PHOTOLYSIS

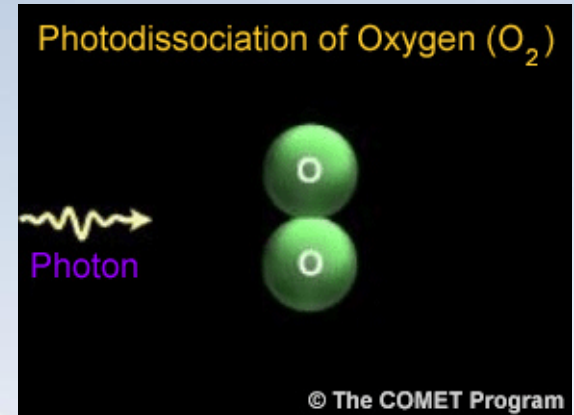Photodissociation of Oxygen (O_2)

Photon

© The COMET Program

Sasha Madronich
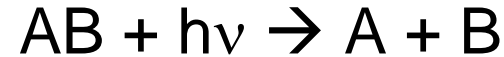*National Center for Atmospheric Research*
Boulder Colorado USA

Boulder, 23 July 2008

NCAR

Quantifying Photolysis Processes

Photolysis reaction: $\qquad$ AB + hν → 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}) $\quad J = \int_{\lambda} F(\lambda)\, \sigma(\lambda)\, \phi(\lambda)\, \mathrm{d}\lambda$

(other names: photodissociation rate coefficient, J-value)

CALCULATION OF PHOTOLYSIS COEFFICIENTS

$$J \; (\text{s}^{-1}) \;\; = \;\; \int_\lambda F(\lambda) \; \sigma(\lambda) \; \phi(\lambda) \; d\lambda$$
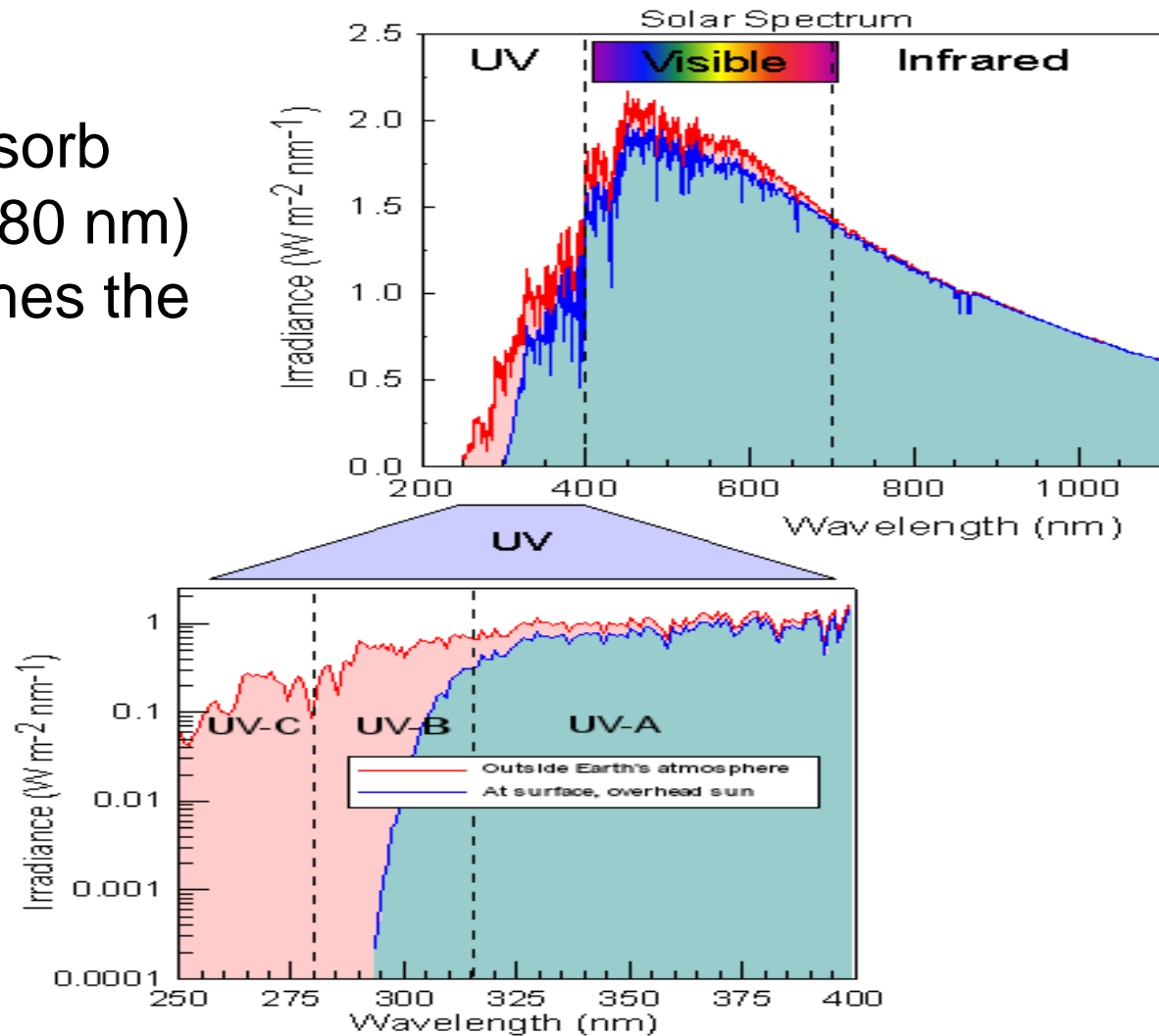
$F(\lambda)$ = spectral actinic flux, quanta $\text{cm}^{-2} \, \text{s}^{-1} \, \text{nm}^{-1}$
$\;\;\;\; \propto$ probability of photon near molecule.

$\sigma(\lambda)$ = absorption cross section, $\text{cm}^2 \, \text{molec}^{-1}$
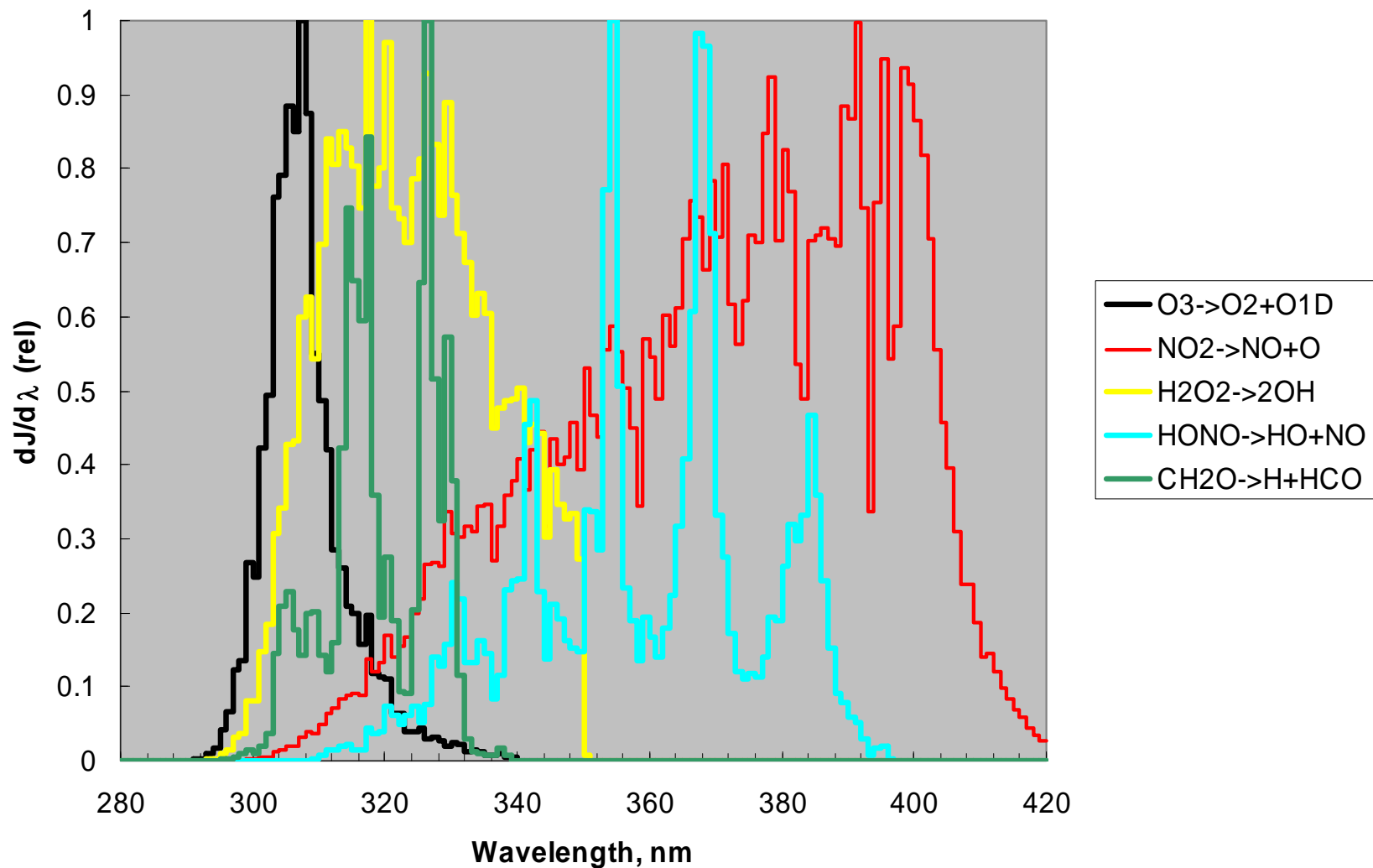$\;\;\;\; \propto$ probability that photon is absorbed.

$\phi(\lambda)$ = 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
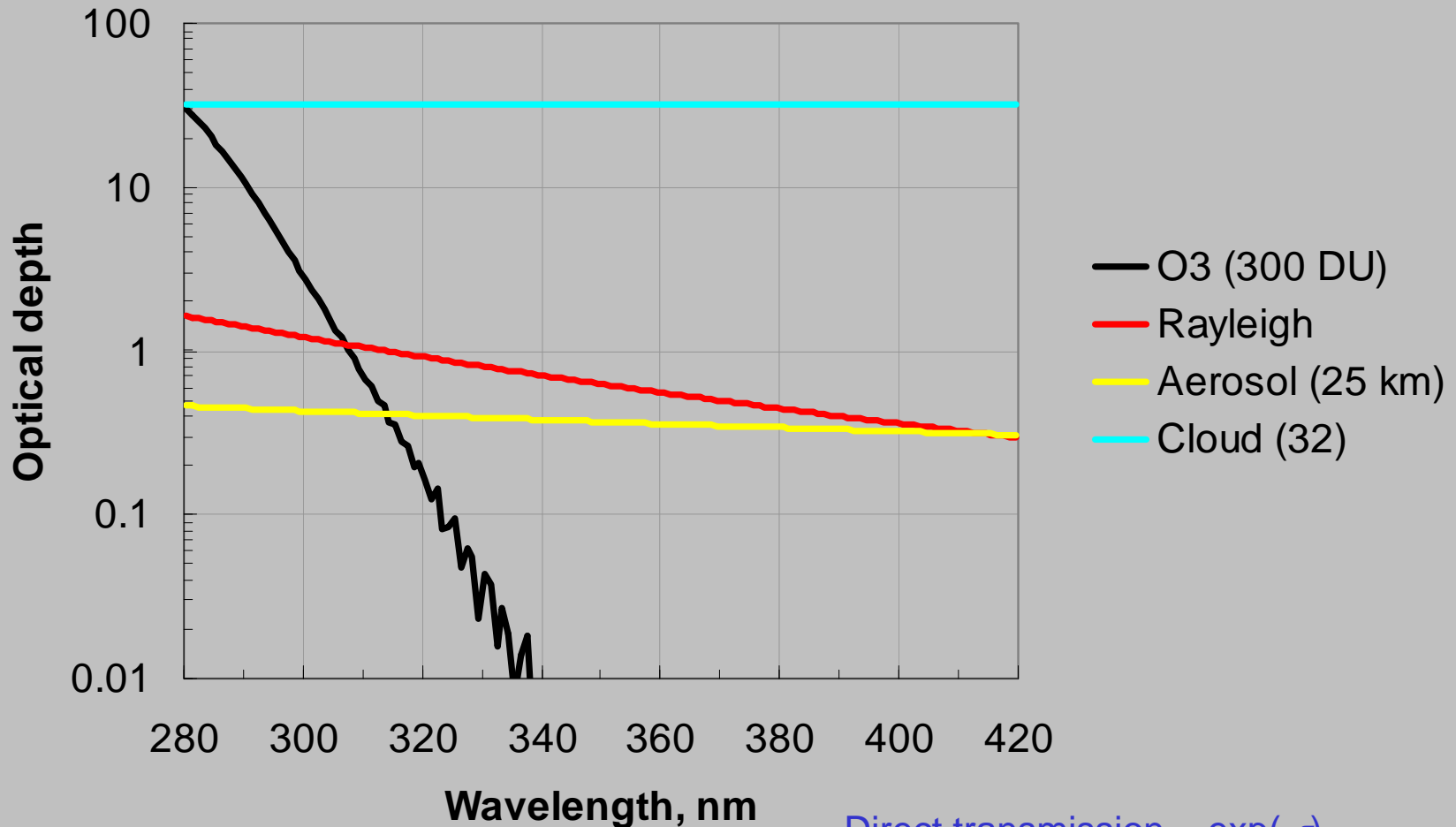
Spectral Region For
Tropospheric Photochemistry

surface, overhead sun

Typical Vertical Optical Depths, τ

O3 (300 DU)
Rayleigh
Aerosol (25 km)
Cloud (32)

Direct transmission = exp($-\tau$)
Diffuse transmission can be much larger

6

DIFFUSE LIGHT - CLEAN SKIES, SEA LEVEL

Irradiance   - - - - - Actinic flux
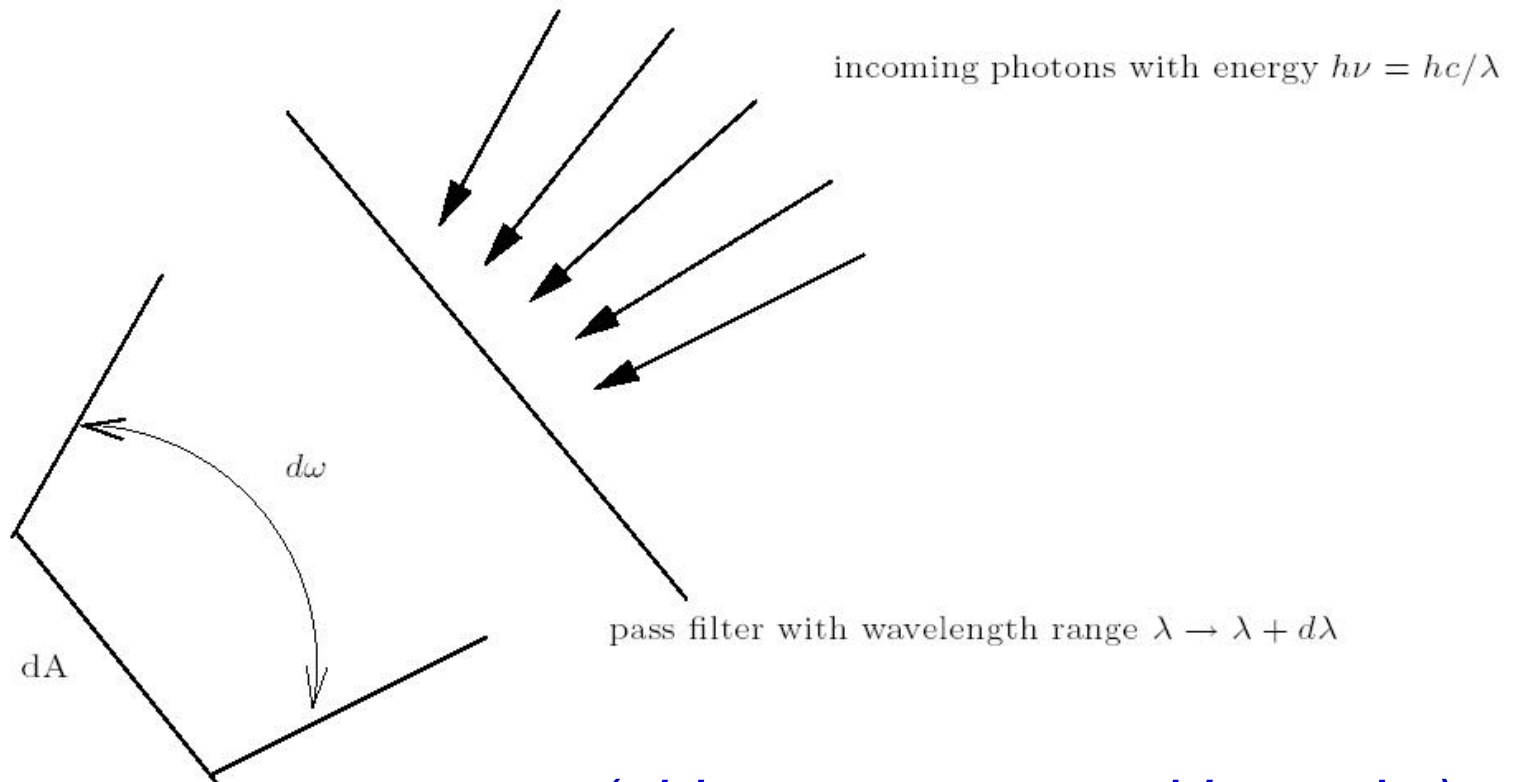
320 nm

550 nm

Diffuse fraction

Solar zenith angle, deg.
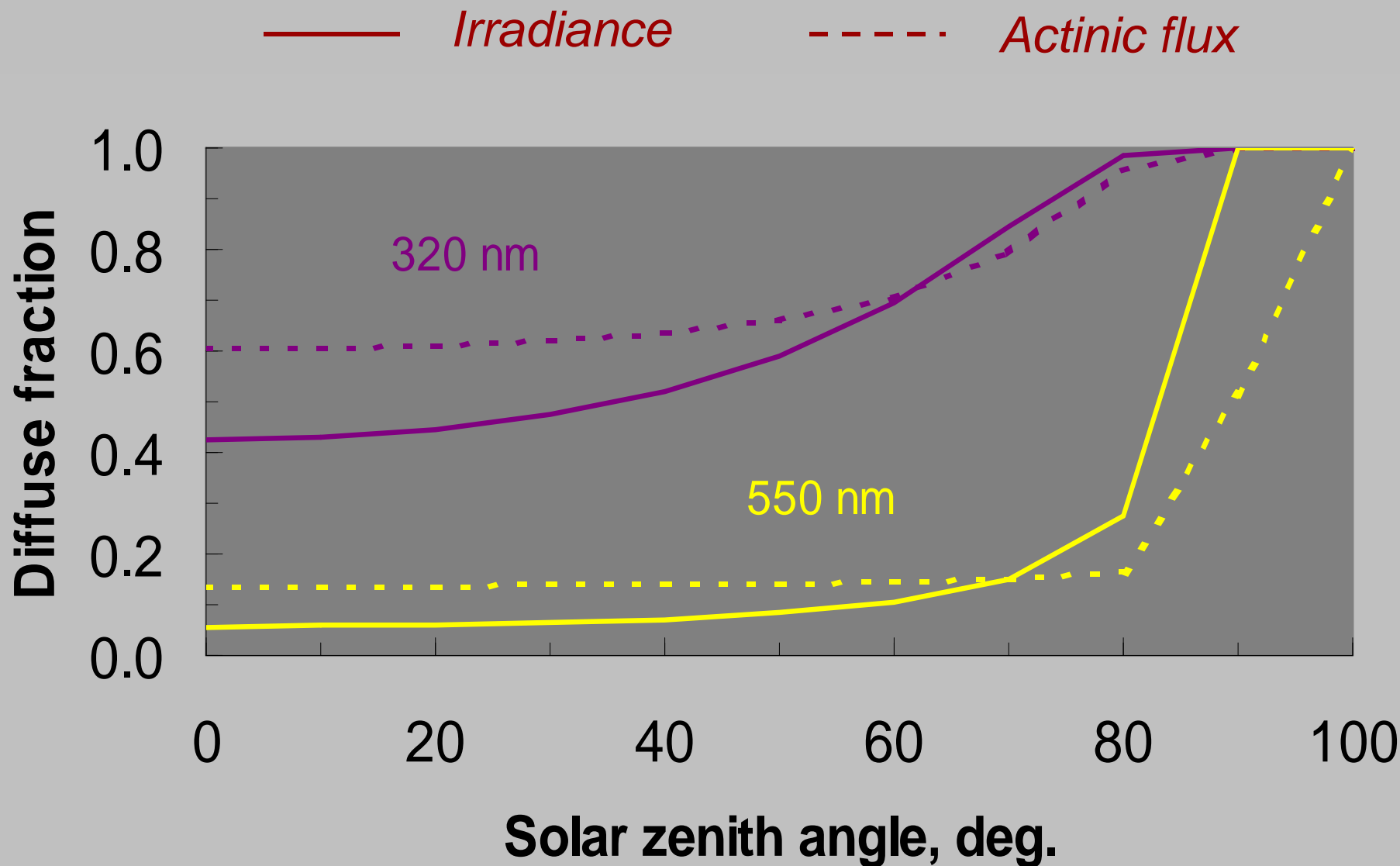
RADIATIVE TRANSFER CONCEPTS

Spectral Radiance, I

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

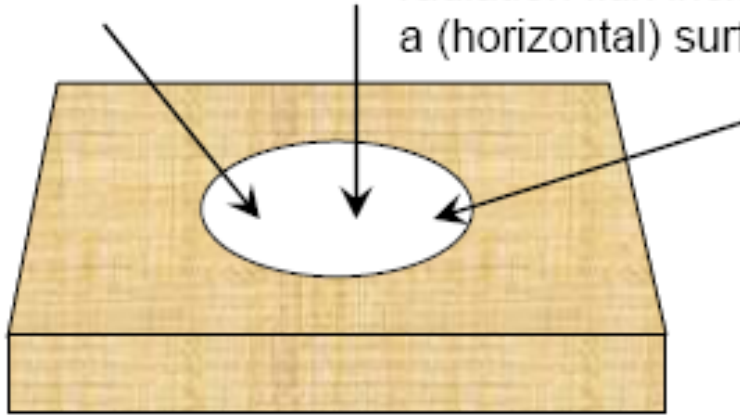units: $J\ s^{-1}\ m^{-2}\ sr^{-1}\ nm^{-1}$

incoming photons with energy $h\nu = hc/\lambda$

$d\omega$

dA

pass filter with wavelength range $\lambda \rightarrow \lambda + d\lambda$

(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.

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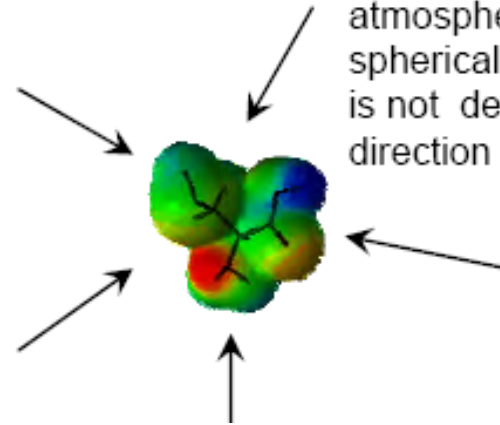
$$F = \int_0^{\pi} \int_0^{2\pi} I(\theta, \varphi) \sin\theta \, \mathrm{d}\varphi \, \mathrm{d}\theta$$
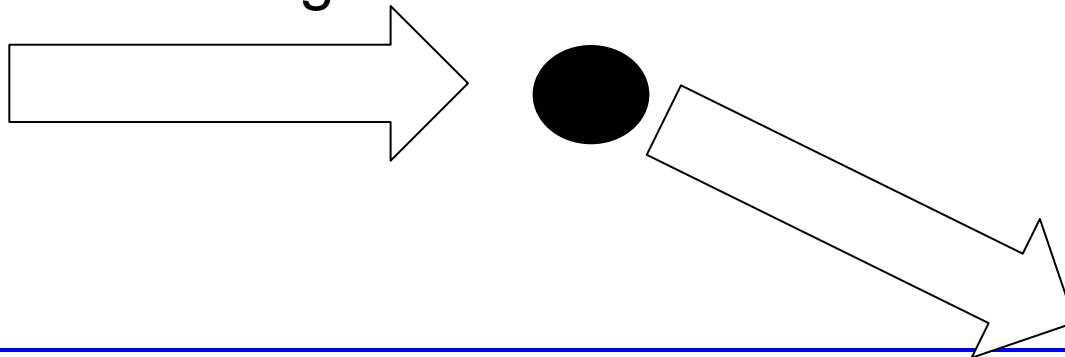
Watts m^{-2}

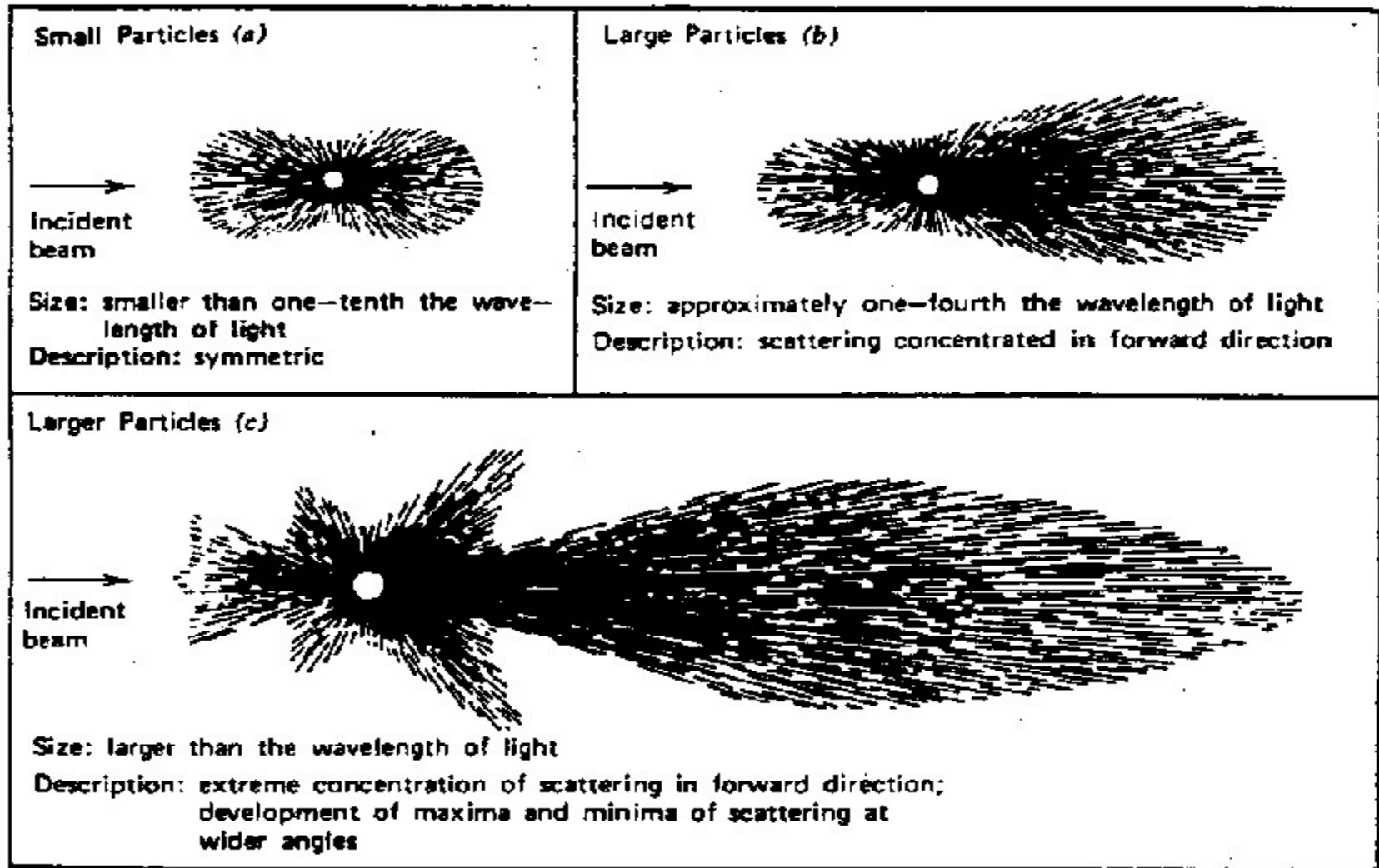Watts m^{-2} or quanta s^{-1} cm^{-2}

Absorption and Scattering

- Absorption – inelastic, loss of radiant energy:
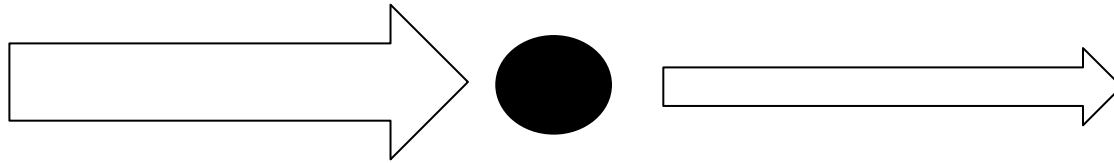
- Scattering – elastic, radiant energy is conserved, direction changes:

SCATTERING PHASE FUNCTIONS

Small Particles (a)

→ Incident beam

Size: smaller than one—tenth the wave—length of light
Description: symmetric

Large Particles (b)

→ Incident beam

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

Larger Particles (c)

→ Incident beam

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
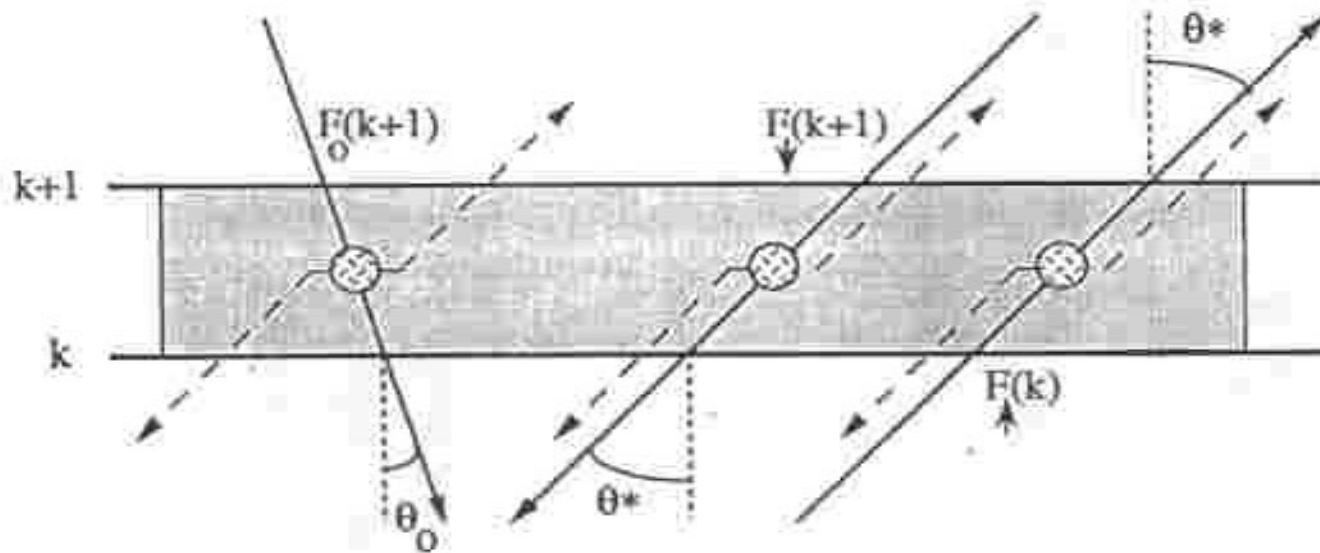
Must specify three optical properties:

  Optical depth, $\Delta\tau$

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

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

For each layer, must specify:

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: $1-1000$

   $\alpha \sim 0$

   cirrus $\sim 1-5$
   cumulonimbus $\sim\, > 100$

For each layer, must specify:

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

range 0 - 1
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:

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
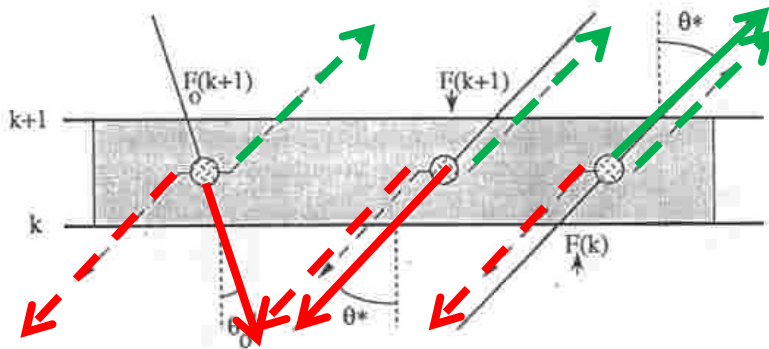   for clouds, typically 0.7-0.9

*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

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

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

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

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

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

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

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

subject to the boundary conditions

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

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

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 = $m + \mathrm{i}k$
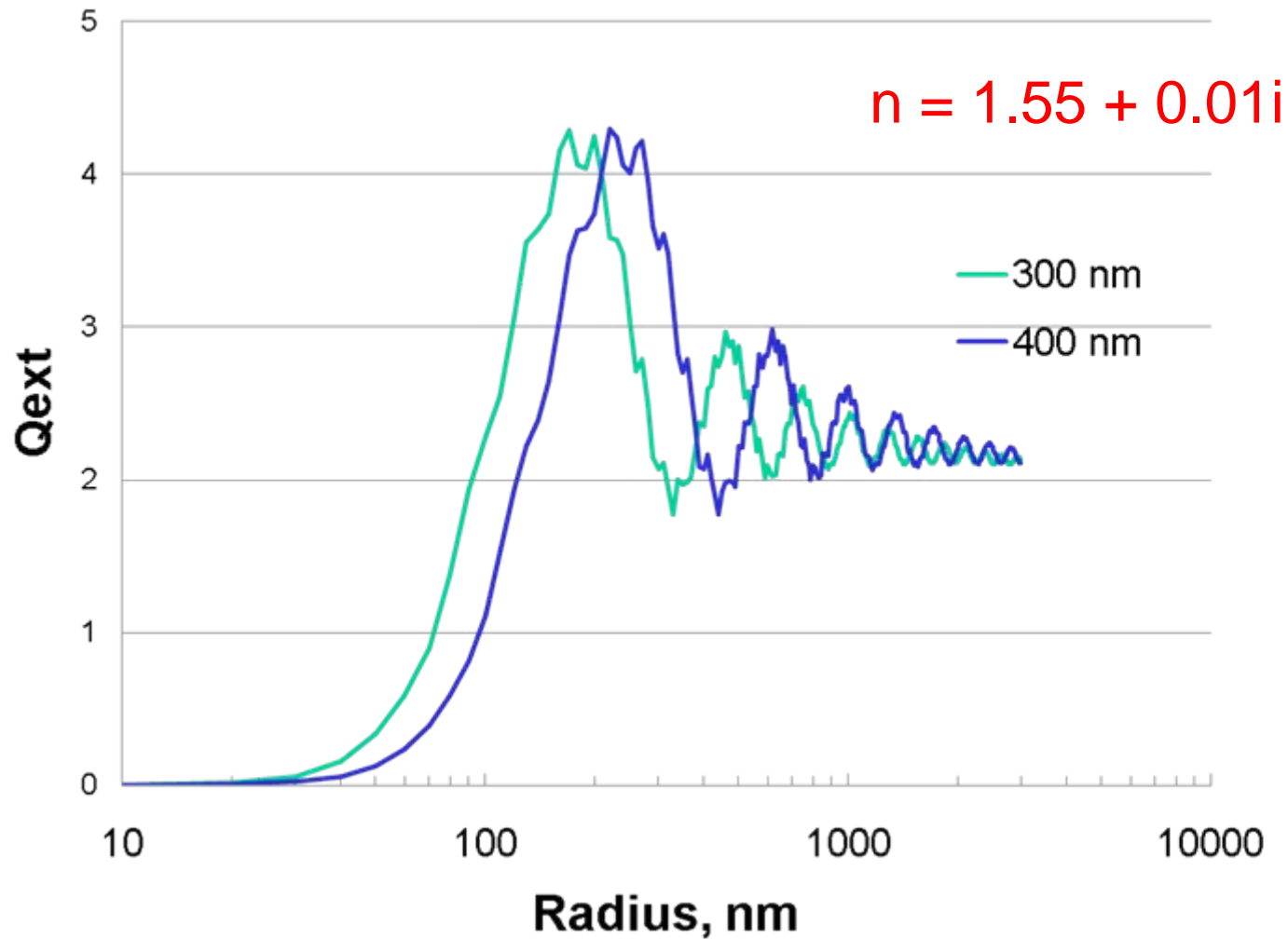Size parameter $\alpha = 2\pi r/\lambda$

Can compute:

Extinction efficiency $\qquad Q_{\mathrm{e}}(r,\lambda,n) \quad \mathrm{x}\ \pi r^2$

Scattering efficiency $\qquad Q_{\mathrm{s}}(r,\lambda,n) \quad \mathrm{x}\ \pi r^2$

Phase function $\qquad\qquad P(\Theta,r,\lambda,n) \quad$ or
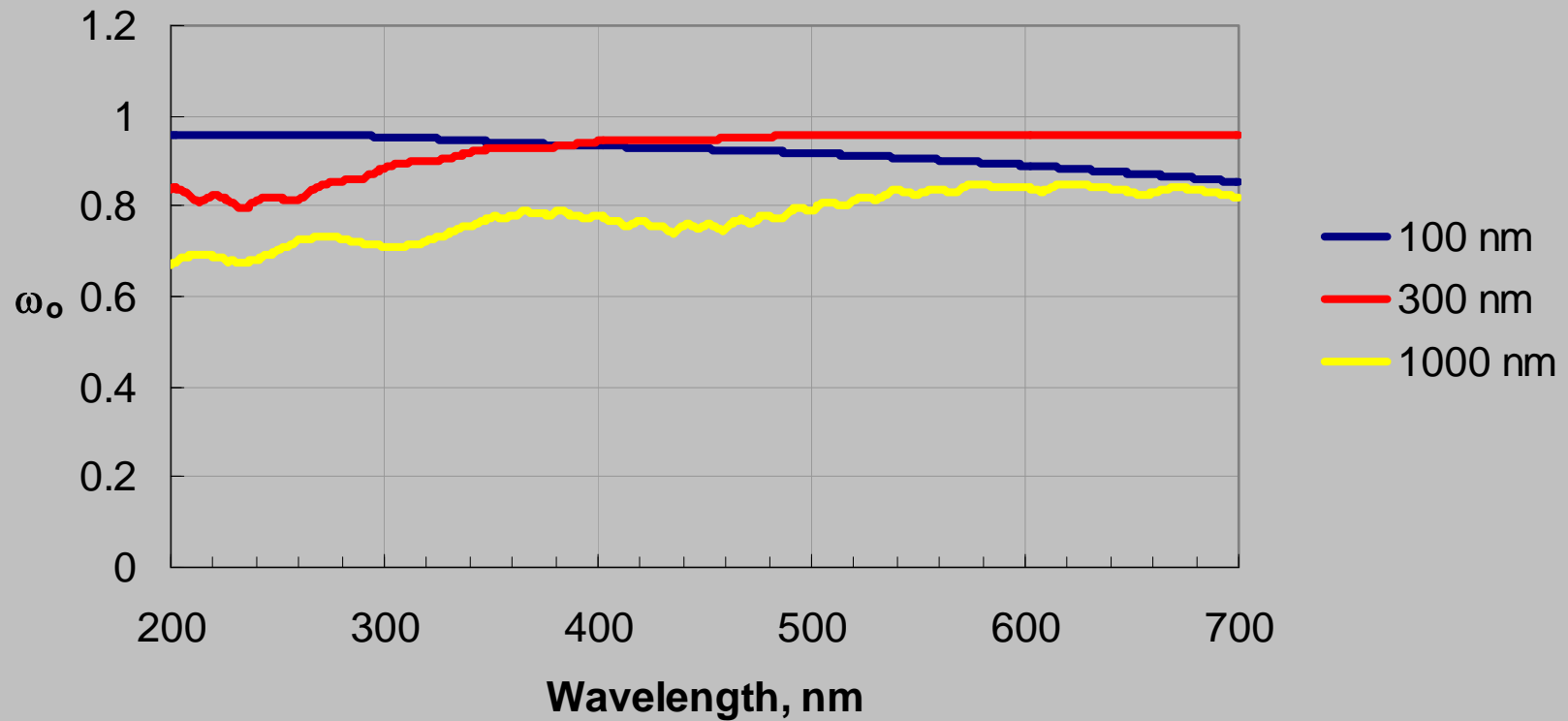asymmetry factor $\qquad\quad g(r,\lambda,n)$

Extinction Efficiency, Q_{ext}

Phase function or Asymmetry factor, g
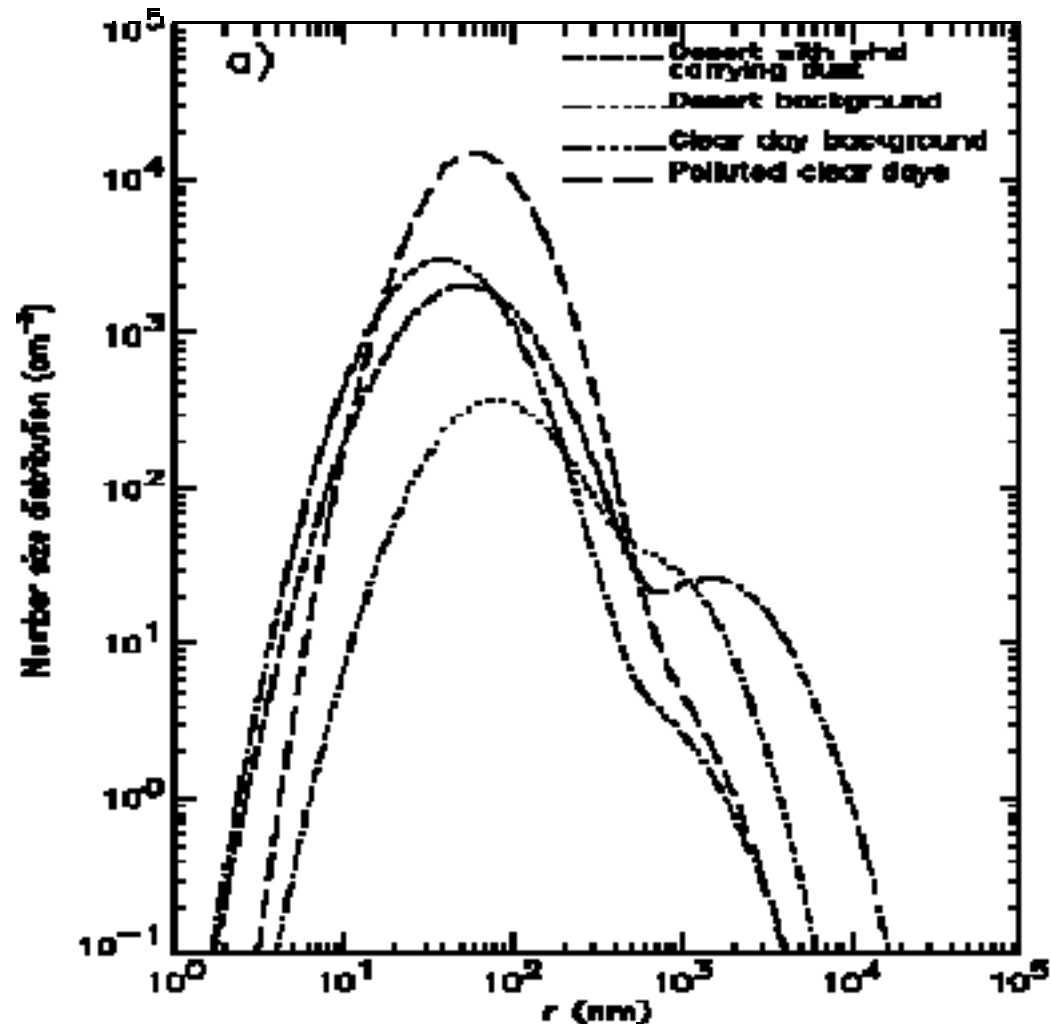
Asymmetry factor, g
n = 1.5 + 0.01 i
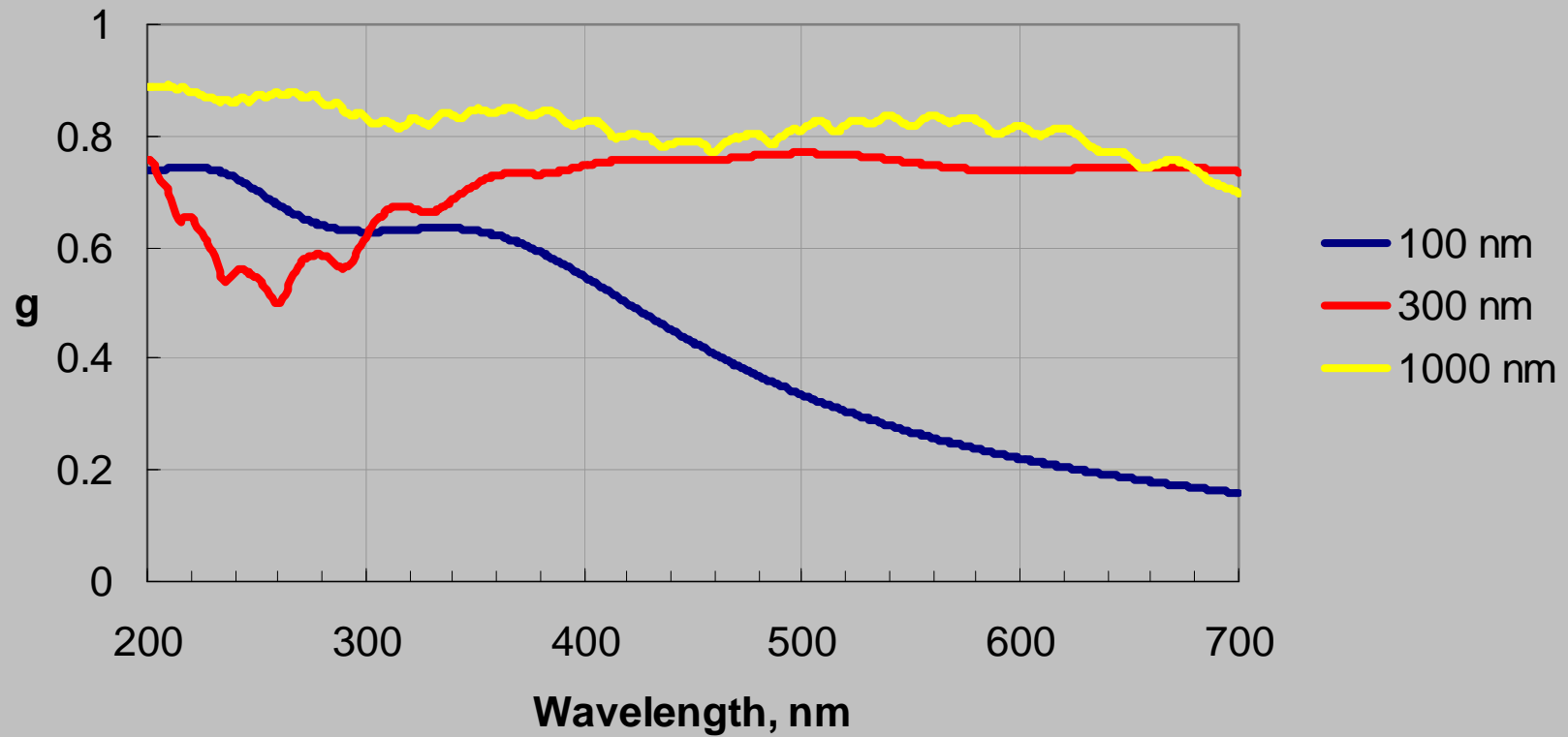
Single Scattering Albedo = Q_{scatt}/Q_{ext}

Single Scattering Albedo, ω_o

n = 1.5 + 0.01 i

Aerosol size distributions

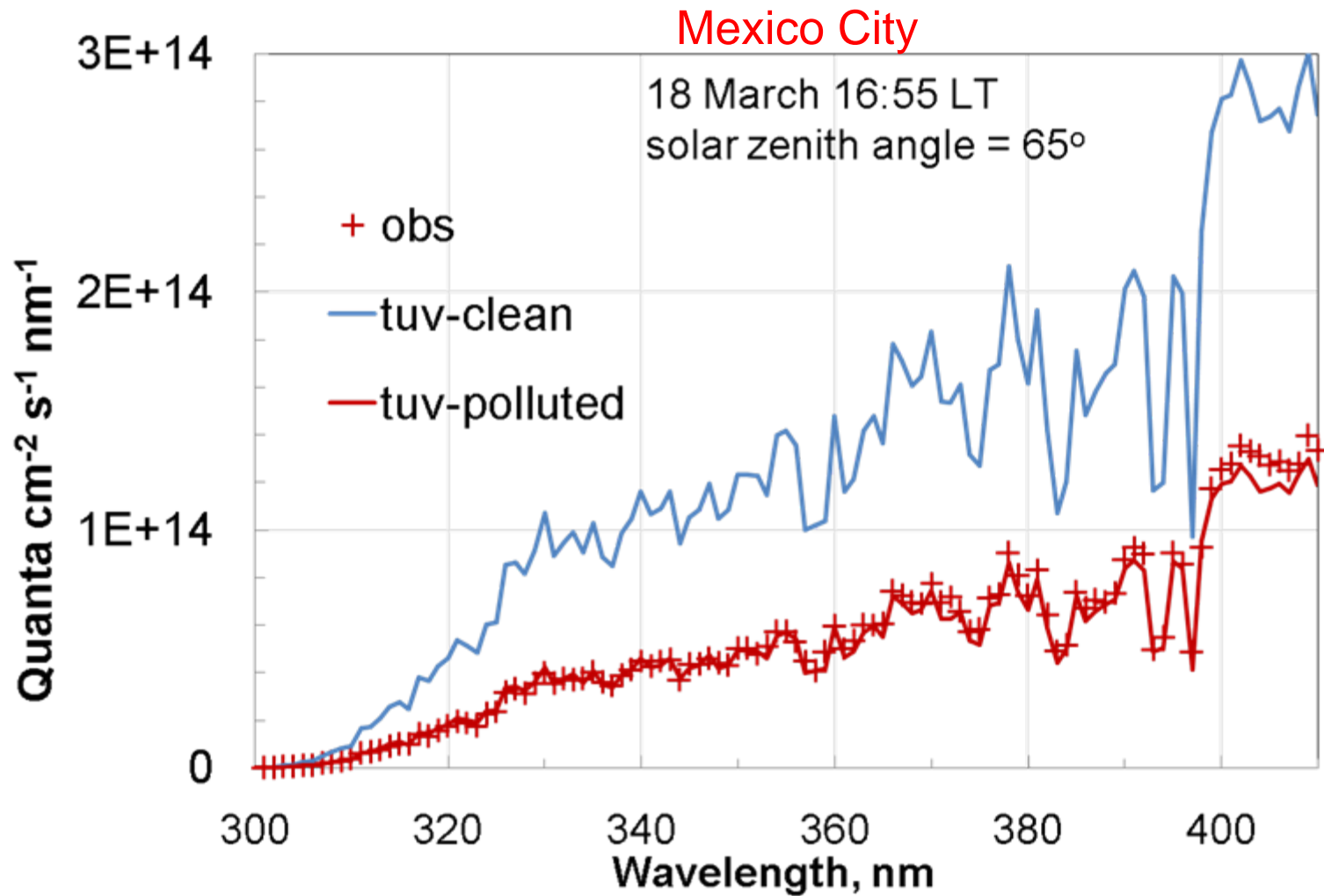# Optical properties of aerosol ensembles

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

Total scattering coefficient =
$$K_s(\lambda) = \int_0^\infty \pi r^2 Q_s(r,\lambda) n(r) \, \mathrm{d}r$$
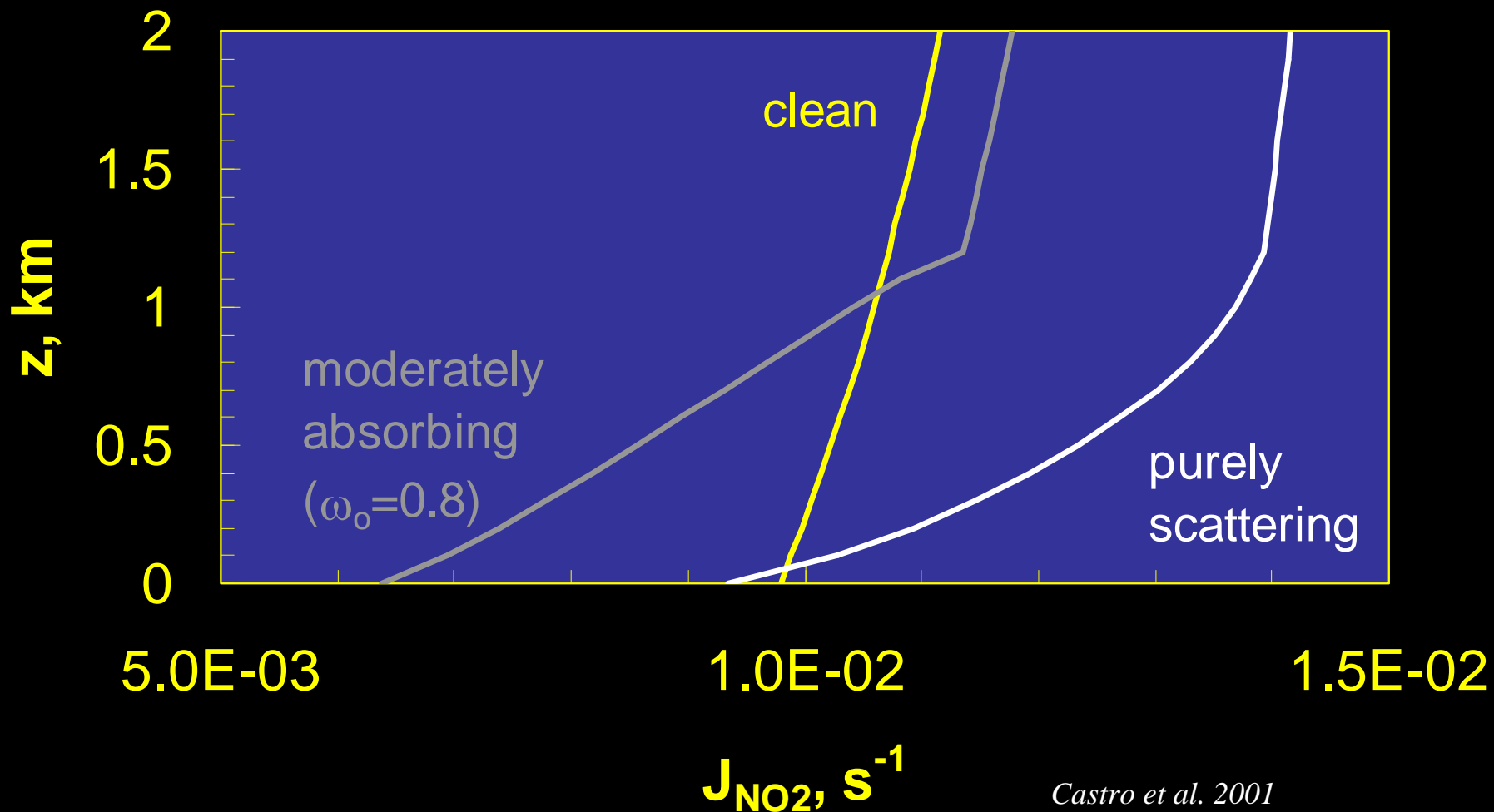
Average single scattering albedo =
$$\varpi_o(\lambda) = K_s(\lambda) / K_e(\lambda)$$

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

UV Actinic Flux Reduction → Slower Photochemistry

Mexico City

18 March 16:55 LT
solar zenith angle = 65°

+ obs
— tuv-clean
— tuv-polluted

Madronich, Shetter, Halls, Lefer, AGU'07

Aerosol Effects
NO$_2$ Photolysis Frequency
19N, April, noon, AOD = 1 at 380 nm

Castro et al. 2001
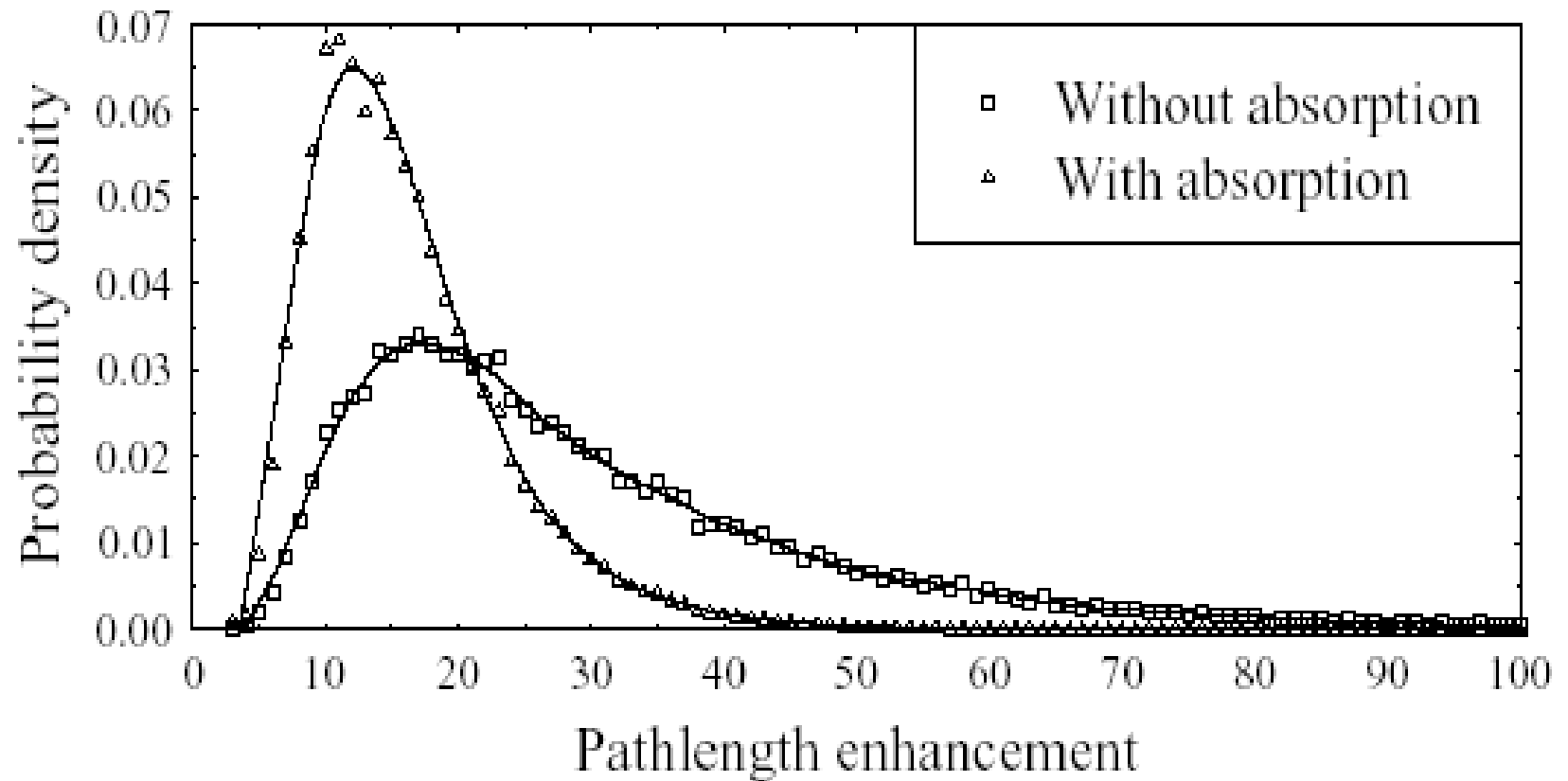
CLOUDS

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

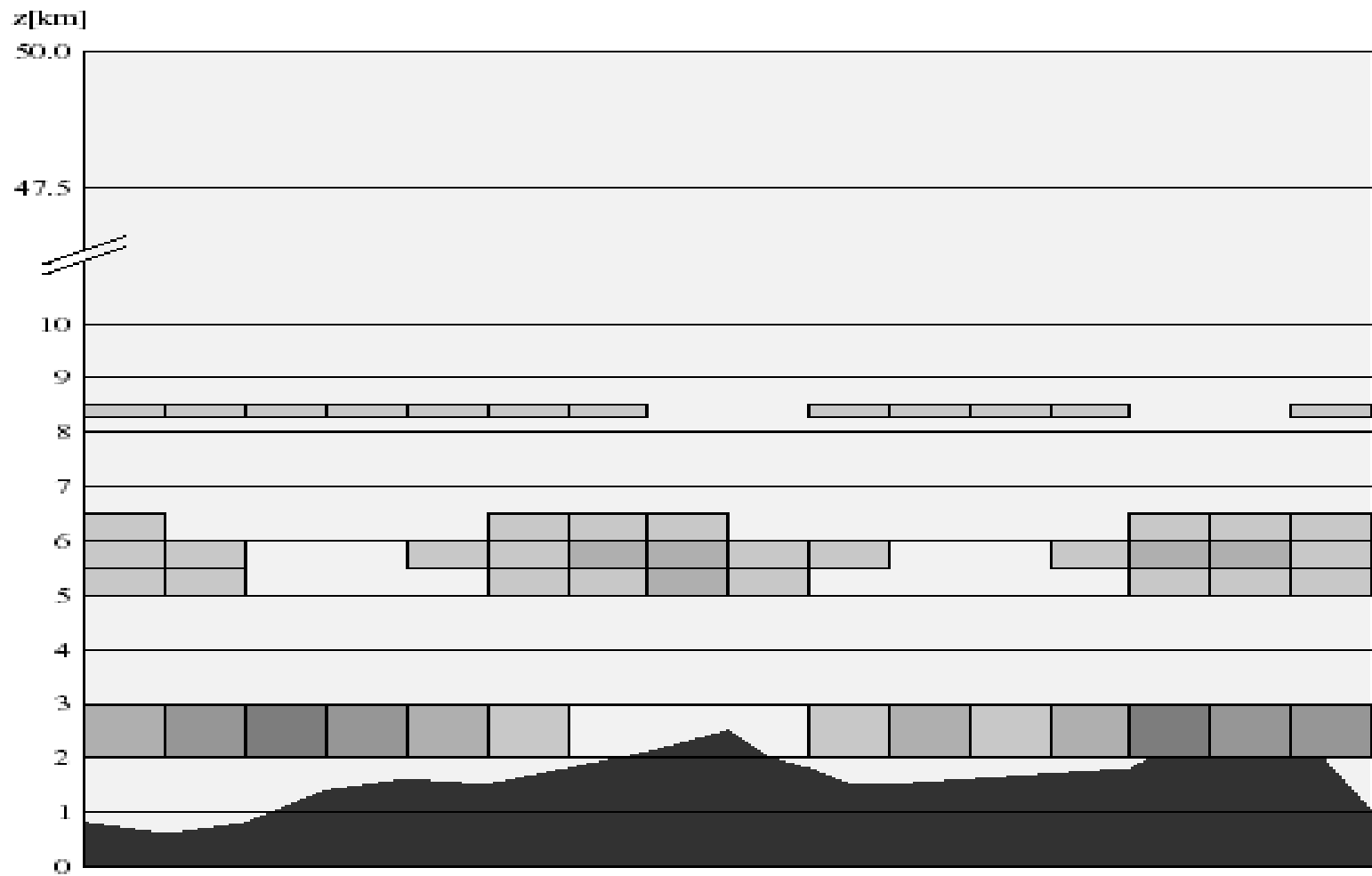**340 nm, sza = 0 deg.,
cloud between 4 and 6 km**

Altitude, km

Actinic flux, quanta cm^{-2} s^{-1}

od = 100
od = 10
od = 0
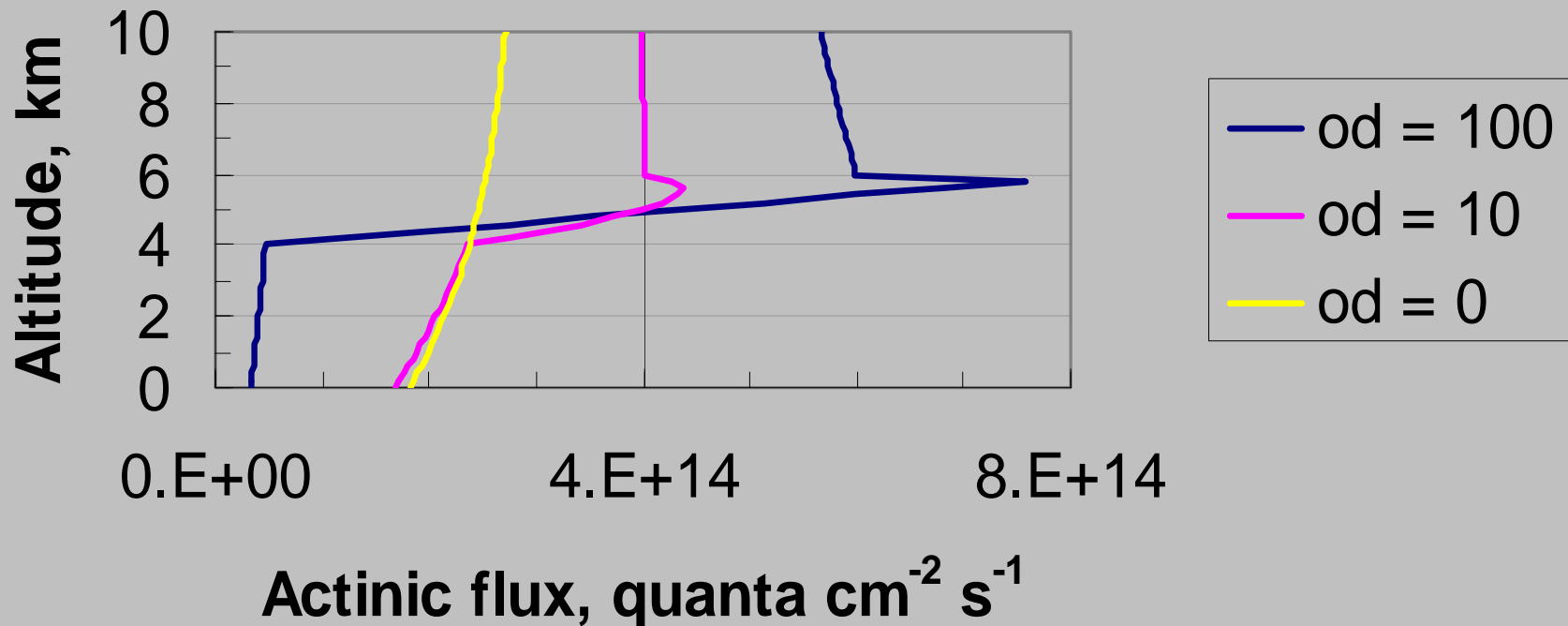
INSIDE CLOUDS:
Photon Path Enhancements

Cumulonimbus, od=400

Broken Clouds

SPECTRAL EFFECTS OF PARTIAL CLOUD COVER

Crafword et al., 2003
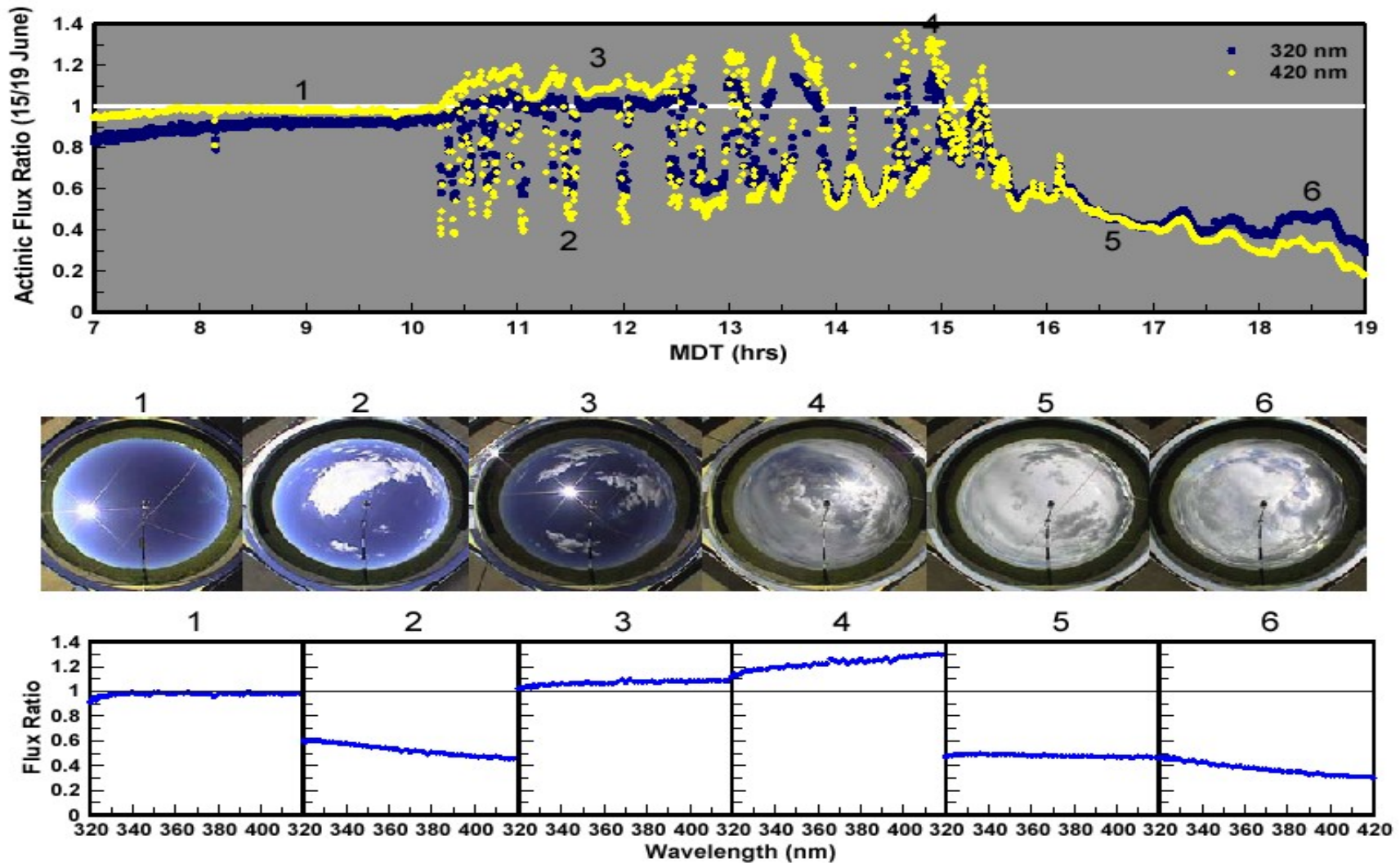
PARTIAL CLOUD COVER
Biomodal distributions

Crafword et al., 2003
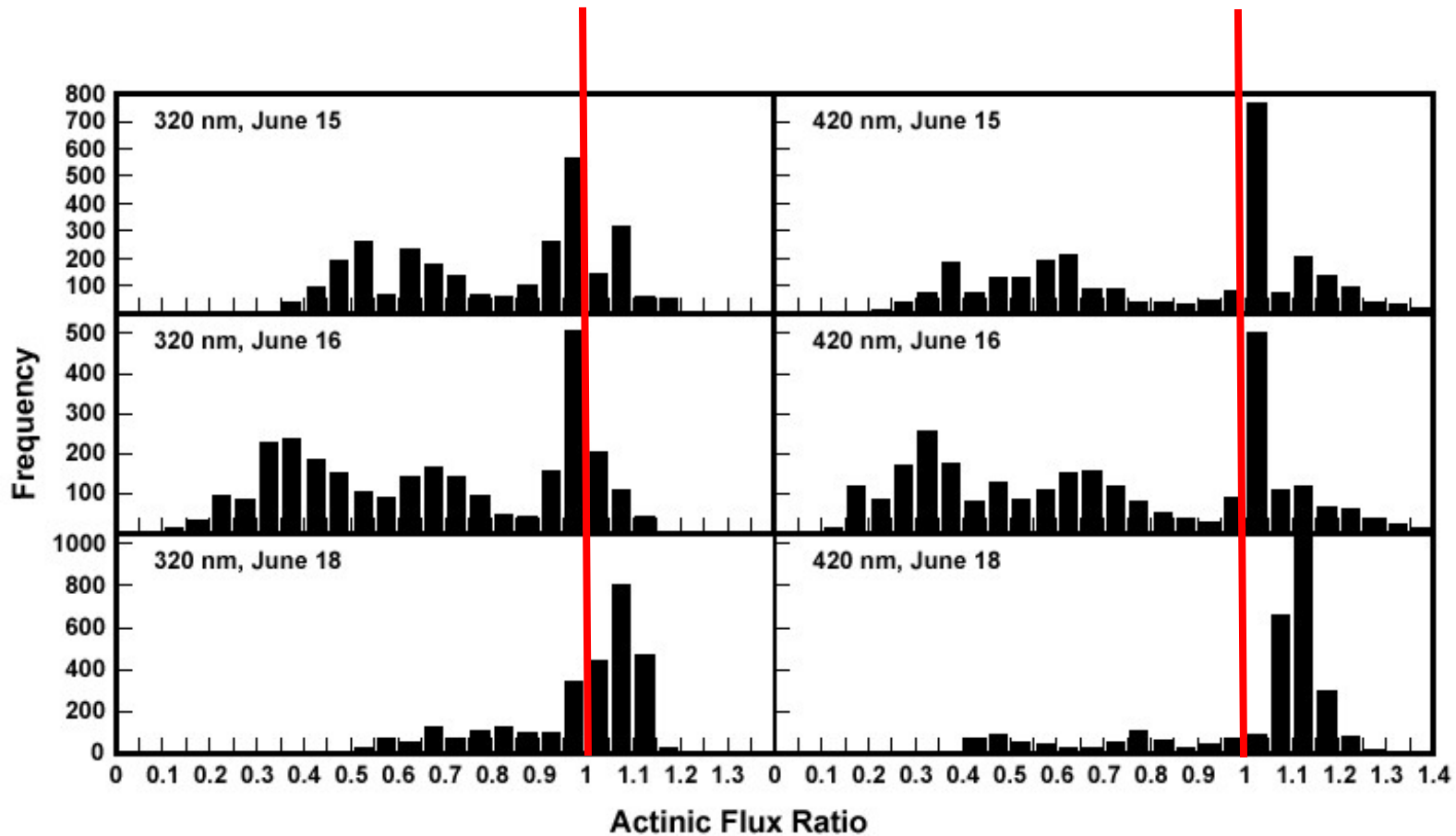
Independent Pixel Approximation

➢ Cloud free:

- S_o = direct sun
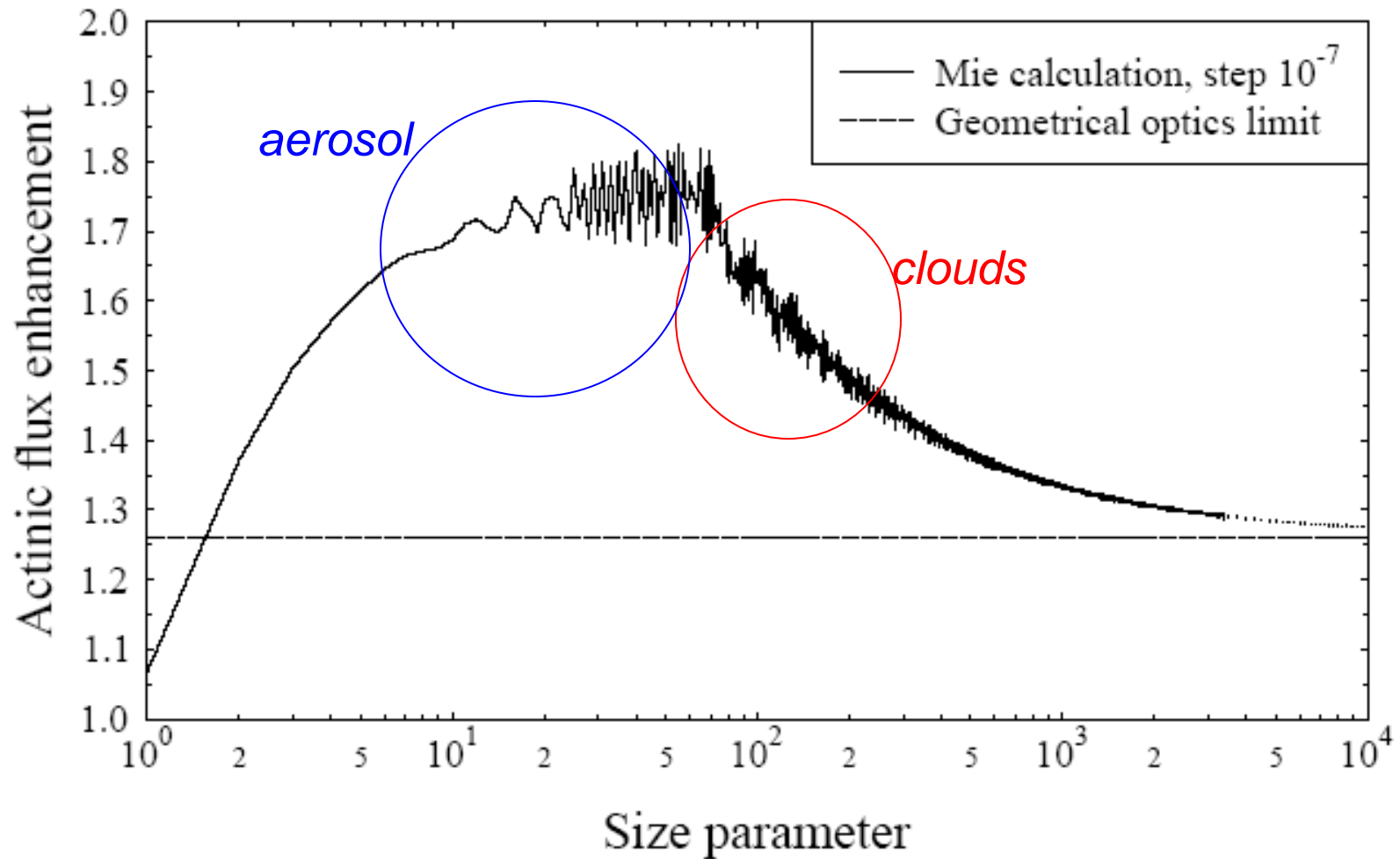- D_o = diffuse light from sky
- G_o = total = $S_o + D_o$

➢ 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

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