PHOTOLYSIS

The driver for photo-oxidation

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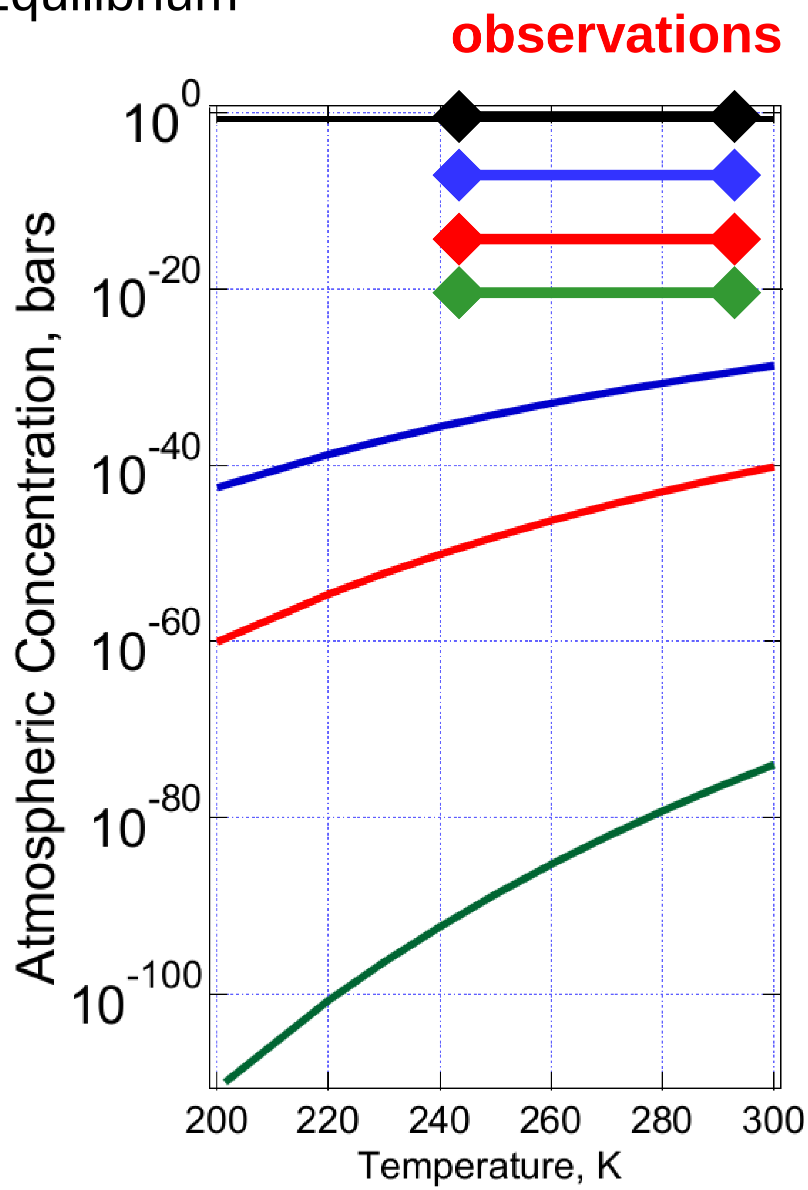
Atmospheric Oxygen

Thermodynamic Equilibrium

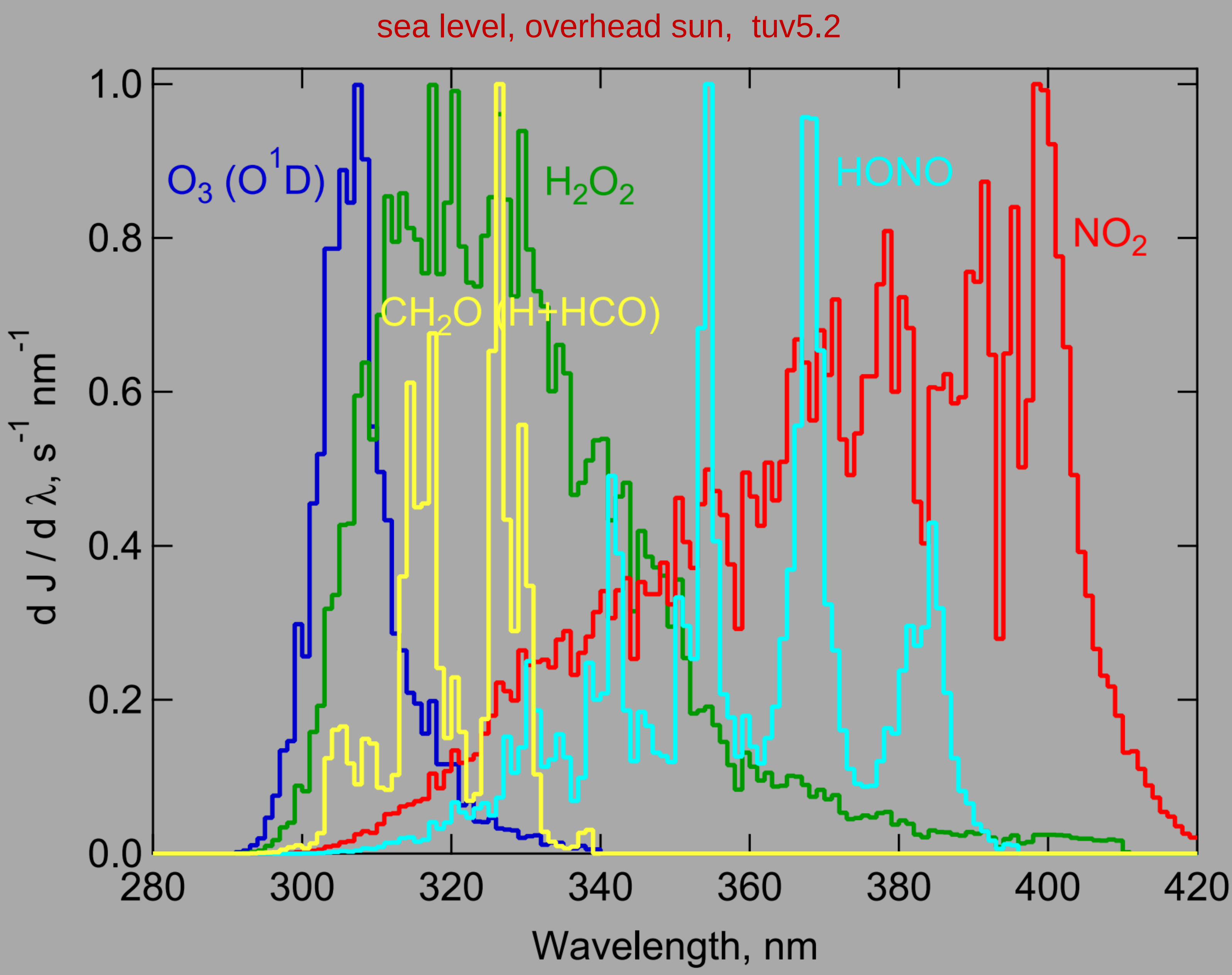
	ΔH_f kcal mol^{-1}
Normal O_2 molecules	0
Ozone, O_3	34.1
Ground state atoms, $O(^3P)$	59.6
Excited atoms, $O^*(^1D)$	104.9



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.

UV-B and UV-A Wavelength: Range and Resolution for Tropospheric Chemistry



Quantifying Photolysis Processes

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

Photolysis rates:

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

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

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

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

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

$\propto$ probability of photon near molecule.

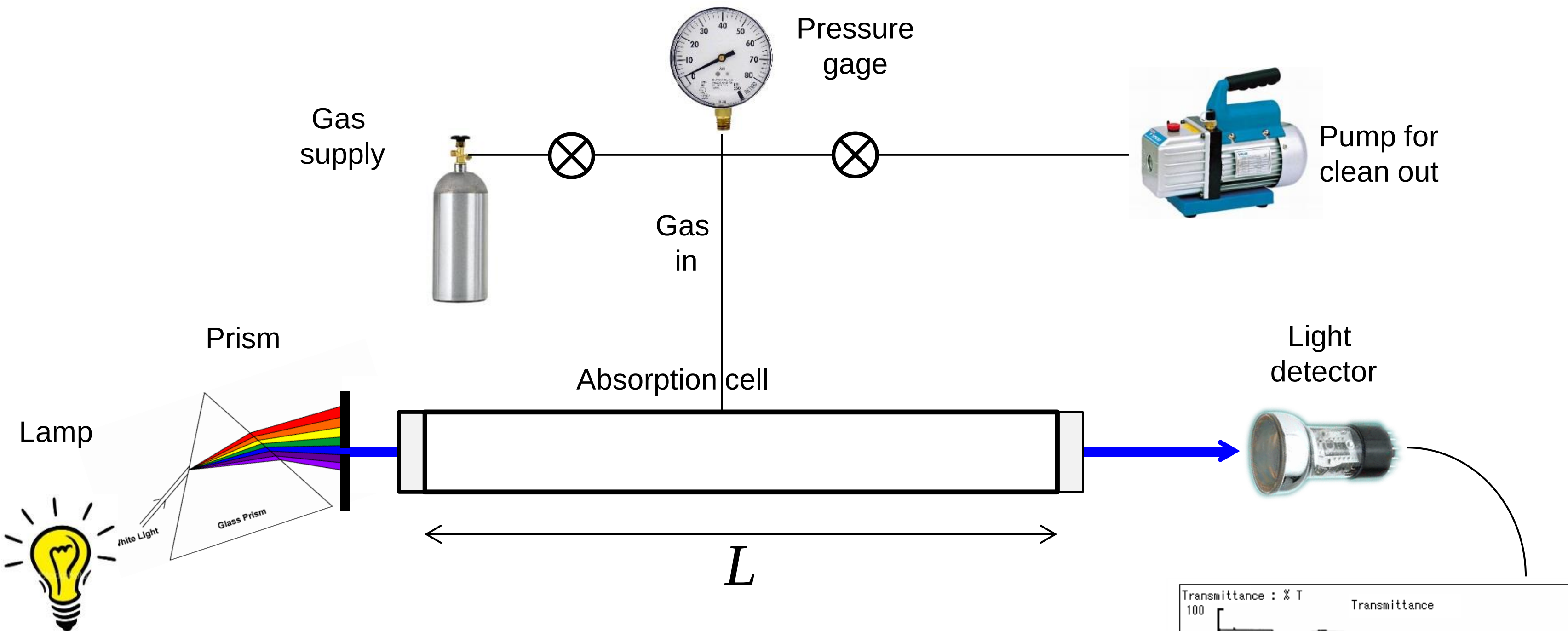
$\sigma(\lambda)$ = absorption cross section, cm^2 $molec^{-1}$

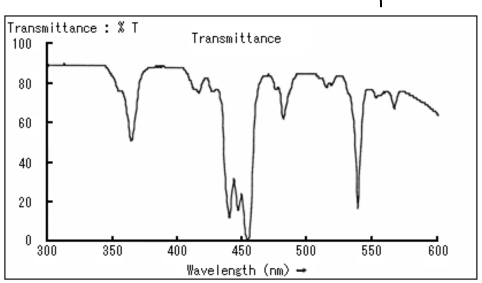
$\propto$ probability that photon is absorbed.

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

$\propto$ probability that absorbed photon causes dissociation.

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



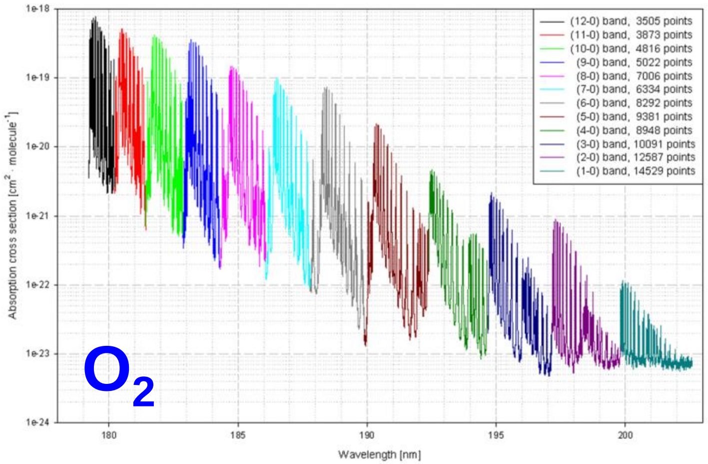


Transmittance = $I / I_o = \exp(-\sigma\, n\, L)$

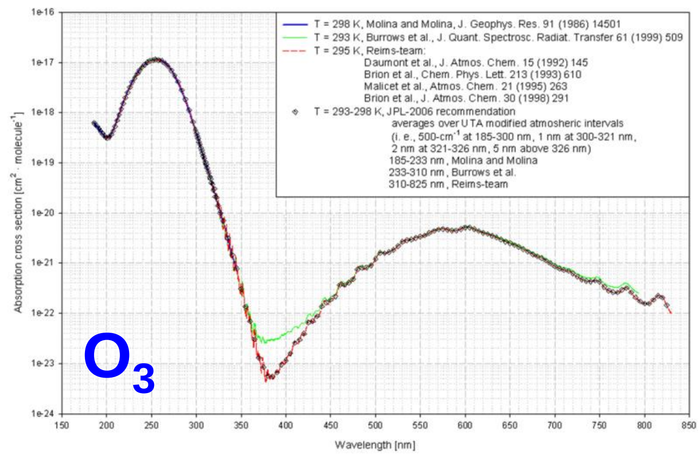
$\sigma = -1/(nL) \ln(I / I_o)$

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

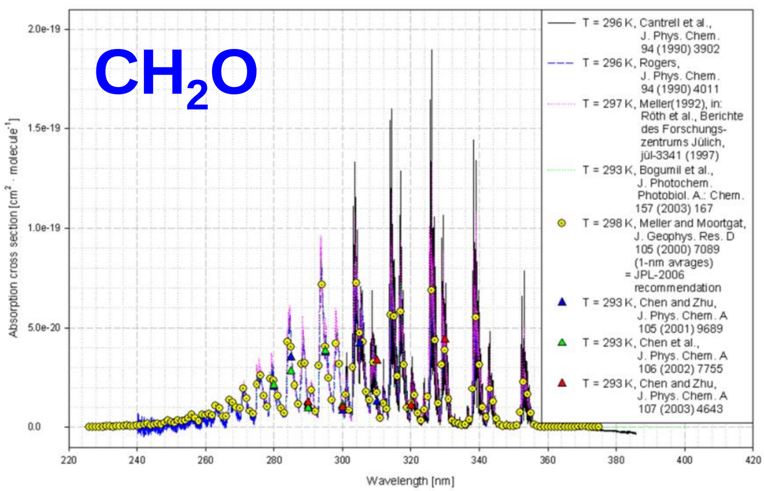
Absorption cross sections $\sigma(\lambda, T)$



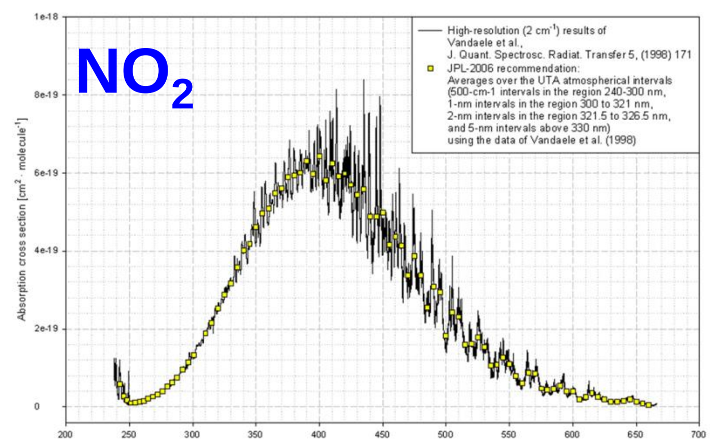
Absorption cross sections in the Schumann-Runge region of oxygen O_2 at 300 K,
Yoshino et al., Planet. Space Sci. 40 (1992) 185



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

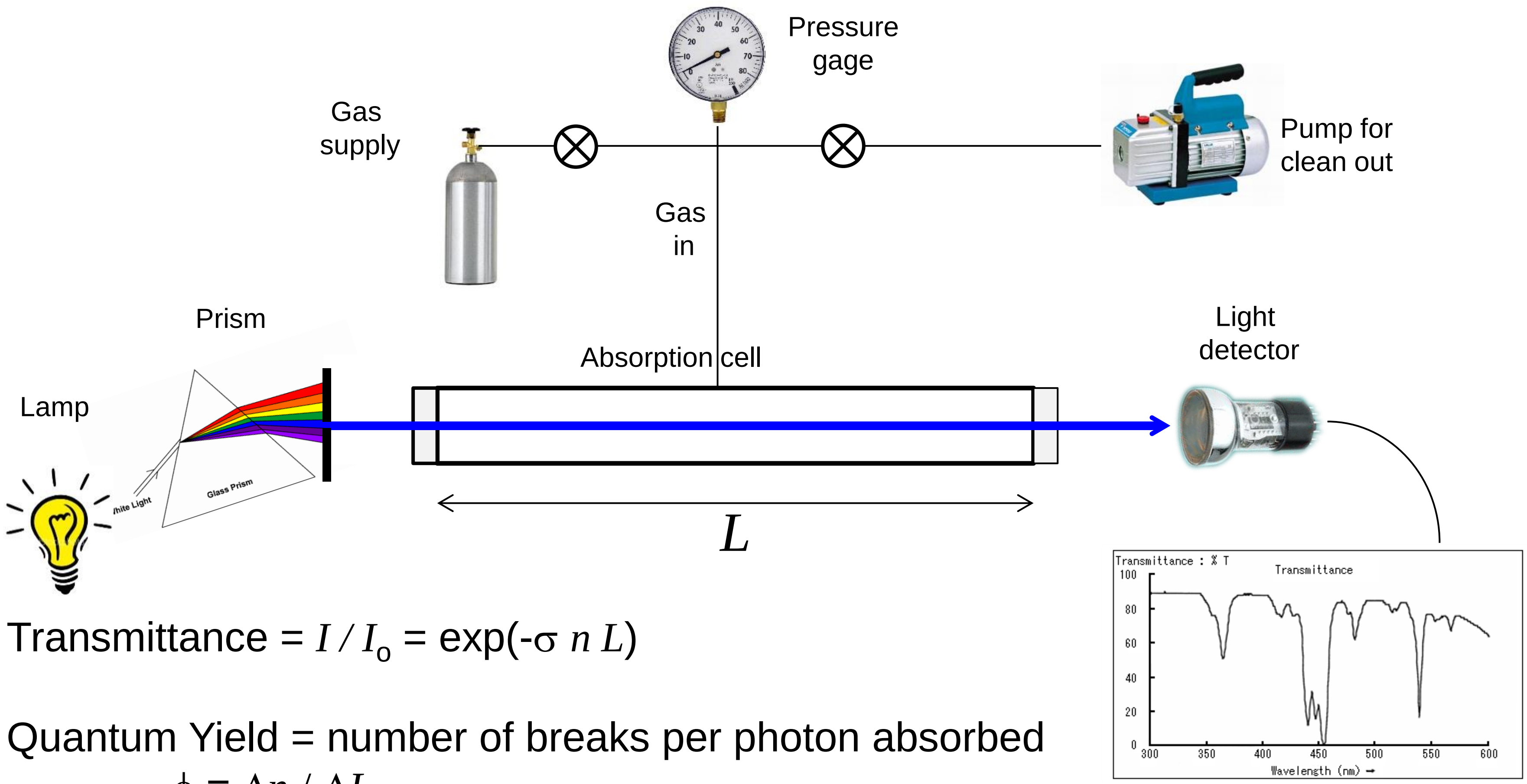


Absorption cross sections of formaldehyde CH_2O at room temperature (results 1990-2003)



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

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



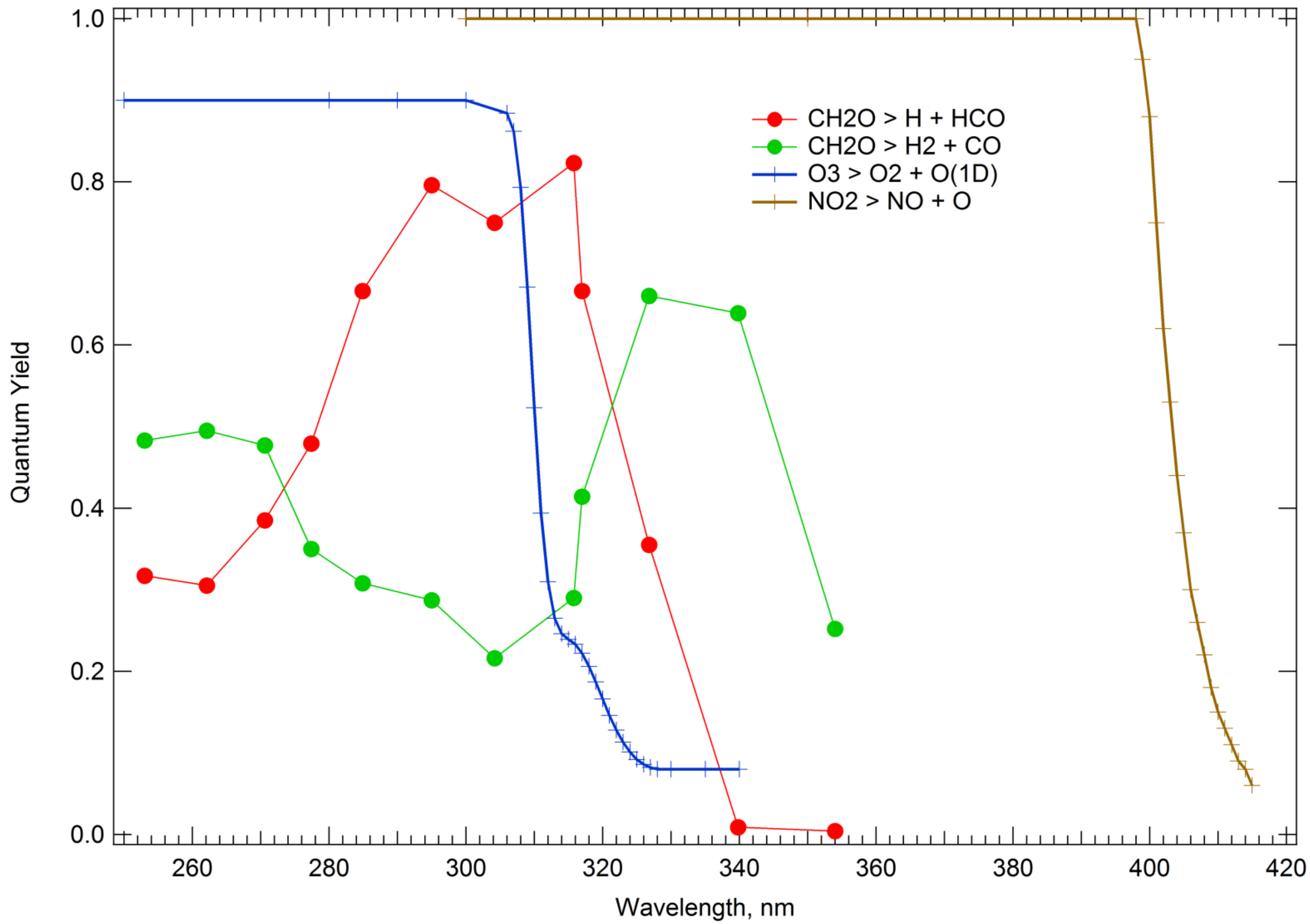
Transmittance = $I / I_o = \exp(-\sigma\, n\, L)$

Quantum Yield = number of breaks per photon absorbed

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

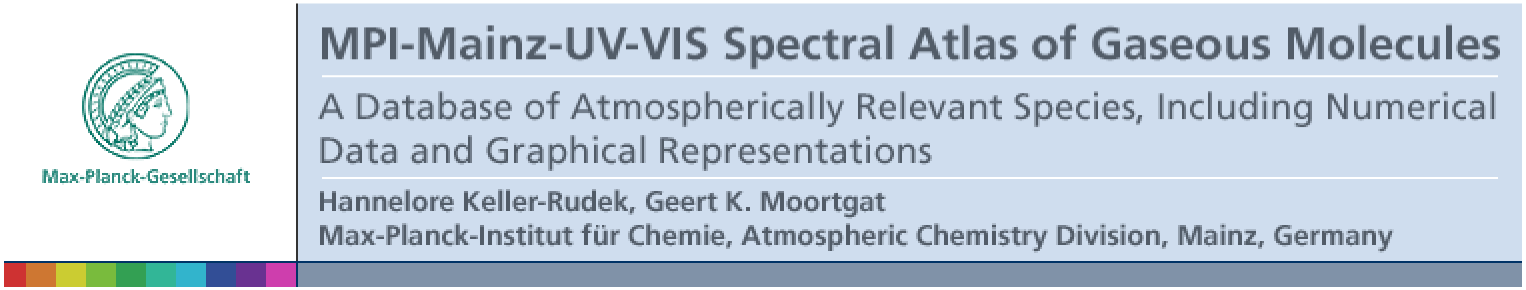
Difficult: must measure absolute change in n (products) and I (photons absorbed)

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

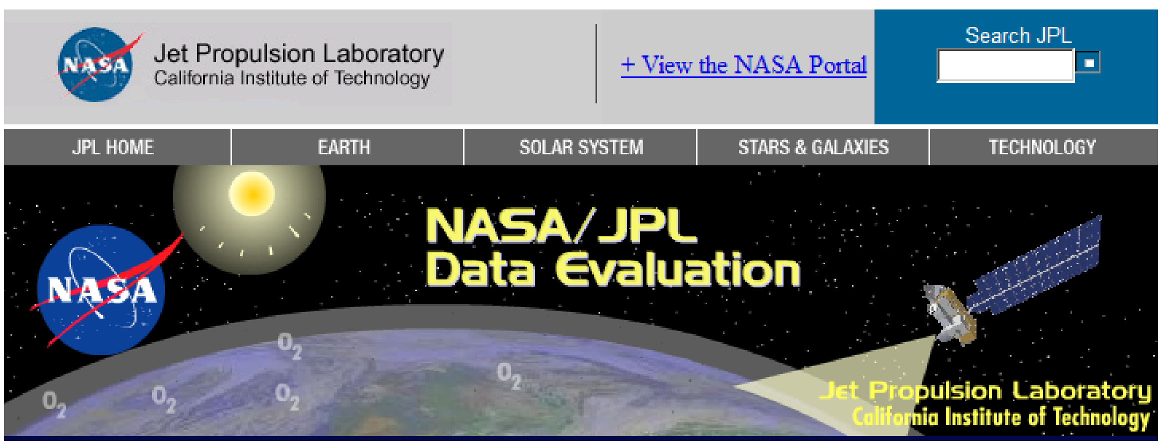


Compilations of Cross Sections & Quantum Yields

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

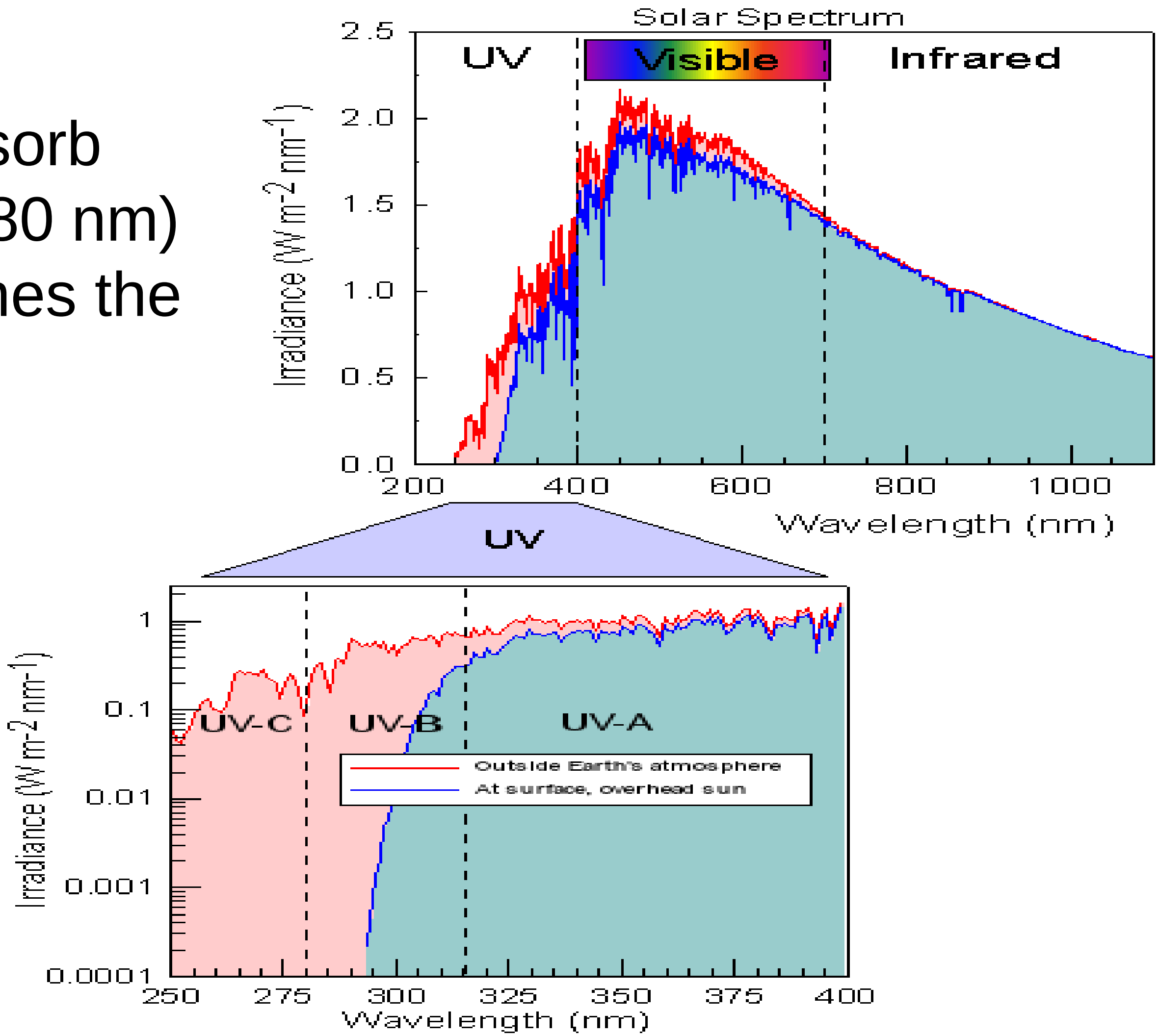


http://jpldataeval.jpl.nasa.gov/



Solar Spectrum

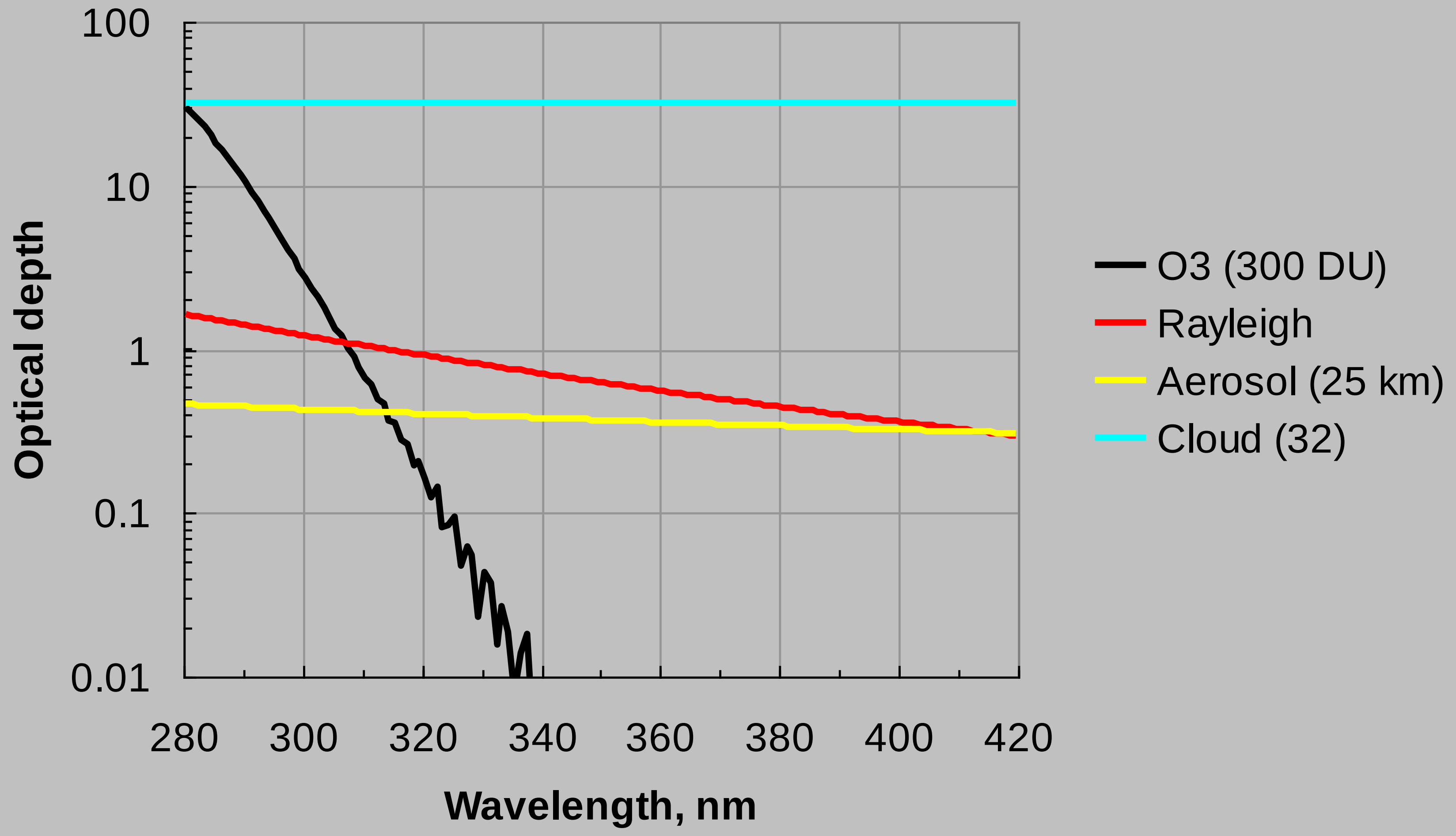
O_2 and O_3 absorb all UV-C (λ<280 nm) before it reaches the troposphere



UNEP, 2002

Atmospheric Optical Depths, τ

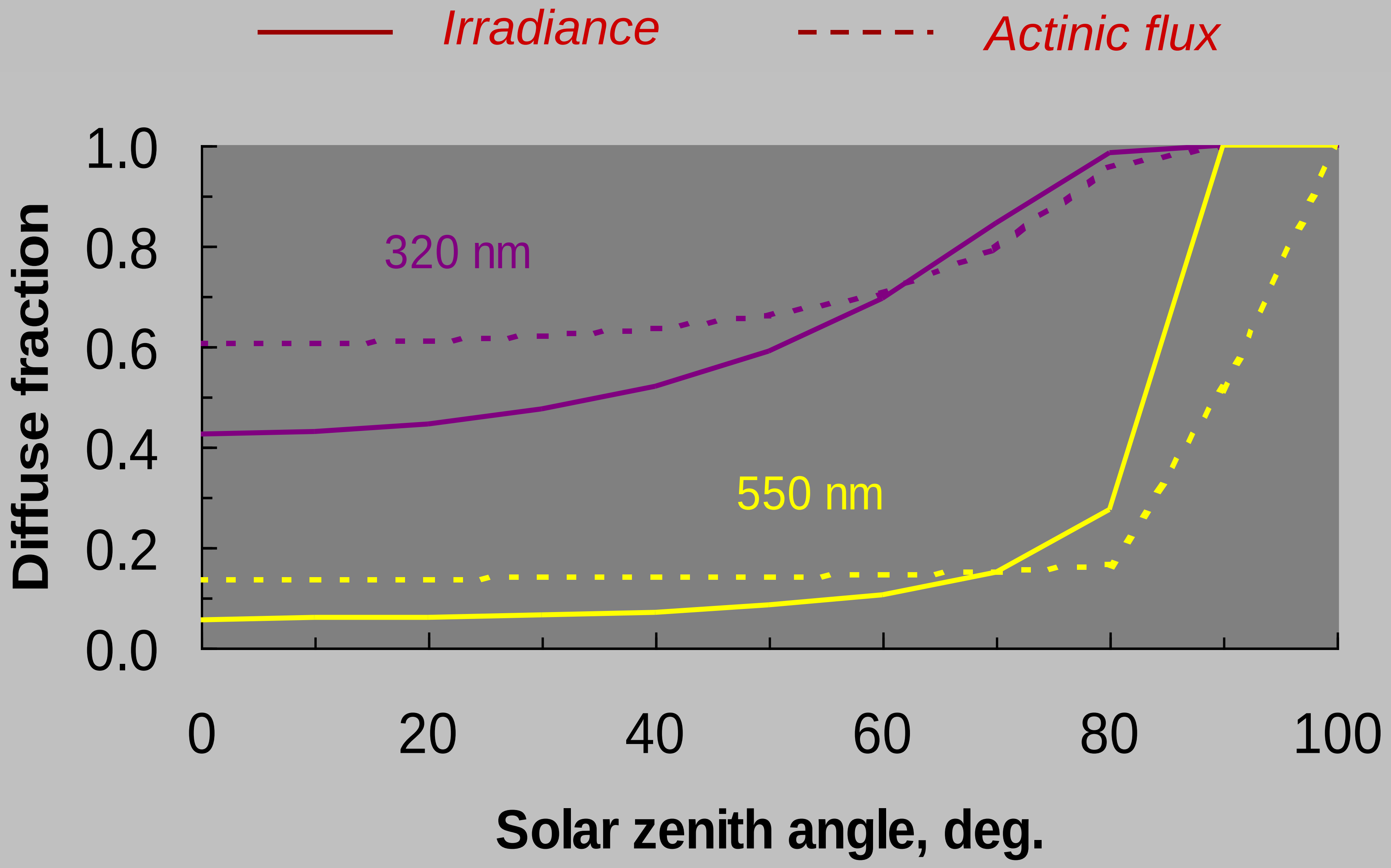
defined by Transmission of a vertical beam = exp (-τ)



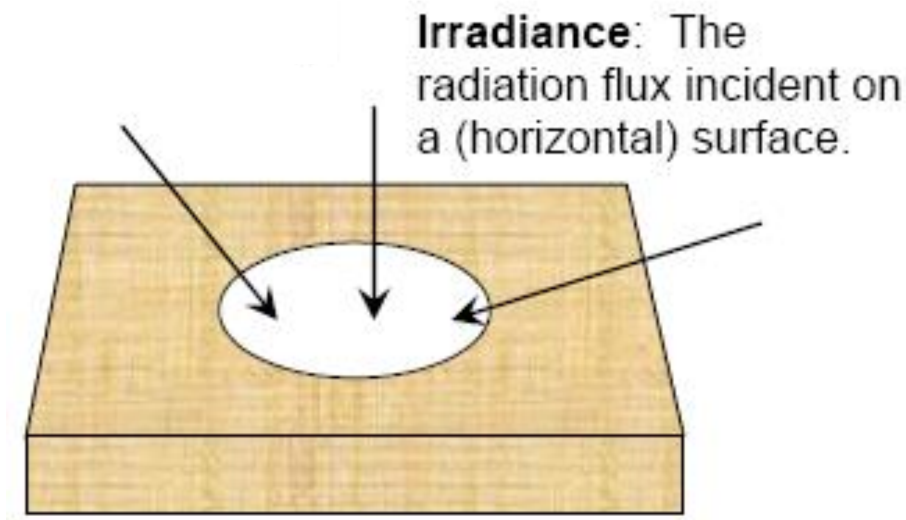
Diffuse transmission can be much larger

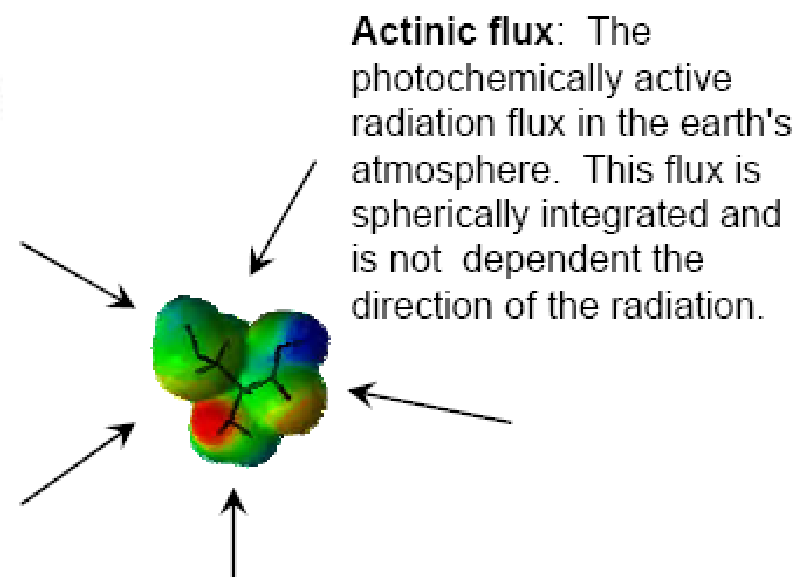
UV: Diffuse Radiation ≥ Direct Solar Beam

clean skies, sea level



INTEGRALS OVER ANGULAR INCIDENCE





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

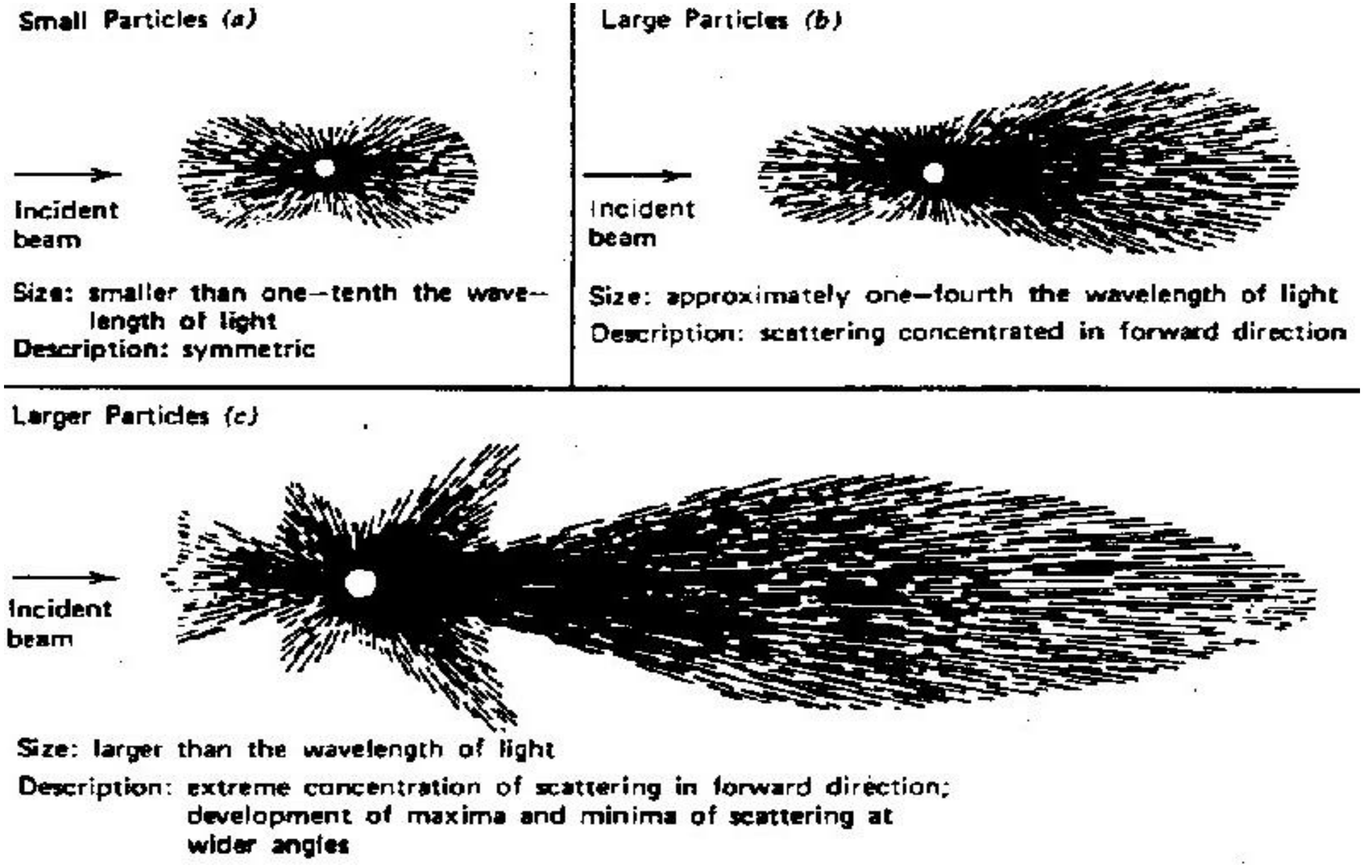
$$F = \int_0^{\pi}\int_0^{2\pi} I(\theta,\varphi)\sin\theta\,\mathrm{d}\varphi\,\mathrm{d}\theta$$

Watts m^{-2}

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

SCATTERING PHASE FUNCTIONS

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



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 $n \to \infty$ but speed $\propto 1/n^2$
- Two-stream family

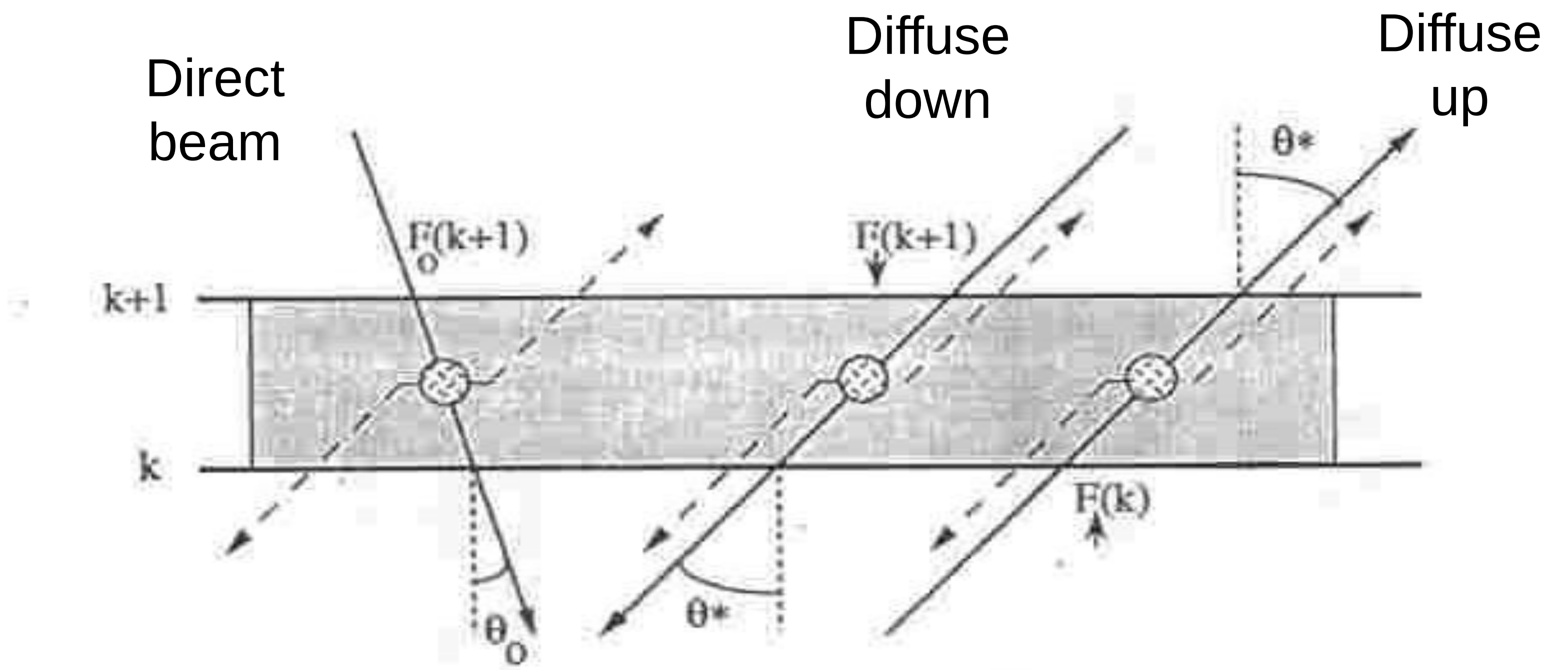
  delta-Eddington, many others

  very fast but not exact
- Monte Carlo

  slow, but ideal for 3D problems
- Others

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

Two-stream methods



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, $\mathbf{g}$: *forward fraction ~ (1+$\mathbf{g}$)/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

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

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

Mie Scattering Theory

For spherical particles, given:

Complex index of refraction: $n = m + \mathrm{i}k$
(composition-dependent)

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

Can compute:

Extinction efficiency $Q_e(\alpha, n) \quad \mathrm{x}\ \pi r^2$

Scattering efficiency $Q_s(\alpha, n) \quad \mathrm{x}\ \pi r^2$

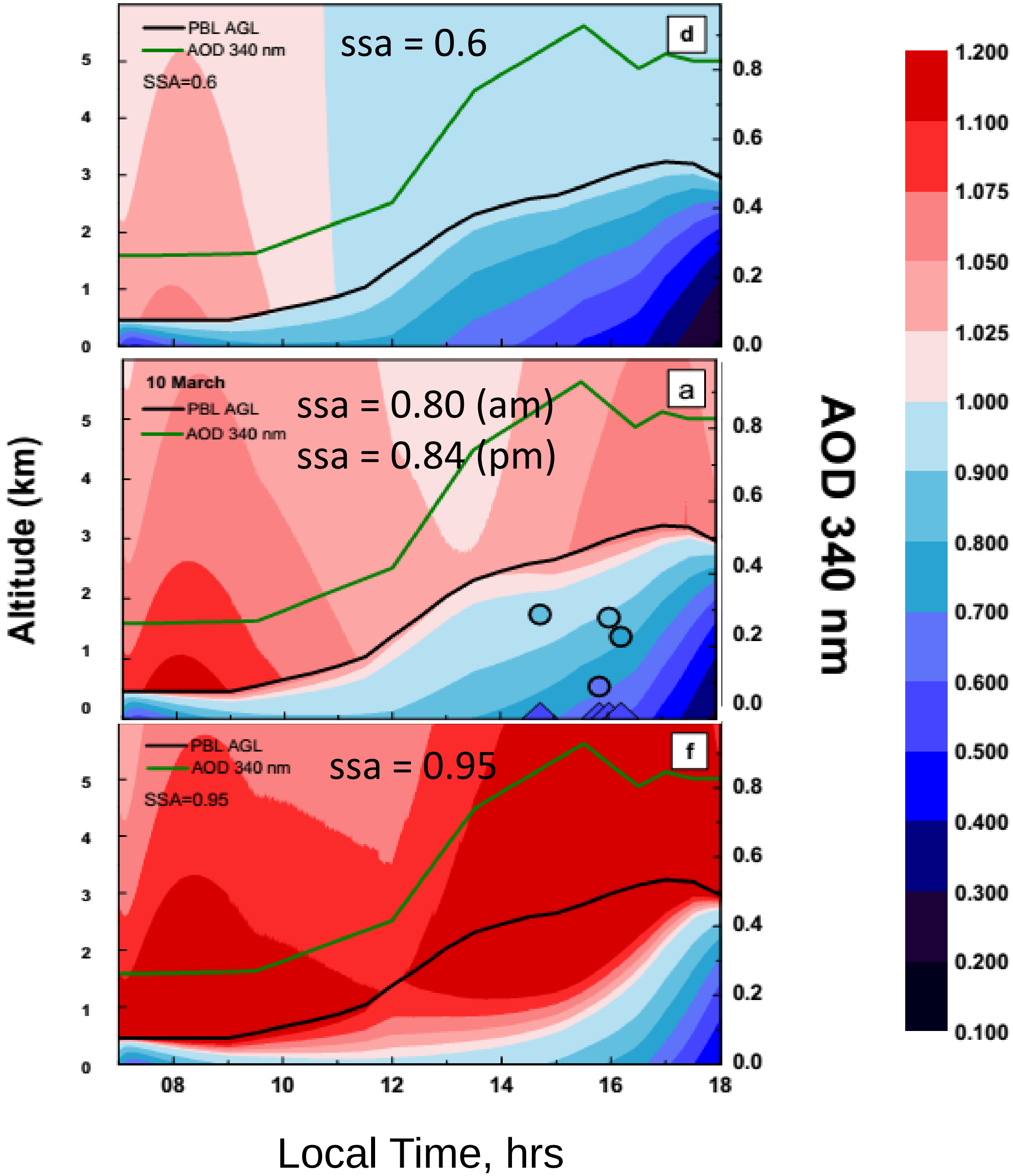
Phase function $P(\Theta, \alpha, n)$
or asymmetry factor $g(\alpha, n)$

Vertical Profile is Very Sensitive to Single Scattering Albedo

Mexico City suburbs (T1) March 2006

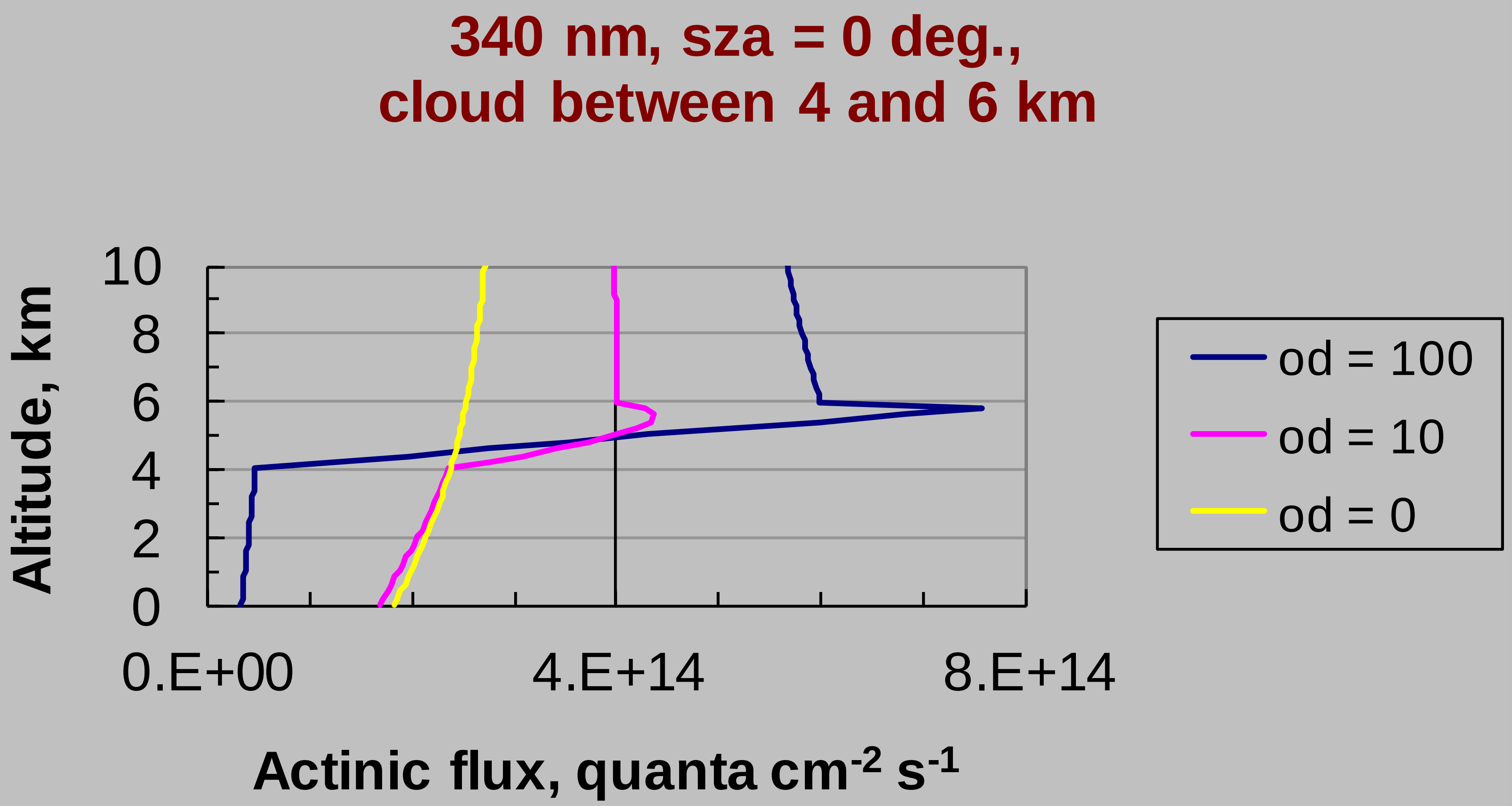
Central panel:
Model with observed ssa, and obs.

Upper and lower panels:
Sensitivity to ssa



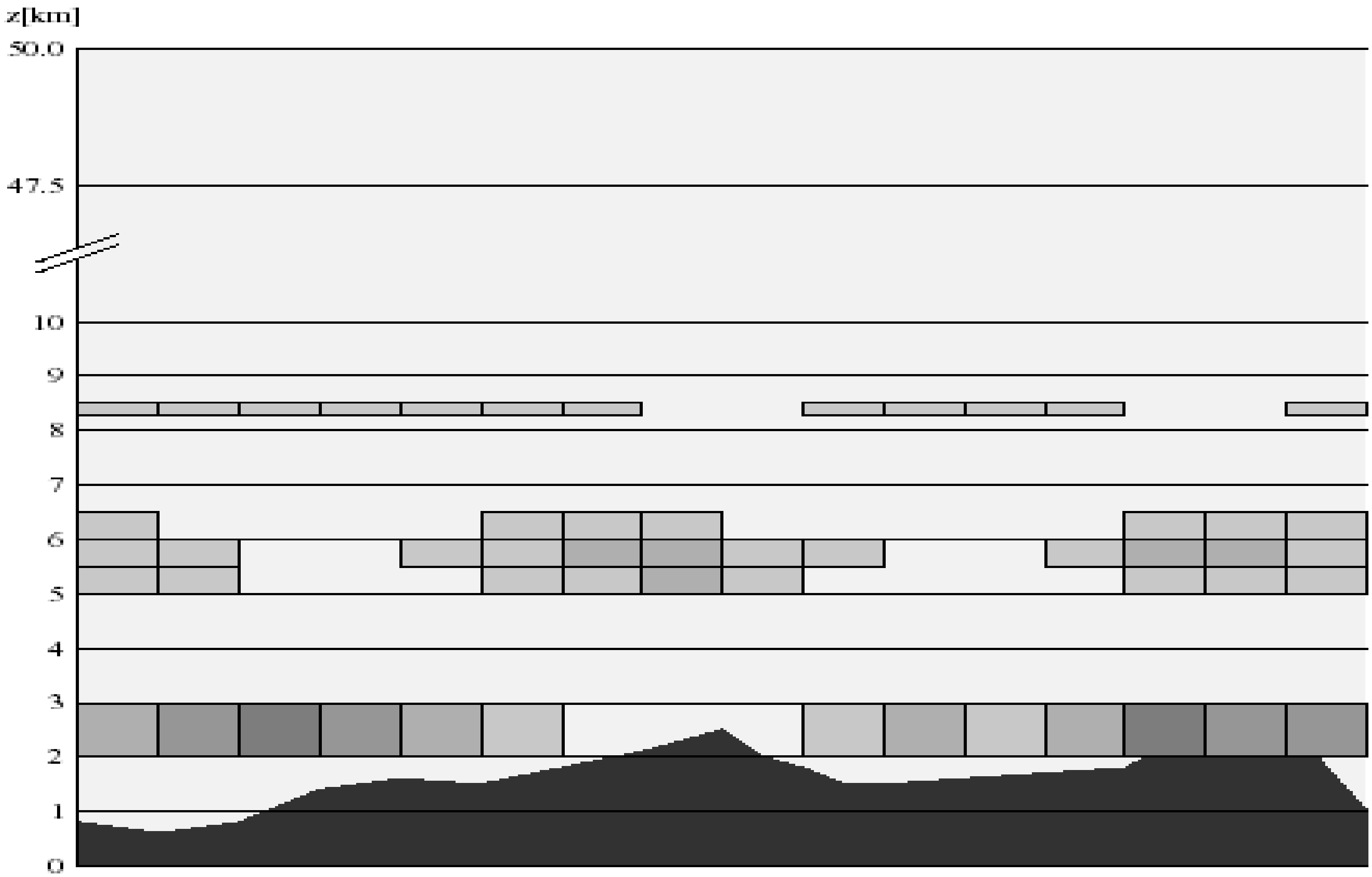
Palancar et al., 2013

EFFECT OF UNIFORM CLOUDS ON ACTINIC FLUX



In liquid spheres, multiply by ~ 1.6

Broken Clouds



Photolysis in WRF-Chem

- Several radiative transfer options:
  - phot_opt = 1 : TUV (140 λs, delta-Eddington)
  - phot_opt = 2 : Fast-J (17 λs, 8-str Feautrier)
  - phot_opt = 3 : F-TUV (17 λs, correction factor, delta-Eddington)

  New option in WRF-Chem v3.9:

  ⇒ phot_opt = 4: updated TUV (140 λs, delta-Eddington)

  ⇒ only works with MOZART_MOSAIC_4BIN_KPP, MOZART_MOSAIC_4BIN_AQ_KPP, and MOZCART_KPP chemical options

- Limitations & advantages
  - Cross section and quantum yield data are hard-coded and not up to date in older schemes;

  ⇒ updated database to the latest TUV model (V5.3, Oct. 2016)

  - Difficult to add new reactions (typically available ~ 20)

  ⇒ 109 reactions relevant for tropo & strato chemistry (e.g. halogens)

List of available photolysis reactions in the updated TUV

No.	Reaction	J
1	O2 -> O + O	(J_o2)
2	O3 -> O2 + O(1D)	(J_o1d)
3	O3 -> O2 + O(3P)	(J_o3p)
4	HO2 -> OH + O	
5	H2O2 -> 2 OH	(J_h2o2)
6	NO2 -> NO + O(3P)	(J_no2)
7	NO3 -> NO + O2	
8	NO3 -> NO2 + O(3P)	
9	N2O -> N2 + O(1D)	(J_n2o)
10	N2O5 -> NO3 + NO + O(3P)	
11	N2O5 -> NO3 + NO2	(J_n2o5b)
12	HNO2 -> OH + NO	
13	HNO3 -> OH + NO2	(J_hno3)
14	HNO4 -> HO2 + NO2	(J_hno4)
15	NO3-(aq) -> NO2(aq) + O-	
16	NO3-(aq) -> NO2-(aq) + O(3P)	
17	CH2O -> H + HCO	(J_ch2or)
18	CH2O -> H2 + CO	(J_ch2om)
19	CH3CHO -> CH3 + HCO	(J_ch3cho_a)
20	CH3CHO -> CH4 + CO	(J_ch3cho_b)
21	CH3CHO -> CH3CO + H	(J_ch3cho_c)
22	C2H5CHO -> C2H5 + HCO	
23	CH3OOH -> CH3O + OH	
24	HOCH2OOH -> HOCH2O. + OH	(J_pooh)
25	CH3ONO2 -> CH3O + NO2	
26	CH3(OONO2) -> CH3(OO) + NO2	
27	CH3CH2ONO2 -> CH3CH2O + NO2	
28	C2H5ONO2 -> C2H5O + NO2	
29	n-C3H7ONO2 -> C3H7O + NO2	
30	1-C4H9ONO2 -> 1-C4H9O + NO2	
31	2-C4H9ONO2 -> 2-C4H9O + NO2	
32	CH3CHONO2CH3 -> CH3CHOCH3 + NO2	
33	CH2(OH)CH2(ONO2) -> CH2(OH)CH2(O.) + NO2	
34	CH3COCH2(ONO2) -> CH3COCH2(O.) + NO2	
35	C(CH3)3(ONO2) -> C(CH3)3(O.) + NO2	
36	C(CH3)3(ONO) -> C(CH3)3(O) + NO	
37	CH3CO(OONO2) -> CH3CO(OO) + NO2	(J_pan_a)
38	CH3CO(OONO2) -> CH3CO(O) + NO3	(J_pan_b)
39	CH3CH2CO(OONO2) -> CH3CH2CO(OO) + NO2	
40	CH3CH2CO(OONO2) -> CH3CH2CO(O) + NO3	
41	CH2=CHCHO -> Products	
42	CH2=C(CH3)CHO -> Products	(J_macr)
43	CH3COCH=CH2 -> Products	(J_mvk)
44	HOCH2CHO -> CH2OH + HCO	(J_glyald_a)
45	HOCH2CHO -> CH3OH + CO	(J_glyald_b)
46	HOCH2CHO -> CH2CHO + OH	(J_glyald_c)
47	CH3COCH3 -> CH3CO + CH3	(J_ch3coch3)
48	CH3COCH2CH3 -> CH3CO + CH2CH3	(J_mek)
49	CH2(OH)COCH3 -> CH3CO + CH2(OH)	(J_hyac_a)
50	CH2(OH)COCH3 -> CH2(OH)CO + CH3	(J_hyac_b)
51	CHOCHO -> HCO + HCO	(J_gly_a)
52	CHOCHO -> H2 + 2CO	(J_gly_b)
53	CHOCHO -> CH2O + CO	(J_gly_c)
54	CH3COCHO -> CH3CO + HCO	(J_mgly)
55	CH3COCOCH3 -> Products	
56	CH3COOH -> CH3 + COOH	
57	CH3CO(OOH) -> Products	
58	CH3COCO(OH) -> Products	
59	(CH3)2NNO -> Products	
60	CF2O -> Products	

**in mozart_mosaic_4bin*

List of available photolysis reactions in the updated TUV

61 Cl2 -> Cl + Cl
62 ClO -> Cl + O(1D)
63 ClO -> Cl + O(3P)
64 ClOO -> Products
65 OClO -> Products
66 ClOOCl -> Cl + ClOO
67 HCl -> H + Cl
68 HOCl -> HO + Cl
69 NOCl -> NO + Cl
70 ClNO2 -> Cl + NO2
71 ClONO -> Cl + NO2
72 ClONO2 -> Cl + NO3
73 ClONO2 -> ClO + NO2
74 CCl4 -> Products
75 CH3OCl -> CH3O + Cl
76 CHCl3 -> Products
77 CH3Cl -> Products
78 CH3CCl3 -> Products
79 CCl2O -> Products
80 CClFO -> Products
81 CCl3F (CFC-11) -> Products
82 CCl2F2 (CFC-12) -> Products
83 CF2ClCFCl2 (CFC-113) -> Products
84 CF2ClCF2Cl (CFC-114) -> Products
85 CF3CF2Cl (CFC-115) -> Products
86 CHClF2 (HCFC-22) -> Products
87 CF3CHCl2 (HCFC-123) -> Products
88 CF3CHFCl (HCFC-124) -> Products
89 CH3CFCl2 (HCFC-141b) -> Products
90 CH3CF2Cl (HCFC-142b) -> Products
91 CF3CF2CHCl2 (HCFC-225ca) -> Products
92 CF2ClCF2CHFCl (HCFC-225cb) -> Products
93 Br2 -> Br + Br
94 BrO -> Br + O
95 HOBr -> OH + Br
96 BrNO -> Br + NO
97 BrONO -> Br + NO2
98 BrONO -> BrO + NO
99 BrNO2 -> Br + NO2
100 BrONO2 -> BrO + NO2
101 BrONO2 -> Br + NO3
102 BrCl -> Br + Cl
103 CH3Br -> Products
104 CHBr3 -> Products
105 CF2Br2 (Halon-1202) -> Products
106 CF2BrCl (Halon-1211) -> Products
107 CF3Br (Halon-1301) -> Products
108 CF2BrCF2Br (Halon-2402) -> Products
109 perfluro 1-iodopropane -> products

Additional file in KPP/mechanisms/$mechanism/
$mechanism.tuv.jmap
Correspondence j_wrfchem with available j_tuv

Photolysis in WRF-Chem

- Ozone column density above the model top:
  - TUV: specified value above the model top (specified_du=325)
  - fast-J: specified value at the model top for the whole domain
  - f-TUV: MOZART model climatology at the top (input file exo_coldens.nc)
  - New TUV: uses ozone climatology distributed from model top to 50km, and then several options available above 50km

- Cloud optical properties:
  - Recalculated in each photolysis scheme, different from physics (e.g. RRTMG)
  - typically, COD calculated from LWP/IWP and effective drop radius (Slingo 1989, with fixed SSA = 0.9999 and f_{assym} = 0.85)
  - Various treatments of Sub-grid cloud overlap
    - Scaled by cloud fraction (fast-J)
    - Max random overlap for f-TUV (expensive)
    - Simplified ($COD_{subgrid} = COD * FCLD^{3/2}$, equivalent to max random overlap)

- Aerosols:

  accounted for through the namelist option **aer_ra_feedback = .true.**

Settings for phot_opt = 4 (default in red)

Download the data file TUV.phot.tar from the ACOM website

(add data directories DATAE1 and DATAJ1, and wrf_tuv_xsqy.nc file)

- phot_opt = 4, 4

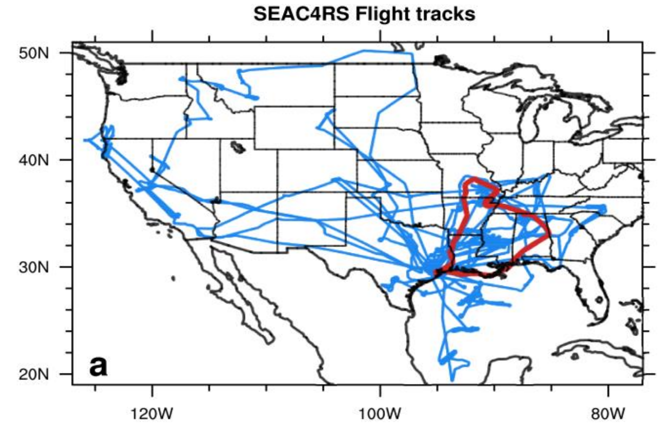
- is_full_tuv = .false. : use wrf_tuv_xsqy.nc table interpolation
- is_full_tuv = .true. : use hard-coded data and formulas (updated)

- du_at_grnd = 300 : default total o3 column density
- has_o3_exo_coldens =.false. : o3 column density above 50 km = 0.
- has_o3_exo_coldens =.true. : o3 column density above 50 km from mozart climatology
- scale_o3_to_grnd_exo_coldens = .true. : total o3 column at ground scaled to climatology
- scale_o3_to_du_at_grnd = .true. : scaled to the du_at_grnd value at the ground

- pht_cldfrc_opt = 1 : grid cell cloud fraction is either 0 or 1
- pht_cldfrc_opt = 2 : grid cell cloud fraction varies between 0 and 1

- cld_od_opt = 1 : cloud optical depth is scaled by cloud fraction
- cld_od_opt = 2 : cloud optical depth is scaled by (cloud fraction)**1.5

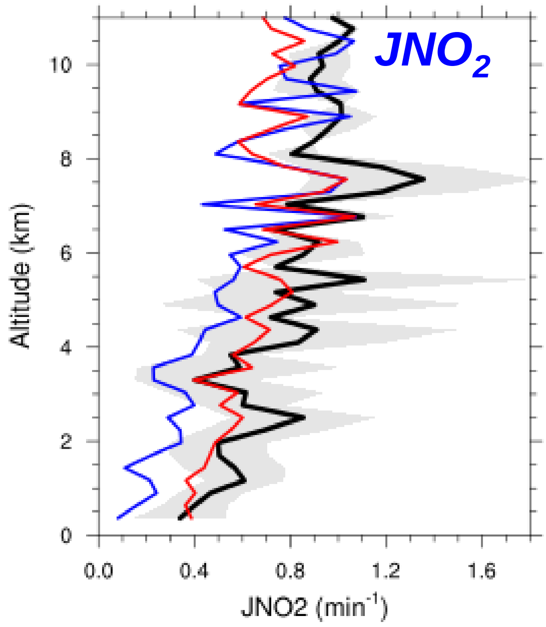
Comparison with the 2013 SEAC^{4}RS flights

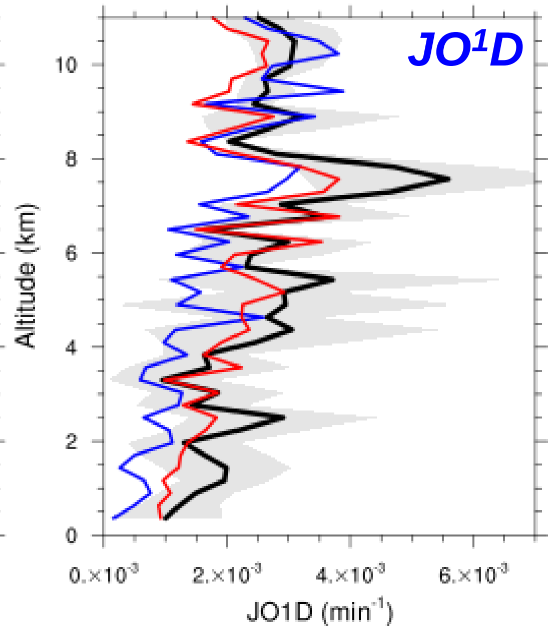


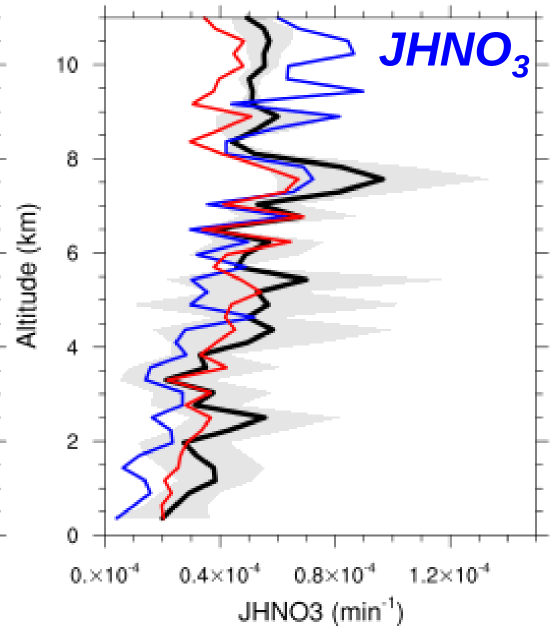
OBS SEAC4RS

Old TUV (phot_opt=1)

New TUV (phot_opt=4)







Comparison with SEAC^{4}RS (14 Aug. 2013)