PHOTOLYSIS

The driver for photo-oxidation

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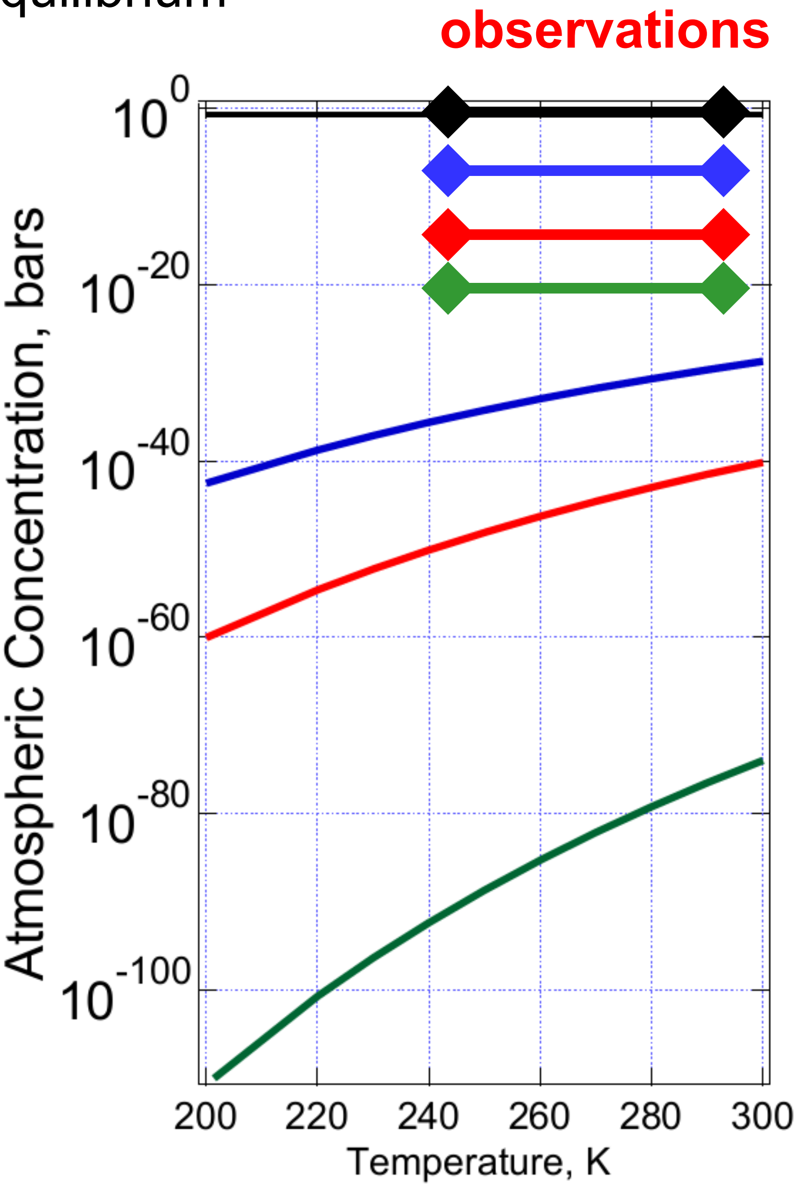
NCAR

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

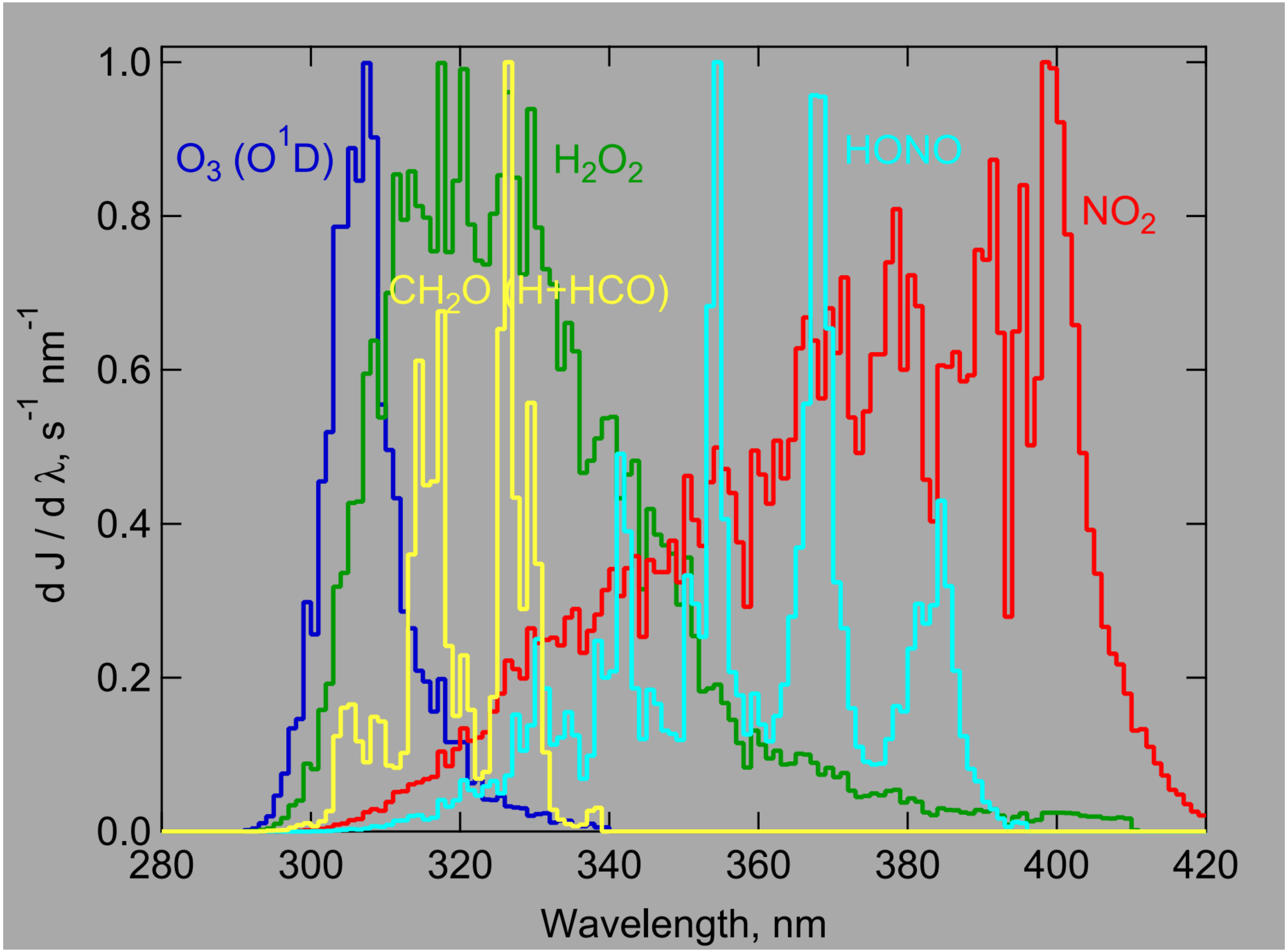


Some Important Photolysis Reactions

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

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

sea level, overhead sun, tuv5.2



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

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

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

$\propto$ probability of photon near molecule.

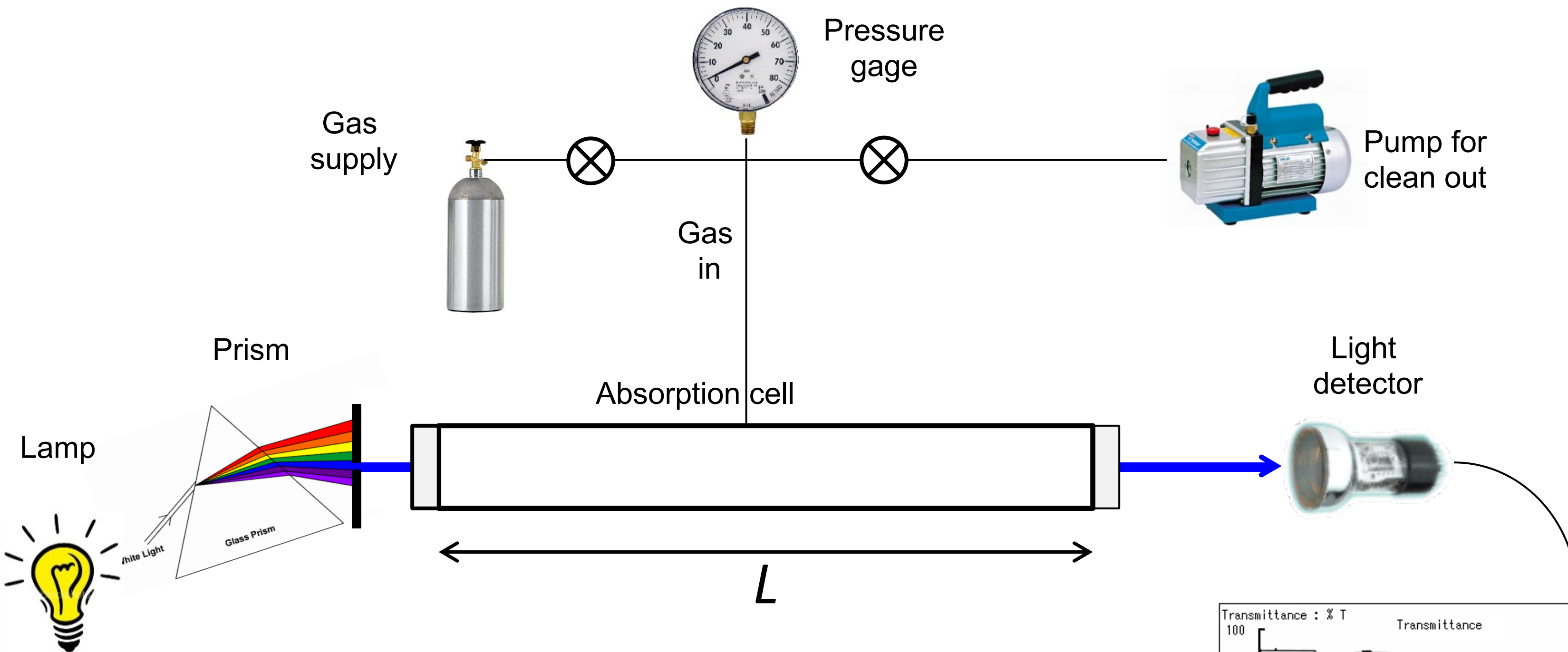
$\sigma(\lambda)$ = absorption cross section, $cm^2\ molec^{-1}$

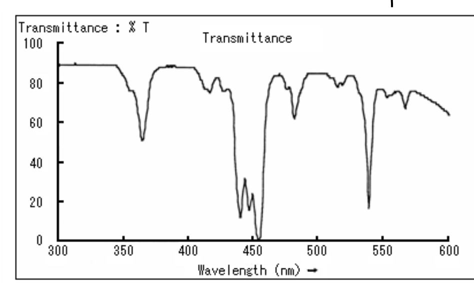
$\propto$ probability that photon is absorbed.

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

$\propto$ probability that absorbed photon causes dissociation.

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



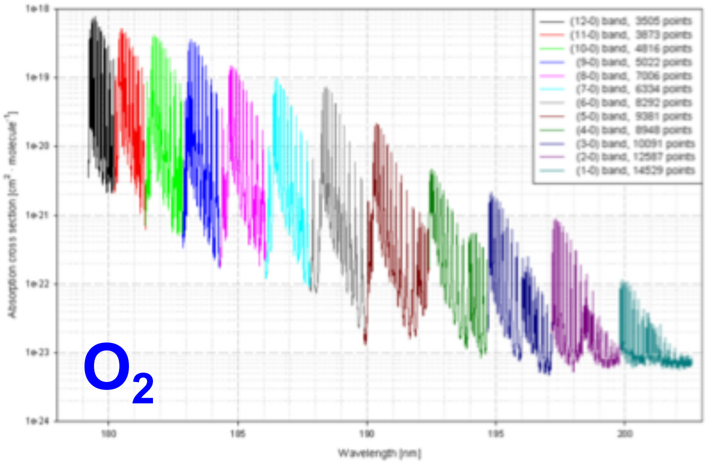


Transmittance = $I / I_o = \exp(-\sigma\, n\, L)$

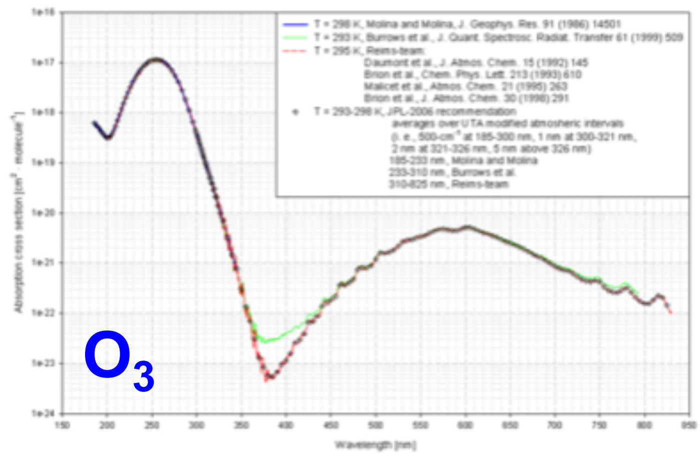
$\sigma = -1/(nL) \ln(I / I_o)$

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

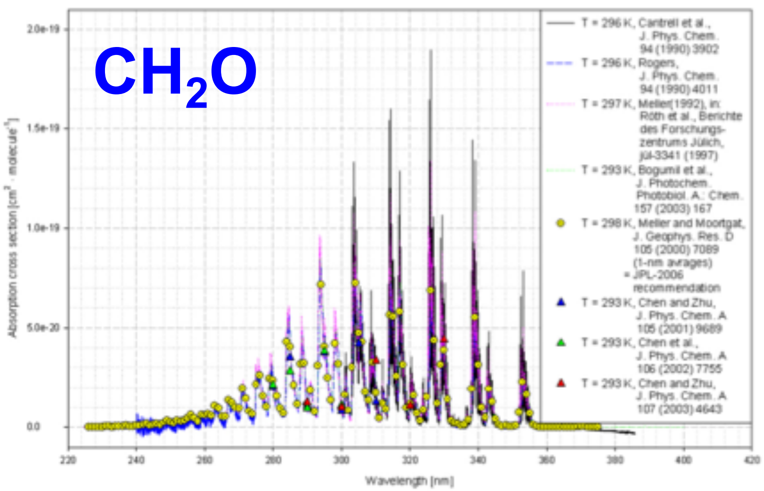
Absorption cross sections $\sigma(\lambda, T)$



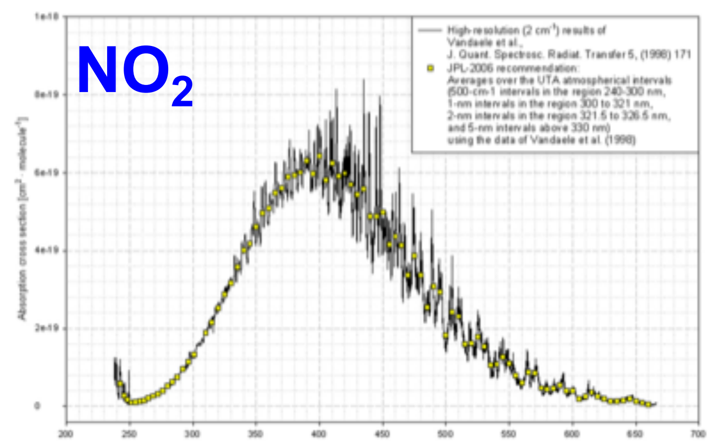
Absorption cross sections in the Schumann-Runge region of oxygen O_2 at 300 K,
Yoshino et al., Planet. Space Sci. 40 (1992) 185



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

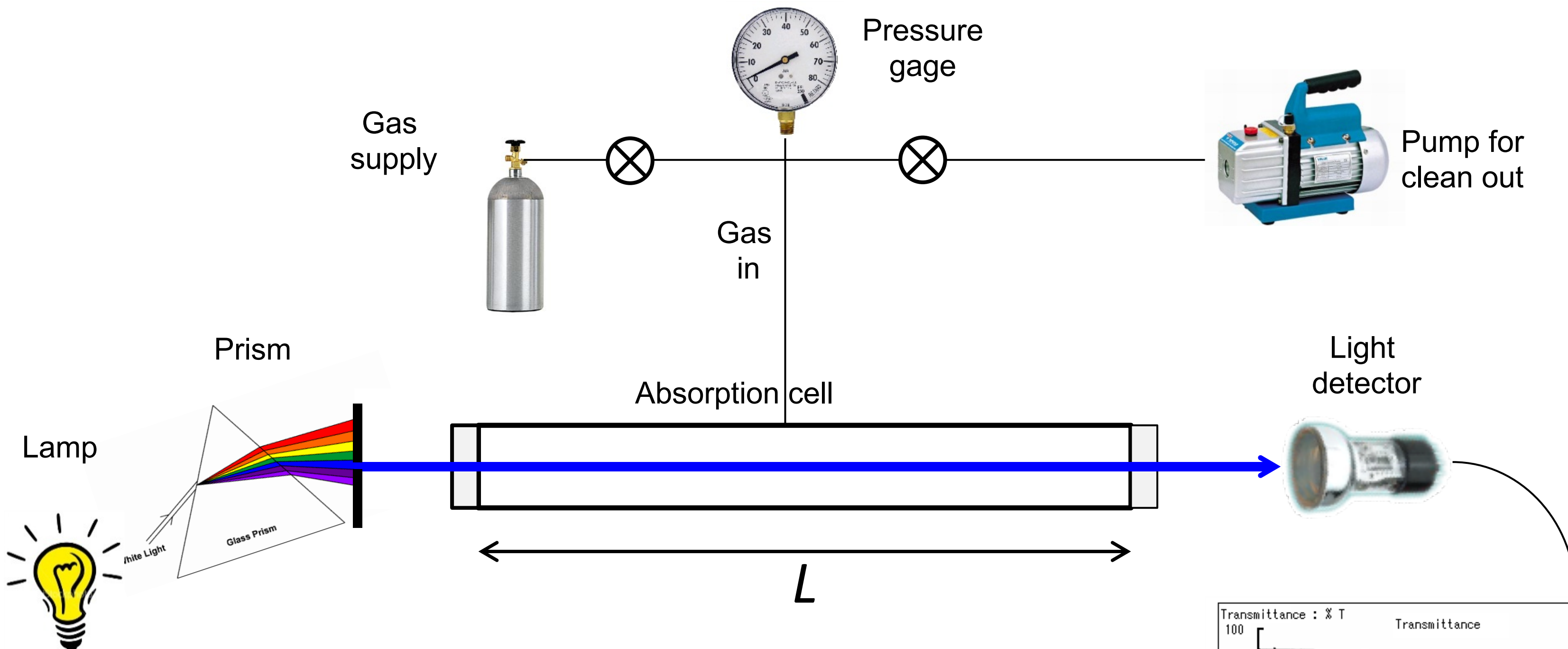


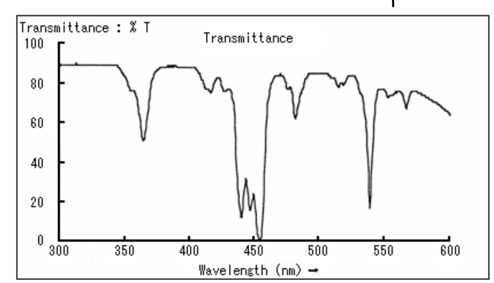
Absorption cross sections of formaldehyde CH_2O at room temperature (results 1990-2003)



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

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





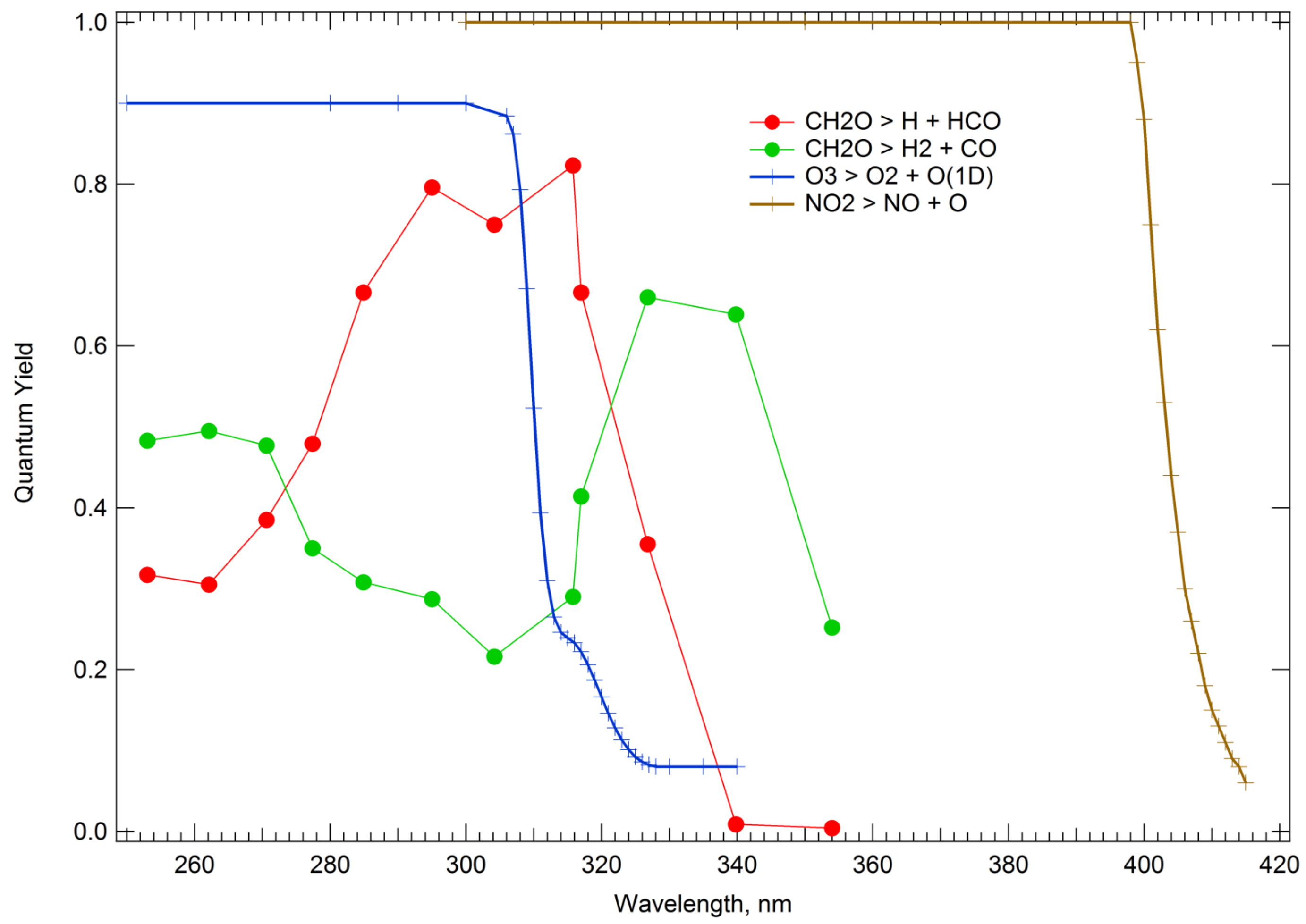
Transmittance = $I / I_o = \exp(-\sigma\, n\, L)$

Quantum Yield = number of breaks per photon absorbed

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

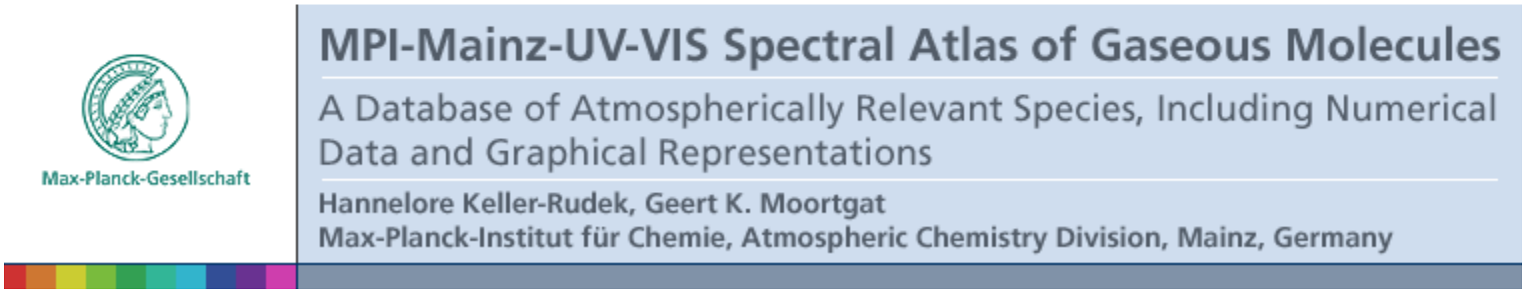
Difficult: must measure absolute change in *n* (products) and *I* (photons absorbed)

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

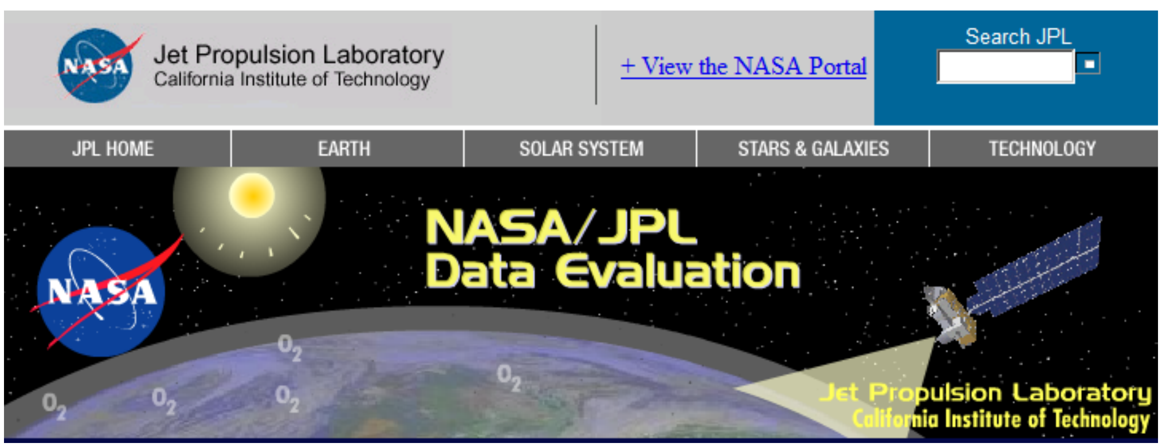


Compilations of Cross Sections & Quantum Yields

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

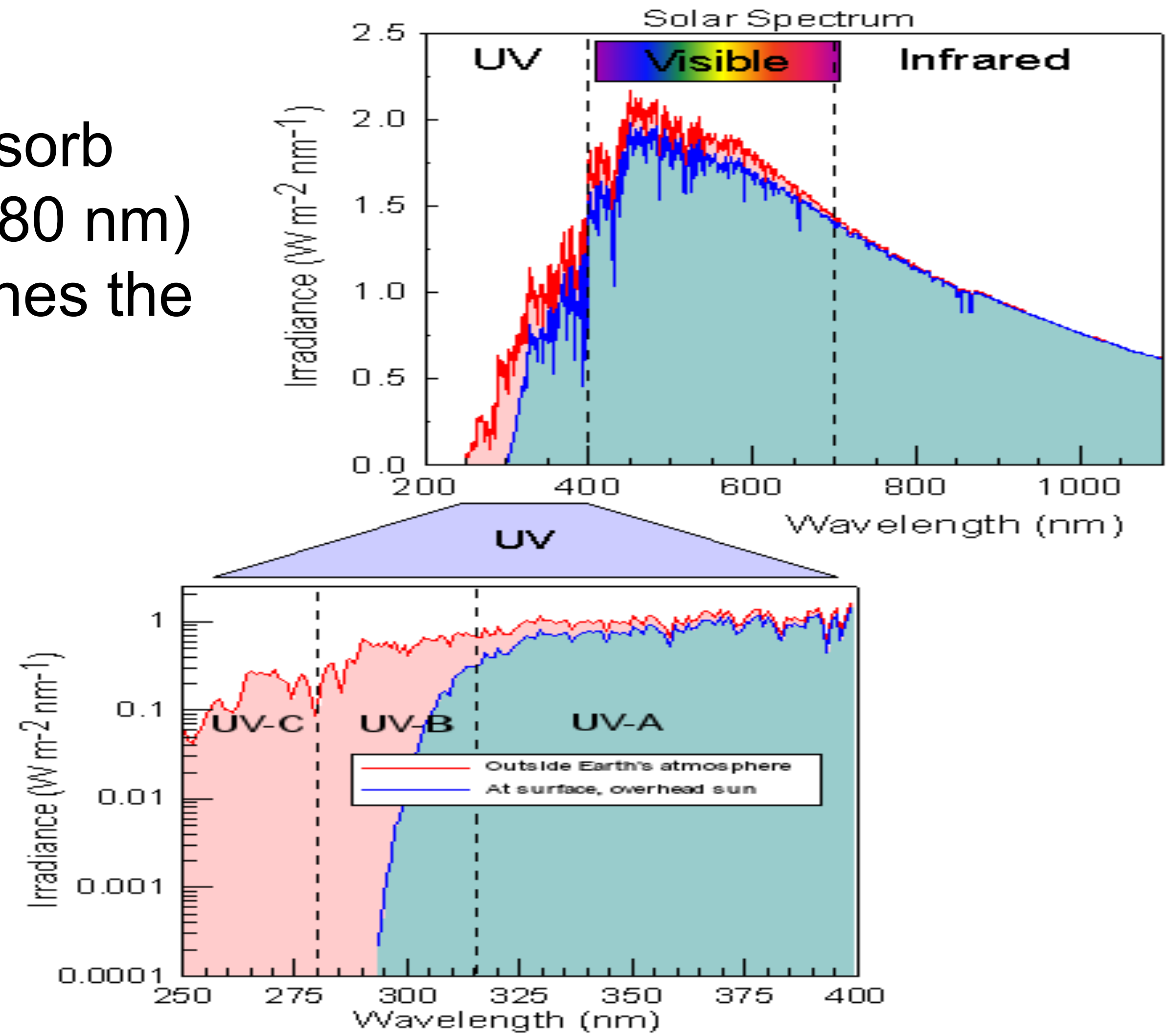


http://jpldataeval.jpl.nasa.gov/



Solar Spectrum

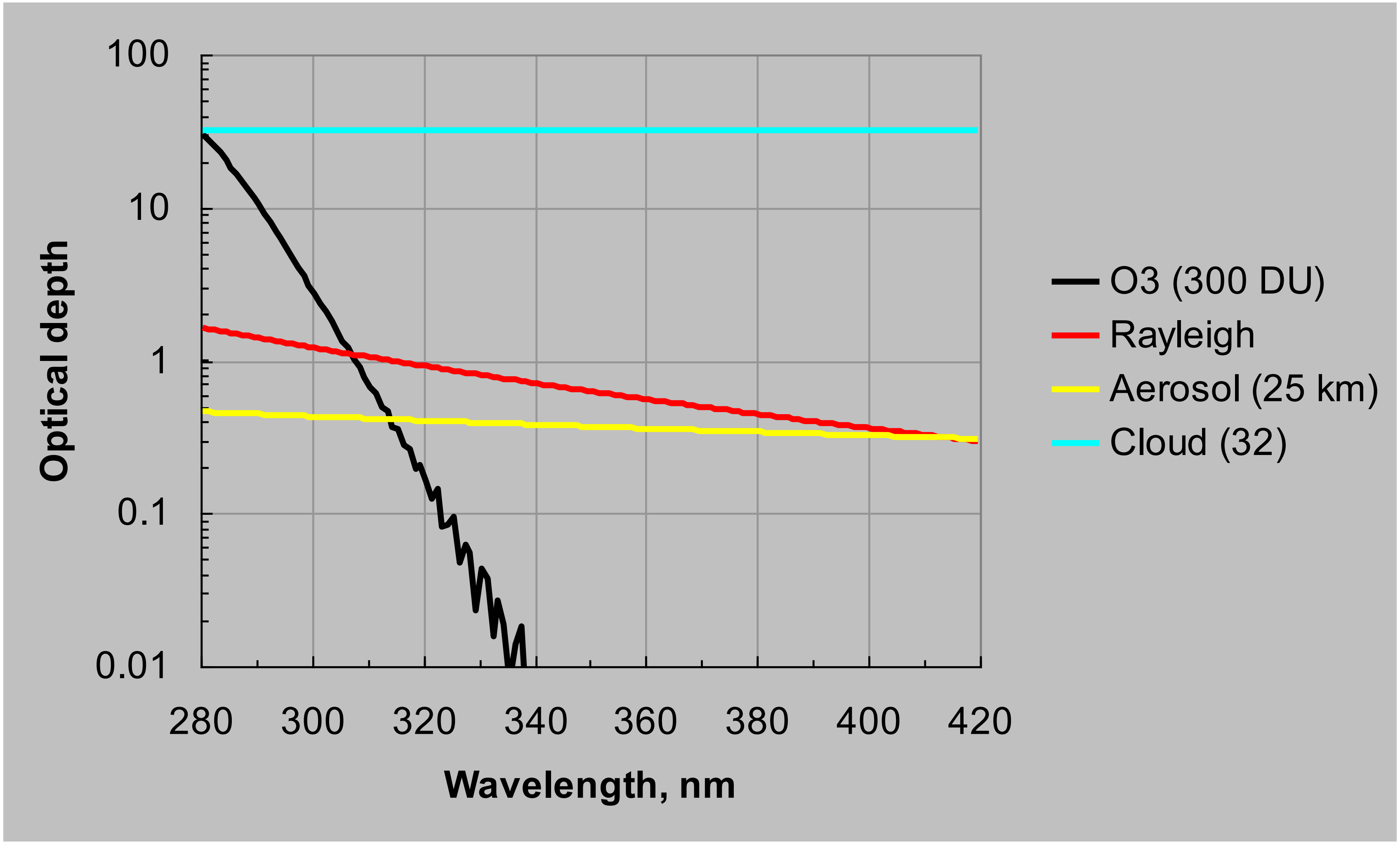
O_2 and O_3 absorb all UV-C (λ<280 nm) before it reaches the troposphere



UNEP, 2002

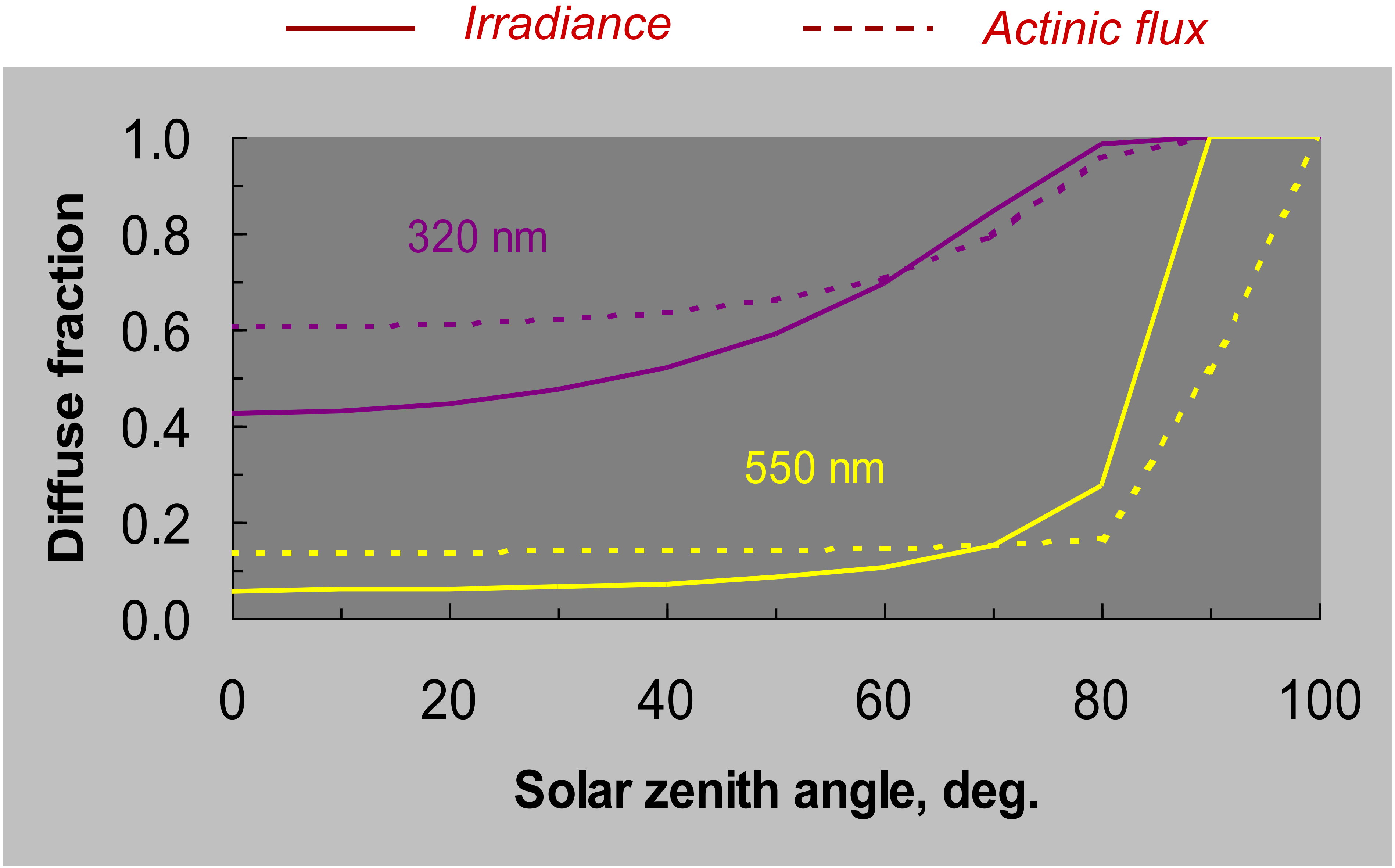
Atmospheric Optical Depths, τ

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



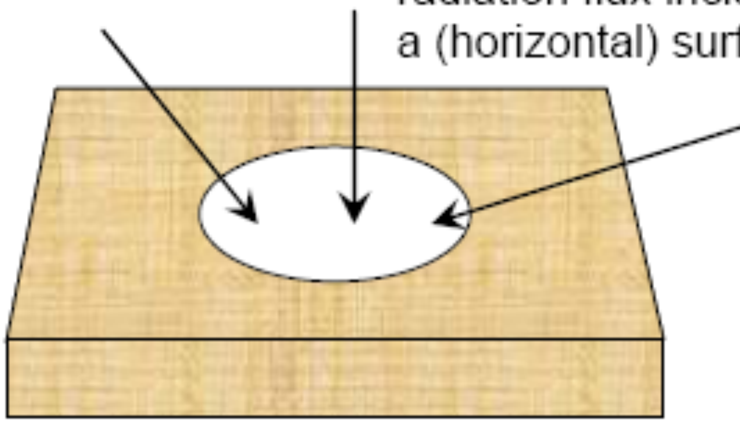
UV: Diffuse Radiation ≥ Direct Solar Beam

clean skies, sea level

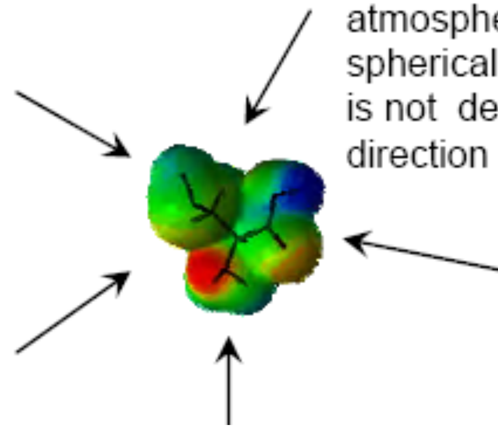


INTEGRALS OVER ANGULAR INCIDENCE

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.



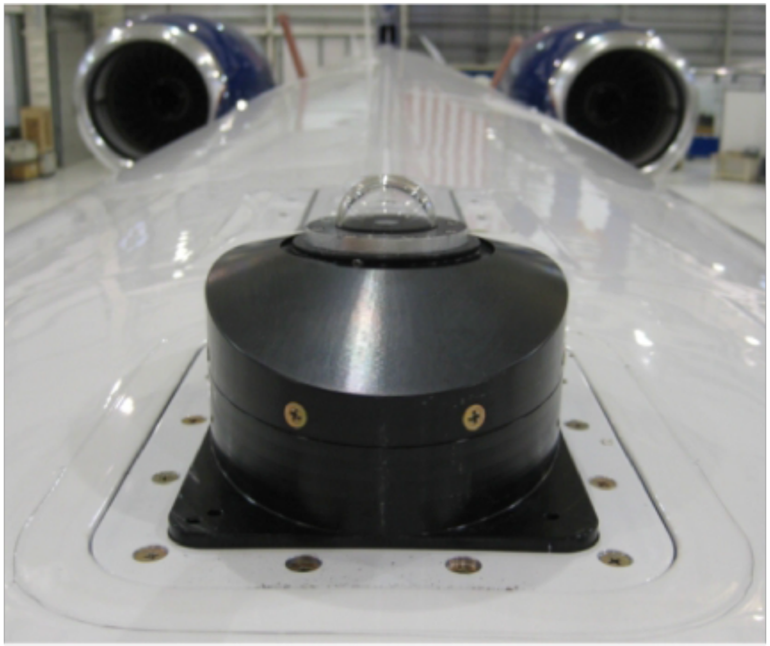
$$E = \int_0^{2\pi}\int_0^{\frac{\pi}{2}} I(\theta,\varphi)\cos\theta\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi$$

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}

Actinic Flux Measurements

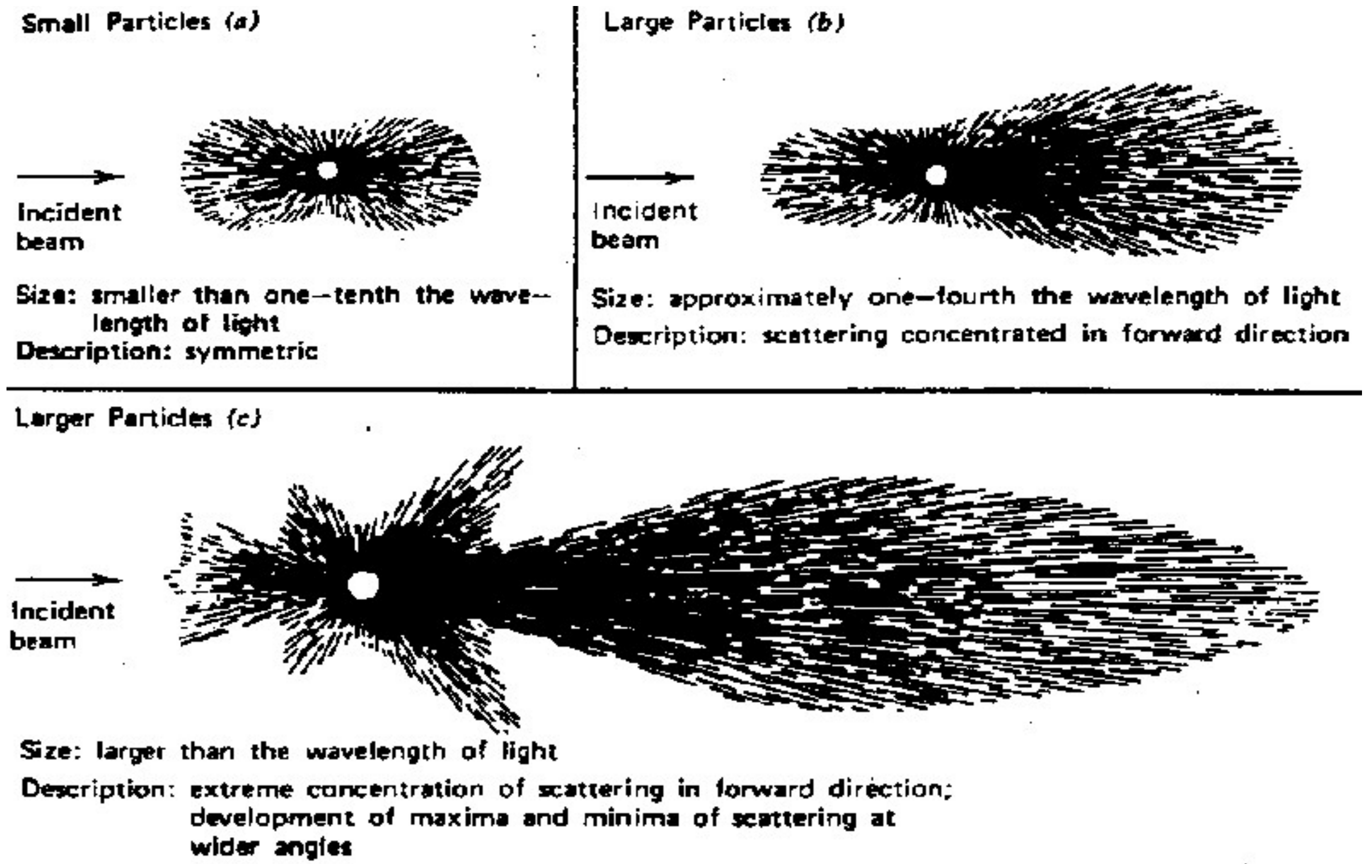


By placing 2 half spheres on the airplane, you can measure the spectral radiation onto a sphere

Combine with cross-sections and quantum yields, integrate
*→ **j-values***

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 $n \rightarrow \infty$ but speed $\propto 1/n^2$

- Two-stream family

  delta-Eddington, many others

  very fast but not exact

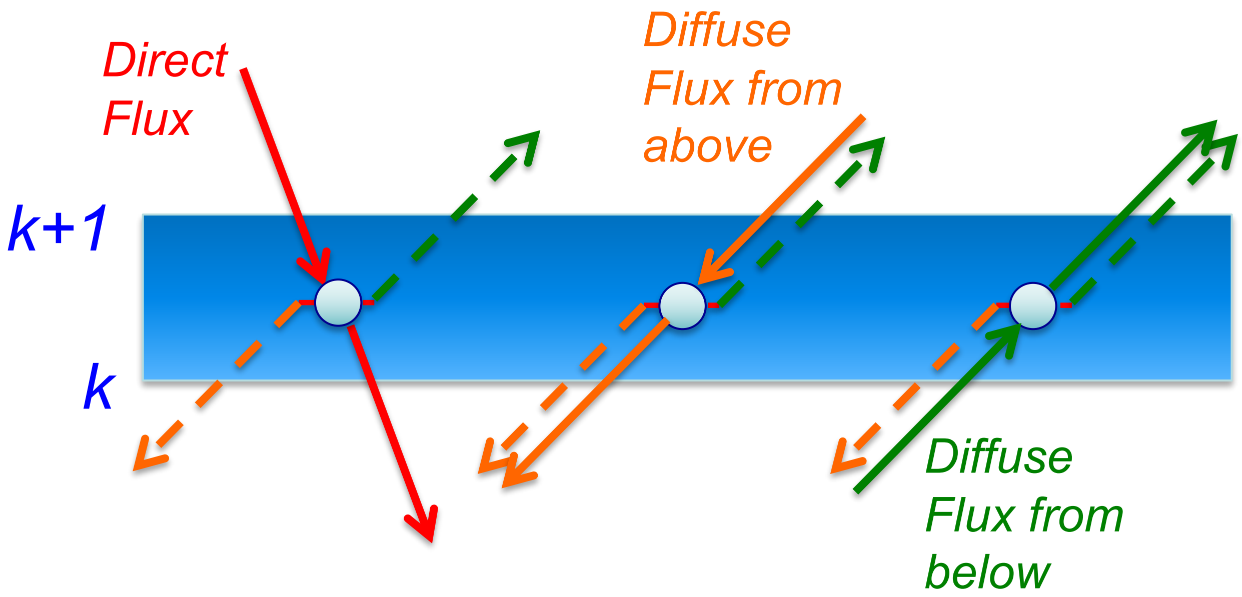
- Monte Carlo

  slow, but ideal for 3D problems

- Others

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

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, ***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: $\Delta\tau(\lambda, z)$ ~ 0 - 30

Rayleigh scatt. ~ 0.1 - 1.0 ~ λ^{-4}

O_3 absorption ~ 0 - 30

for aerosols: 0.01 - 5.0

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

(α =Angstrom exponent)

for clouds: 1-1000

$\alpha \sim 0$

cirrus ~ 1-5

cumulonimbus ~ > 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*(λ, *z*) = first moment of phase function

range -1 to + 1

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

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

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: $n = m + ik$
(composition-dependent)

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

Can compute:

Extinction efficiency $Q_e(\alpha, n) \times \pi r^2$

Scattering efficiency $Q_s(\alpha, n) \times \pi r^2$

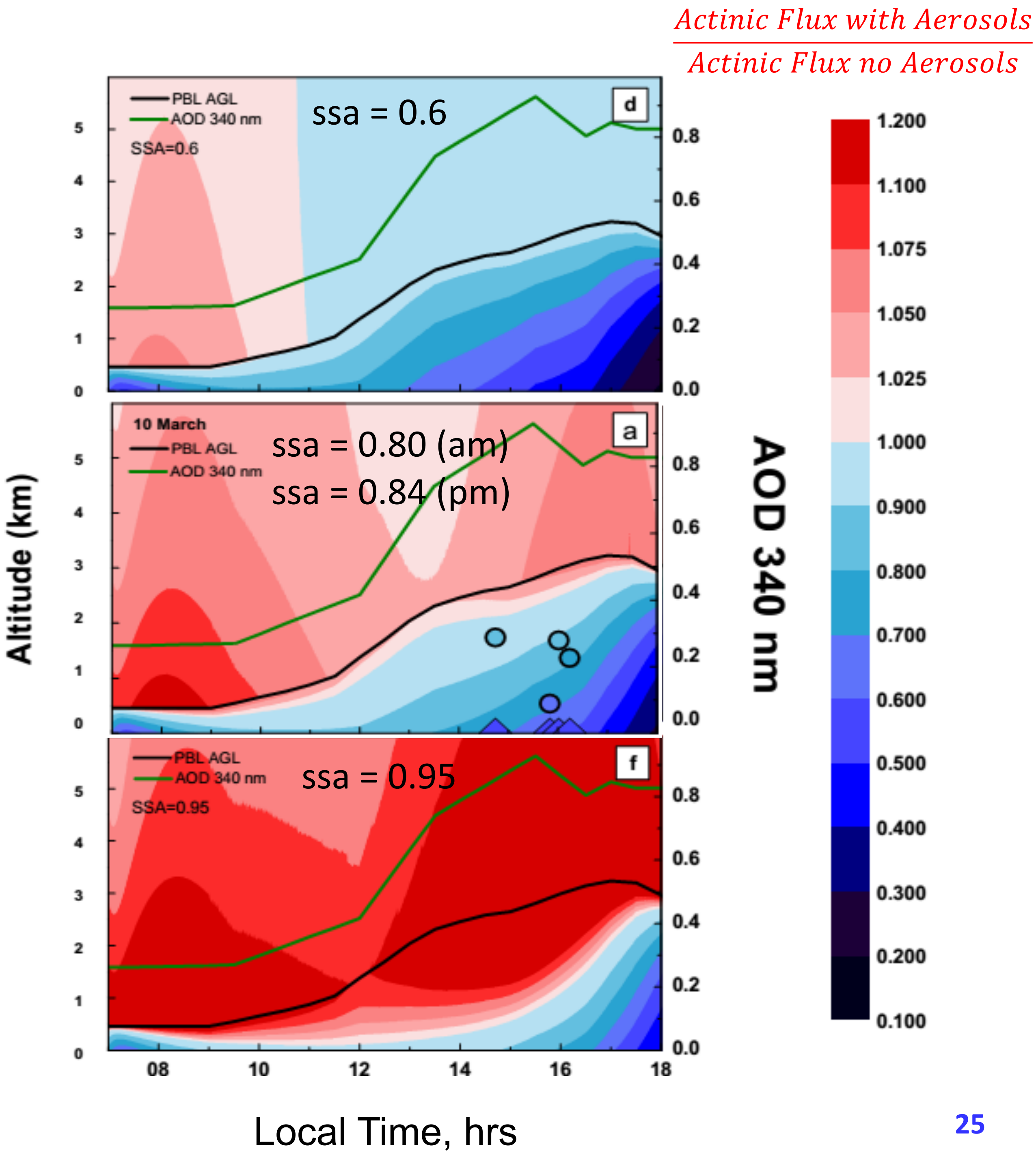
Phase function $P(\Theta, \alpha, n)$
or asymmetry factor $g(\alpha, n)$

Actinic Flux is Very Sensitive to Single Scattering Albedo

Mexico City suburbs (T1)
March 2006

Central panel:
Model with observed ssa, and obs.

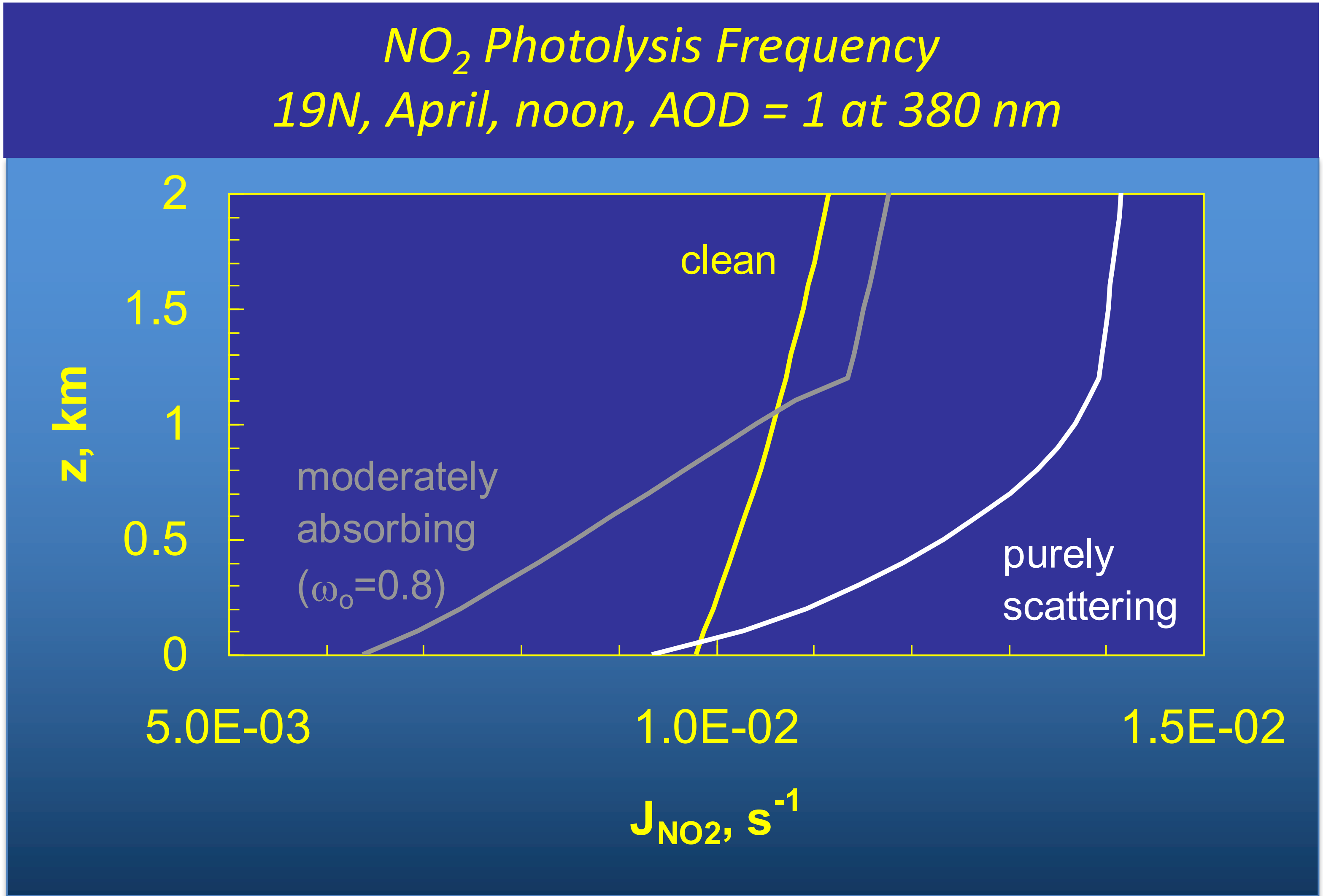
Upper and lower panels: Sensitivity to ssa



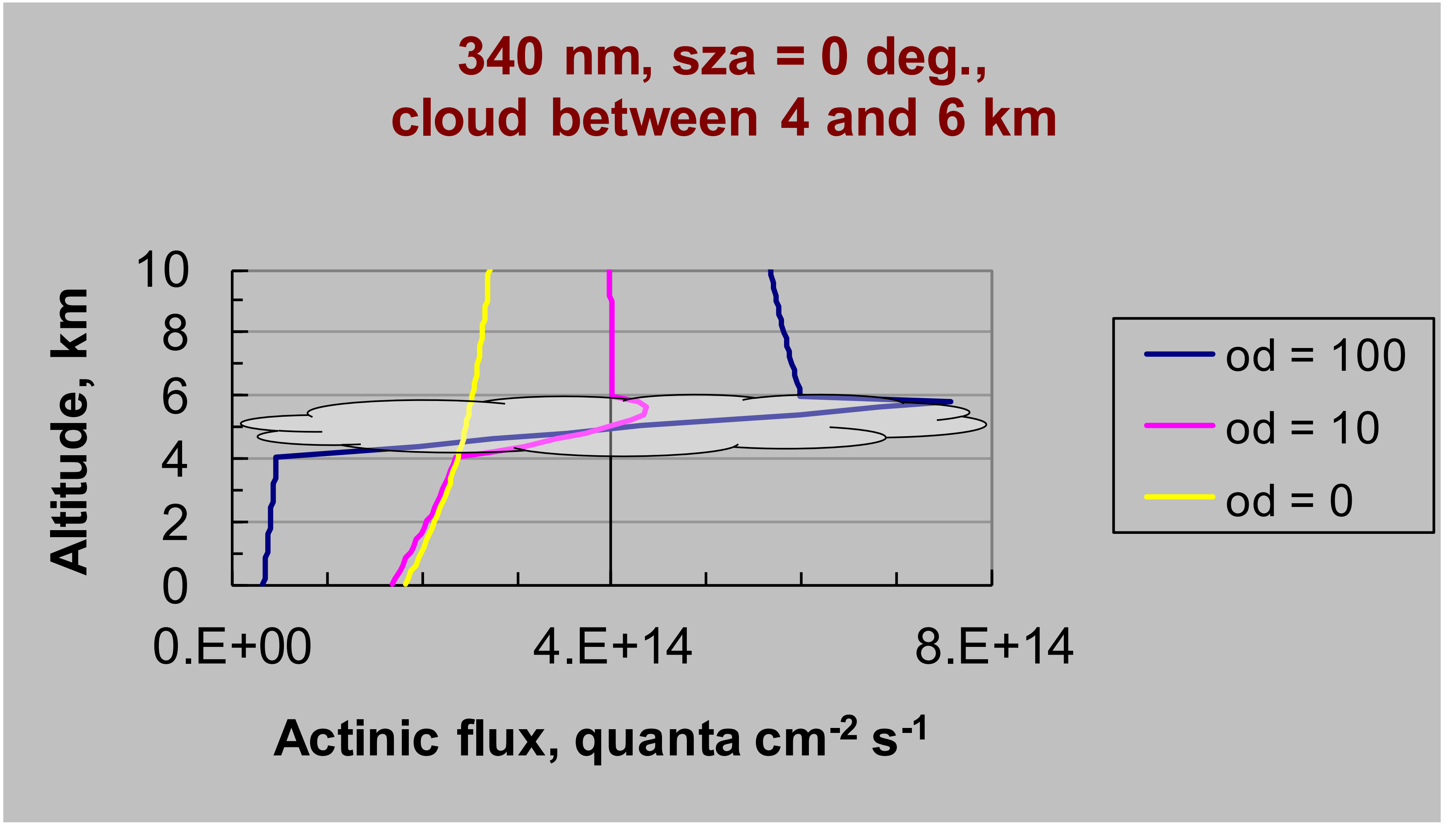
Palancar et al., 2013

Effects on the Radiation

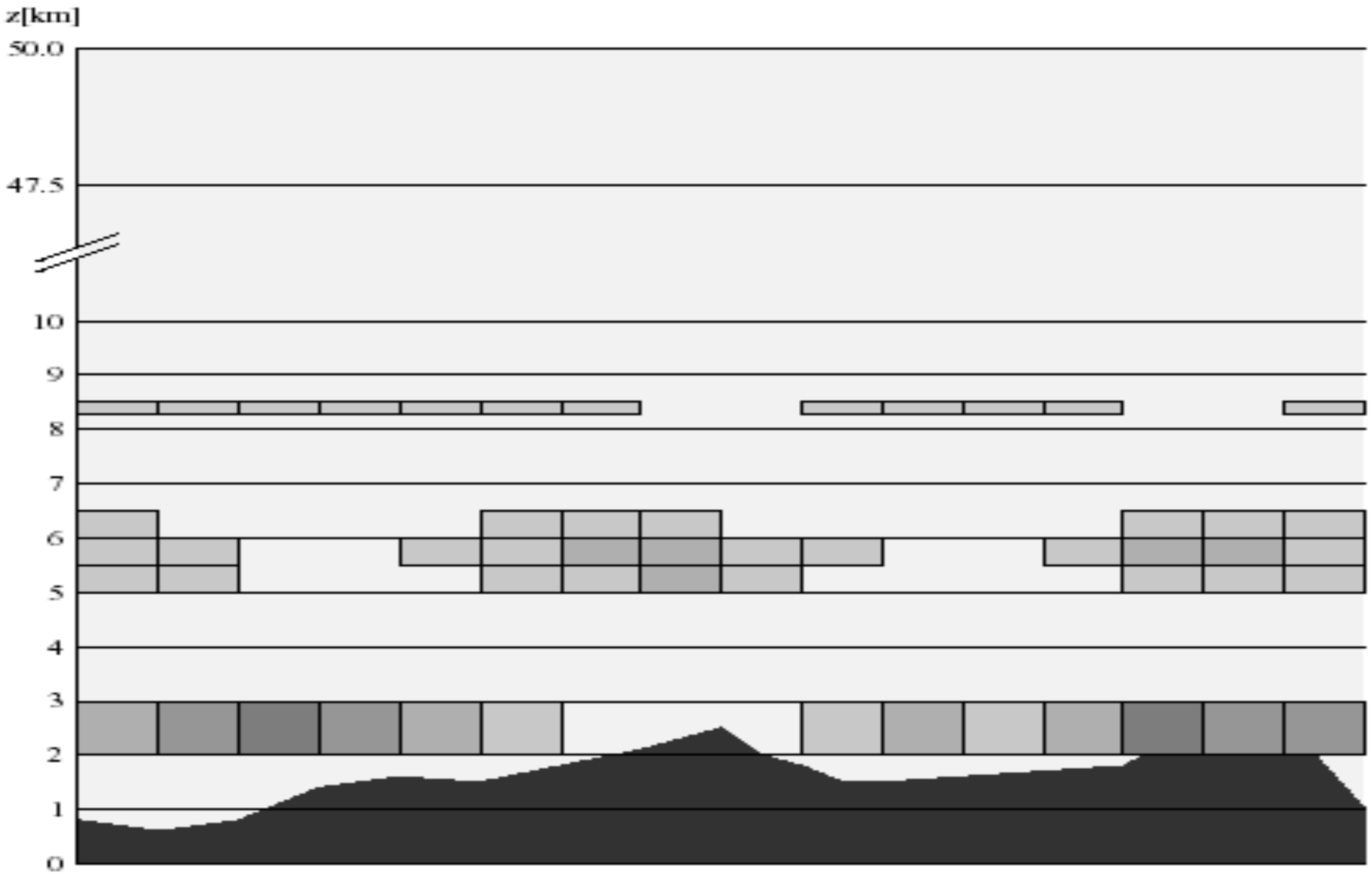
- Aerosols affect radiation – either scatter or absorb
- Clouds affect radiation – scattering



EFFECT OF UNIFORM CLOUDS ON ACTINIC FLUX



Broken Clouds



Photolysis in WRF-Chem

- Several radiative transfer options:
  - phot_opt = 1 : Madronich 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)

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

  New option in WRF-Chem v3.9:

  ⇒ 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;

  ⇒ phot_opt = 4 has updated database to the latest TUV model (V5.3, Oct. 2016)

  Difficult to add new reactions (typically available ~ 20)

  ⇒ 109 reactions relevant for tropospheric & stratospheric chemistry

List of available photolysis reactions in the updated TUV

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	perfluoro 1-iodopropane -> products

Additional file in KPP/mechanisms/$mechanism/

$mechanism.tuv.jmap

Provides mapping of j_wrfchem with available j_tuv

Photolysis in WRF-Chem

- Ozone column density above the model top:
  1) TUV: specified value above the model top (specified_du=325)
  2) fast-J: specified value at the model top for the whole domain
  3) f-TUV: WACCM model climatology at the top (input file exo_coldens.nc)
  4) 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 WACCM 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

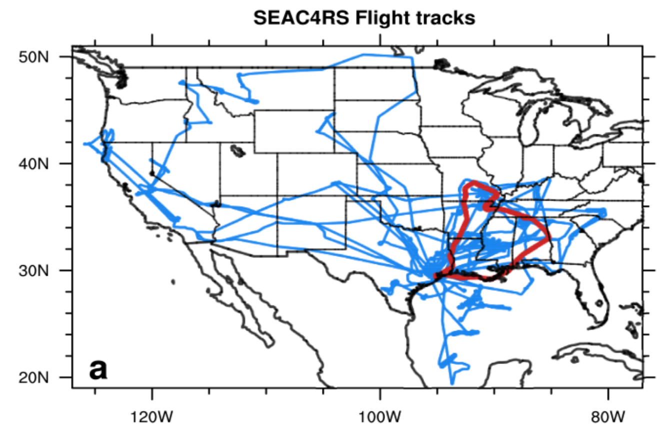
- cld_od_opt = 1 : cloud optical depth is scaled by cloud fraction
- cld_od_opt = 2 : cloud optical depth is scaled by (cloud fraction)**1.5

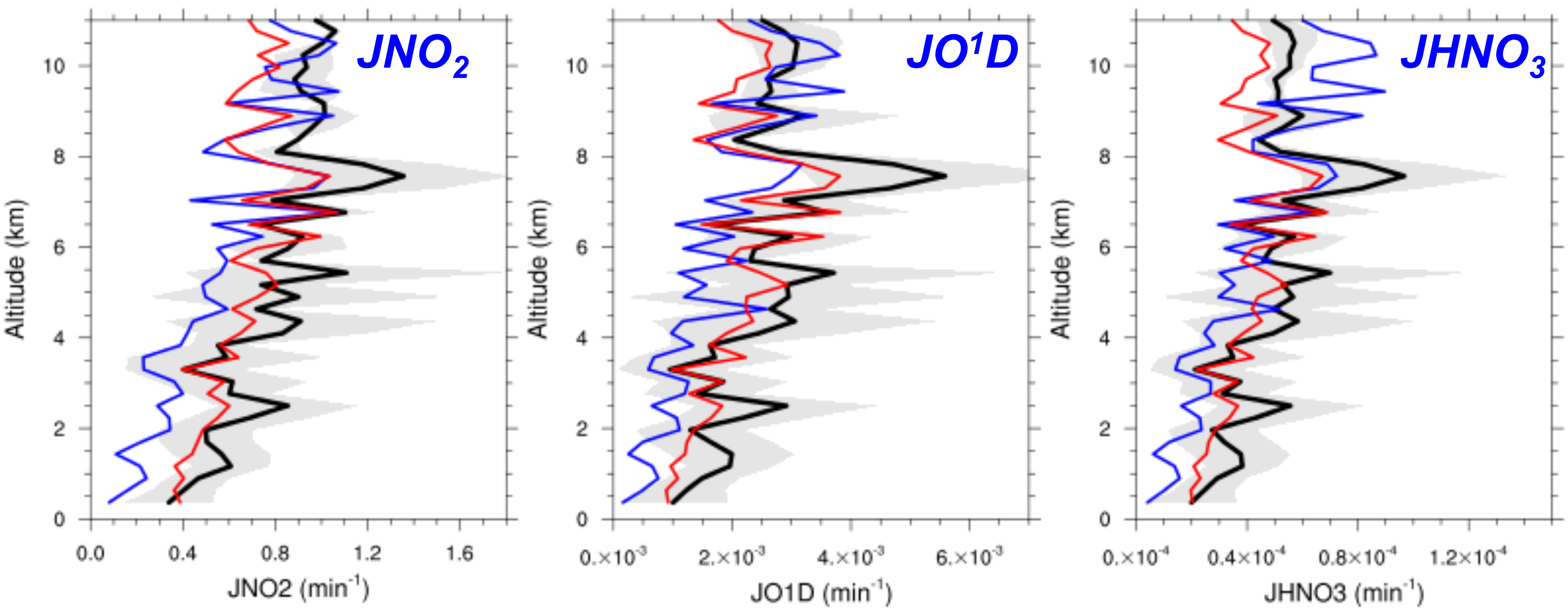
Comparison with the 2013 SEAC⁴RS flights

OBS SEAC4RS

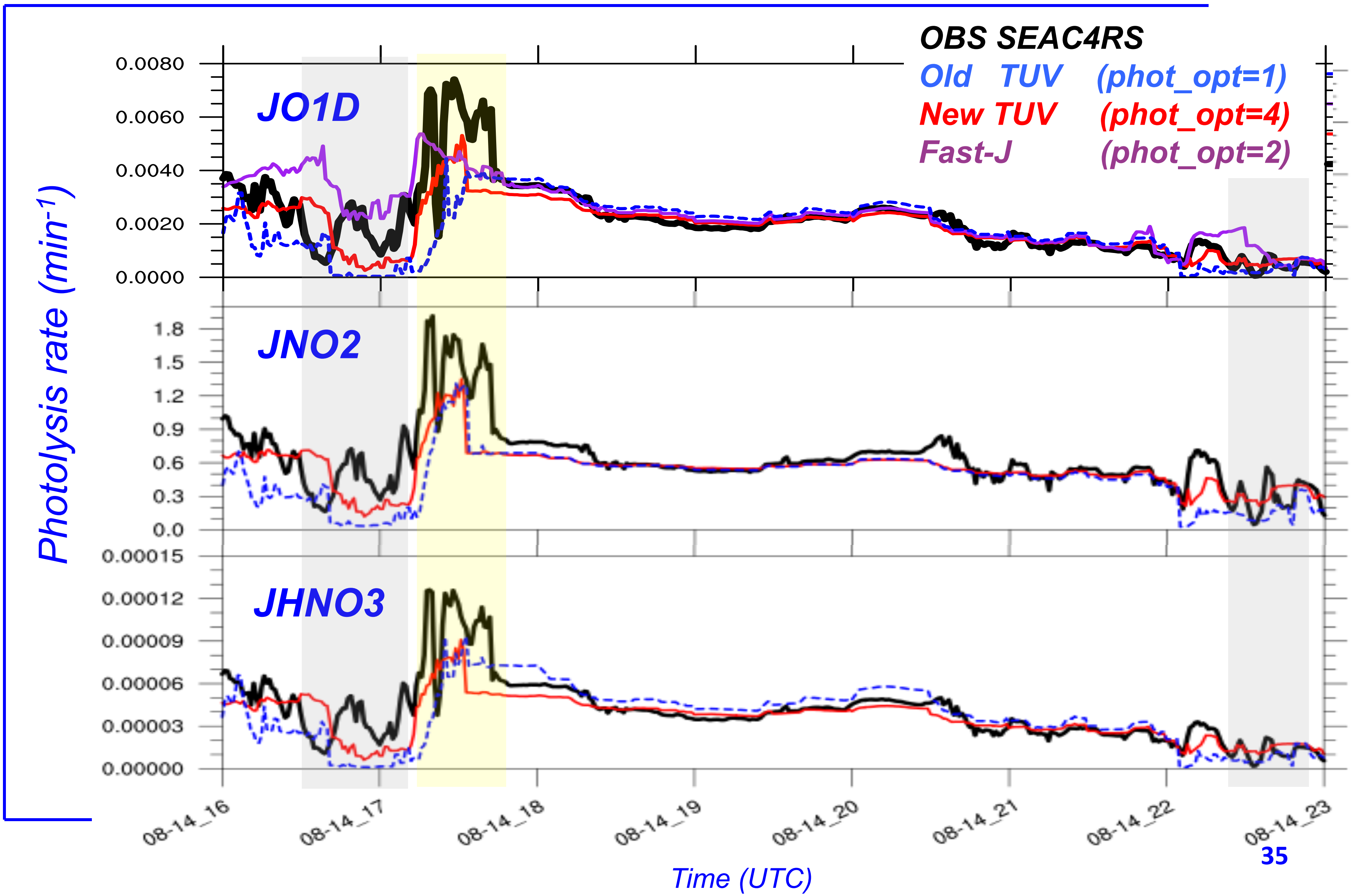
Old TUV (phot_opt=1)

New TUV (phot_opt=4)





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



http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/

QUICK TUV CALCULATOR

This web page runs the *4.1* version of the TUV model. You can run the model for a specified latitude, longitude and time (input option 1), or for a given solar zenith angle (input option 2). In either case, you must also specify the additional parameters in the second column. Also, you may select to print out the photolysis rates and/or the solar actinic flux spectrum at a given altitude above the surface (output option 1), or the erythemal UV and/or solar irradiance at that altitude (output option 2). For any problem, or to send comments, email TUV administrators.

◉ INPUT OPTION 1	OTHER INPUT PARAMETERS	◉ OUTPUT OPTION 1 (for Atmospheric Science)
LATITUDE (deg): 0	DATE (YYMMDD): 000630	☑ MOLECULAR PHOTOLYSIS FREQUENCIES (s-1)
LONGITUDE (deg): 0	OVERHEAD OZONE COLUMN (du): 300	☐ ACTINIC FLUX, SPECTRAL (quanta s-1 cm-2 nm-1)
TIME (hh:mm:ss, GMT): 12:00:00	SURFACE ALBEDO (0-1): 0.1	○ OUTPUT OPTION 2 (for Biology)
○ INPUT OPTION 2	GROUND ELEVATION (km asl): 0	☑ IRRADIANCE, WEIGHTED (W m-2)
SOLAR ZENITH ANGLE (deg): 0	MEASUREM. ALTITUDE (km asl): 0	☐ IRRADIANCE, SPECTRAL (W m-2 nm-1)

RADIATION TRANSFER MODEL

◉ Pseudo-spherical 2 streams (faster, less accurate)
○ Pseudo-spherical discrete ordinate 4 streams (slower, more accurate)

GO!