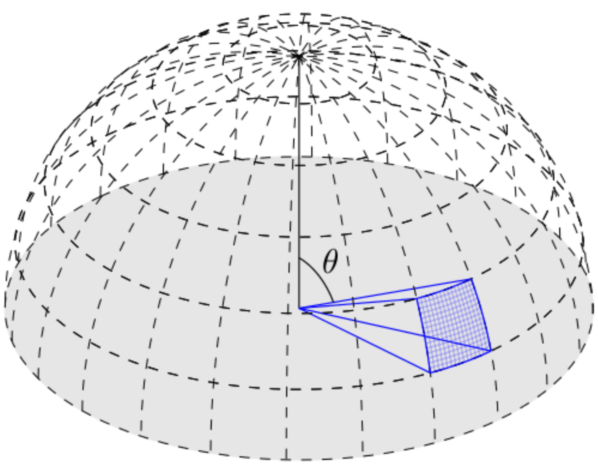
Solid Angle

(units = steradians, sr)

Solid Angle ≡ area of patch on unit sphere ($R = 1$)

e.g.:
hemisphere = 2π sr
full sphere = 4π sr
Sun (seen from Earth) ≈ 7×10^{-5} sr





Spherical coordinates:

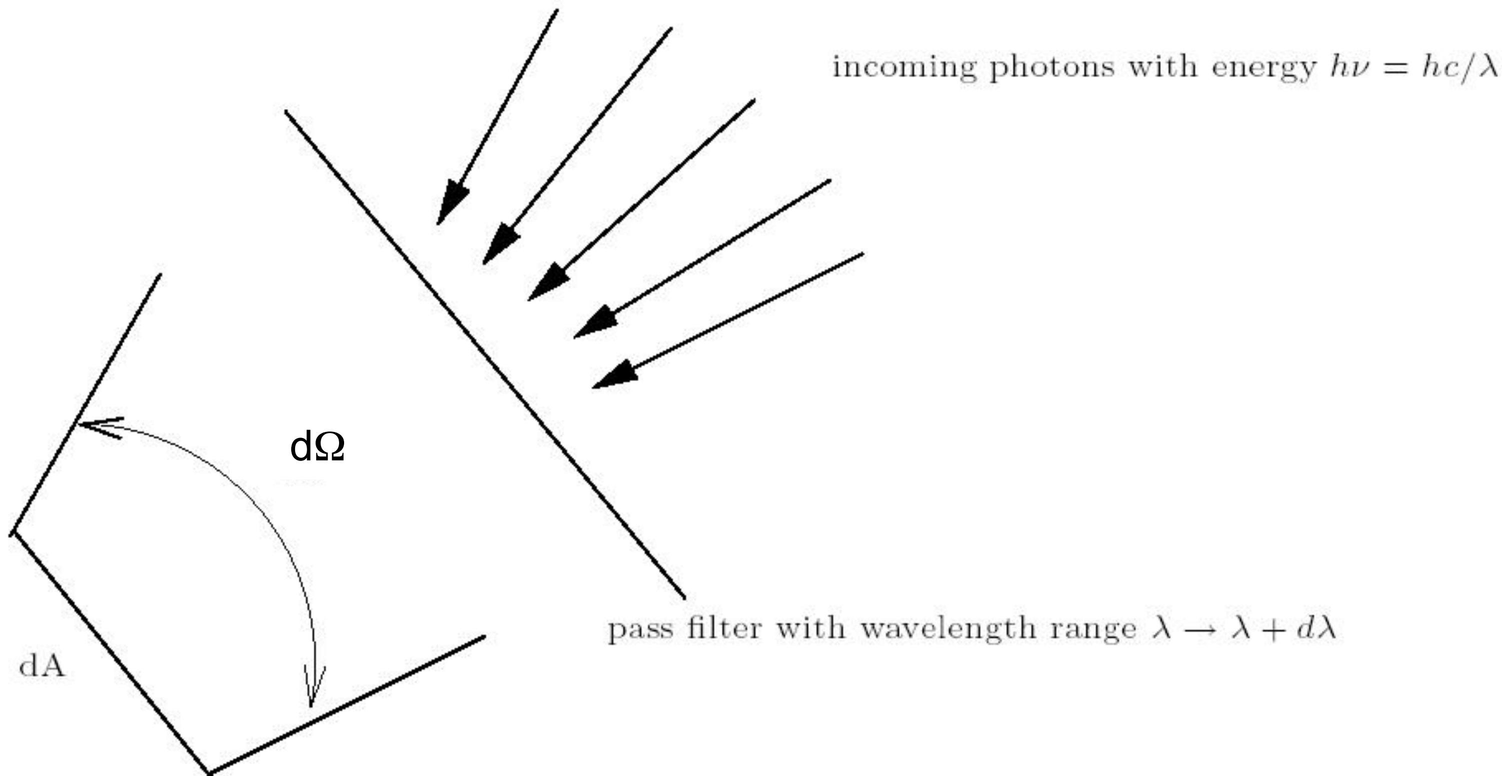
θ = zenith angle = Angle from vertical axis

ϕ = azimuth angle = angle in horizontal plane, from a reference direction, usually North

Spectral Radiance, I

$$I(\lambda,\theta,\phi) = N(hc/\lambda) / (dt\ dA\ d\Omega\ d\lambda)$$

units: J s^{-1} m^{-2} sr^{-1} nm^{-1}



(old name = Specific Intensity)

Definition of Optical Depth

$\mathrm{d}I/\mathrm{d}z = - \sigma\, n\, I$

(integral form) $I(z_2) = I(z_1) \exp [- \sigma\, n\, (z_2 - z_1)]$

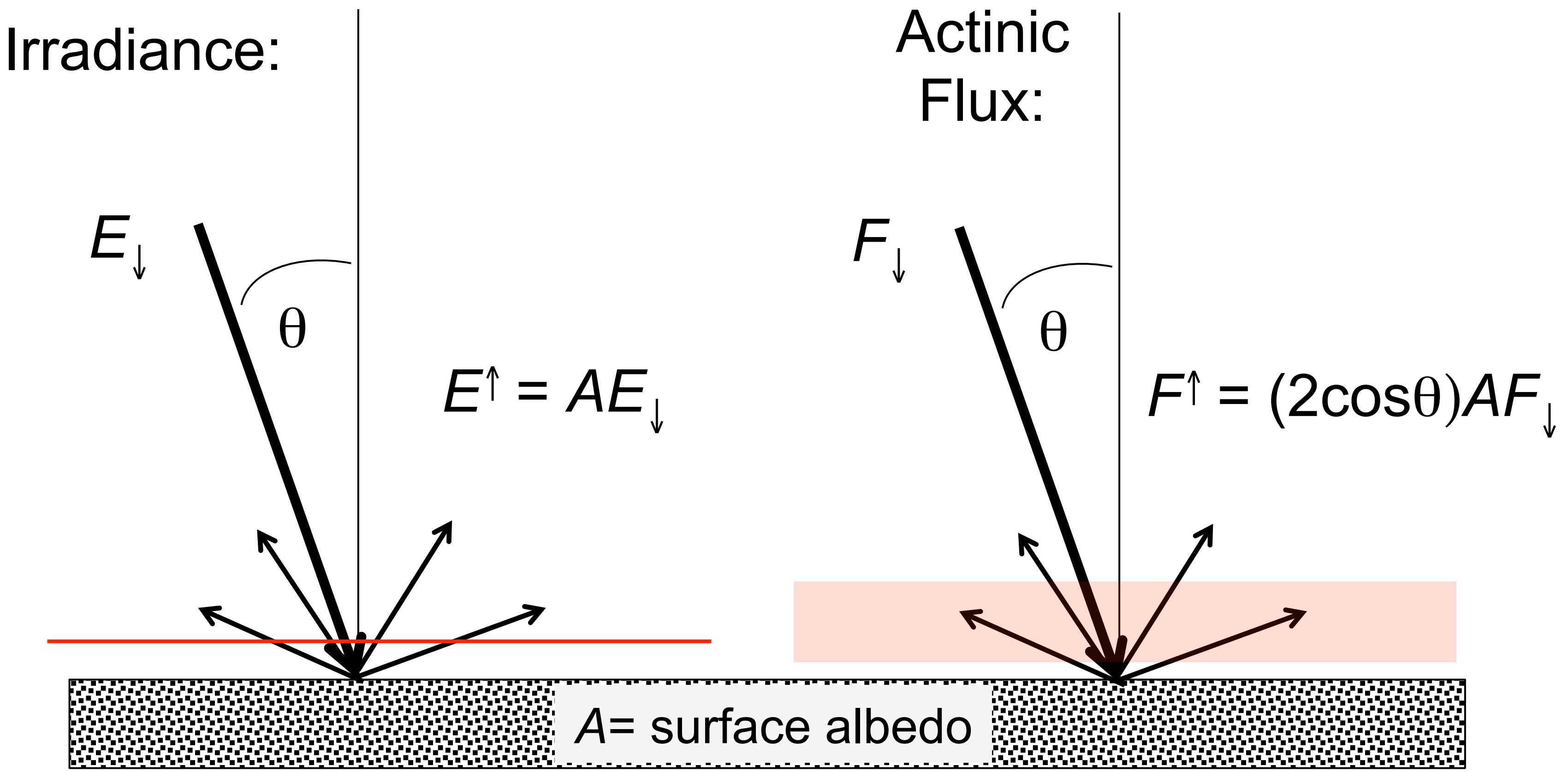
Beer-Lambert Law: $I(z_2) = I(z_1) \exp [- \sigma\, n\, (z_2 - z_1)]$

If σ and/or n depend on z, then

$$\tau = \int_{z1}^{z2} \sigma(z) n(z)\, \mathrm{d}\, z$$

Optical depth: $\tau = \sigma\, n\, (z_2 - z_1)$

Lambertian (isotropic) Reflection
(e.g. approximately true for snow)



Limit for overhead sun, $A = 1$, $\theta = 0^o$:

$E^\uparrow = E_\downarrow$ (conservation of energy), but $F^\uparrow = 2F_\downarrow$ (not conserved)

Mie Scattering Theory

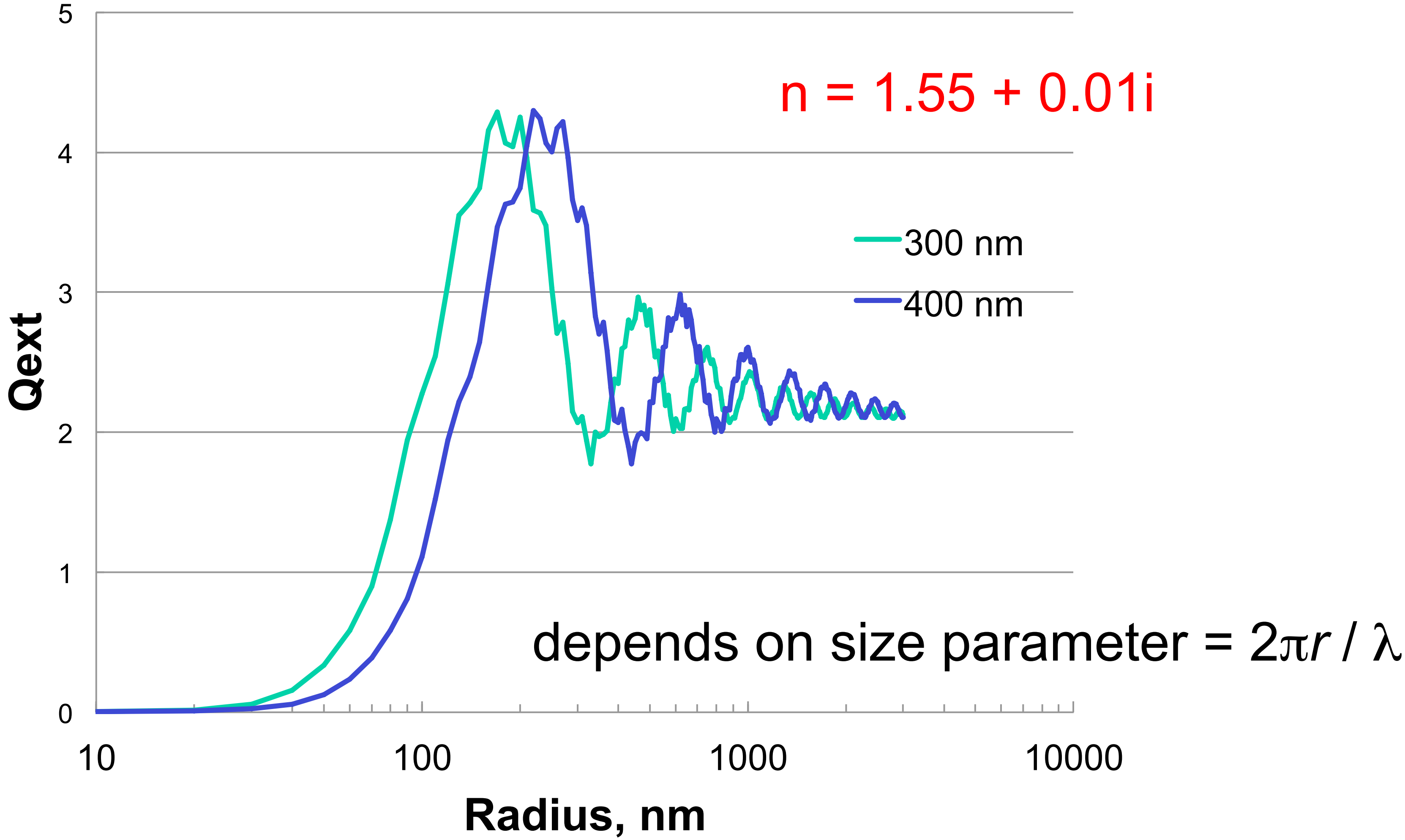
For spherical particles, given:

Complex index of refraction: $n = m + \mathrm{i}k$
Size parameter: $\alpha = 2\pi r / \lambda$

Can compute:

Extinction efficiency	$Q_e(\alpha, n) \quad \times \pi r^2$
Scattering efficiency	$Q_s(\alpha, n) \quad \times \pi r^2$
Phase function	$P(\Theta, \alpha, n)$
or asymmetry factor	$g(\alpha, n)$

Extinction Efficiency, Q_{ext}



EFFECT OF CLOUDS (UNIFORM LAYER)

- Above cloud: - high radiation because of reflection
- Below cloud: - lower radiation because of attenuation by cloud
- Inside cloud: - complicated behavior
  - Top half: very high values (for high sun)
  - Bottom half: lower values

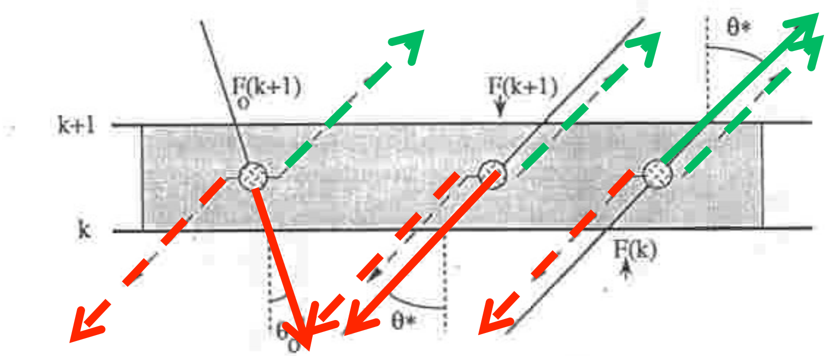
SIMPLE 2-STREAM METHOD:

3 Equations for each layer

$$F_o(k) = F_o(k+1)e^{-\Delta\tau/\cos\theta_o}$$

$$F_\downarrow(k) = F_\downarrow(k+1)e^{-\Delta\tau/\cos\theta^*} + f\omega_o F_o(k+1)(1-e^{-\Delta\tau/\cos\theta_o}) + f\omega_o F_\downarrow(k+1)(1-e^{-\Delta\tau/\cos\theta^*}) + (1-f)\omega_o F_\uparrow(k)(1-e^{-\Delta\tau/\cos\theta^*})$$

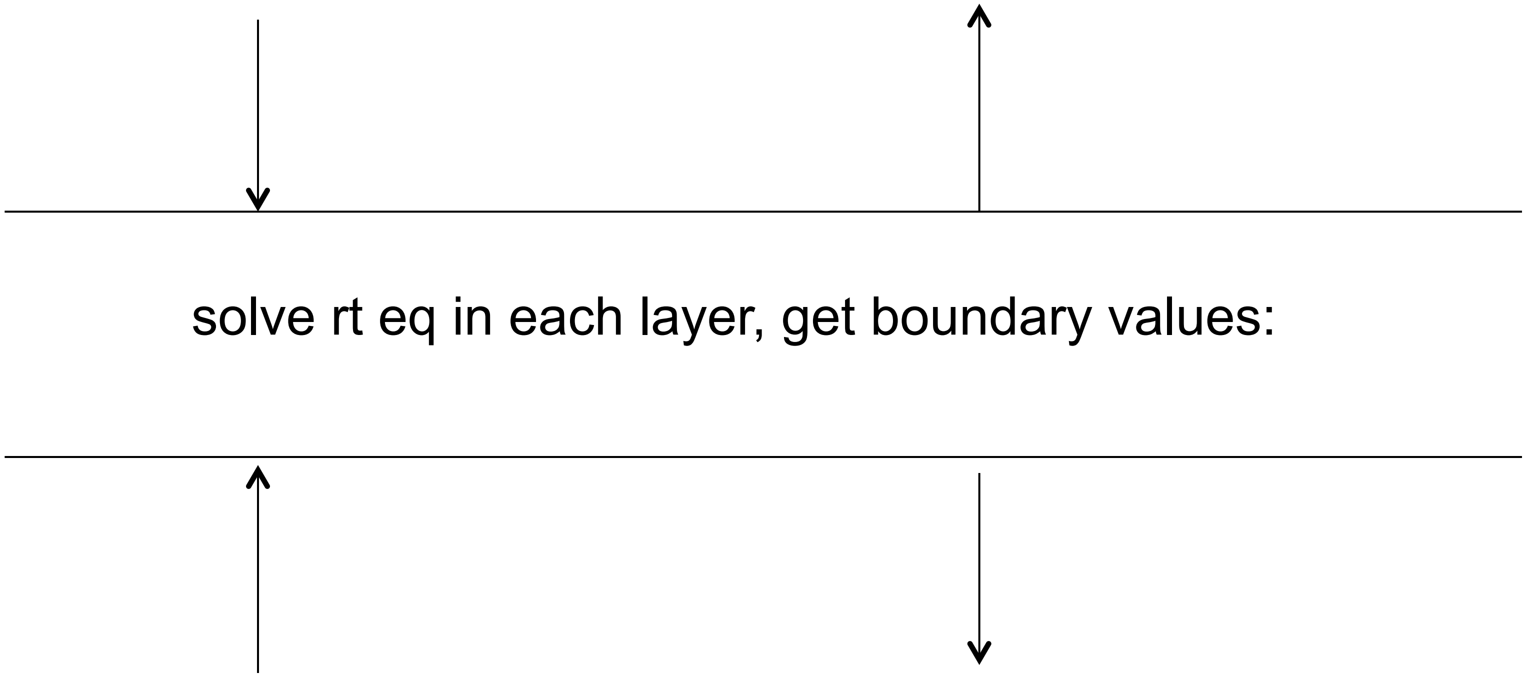
$$F_\uparrow(k+1) = F_\uparrow(k)e^{-\Delta\tau/\cos\theta^*} + (1-f)\omega_o F_o(k+1)(1-e^{-\Delta\tau/\cos\theta_o}) + (1-f)\omega_o F_\uparrow(k)(1-e^{-\Delta\tau/\cos\theta^*}) + f\omega_o F_\downarrow(k)(1-e^{-\Delta\tau/\cos\theta^*})$$



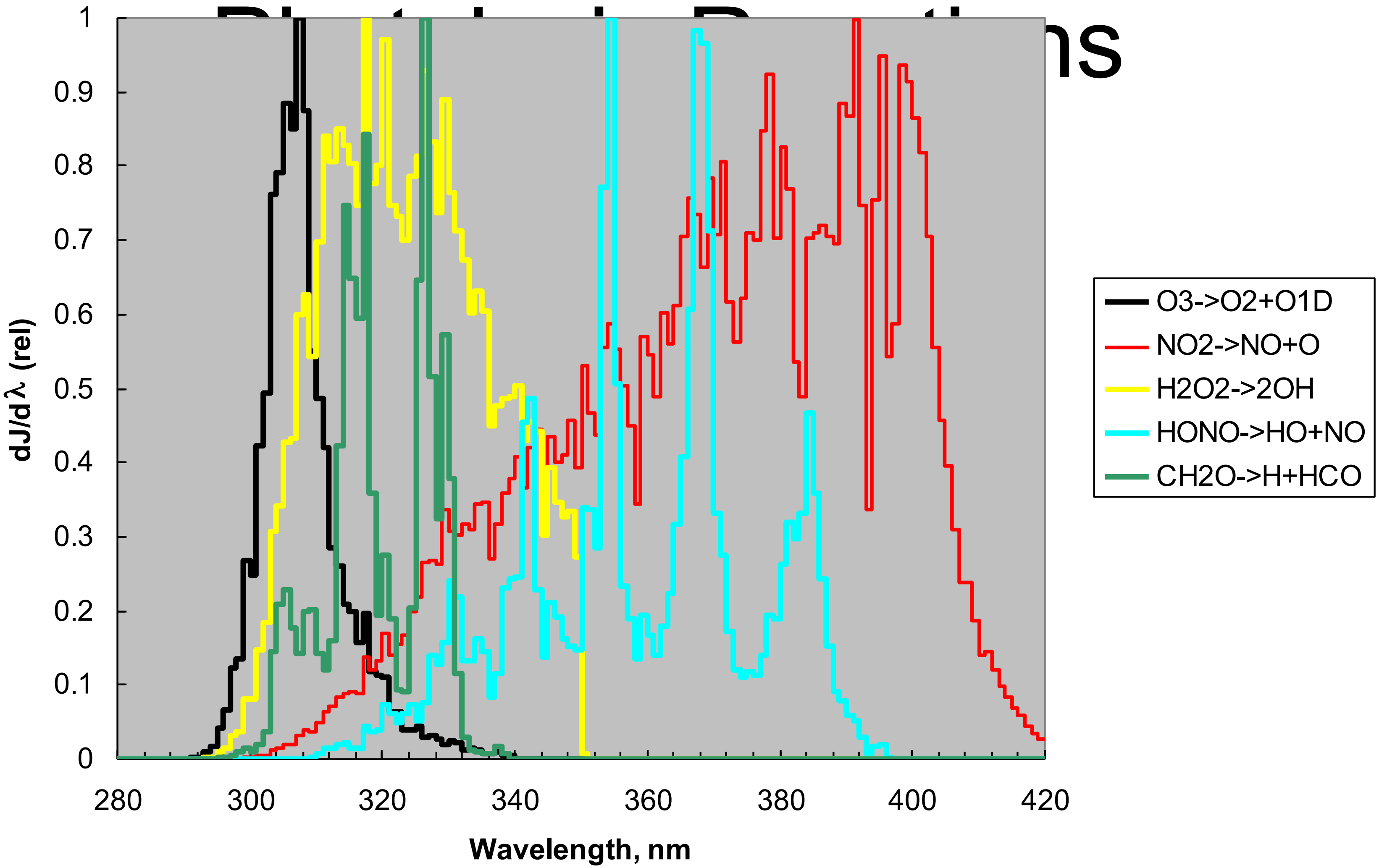
subject to the boundary conditions

at top ($k = N$): $F_o(N) = F_\infty \cos\theta_o$ and $F\downarrow(N) = 0$

at bottom ($k = 1$): $F\uparrow(1) = A[F_o(1) + F\downarrow(1)]$


solve rt eq in each layer, get boundary values:

Wavelengths for Different



surface, overhead sun