Impact of recent laboratory N_2 data to our understanding of thermospheric NO

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Overview

- Reaction of the first excited state of atomic nitrogen, $N(^2D)$, with O_2 is the principal chemical source of NO throughout thermosphere.
- Reaction of ground state atomic nitrogen, $N(^4S)$, with NO is the principal NO chemical sink throughout thermosphere.
- Laboratory evidence has appeared for NO product from $N_2(A)$ +O reaction. [1]
- Include $N_2(A)$ in photochemical model to evaluate claimed thermospheric NO increase of 200-300%. [2]
- How do new N_2 electron-impact excitation cross-sections [3] affect determination of $N_2(A)$ production?

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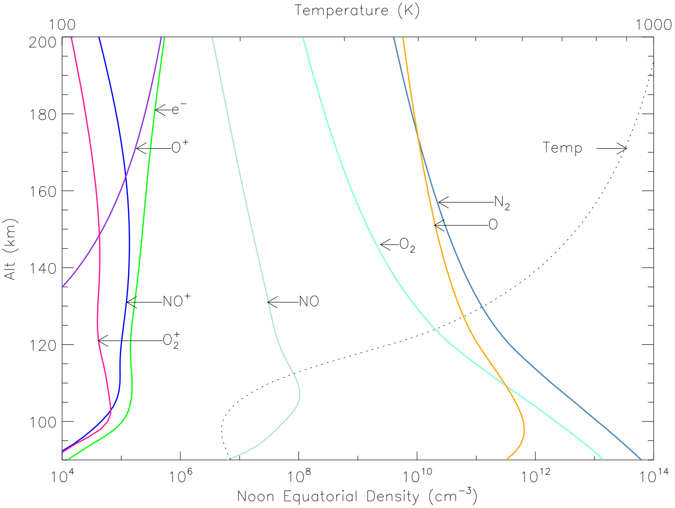
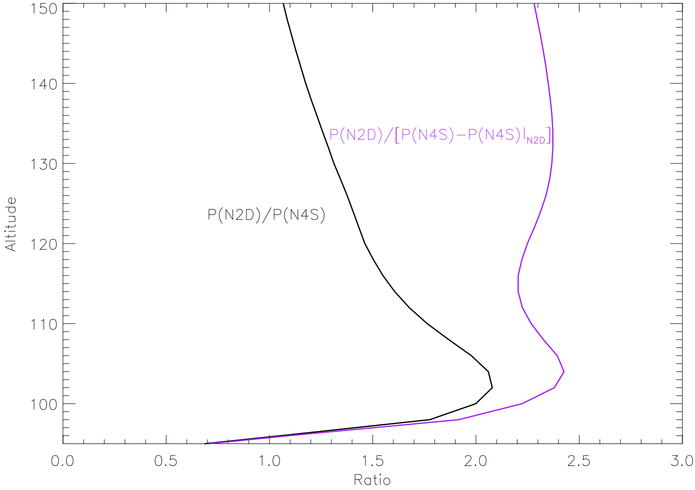
[1] Thomas J., Kaufman F., *J.Phys.Chem.*, **1996**
[2] Campbell, L. et al. *J.Geophys.Res.*, **2007**
[3] Johnson, P. et al. *J.Phys.B*, **2005**; Malone, C. et al. *J.Phys.B*, **2009**

Ionosphere/Thermosphere Overview



N(^{2}D) and N(^{4}S) Production



$N_2^+ + O$: Principal Source of NO^+, $N(^2D)$, and NO

Ionized N_2 leads to $N(^2D)$

$$N_2 + e^* \rightarrow N_2^+ + 2e$$

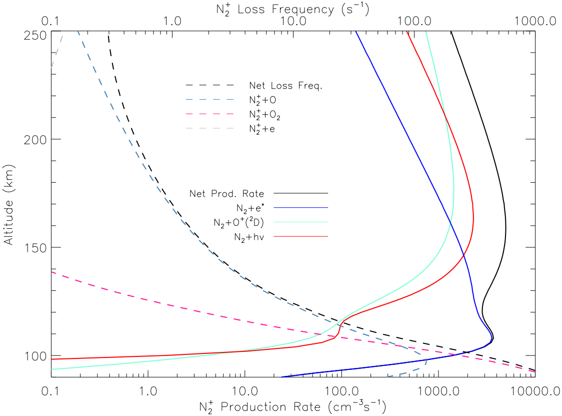
$$N_2^+ + O \rightarrow NO^+ + N(^2D)$$

$$\underline{NO^+ + e \rightarrow N(^2D) + O}$$

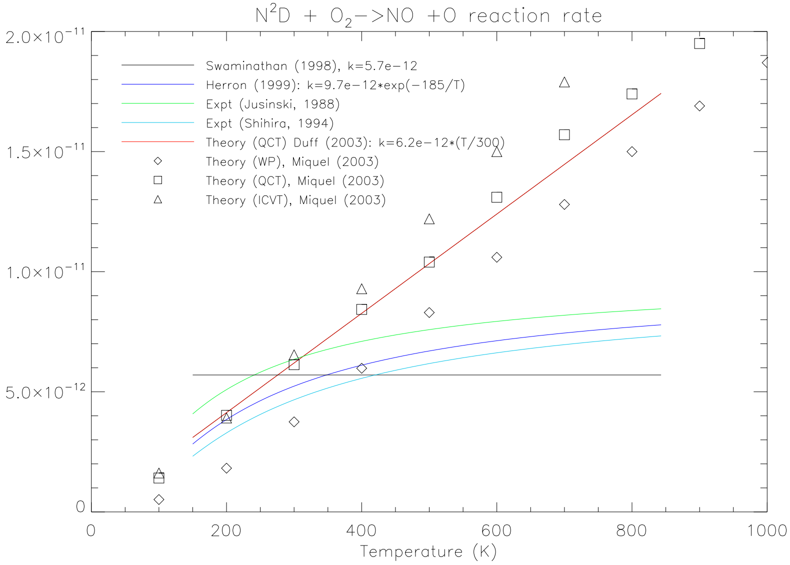
$$N_2 + e^* \rightarrow 2N(^2D)$$

which leads to NO:

$$N(^2D) + O_2 \rightarrow NO + O.$$



N(^{2}D)+O_2 Rate



N2D + O2->NO +O reaction rate
2.0×10-11
1.5×10-11
1.0×10-11
5.0×10-12
0
0
200
400
600
800
1000
Temperature (K)
Swaminathan (1998), k=5.7e-12
Herron (1999): k=9.7e-12*exp(-185/T)
Expt (Jusinski, 1988)
Expt (Shihira, 1994)
Theory (QCT) Duff (2003): k=6.2e-12*(T/300)
Theory (WP), Miquel (2003)
Theory (QCT), Miquel (2003)
Theory (ICVT), Miquel (2003)

New Lab Data [4]

Excited N_2 leads to NO

$$N_2 + e^* \rightarrow N_2(A) + e$$

$$N_2(A) + O \rightarrow NO + N(^2D)$$

$$\underline{N(^2D) + O_2 \rightarrow NO + O}$$

$$N_2 + O_2 + e^* \rightarrow 2NO + e$$

N_2 Dissociation:
Branching Ratio N(^{2}D)≈.5

$$N_2 + e^* \rightarrow N(^4S) + N(^2D) + e$$

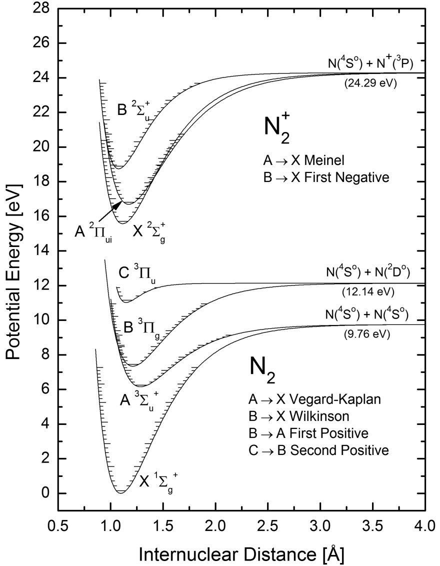
$$N(^4S) + NO \rightarrow N_2 + O$$

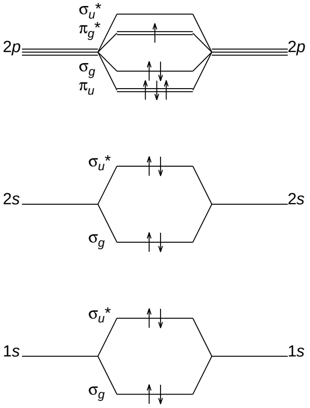
$$\underline{N(^2D) + O_2 \rightarrow NO + O}$$

$$O_2 + e^* \rightarrow 2O + e$$

[4] Thomas, J. & F. Kaufman, *J.Phys.Chem.*, **1996**

N_2 Electronic States (courtesy D. Sentman, UAF)





$N_2(A) = [KL] 1\pi_u^3 3\sigma_g^2 3\sigma_u^1$

Outline of NOx 1D Photochemical Model[7]

- Inputs: neutral atmosphere (N_2,O_2, O) and temperature from NRLMSIS[5]; daily F10.7 scaled EUV solar spectrum; photoionization, photoabsorption, electron-impact cross sections and photoelectron spectrum from GLOW[6].
- Solves continuity equation. 12 species: NO, $N(^4S)$, $N(^2D)$, $N(^2P)$, $N_2(A)$, NO^+, N_2^+, N^+, O_2^+, $O^+(^4S)$, $O^+(^2D)$, e^-.
- Vertical diffusion included only for NO and $N(^4S)$: BC at 40 km (photochemical equilibrium) and 250 km (diffusive equilibrium).
- Δz=2 km, Δt=5 min. Solar inputs and neutral atmosphere updated every hour.

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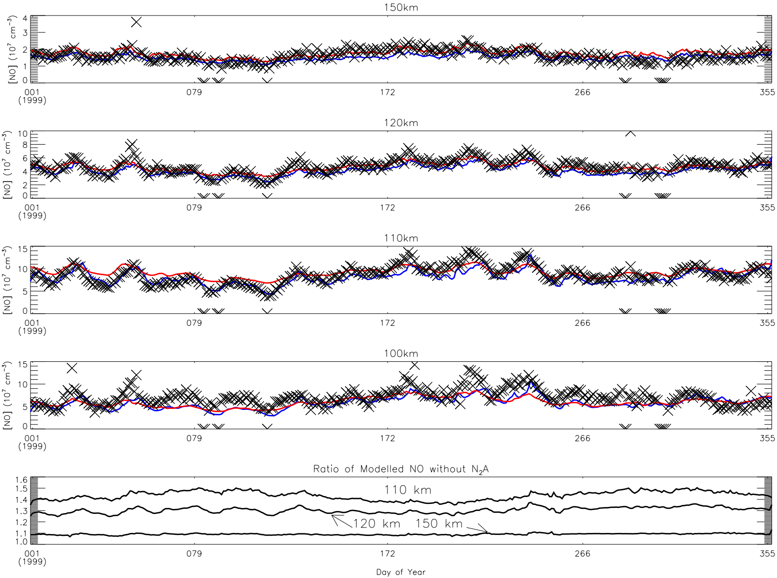
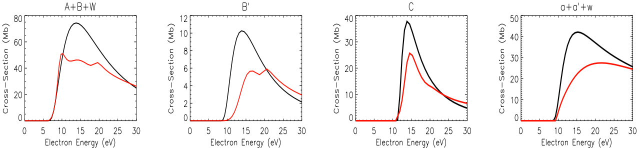
[5]Picone, J et al., *J.Geophys.Res*, **2002**
[6]Solomon, S. et al. *J.Geophys.Res.*, **1988**
[7]Bailey, S. et al. *J.Geophys.Res.*, **2002**

Comparison of Model with SNOE NO



New Electron Impact Excitation Cross Sections[8] [9]



Net N_2(A) cross section$=\sigma_{eff}(A)=\sigma(A, B, W) + \sigma(B') + \sigma(C)$.
For 12 eV photoelectrons:

- σ(A,B,W) lower by about 30%.
- σ(B') relatively unimportant.
- σ(C) lower by about 50%.
- σ(a,a',w) lower by *a factor of 3*.

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[8] Johnson, P. et al. *J.Phys.B*, **2005**
[9] Malone, C. et al. *J.Phys.B*, **2009**

Equilibrium Photoelectron Calculation

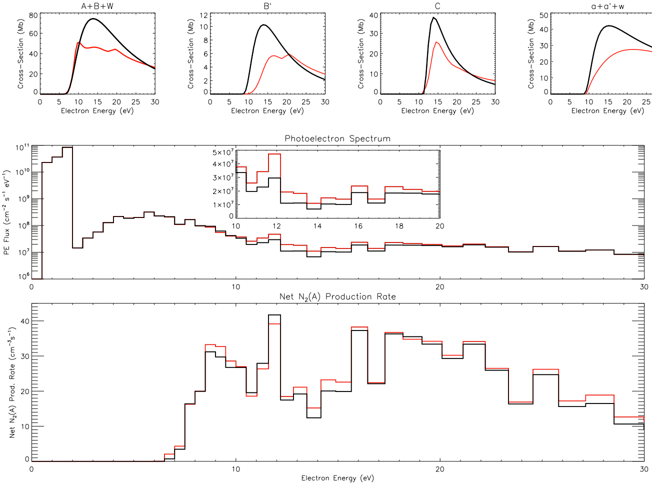
Full two-stream GLOW calculation[10] necessary in F-region. In mid-latitude E-region, equilibrium can be assumed and the local photoelectron flux, ϕ, is given by:

$$\phi(E) = \frac{P}{L} = \frac{P_{direct}(E) + P_{cascade}(E', E) + P_{secondary}(E', E)}{L(E, E'')}$$

- P_{direct}=direct photoionization (photoelectric effect).
- $P_{cascade}$=collisional energy loss from higher energy photoelectrons (E+IP>E'>E).
- $P_{secondary}$=photoelectron ionization (E'>E+IP).
- L=collisional energy loss to lower energy photoelectrons (E>E").

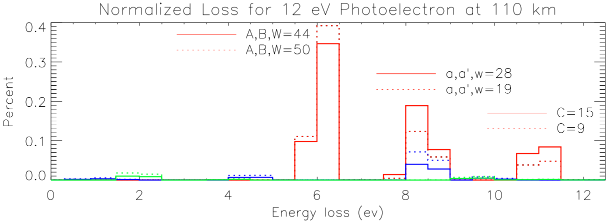
[10] Bailey, S.M., C.A. Barth, S.C. Solomon, *JGR*, **107**, 2002

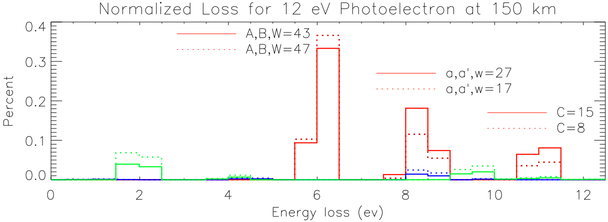
Effect on $N_2(A)$ Production at 150 km



$$P_A(E) = [N_2]\phi(E)\sigma_{eff}(E)\Delta E$$

Competition Among Channels: Normalized Loss, η



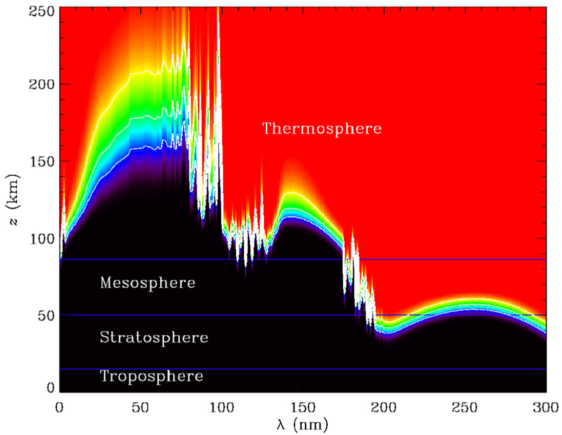


$$P_A = P_{pe} \cdot \eta(A)$$

Conclusions

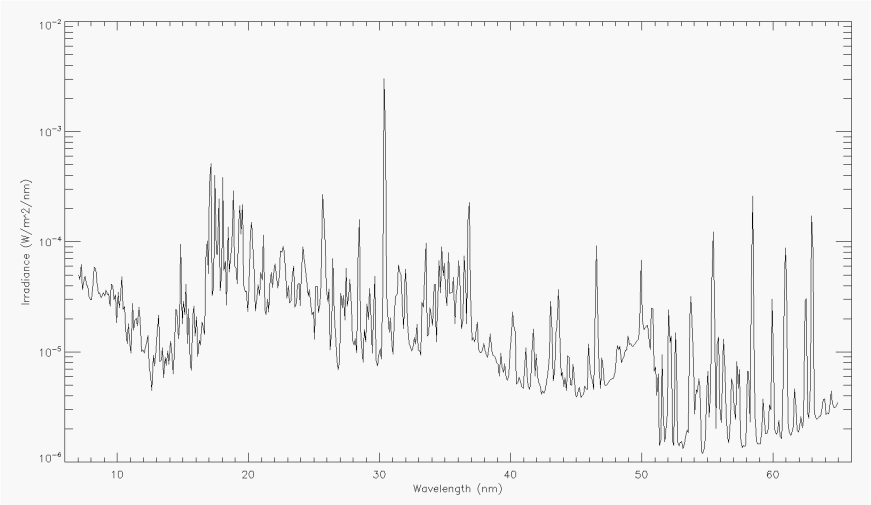
- $N(^2D)$ production from ion-neutral chemistry responsible for NO peak at 110 km.
- NO appears well-modelled but large uncertainties still exist.
- Temperature dependence and branching ratios for key rates need further laboratory investigation.
- $N_2(A)$ is an important (30-70%) contributor to NO.
- Reduction of electron impact N_2 excitation cross sections by $\approx 40\%$ has little effect on $N_2(A)$ production rates because photoelectron flux increased by corresponding amount.

Deposition of Solar Irradiance (lasp.colorado.edu)

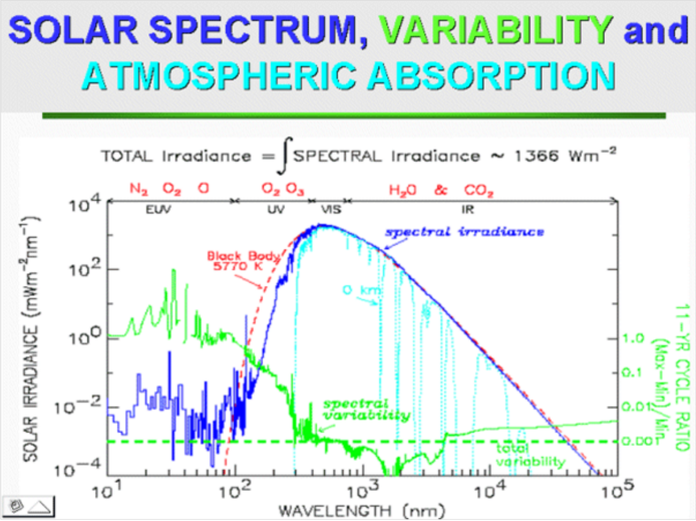


$$\tau(\lambda, z) = \sum_{i=N_2,O_2,O} \int_z^\infty n_i(z)\sigma(\lambda)dz$$

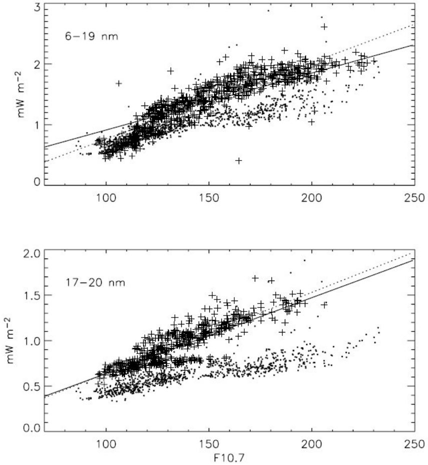
SDO/EVE Solar Spectrum



Solar Irradiance Variability (courtesy of Judith Lean, NRL)

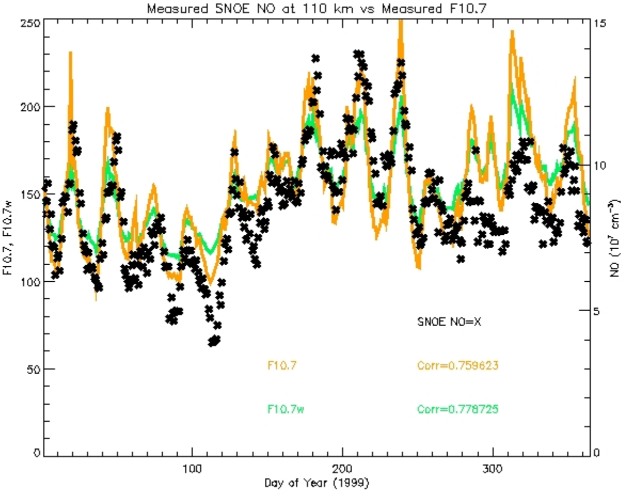


Correlation of F10.7 with Measured X-ray Irradiance[11]

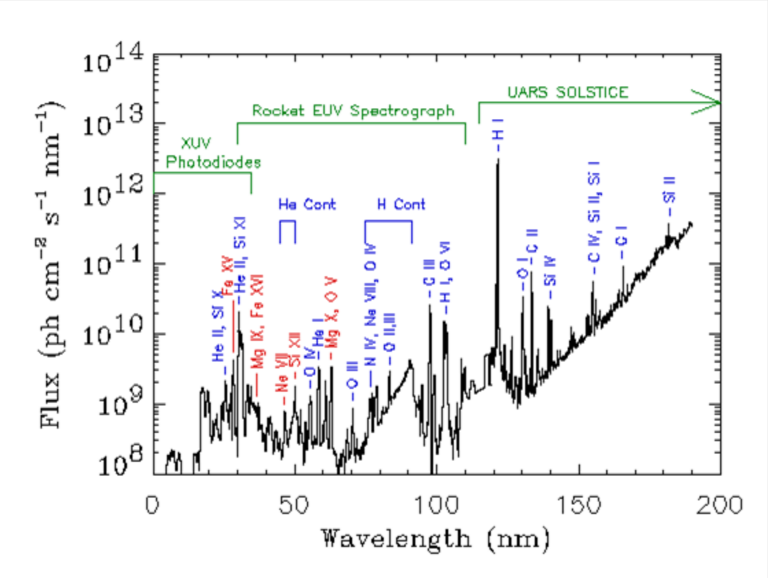


[11] Bailey et al, *Advances in Space Research*, **2005**

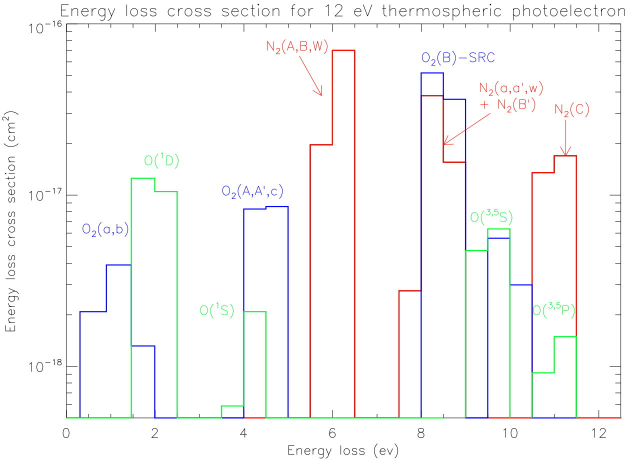
Correlation of Measured NO with Measured F10.7



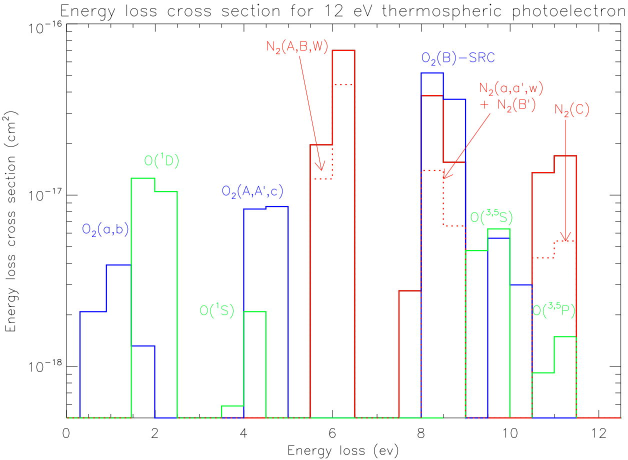
EUV Reference Spectrum (lasp.colorado.edu)



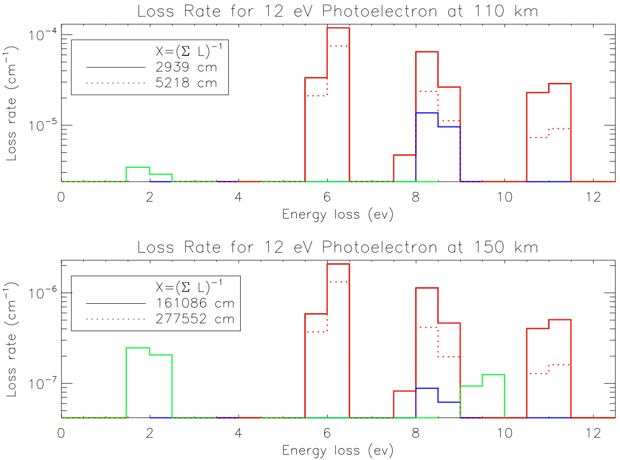
Energy Loss Cross Sections



Energy Loss Cross Sections



Energy Loss Rates



$$L_{net}(E) = \sum_{i=O,O_2,N_2}^{E' \leq E} n_i \sigma(E, E')$$