PHOTOLYSIS

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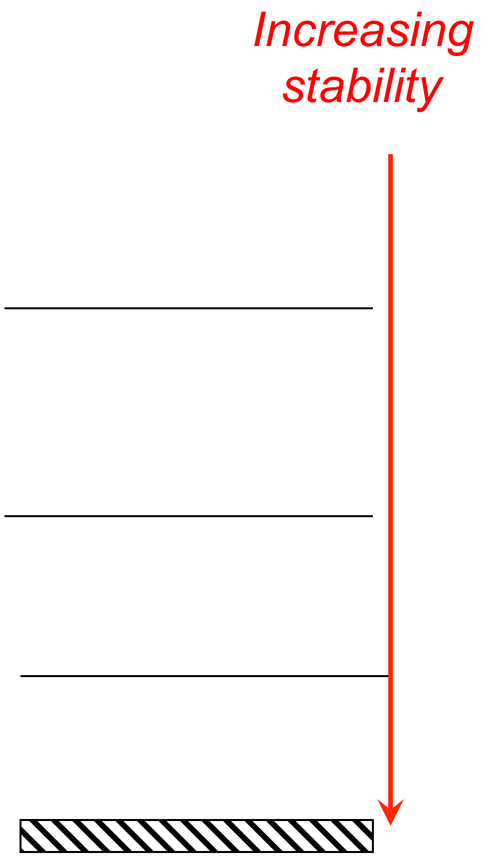
NCAR

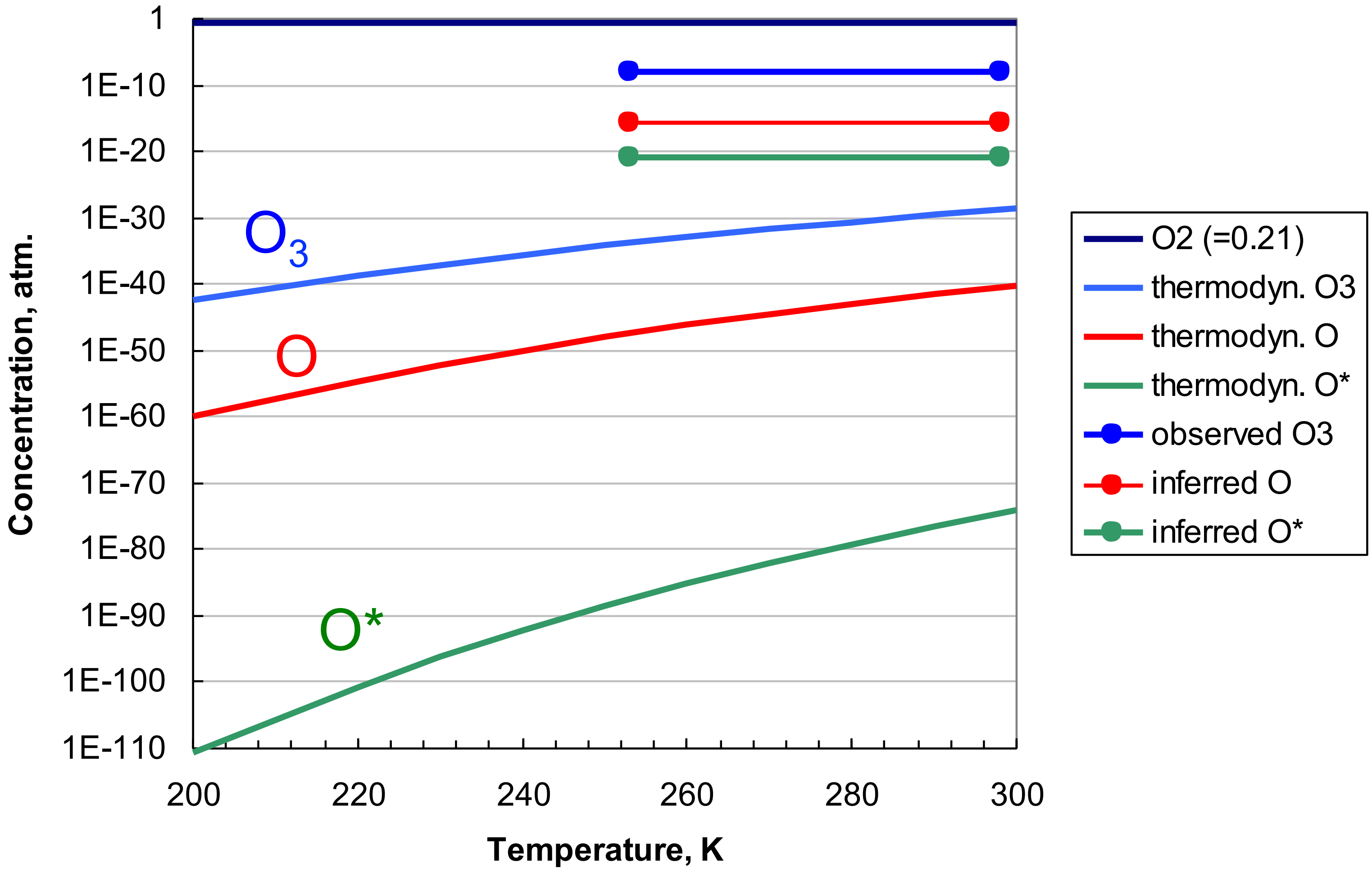
Energetics of Oxygen in the Atmosphere

		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

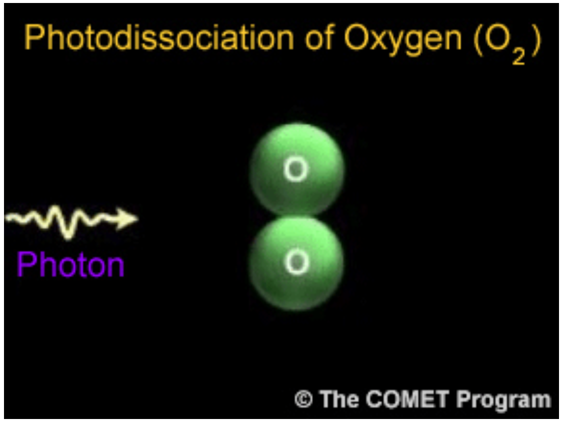


Photochemistry

- 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>

Some Important Photolysis Reactions

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

Quantifying Photolysis Processes

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

Photolysis rates:

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

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

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

(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.

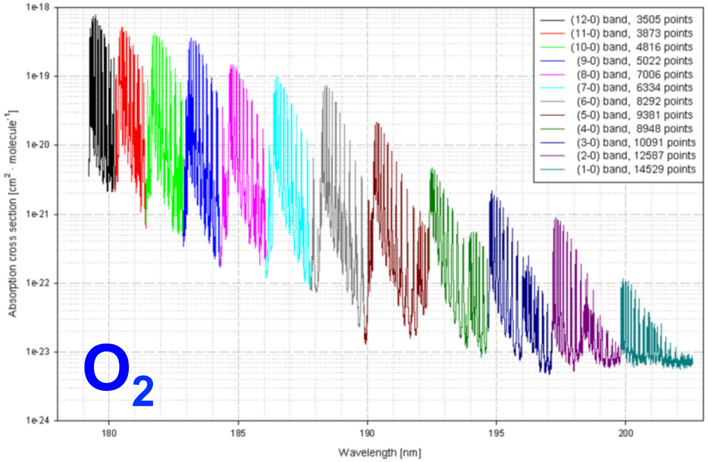
$\sigma(\lambda)$ = absorption cross section, $\mathrm{cm}^2\ \mathrm{molec}^{-1}$

$\propto$ probability that photon is absorbed.

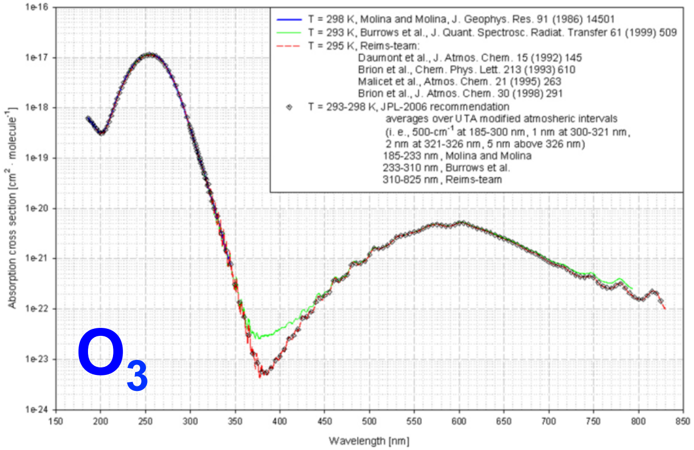
$\phi(\lambda)$ = photodissociation quantum yield, molec quanta^{-1}

$\propto$ probability that absorbed photon causes dissociation.

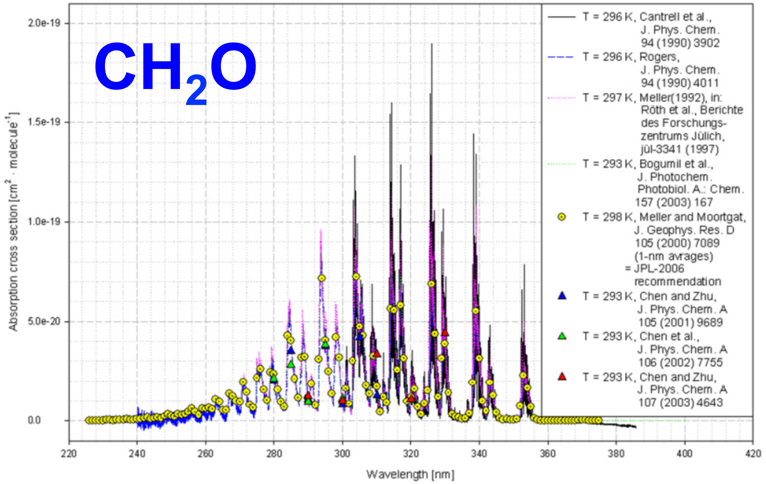
Absorption cross sections



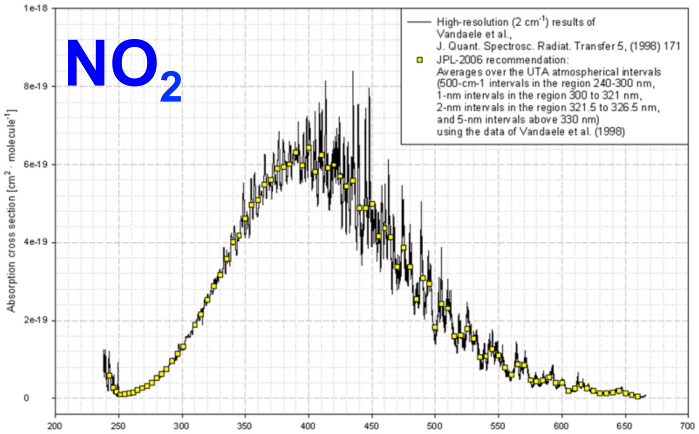
Absorption cross sections in the Schumann-Runge region of oxygen O_2 at 300 K,
Yoshino et al., Planet. Space Sci. 40 (1992) 185



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

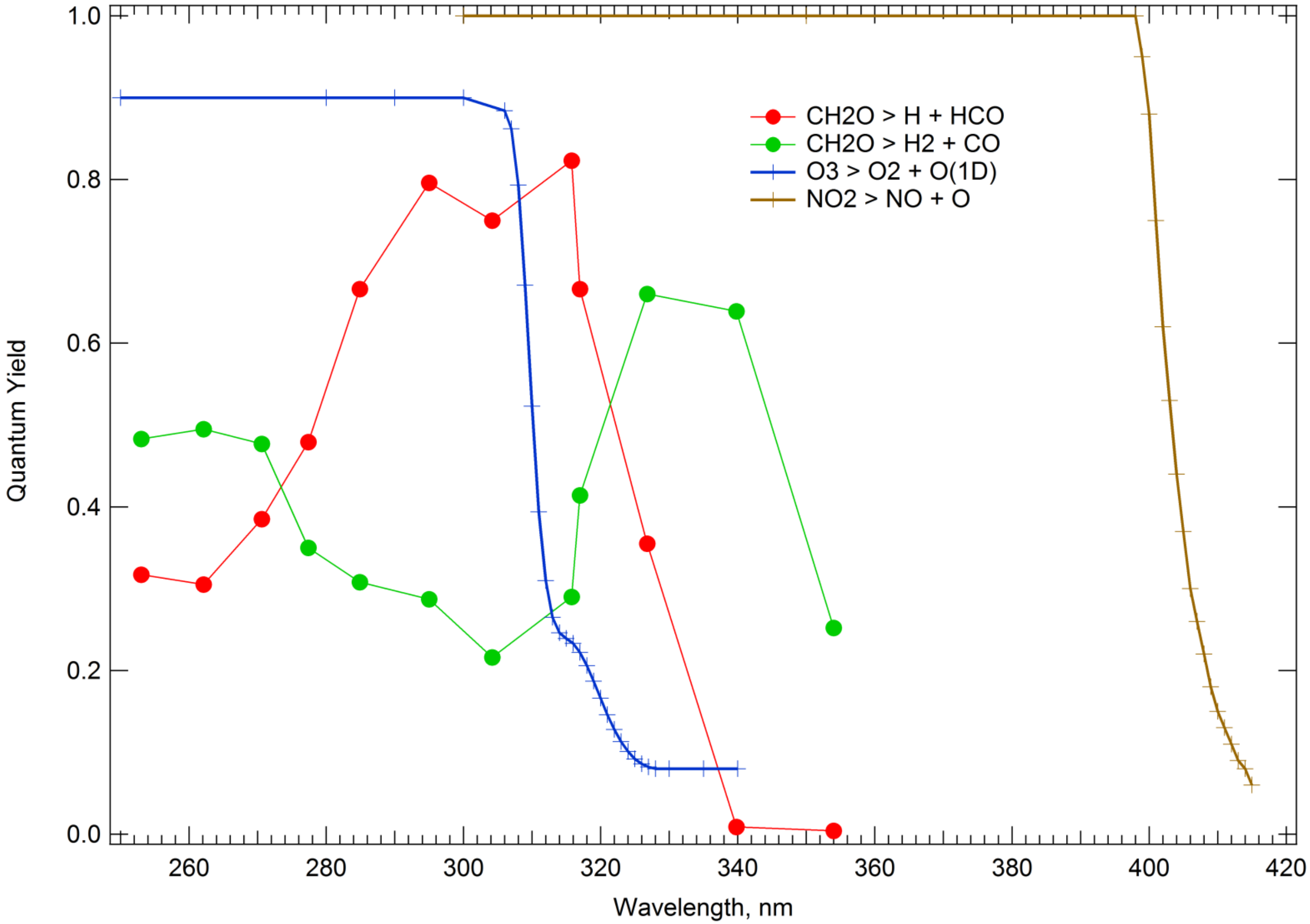


Absorption cross sections of formaldehyde CH_2O at room temperature (results 1990-2003)



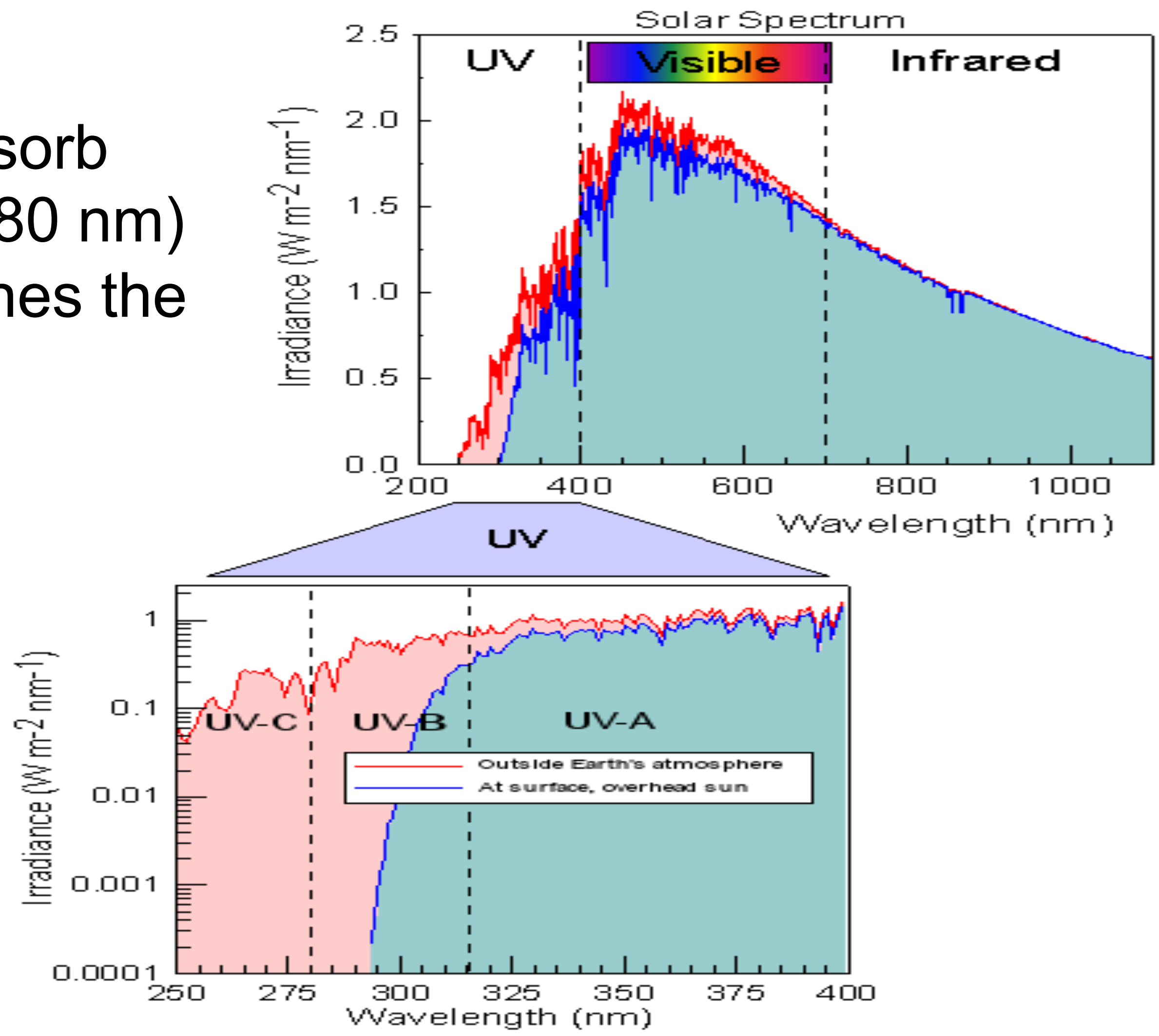
Absorption cross sections of nitrogen dioxide NO_2 at 294 K
Results from the year 1998 and JPL-2006 recommendation

Photodissociation Quantum Yields



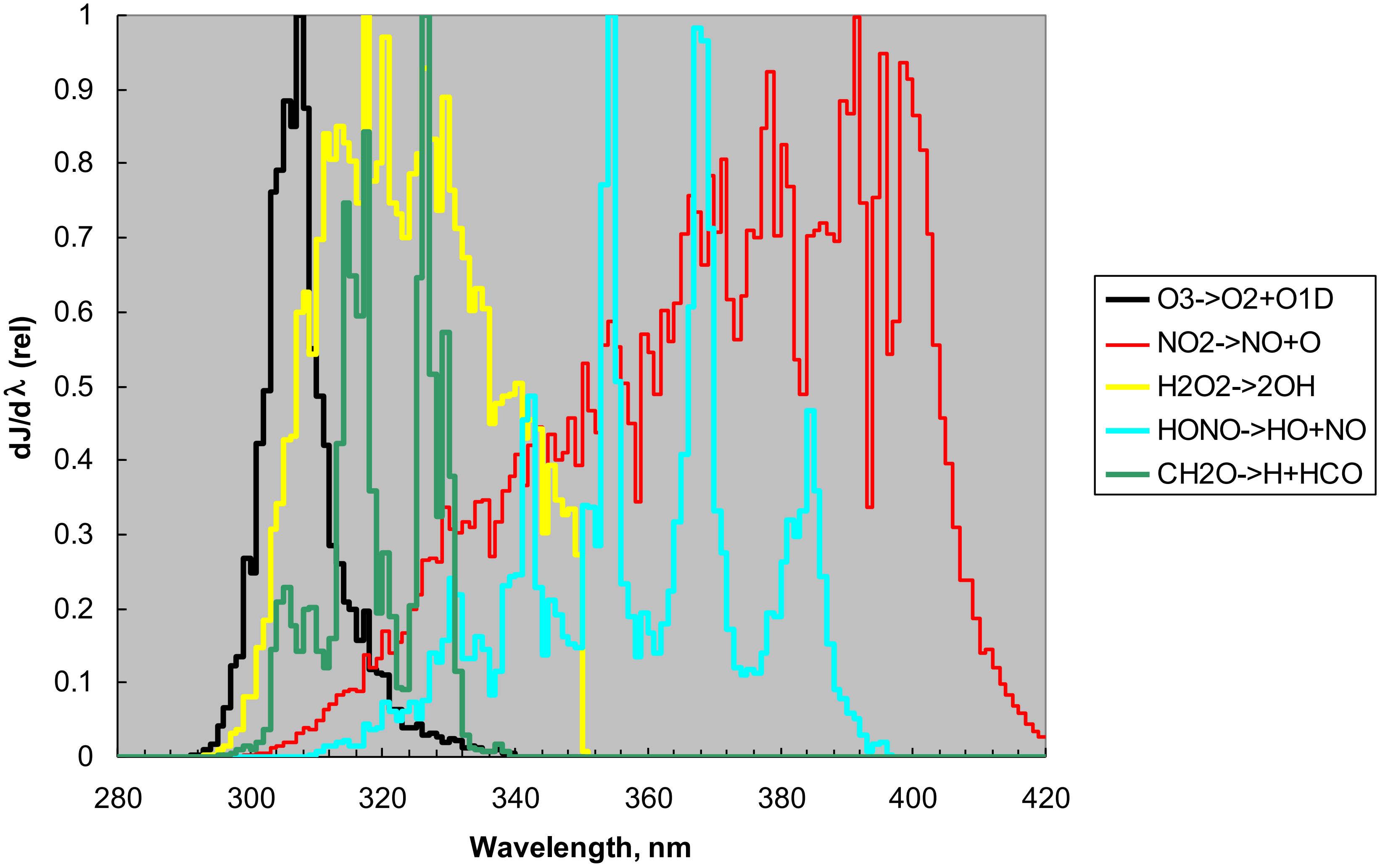
Solar Spectrum

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



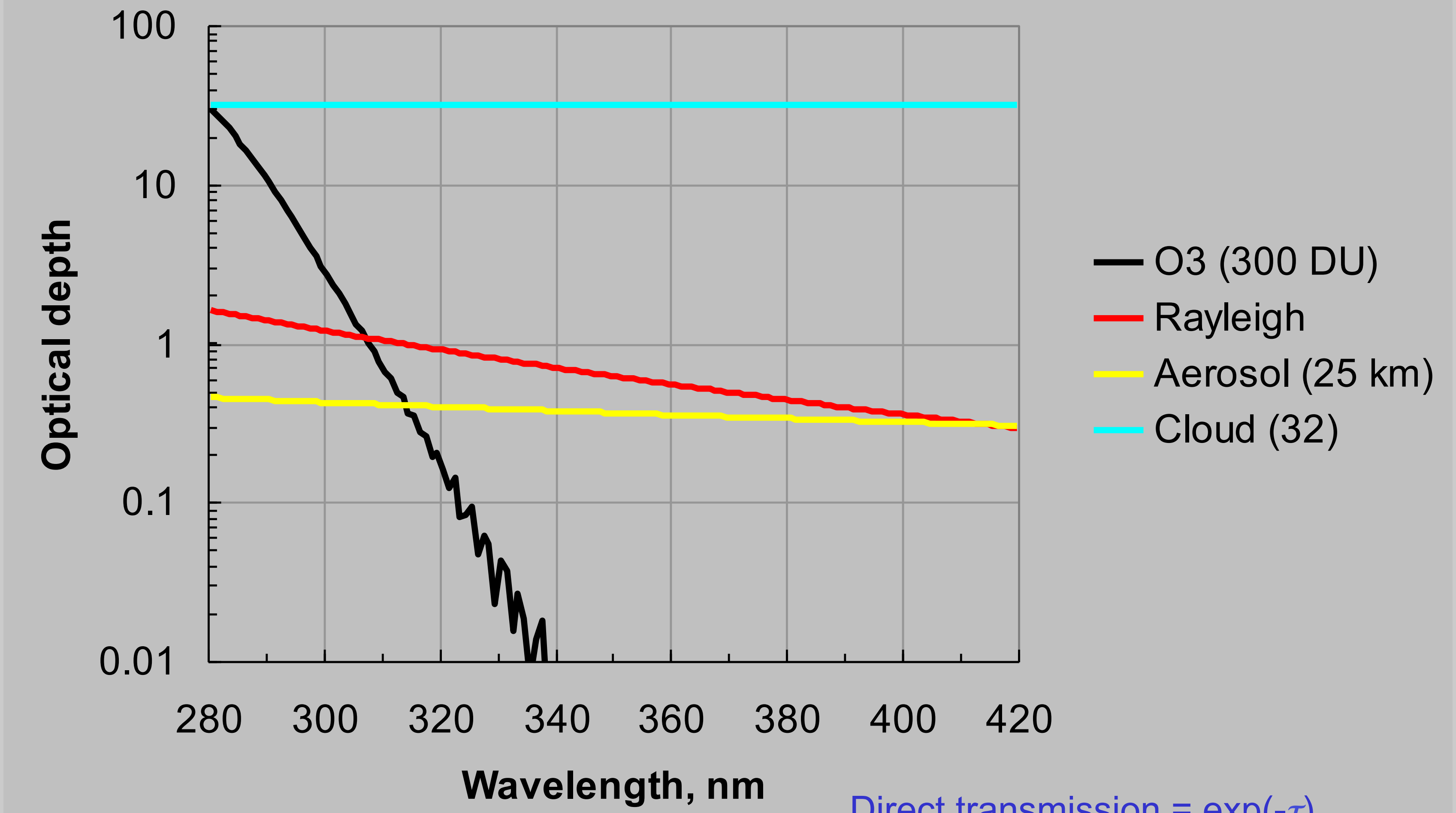
UNEP, 2002

Spectral Region For Tropospheric Photochemistry



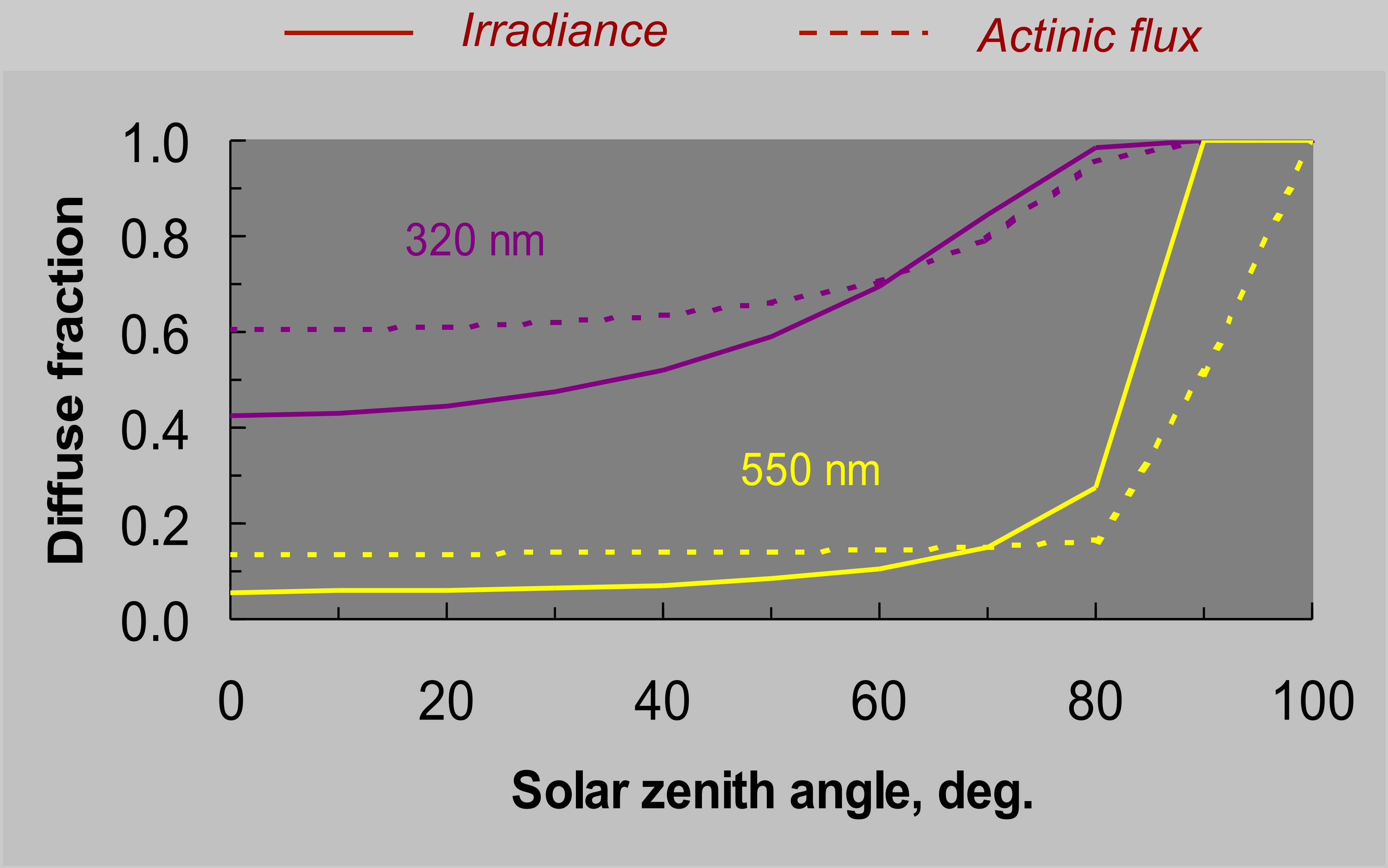
surface, overhead sun

Typical Vertical Optical Depths, τ



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

DIFFUSE LIGHT - CLEAN SKIES, SEA LEVEL

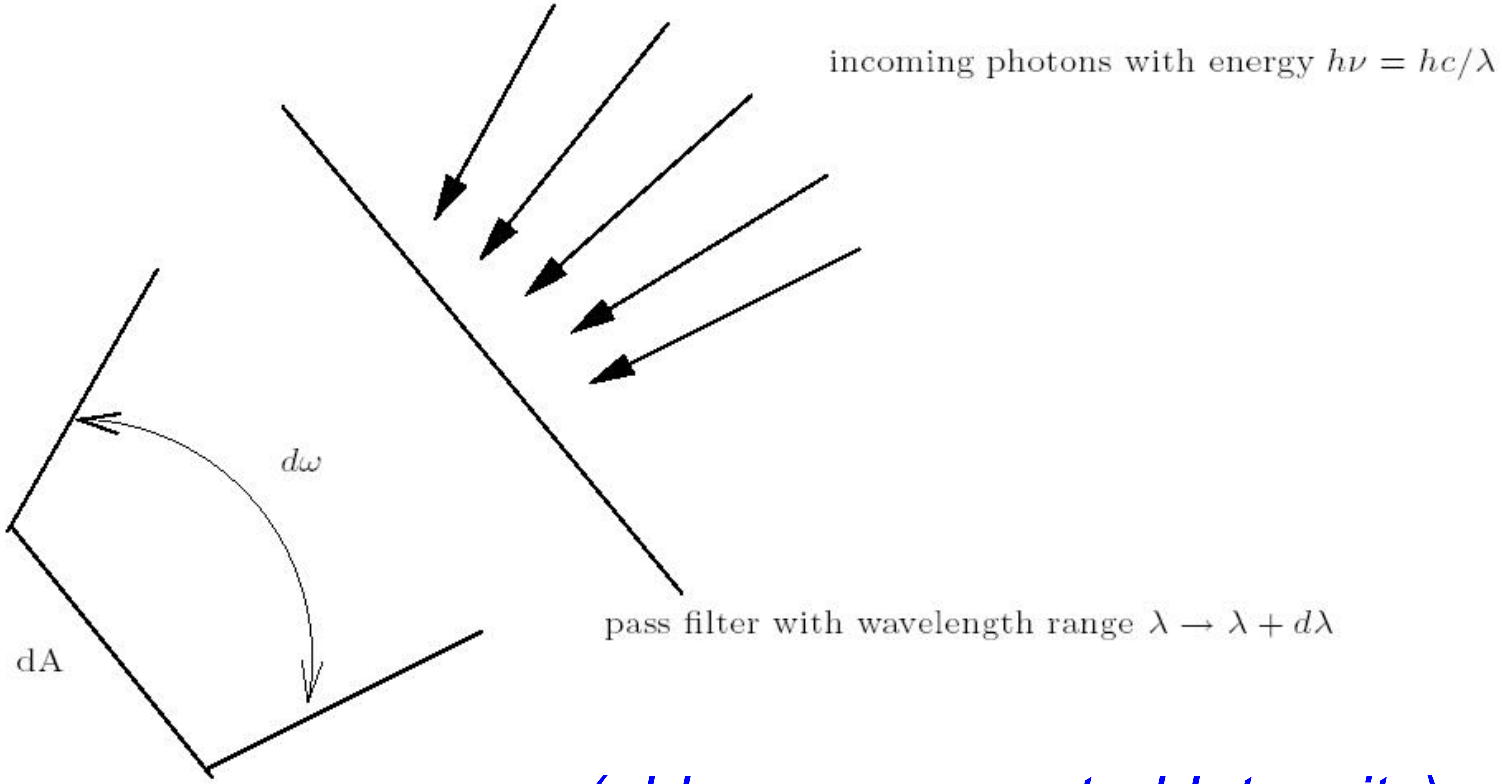


RADIATIVE TRANSFER CONCEPTS

Spectral Radiance, *I*

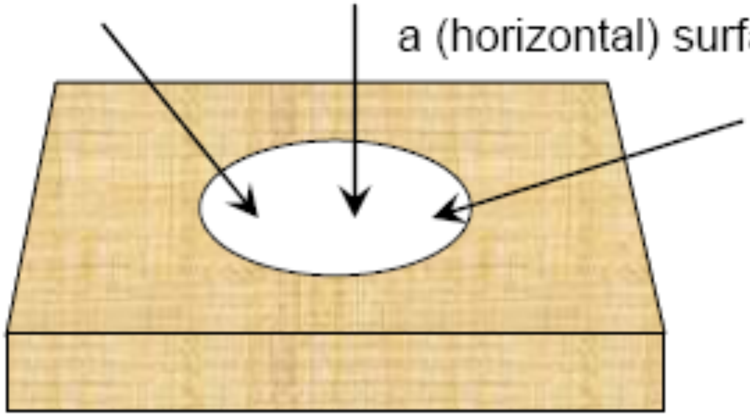
$I(\lambda,\theta,\phi) = N(hc/\lambda) / (dt\ dA\ d\omega\ d\lambda)$

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

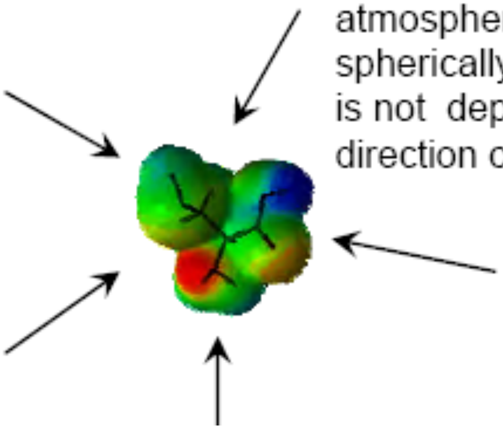


(old name = spectral Intensity)

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.

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

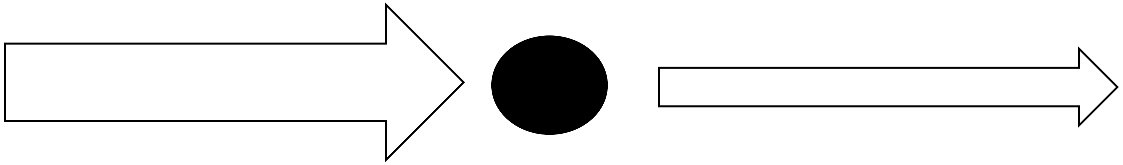
Watts m^{-2}

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

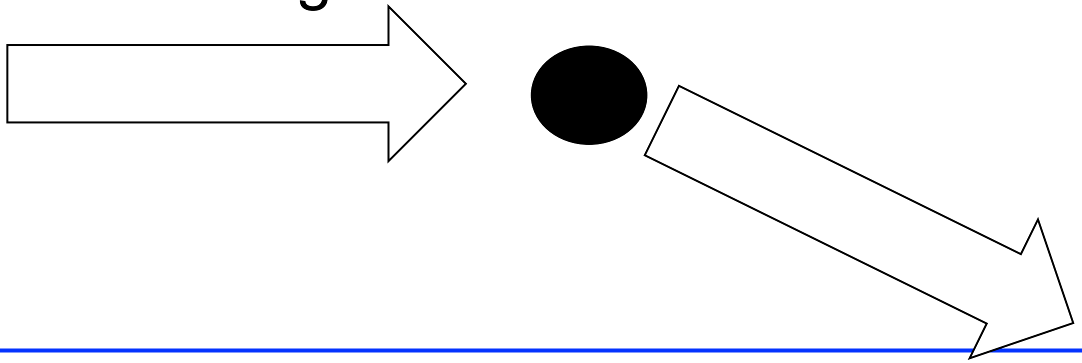
Watts m^{-2} or quanta s^{-1} cm^{-2}

Absorption and Scattering

- Absorption – inelastic, loss of radiant energy:

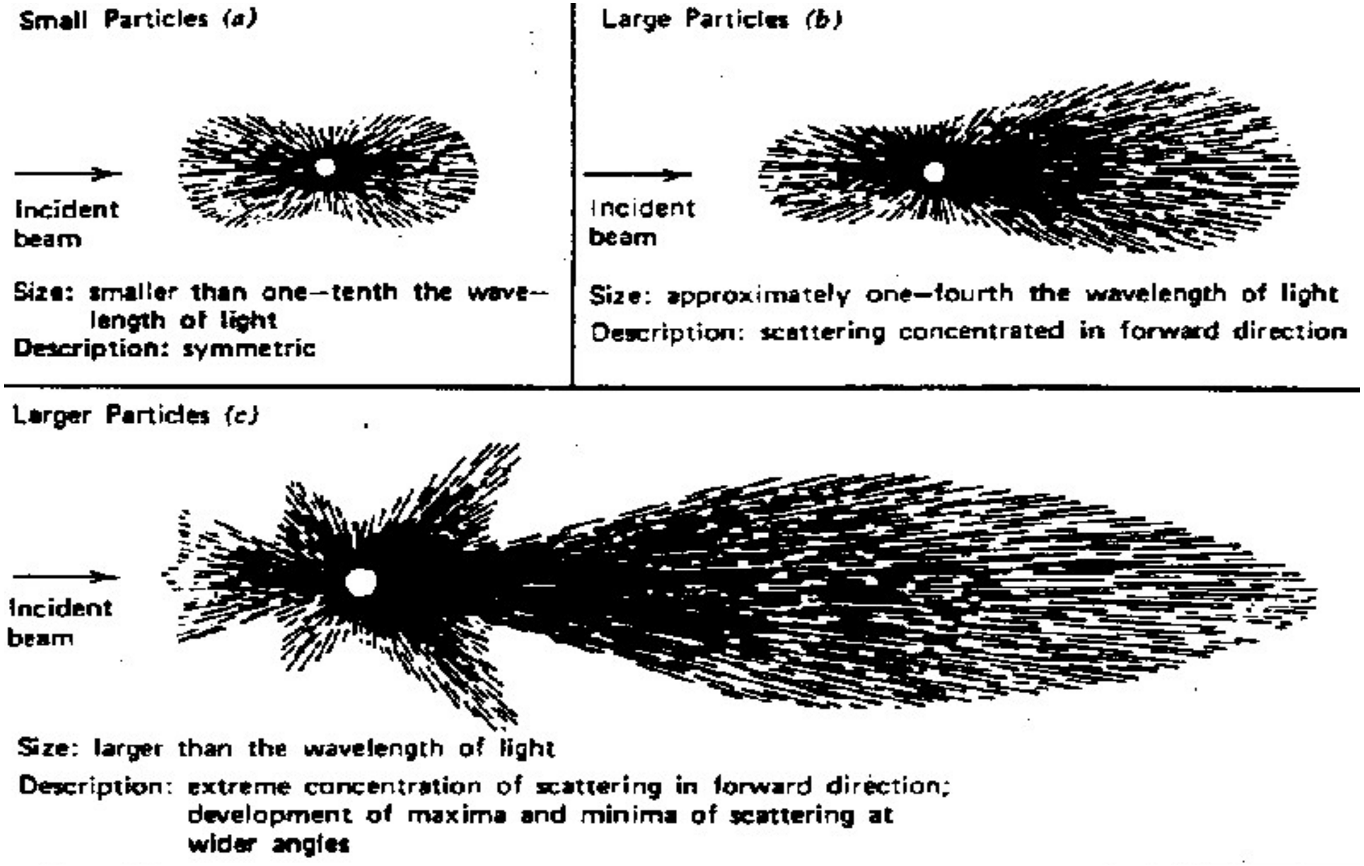


- Scattering – elastic, radiant energy is conserved, direction changes:



SCATTERING PHASE FUNCTIONS

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



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

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

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

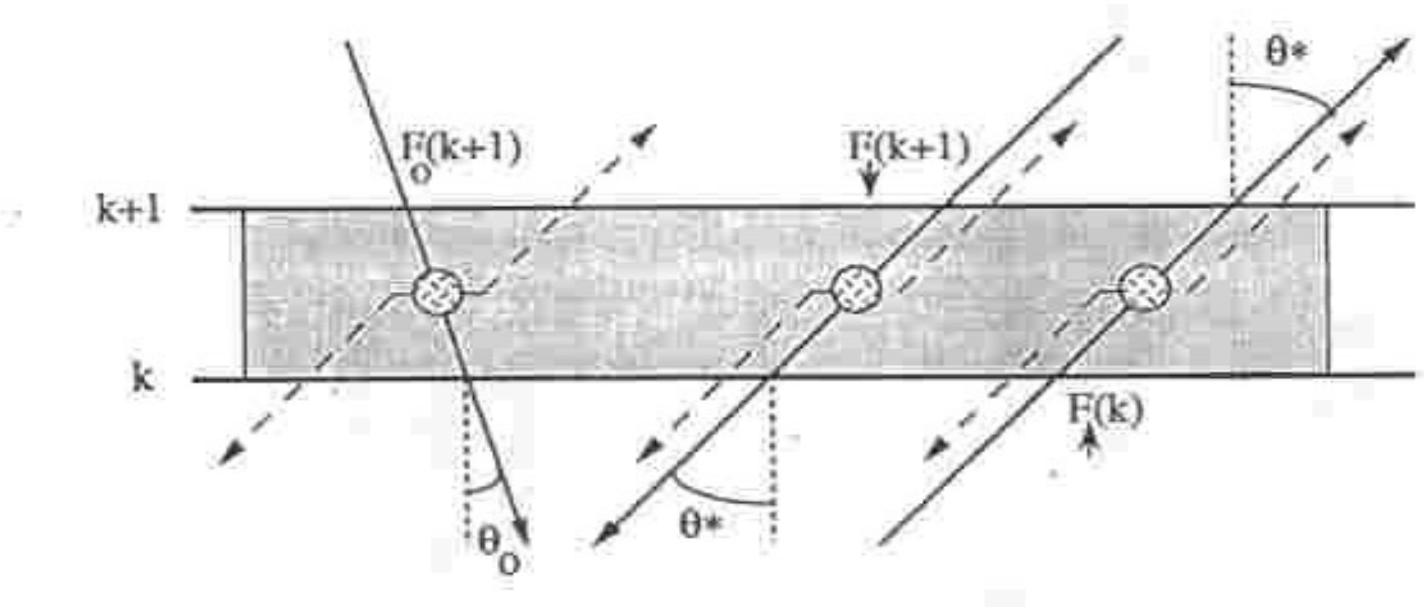
- Monte Carlo

    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

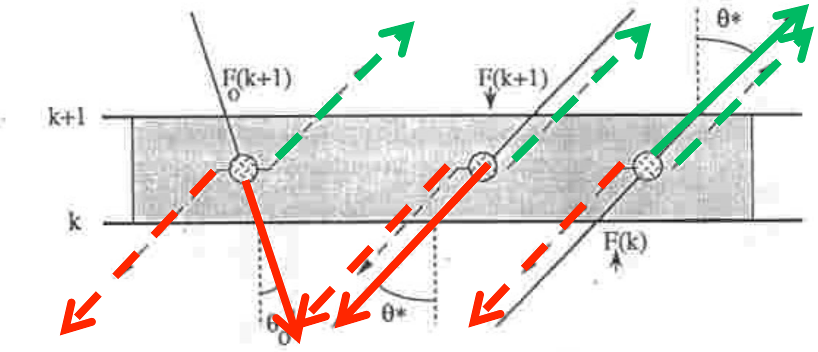
strongly dependent on particle size
- for aerosols:, typically 0.5-0.7
- for clouds, typically 0.7-0.9

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

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



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:

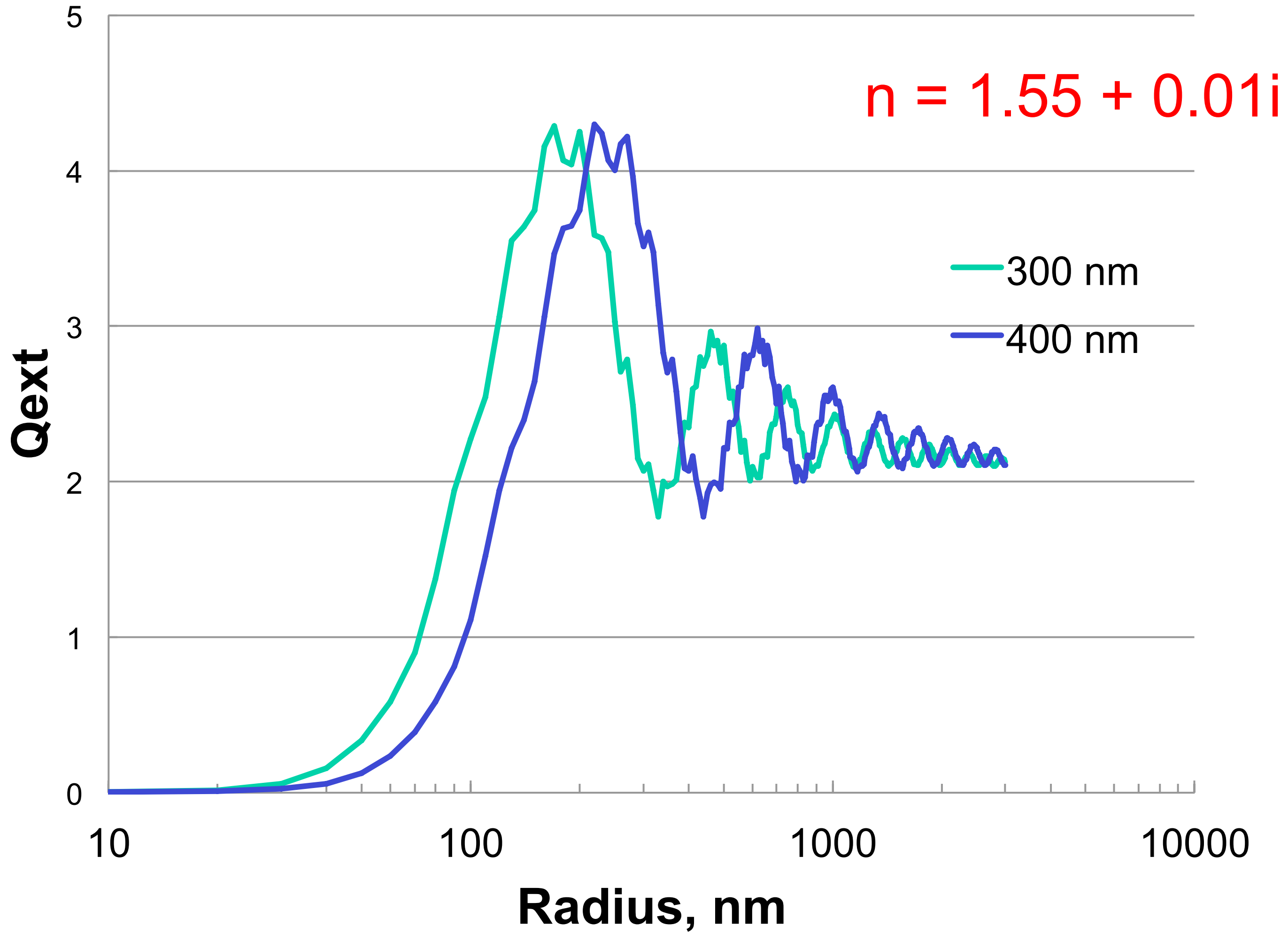
Complex index of refraction: $n = m + \mathrm{i}k$

Size parameter: $\alpha = 2\pi r / \lambda$

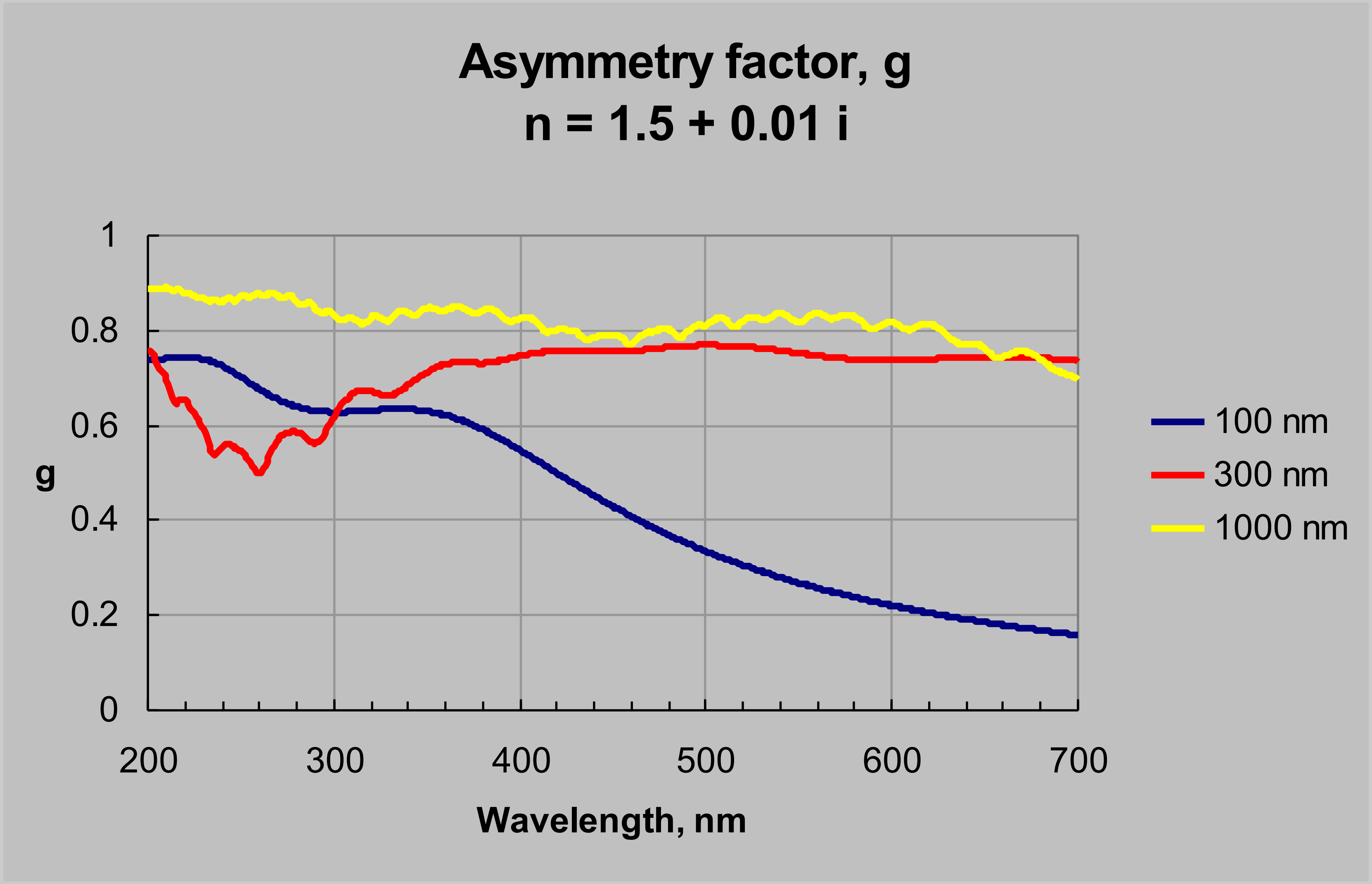
Can compute:

Extinction efficiency	$Q_\mathrm{e}(\alpha, n)$ x πr^2
Scattering efficiency	$Q_\mathrm{s}(\alpha, n)$ x πr^2
Phase function	$P(\Theta, \alpha, n)$
or asymmetry factor	$g(\alpha, n)$

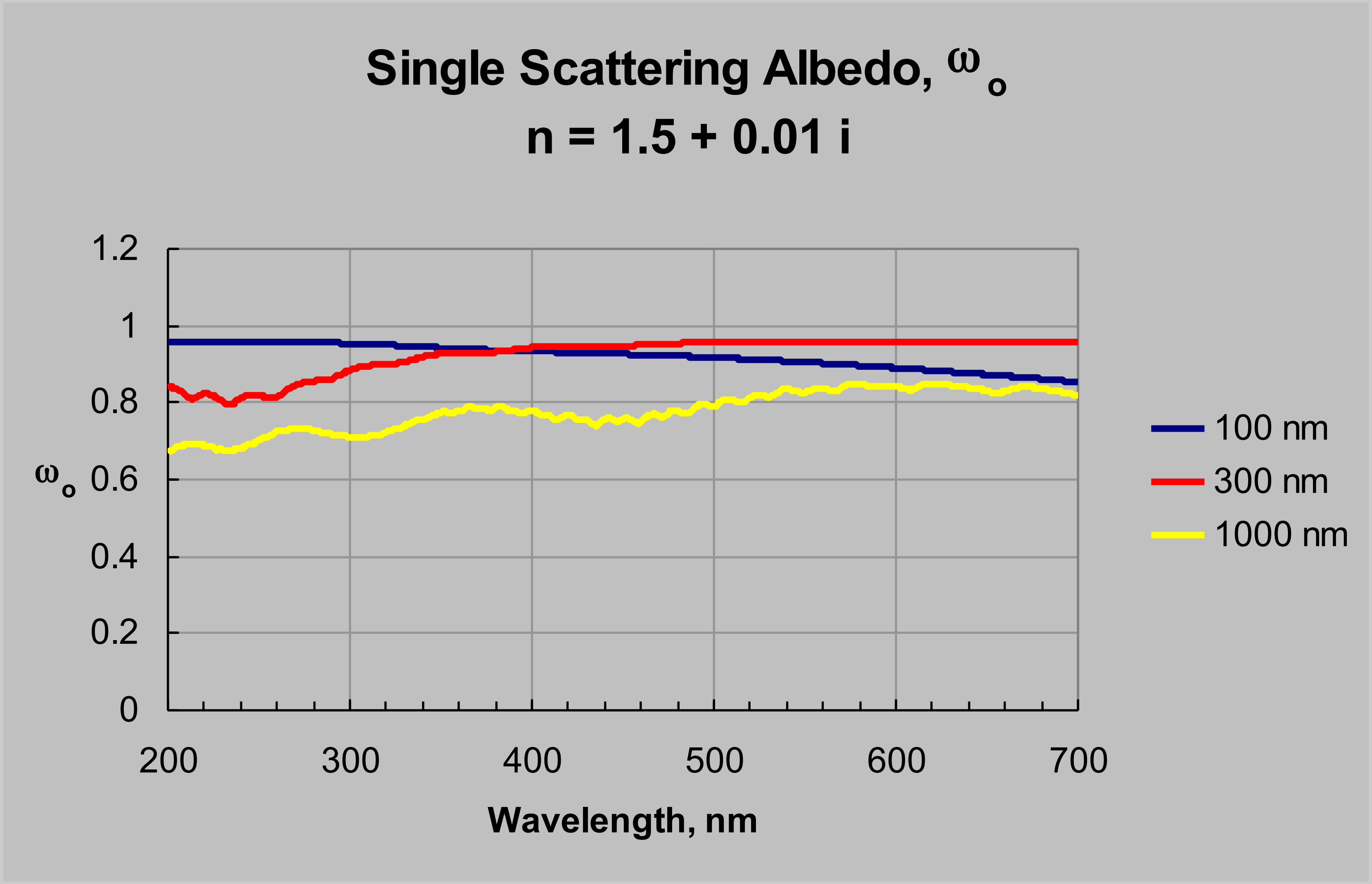
Extinction Efficiency, Q_{ext}



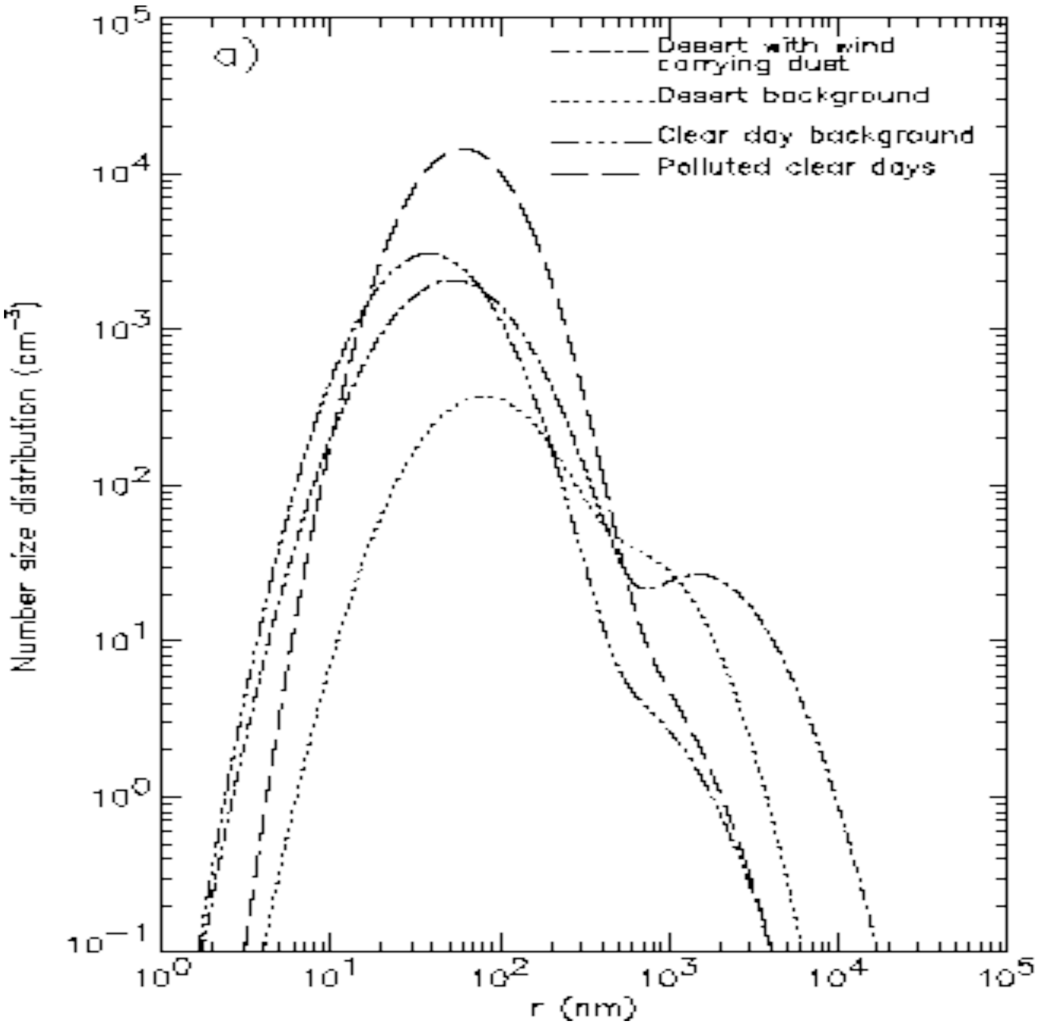
Phase function or Asymmetry factor, g



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



Aerosol size distributions



Optical properties of aerosol ensembles

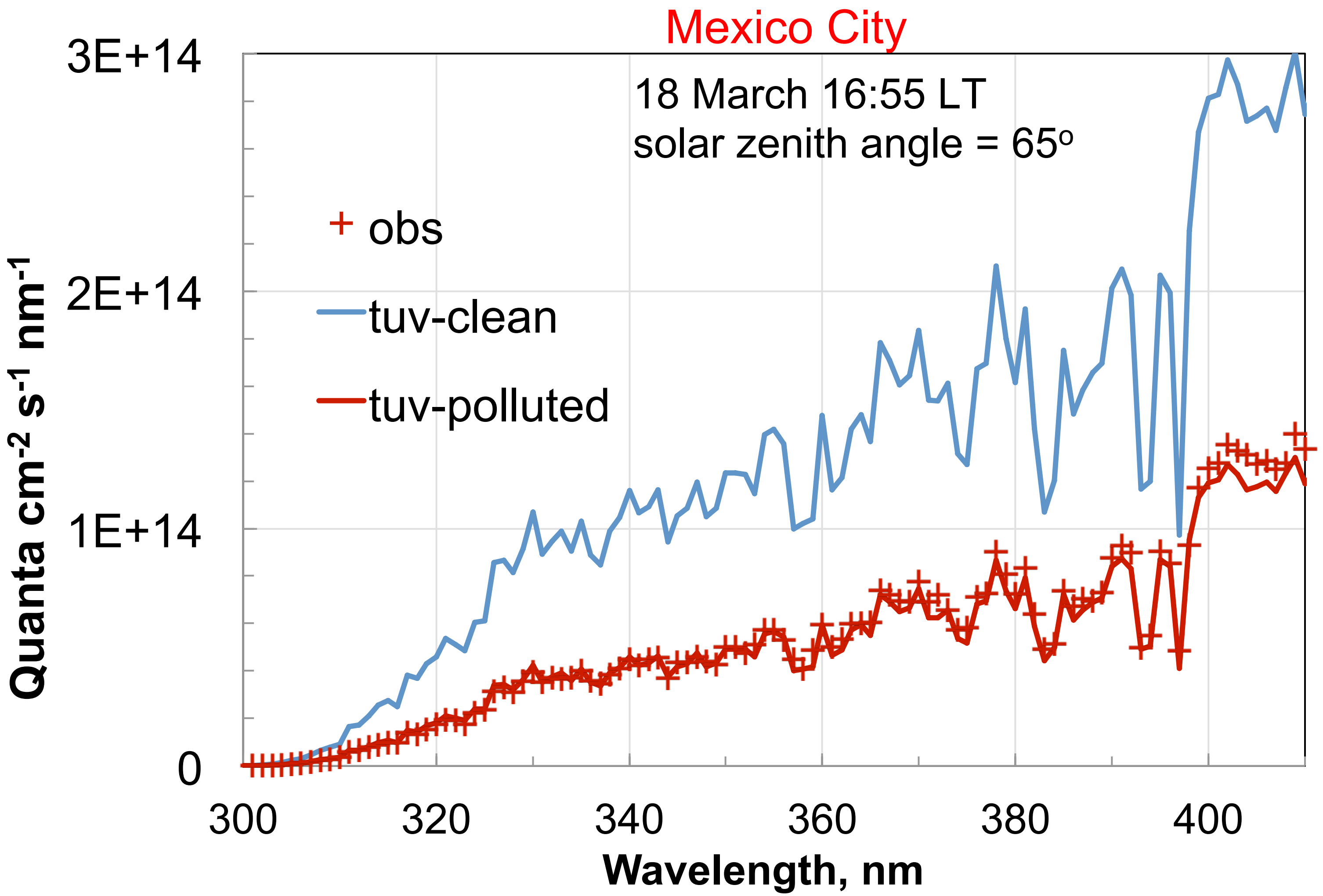
Total extinction coefficient =
$$K_e(\lambda) = \int_0^\infty \pi r^2 Q_e(r,\lambda) n(r)\,\mathrm{d}r$$

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



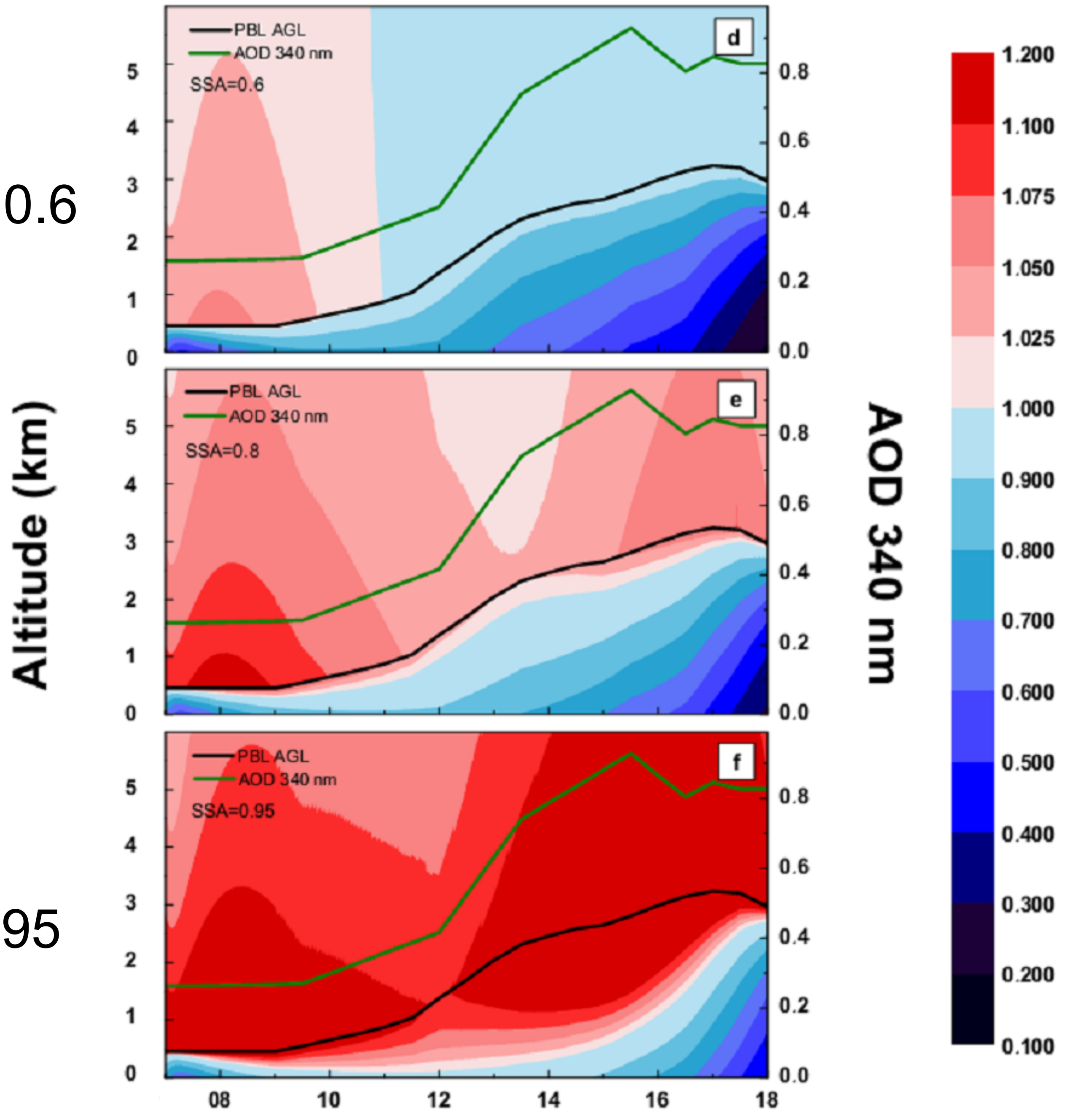
Madronich, Shetter, Halls, Lefer, AGU'07

Effect of aerosols on PBL actinic flux

ssa = 0.6

ssa = 0.8

ssa = 0.95

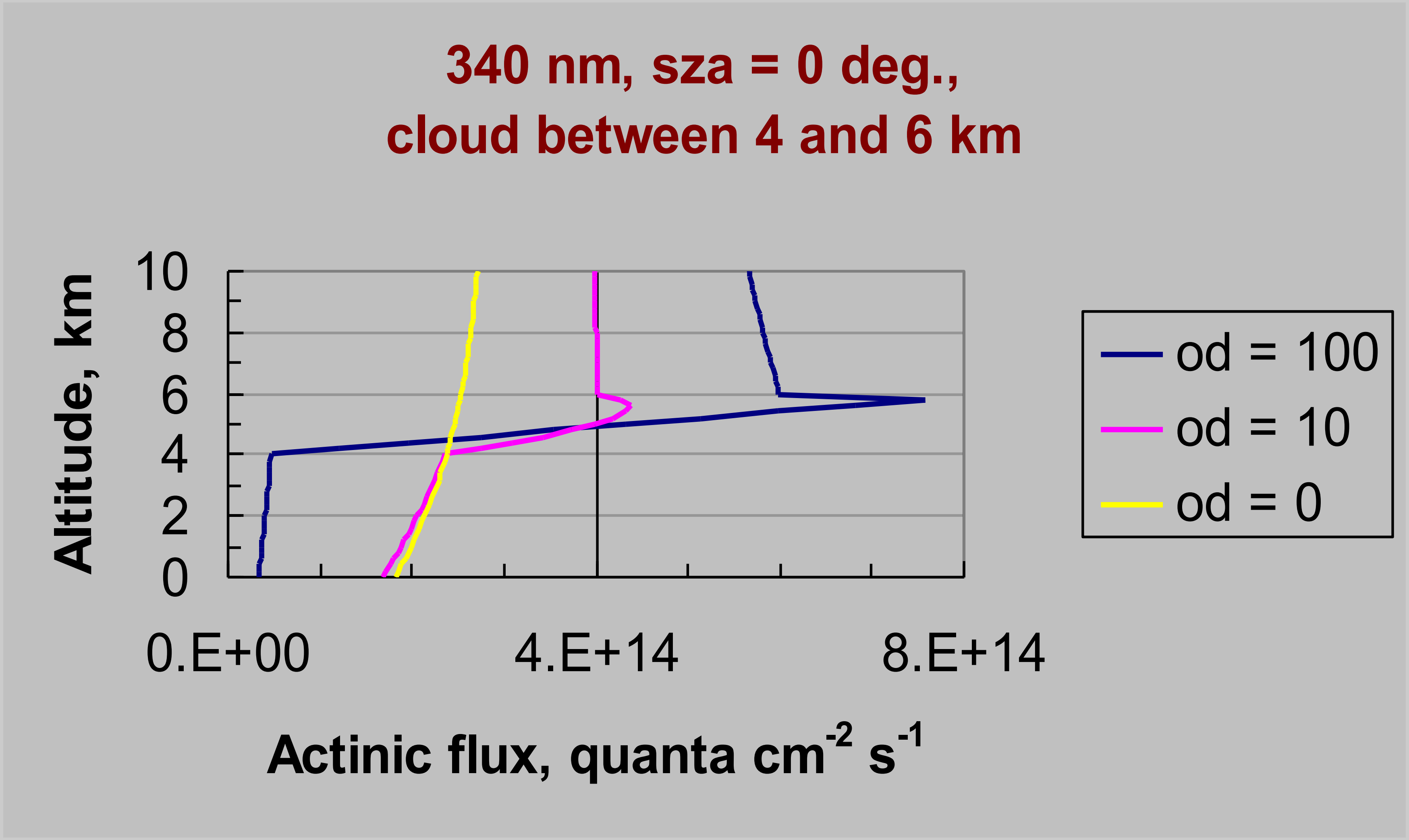


CLOUDS

UNIFORM CLOUD LAYER

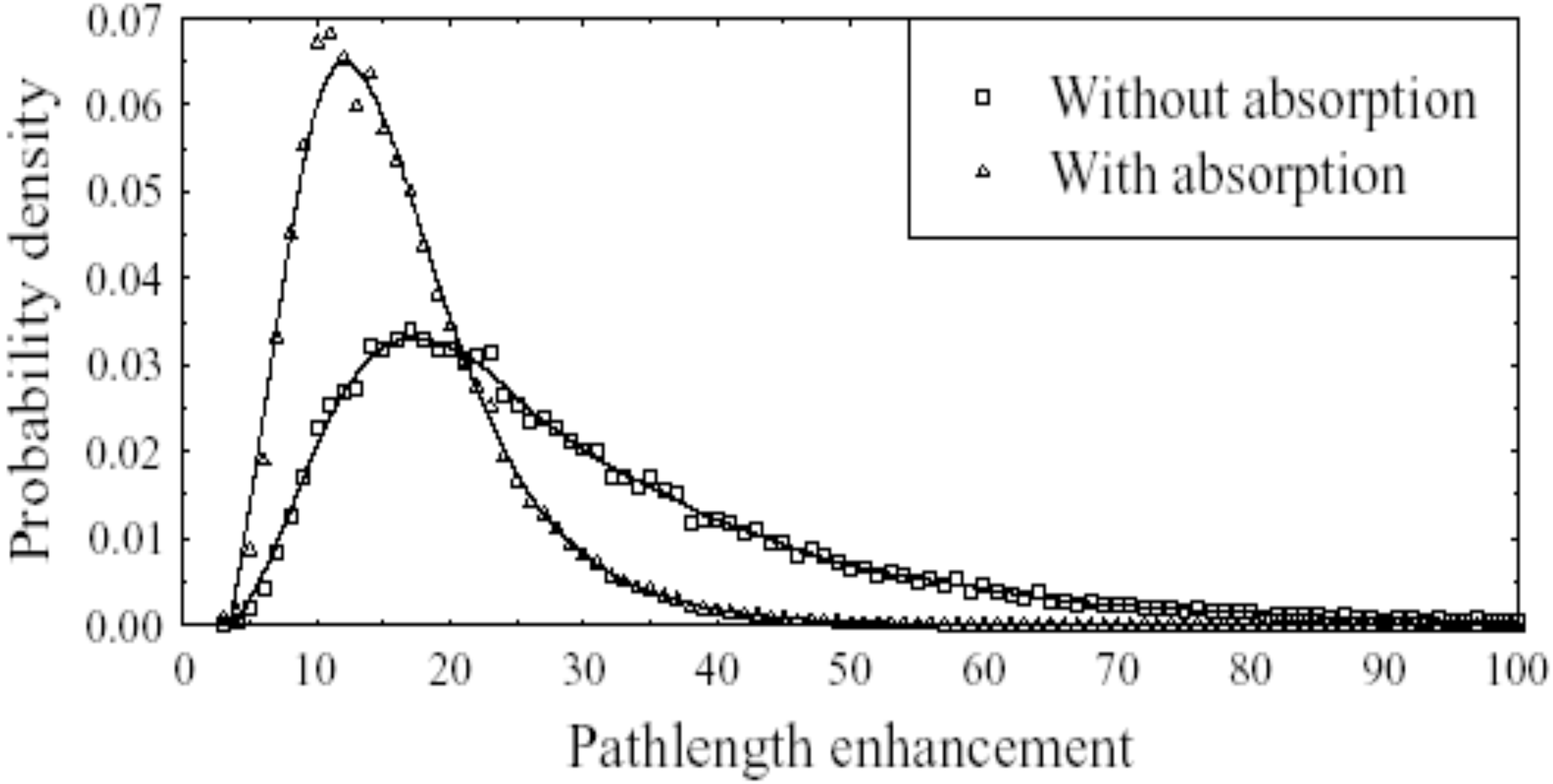
- Above cloud: - high radiation because of reflection
- Below cloud: - lower radiation because of attenuation by cloud
- Inside cloud: - complicated behavior
  - Top half: very high values (for high sun)
  - Bottom half: lower values

EFFECT OF UNIFORM CLOUDS ON ACTINIC FLUX



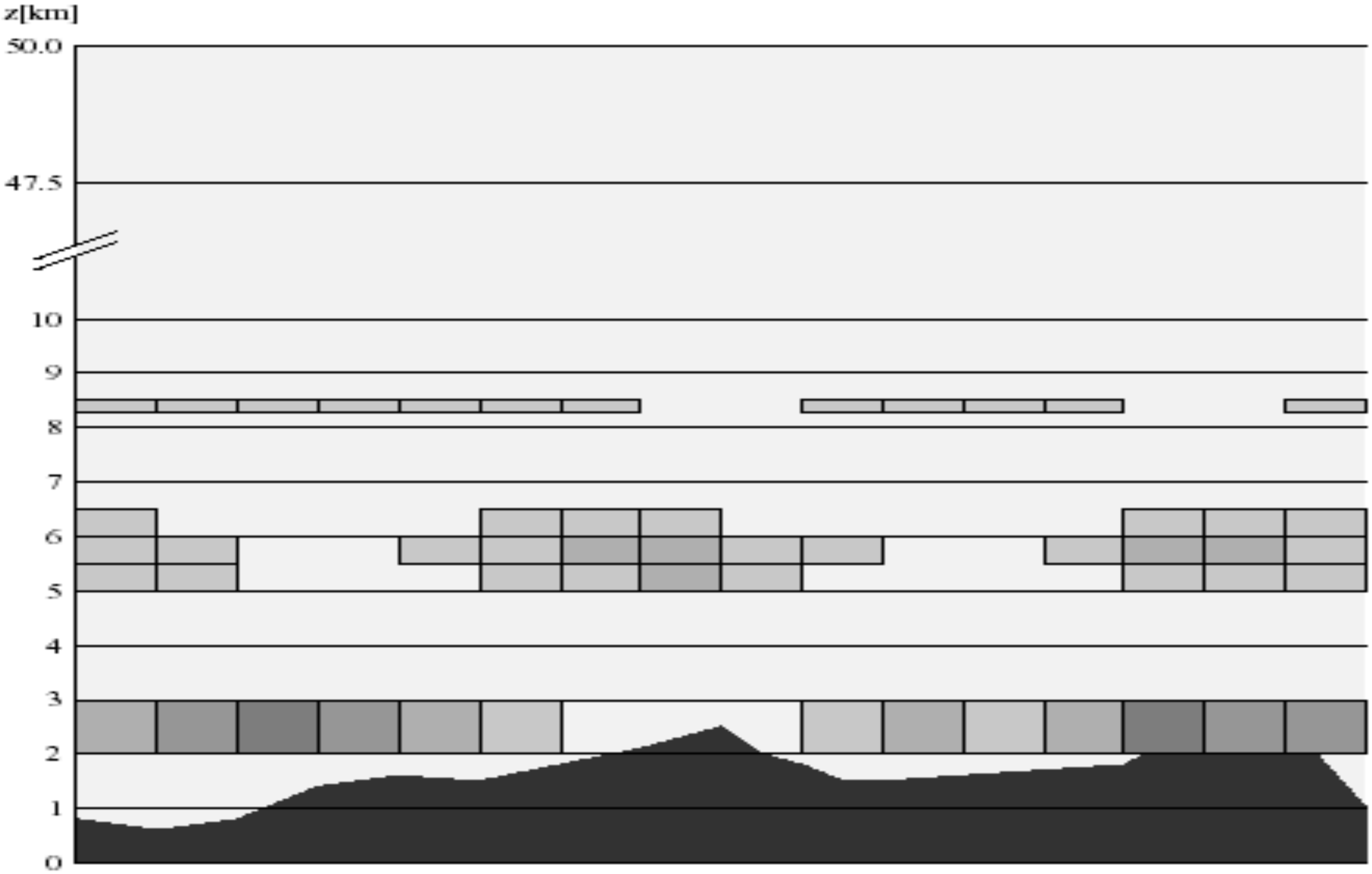
INSIDE CLOUDS:
Photon Path Enhancements

Cumulonimbus, od=400

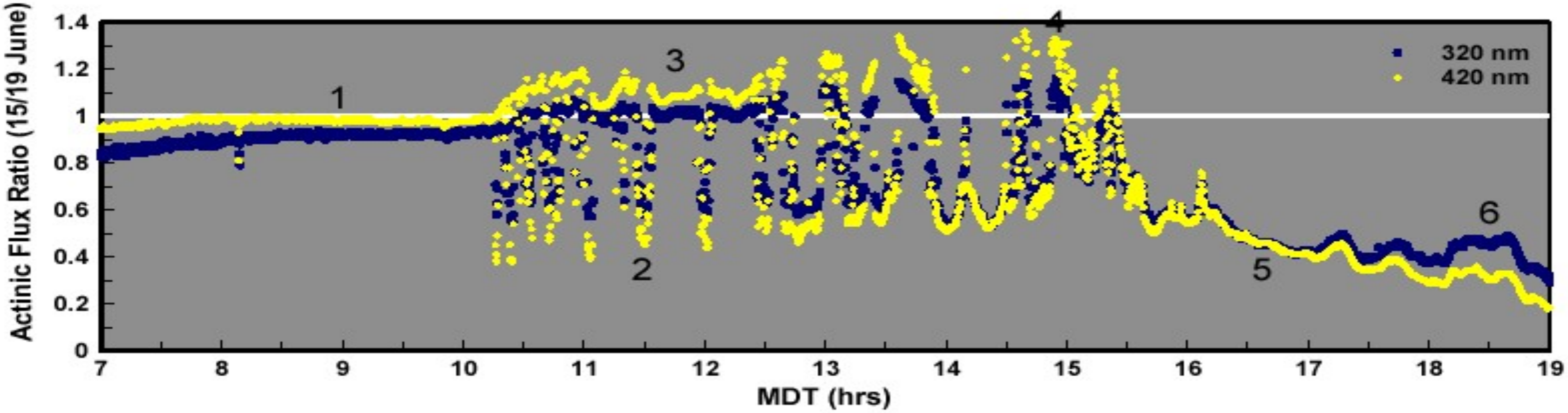


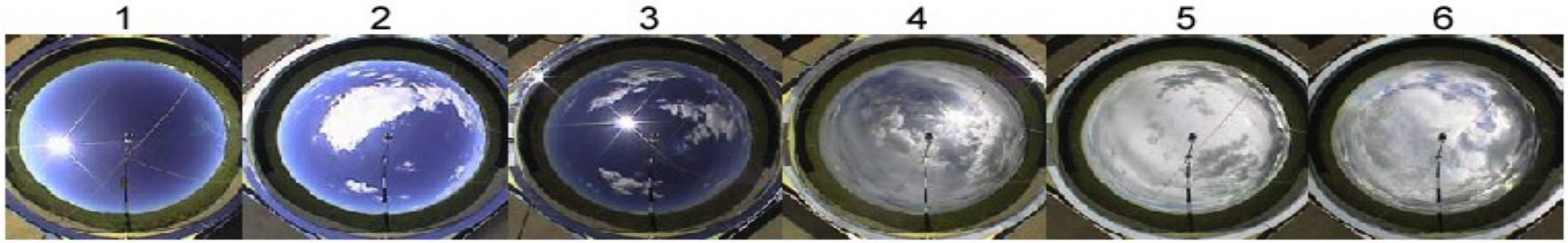
Mayer et al., 1998

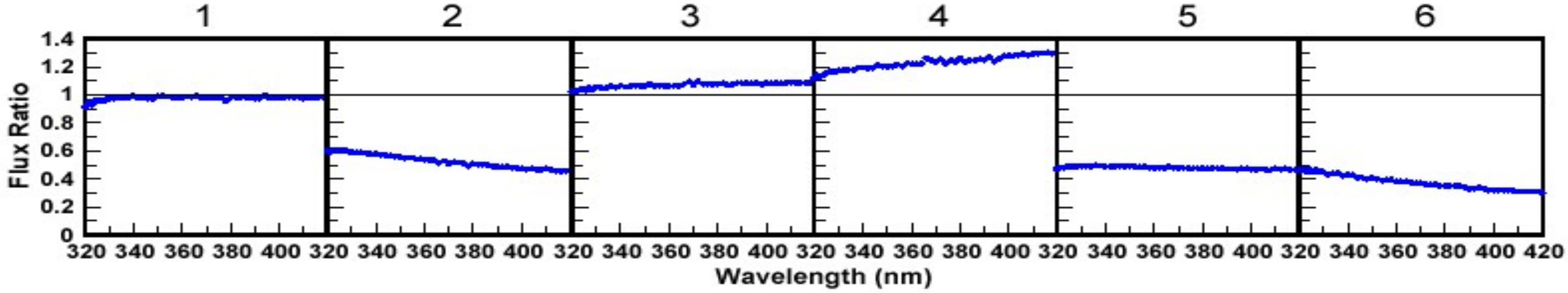
Broken Clouds



SPECTRAL EFFECTS OF PARTIAL CLOUD COVER



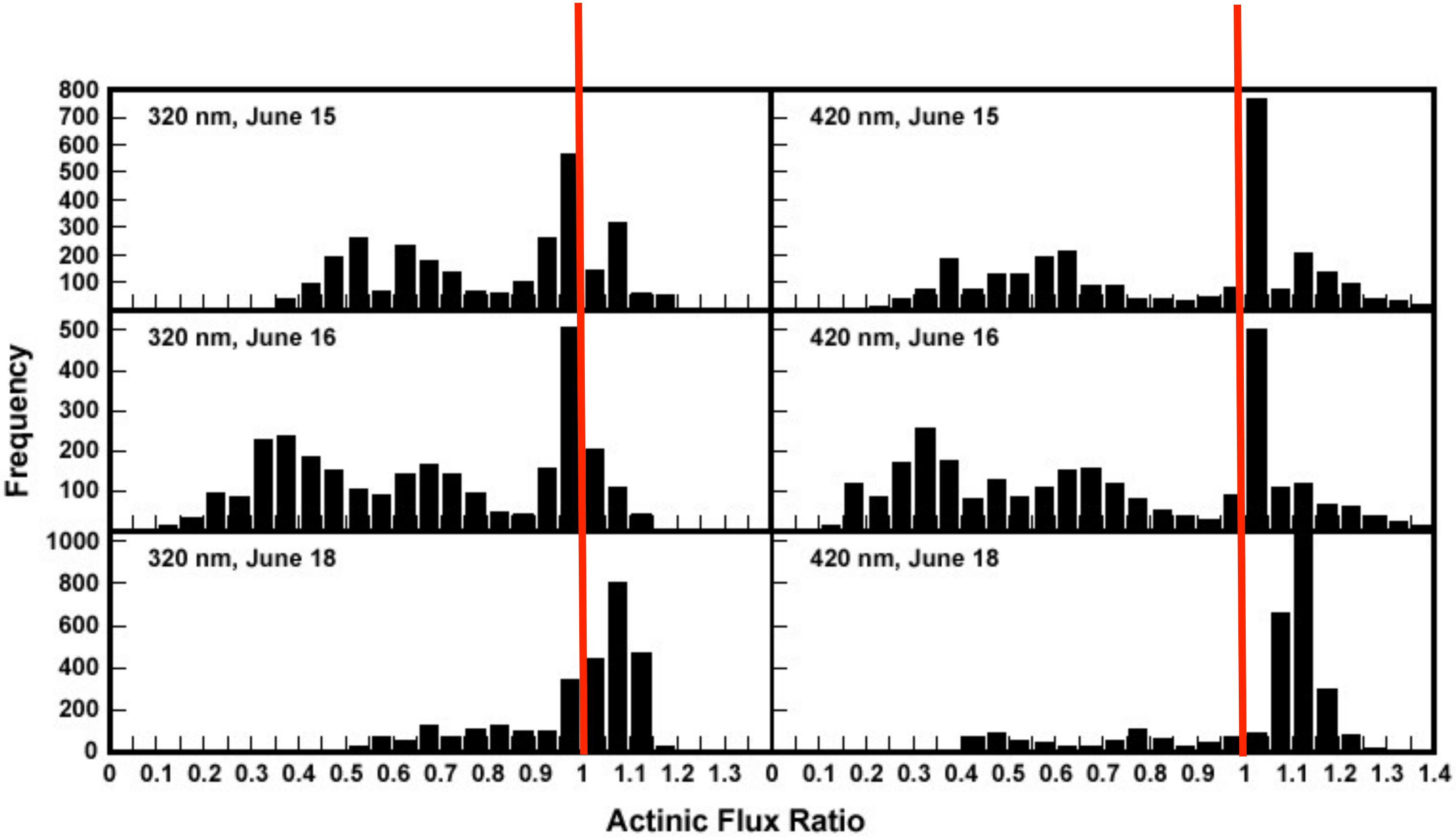




Crafword et al., 2003

PARTIAL CLOUD COVER

Biomodal distributions



Crafword et al., 2003

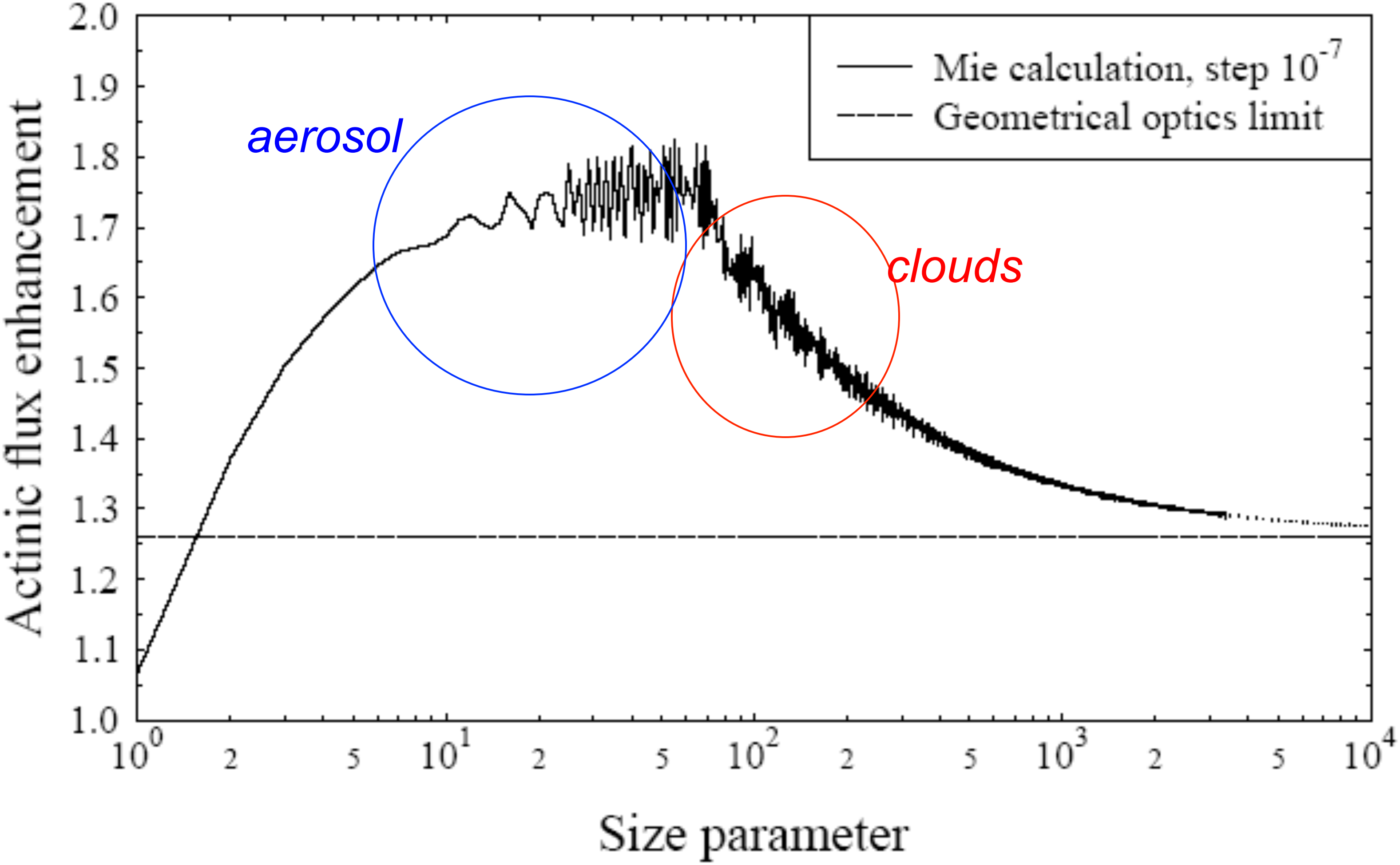
Independent Pixel Approximation

- 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)
  - 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