

## Chemistry of Atmospheres: Notes for lecture 1

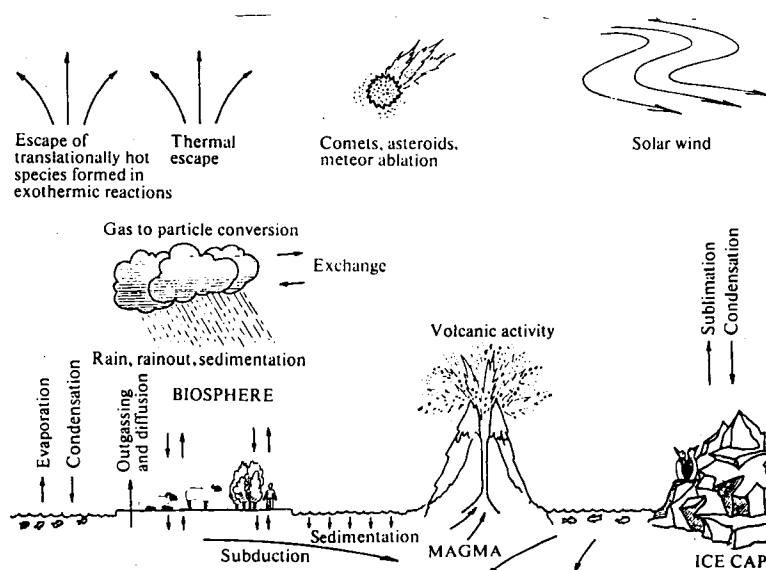
### 1.1 Major constituents of Earth's atmosphere (dry) at sea level; concentrations at STP

Species	RMM	Percentage	Concentration (molecule cm <sup>-3</sup> )
N <sub>2</sub>	28.02	78.08	2.098 × 10 <sup>19</sup>
O <sub>2</sub>	32.00	20.95	5.629 × 10 <sup>18</sup>
Ar	39.95	0.934	2.510 × 10 <sup>17</sup>
CO <sub>2</sub>	44.01	0.36	9.672 × 10 <sup>15</sup>

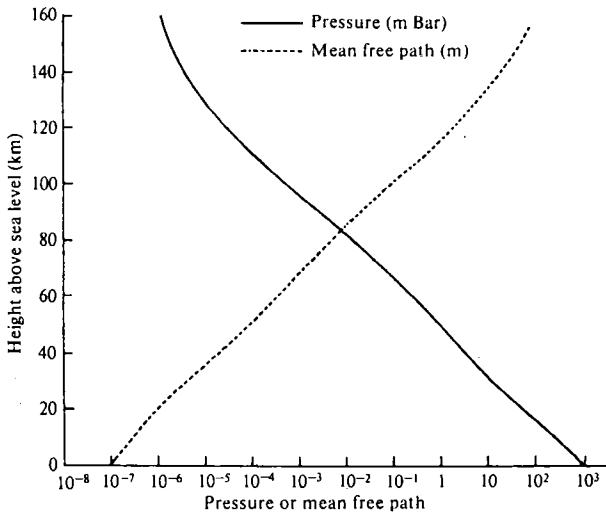
Total mass of Earth's atmosphere – 5 × 10<sup>18</sup>kg; 50% lies below 5.5km altitude, 99% below 30km.

### 1.2 Tropospheric gases

Species	Mixing ratio	Source/10 <sup>9</sup> kg yr <sup>-1</sup>	
		Man	Natural
CH <sub>4</sub> , HCs	1.7 × 10 <sup>-6</sup> (CH <sub>4</sub> )	188	1800
CO <sub>2</sub>	0.36	2 × 10 <sup>4</sup>	10 <sup>6</sup>
CO	4 - 20 × 10 <sup>-8</sup>	600	2500
N <sub>2</sub> O	3.0 × 10 <sup>-7</sup>		
NO <sub>x</sub>	5 - 200 × 10 <sup>-10</sup>	90	1200
NH <sub>3</sub>	<1 × 10 <sup>-8</sup>	7	1200
SO <sub>2</sub>	1.1 × 10 <sup>-10</sup>	207	~10
H <sub>2</sub> S, CH <sub>3</sub> SCH <sub>3</sub> , CH <sub>3</sub> SSCH <sub>3</sub>	1 × 10 <sup>-10</sup>	2 (H <sub>2</sub> S)	50 (H <sub>2</sub> S)
COS	5 × 10 <sup>-10</sup>		
H <sub>2</sub> O	10 <sup>-5</sup> - 10 <sup>-2</sup>		[weather]
O <sub>3</sub>	1 - 4 × 10 <sup>-8</sup>	[chemistry]	[chemistry]



### 1.3 Representation of the cyclic processes of biogeochemistry that exchange constituents between air, land, and sea



**1.4** Pressure and mean free path as a function of altitude.

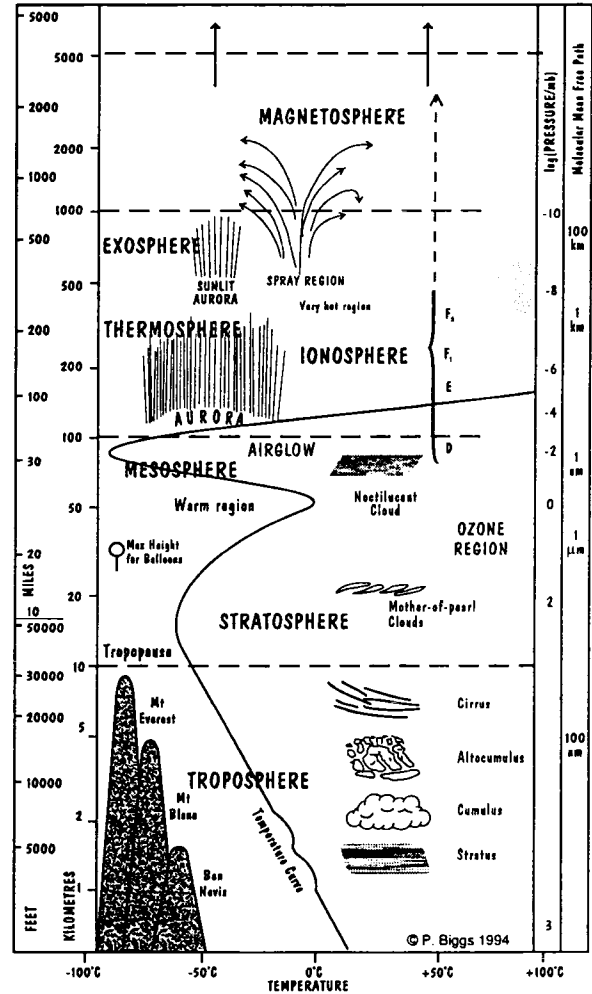
The hydrostatic equation is

$$\frac{dp}{p} = - \frac{dz}{(kT/mg)}$$

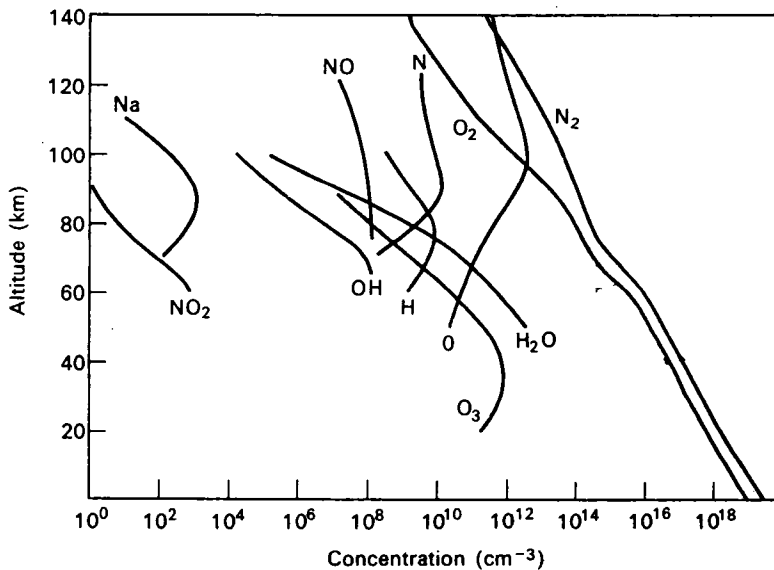
where  $p$  is the pressure, and  $z$  the altitude. For constant  $g$  and  $T$ , this equation can be integrated to

$$p = p_0 \exp(-mgz/kT)$$

The characteristic length  $H = kT/mg$  is called the *scale height*, and is about 6 to 9km.



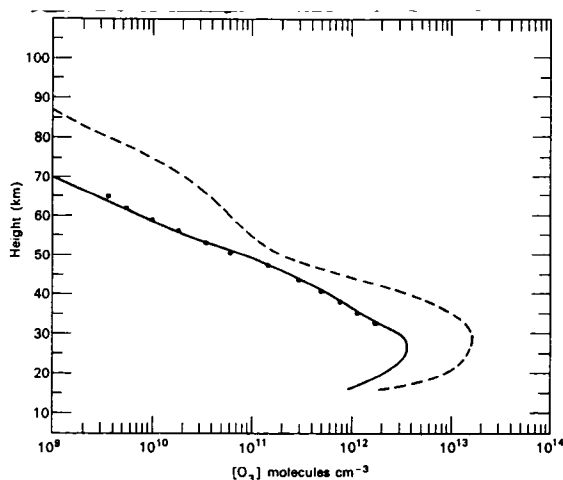
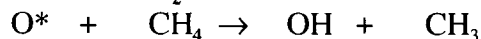
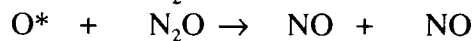
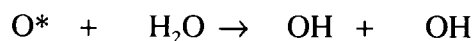
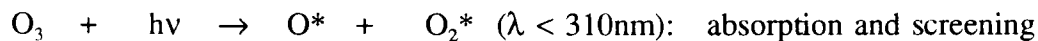
**1.5** The temperature structure in the Earth's atmosphere and the atmospheric regions.



**1.6** Representative concentration profiles of neutral species in the atmosphere

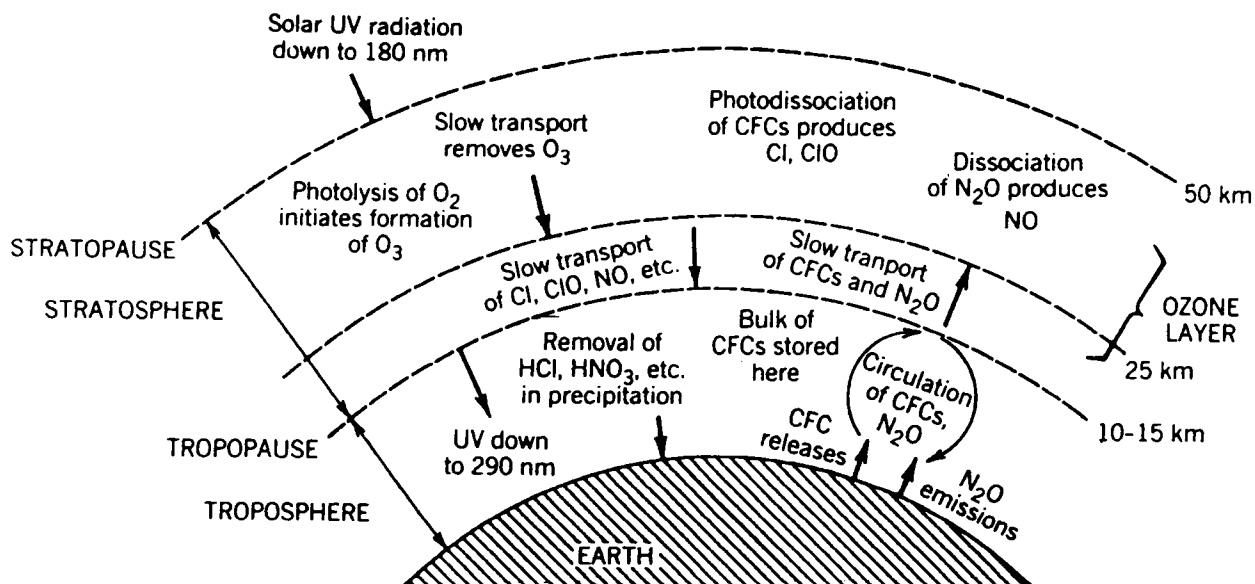
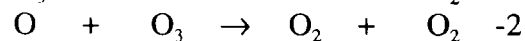
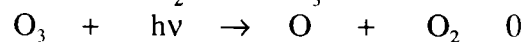
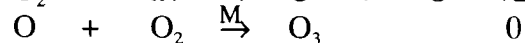
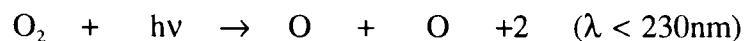
## Chemistry of Atmospheres: Notes for lecture 2

### 2.1 The importance of ozone



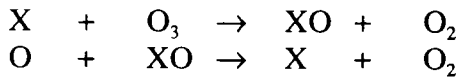
### 2.2 Ozone profile: measured and calculated (Chapman reactions only)

### 2.3 The Chapman reactions

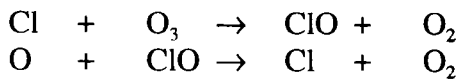
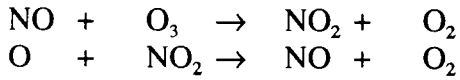
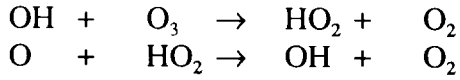


### 2.4 Chemistry involved in ozone formation and removal by trace catalysts

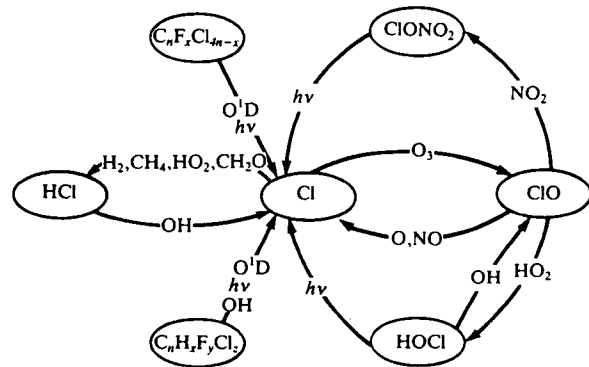
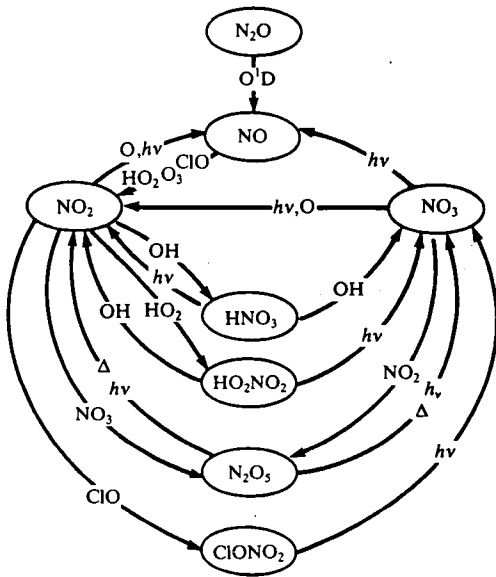
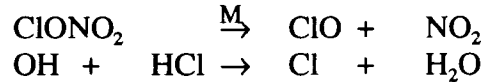
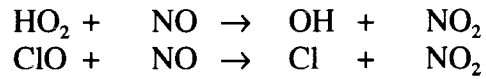
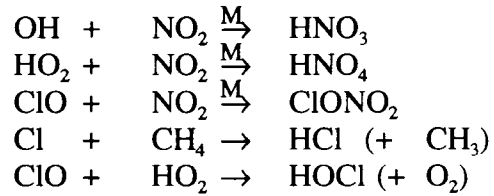
### 2.5 Catalytic cycles



X = OH, NO, Cl

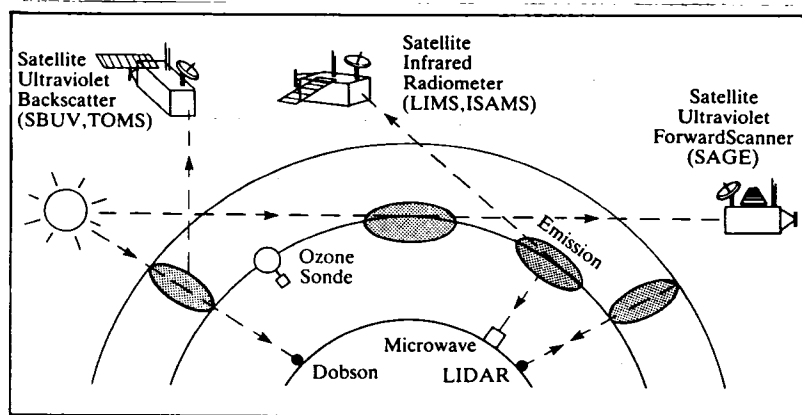


### 2.6 Reservoirs and cross cycles



### 2.7 Chemical cycles for NO<sub>x</sub> species

### 2.8 Chemical cycles for ClO<sub>x</sub> species



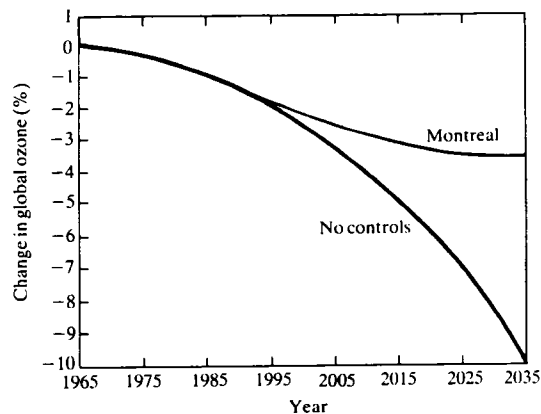
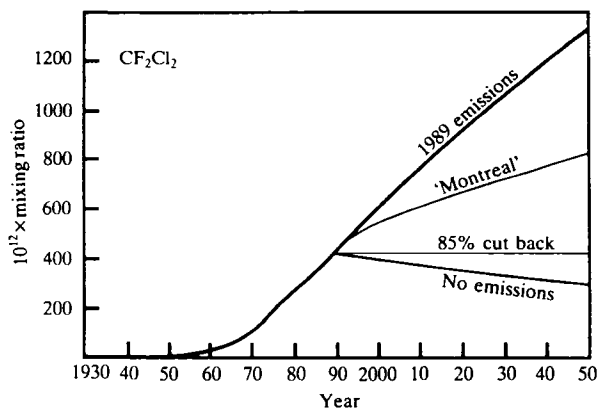
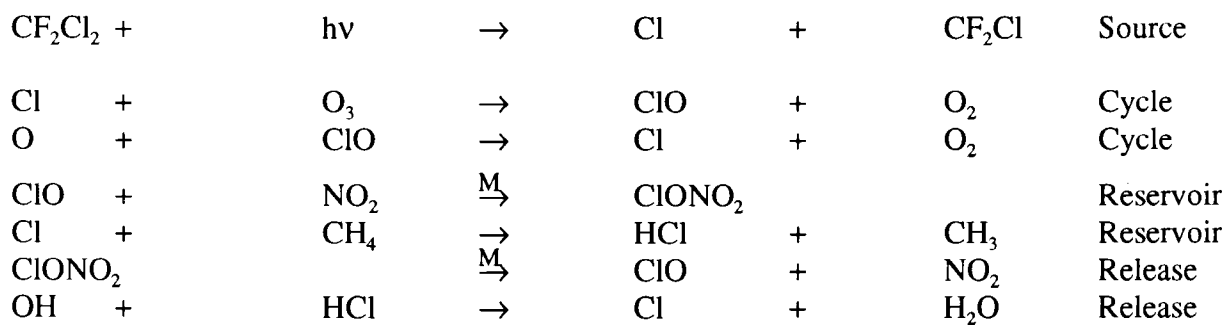
### 2.9 Some techniques for measuring stratospheric ozone concentrations

## Chemistry of Atmospheres: Notes for lecture 3

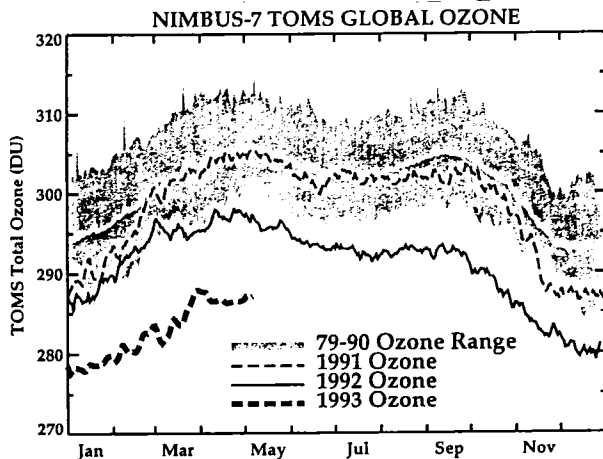
### 3.1 Sources of catalytic species

Family	X	XO	Sources	
HO <sub>x</sub>	OH	HO <sub>2</sub>	O( <sup>1</sup> D) + H <sub>2</sub> O	O( <sup>1</sup> D) + CH <sub>4</sub>
NO <sub>x</sub>	NO	NO <sub>2</sub>	Lightning; ionosphere	O( <sup>1</sup> D) + N <sub>2</sub> O
ClO <sub>x</sub>	ClO	ClO	CH <sub>3</sub> Cl + hv	CF <sub>2</sub> Cl <sub>2</sub> + hv, etc: MAN

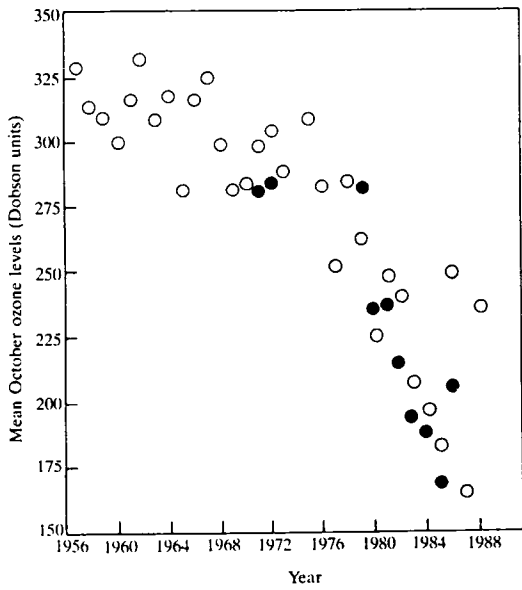
### 3.2 Reminder of chlorine chemistry



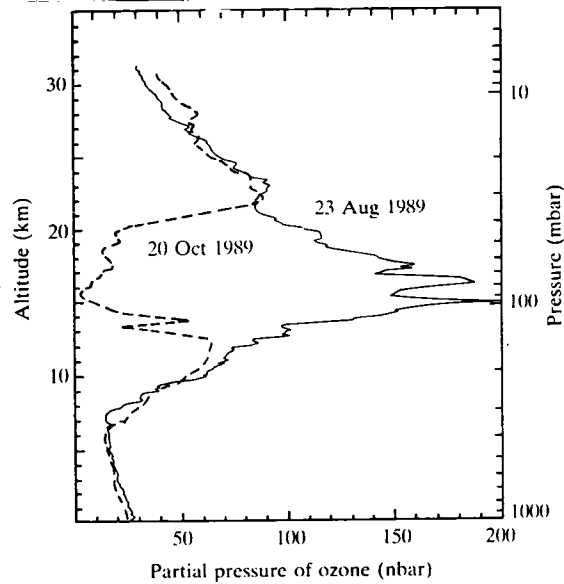
### 3.3 Projected time history of (a) CF<sub>2</sub>Cl<sub>2</sub> concentrations; and (b) changes of ozone concentrations



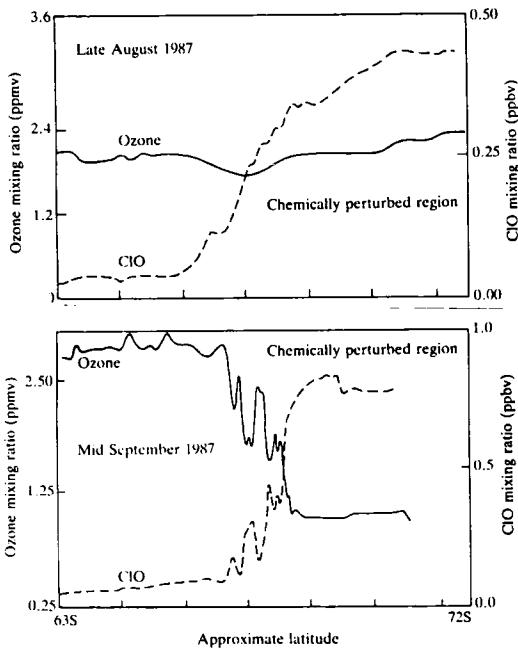
### 3.4 Recent TOMS measurements of zonally-averaged ozone, 30-60°N



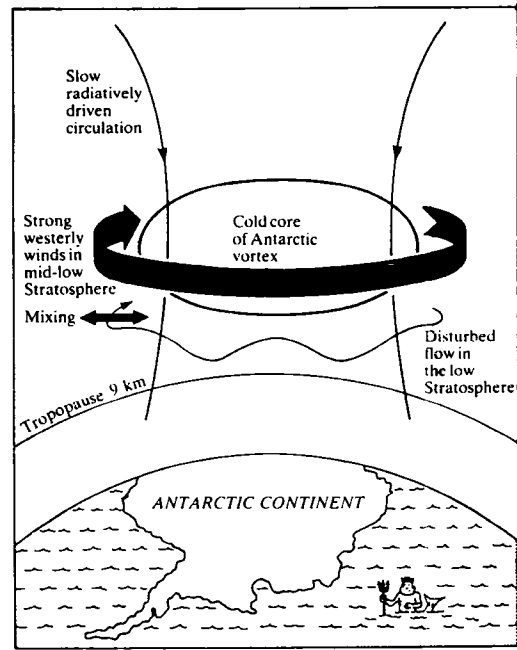
3.5 Decline in October [O<sub>3</sub>], Halley Bay



3.6 Ozone height profiles in Antarctic, 1989

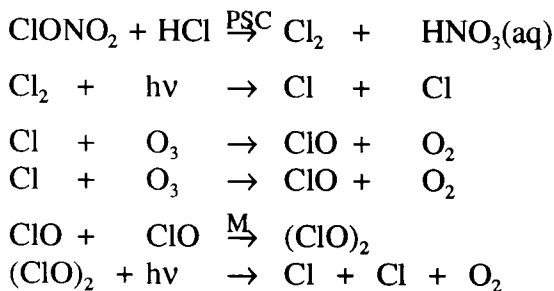


3.7 O<sub>3</sub> and ClO in August and September

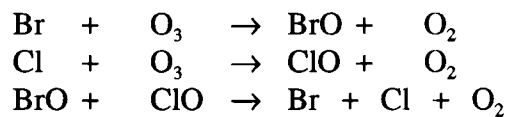
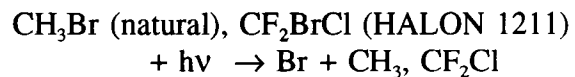


3.8 The Antarctic winter vortex

3.9 Ozone hole chemistry (chlorine)



3.10 Importance of bromine



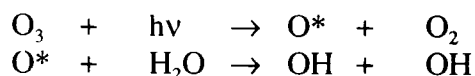
BrO + ClO → Br + OClO  
is only known stratospheric source of OClO

All reservoirs of Br (BrCl, HBr, BrONO<sub>2</sub>) are rapidly photolysed to regenerate X atoms.

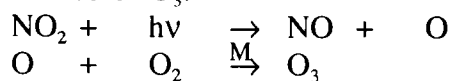
## Chemistry of Atmospheres: Notes for lecture 4

### 4.1 Initial oxidation steps by day

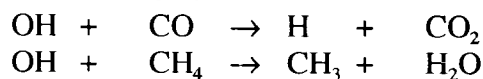
#### Initiation



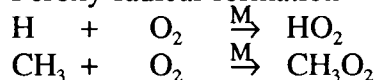
#### Source of O<sub>3</sub>:



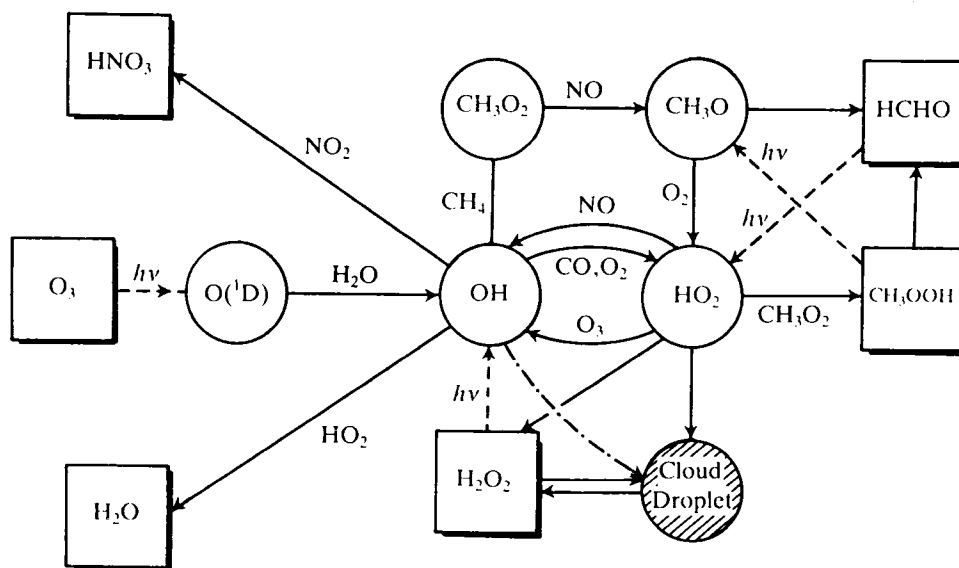
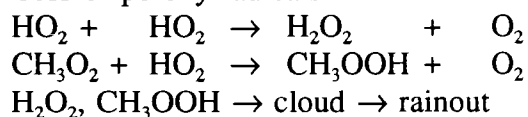
#### Attack of OH:



#### Peroxy radical formation



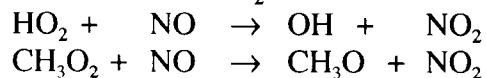
#### Loss of peroxy radicals



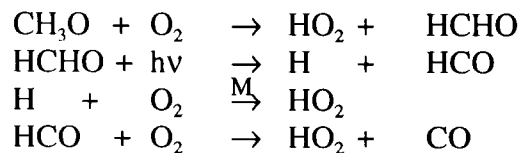
### 4.2 Chemistry of the troposphere

#### 4.3 Cyclic processes: NO

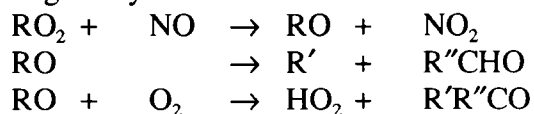
##### Conversion to NO<sub>2</sub>:



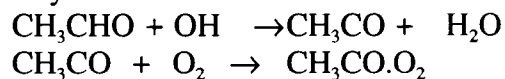
##### Fate of CH<sub>3</sub>O:

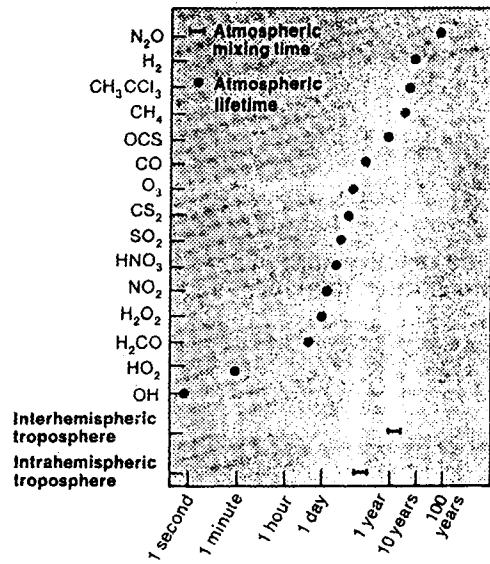
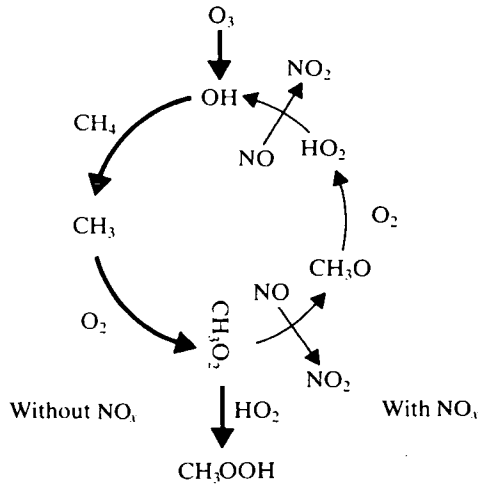


##### Higher hydrocarbons:



##### Acyl radicals:



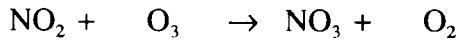


4.4 Importance of NO<sub>x</sub> in methane oxidation

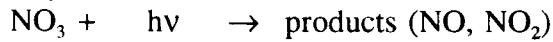
4.5 Atmospheric lifetimes of trace gases

4.6 The nitrate radical

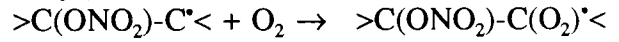
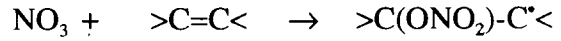
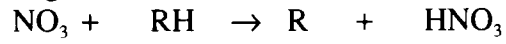
Formation:



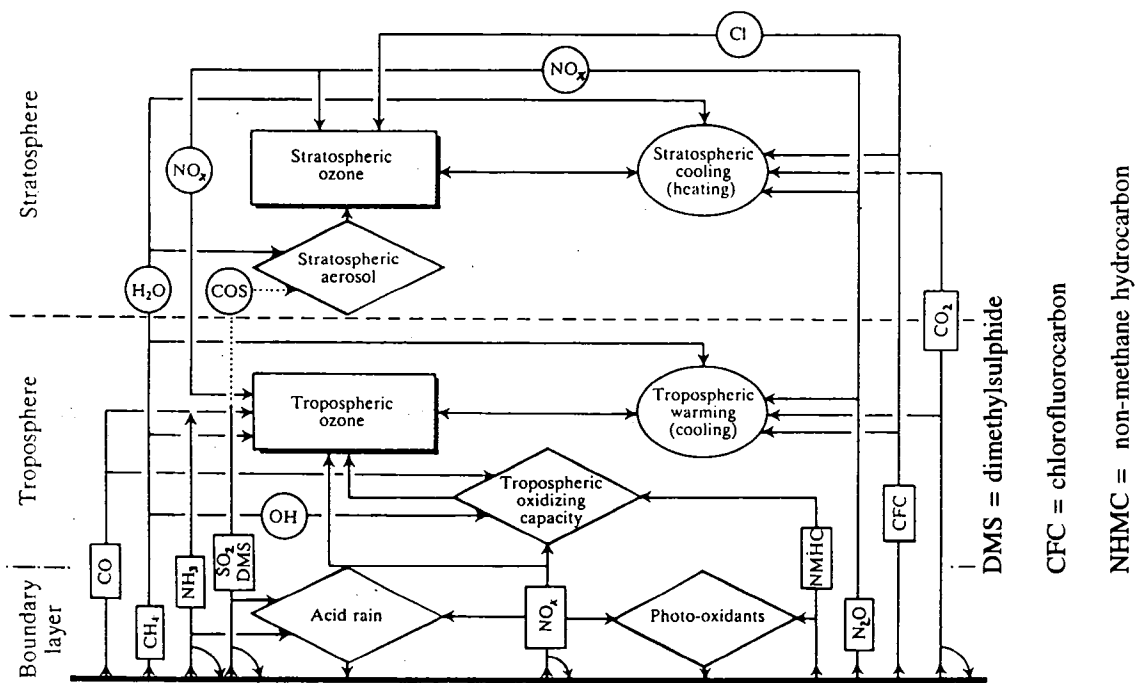
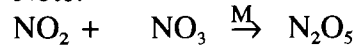
Daytime:



Night-time:



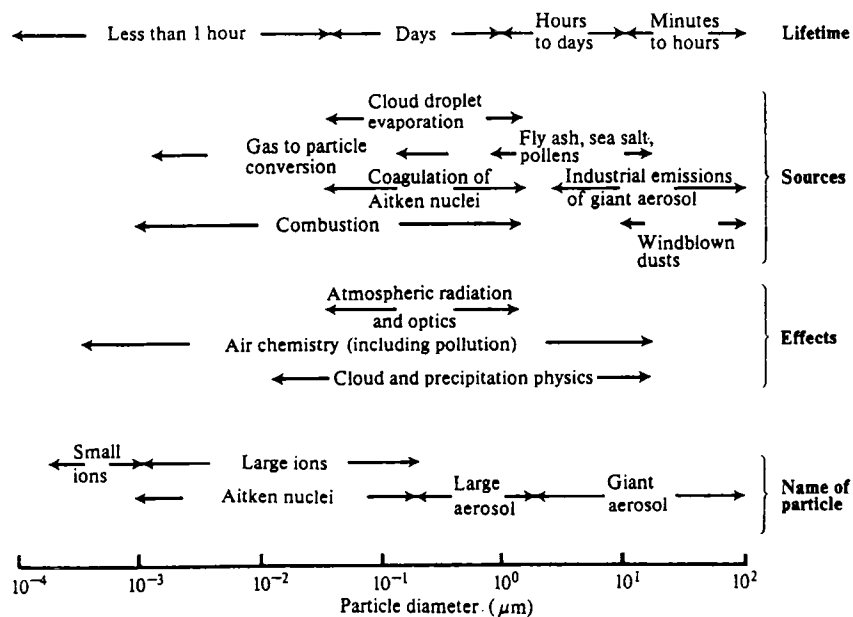
Note:



4.7 Feedbacks in atmospheric chemistry



## Chemistry of Atmospheres: Notes for lecture 5



### 5.1 Effects, sources and lifetimes of atmospheric particles

#### 5.2 Heterogeneous processes:

- (i) Condensation of single component;
- (ii) Reaction of gases to form particle;
- (iii) Reactions of gases on existing particle;
- (iv) Reactions within particles themselves.

Process (iii) - condensation of gases on pre-existing particles - is sometimes called *aerosol scavenging*. It affects bulk tropospheric chemistry by providing a sink for, eg,  $\text{HNO}_3$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{H}_2\text{O}_2$ ,  $\text{HO}_2$  and organic nitrates and peroxides. "Rainout" removes these aerosols.

In process (iv), clouds offer a medium for aqueous-phase reactions, and have large influence on troposphere: Three reasons:

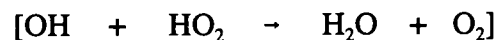
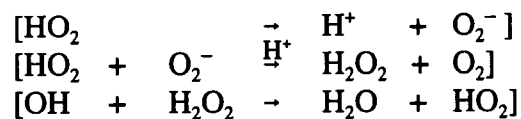
- (a) concentration in solution enhances rates (especially of 2nd order processes);
- (b) activation energies often less in solution than in gas phase; and, a **special feature**,
- (c) high solubility of certain key compounds such as  $\text{HO}_2$  and  $\text{N}_2\text{O}_5$ . Reactions of these species within droplet ensures that dissolution is irreversible and partitioning into aqueous phase is thus strongly favoured despite relatively small fractional volume of  $\text{H}_2\text{O}$  droplets (ca.  $10^{-6}$ )

#### 5.3 Examples of droplet chemistry

Hydration of anhydrides

$[\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_3]$   
most important. Rate limited by gas-phase diffusion and transfer through interface.

Radical sinks:



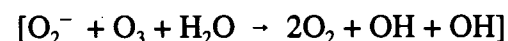
Thus oxidizing capacity of troposphere can be affected by droplet chemistry.

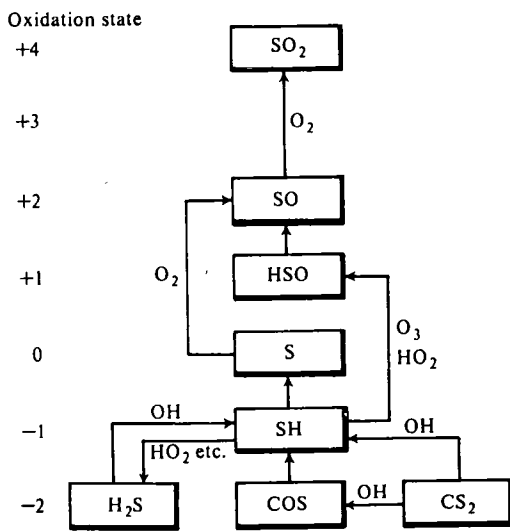
Because  $\text{HO}_2$  is highly soluble, and  $\text{NO}$  is relatively *insoluble*,  $\text{HO}_2$  and  $\text{NO}$  are separated by droplets, and the reaction



that ultimately yields  $\text{O}_3$  in the gas phase is inhibited.

There are also reactions that destroy  $\text{O}_3$ , such as

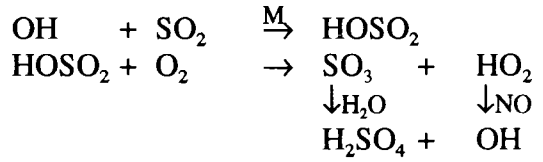




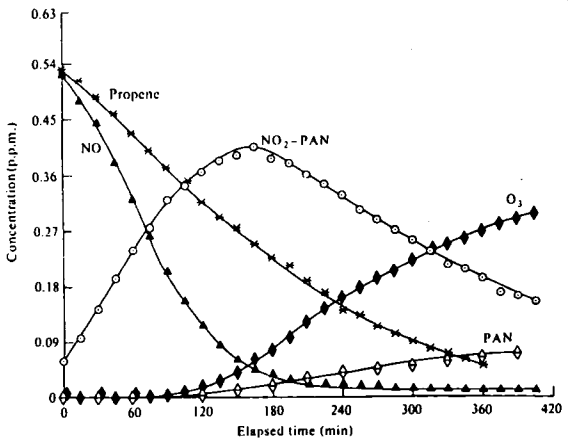
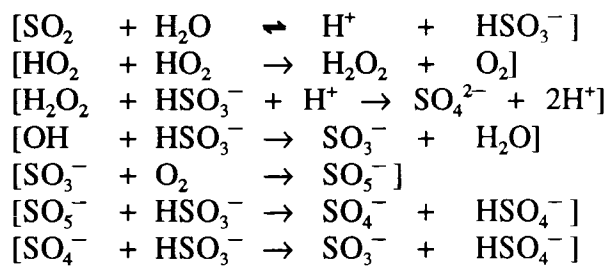
5.4 Oxidation of reduced S to SO<sub>2</sub>

5.5 Oxidation of S(IV) to S(VI)

Gas phase:



Droplets:



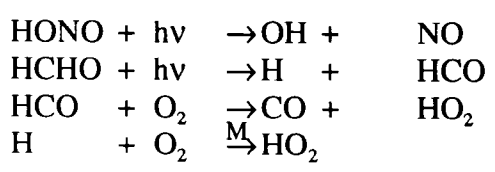
5.6 Smog chamber results

5.7 Photochemical smog chemistry

Exaggerated form of normal tropospheric oxidation: see notes 4.1 to 4.4 for the chemical steps.

Note that NO is converted NO<sub>2</sub>, which is a photochemical source of O<sub>3</sub>.

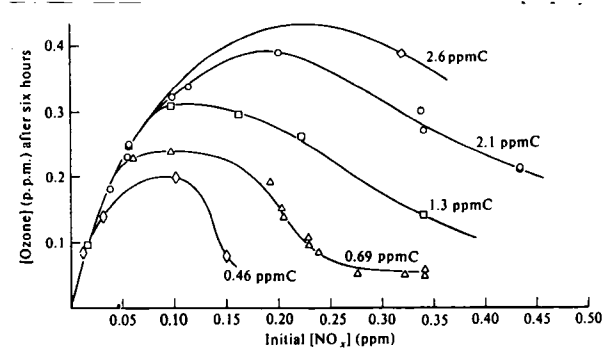
Aldehydes, which are intermediate oxidation products, and HONO are additional photochemical sources of radicals



5.8 Alkenes and PAN

Alkenes RCH=CH<sub>2</sub> react with OH to yield a radical RCHCH<sub>2</sub>OH that adds O<sub>2</sub> to form a peroxy radical RCH(O<sub>2</sub>)CH<sub>2</sub>OH. As with RO<sub>2</sub>, this radical converts NO to NO<sub>2</sub>, and itself yields an oxy radical, RCH(O)CH<sub>2</sub>OH that decomposes to RCHO and CH<sub>2</sub>OH. In the atmosphere, CH<sub>2</sub>OH reacts exclusively with O<sub>2</sub> to form HCHO and HO<sub>2</sub>. Finally, reaction of HO<sub>2</sub> with NO regenerates the starting radical, OH.

Peroxyacetyl nitrate, PAN (ethane peroxy nitric anhydride: CH<sub>3</sub>CO.O<sub>2</sub>.NO<sub>2</sub>) is formed as an adduct between NO<sub>2</sub> and the peroxyacetyl radical derived from CH<sub>3</sub>CHO (see end of note 4.3). CH<sub>3</sub>CHO is an intermediate in the oxidation of both saturated and unsaturated hydrocarbons.



5.9 Effect of altering HC/NO<sub>x</sub> ratio

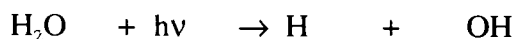
## Chemistry of Atmospheres: Notes for lecture 6

### 6.1 Mesosphere and thermosphere

Higher energy neutral chemistry and ionic processes become important.

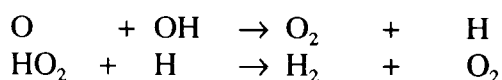
Photolysis of O<sub>2</sub> and gravitational separation means that O atoms begin to dominate over other neutral species (see note 1.6).

Wavelengths are short enough ( $\lambda < 175\text{nm}$ ) to photodissociate water



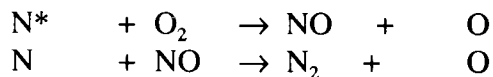
and an upward flow of H<sub>2</sub>O must compensate.

Reactions such as

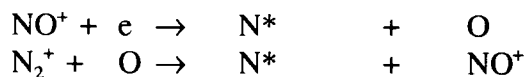


interconvert HO<sub>x</sub> species. H atoms escape from the exosphere.

Important reactions involving NO include



N\* here represents N(<sup>2</sup>D), which may be formed in processes such as



so that ion reactions affect neutral chemistry.

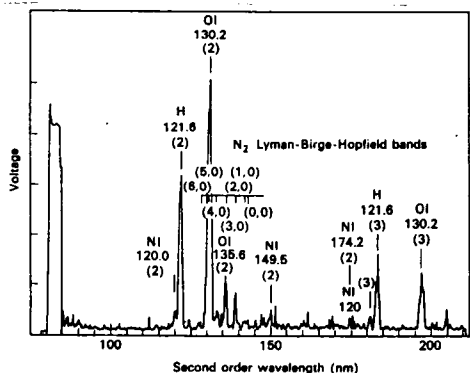
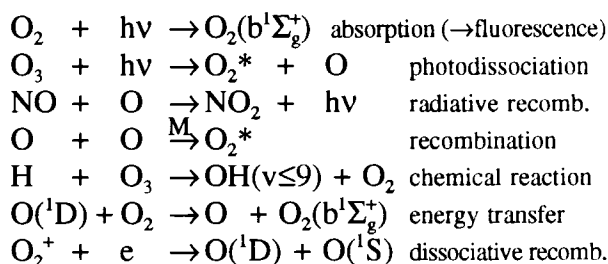
### 6.2 Airglow and aurora

*Airglow* results from the interaction of atmospheric constituents with one another and with sunlight. *Auroras* are more intense, but are mainly observed near the magnetic poles, and are excited by impact of energetic electrons and protons arriving from the Sun.

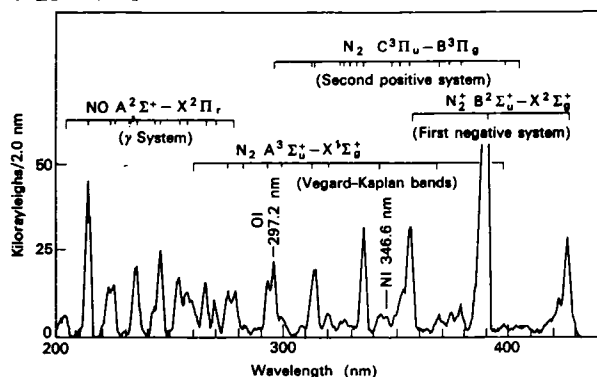
Notes 6.3 and 6.4 below reproduce parts of the UV airglow. Other very important components in the visible and near-ir include

$\lambda/\text{nm}$	Species	Name of emission
557.7	O( <sup>1</sup> S)	"Auroral" green line
589.3	Na( <sup>2</sup> P)	Sodium resonance line
630.0	O( <sup>1</sup> D)	Oxygen red line
761.9	O <sub>2</sub> (b <sup>1</sup> $\Sigma_g^+$ )	Atmospheric band
1270	O <sub>2</sub> (a <sup>1</sup> $\Delta_g$ )	IR atmospheric band
2800 etc	OH ( $v \leq 9$ )	Meinel bands

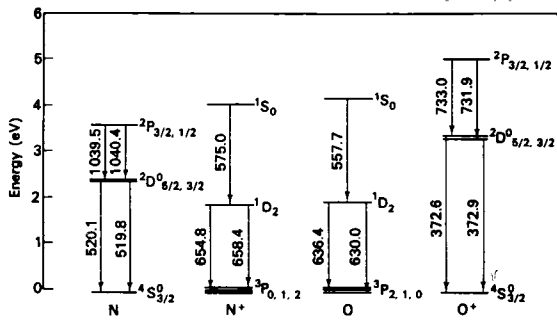
Excitation mechanisms include



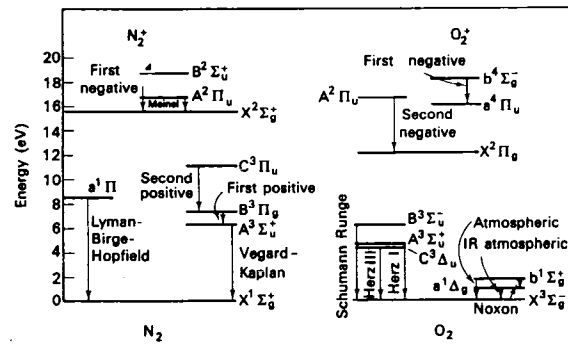
### 6.3 UV dayglow: 110-210nm



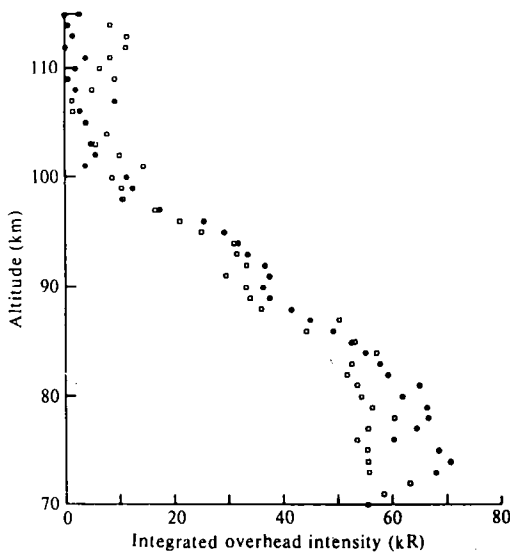
### 6.4 UV dayglow: 200-430nm



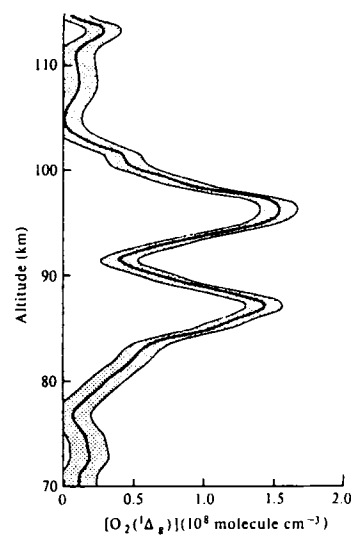
6.5 Energy levels of atoms and atomic ions (nb 1eV = 8065.7cm<sup>-1</sup> = 96.5kJ mol<sup>-1</sup>)



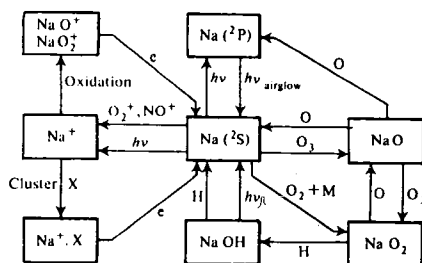
6.6 Energy levels of molecules and molecular ions



6.7 Nightglow IR atmospheric band



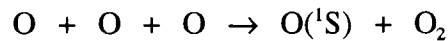
6.8 [O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>)] derived from profile of fig. 6.7



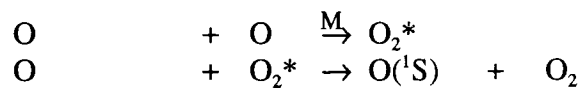
6.9 Mesospheric chemistry of sodium

6.10 Nightglow oxygen emission chemistry

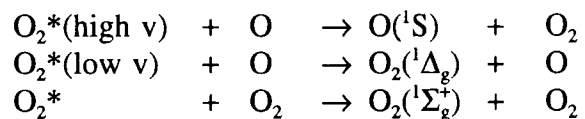
Chapman:



Barth:



Generalized scheme:



Perhaps O<sub>2</sub>\* can be equated with O<sub>2</sub>(c<sup>1</sup>Σ<sub>u</sub><sup>-</sup>)