Photolysis of O_2

Key to Chemistry of Middle Atmosphere

by John Iorio

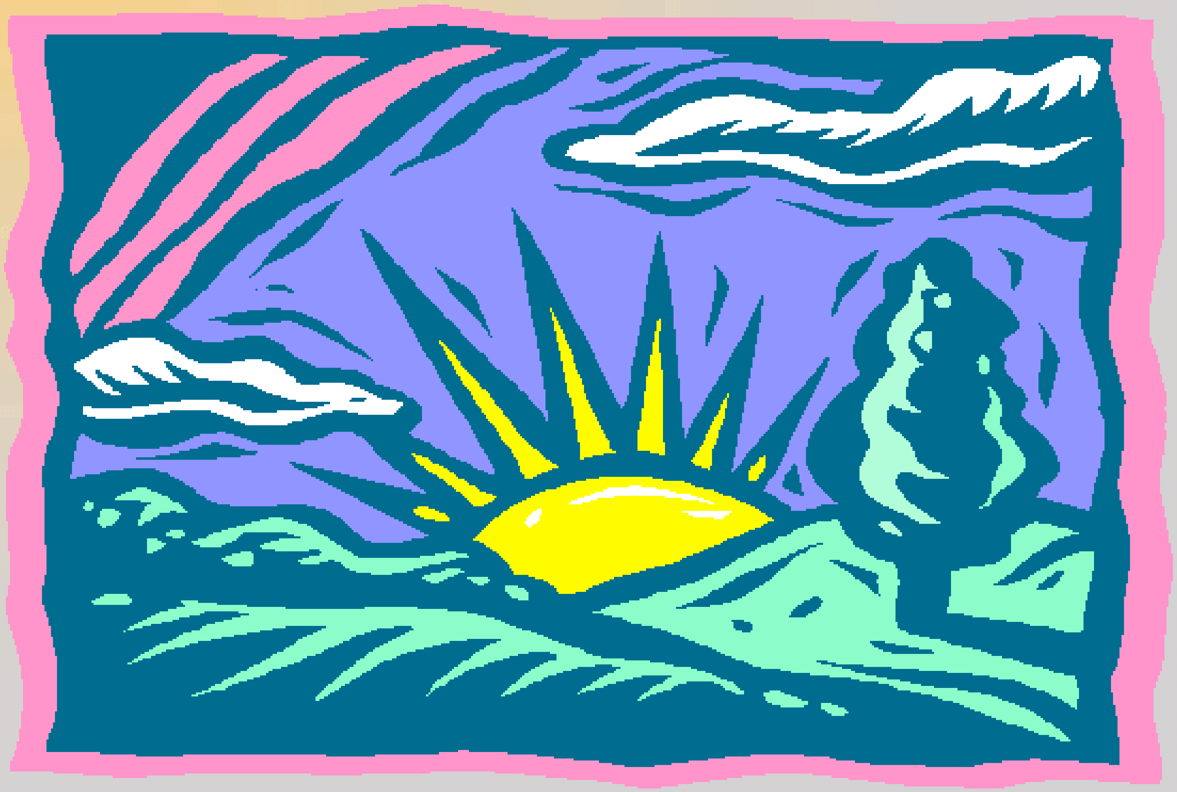
Significance

- Strato- and Mesospheric Climate
- Main Source of Sratospheric Ozone
  - $O_2 + hv \rightarrow O + O$
  - $O + O_2 + M \rightarrow O_3 + M$

My Work

- Fast Calculation of JO_2
- Check on existing TUV (Tropospheric UV-Visible) Model
- Explore TUV Errors

From Sunrise to Sunset



Principles of O_2 Photolysis

- $J = \int F(\lambda)\, \sigma(\lambda)\, \Phi(\lambda)\, d\lambda$ – at a given altitude
  - J = photolysis rate (s^{-1})
  - $F(\lambda)$ = spectral solar flux at given altitude and solar zenith angle
  - $\sigma(\lambda)$ = absorption x-section of molecule
  - $\Phi(\lambda)$ = photodissociation efficiency (taken to be 1)
- Occurs at $\lambda < 240$ nm
  - Lyman-α, Schumann Runge Continuum, SR Bands, Herzberg Continuum

Solar Spectrum

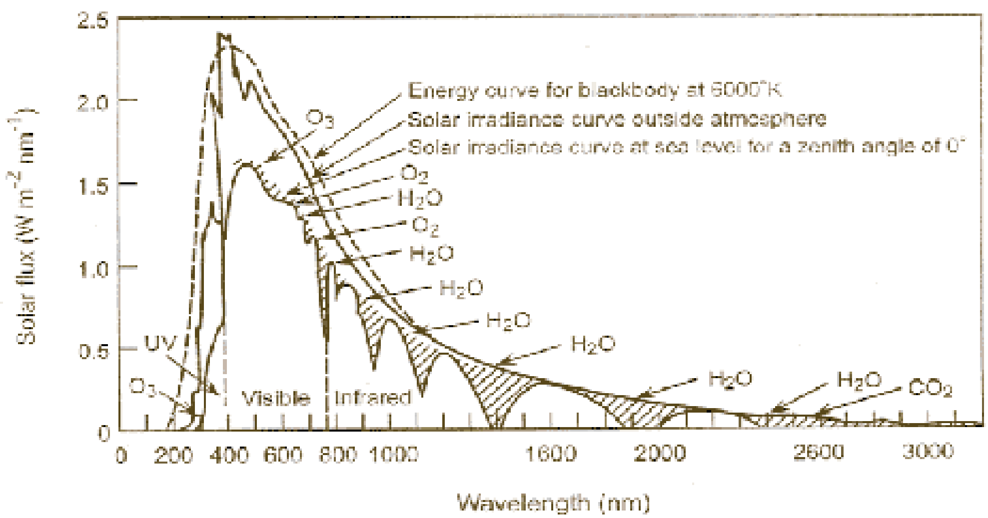


FIGURE 3.12 Solar flux outside the atmosphere and at sea level, respectively. The emission of a blackbody at 6000 K is also shown for comparison. The species responsible for light absorption in the various regions (O_3, H_2O, etc.) are also shown (from Howard *et al.*, 1960).

σ(λ) for O2

- Photolysis prevalent where the x-section and solar flux curves are both high

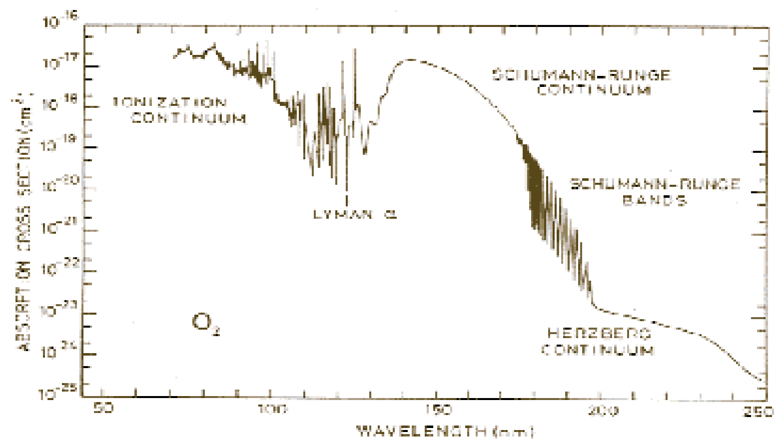


Fig. 4.26. Spectral distribution of the absorption cross section of molecular oxygen.

My Code As an Approximation

- Breaks up each band/cont. into bins
  - J calculated for each bin, summed over all bins
  - As few λ bins as possible – computer time
- SRC (121.9nm-175.4nm) and HC(192nm-240nm)
  - Beer-Lambert Law
    - $J = \int (F_{\infty}) (\sigma O_2) (e^{(-\sigma O_2 \times NO_2)}) \, d\lambda$
      - F_{∞} = Solar Flux at top of atmosphere
      - NO_2 = Slant O_2 Column (function of altitude and zenith angle)
  - Interpolation of Flux and Cross-Section Data onto my grid

Schumann-Runge Continuum

- 1 bin used – 54 nm
- $\sigma(\lambda)$: weighted by the flux over the bin

Herzberg Continuum

- 1 bin – 46 nm
- Yoshino – Polynomial Expression for $\sigma(\lambda)$
- Pre-calculated exact avg. σ over interval

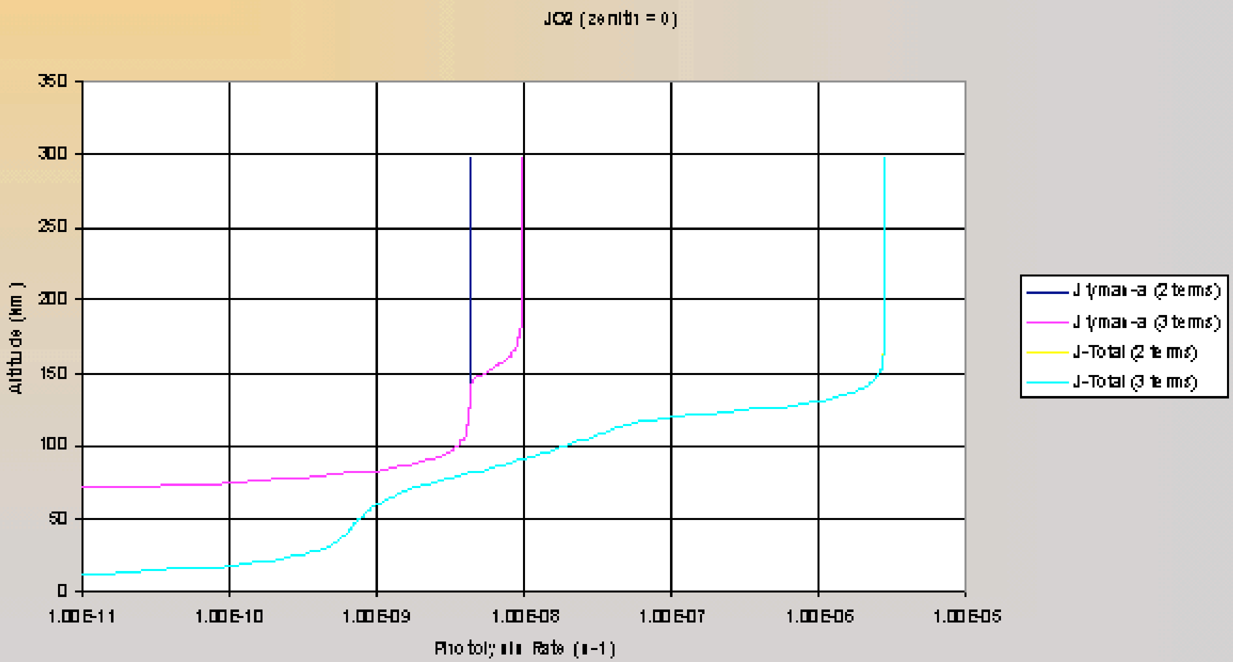
Lyman-α and SRB: Kockarts's Parameterization

- $J = \int (F_\infty)(R)\, d\lambda$
- Essentially Beer-Lambert Law, $R = (\sigma O_2)(e^{(-\sigma O_2 \times NO_2)})$
- Exact R in both bands calculated using Beer – Lambert at fine λ scales
- Kockarts develops close approximations to save computer time

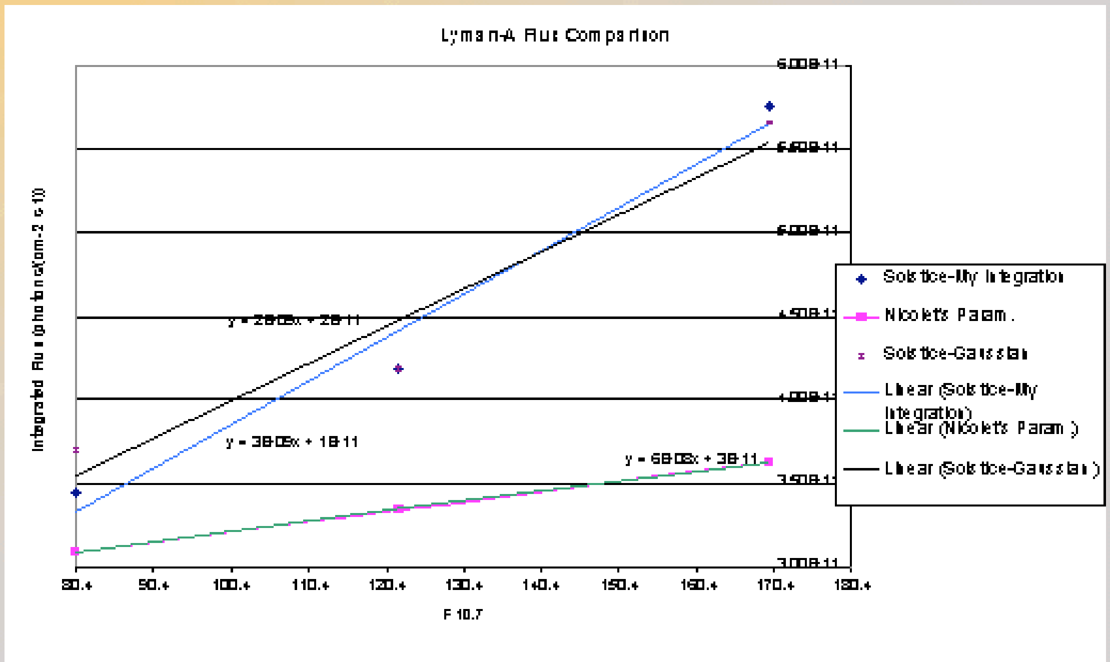
Lyman-α Parameterization

- $R = {}^{3}\Sigma_{i=1}\, a_i(e^{(-b_i \times NO_2)})$
  - R function of NO_2 only
  - A and B: coefficients determined by fitting to exact R vs. NO_2 curve
- 1 bin
- Took out third term - anomalous results in mesosphere (b_1 = 8.22E-21, b_2 = 1.63E-20, b_3 = 4.85E-17)

J for lyman-α (3 terms vs. 2)



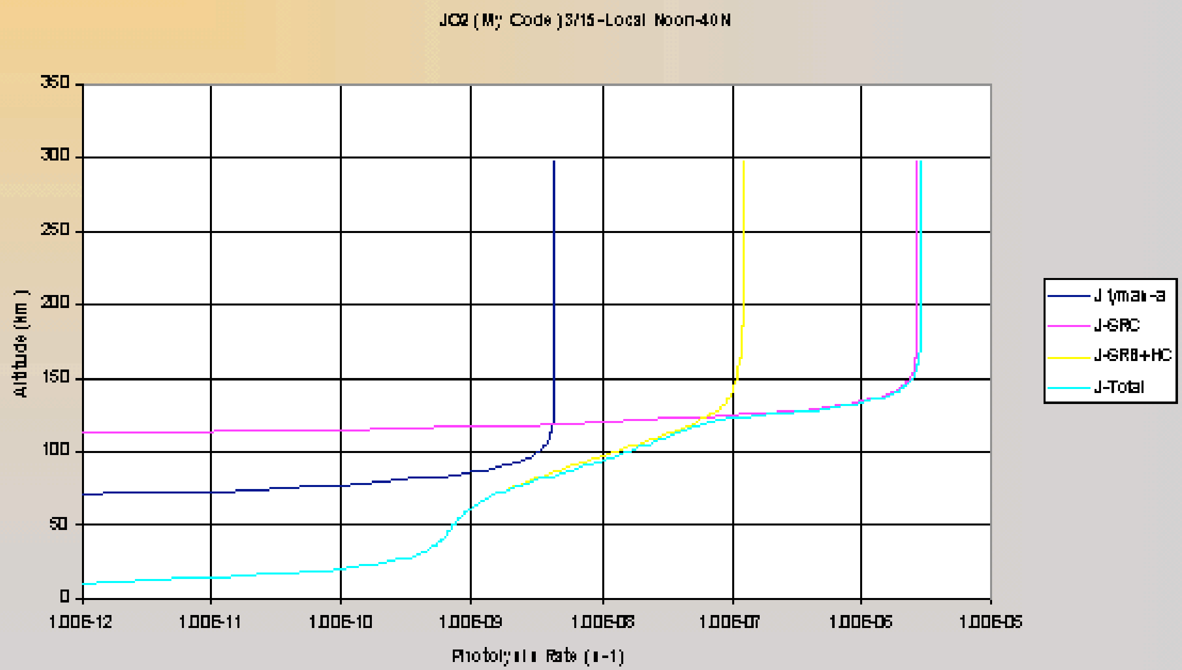
Lyman-α Solar Flux



SRB parameterization

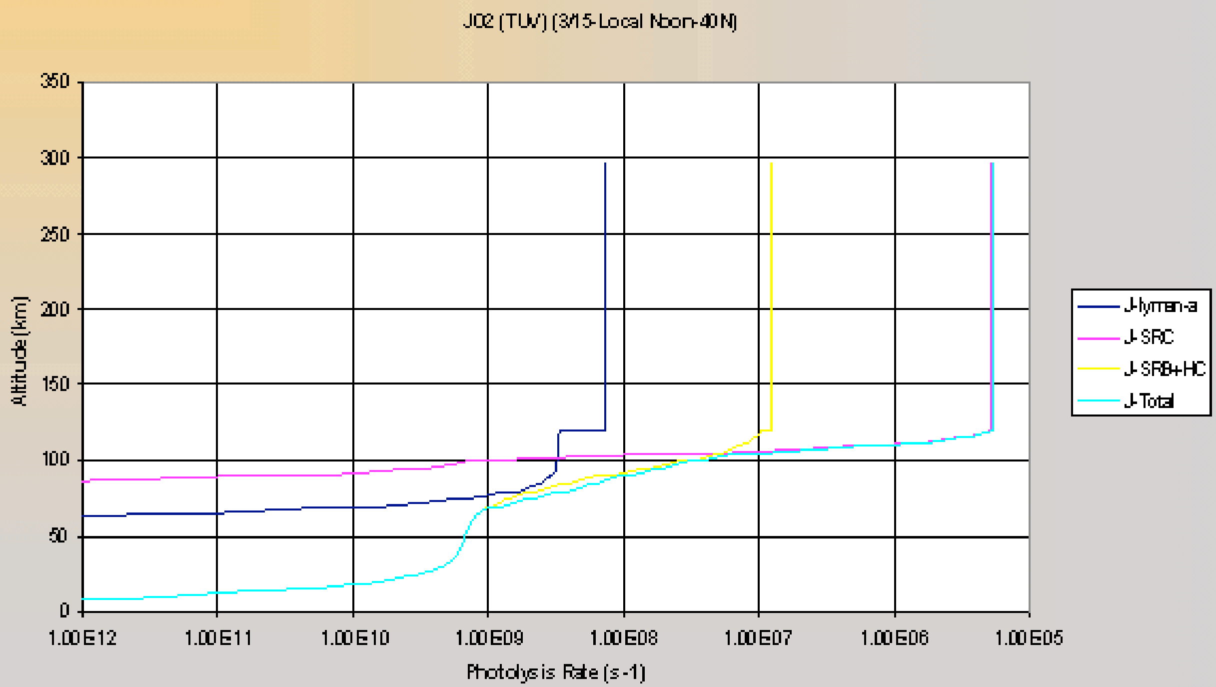
- $R_j = {}^6\Sigma_{i=1}\ a_{2i-1}(e^{(-a_{2i} \times NO_2)})$
  - j is 500 cm^{-1} bin
  - 16 bins in original param.
  - cut down to 13 by averaging adjacent bins with close R values

My Code



JO2 (My Code)3/15-Local Noon-40 N
350
300
250
200
150
100
50
0
Altitude (km)
1.00E-12
1.00E-11
1.00E-10
1.00E-09
1.00E-08
1.00E-07
1.00E-06
1.00E-05
Photolysis Rate (s-1)
J Lyman-a
J-SRC
J-SRB+HC
J-Total

TUV

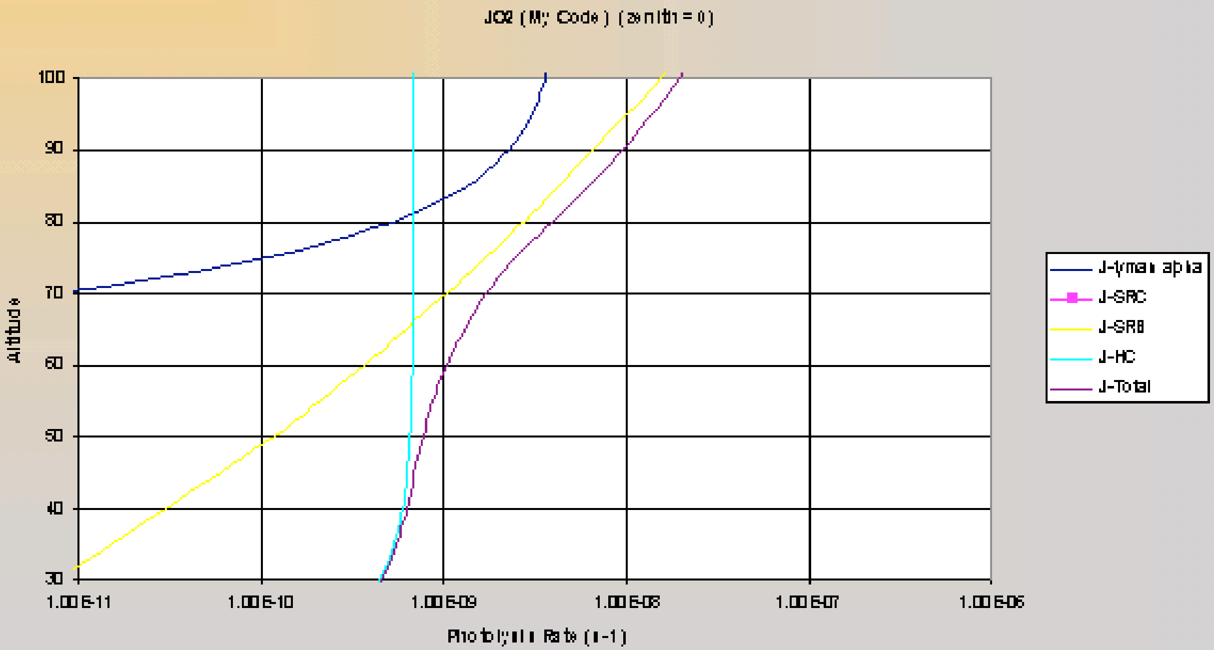


J02 (TUV) (3/15-Local Noon-40N)
350
300
250
200
150
100
50
0
Altitude (km)
1.00E12
1.00E11
1.00E10
1.00E09
1.00E08
1.00E07
1.00E06
1.00E05
Photolysis Rate (s-1)
J-lyman-a
J-SRC
J-SRB+HC
J-Total

Problems in TUV

- 2 bins for Schumann-Runge Continuum
  - 2^{nd} bin (123nm-175nm)
- Lyman-α param. (used all 3 terms)
- High Altitude Problems

Comparison of J (my code)



Comparison of J ("Aeronomy of Middle Atm.")

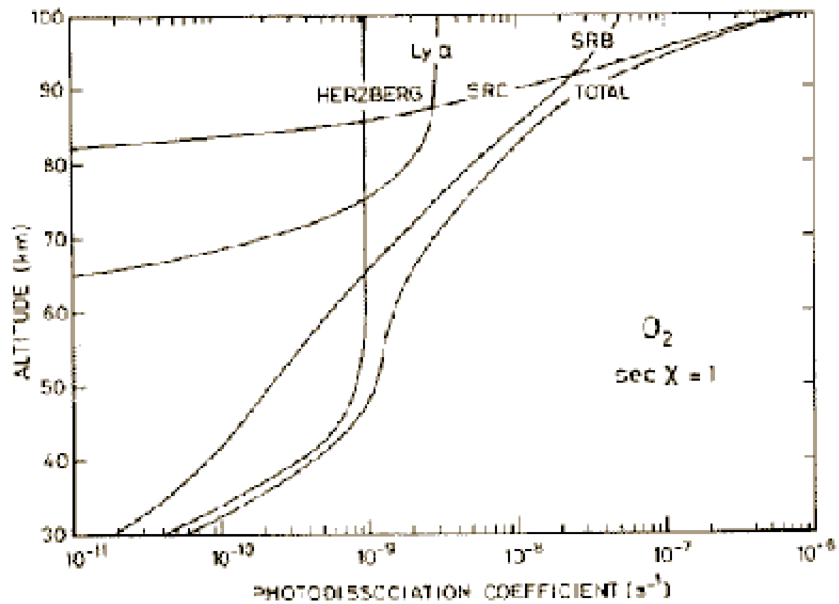
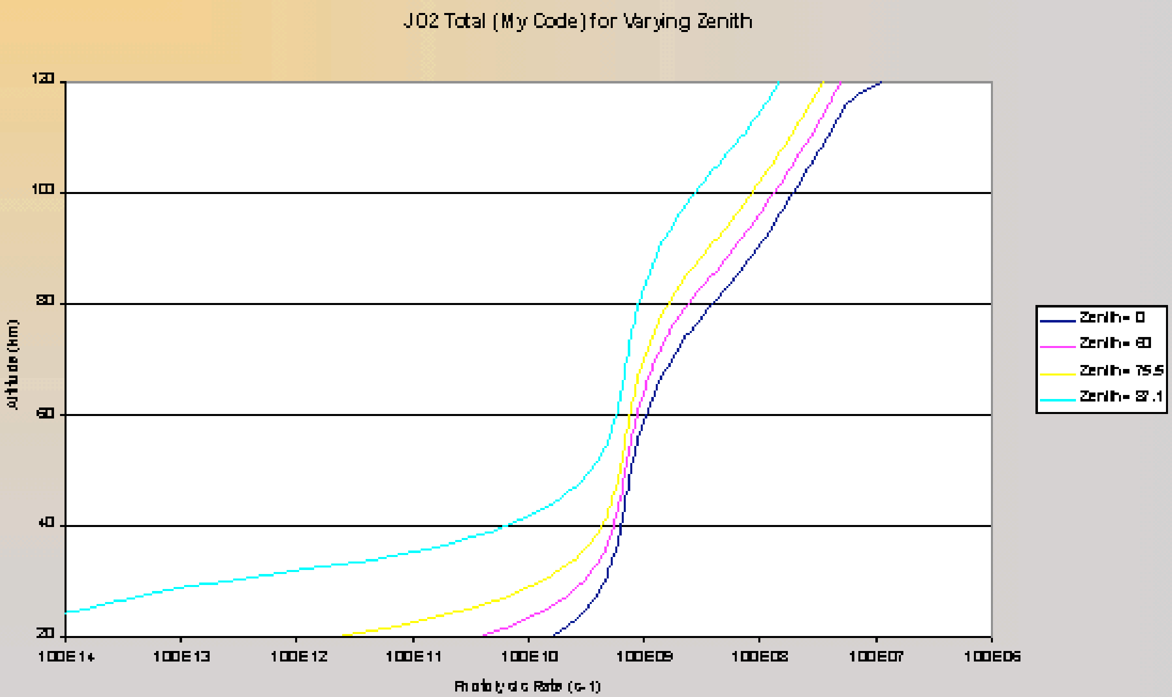
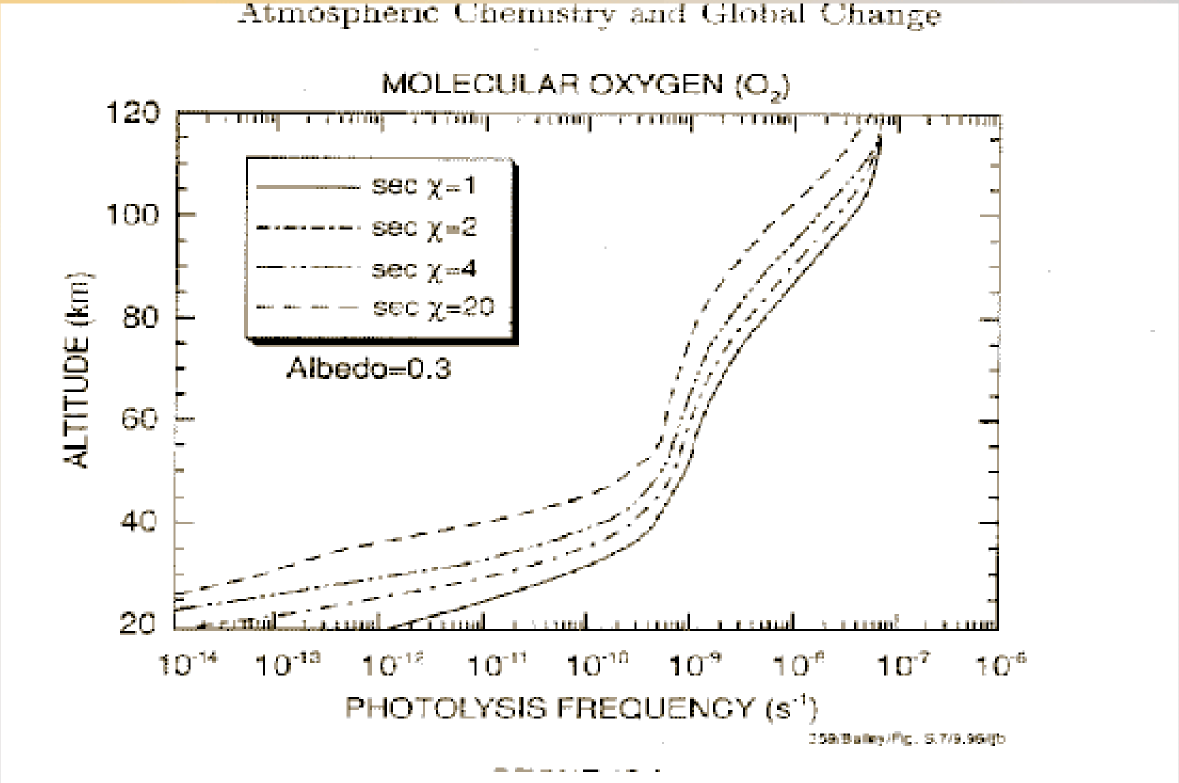


Fig. 4.31. Contribution of each spectral region to the photodissociation of molecular oxygen as a function of altitude.

Comparison of J Total (effects of zenith angle) – My Code



Comparison of J Total (effects of zenith angle) – "Atm. Chem. And Global Change"



Conclusions/Future Work

- Results from my code are preliminary
- Try using more than 1 bin for Schumann-Runge Continuum and Herzberg Continuum
- 3rd term in lyman-alpha param. is wrong
    - Use only first 2 terms
- Incorporate into TUV (replace O_2 photolysis calculation with my code)
    - Include effects of O_3 absorption and scattering

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