Adding new photolysis in GEOS-Chem

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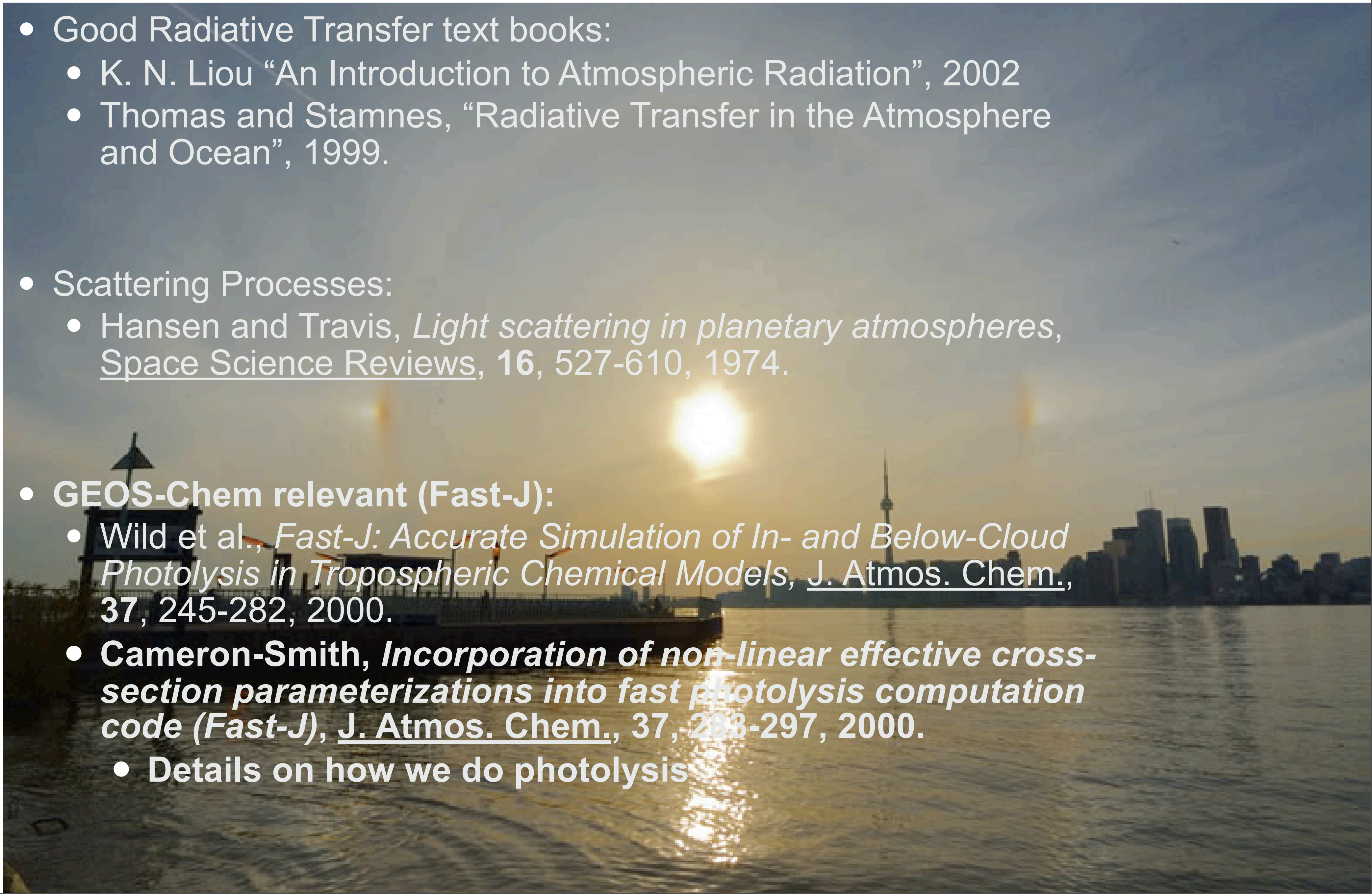
Grad Student Forum, 6/2/2011

Side-note: Good References



- Good Radiative Transfer text books:
  - K. N. Liou “An Introduction to Atmospheric Radiation”, 2002
  - Thomas and Stamnes, “Radiative Transfer in the Atmosphere and Ocean”, 1999.
- Scattering Processes:
  - Hansen and Travis, *Light scattering in planetary atmospheres*, Space Science Reviews, **16**, 527-610, 1974.
- **GEOS-Chem relevant (Fast-J):**
  - Wild et al., *Fast-J: Accurate Simulation of In- and Below-Cloud Photolysis in Tropospheric Chemical Models*, J. Atmos. Chem., **37**, 245-282, 2000.
  - **Cameron-Smith, *Incorporation of non-linear effective cross-section parameterizations into fast photolysis computation code (Fast-J)*, J. Atmos. Chem., 37, 283-297, 2000.**
    - **Details on how we do photolysis**

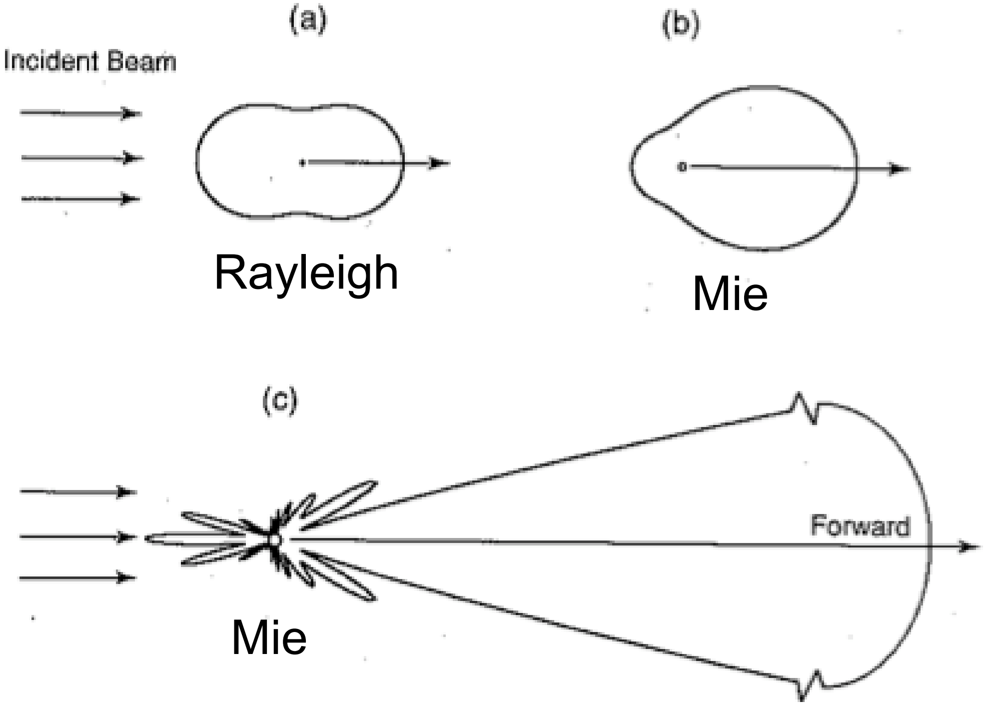
Radiative transfer: solving the Schwartzchild eq'n

source fn' →
$$S(\tau,\hat{\Omega}) = \underbrace{[1-a]B(T)}_{\text{thermal emission}} + \underbrace{S^*(\tau,\hat{\Omega})}_{\text{first-order scattering}} + \underbrace{\frac{a}{4\pi}\int_{4\pi} p(\hat{\Omega}',\hat{\Omega})I_d(\hat{\Omega}')dw'}_{\text{multiple scattering}}$$

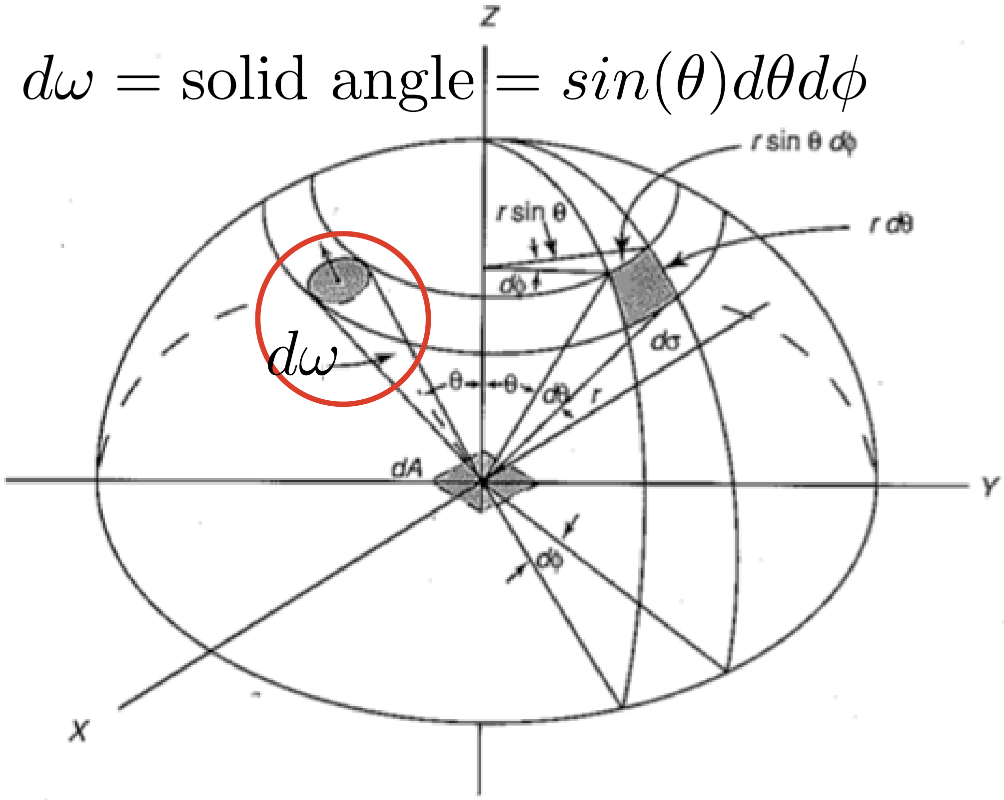
Solving for the radiation field throughout atmosphere

Full integro-differential eq. →
$$\mu\frac{dI(\tau;\mu,\phi)}{d\tau} = \underbrace{I(\tau,\hat{\Omega})e^{-(\Delta\tau/\mu)}}_{\text{attenuated solar beam}} + \underbrace{\int_{\Delta\tau} S(\tau',\hat{\Omega})e^{-(\tau'-\tau)/\mu}\frac{d\tau'}{\mu}}_{\text{attenuated source fn'}}$$

Light scattering processes
(O2, N2, Ag, particles)



$$d\omega = \text{solid angle} = sin(\theta)d\theta d\phi$$



Fast-J

$$\mu \frac{d\mathbf{I}(\tau;\mu,\phi)}{d\tau} = \mathbf{I}(\tau;\mu,\phi) - \mathbf{J}(\tau;\mu,\phi)$$

- Guassian Quadrature-based radiative transfer calculations: 8-stream multiple scattering.
- Psuedo-spherical (treat spherical geometry for irradiance, plane-parallel approx. for diffuse radiation)
- Treatment of aerosol and clouds based on full optical columns of thickness + assumptions on random overlap of clouds.
- Another important time-saver: We don't want to integrate over fine spectral structure online. Pre-select, average bins to get mean radiances for photochem.

Guass-quadrature used for angular integration of multiple scattering. Done for computational efficiency. **Maximizes the accuracy** of the solution with the **minimum number of points (evaluations)**. For *n* integration points, integrate polynomial of *2n-1* exactly.

7 λ bins:

289.00 - 298.25 nm
298.25 - 307.45 nm
307.45 - 312.45 nm
312.45 - 320.30 nm
320.30 - 345.00 nm
345.00 - 412.45 nm
412.45 - 850.00 nm

How are J-values calculated?

On paper

for chemical
tracer “w”

Actinic Flux
(online by Fast-J)

$$J_w = \int_0^\infty \Omega_w(\lambda)\boxed{\phi_\lambda}(\lambda)d\lambda$$

where, $\Omega_w(\lambda) = \boxed{q_w}(\lambda)\boxed{\sigma_w}(\lambda)$

quantum yield

x-section

Problem: we could discretize this, but then we’d have to integrate over really fine Δλ’s on-line... too slow.

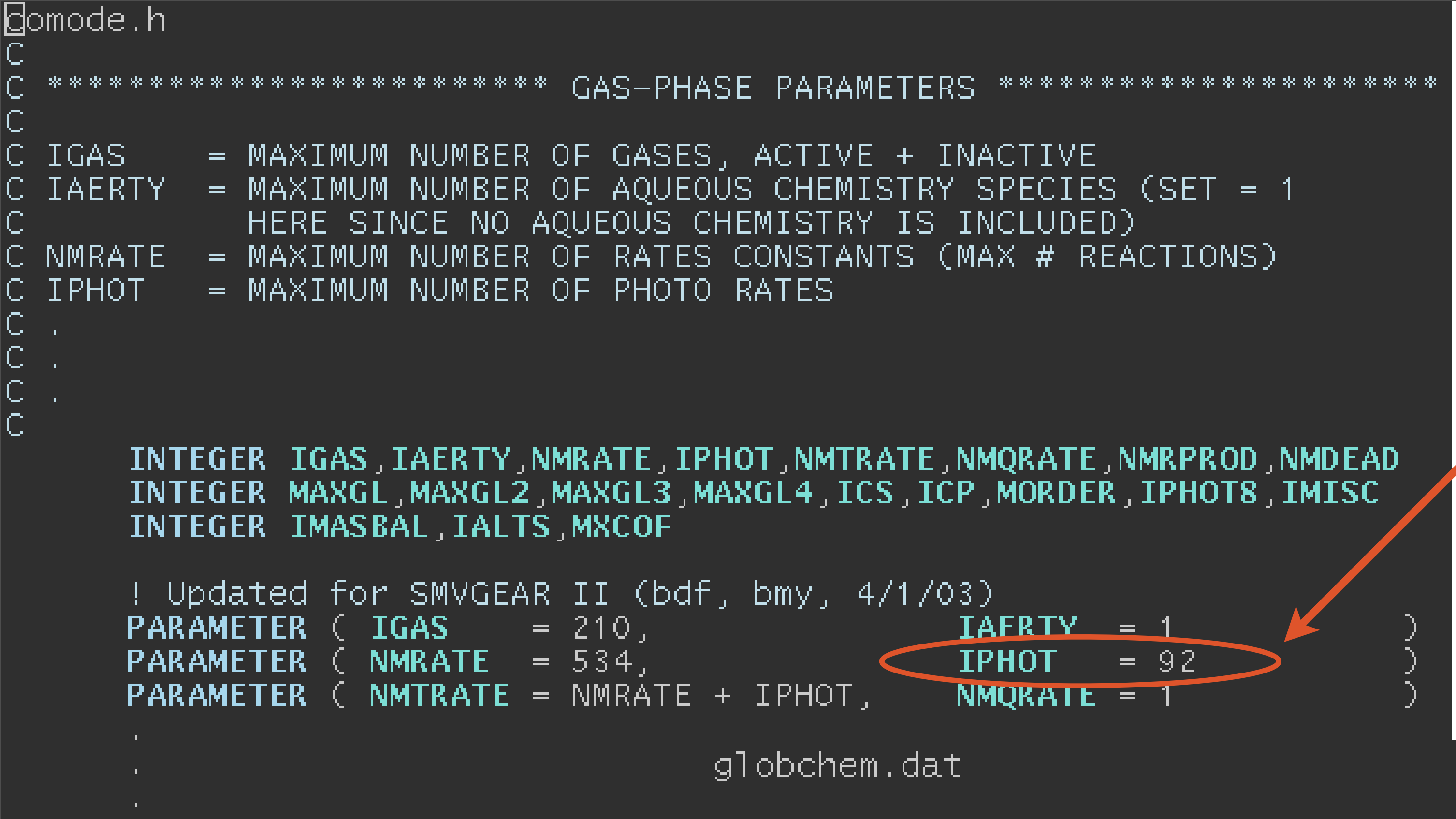
One of Fast-J’s tricks

We can get away with larger Δλ bins if we make assume “grey atmosphere” for each bin to **pre-compute** the cross-sections, Ω.

- In other words, we take the average cross-section for each Δλ bin, weighted by a solar flux spectrum.

$$\overline{\Omega_w}(i) = \frac{\int_{\Delta\lambda(i)} \Omega_w(\lambda)\phi_\lambda(\lambda)d\lambda}{\int_{\Delta\lambda(i)} \phi_\lambda(\lambda)d\lambda}$$

$$J_w = \sum_i \overline{\Omega_w}(i)\Phi_\lambda(i)$$

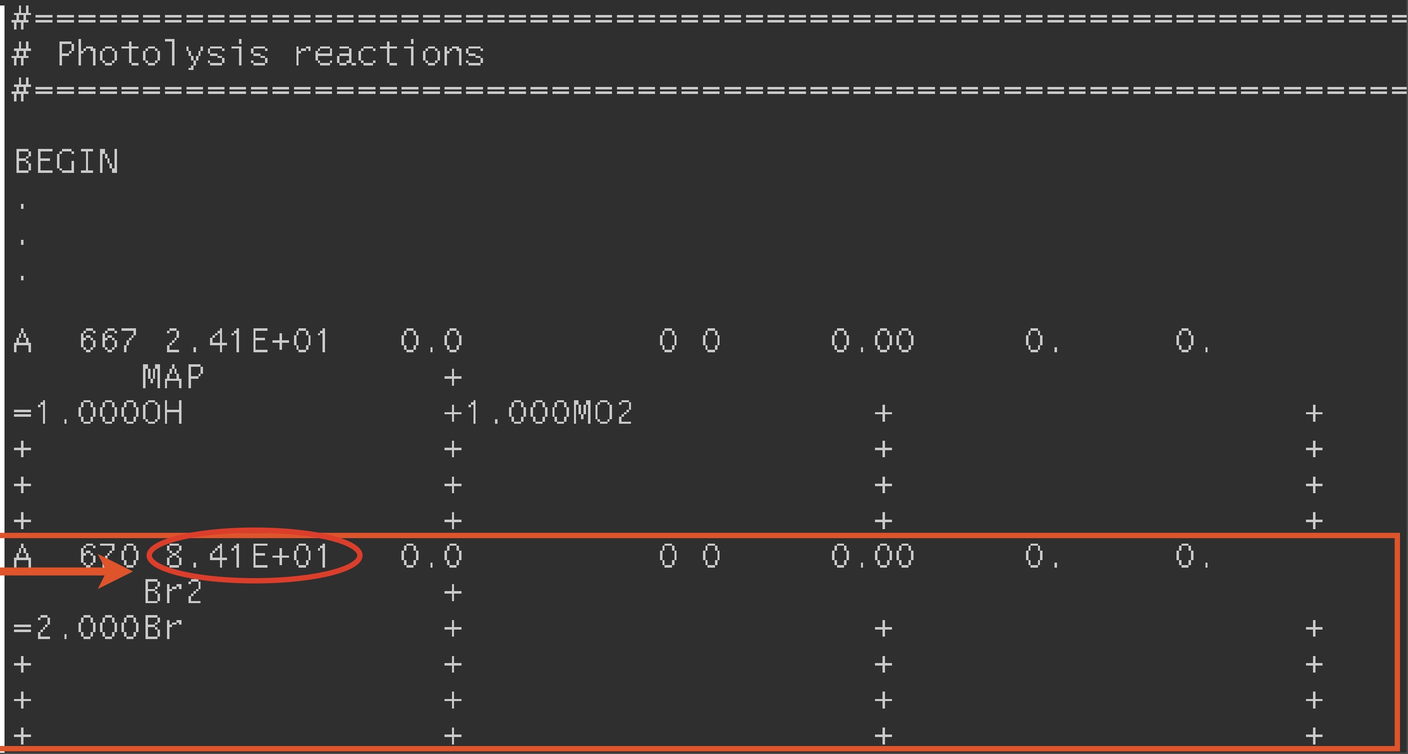


```
comode.h
C
C ************************ GAS-PHASE PARAMETERS **********************
C
C IGAS     = MAXIMUM NUMBER OF GASES, ACTIVE + INACTIVE
C IAERTY   = MAXIMUM NUMBER OF AQUEOUS CHEMISTRY SPECIES (SET = 1
C            HERE SINCE NO AQUEOUS CHEMISTRY IS INCLUDED)
C NMRATE   = MAXIMUM NUMBER OF RATES CONSTANTS (MAX # REACTIONS)
C IPHOT    = MAXIMUM NUMBER OF PHOTO RATES
C .
C .
C .
C
      INTEGER IGAS,IAERTY,NMRATE,IPHOT,NMTRATE,NMQRATE,NMRPROD,NMDEAD
      INTEGER MAXGL,MAXGL2,MAXGL3,MAXGL4,ICS,ICP,MORDER,IPHOT8,IMISC
      INTEGER IMASBAL,IALTS,MXCOF

      ! Updated for SMVGEAR II (bdf, bmy, 4/1/03)
      PARAMETER ( IGAS    = 210,              IAERTY  = 1        )
      PARAMETER ( NMRATE  = 534,              IPHOT   = 92       )
      PARAMETER ( NMTRATE = NMRATE + IPHOT,   NMQRATE = 1        )
      .
      .
      .
```

1. **comode.h:** Increase IPHOT to make room for new photo. rxns

globchem.dat



```
#================================================================
# Photolysis reactions
#================================================================

BEGIN
.
.
.
A   667  2.41E+01    0.0          0 0      0.00      0.      0.
       MAP                +
=1.0000H                  +1.000MO2            +                    +
+                         +                    +                    +
+                         +                    +                    +
+                         +                    +                    +
A   670  8.41E+01    0.0          0 0      0.00      0.      0.
       Br2                +
=2.000Br                  +                    +                    +
+                         +                    +                    +
+                         +                    +                    +
+                         +                    +                    +
```

2. **globchem.dat**: Add lines for each new photolysis reaction

Note:
- Arbitrary number, **unless** the rxn has multiple branches
  - only 3rd digit matters
  - “8.4**1**E+01” for branch 1
  - “8.4**2**E+01” for branch 2

3. **jv_spec.dat:**

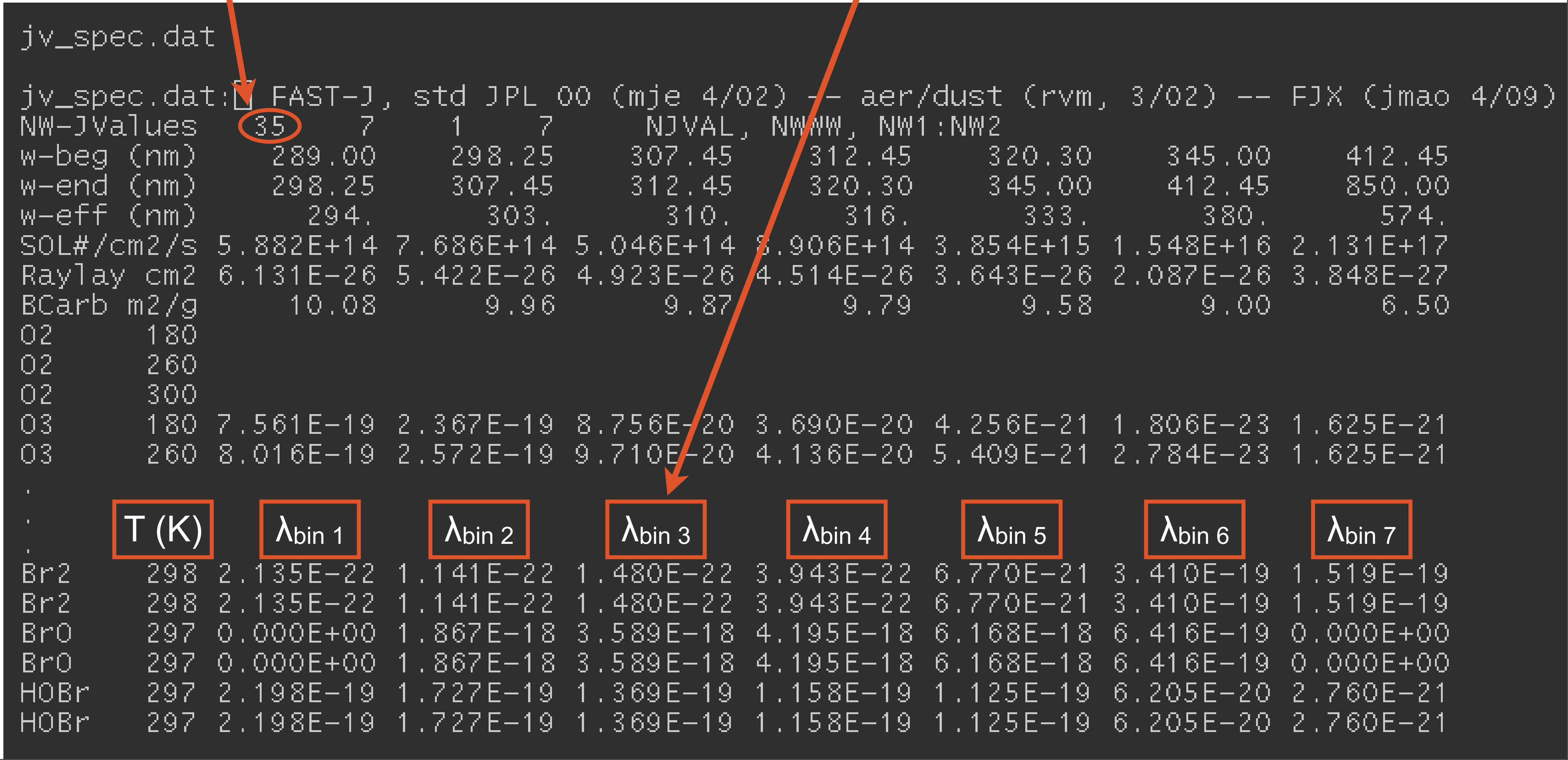
Photolysis rate calculation online for each i^{th} bin: →

$$J_w = \sum_i \overline{\Omega_w}(i)\Phi_\lambda(i)$$

Note: pre-calculation includes quantum yield

$$\overline{\Omega_w}(i) = \frac{\int_{\Delta\lambda(i)} \Omega_w(\lambda)\phi_\lambda(\lambda)d\lambda}{\int_{\Delta\lambda(i)} \phi_\lambda(\lambda)d\lambda}$$

Increase NJVAL to make room for new photo. rxns



```
jv_spec.dat

jv_spec.dat:□ FAST-J, std JPL 00 (mje 4/02) -- aer/dust (rvm, 3/02) -- FJX (jmao 4/09)
NW-JValues   35      7      1      7      NJVAL, NWWW, NW1:NW2
w-beg (nm)     289.00     298.25     307.45     312.45     320.30     345.00     412.45
w-end (nm)     298.25     307.45     312.45     320.30     345.00     412.45     850.00
w-eff (nm)       294.       303.       310.       316.       333.       380.       574.
SOL#/cm2/s 5.882E+14 7.686E+14 5.046E+14 8.906E+14 3.854E+15 1.548E+16 2.131E+17
Raylay cm2 6.131E-26 5.422E-26 4.923E-26 4.514E-26 3.643E-26 2.087E-26 3.848E-27
BCarb m2/g      10.08       9.96       9.87       9.79       9.58       9.00       6.50
O2       180
O2       260
O2       300
O3       180 7.561E-19 2.367E-19 8.756E-20 3.690E-20 4.256E-21 1.806E-23 1.625E-21
O3       260 8.016E-19 2.572E-19 9.710E-20 4.136E-20 5.409E-21 2.784E-23 1.625E-21
.
.
.
Br2      298 2.135E-22 1.141E-22 1.480E-22 3.943E-22 6.770E-21 3.410E-19 1.519E-19
Br2      298 2.135E-22 1.141E-22 1.480E-22 3.943E-22 6.770E-21 3.410E-19 1.519E-19
BrO      297 0.000E+00 1.867E-18 3.589E-18 4.195E-18 6.168E-18 6.416E-19 0.000E+00
BrO      297 0.000E+00 1.867E-18 3.589E-18 4.195E-18 6.168E-18 6.416E-19 0.000E+00
HOBr     297 2.198E-19 1.727E-19 1.369E-19 1.158E-19 1.125E-19 6.205E-20 2.760E-21
HOBr     297 2.198E-19 1.727E-19 1.369E-19 1.158E-19 1.125E-19 6.205E-20 2.760E-21
```

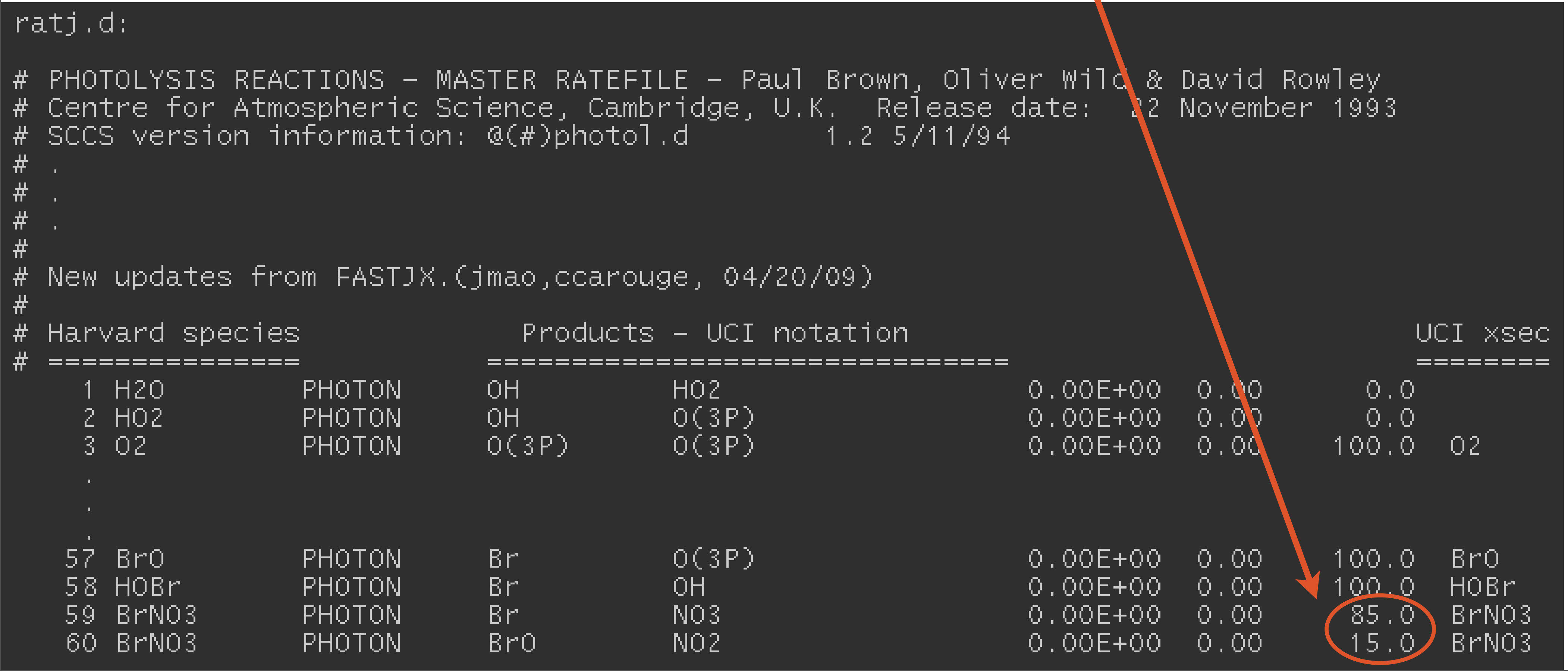
4. **ratj.d:**

Photolysis rate calculation online for each ith bin: →

$$J_w = \sum_i \overline{\Omega_w}(i)\Phi_\lambda(i)$$

$$\overline{\Omega_w}(i) = \frac{\int_{\Delta\lambda(i)} \Omega_w(\lambda)\phi_\lambda(\lambda)d\lambda}{\int_{\Delta\lambda(i)} \phi_\lambda(\lambda)d\lambda}$$

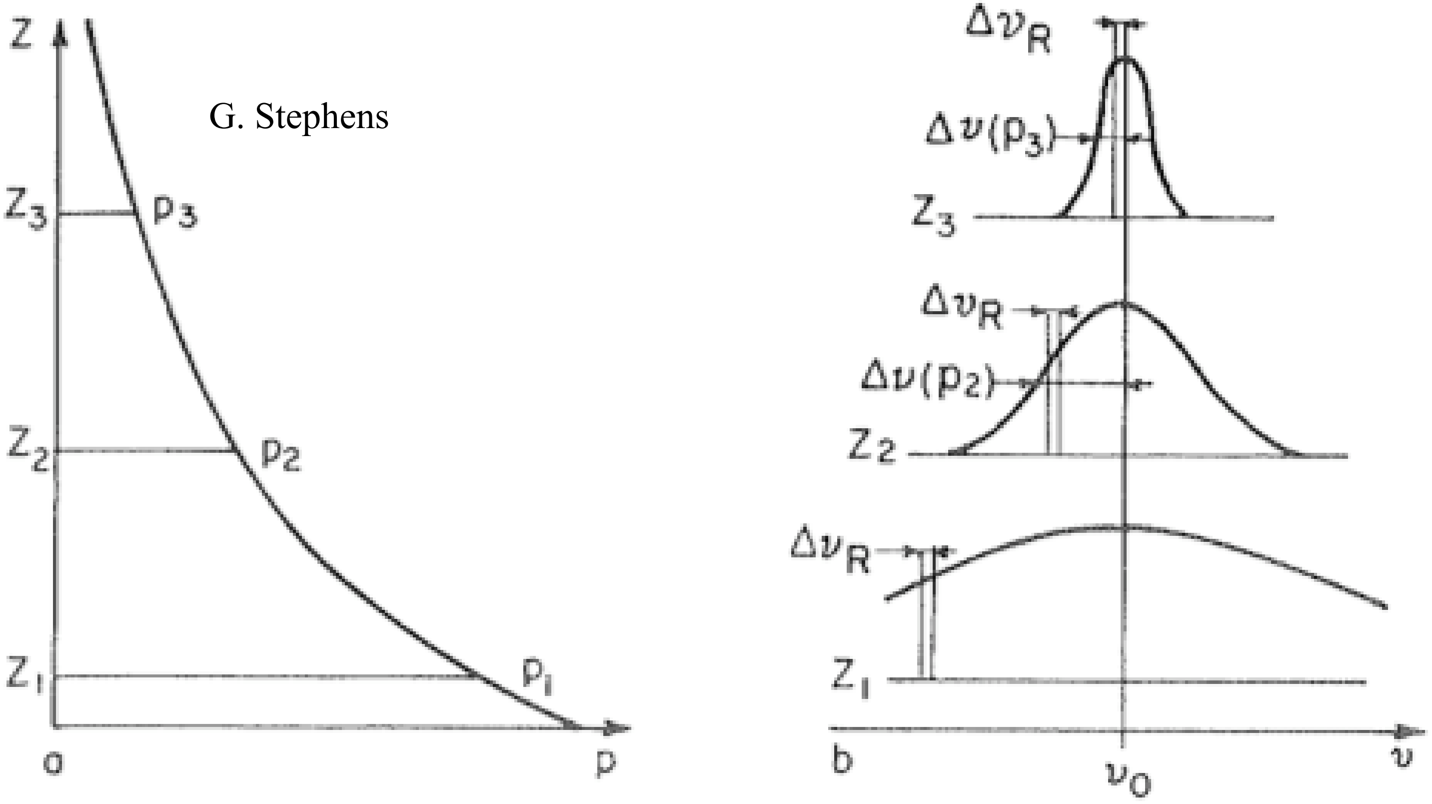
Branching ratio



```
ratj.d:

# PHOTOLYSIS REACTIONS - MASTER RATEFILE - Paul Brown, Oliver Wild & David Rowley
# Centre for Atmospheric Science, Cambridge, U.K.  Release date:  22 November 1993
# SCCS version information: @(#)photol.d        1.2 5/11/94
# .
# .
# .
#
# New updates from FASTJX.(jmao,ccarouge, 04/20/09)
#
# Harvard species               Products - UCI notation                              UCI xsec
# ===============            ===============================                         ========
    1 H2O          PHOTON     OH          HO2                   0.00E+00  0.00       0.0
    2 HO2          PHOTON     OH          O(3P)                 0.00E+00  0.00       0.0
    3 O2           PHOTON     O(3P)       O(3P)                 0.00E+00  0.00     100.0  O2
    .
    .
    .
   57  BrO         PHOTON     Br          O(3P)                 0.00E+00  0.00     100.0  BrO
   58  HOBr        PHOTON     Br          OH                    0.00E+00  0.00     100.0  HOBr
   59  BrNO3       PHOTON     Br          NO3                   0.00E+00  0.00      85.0  BrNO3
   60  BrNO3       PHOTON     BrO         NO2                   0.00E+00  0.00      15.0  BrNO3
```

More advanced: Some absorbers need pressure-broadening accounted for



G. Stephens

- **For how to include in Fast-J, Cameron-Smith 2000; also GC wiki**
- **Lineshape: convolution of pressure and Doppler broadening**
  - **Pressure Broadening: f(P)**
    - Derivation is difficult: depends on potential wells of colliding molecules
    - Simplified semiclassical model gives nice estimation - disruption of infinite cosine
  - **Doppler broadening: f(λ,T)**
    - Essentially invariant in altitude (T dependence is weak)