PHOTOLYSIS

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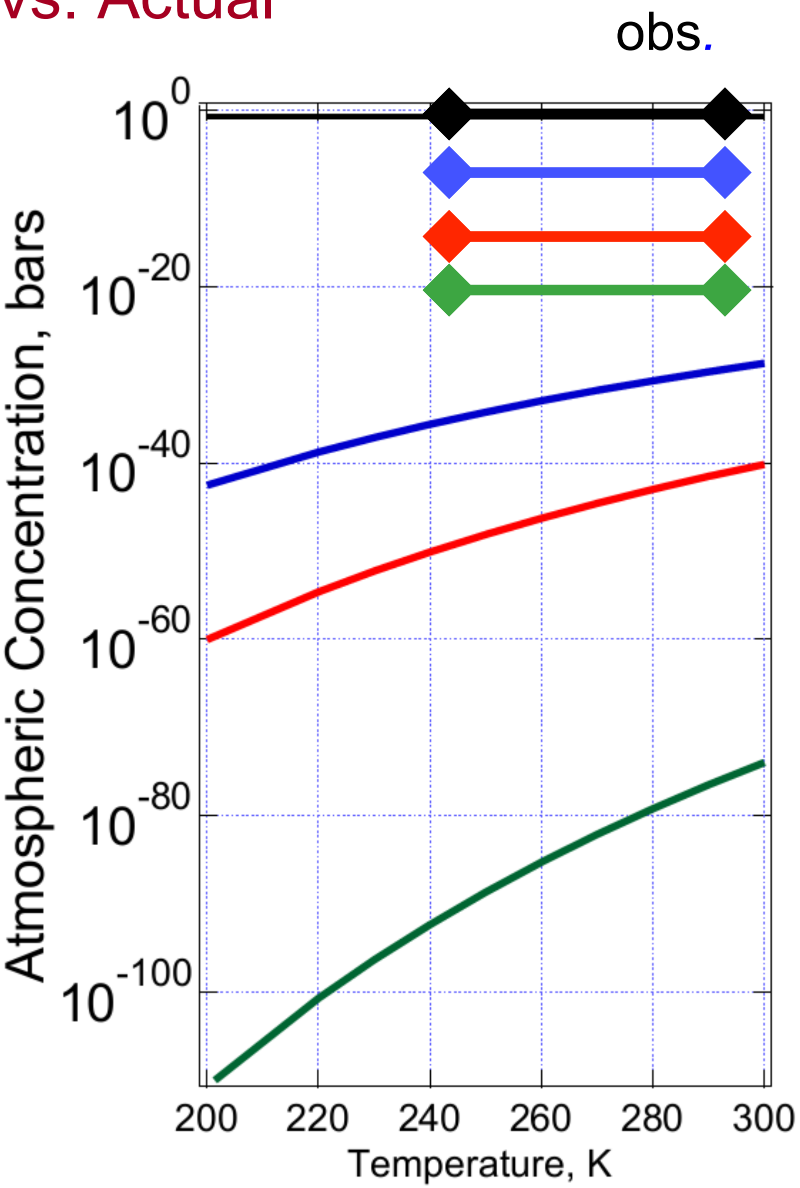
NCAR

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

$O_2 + h\nu\ (\lambda < 240\ \mathrm{nm}) \rightarrow O + O$	source of O_3 in stratosphere
$O_3 + h\nu\ (\lambda < 340\ \mathrm{nm}) \rightarrow O_2 + O(^1D)$	source of OH in troposphere
$NO_2 + h\nu\ (\lambda < 420\ \mathrm{nm}) \rightarrow NO + O(^3P)$	source of O_3 in troposphere
$CH_2O + h\nu\ (\lambda < 330\ \mathrm{nm}) \rightarrow H + HCO$	source of HOx, everywhere
$H_2O_2 + h\nu\ (\lambda < 360\ \mathrm{nm}) \rightarrow OH + OH$	source of OH in remote atm.
$HONO + h\nu\ (\lambda < 400\ \mathrm{nm}) \rightarrow OH + NO$	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 cm^{-2} s^{-1} nm^{-1}

$\propto$ probability of photon near molecule.

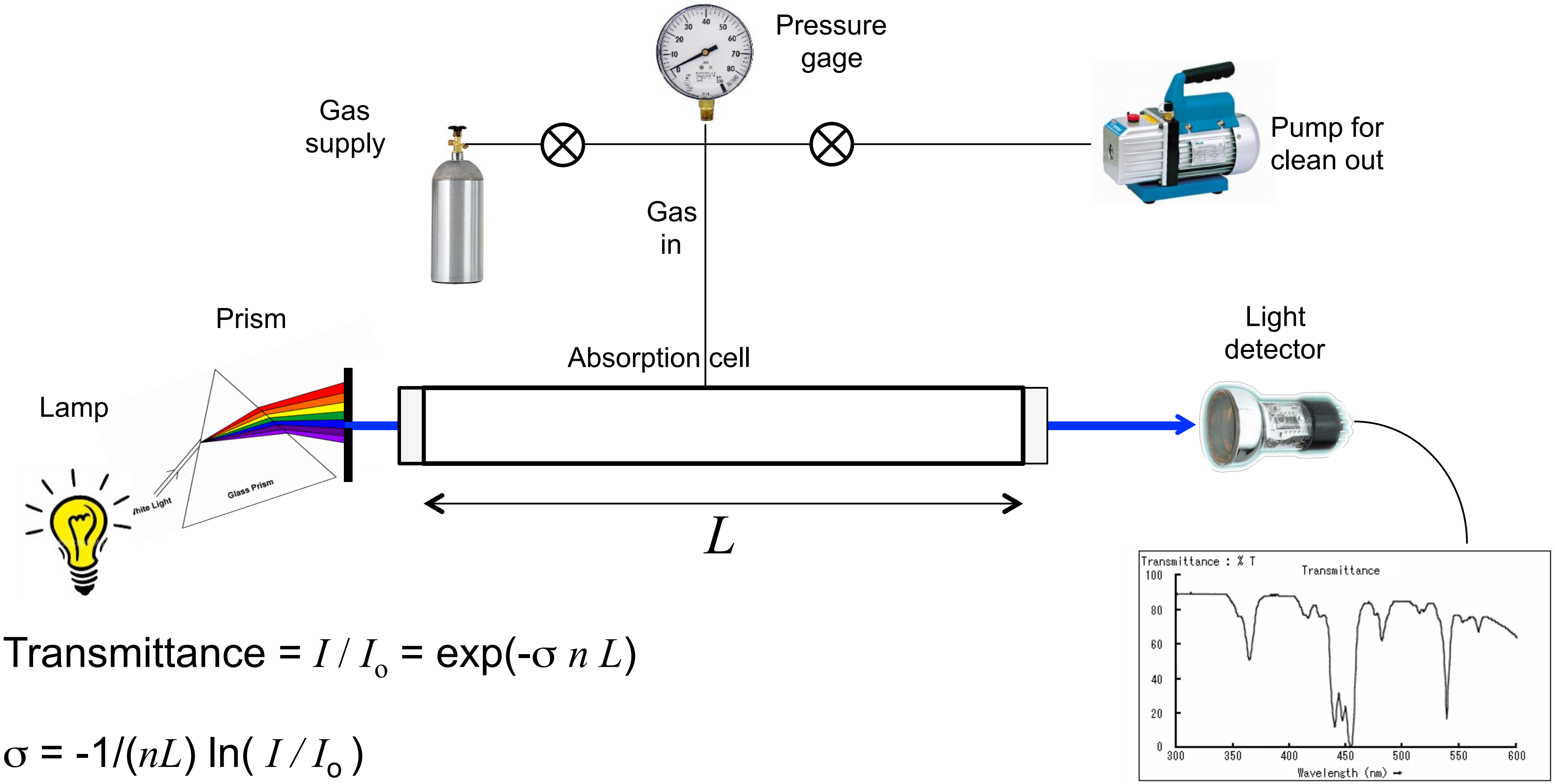
$\sigma(\lambda)$ = absorption cross section, cm^2 molec^{-1}

$\propto$ probability that photon is absorbed.

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

$\propto$ probability that absorbed photon causes dissociation.

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

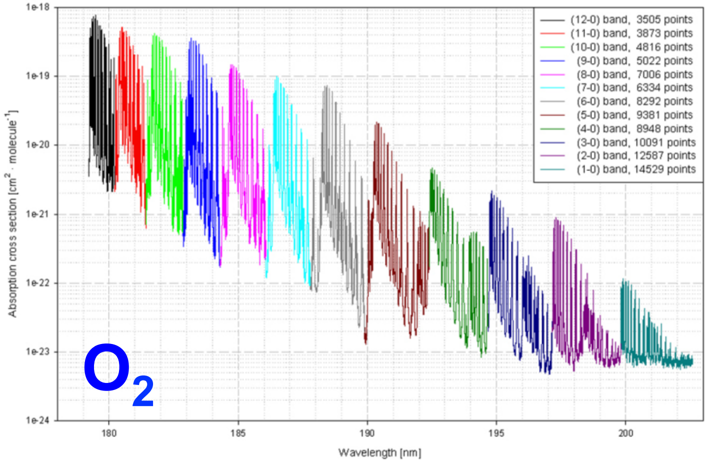


Transmittance = $I / I_o = \exp(-\sigma\, n\, L)$

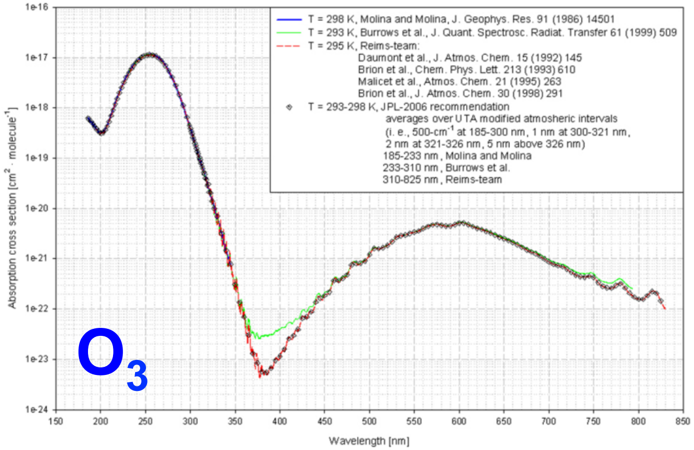
$\sigma = -1/(nL)\ \ln(\, I / I_o\,)$

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

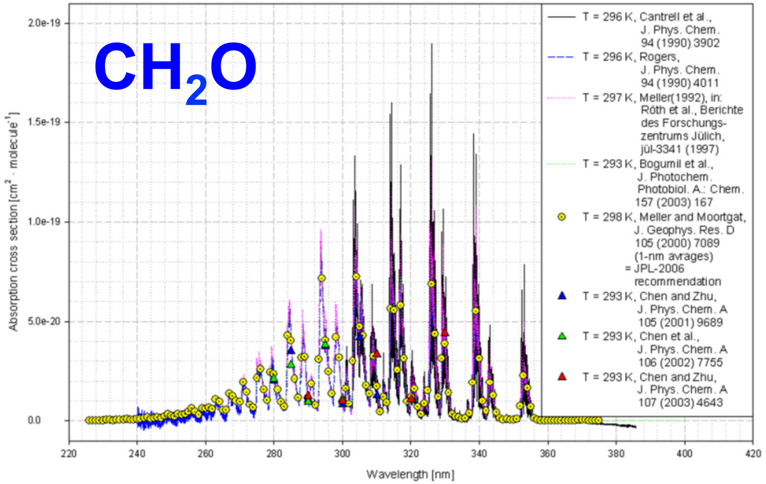
Absorption cross sections $\sigma(\lambda, T)$



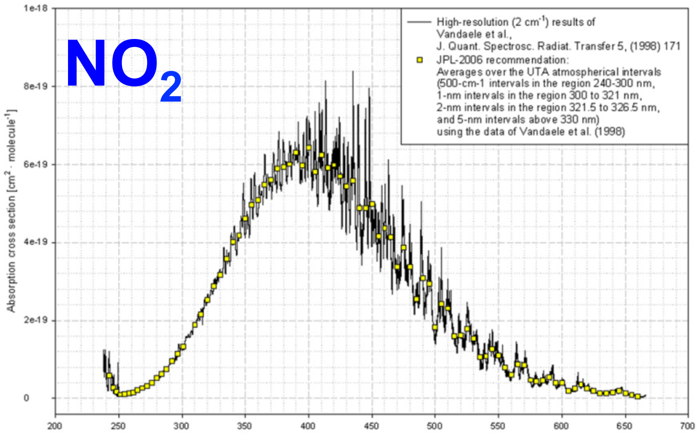
Absorption cross sections in the Schumann-Runge region of oxygen O_2 at 300 K,
Yoshino et al., Planet. Space Sci. 40 (1992) 185



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

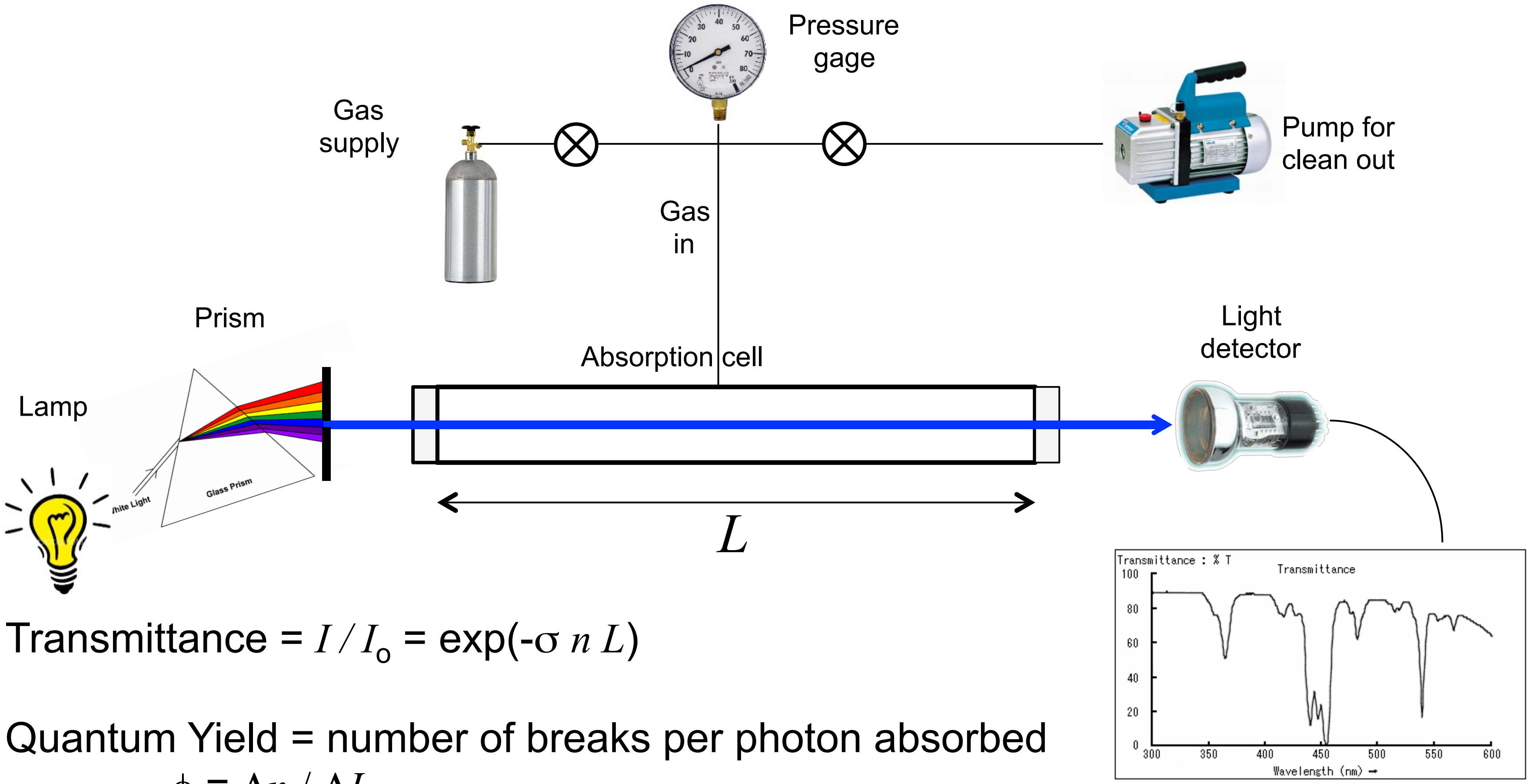


Absorption cross sections of formaldehyde CH_2O at room temperature (results 1990-2003)



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

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



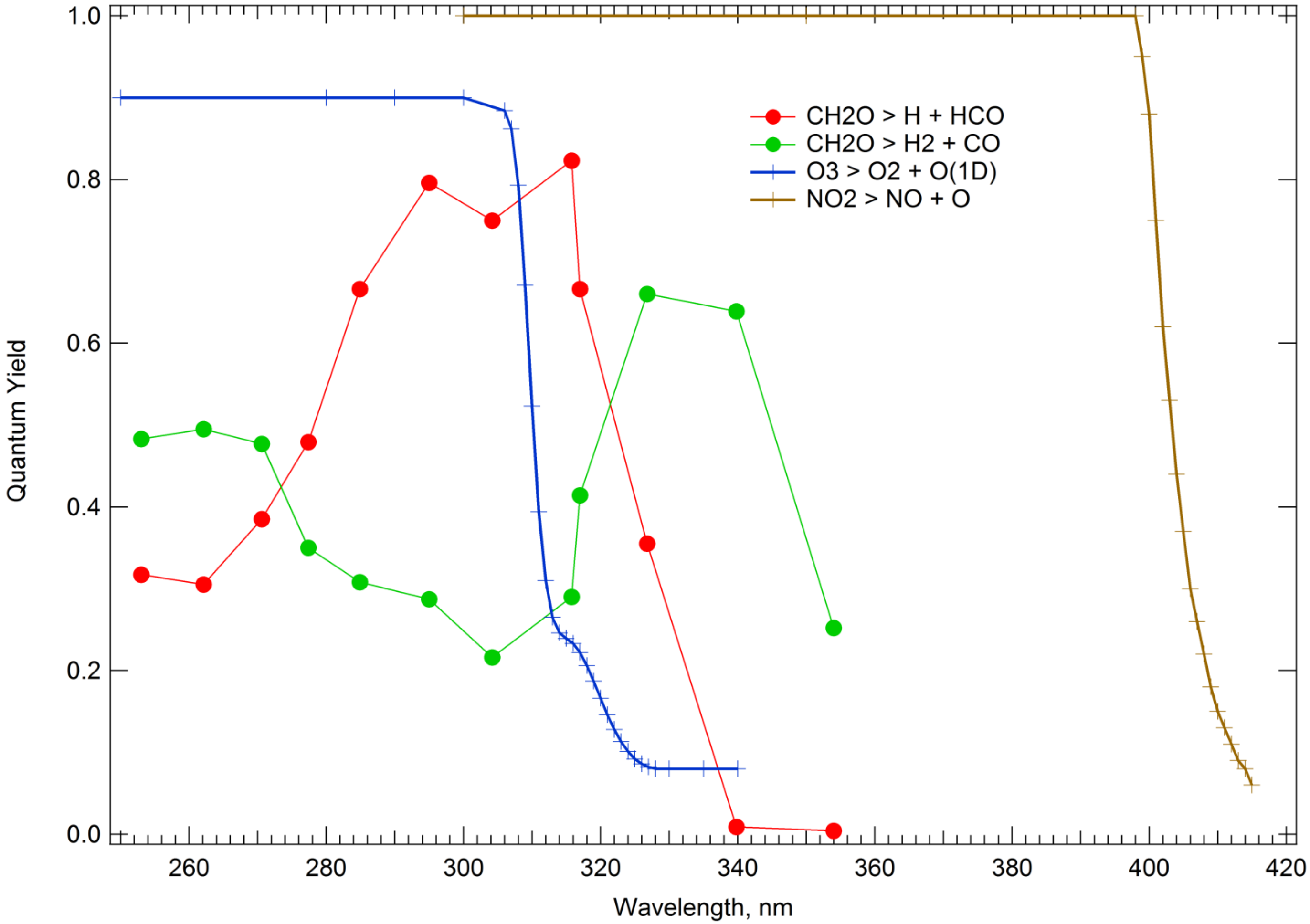
Transmittance = $I / I_o = \exp(-\sigma\, n\, L)$

Quantum Yield = number of breaks per photon absorbed

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

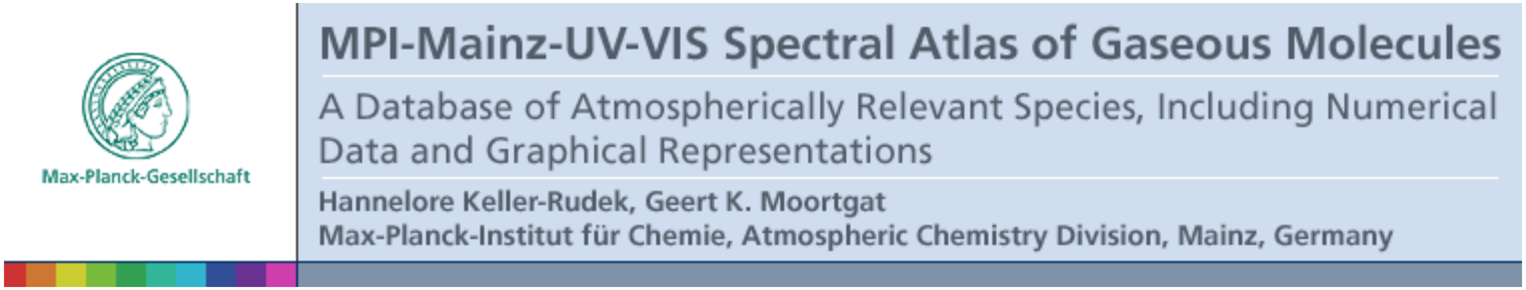
Difficult: must measure absolute change in n (products) and I (photons absorbed)

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



Compilations of Cross Sections & Quantum Yields

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

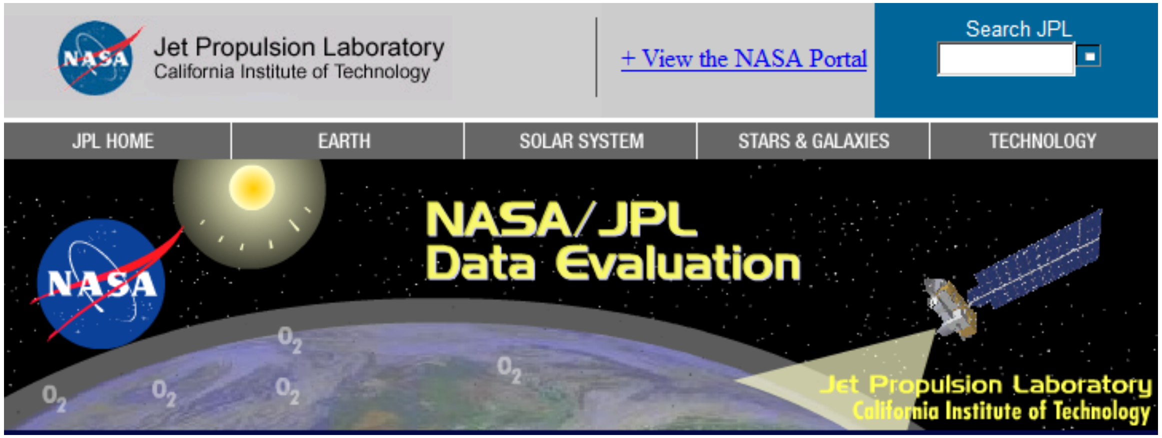


MPI-Mainz-UV-VIS Spectral Atlas of Gaseous Molecules

A Database of Atmospherically Relevant Species, Including Numerical Data and Graphical Representations

Hannelore Keller-Rudek, Geert K. Moortgat
Max-Planck-Institut für Chemie, Atmospheric Chemistry Division, Mainz, Germany

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

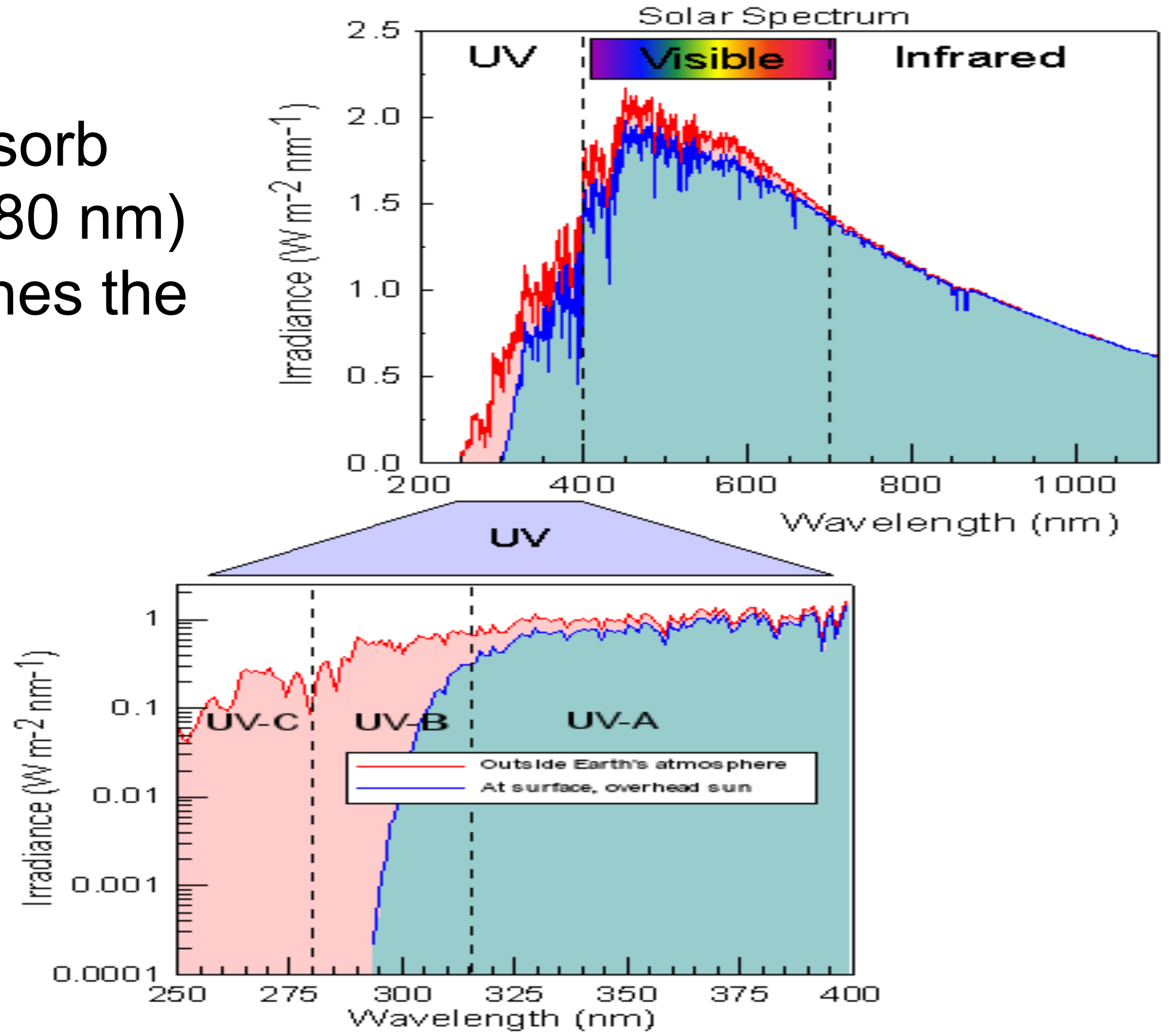


NASA/JPL Data Evaluation

RADIATIVE TRANSFER CONCEPTS

Solar Spectrum

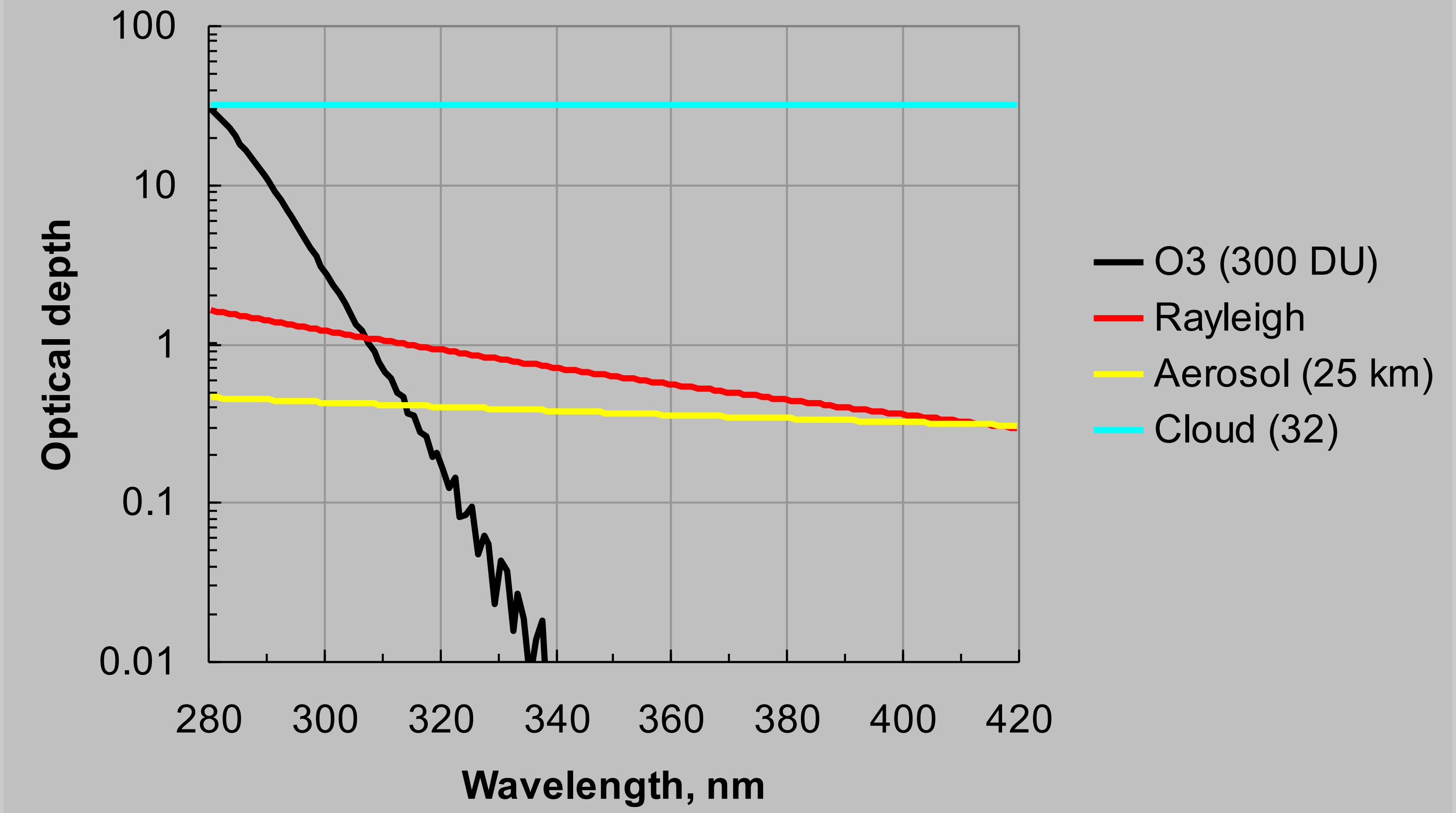
O_2 and O_3 absorb all UV-C (λ<280 nm) before it reaches the troposphere



UNEP, 2002

Atmospheric Optical Depths, τ

defined by Transmission of a vertical beam = exp ($-\tau$)

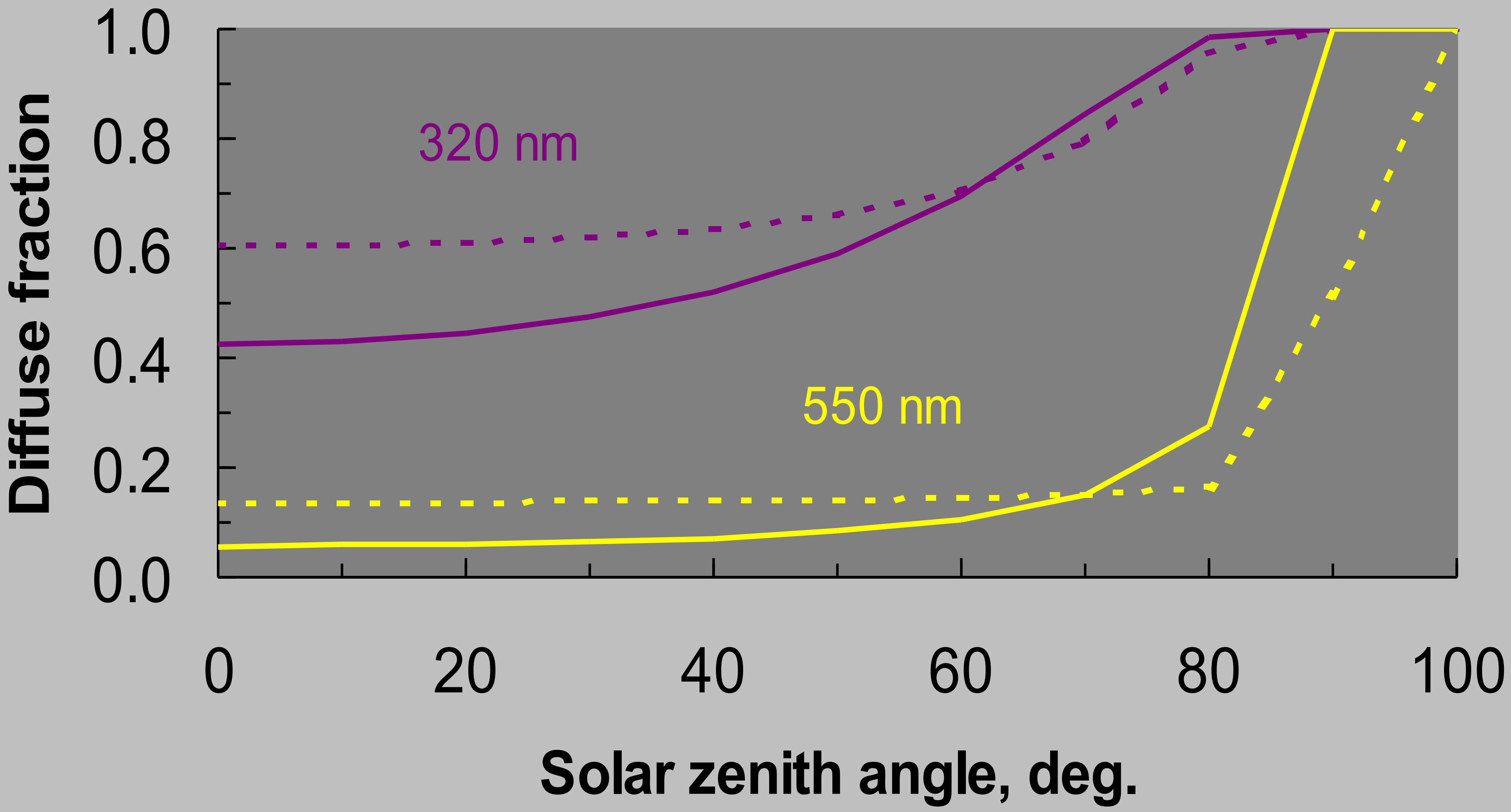


Diffuse transmission can be much larger

UV: Diffuse Radiation ≥ Direct Solar Beam

clean skies, sea level

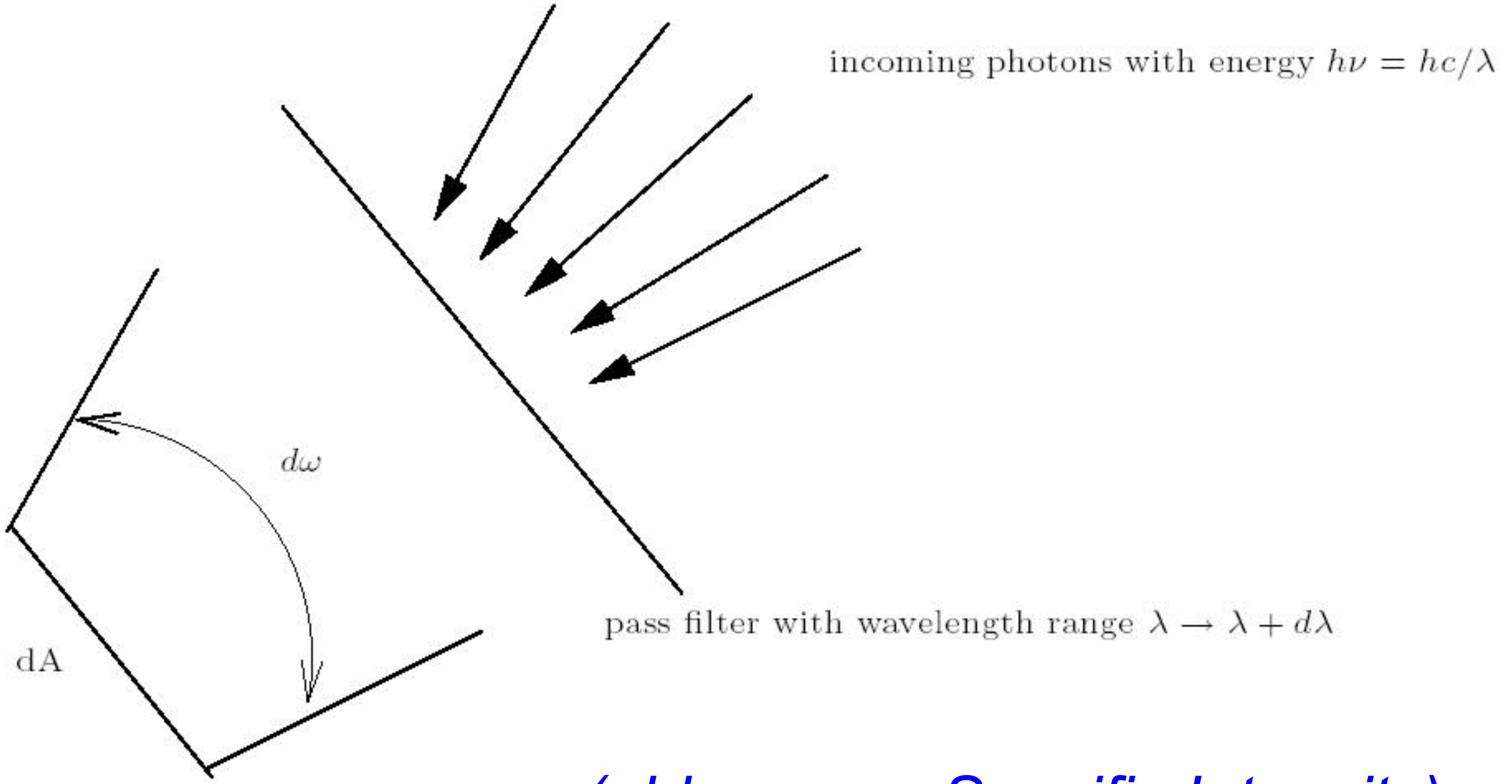
——— *Irradiance* - - - - - *Actinic flux*



Spectral Radiance, I

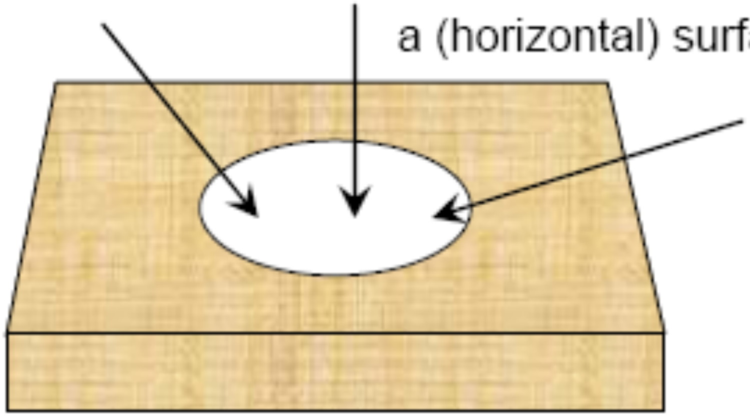
$$I(\lambda,\theta,\phi) = N(hc/\lambda) \,/\, (dt\ dA\ d\omega\ d\lambda)$$

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

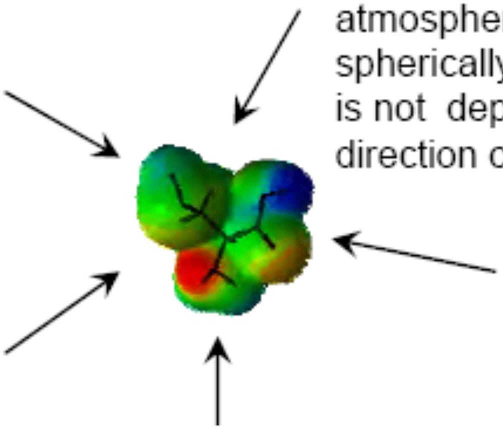


(old name = Specific Intensity)

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.

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

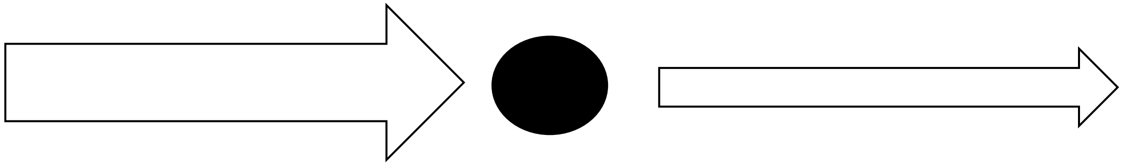
$$F = \int_0^{\pi}\int_0^{2\pi} I(\theta,\varphi)\sin\theta\,\mathrm{d}\varphi\,\mathrm{d}\theta$$

Watts m^{-2}

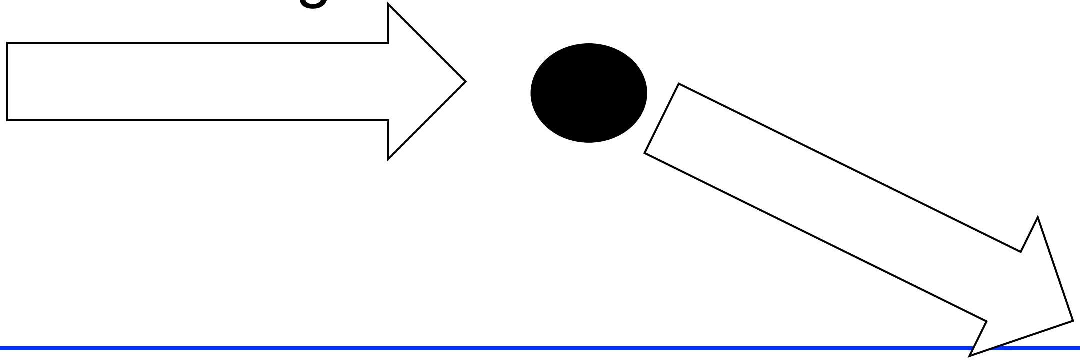
Watts m^{-2} or quanta s^{-1} cm^{-2}

Absorption and Scattering

- Absorption – inelastic, loss of radiant energy:

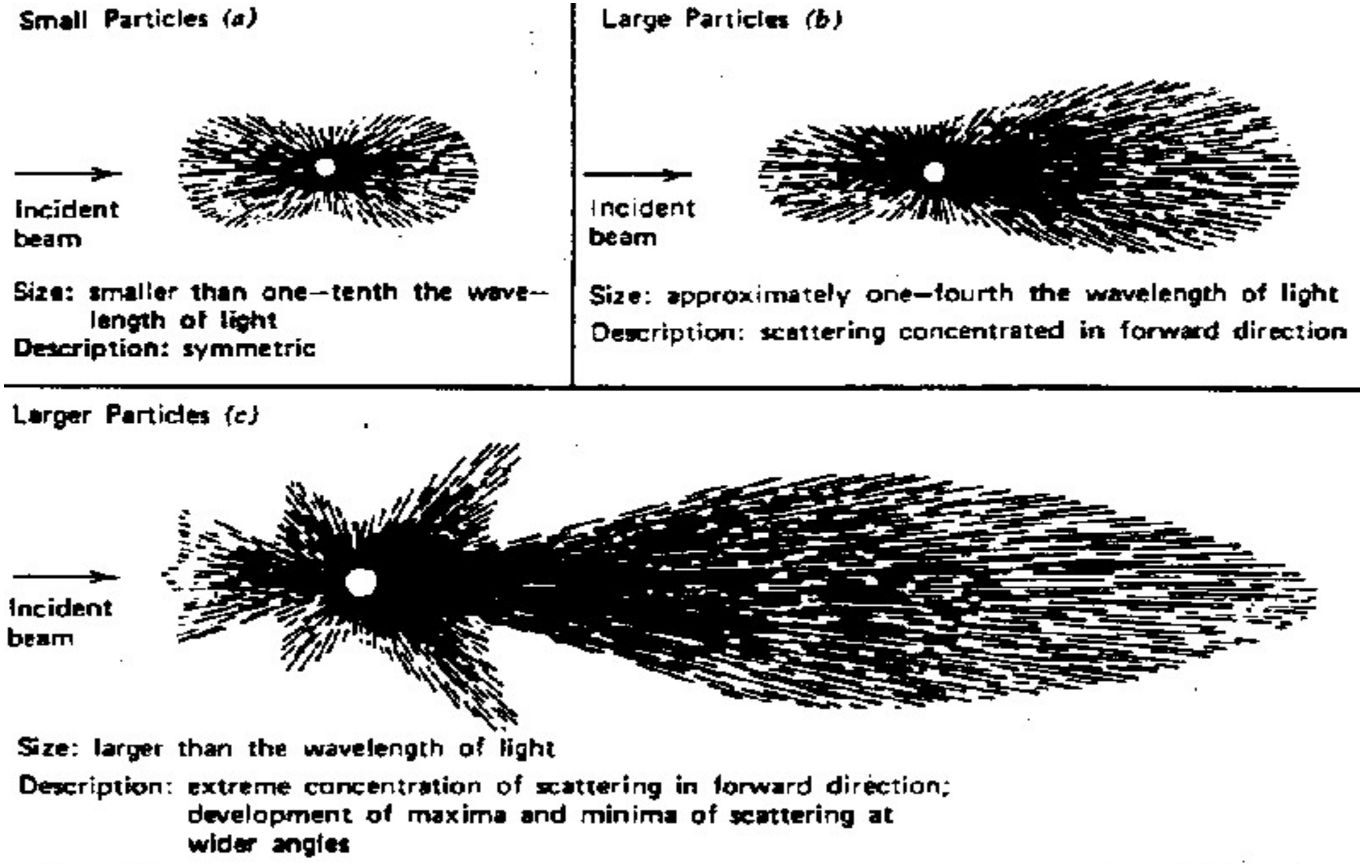


- Scattering – elastic, radiant energy is conserved, direction changes:



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

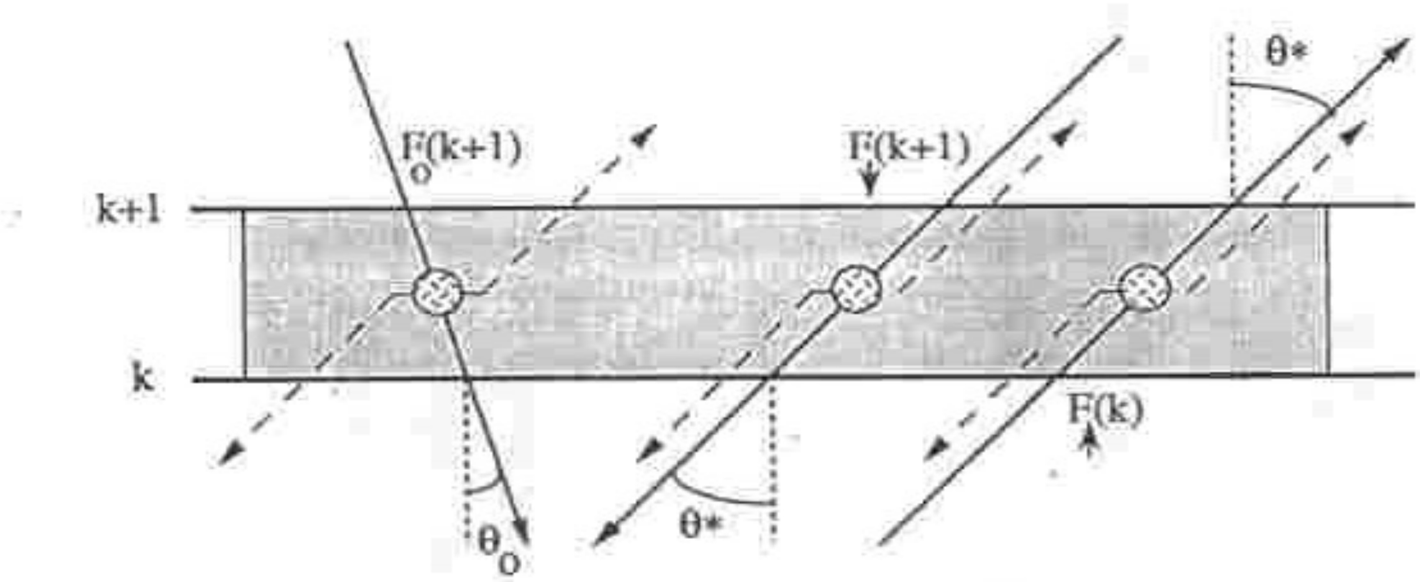
- Monte Carlo

  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: $0.01 - 5.0$

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

(α =*Angstrom exponent*)

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

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

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*

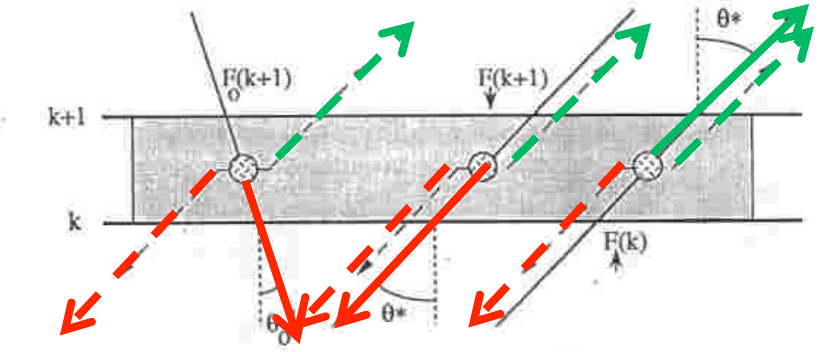
SIMPLE 2-STREAM METHOD:

3 Equations for each layer

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

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

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



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:

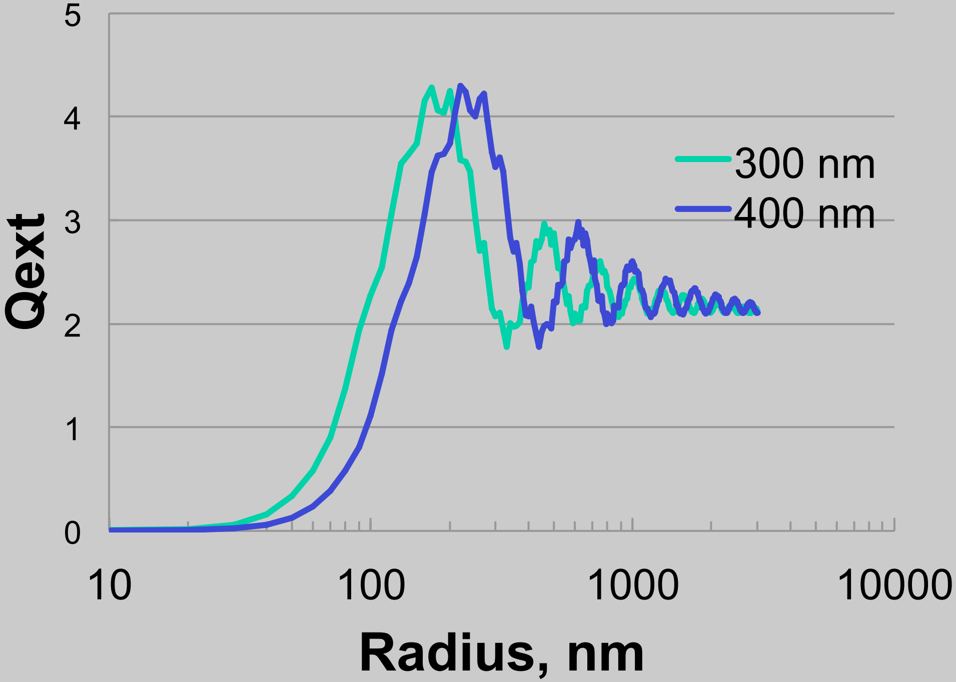
Complex index of refraction: $n = m + \mathrm{i}k$
Size parameter: $\alpha = 2\pi r / \lambda$

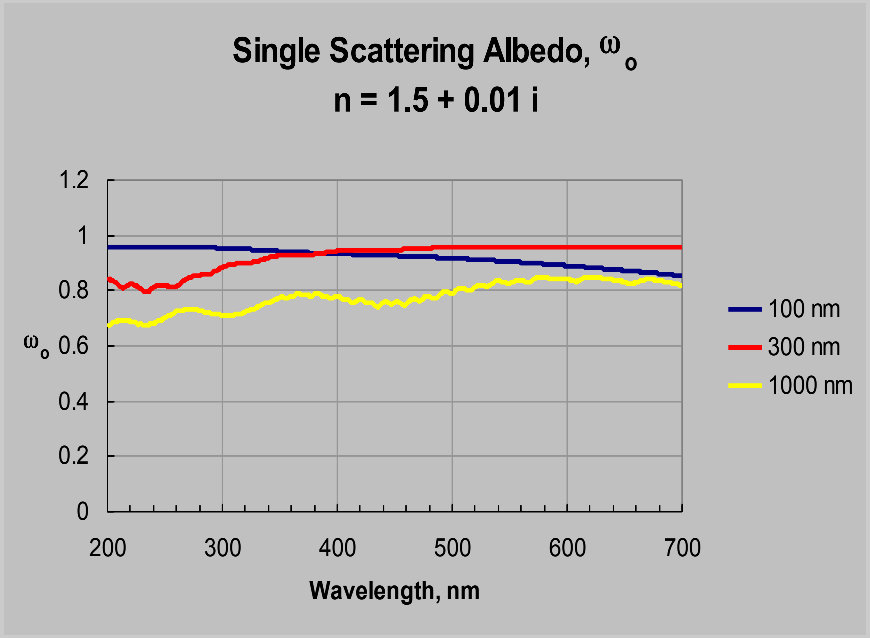
Can compute:

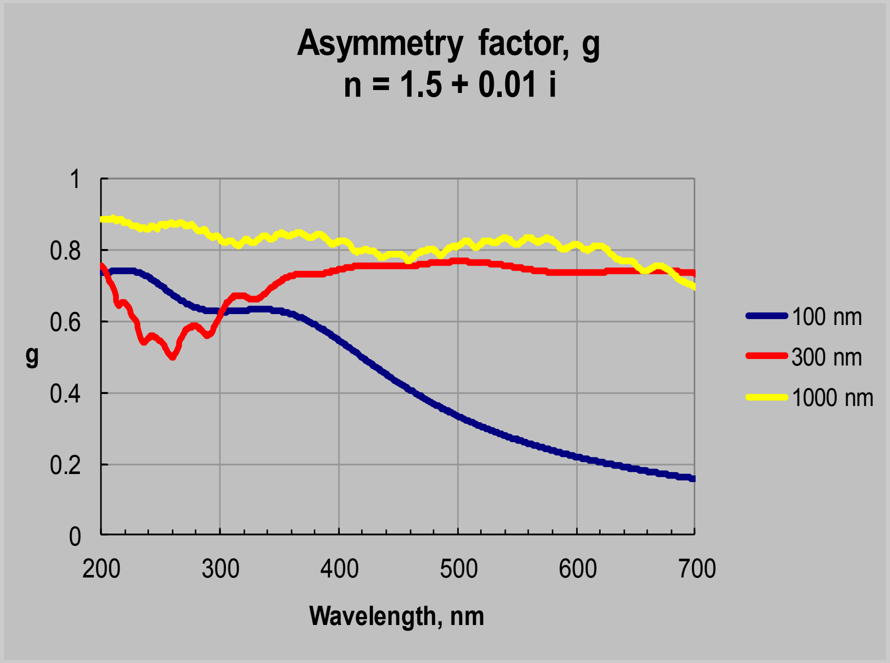
Extinction efficiency	$Q_\mathrm{e}(\alpha, n)$	x πr^2
Scattering efficiency	$Q_\mathrm{s}(\alpha, n)$	x πr^2
Phase function	$P(\Theta, \alpha, n)$	
or asymmetry factor	$g(\alpha, n)$	

Mie Theory
Typical Results

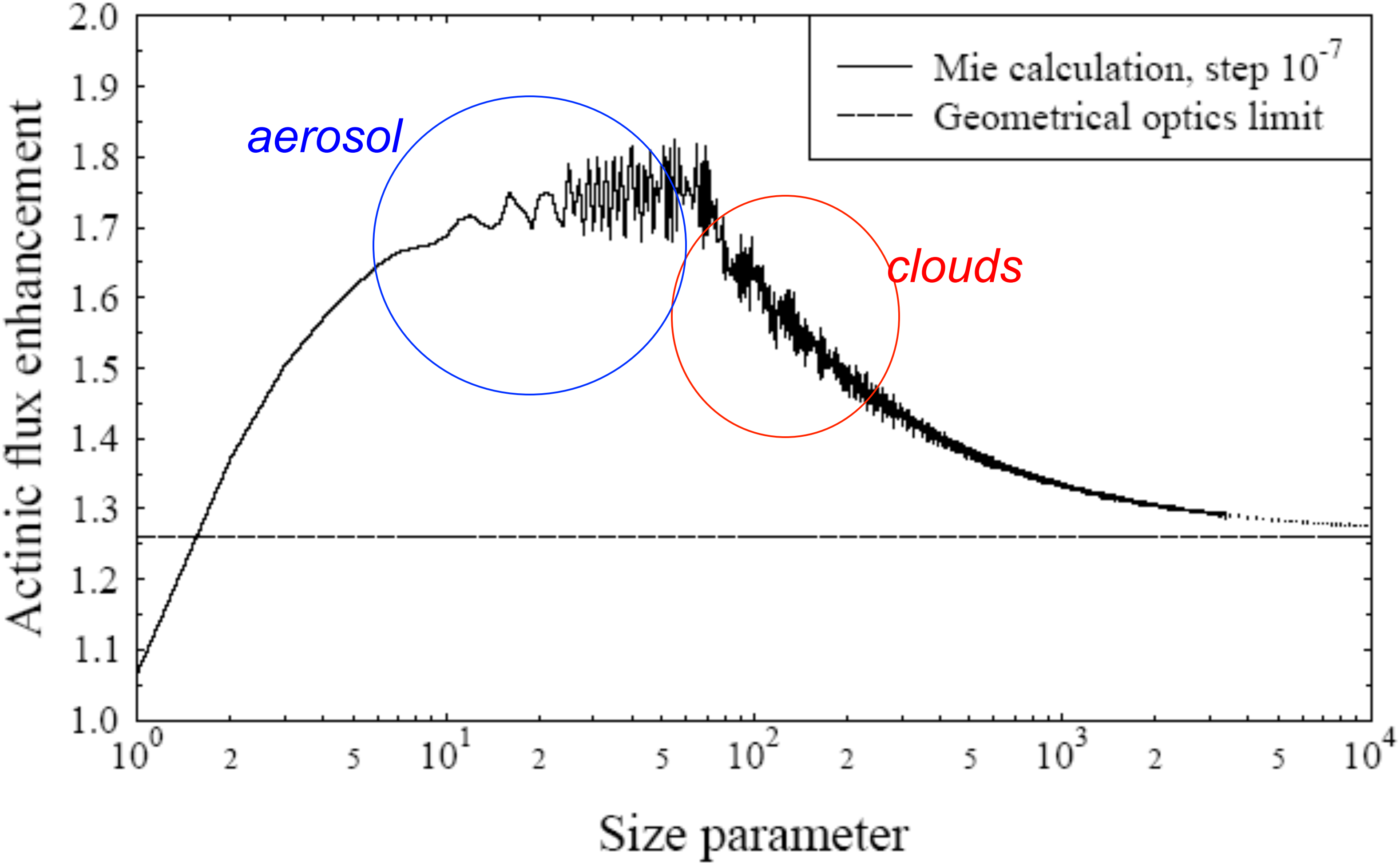
$$\alpha = 2\pi r / \lambda$$




Single Scattering Albedo, ω_o
n = 1.5 + 0.01 i

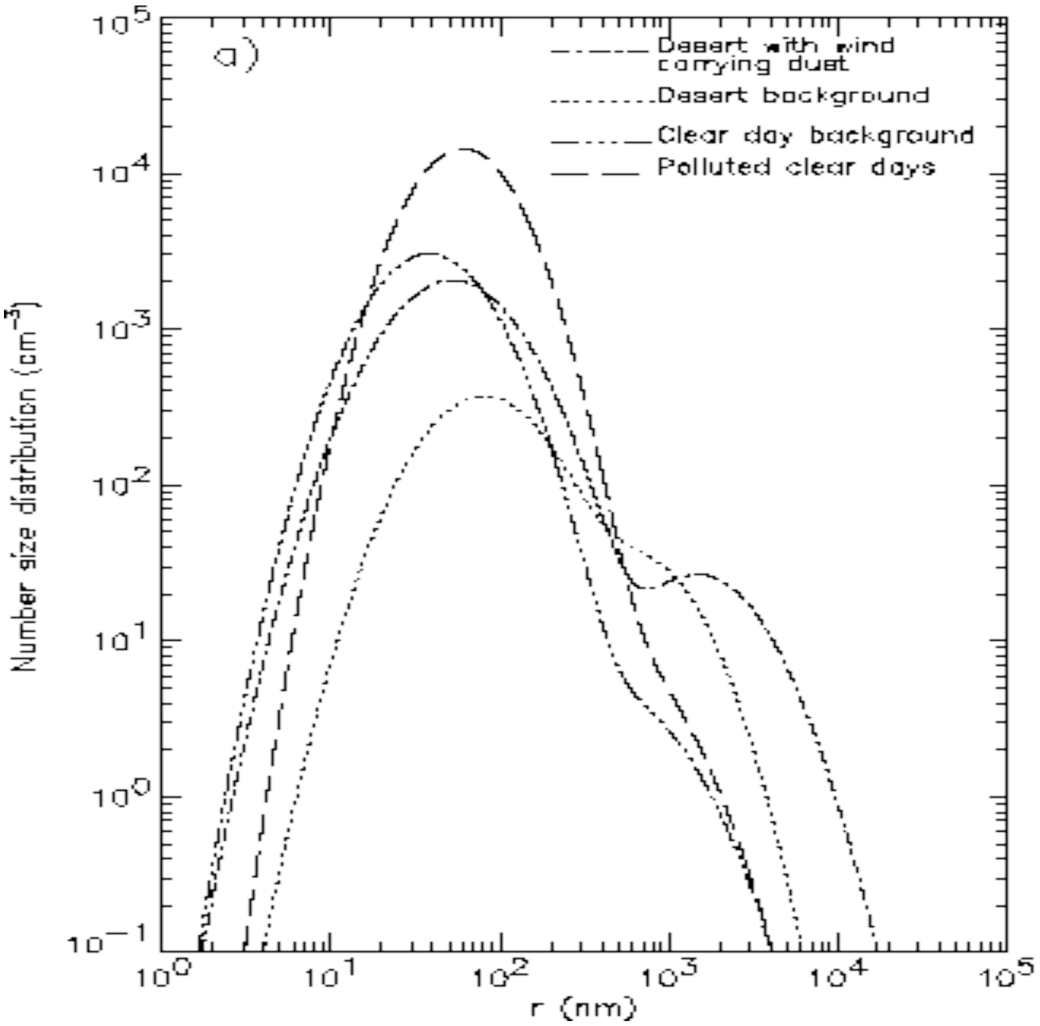

Asymmetry factor, g
n = 1.5 + 0.01 i

Radiation Inside Liquid Spheres



Mayer and Madronich, 2004

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 = $$\varpi_o(\lambda) = K_s(\lambda)/K_e(\lambda)$$

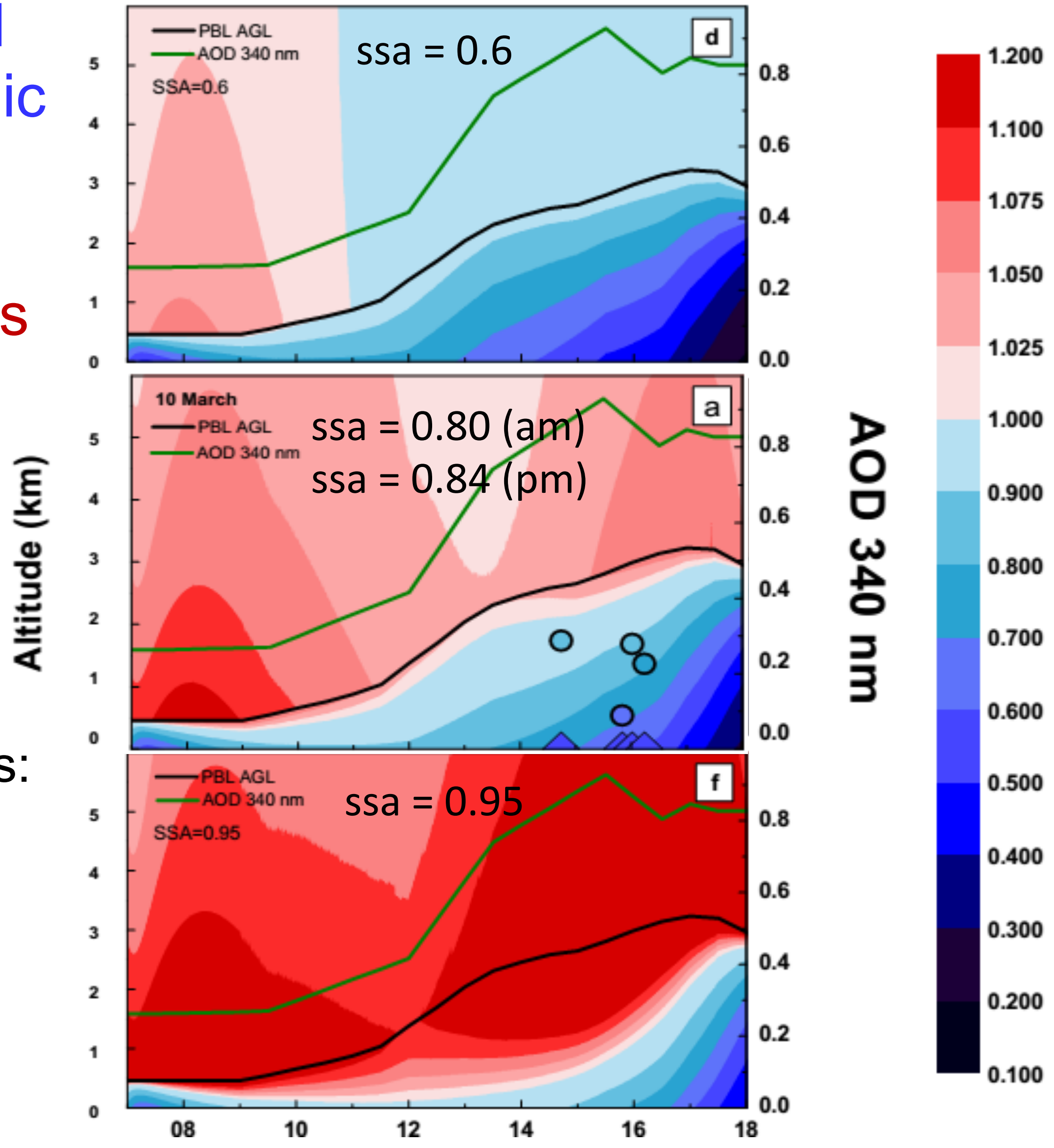
Average asymmetry factor = $$\bar{g}(\lambda) = \frac{\int_0^\infty g(r,\lambda)\pi r^2 Q_s(r,\lambda) n(r)\,\mathrm{d}r}{\int_0^\infty \pi r^2 Q_s(r,\lambda) n(r)\,\mathrm{d}r}$$

Enhancements and Reductions of Actinic Flux by Aerosols

Mexico City suburbs (T1) March 2006

Central panel:
Model with observed ssa, and obs.

Upper and lower panels:
Sensitivity to ssa


ssa = 0.6

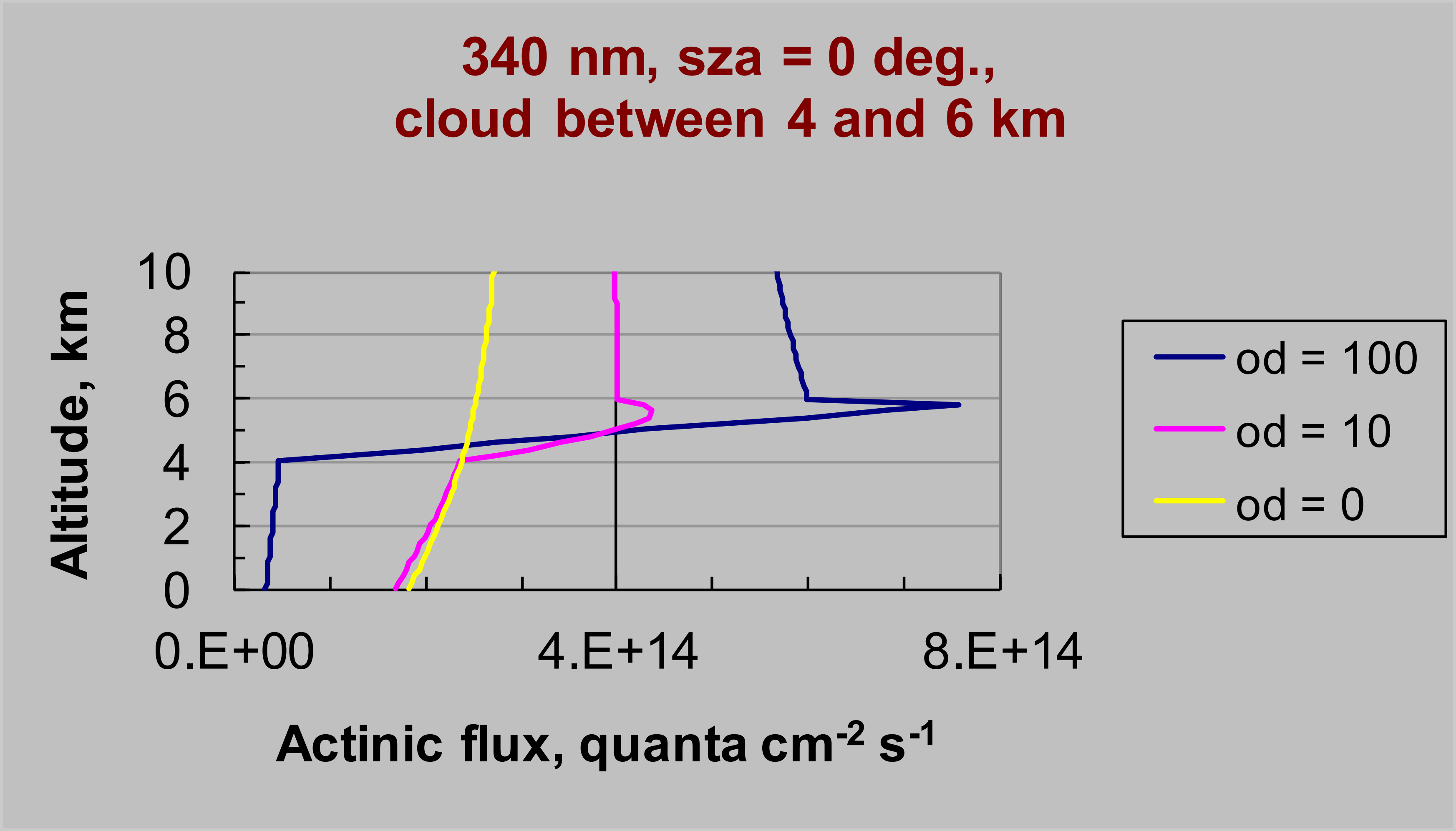
ssa = 0.80 (am)
ssa = 0.84 (pm)

ssa = 0.95

Palancar et al., 2013

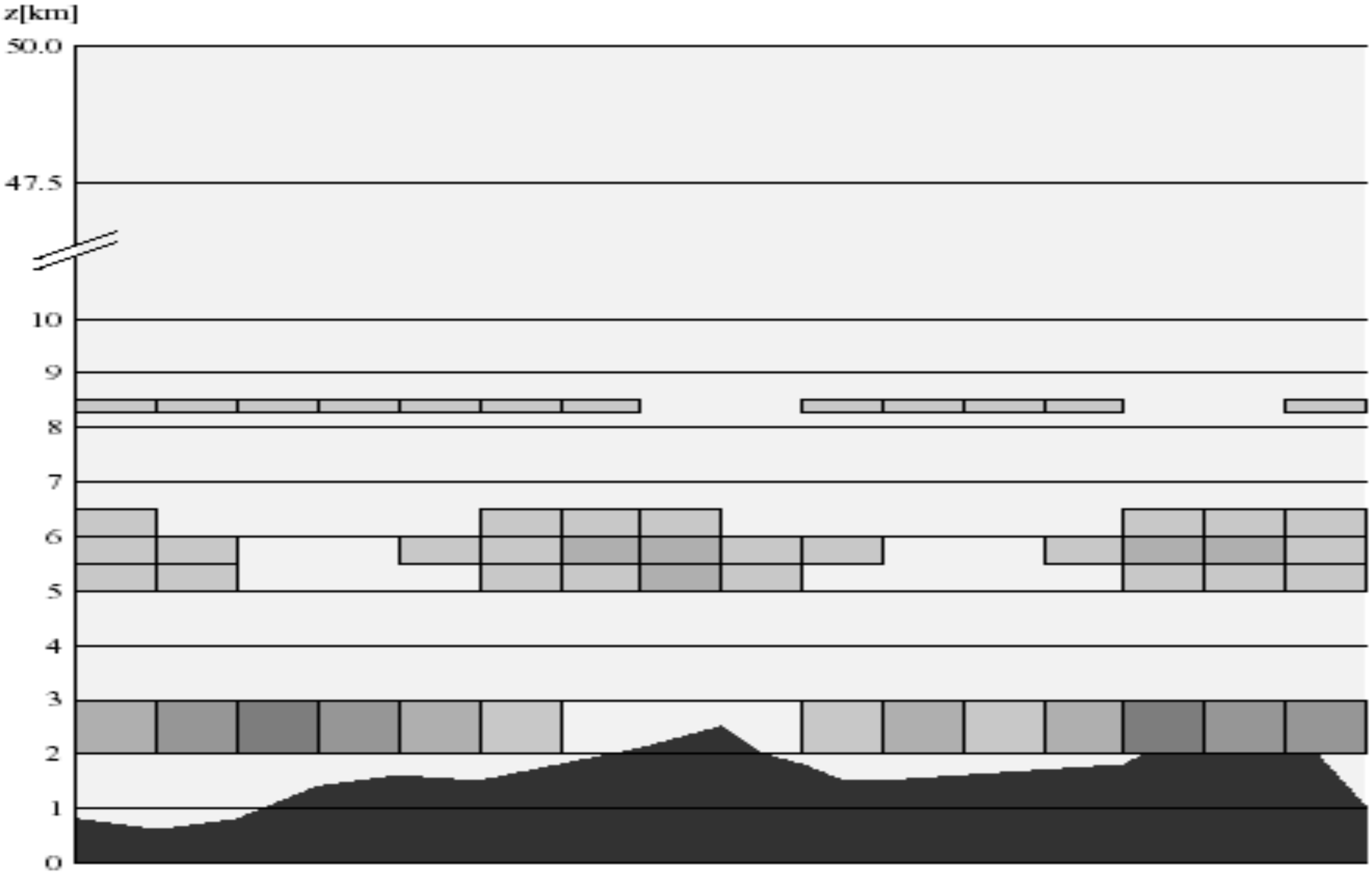
CLOUDS

EFFECT OF UNIFORM CLOUDS ON ACTINIC FLUX



In liquid spheres, multiply by ~ 1.6

Broken Clouds



Photolysis 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

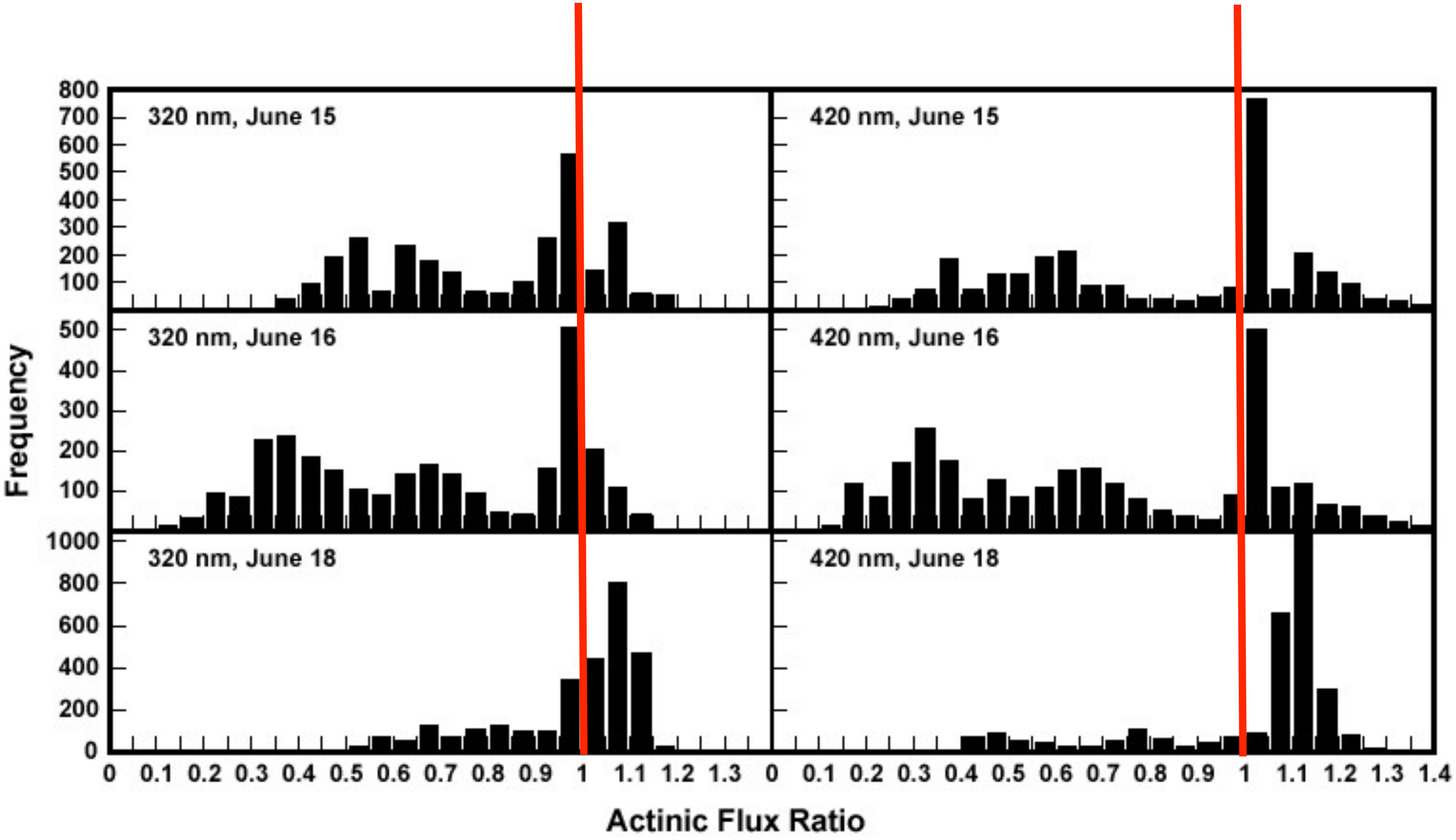
- Aerosols:
  - mixing rules for index of refraction
  - Mie scattering integrated over size distributions,
  - Different core-shell options

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: $G_B = S_1 + cD_1 + (1-c)D_o$

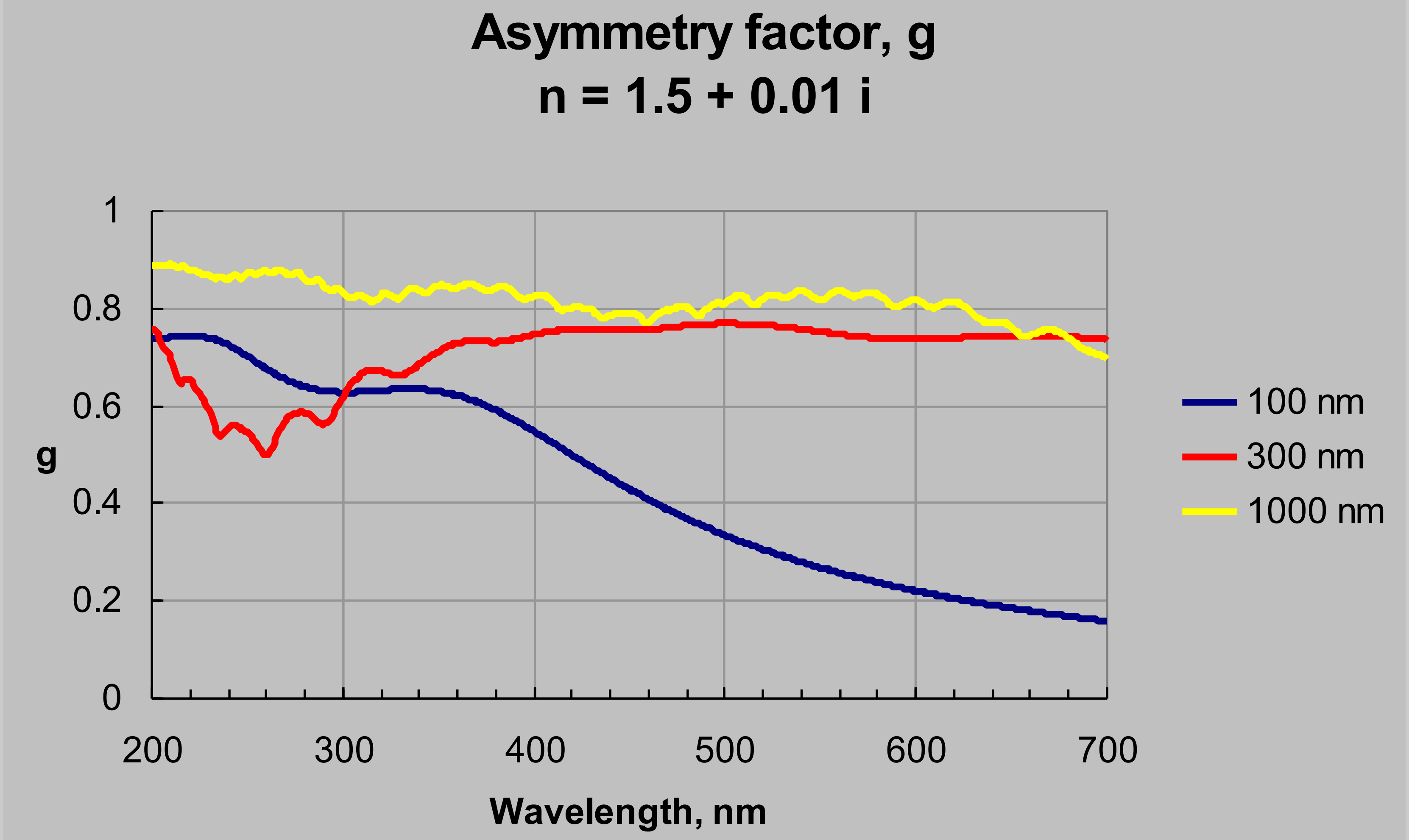
PARTIAL CLOUD COVER

Biomodal distributions

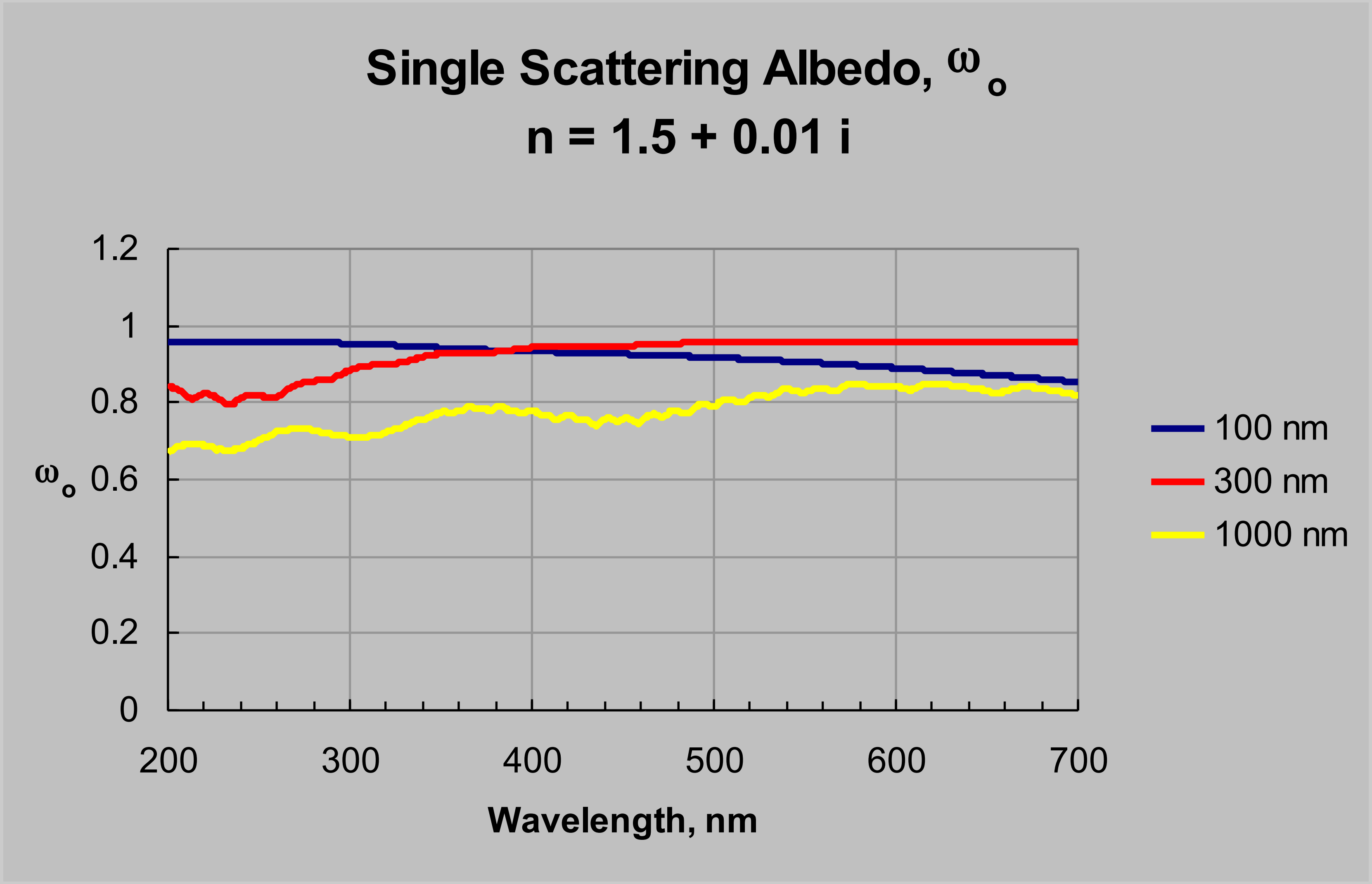


Crafword et al., 2003

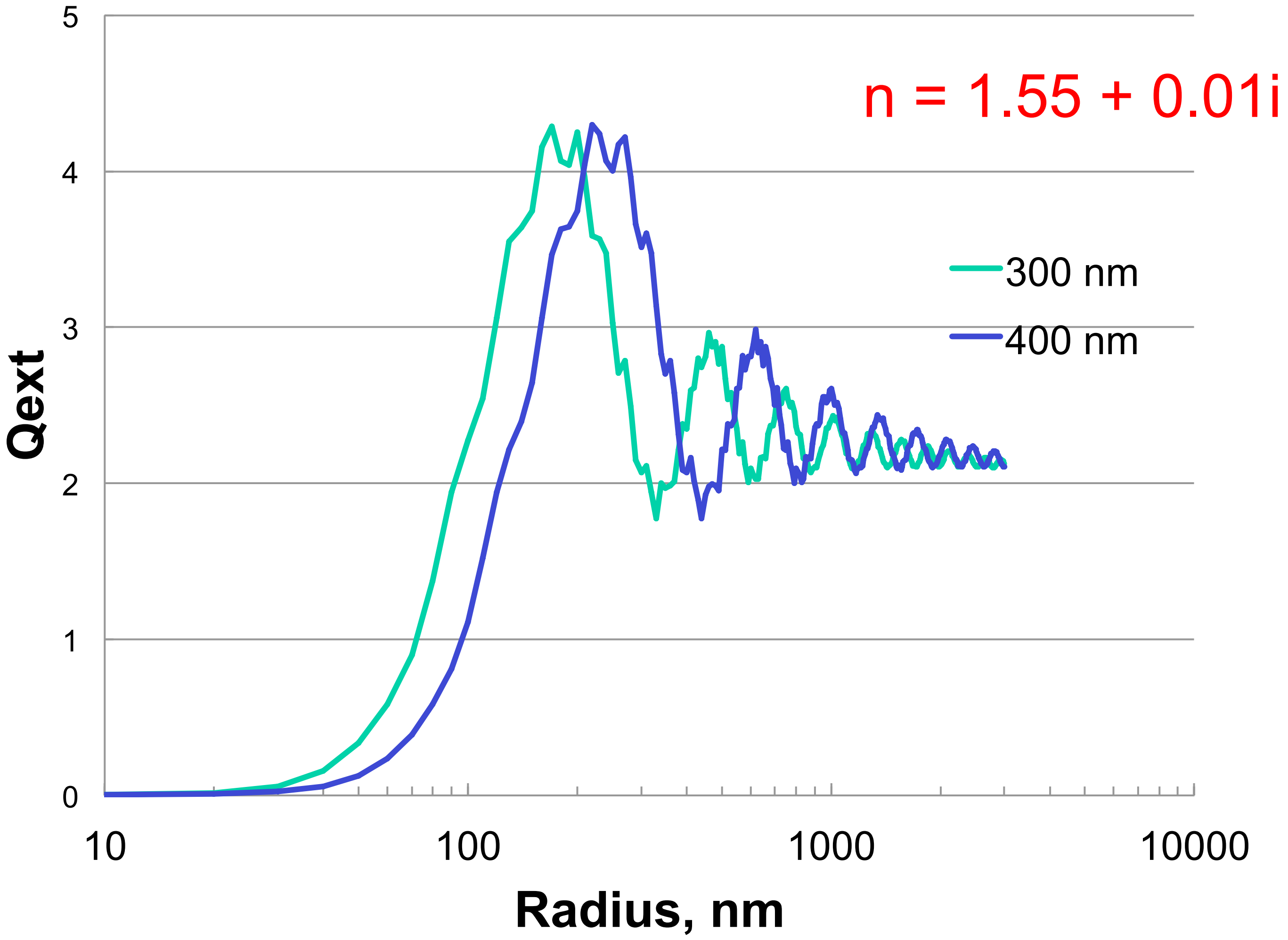
Phase function or Asymmetry factor, g



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

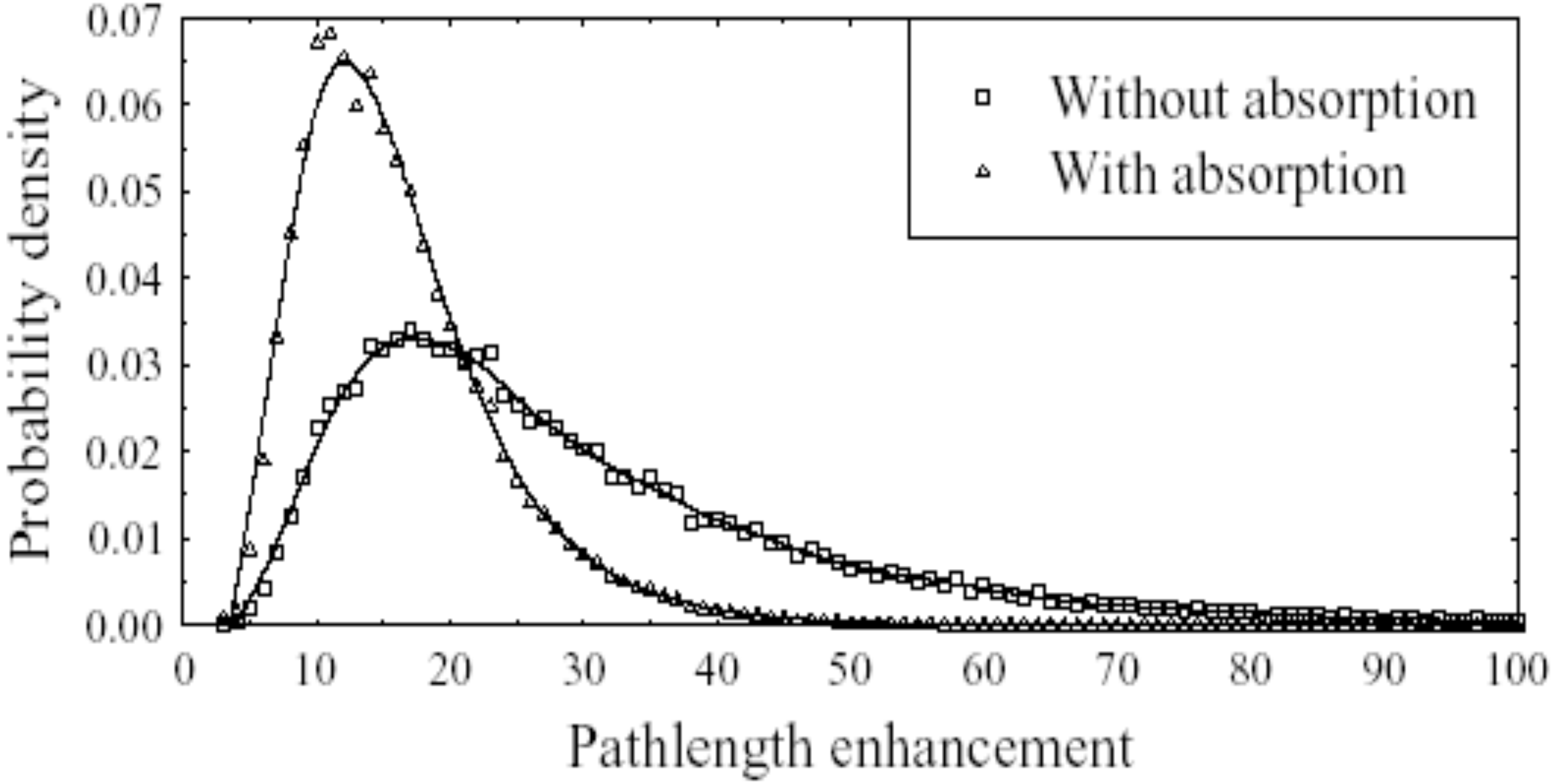


Extinction Efficiency, Q_{ext}



INSIDE CLOUDS:
Photon Path Enhancements

Cumulonimbus, od=400

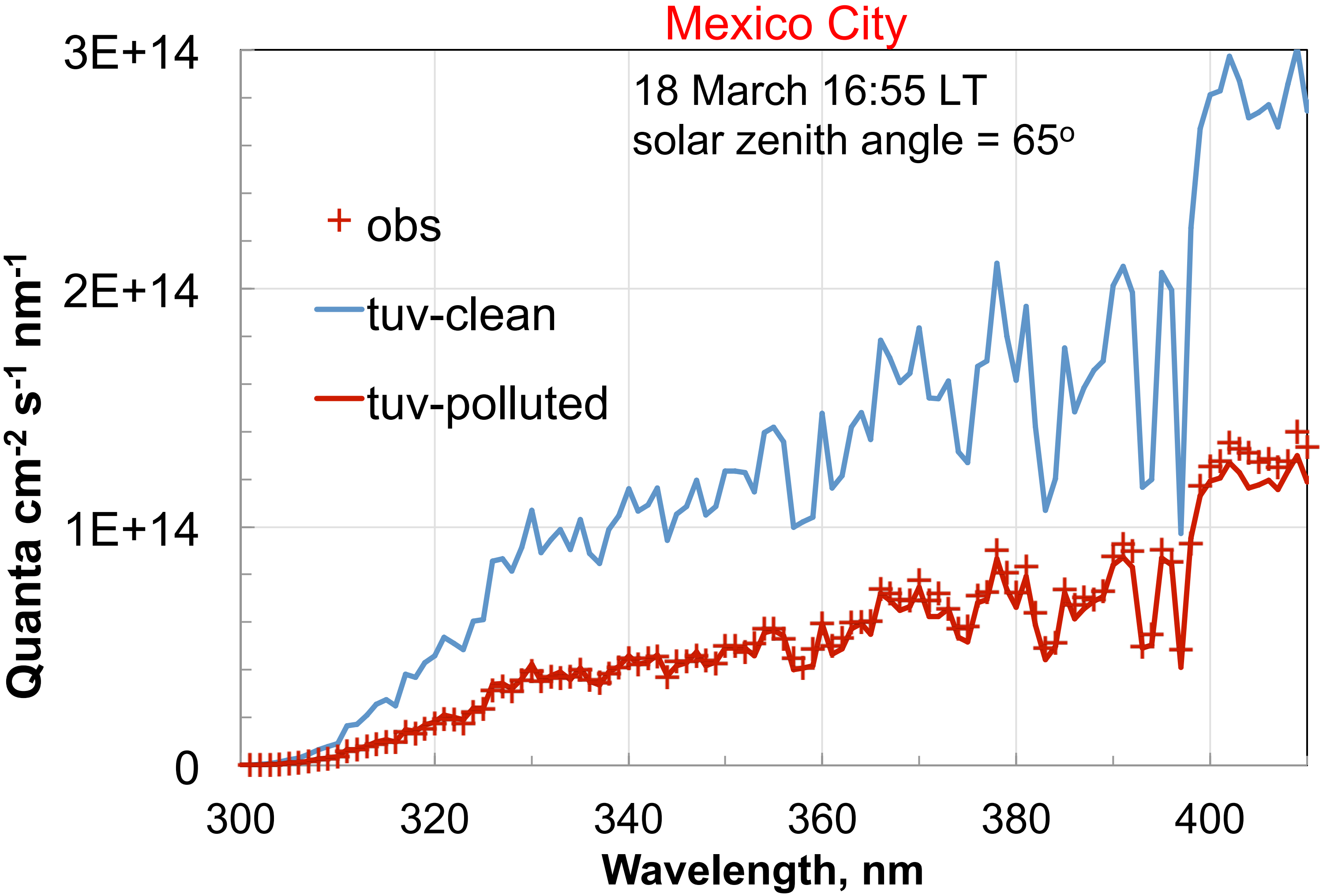


Mayer et al., 1998

UNIFORM CLOUD LAYER

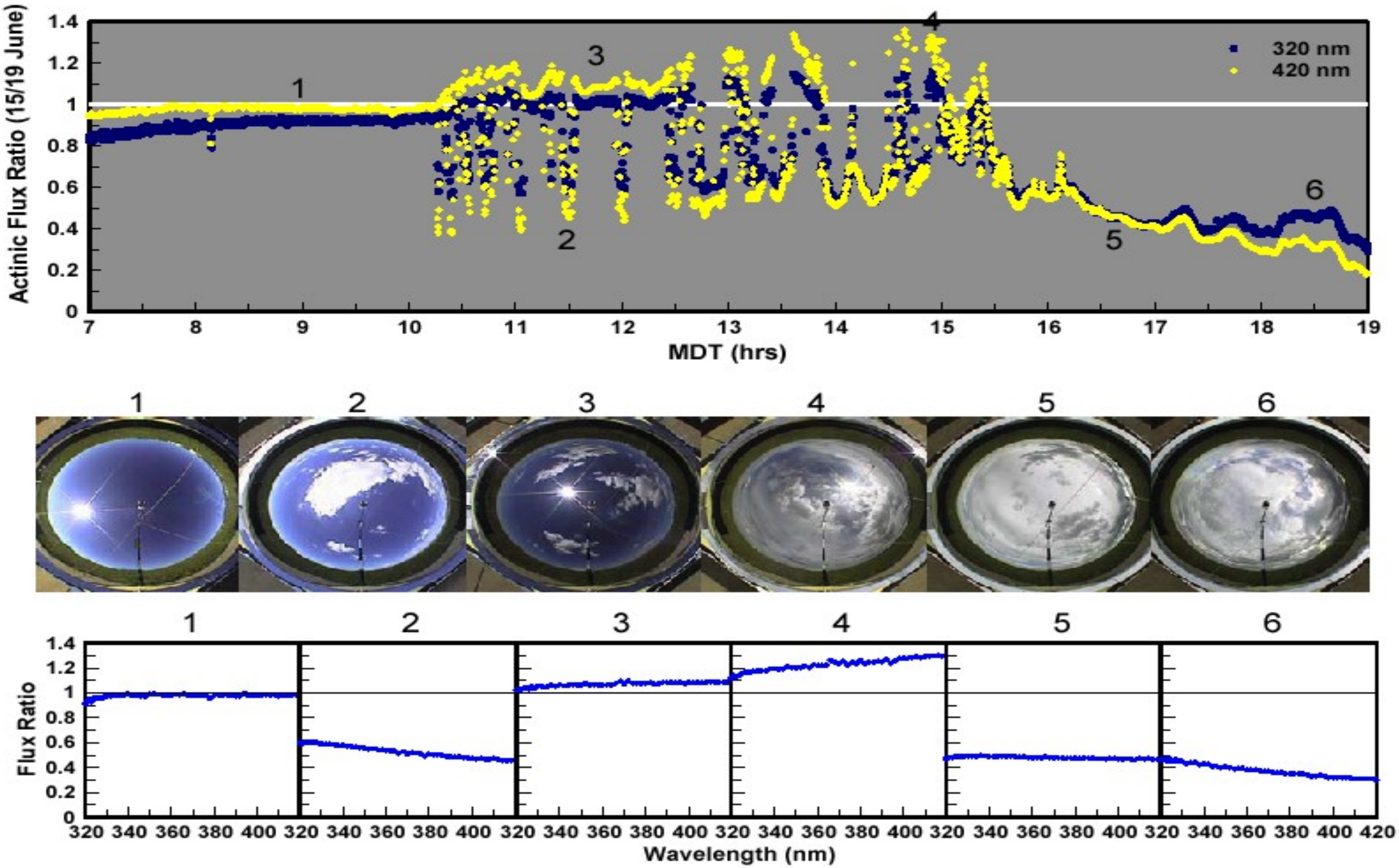
- Above cloud: - high radiation because of reflection
- Below cloud: - lower radiation because of attenuation by cloud
- Inside cloud: - complicated behavior
  - Top half: very high values (for high sun)
  - Bottom half: lower values

UV Actinic Flux Reduction → Slower Photochemistry



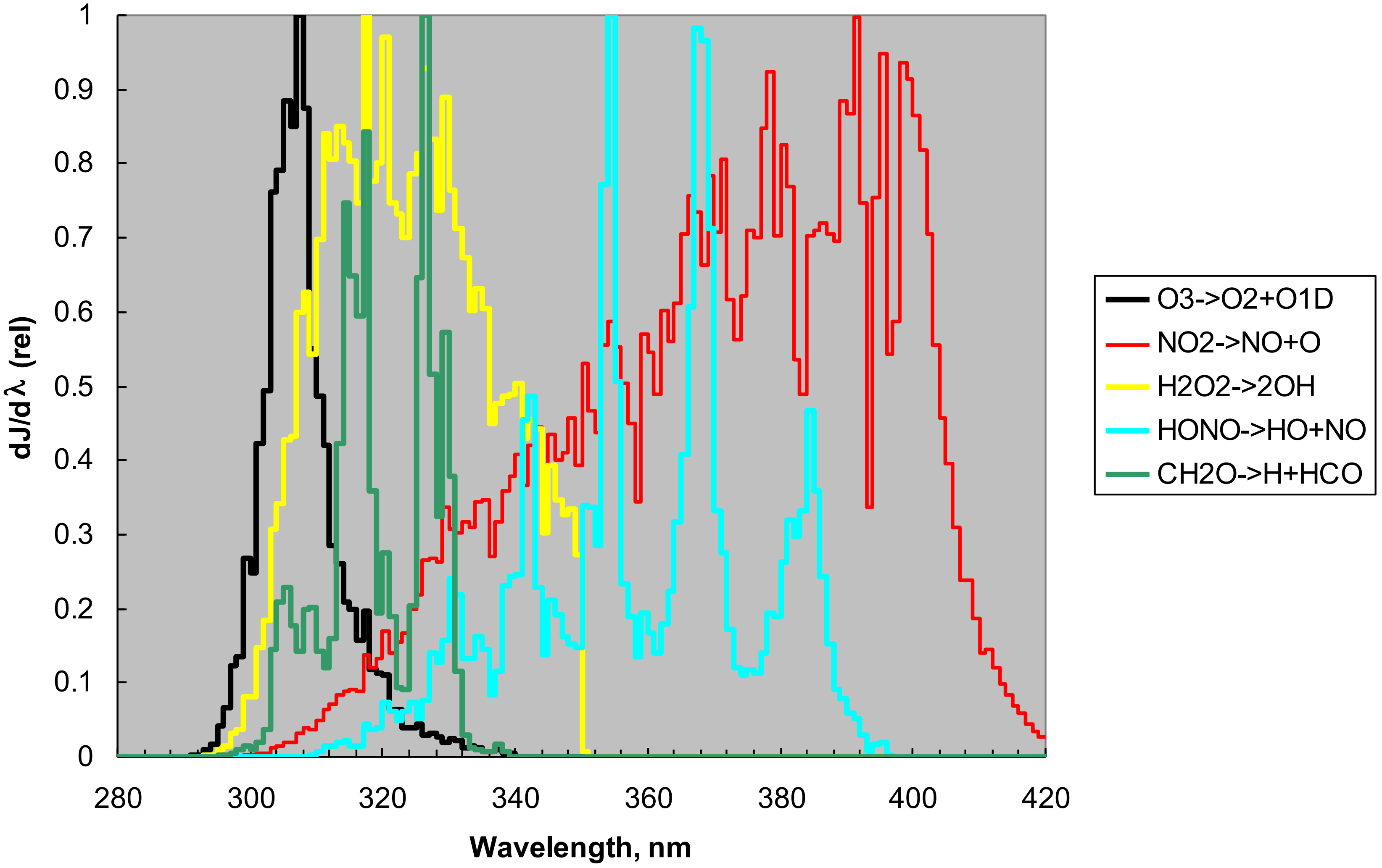
Madronich, Shetter, Halls, Lefer, AGU'07

SPECTRAL EFFECTS OF PARTIAL CLOUD COVER



Crafword et al., 2003

Spectral Region For Tropospheric Photochemistry



surface, overhead sun