PHOTOLYSIS

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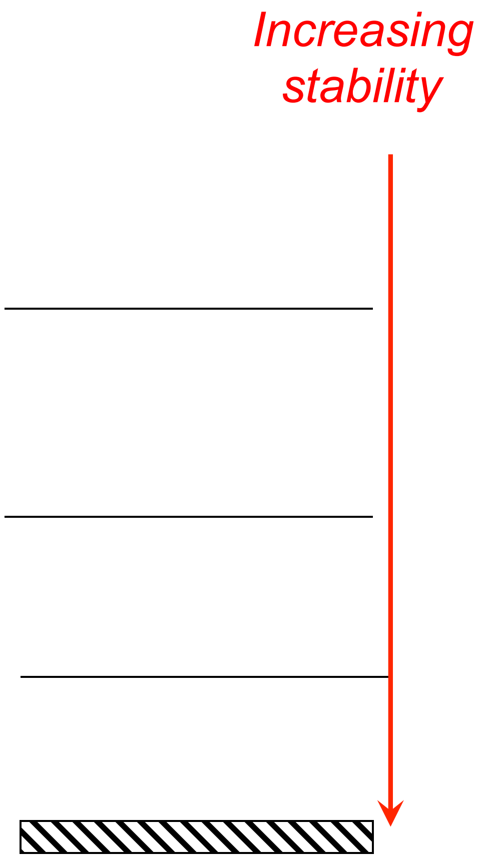
NCAR

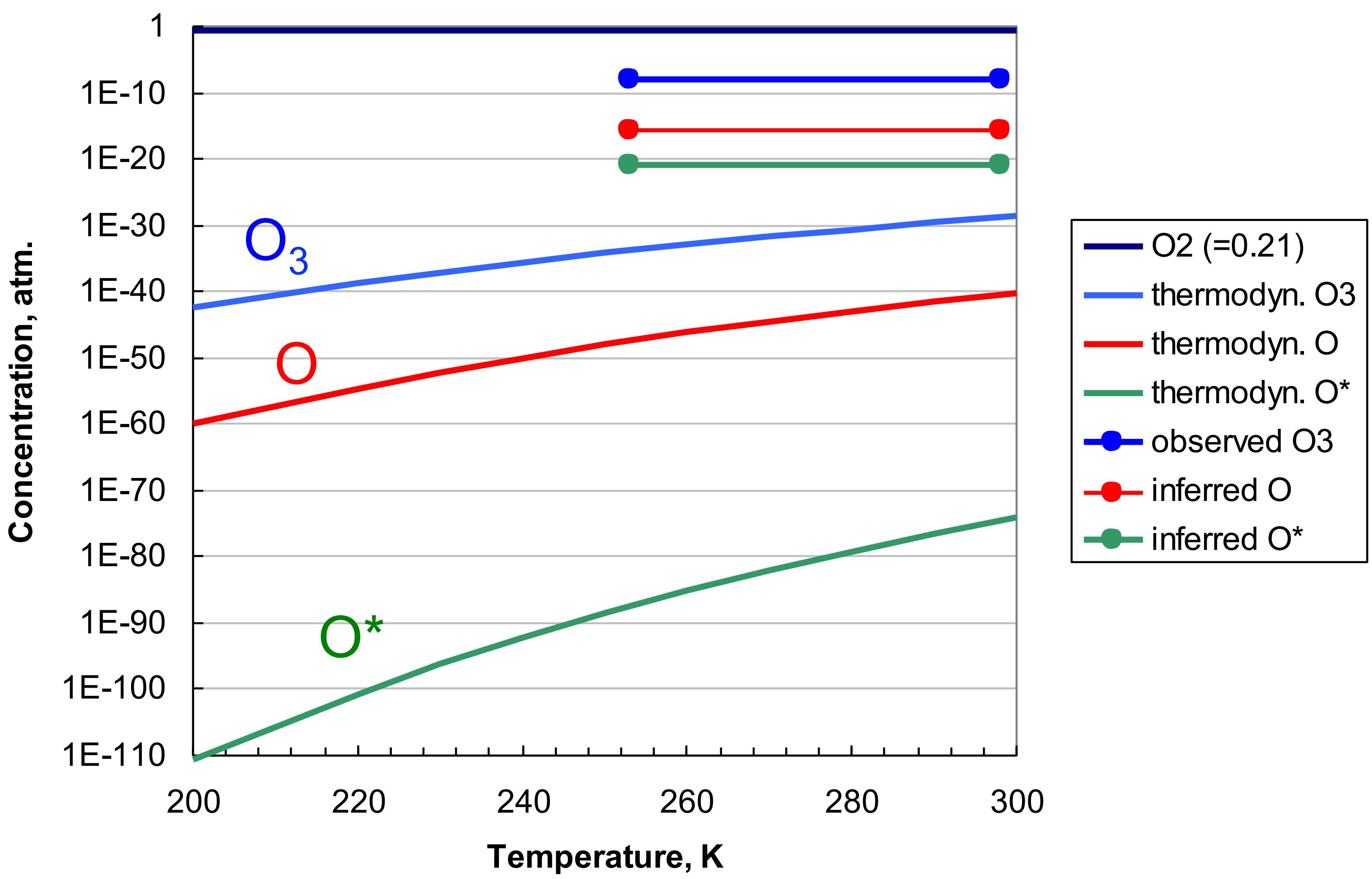
Energetics of Oxygen in the Atmosphere

		ΔH_f(298K) kcal mol^{-1}
Excited atoms	$O^*(^1D)$	104.9
Ground state atoms	$O\ (^3P)$	59.6
Ozone	O_3	34.1
Normal molecules	O_2	0



Atmospheric Oxygen

Thermodynamic vs. Actual



Photochemistry

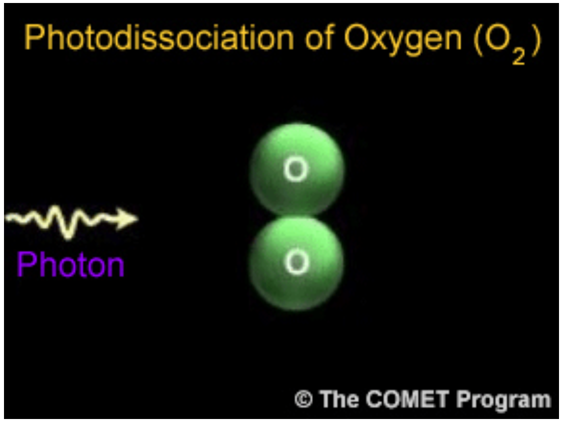
- Thermodynamics alone cannot explain atmospheric amounts of O_3, O, O*

- Need
  - energy input, e.g.

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

  - chemical reactions, e.g.

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



<u>= Photochemistry</u>

Quantifying Photolysis Processes

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

Photolysis rates:

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

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

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

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

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

$\propto$ probability of photon near molecule.

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

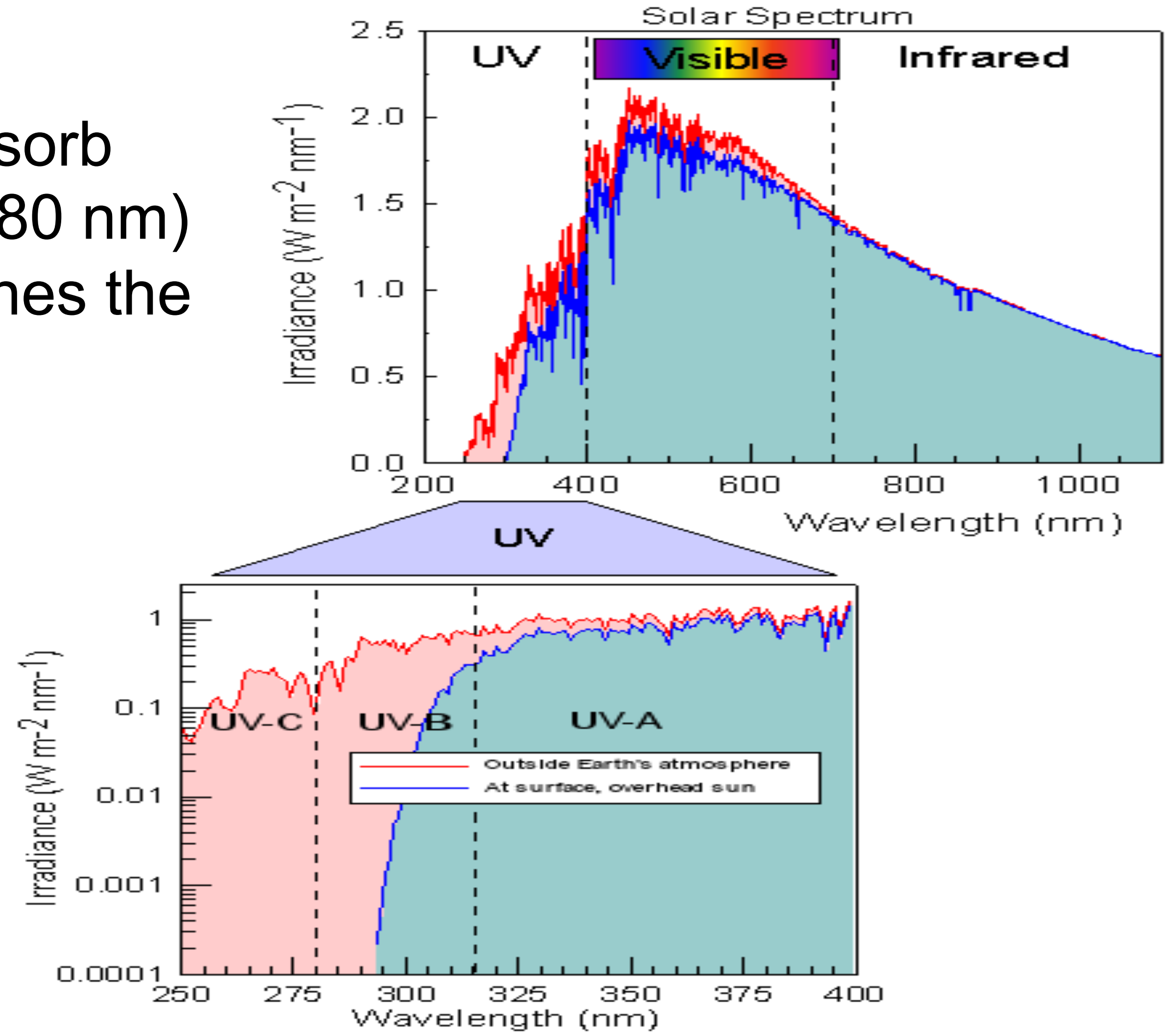
$\propto$ probability that photon is absorbed.

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

$\propto$ probability that absorbed photon causes dissociation.

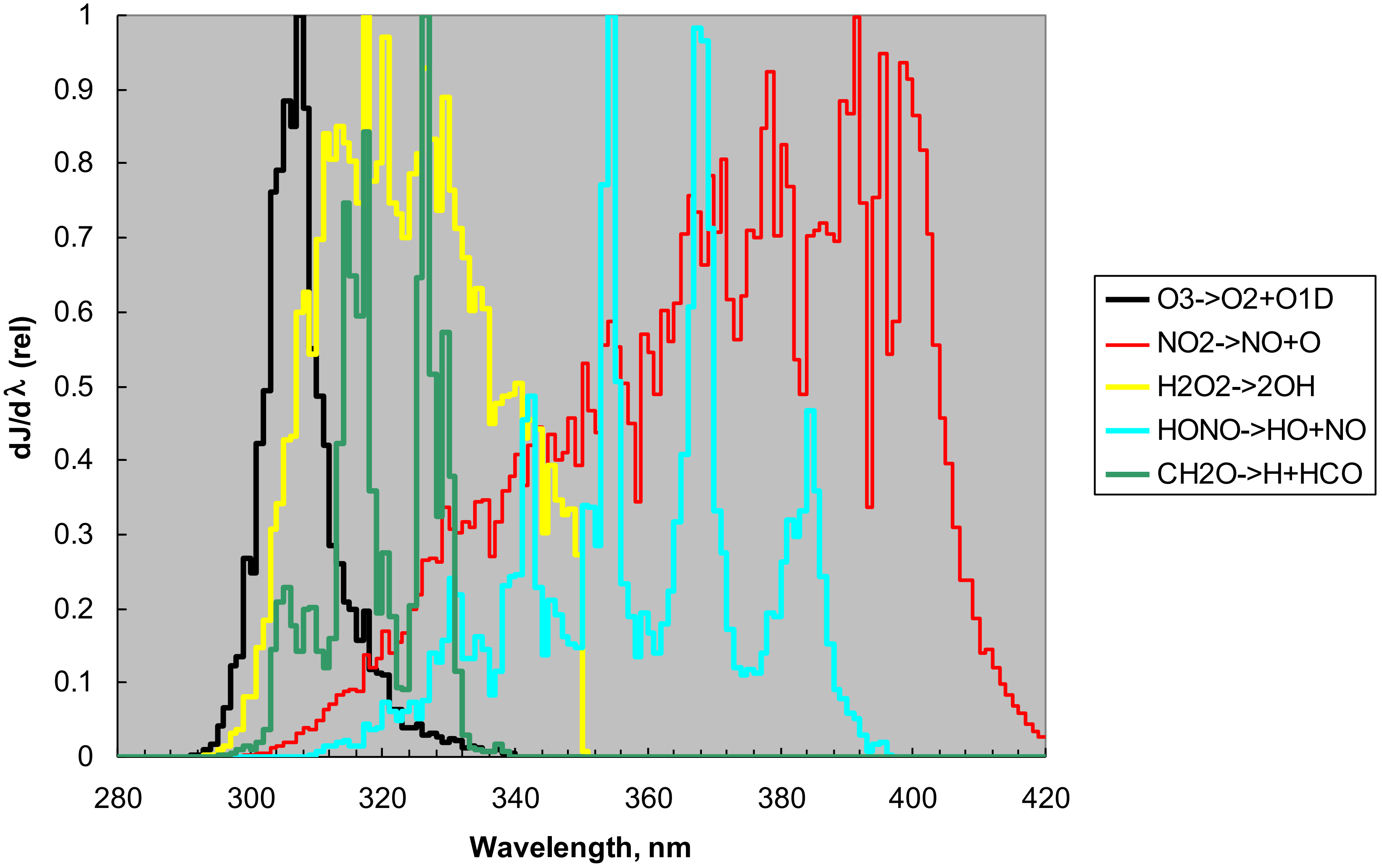
Solar Spectrum

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



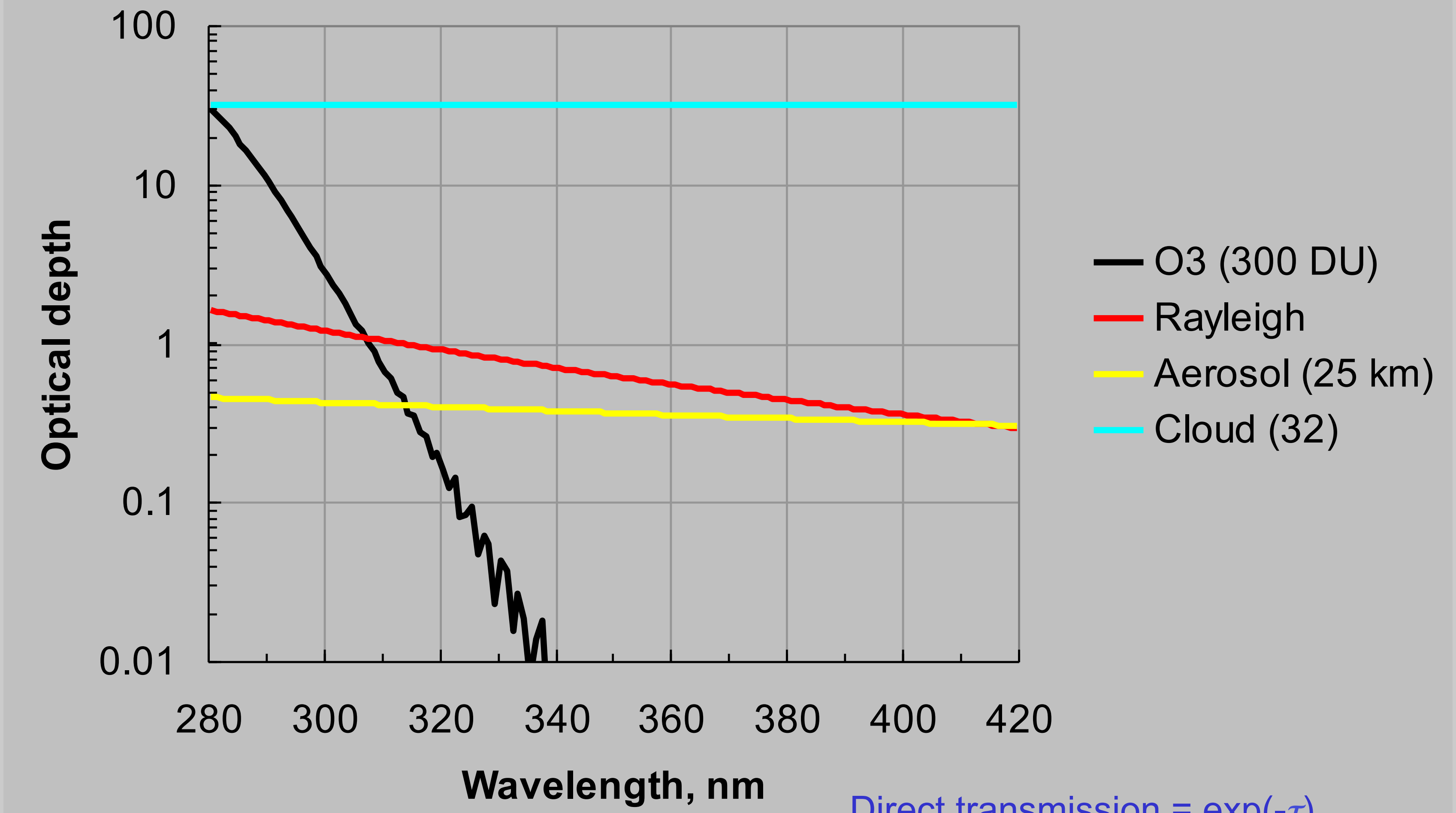
UNEP, 2002

Spectral Region For Tropospheric Photochemistry



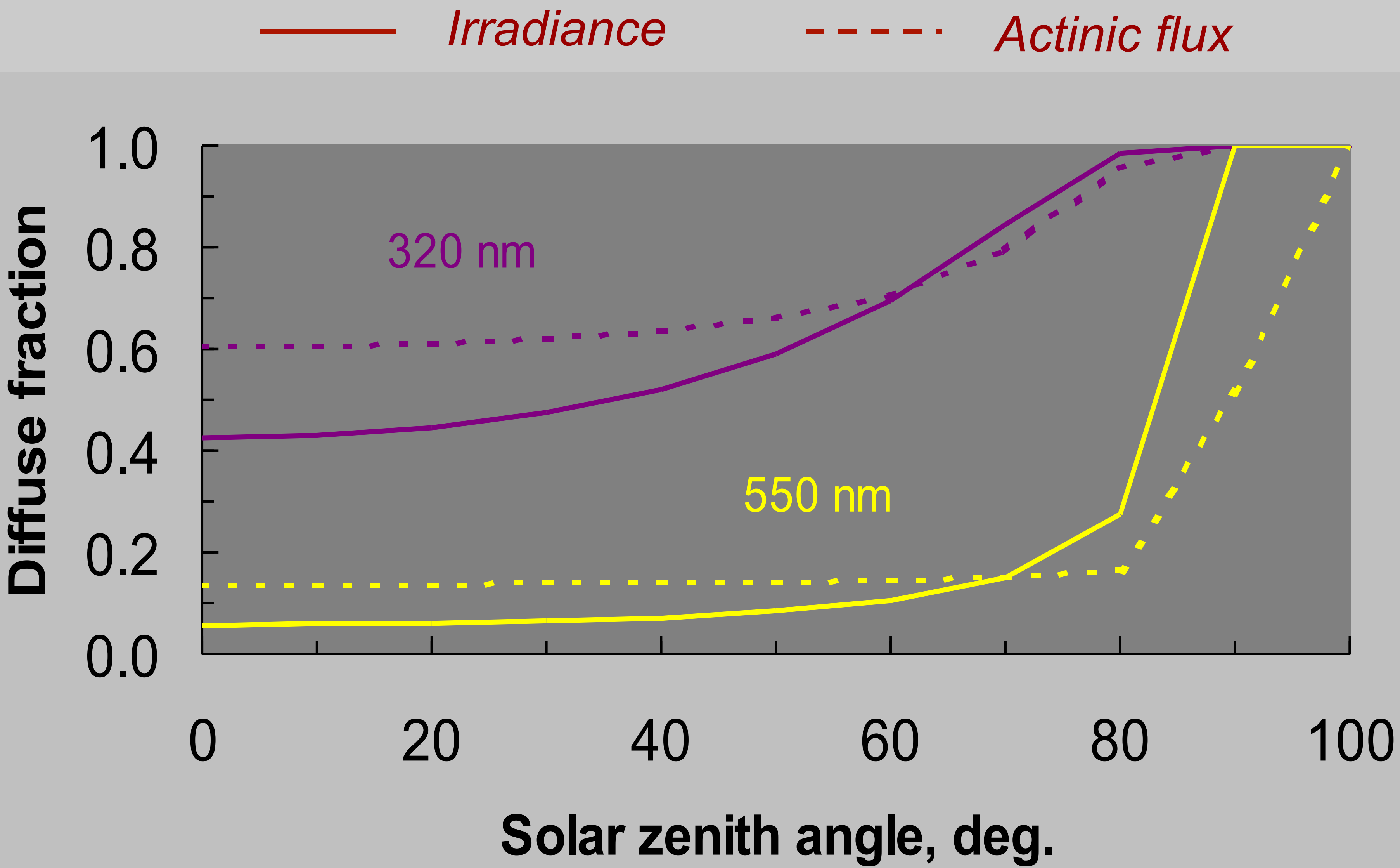
surface, overhead sun

Typical Vertical Optical Depths, τ



Direct transmission = exp(-τ)
Diffuse transmission can be much larger

DIFFUSE LIGHT - CLEAN SKIES, SEA LEVEL

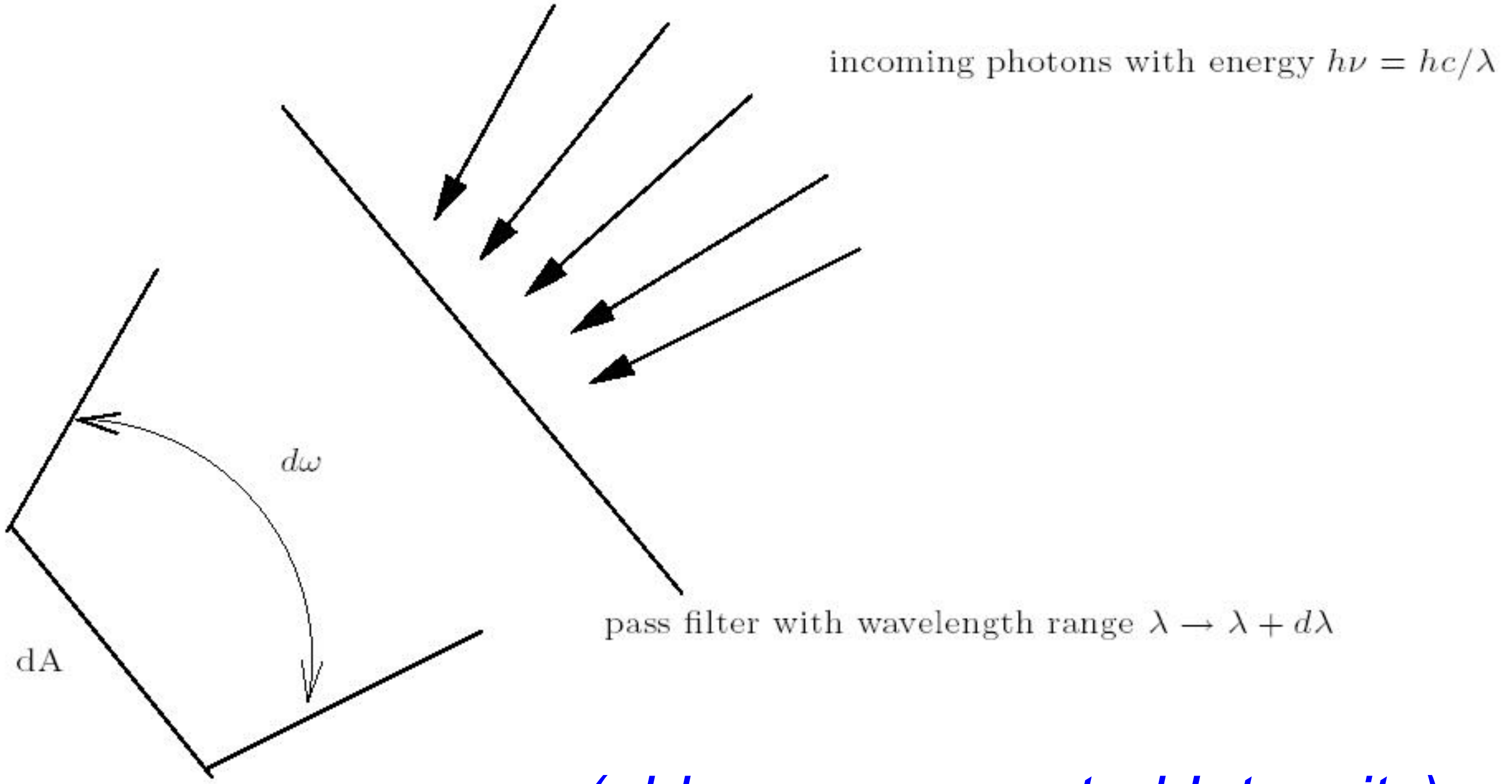


RADIATIVE TRANSFER CONCEPTS

Spectral Radiance, I

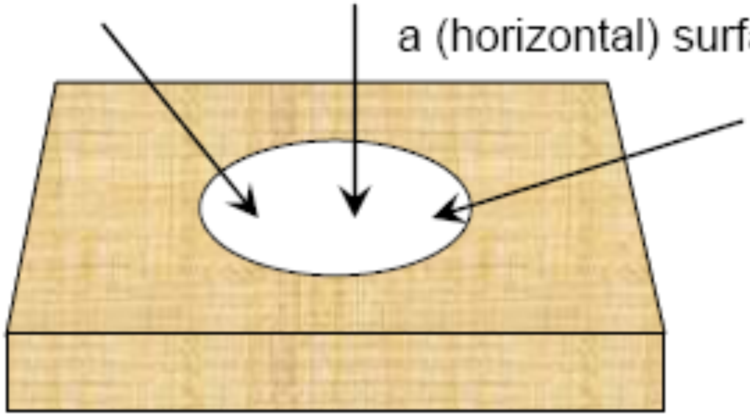
$I(\lambda,\theta,\phi) = N(hc/\lambda) / (dt\ dA\ d\omega\ d\lambda)$

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

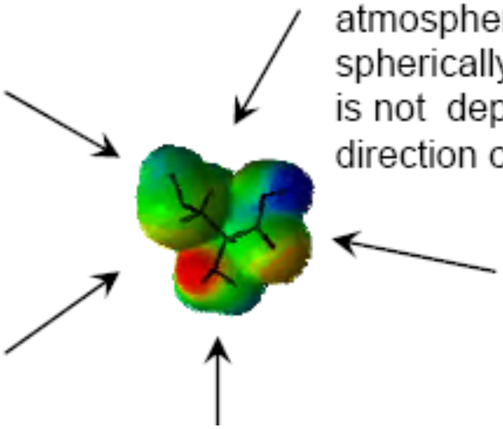


(old name = spectral Intensity)

INTEGRALS OVER ANGULAR INCIDENCE



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.

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

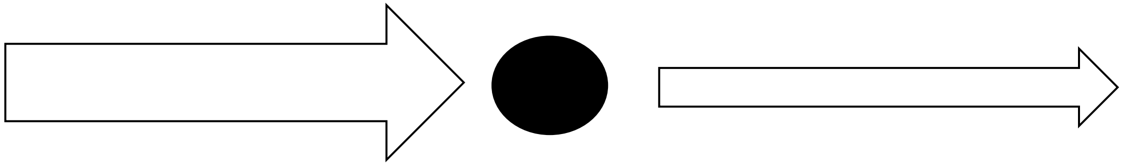
$$F = \int_0^{\pi}\int_0^{2\pi} I(\theta,\varphi)\sin\theta\,\mathrm{d}\varphi\,\mathrm{d}\theta$$

Watts m^{-2}

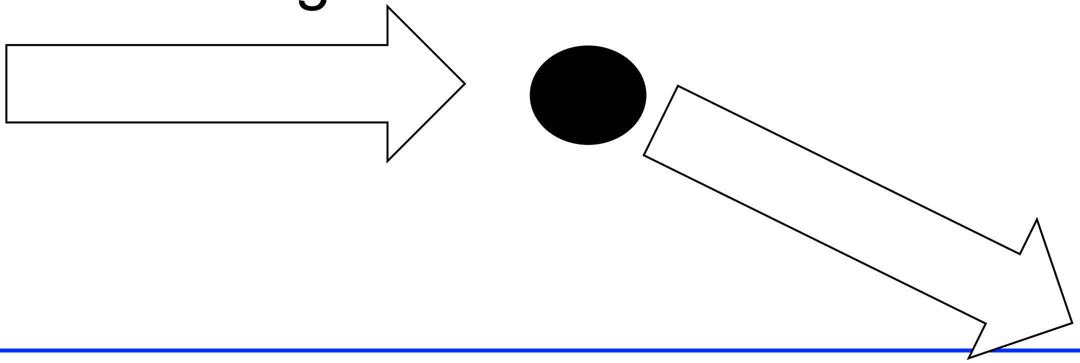
Watts m^{-2} or quanta s^{-1} cm^{-2}

Absorption and Scattering

- Absorption – inelastic, loss of radiant energy:

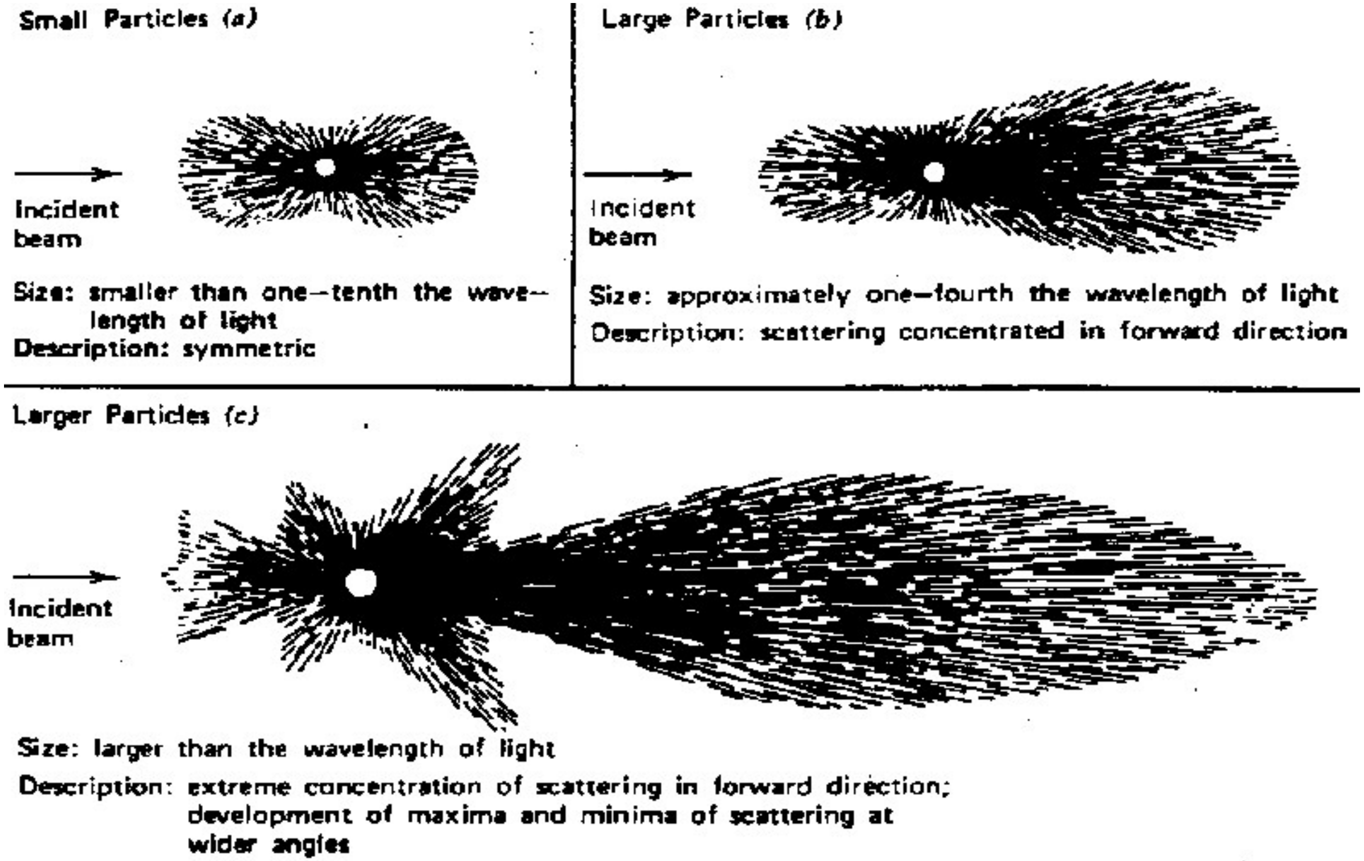


- Scattering – elastic, radiant energy is conserved, direction changes:



SCATTERING PHASE FUNCTIONS

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



Small Particles *(a)*

Size: smaller than one-tenth the wavelength of light
Description: symmetric

Large Particles *(b)*

Size: approximately one-fourth the wavelength of light
Description: scattering concentrated in forward direction

Larger Particles *(c)*

Size: larger than the wavelength of light
Description: extreme concentration of scattering in forward direction; development of maxima and minima of scattering at wider angles

The Radiative Transfer Equation

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)

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

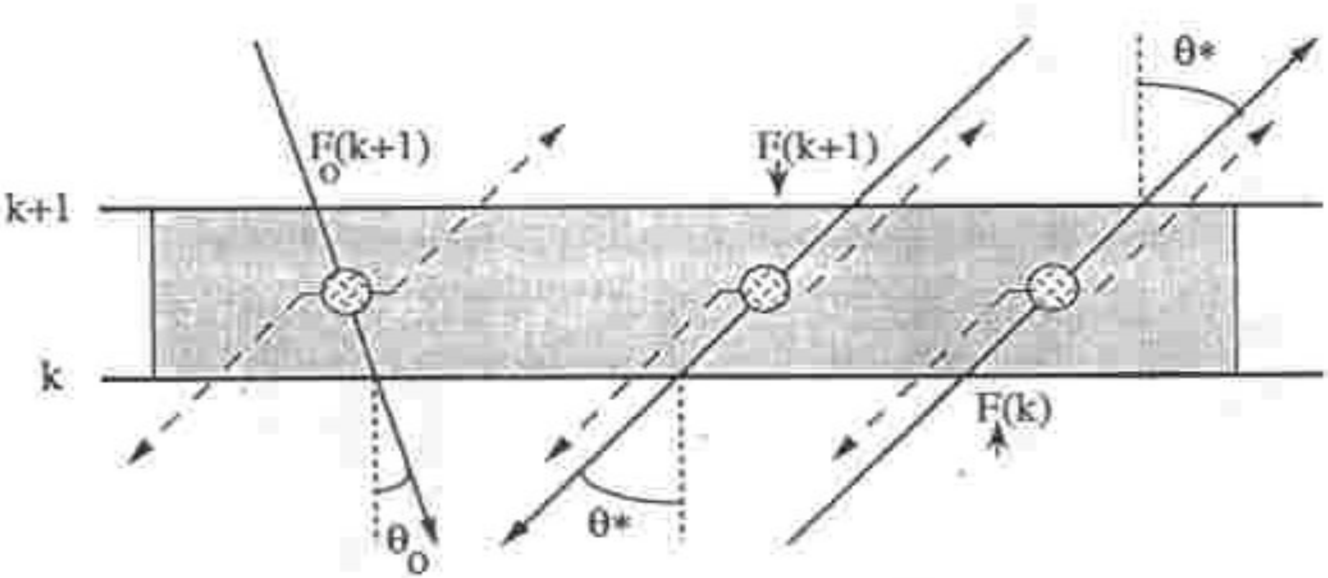
  delta-Eddington, many others

  very fast but not exact
- Monte Carlo

  slow, but ideal for 3D problems
- Others

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

Multiple Atmospheric Layers
Each Assumed to be Homogeneous



Must specify three optical properties:

Optical depth, $\Delta\tau$

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

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

For each layer, must specify $\Delta\tau$, ω_o, g:

1. Vertical optical depth, $\Delta\tau(\lambda, z) = \sigma(\lambda, z)\, n(z)\, \Delta z$

for molecules: $\Delta\tau(\lambda, z) \sim 0 - 30$

Rayleigh scatt. $\sim 0.1 - 1.0 \sim \lambda^{-4}$

O_3 absorption $\sim 0 - 30$

for aerosols: $0.01 - 5.0$

$\Delta\tau(\lambda, z) \sim \lambda^{-\alpha}$

for clouds: $1\text{-}1000$

$\alpha \sim 0$

cirrus $\sim 1\text{-}5$

cumulonimbus $\sim > 100$

For each layer, must specify $\Delta\tau$, ω_o, g:

2. Single scattering albedo, $\omega_o(\lambda, z) =$ scatt./(scatt.+abs.)

range 0 - 1

limits: pure scattering = 1.0
pure absorption = 0.0

for molecules, strongly λ-dependent, depending on absorber amount, esp. O_3

for aerosols:

sulfate ~ 0.99
soot, organics ~ 0.8 or less,
not well known but probably higher at shorter λ, esp. in UV

for clouds: typically 0.9999 or larger (vis and UV)

For each layer, must specify $\Delta\tau$, ω_o, g:

3. Asymmetry factor, $g(\lambda, z)$ = first moment of phase function

$$g = \frac{1}{2}\int_{-1}^{+1} P(\Theta)\cos\Theta \, d(\cos\Theta)$$

range -1 to + 1

- pure back-scattering = -1
- isotropic or Rayleigh = 0
- pure forward scattering = +1

strongly dependent on particle size

- for aerosols:, typically 0.5-0.7
- for clouds, typically 0.7-0.9

Mie theory for spherical particles: can compute $\Delta\tau$, ω_o, g
from knowledge of λ*, particle radius and complex index of refraction*

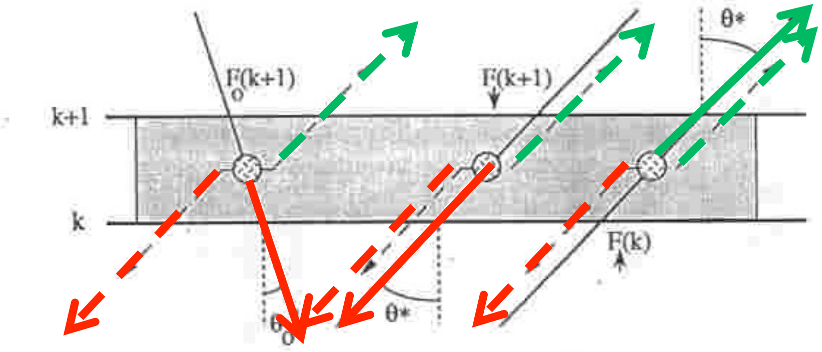
SIMPLE 2-STREAM METHOD:

3 Equations for each layer

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

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

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



subject to the boundary conditions

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

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

AEROSOLS

Many different types of aerosols

- Size distributions
- Composition (size-dependent)

Need to determine aerosol optical properties:

$\tau(\lambda)$ = optical depth
ω_o = single scattering albedo
$P(\Theta)$ = phase function or g = asymmetry factor

Mie Scattering Theory

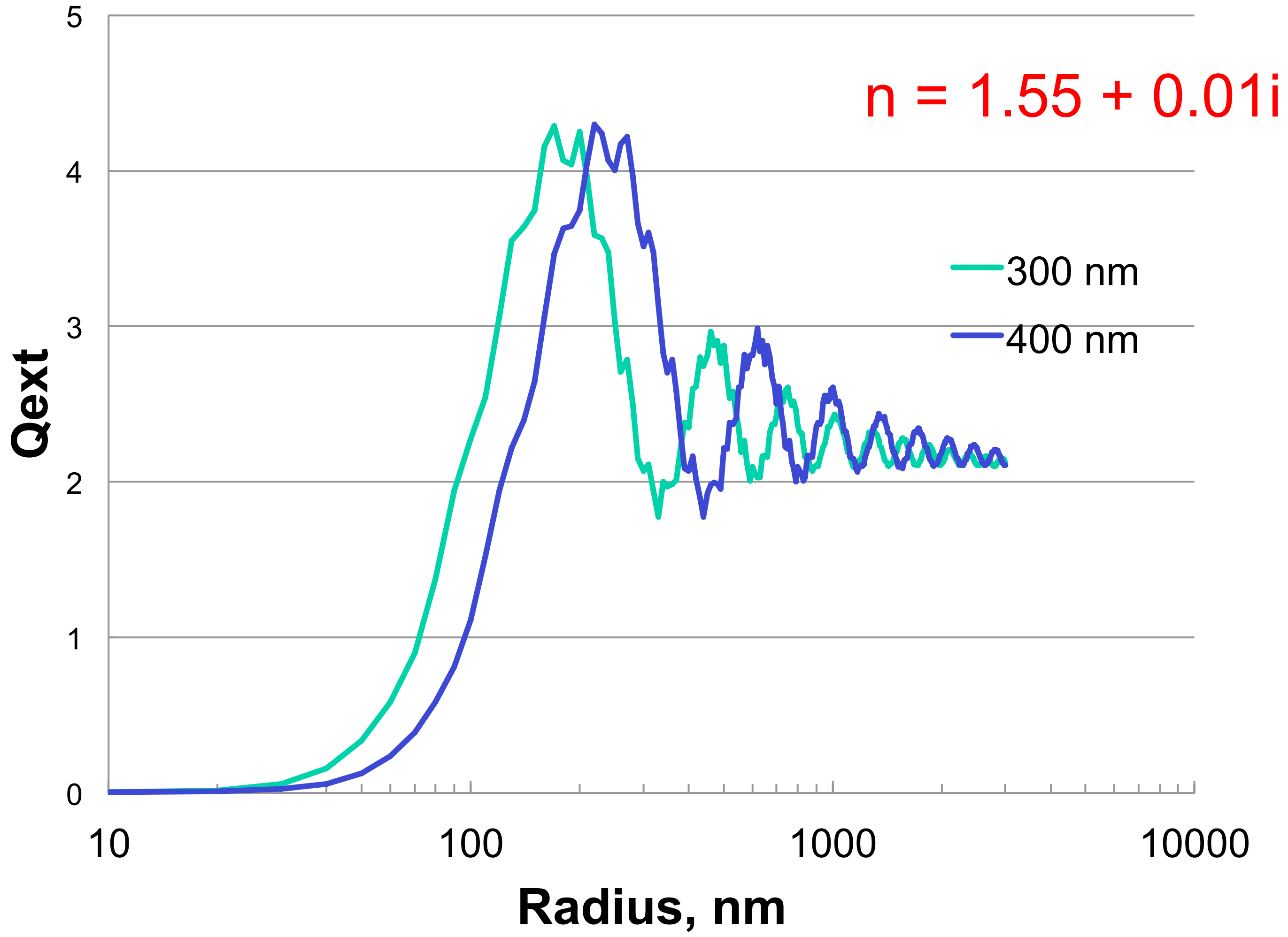
For spherical particles, given:

Complex index of refraction: $n = m + ik$
Size parameter: $\alpha = 2\pi r / \lambda$

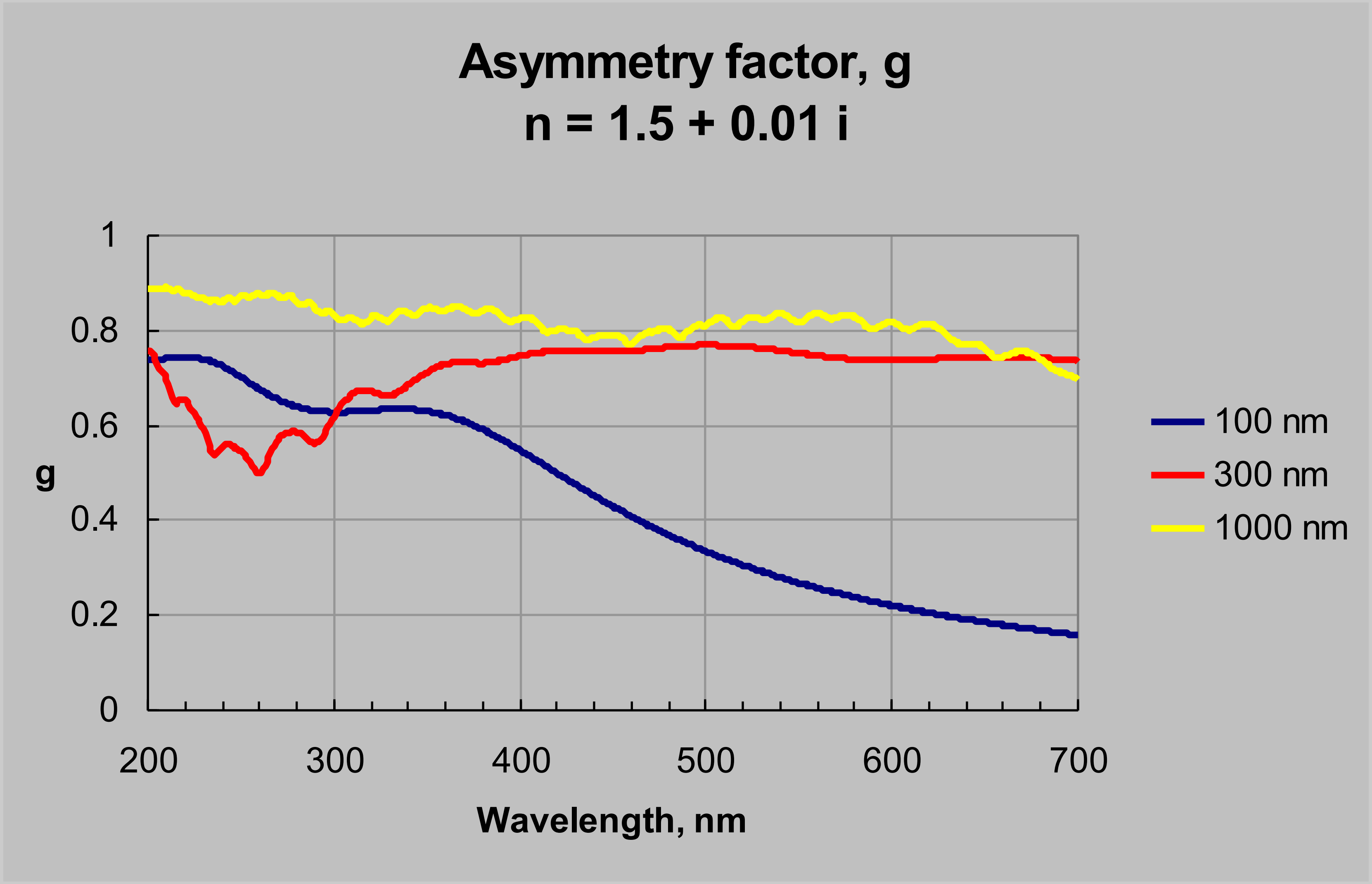
Can compute:

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

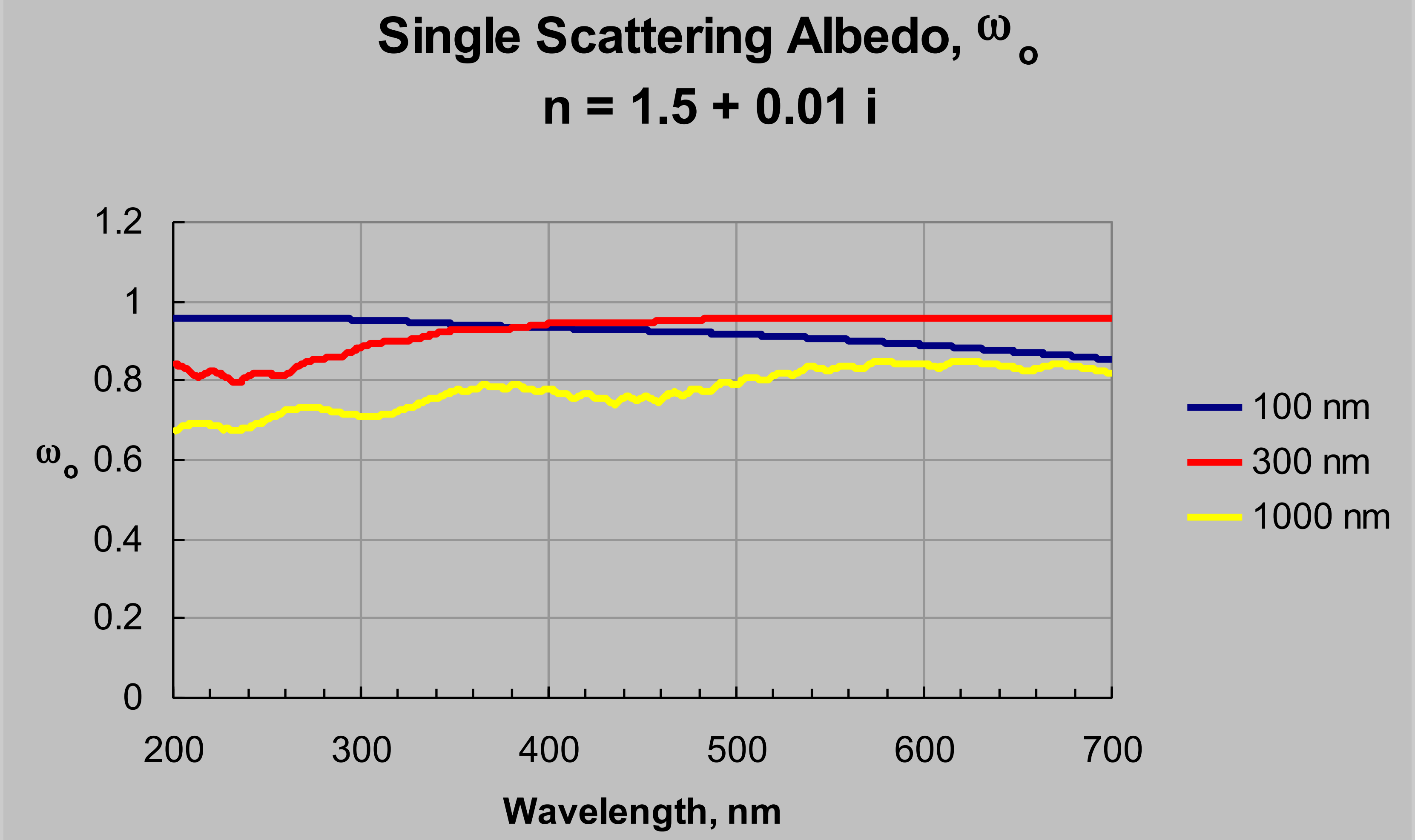
Extinction Efficiency, Q_{ext}



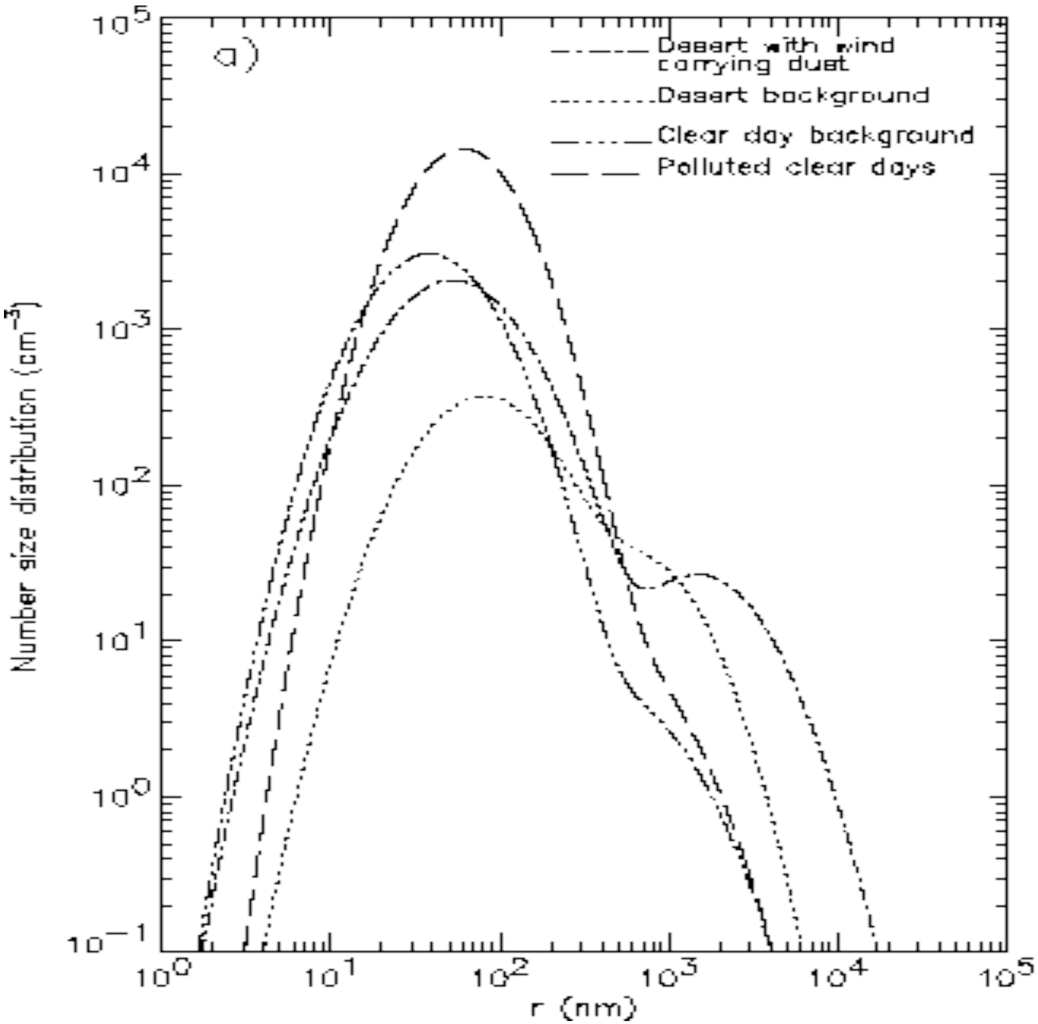
Phase function or Asymmetry factor, g



Single Scattering Albedo = Q_{scatt}/Q_{ext}



Aerosol size distributions



Optical properties of aerosol ensembles

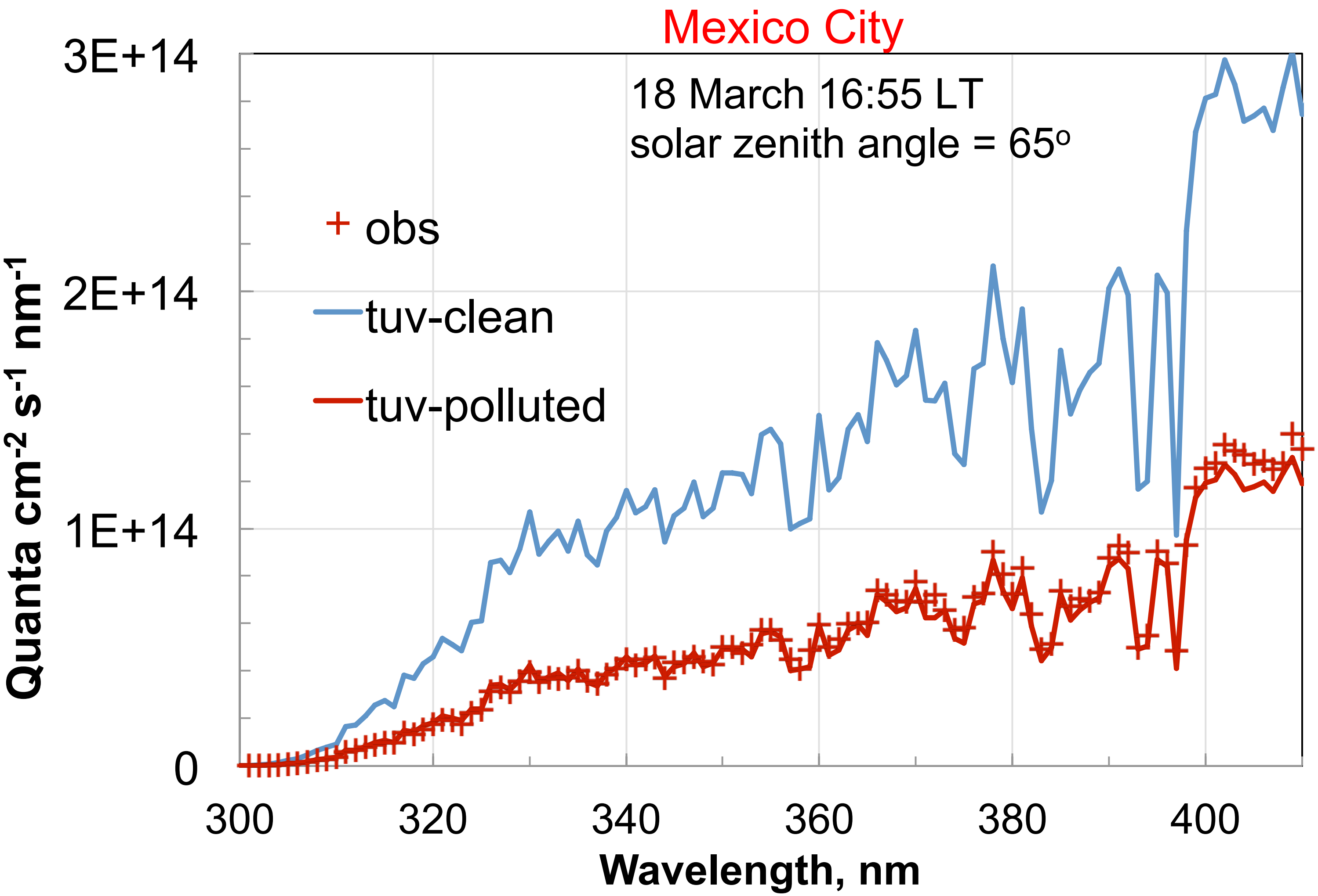
Total extinction coefficient = $$K_e(\lambda) = \int_0^\infty \pi r^2 Q_e(r,\lambda) n(r)\,\mathrm{d}r$$

Total scattering coefficient = $$K_s(\lambda) = \int_0^\infty \pi r^2 Q_s(r,\lambda) n(r)\,\mathrm{d}r$$

Average single scattering albedo = $$\varpi_o(\lambda) = K_s(\lambda) / K_e(\lambda)$$

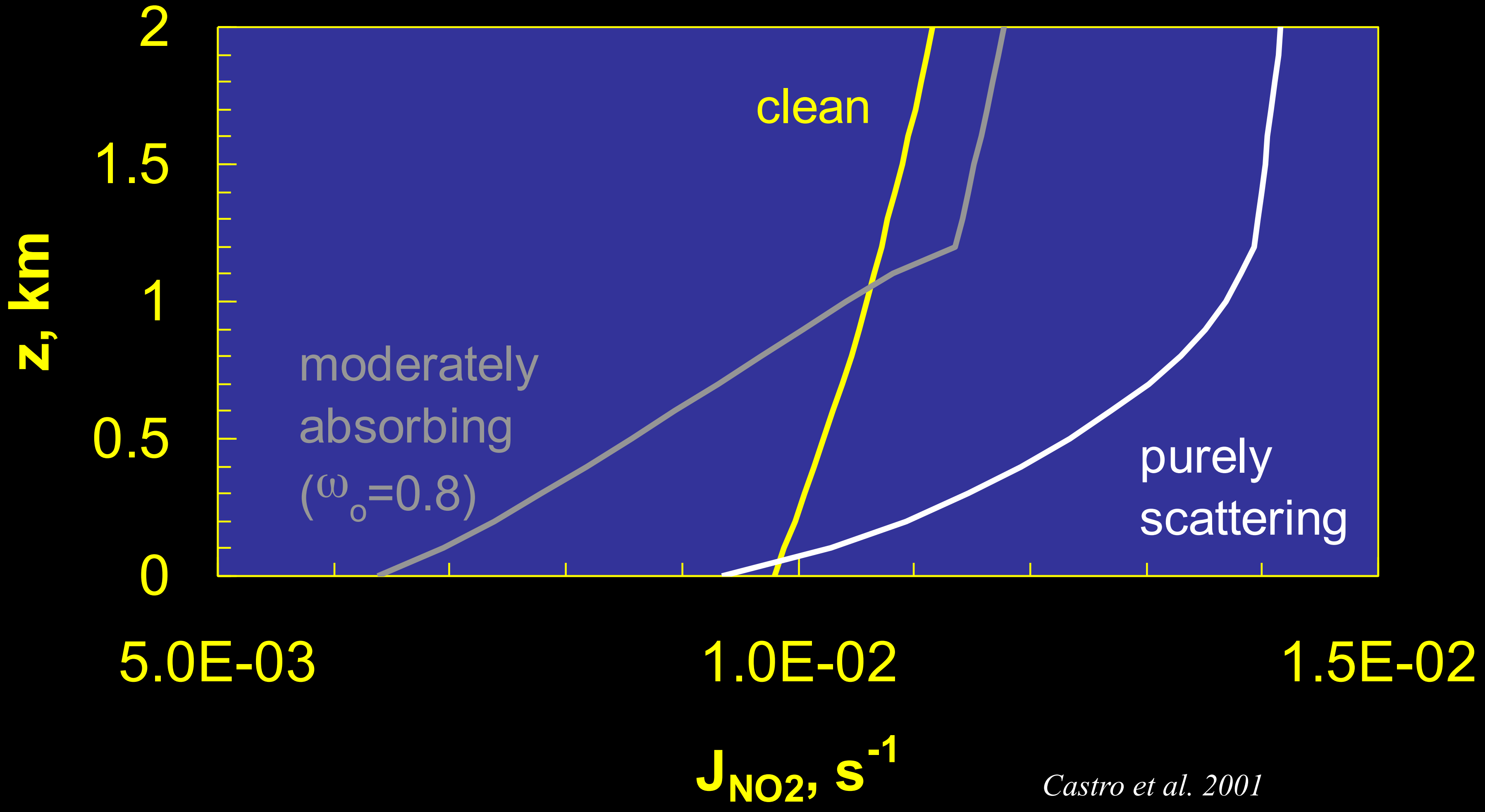
Average asymmetry factor = $$\bar{g}(\lambda) = \frac{\int_0^\infty g(r,\lambda) \pi r^2 Q_s(r,\lambda) n(r)\,\mathrm{d}r}{\int_0^\infty \pi r^2 Q_s(r,\lambda) n(r)\,\mathrm{d}r}$$

UV Actinic Flux Reduction → Slower Photochemistry



Madronich, Shetter, Halls, Lefer, AGU'07

Aerosol Effects
NO_2 Photolysis Frequency
19N, April, noon, AOD = 1 at 380 nm



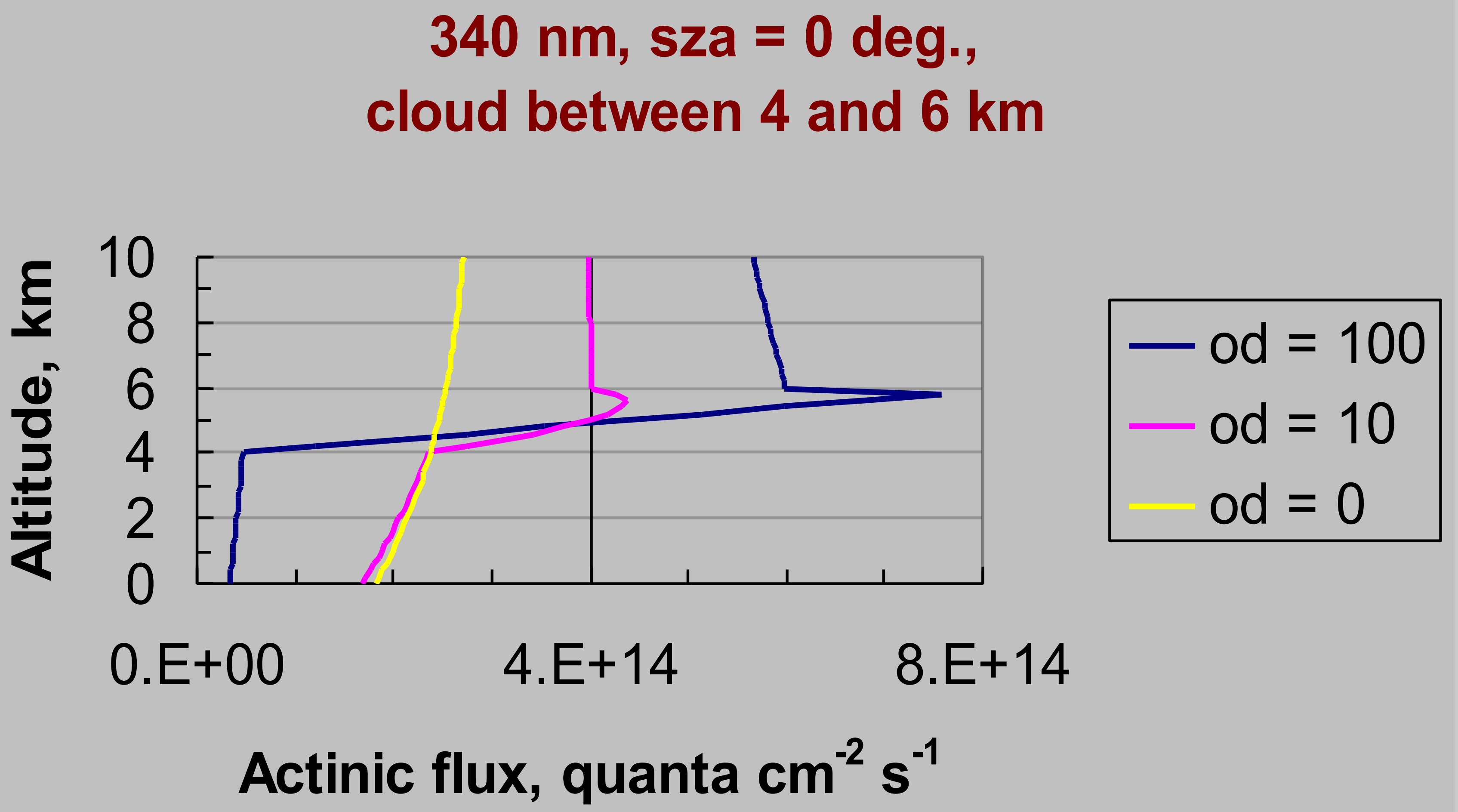
Castro et al. 2001

CLOUDS

UNIFORM CLOUD LAYER

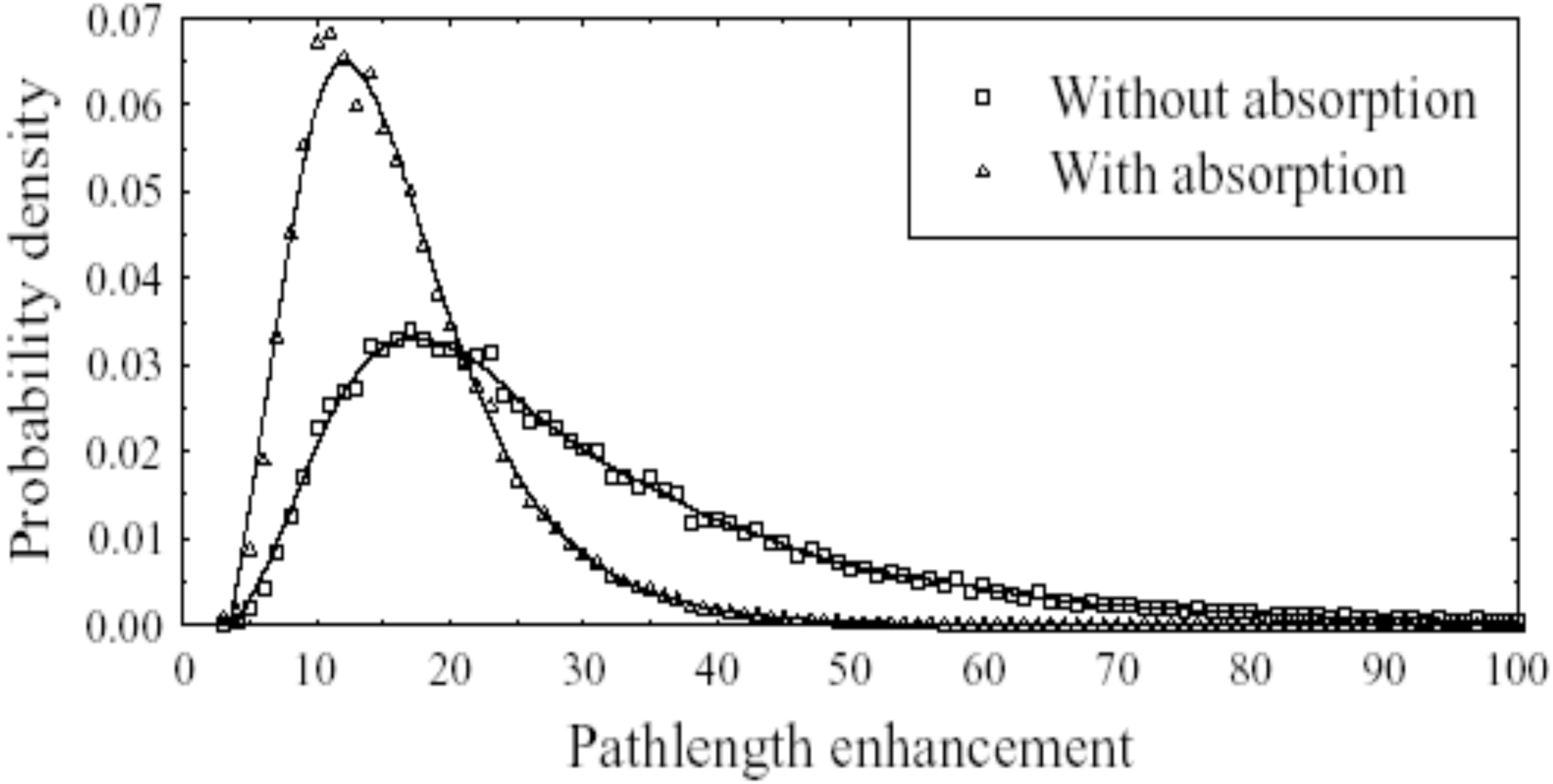
- Above cloud: - high radiation because of reflection
- Below cloud: - lower radiation because of attenuation by cloud
- Inside cloud: - complicated behavior
  - Top half: very high values (for high sun)
  - Bottom half: lower values

EFFECT OF UNIFORM CLOUDS ON ACTINIC FLUX



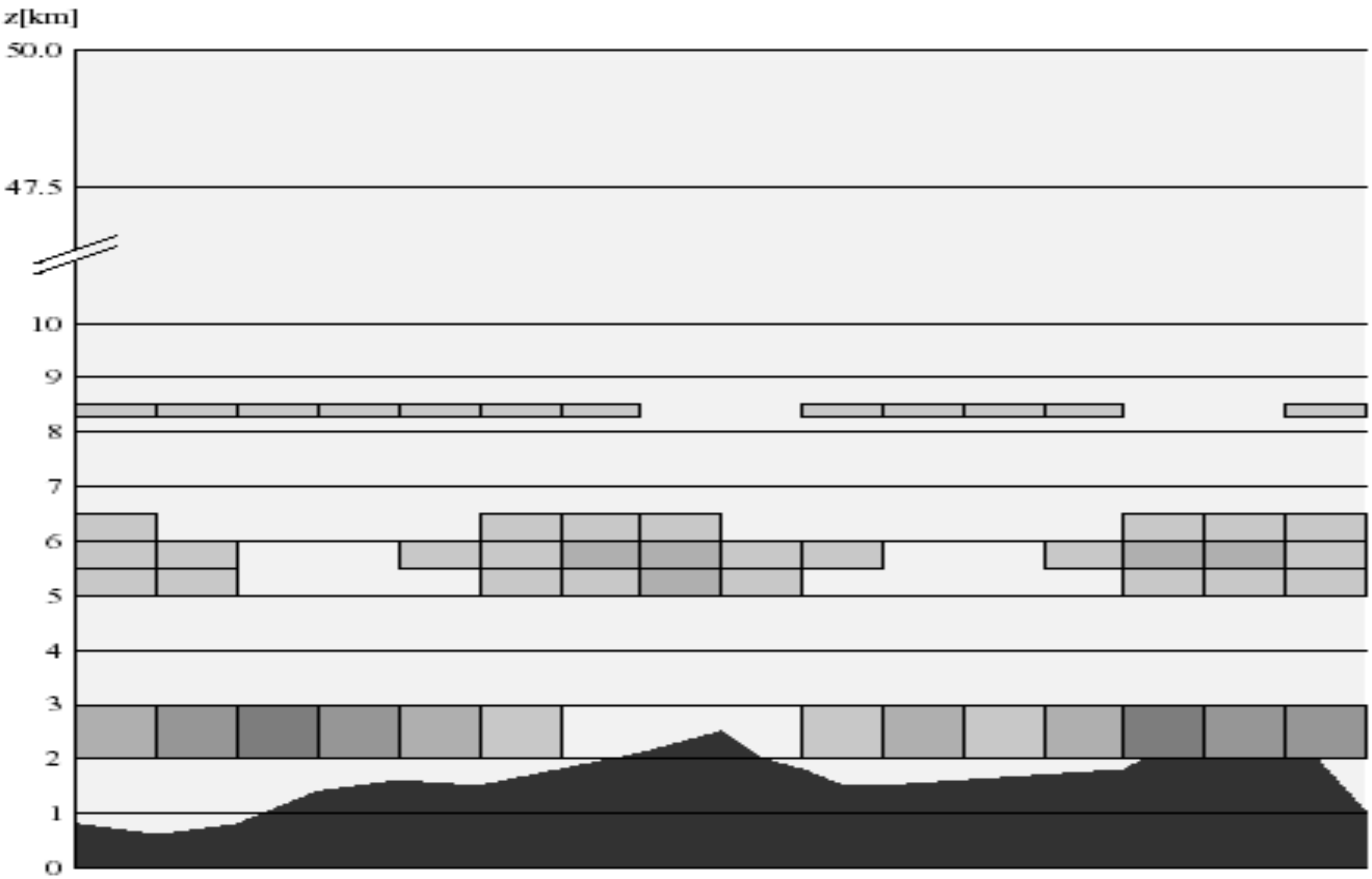
INSIDE CLOUDS:
Photon Path Enhancements

Cumulonimbus, od=400

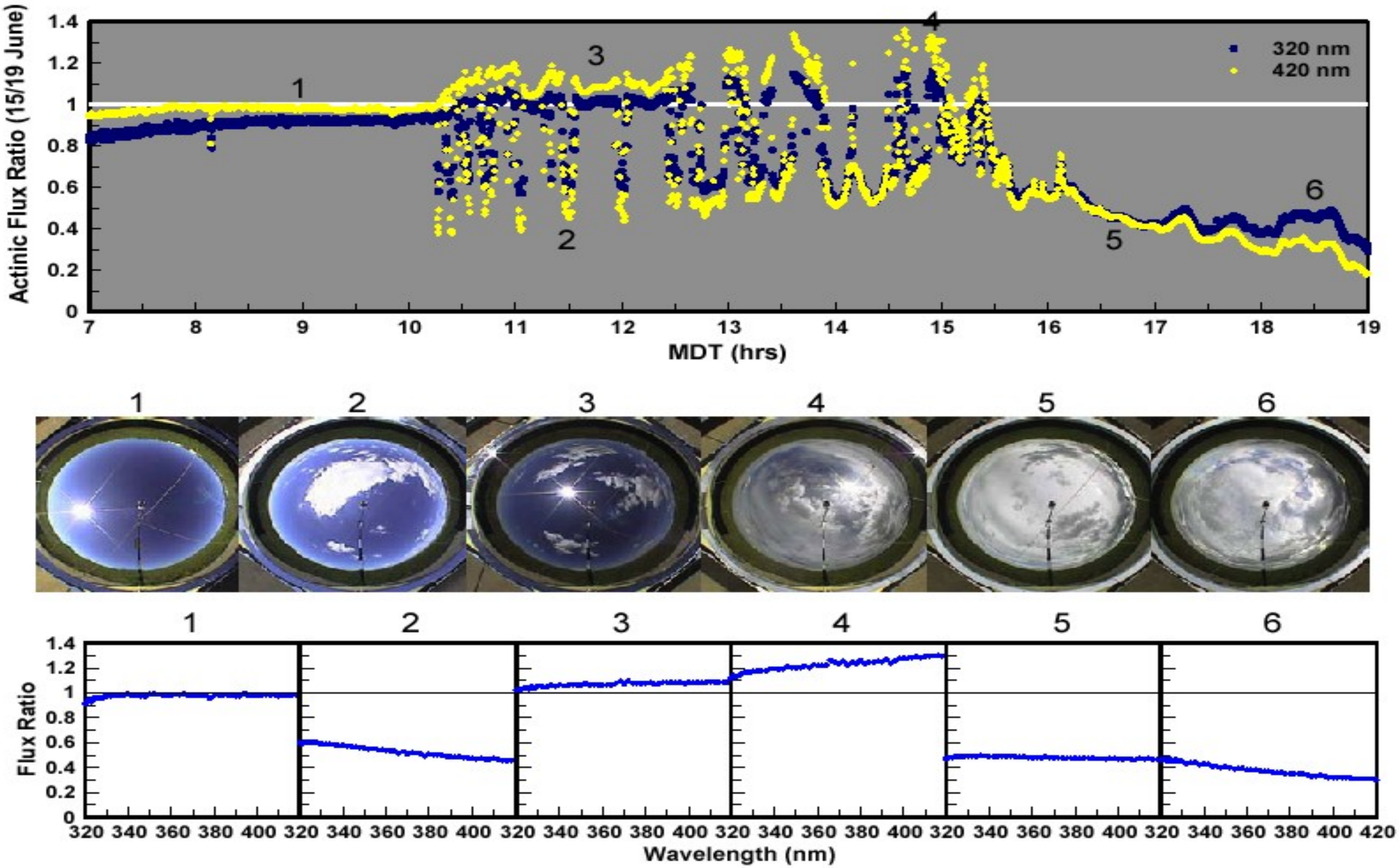


Mayer et al., 1998

Broken Clouds



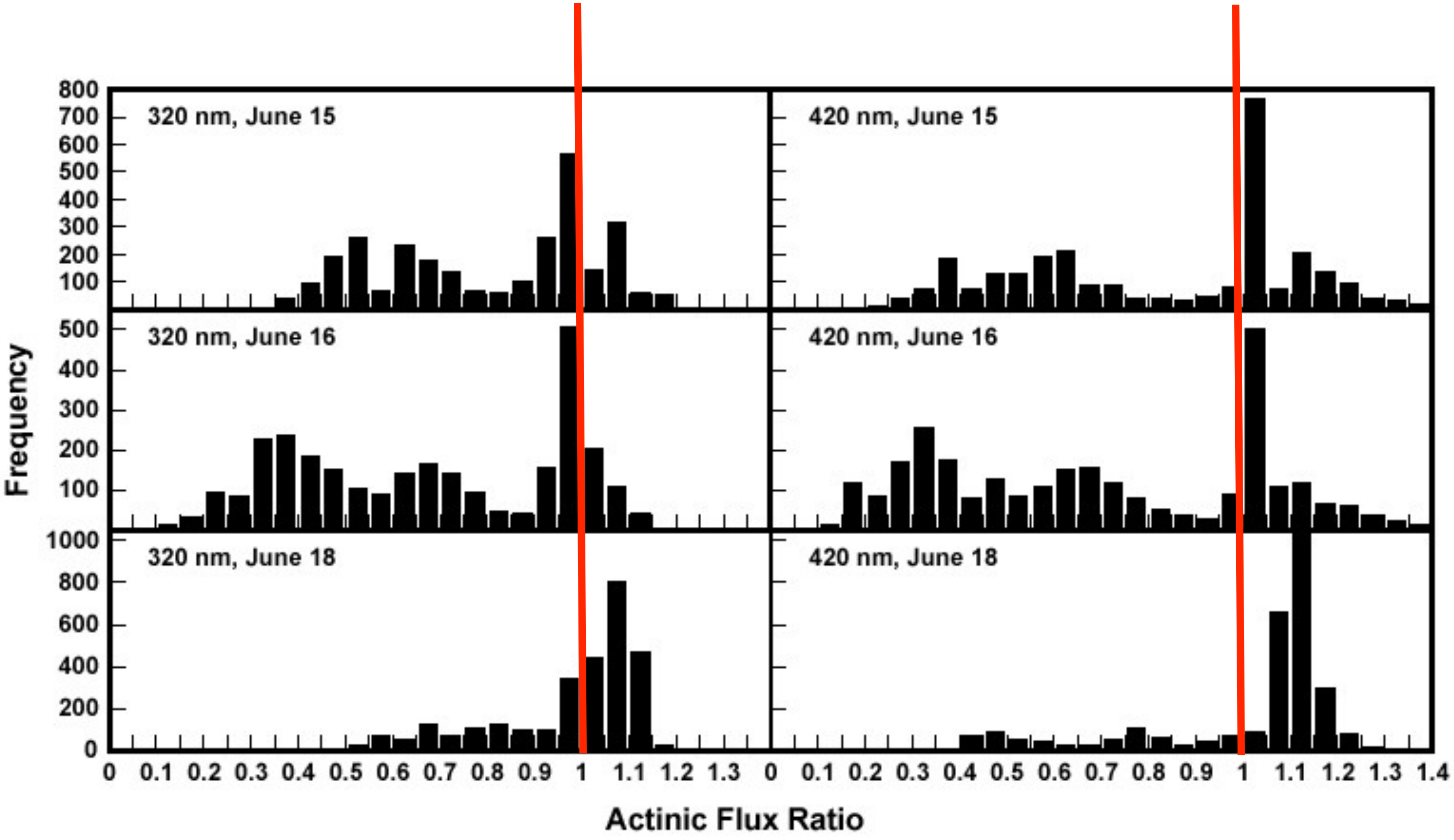
SPECTRAL EFFECTS OF PARTIAL CLOUD COVER



Crafword et al., 2003

PARTIAL CLOUD COVER

Biomodal distributions

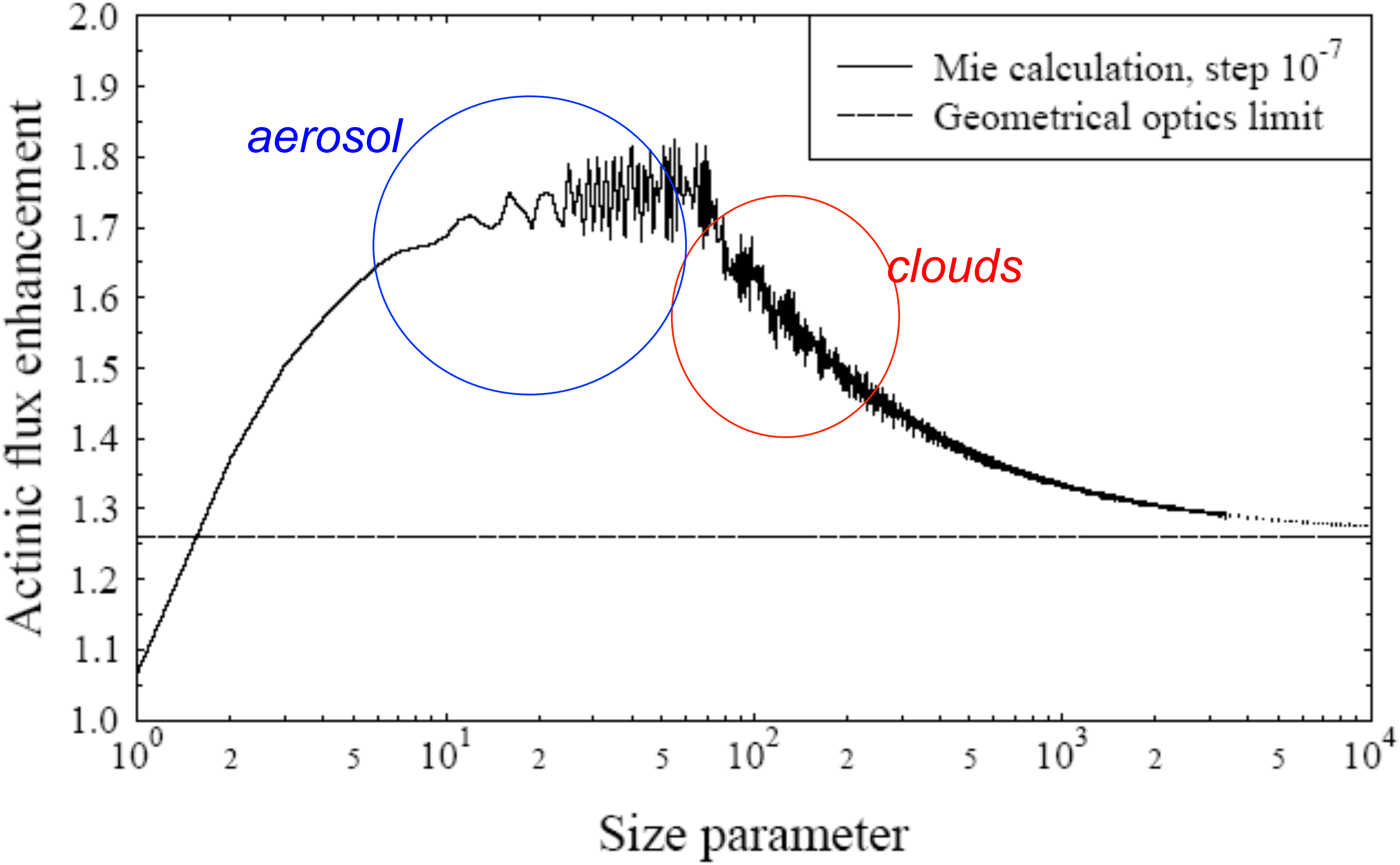


Crafword et al., 2003

Independent Pixel Approximation

- Cloud free:
  - S_o = direct sun
  - D_o = diffuse light from sky
  - G_o = total = $S_o + D_o$
- Completely covered by clouds:
  - S_1 = direct sun (probably very small)
  - D_1 = diffuse light from base of cloud
  - G_1 = total = $S_1 + D_1$
- Mix: Clouds cover a fraction *c* of the sky
  - If sun is not blocked: $G_{NB} = S_o + cD_1 + (1-c)D_o$
  - If sun is blocked: $G_B = S_1 + cD_1 + (1-c)D_o$

Photochemistry Inside Liquid Particles



Mayer and Madronich, 2004

Implementation in WRF-Chem

- Several radiative transfer options:
  - TUV (delta-Eddington, 140 λ's)
  - Fast-J (8-str Feautrier, 17 λ's)
  - Fast-TUV (delta-Eddington, 17 λ's, correction table)
- Sub-grid cloud overlap schemes
  - Max overlap if vertically contiguous, random otherwise
  - Other overlap schemes?
  - Aqueous photochemistry enhancements?
- Aerosols:
  - mixing rules for index of refraction
  - Mie scattering integrated over size distributions, core-shell options