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H4. SMR/1247
Lecture Note: 25

WORKSHOP ON PHYSICS OF MESOSPHERE-STRATOSPHERE-TROPOSPHERE INTERACTIONS WITH SPECIAL EMPHASIS ON MST RADAR TECHNIQUES

(13 - 24 November 2000)

AN INTRODUCTION TO ATMOSPHERIC CHEMISTRY

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An introduction to atmospheric chemistry

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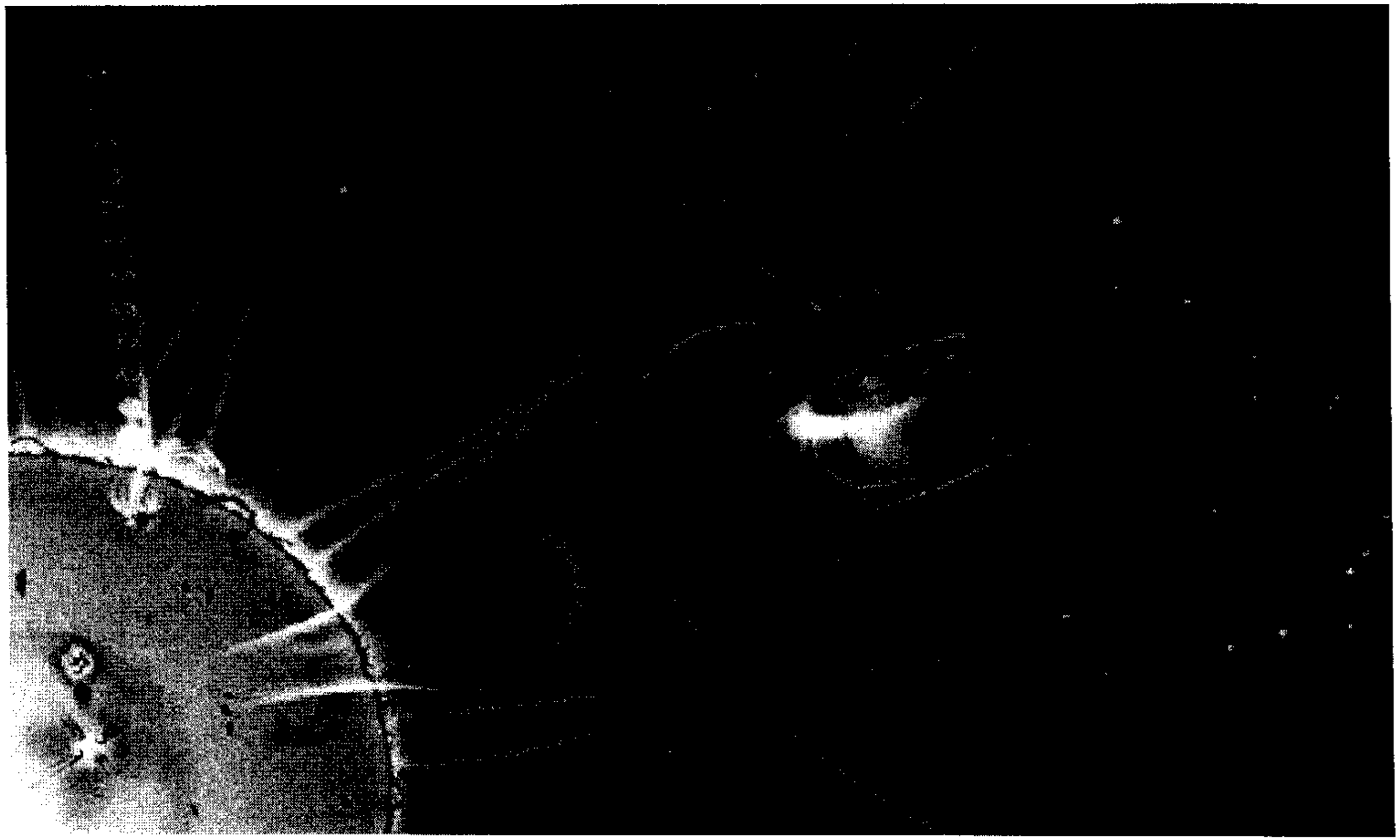
The earth space environment



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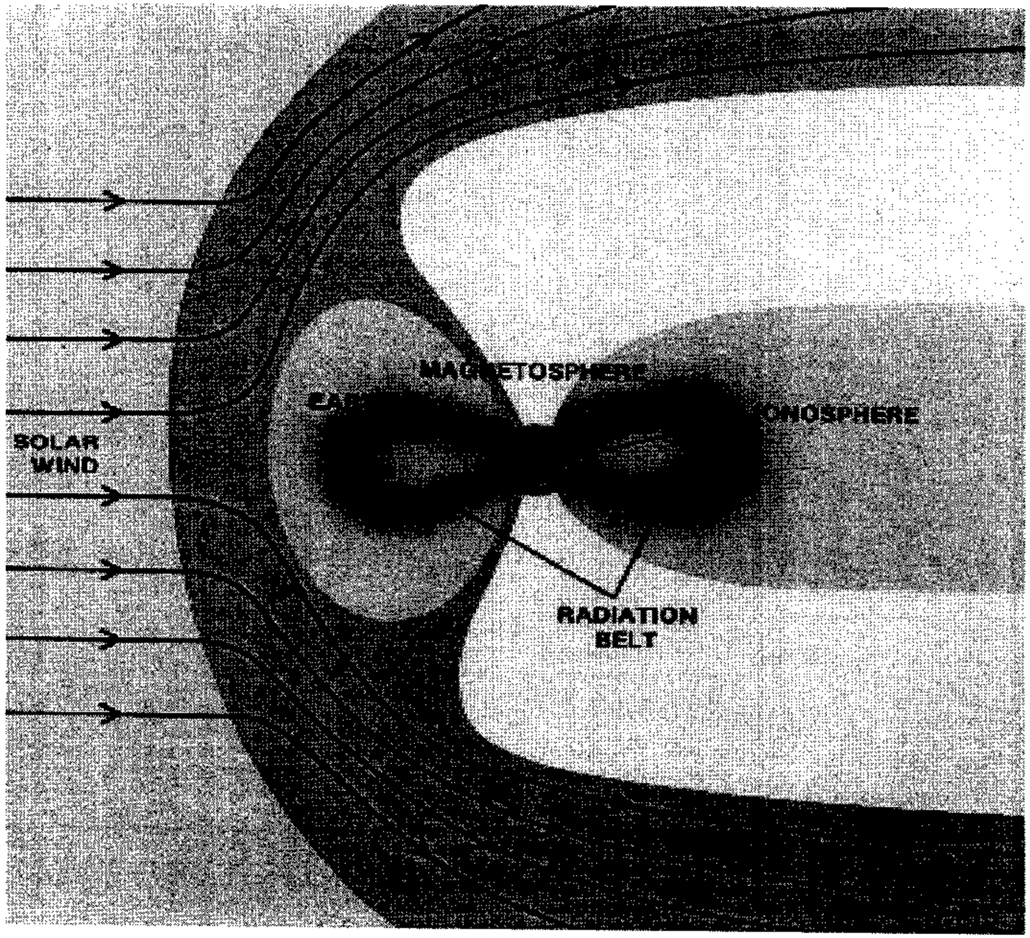
A closer look



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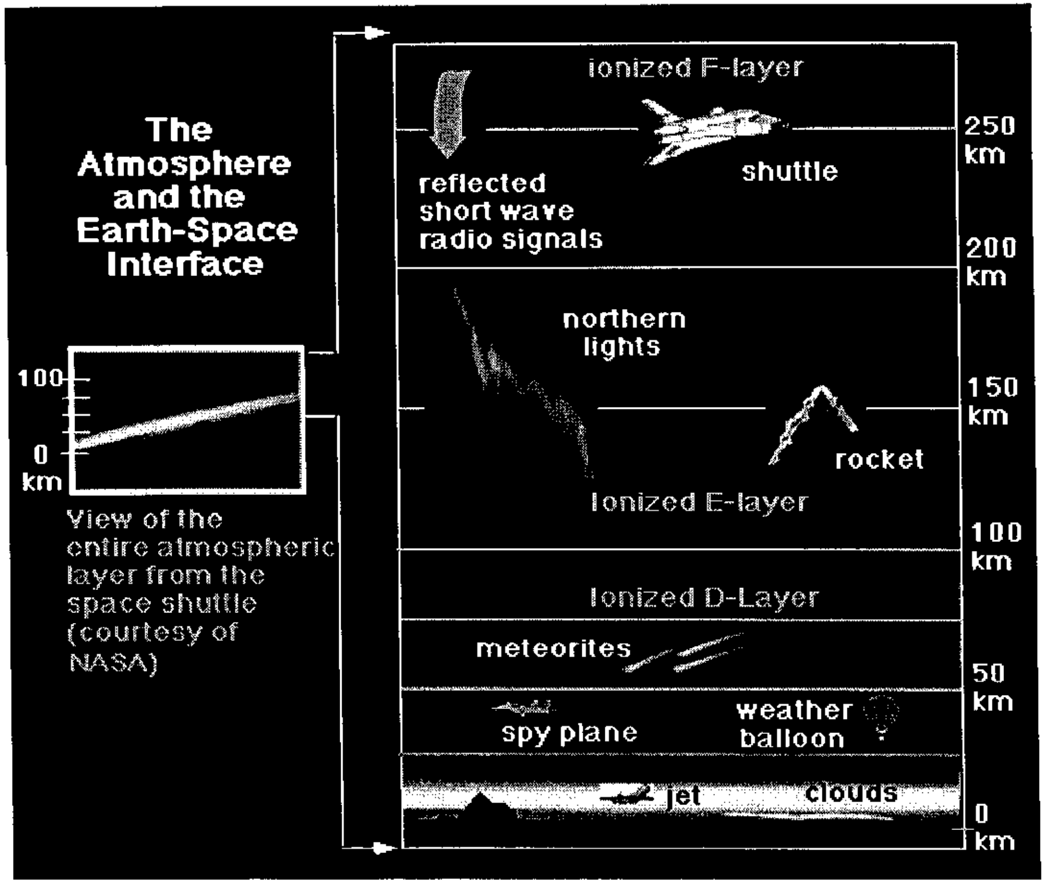
Atmospheric environment and human activities



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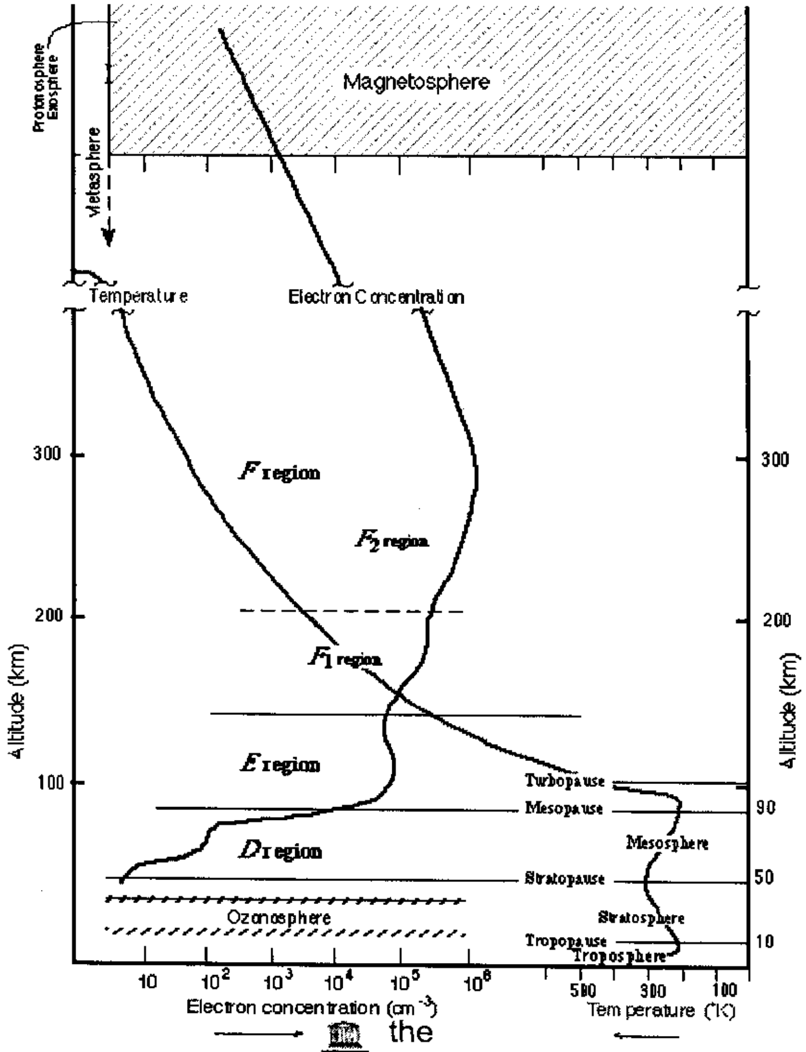
The atmospheric system



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The study of the atmospheric system

- The *atmospheric system* is not normally studied as a *system* but taking only into account one particular element of the system as the *ionospheric* (ionized species) *properties* or the *chemical* or *dynamical processes*.
- This approach reduces the possibilities of a full understanding of the atmospheric system behavior as a whole.

Atmospheric chemistry and the middle atmosphere

- The atmosphere of the Earth is made up of a large number of chemical constituents.
- The most abundant or major constituents are N_2, O_2 and Ar.
- Many more constituents are produced in the atmosphere itself by photochemical processes or at the surface by different natural processes or by human activity.
- The latter species are known as source gases. They are as examples: H_2O, CO_2, CH_4, N_2O, and CH_3Cl.

The middle atmosphere

- The region of the *middle atmosphere* (20-100 km) is chemically the most active one.
- The starting *processes* are photochemical reactions due mainly by the solar electromagnetic radiation in the UV and X regions of the spectrum.

Main photochemical processes

Photodissociation: $AB + h\nu \rightarrow A + B$

(wavelenght > 130 nm)

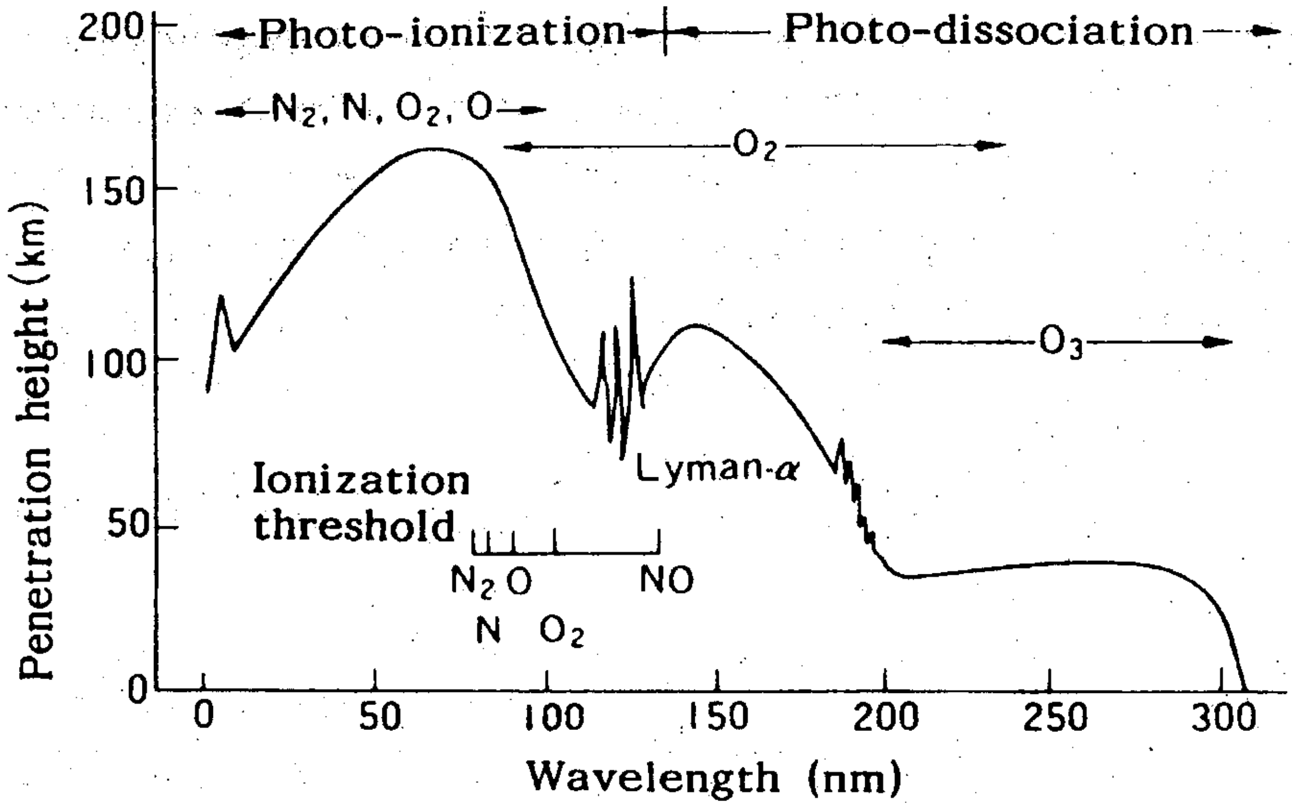
Photoexcitation: $AB + h\nu \rightarrow AB^*$

(wavelenght < 310 nm)

Photoionization: $A + h\nu \rightarrow A^+ + e$

(wavelenght < 100 nm)

Penetration heights



Chemical reactions in the middle atmosphere

- The initial photochemical processes start large chains of chemical reactions among neutral and ionized species in the middle atmosphere.
- Reactions involving neutrals give rise to complex families of Oxygen, Carbon, Hydrogen, Nitrogen and Chlorine compounds.
- Reactions involving ionized species generate series of both positive and negative molecular ions. The presence of these last species is the main chemical characteristic of the D-region of the ionosphere.

Initial steps of the oxygen chemistry

Photodissociation of O_2 in the stratosphere and mesosphere $\xrightarrow{\lambda<242.4nm}$ produces atomic oxygen O

atomic oxygen O $\xrightarrow{\text{reacting with } O_2+M}$ produces O_3

Photodissociation of $O_3 \xrightarrow{\lambda<310nm}$ produces $O_2(^1\Delta_g)$ + $O(^1D)$

deactivation of $O_2(^1\Delta_g) \rightarrow$
can produce infrarred emission at $\lambda = 1.27\mu m$

(*O and O_3 generate series of reactions that involve most families of compounds*)

Initial steps of hydrogen chemistry

Photodissociation of water vapor in the upper mesosphere $\xrightarrow{\lambda < 200nm}$ produces H + OH (hydrogen free radicals)

Water vapor in the stratosphere and mesosphere $\xrightarrow{\text{reacting with } O(^1D)}$ produces OH

OH radical with CH_4 $\xrightarrow{\text{through oxidation}}$ produces methyl radical CH_3

(*Methyl radical initiates a chain of reactions that includes also Cl*)

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Initial steps of carbon chemistry

OH radical and O(^{1}D) reacting with CH_4 in the stratosphere $\xrightarrow{\text{through oxidation}}$ produces methyl radical CH_3

CH_3 reacting in chain with O_2 and NO $\xrightarrow{\text{through photodissociation}}$ produces O and finally O_3

(*this last mechanism produces photochemical smog in the troposphere*)

Initial steps of nitrogen chemistry

N_2 is photochemically inactive,

N_2O is introduced in the stratosphere from the soil by denitrification and vertical motion.

N_2O reacting with O and O_3 $\rightarrow$ produces NO and NO_2

(*nitrogen oxides destroy catalytically O and O_3 and react with other compounds*)

Basics of chlorine chemistry

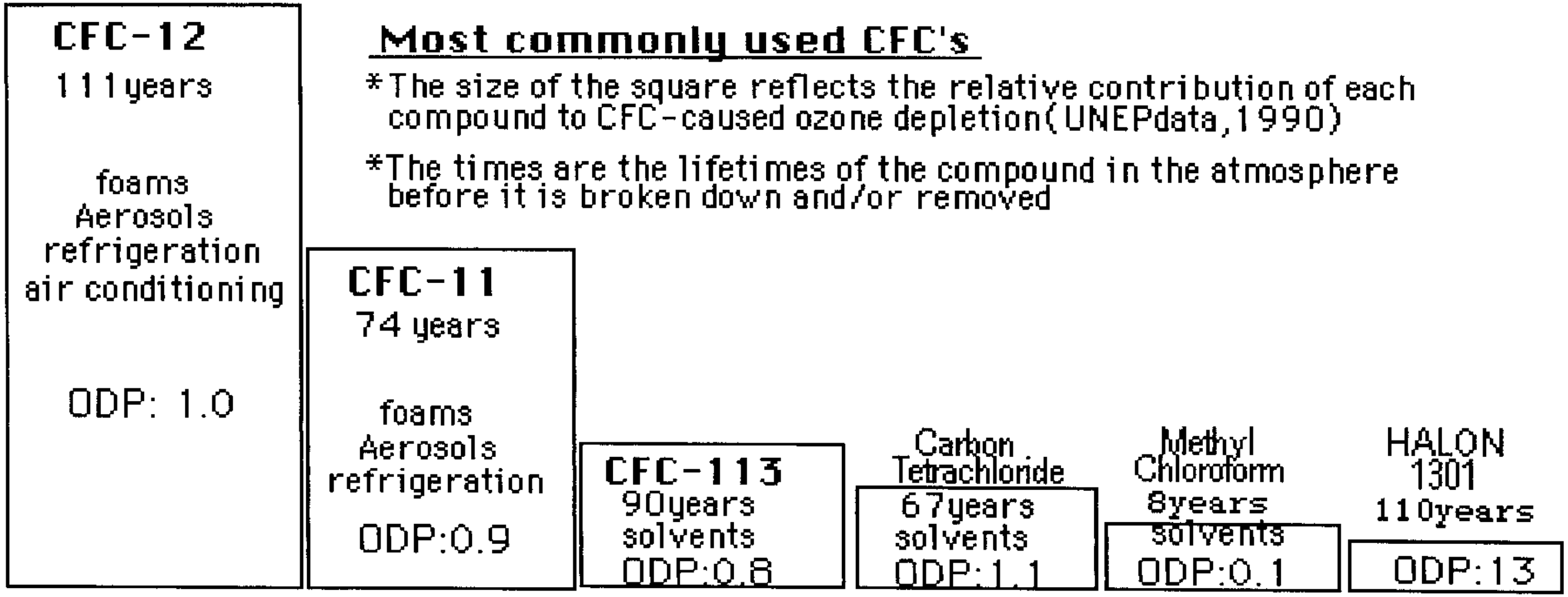
Anthropogenic chlorofluorcarbons (CFC) (like $CFCl_3$) are produced at ground level and, being stable, are transported toward the stratosphere.

These compounds are dissociated by UV radiation or by reaction with $O(^1D)$ producing free Cl

Free Cl regenerates itself reacting in chain with O_3 (forming the very active ozone destroyer ClO), O and NO or generate inactive compounds like $ClNO_2$.

(Through these processes chlorine is an effective destroyer of stratospheric O_3)

Anthropogenic CFC and their lifetime



Polar stratosphere

- During the winter polar night, sunlight does not reach the south pole. A strong circumpolar wind called "polar vortex" develops in the middle to lower stratosphere. This has the effect of isolating the air over the polar region.
- In absence of sunlight, the air within the polar vortex can get very cold and Polar Stratospheric Clouds (or PSCs for short) can form once the air temperature gets to below about -80C. These clouds first form as nitric acid trihydrate.

Polar stratosphere and chlorine

- As the temperature gets colder however, larger droplets of water-ice with nitric acid dissolved in them can form. However, their exact composition is still the subject of intense scientific investigation. PSCs are the medium on which reservoir chlorine compounds: hydrochloric acid (HCl) and chlorine nitrate (ClONO2) are converted into ozone-destroying chlorine radicals (like ClO that is 100 times more abundant inside the polar vortex than at diddle latitudes).

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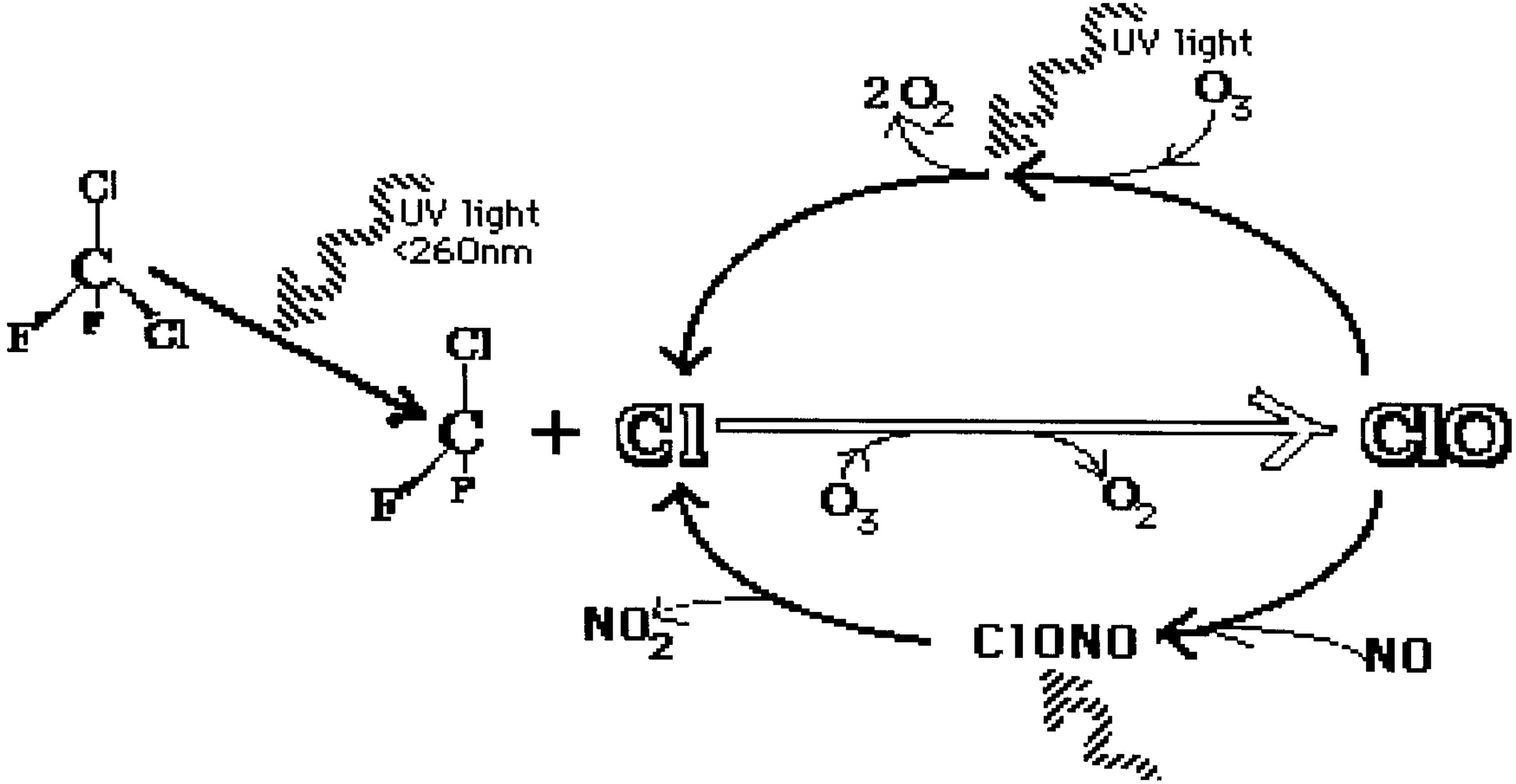
Ozone destruction by Cl



Ozone destruction

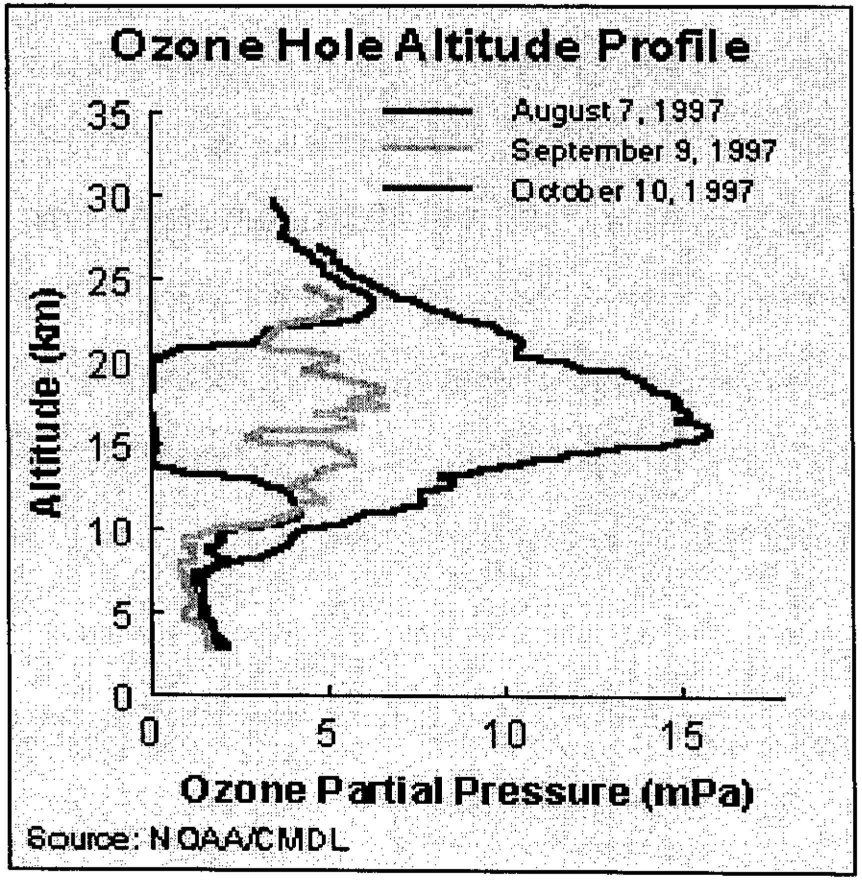
- It is estimated that one free chlorine can degrade over 100,000 molecules of ozone before it is removed from the stratosphere or becomes part of an inactive compound.
- These inactive compounds, for example ClONO2, are collectively called 'reservoirs'. They hold chlorine in an inactive form but can release a free chlorine by photodissociation by solar radiation.

The so called "ozone hole"

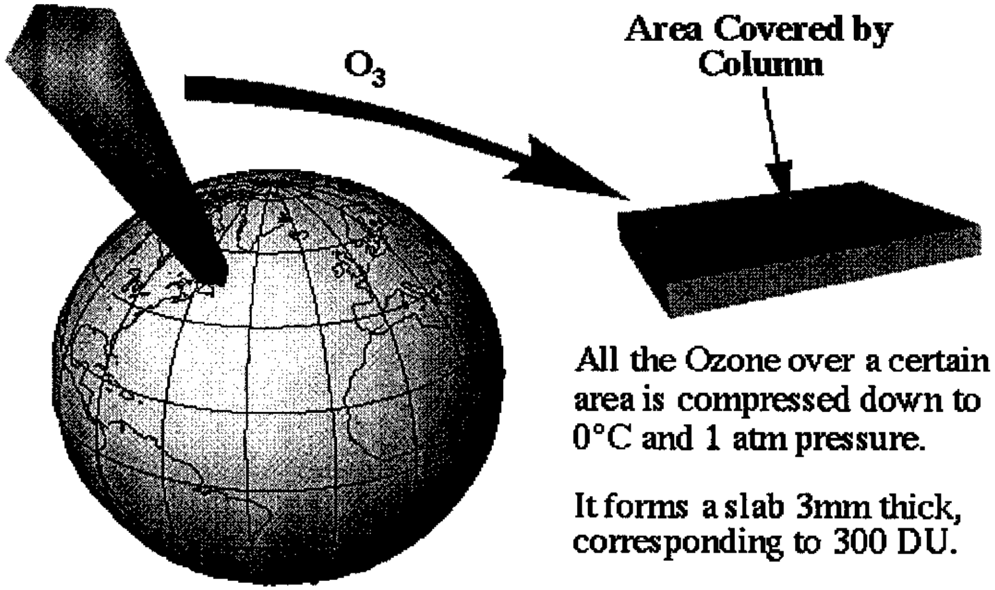
- Dramatic loss of ozone in the lower stratosphere over Antarctica was first noticed in the 1970s by a research group from the British Antarctic Survey (BAS).
- Recent results from the European campaign SESAME (1994-95) indicate significant ozone loss within the Arctic vortex.

- **Firm evidence has been produced that there had been an ozone decrease over the heavily populated northern mid-latitudes (30-60N). However, unlike the sudden and near total loss of ozone over Antarctica at certain altitudes, the loss of ozone in mid-latitudes is much less and much slower - only a few percentage per year.**

Profile of ozone deplition

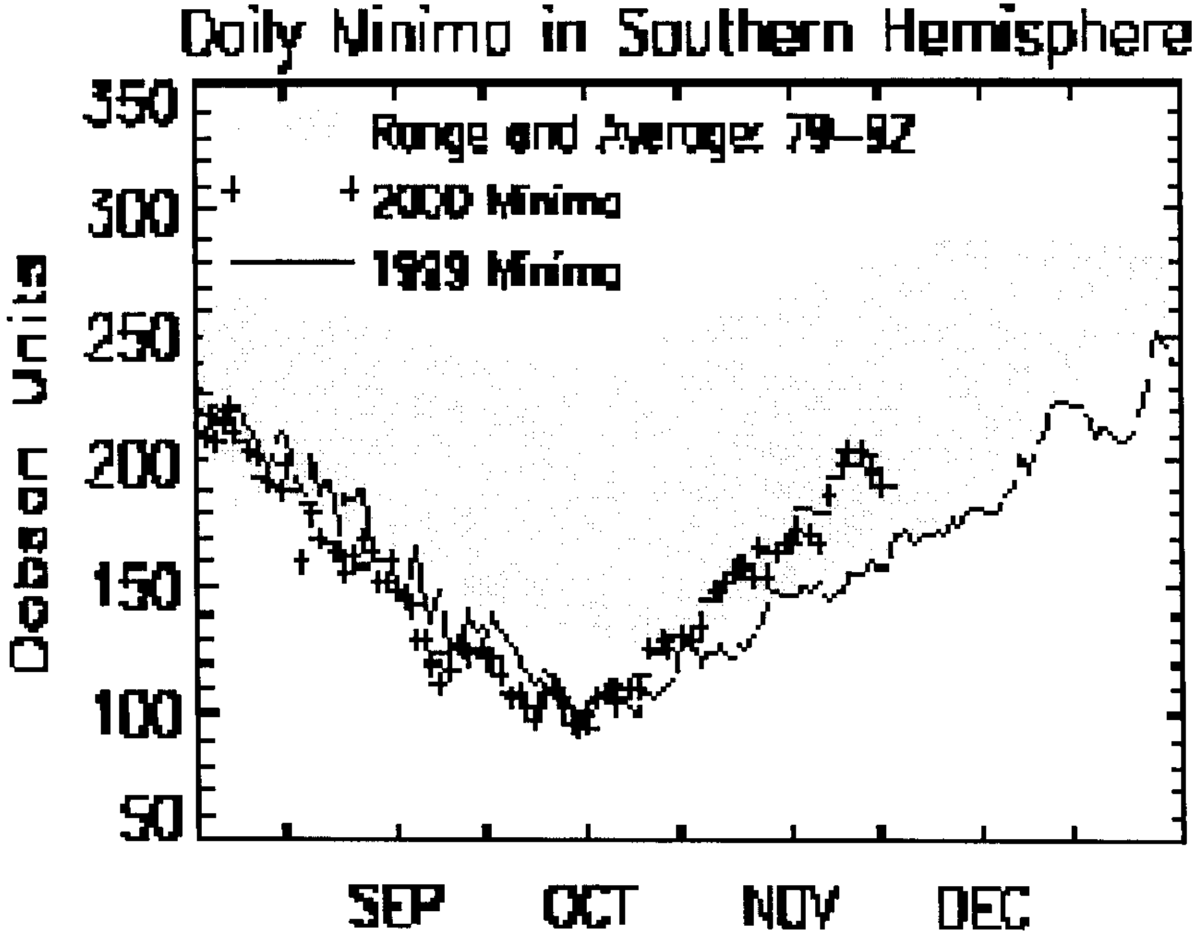


Ozone measurements: the Dobson Unit



1 Dobson Unit (DU) is defined to be 0.01 mm thickness at STP(0 deg C and 1 atmosphere pressure)

Ozone deplition minima



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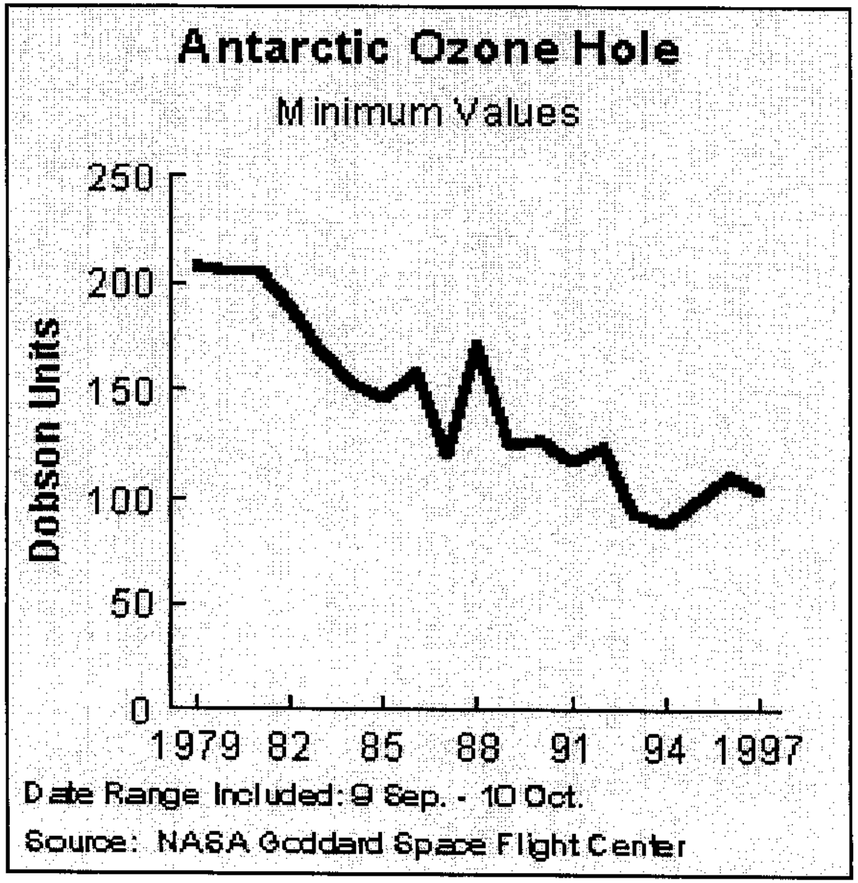
Evolution of ozone deplition minimum (1)



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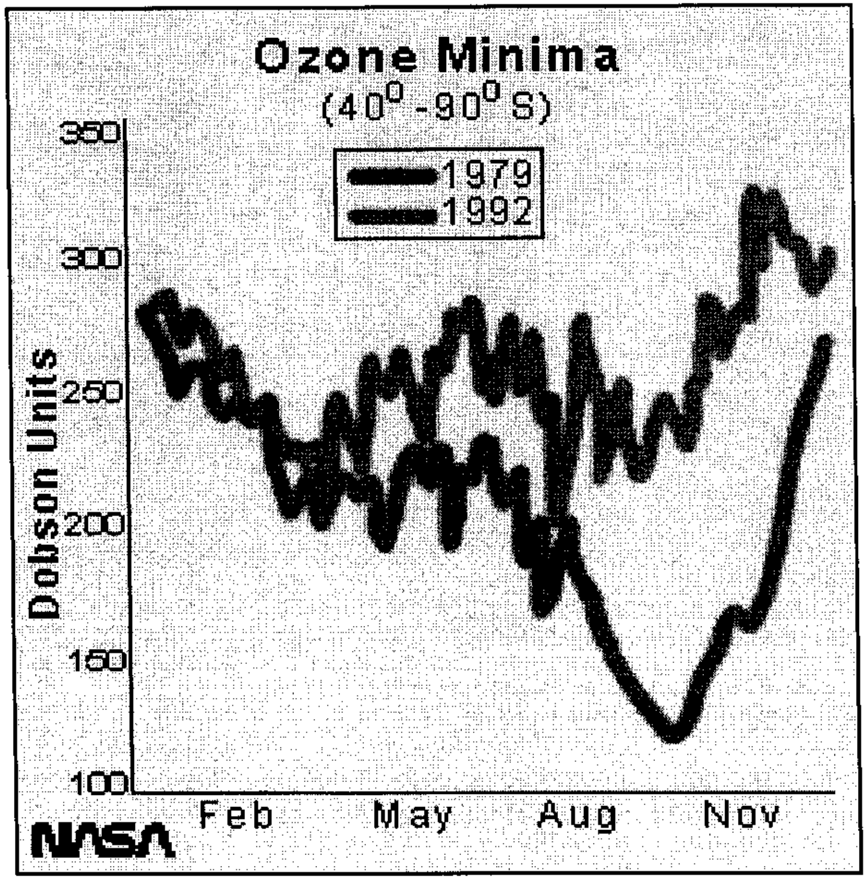
Evolution of ozone deplition minimum (2)



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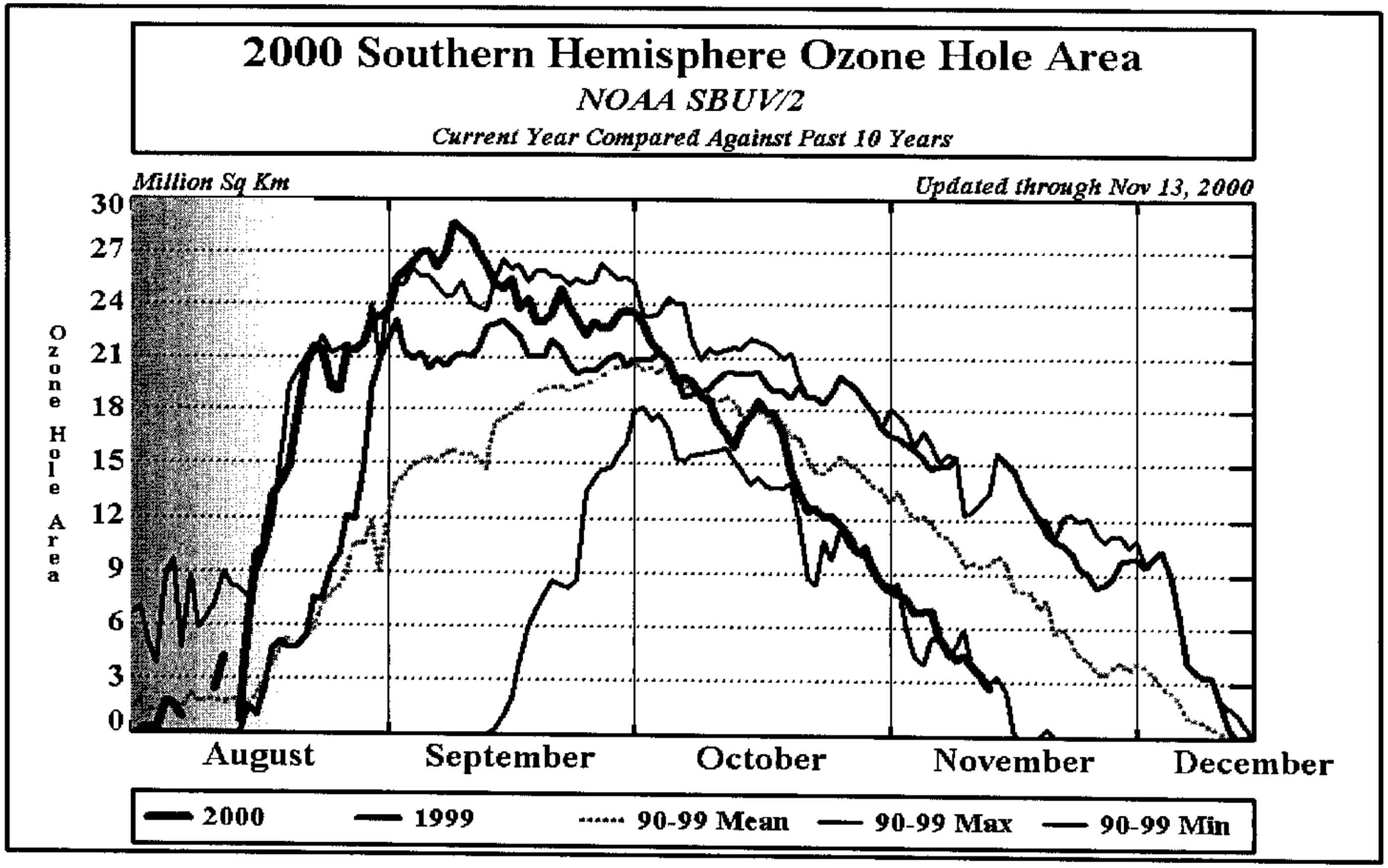
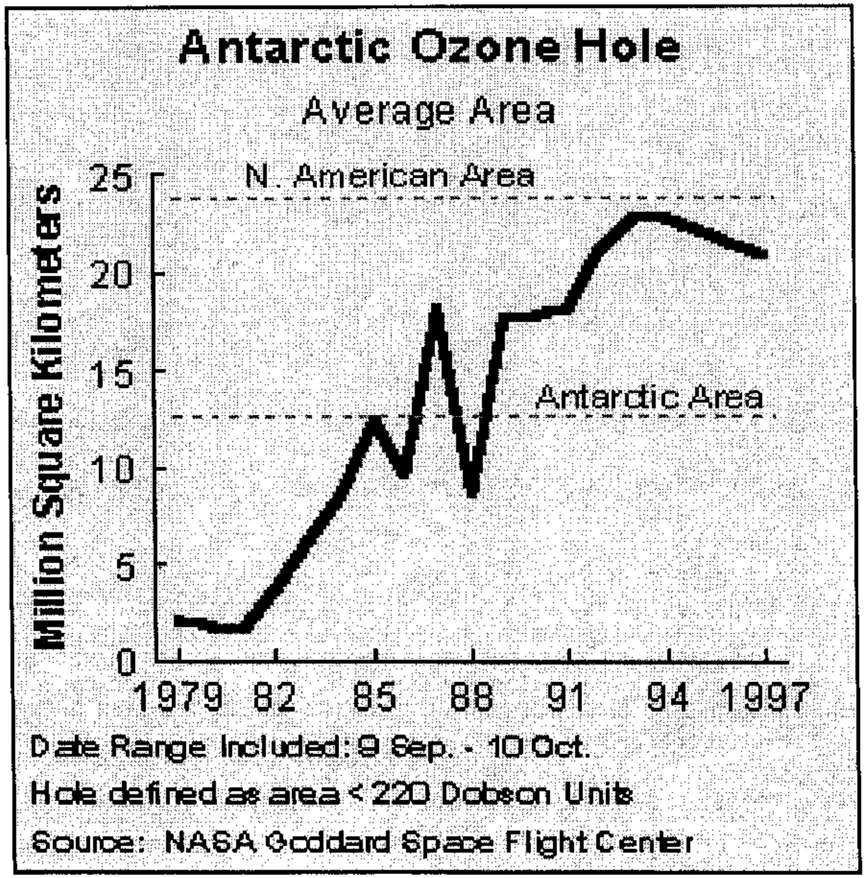
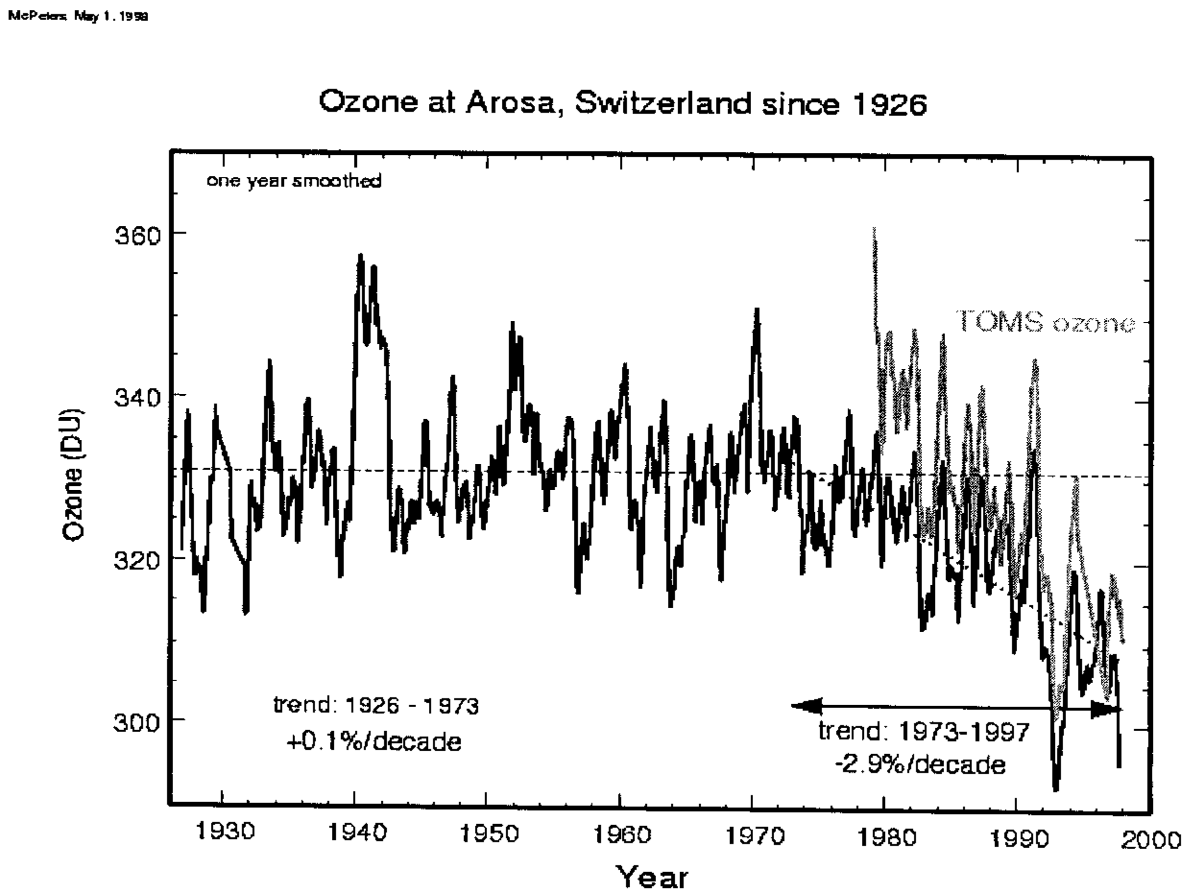
Southern hemisphere ozone deplition area (1)



Southern hemisphere ozone deplition area (2)



Northern hemisphere ozone (1)



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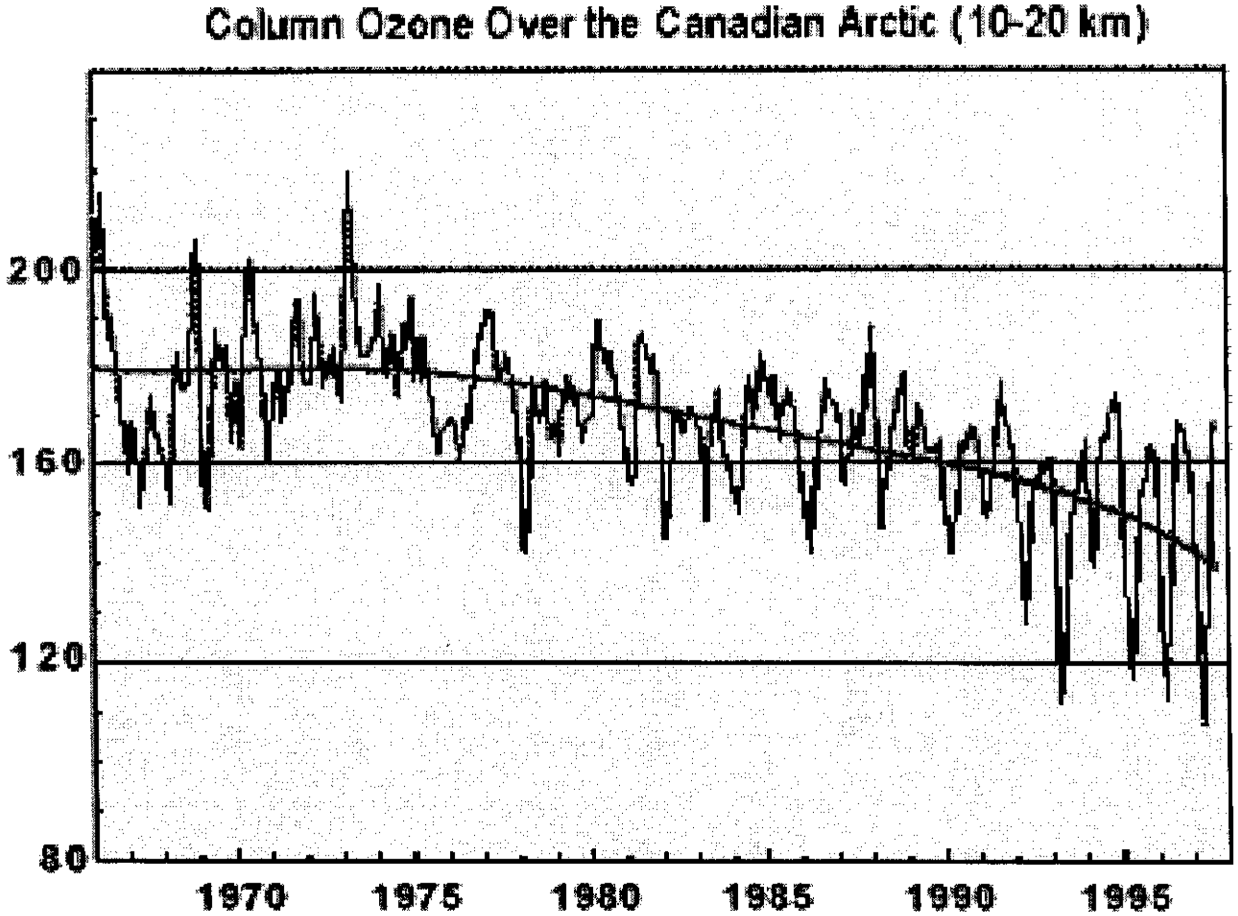
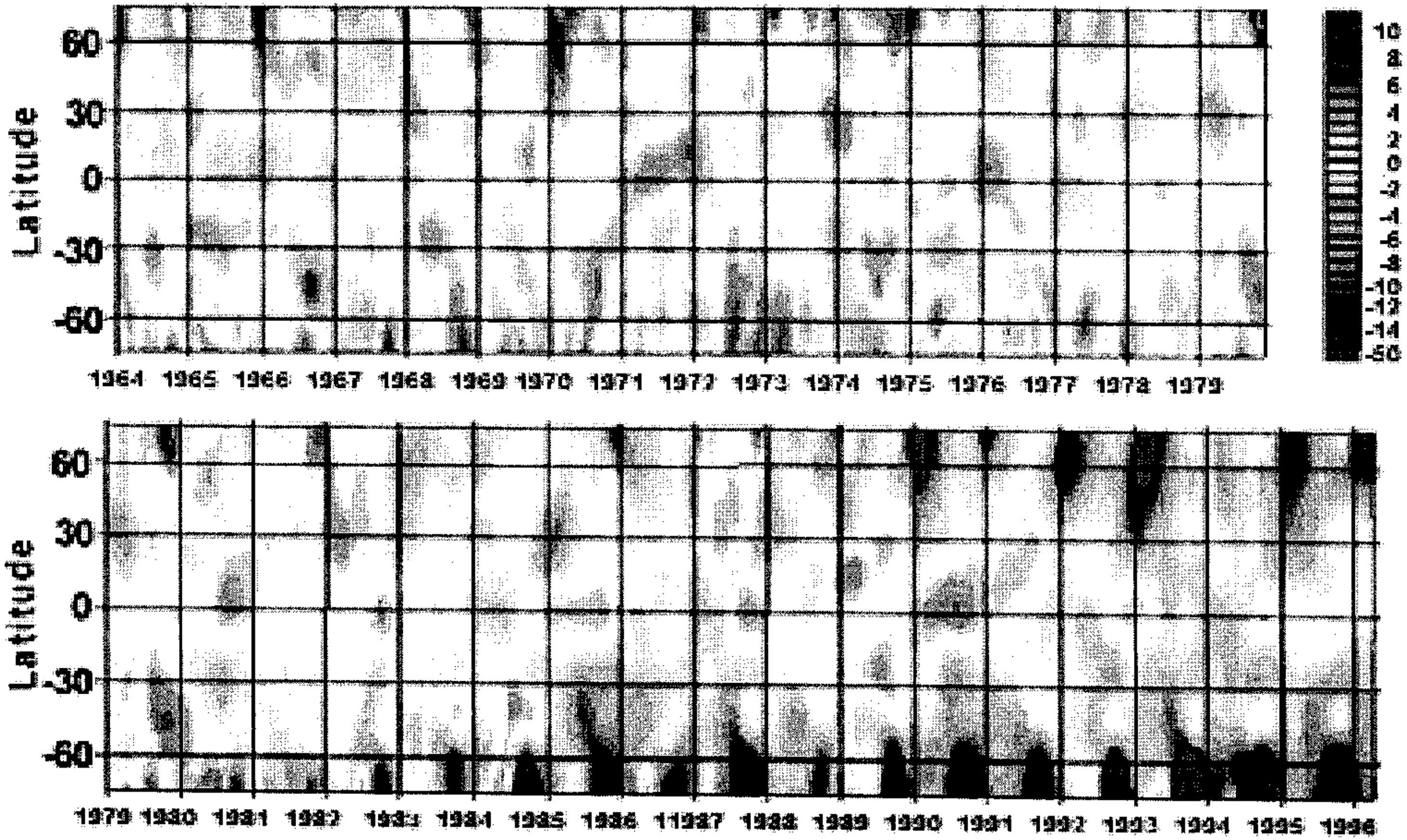
Northern hemisphere ozone (2)



Evolution of global ozone (1)

Global Deviations 1964 - 1996



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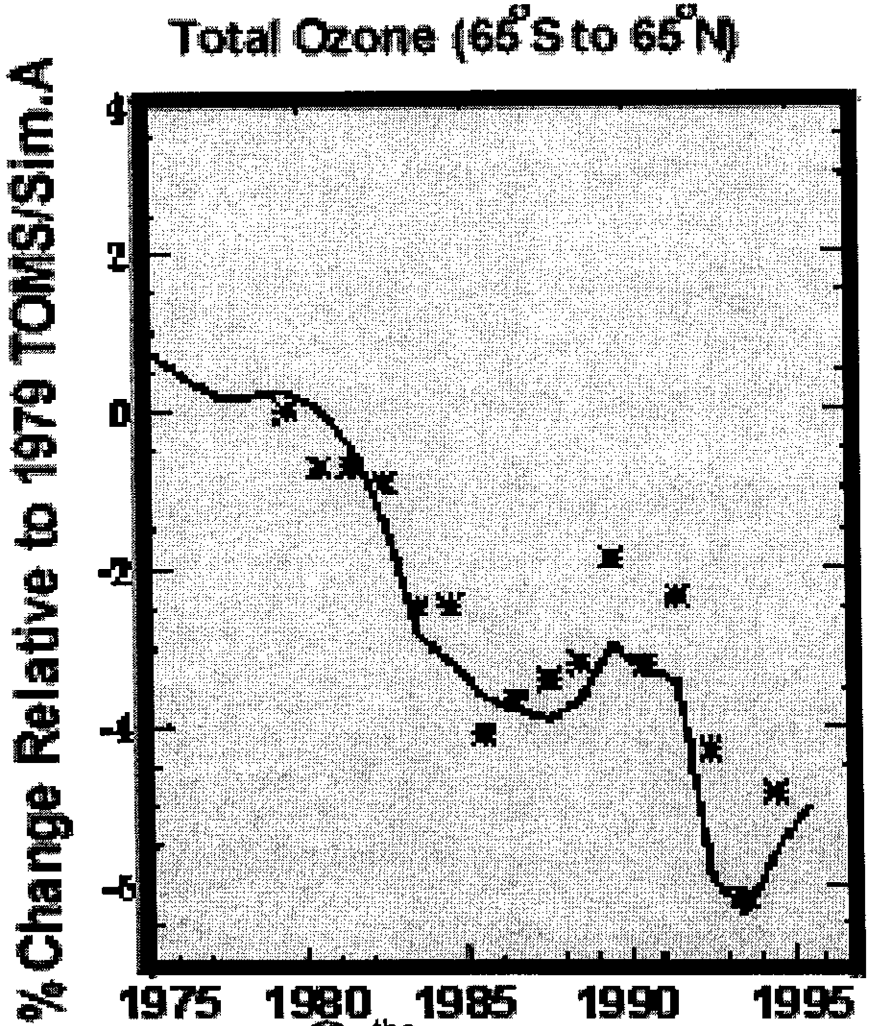
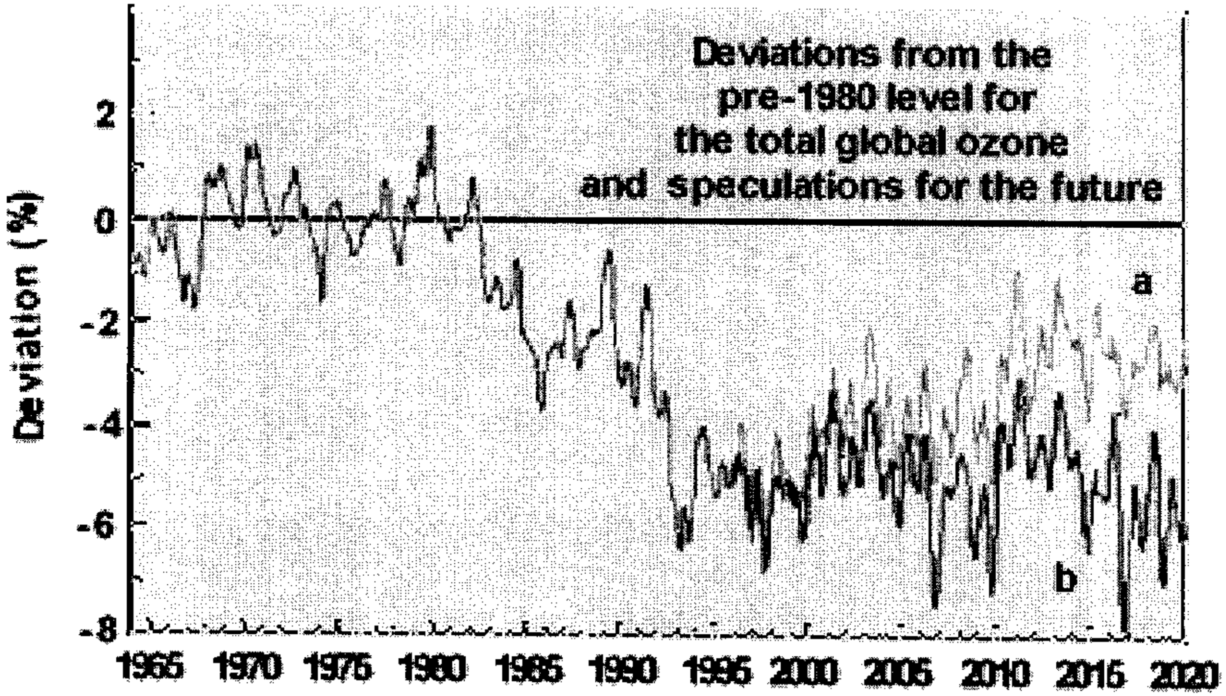
Evolution of global ozone (2)



Evolution of global ozone (2)



a) the best case scenario
b) all ozone depleting substances remain at their 1997 levels

Basic chemical kinetics of interest to lower ionosphere

Photoionization:

$$A + h\nu \rightarrow A^{+} + e$$

Photoionization rate:

$$\frac{d(A)}{dt} = -J_{A}(A) = q$$

where:

(A) concentration in cm^{-3}

J_A photoionization coefficient in s^{-1}

q ion-pair production rate

from $\frac{d(A)}{dt} = -J_A dt$ is $\ln(A) = -J_A t + c$

if $(A) = (A)_0$ at $t = 0$:

$$(A) = (A)_0{}^{-J_A t}$$

and

$\tau_A = \frac{1}{J_A}$ is the lifetime of specie A in s

For a single solar wavelenght ionizing species A :

$$J_A = \eta_i \cdot \sigma_i I_\infty e^{-\tau \sec\chi}$$

η_A **quantum efficiency of photoionization**

σ_A **absorption cross section for photoionization**

I_∞ **intensity of incident ionizing radiation**

$$\tau = \int_s \sigma_a N(s) ds$$ **optical depth**

σ_a **total absorption cross section**

s **slant path of the ray**

χ **solar zenith angle**

Ionization processes in the lower ionosphere

Lα (1215 Å) ionizes NO

EUV (1027 - 1118 Å) ionize $O_2(^1\Delta_g)$

EUV ionize O_2 and N_2

X – rays (2 - 8 Å) ionize all constituents

Galactic Cosmic Rays ionize all constituents

Energetic Solar / Auroral particles ionize all constituents

X - rays/γ - rays from neutron stars (including flares) ionize all constituents

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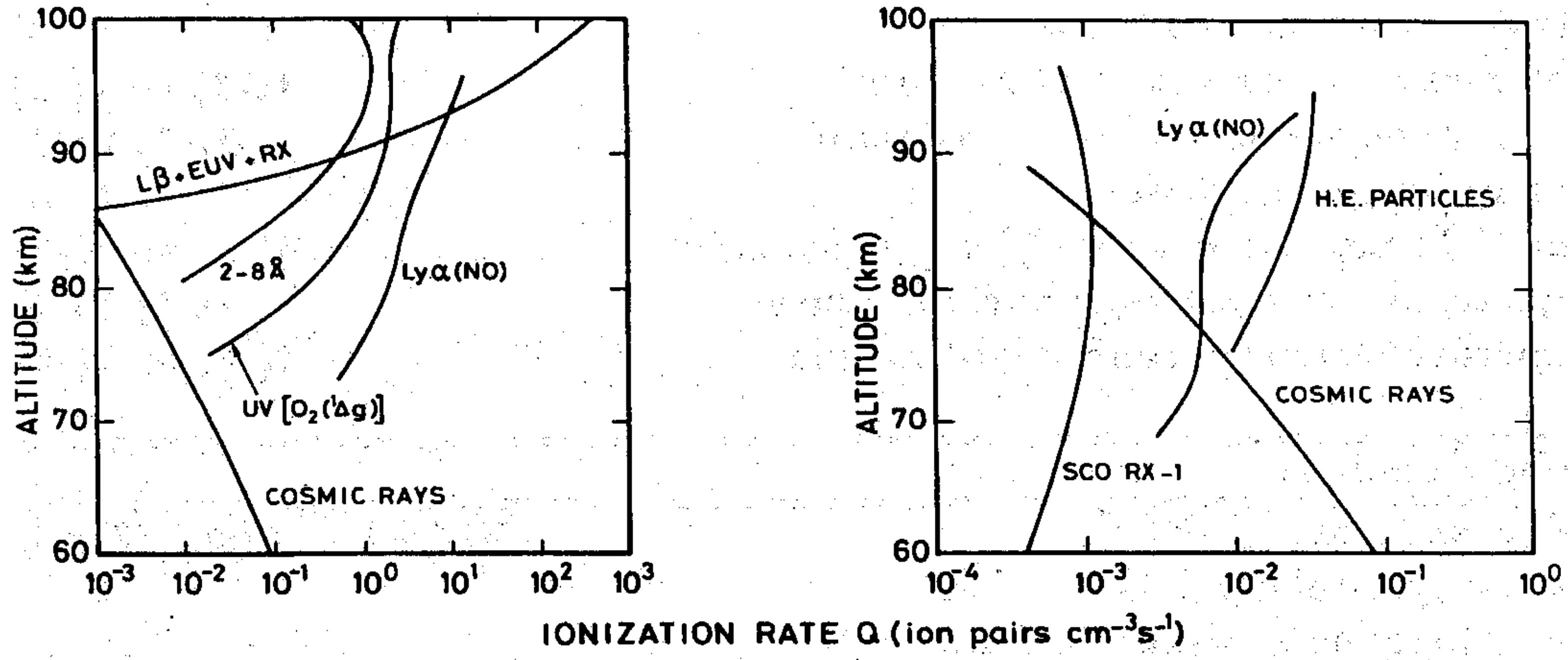
Ionization rates in the lower ionosphere (day and night)



Ionization of NO

For the ionization of NO in the lower ionosphere:

$I_{\infty}(L\alpha) = (3 \pm 1)x10^{11} \quad cm^{-2}s^{-1}$

$\sigma_{NO} = 2x10^{-18} cm^{-2}$

$\sigma_{aO_2} = 1x10^{-20} cm^{-2}$

if:

$N_{O_2}(s, \chi)$ is the integrated molecular concentration along the path s at a zenith solar angle χ

$$J_{NO} = (6 \pm 2)x10^{-7} \exp[-1x10^{-20} N_{O_2}(s, \chi)] \; s^{-1}$$

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Two bodies reaction

General two bodies reaction:

$$A+B \xrightarrow{k_r} C+D$$

Rate of reaction (molec cm^{-3}s^{-1})

$$\frac{d(C)}{dt}=\frac{d(D)}{dt}=-\left(\frac{d(A)}{dt}\right)=-\left(\frac{d(B)}{dt}\right)=k_r(A)(B)$$

where k_r is the rate constant (cm^{-3}molec^{-1}s^{-1})

$$(A) \approx (A)_0 e^{-k_r (B)}$$

$$\tau_A = \frac{1}{k_r (B)} \text{ in s}$$

Production and loss of a species

$$X + h\nu \xrightarrow{J_x} A + \text{Products}$$

$$A + B \xrightarrow{k_1} \text{Products}$$

$$A + B + M \xrightarrow{k_2} \text{Products}$$

$$A + F \xrightarrow{k_3} \text{Products}$$

$$G + H \xrightarrow{k_4} A + \text{Products}$$

$$\frac{d(A)}{dt} = J_x(X) + k_4(G)(H) - k_1(A)(B) - k_2(A)(C)(M) - k_3(A)(F)$$

lifetime of species A: $$\tau_A = \frac{1}{k_1(B) + k_2(C)(M) + k_3(F)}$$

Steady state

- If the chemical timelife of species A is short compared with transport times and if the concentration of B,C,F,G and H are not changing over the time considered, photochemical stationary state (*steady state*) can be assumed.
- In this case species A is in instantaneous equilibrium and its concentration is determined by its sources and sinks.

Continuity equations

$$\frac{d(A)}{dt} = \sum_i P_i - \sum_i L_i(A) = 0$$

$$(A) = \frac{\sum_i P_i}{\sum_i L_i}$$

$$(A) = \frac{J_X + k_4(G)(H)}{k_1(B) + k_2(C)(M) + k_3(F)}$$

Basic reactions in the lower ionosphere

$XY + h\nu \rightarrow XY^{+} + e$	Photoionization
$X + e^{*} \rightarrow X^{+} + 2e$	Ionization by energetic particles
$X^{+} + Y \rightarrow Y^{+} + X$	Charge exchange
$X^{+} + e \rightarrow \text{neutrals}$	Ion-electron recombination
$e + Z + M \rightarrow Z^{-} + M$	Attachment
$Z^{-} + h\nu \rightarrow Z + e$	Photodetchment
$Z^{-} + M \rightarrow Z + M + e$	Collisional detachment
$X^{+} + Z^{-} \rightarrow \text{neutrals}$	Ion-ion recombination
$X^{+} \cdot M + H_2O \rightarrow X^{+} \cdot H_2O + M$	Ion clustering (ion hydration)

Recombination processes

Radiative recombination:

$$X^{+} + e \xrightarrow{\alpha_R} X + h\nu$$

Dissociative recombination:

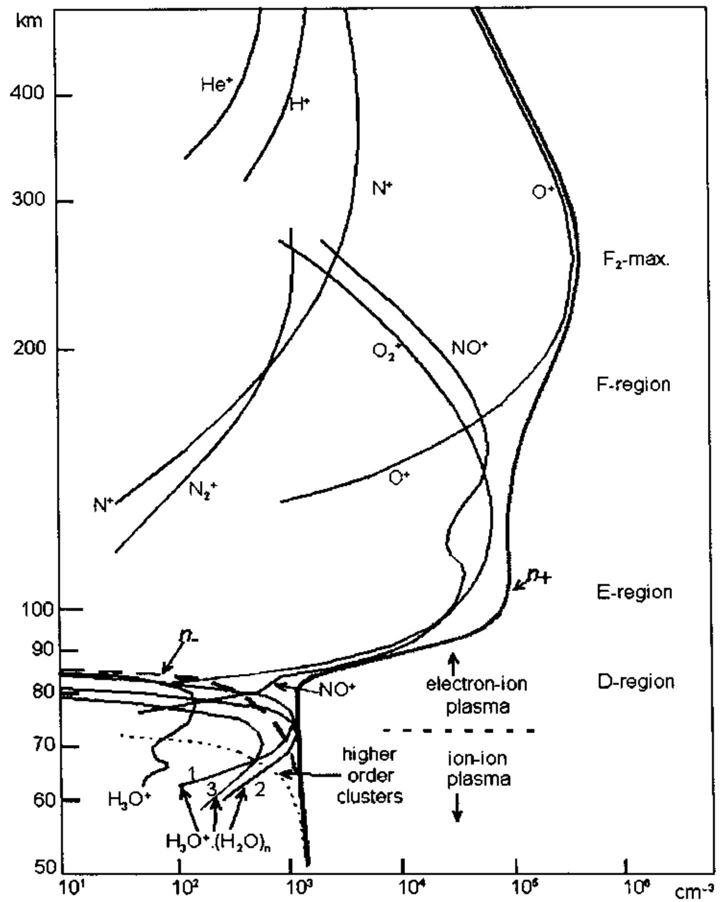
$$XY^{+} + e \xrightarrow{\alpha_D} X + Y$$

Ion-ion recombination:

$$XY^{+} + Z^{-} \xrightarrow{\alpha_i} \text{neutrals}$$

Ionic composition

Ionic composition of the atmosphere



- **Due to the complex ionic chemistry ionic species both positive and negative are important minor constituents of the atmosphere.**

Ionized species continuity equations

Assume that:

(N^+) Concentration of positive ions

(N^-) Concentration of negative ions

(e) Concentration of electrons

(N_a) Concentration of neutrals forming initial negative ions

β_a Electron - neutral attachment rate coefficient

K_d Total detachment processes rate

α_i Ion – ion recombination rate coefficient

Electron and ion continuity equations

$$\frac{d(N^+)}{dt} = q - \alpha_D(N^+)(e) - \alpha_i(N^+)(e) = q - \alpha_{eff}(N^+)(e)$$

$$\frac{d(N^-)}{dt} = \beta_a(N_a)(e) - K_d(N^-) - \alpha_i(N^+)(N^-)$$

$$\frac{d(e)}{dt} = q + K_d(N^-) - \alpha_D(N^+)(e) - \beta_a(N_a)(e)$$

$$= q - \left[\alpha_D(N^+) - \beta_a(N_a) + K_d\lambda\right](e)$$

where:

$$\alpha_{eff} = \alpha_D + \alpha_i\lambda$$

$$\lambda = \frac{(N^-)}{(e)}$$

Electron to negative ions ratio

for steady state conditions is:

$$\lambda = \frac{\beta_a (N_a)}{K_d} = \frac{\text{electron neutral attachment rate}}{\text{total detachment rate}}$$

when $\lambda \to 0$ ($k_a(N_a) \to 0$ or $N^- \to 0$) then:

$$\frac{d(e)}{dt} = q - \alpha_D (N^+)(e)$$ that is the continuity equation in absence of negative ions (E-region)

A different "effective" continuity equations system

$$\frac{d(N_e)}{dt} = \sum q - \beta_{eff}(e) - \alpha_D(e)(N^+)$$

$$\frac{d(N^-)}{dt} = \beta_{eff}(e) - \alpha_i(N^-)(N^+)$$

$$(N^+) = (N^-) + (e)$$

$$\beta_{eff} = \sum_i \beta_i (N)^n \{1 - \Lambda_i\} \quad \text{in } s^{-1}$$

β_i attachment rate constant which produces the i-st initial negative ion

$(N)^n$ neutral species concentration with n depending upon the reaction type (two-body, three-body, etc.)

Λ_i weighted dechament rates function of neutrals concentration and rate constants

A simplified negative ions reaction scheme

$$(e) + O_2 + O_2 \xrightarrow{k_1} O_2^- + O_2$$

$$O_2^- + O \xrightarrow{k_2} e + O_3$$

$$O_2^- + O_2(^1\Delta_g) \xrightarrow{k_3} e + 2O_2$$

$$O_2^- + O_3 \xrightarrow{k_4} O_3^- + O_2$$

$$O_2^- + O_2 + M \xrightarrow{k_5} O_2 \cdot O_2^- + M$$

$$O_2^- + NO_2 \xrightarrow{k6} NO_2^- + O_2$$

$$O_3^- + O \xrightarrow{k_7} O_2^- + O_2$$

$$O_3^- + O \xrightarrow{k_8} e + 2O_2$$

$$O_3^- + O_3 \xrightarrow{k_9} e + 3O_2$$

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Effective attachment coefficient

By solving the continuity equations that corresponds to the previous set of reactions for electrons and the negative ions that produces electrons by detachment:

$$\beta_{eff} = k_1(O_2)^2\left\{1-\left(\frac{k_3(O_2{}^1\Delta_g)}{A}+\frac{k_4(O_3)}{A\cdot B}\left[k_8(O)+k_9(O_3)\right]\right)\right\}$$

where

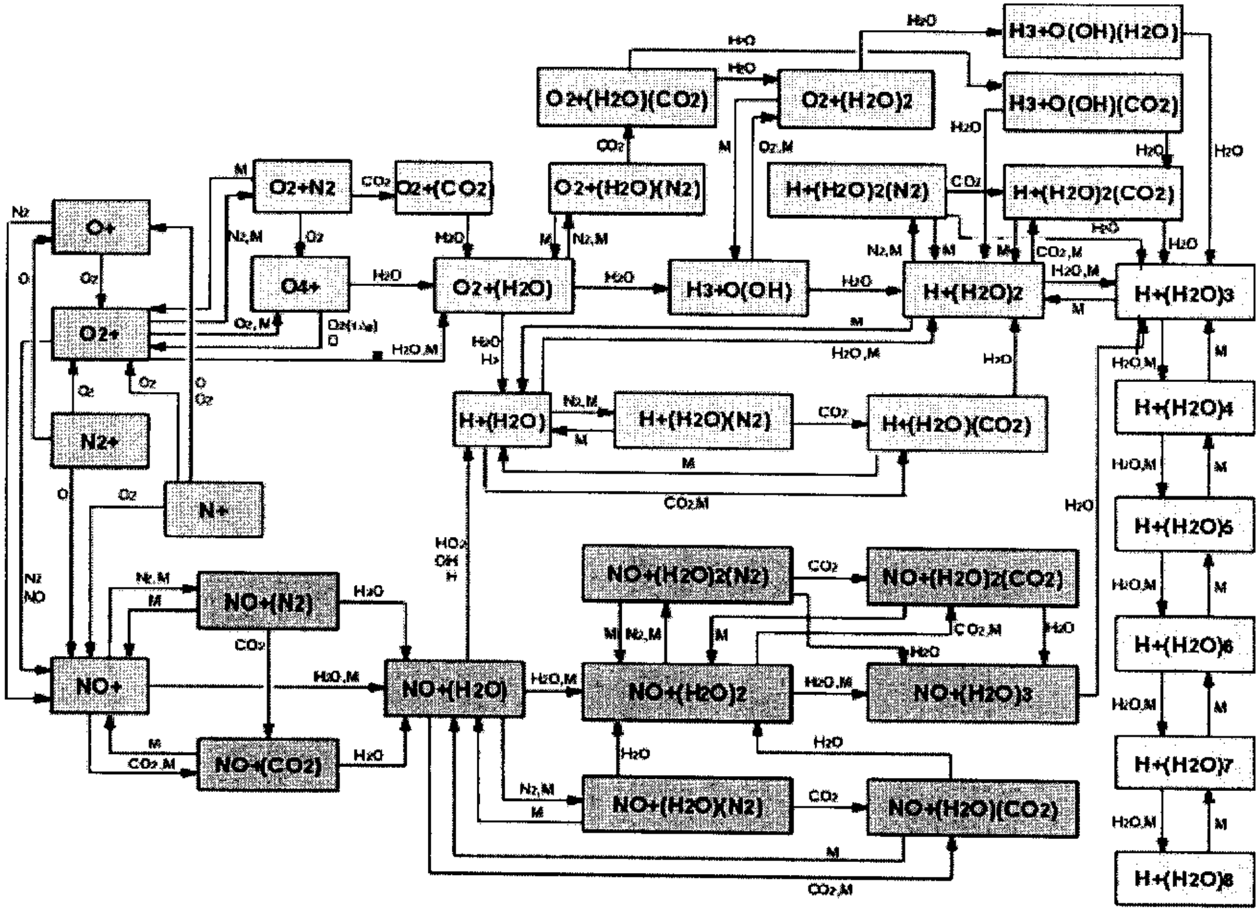
$$A = k_2(O)+k_3(O_2{}^1\Delta_g)+k_4(O_3)+k_5(O_2)(M)+k_6(NO_2)$$

$$B = k_7(O)+k_8(O)+k_9(O_3)$$

and

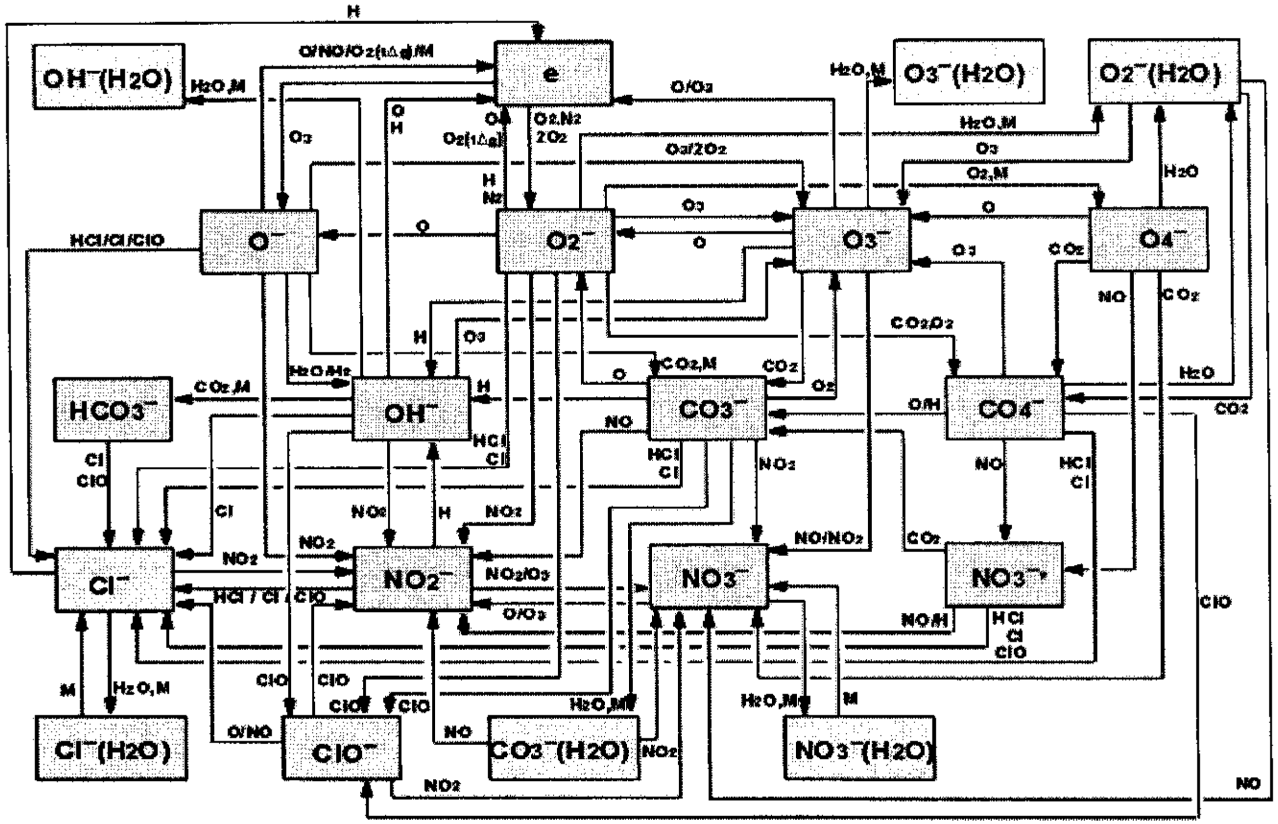
$$\Lambda = \frac{k_3(O_2{}^1\Delta_g)}{A}+\frac{k_4(O_3)}{A\cdot B}\left[k_8(O)+k_9(O_3)\right]$$

Sodankylä Ion Chemistry
Modeling the Chemistry of the Lower Ionosphere



Positive ion reaction scheme

Sodankylä Ion Chemistry
Modeling the Chemistry of the Lower Ionosphere



Negative ion reaction scheme

Same references: Books and a paper

Books

- W. Dieminger,G.K. Hartmann and R. Leitinger; "The Upper Atmosphere, Data Analysis and Interpretation", Springer -Verlag, 1996
- T. Shimazaki; " Minor constituents in the middle atmosphere", D. Reidel P.C., 1985
- G. Brasseur and S. Solomon; " Aeronomy of the middle atmosphere", D. Reidel P. C., 1986

Referenced paper

- S. M. Radicella and V. Restbergs, "Oxygen allotropes concentrations and electron density profiles in the nighttime D-region", Journal of Atmospheric and Terrestrial Physics, Vol. 43, p. 1-6. (1981).

Same references: web pages

- *The Science of Ozone Depletion* in http://www.epa.gov/docs/ozone/science/science.html
- *The ozone hole tour* in http://www.atm.ch.cam.ac.uk/tour/index.html
- *Ion chemistry of the terrestrial atmosphere* in http://www.jh-inst.cas.cz/~spanel/atmosph.htm
- *Sodankylä Ion Chemistry, Modelling the Chemistry of the Lower Ionosphere* in http://space.sgo.fi/SIC/sic.html