CH2501 – Chemistry of the Atmosphere

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1. INTRODUCTION: Molecules in the Atmosphere

The goal of this module is to provide an introduction to the composition of the Earth's atmosphere and the chemistry that underpins it. We will also look at how human activity impacts the atmosphere and the wider environmental consequences of this activity.

2. ROLES PLAYED BY THE ATMOSPHERE

The atmosphere is composed of 78.1% N_2, 21.0% O_2, 0.9% Ar, 0.04% CO_2 and smaller amounts of other gases. The N_2 in the atmosphere, aside from providing an end nitrogen source for living things to make proteins (not directly, see below), it serves as an important gas for the dilution of the oxygen content of the atmosphere. Without it, organic matter would too rapidly burn at the Earth's surface. The O_2 is of course essential for respiration and therefore life. It is also a constituent component of combustion. CO_2 is a required compound in plant photosynthesis. It also contributes to preventing heat from the Earth's surface from escaping and so helps to moderate the temperature. In a similar fashion, the water vapour (0-4%) also prevents heat loss from the Earth as part of a natural greenhouse effect that is essential for life on Earth. Atmospheric molecules in upper atmosphere absorb harmful UVC radiation to undergo photochemistry. As a function of this photochemistry, temperature gradients develop that are dependent on altitude. These temperature gradients also give rise to the weather. A trace gas worth noting is O_3, which forms a layer in the atmosphere that provides further protection to harmful UVB and some UVA radiation.
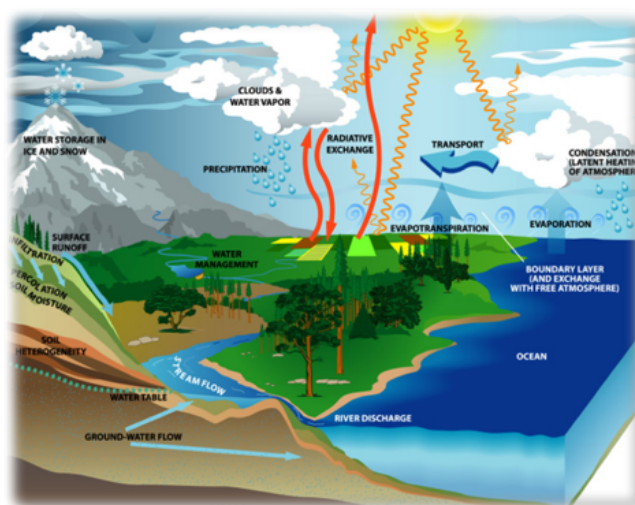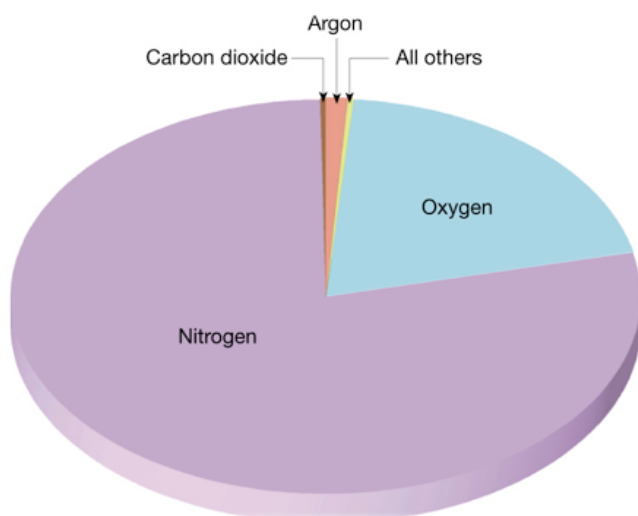

2.1 THE ATMOSPHERE AS A RECYCLER OF ELEMENTS

The atmosphere contributes to the recycling of water, carbon, nitrogen and oxygen and, partly sulfur, phosphorus, and as salt spray, NaCl.

2.1.1 THE ATMOSPHERE AS A RECYCLER OF ELEMENTS: WATER CYCLE

Nearly all of the water on Earth is salty (97.5%) and found in the oceans. Of the remaining water, 99 percent is locked as underground water or ice. This leaves < 1% of fresh water present in lakes and rivers. Fresh water supply is an essential component of nearly all ecosystems (excluding sea water-based ecosystems). Humans have developed technologies to exploit fresh water supplies and so increase water availability, such as digging wells to harvest groundwater and storing rainwater. Humans have

also invented techniques for desalination to obtain drinkable water from the ocean, but this is very energy intensive. The supply of fresh water continues to be a major economic, political and sociological issue in modern times.

The water cycle is driven by the Sun's energy as it warms the oceans and other surface waters. In terms of the water cycle, important processes include: evaporation (water to water vapour) and sublimation (ice to water vapour); condensation (into clouds) and precipitation (rain, hail or snow); subsurface water flow; snowmelt and surface runoff; stream flow. In most natural terrestrial environments rain encounters vegetation before it reaches the soil surface. A significant percentage of water evaporates immediately from the surfaces of plants. The roots of plants will take up most water in the soil. The plant will use some of this water for its own metabolism, and some of that will find its way into animals that eat the plants, but much of it will be lost back to the atmosphere through a process known as evapotranspiration. Water in the soil that is not taken up by plants and that does not evaporate is able to percolate into the subsoil and bedrock. Here it forms groundwater. Most groundwater reservoirs, or aquifers, are the source of drinking or irrigation water drawn up through wells. In many cases these aquifers are being depleted faster than they are being replenished by water percolating down from above. Rain and surface runoff are major ways in which minerals, including carbon, nitrogen, phosphorus, and sulfur, are cycled from land to water.
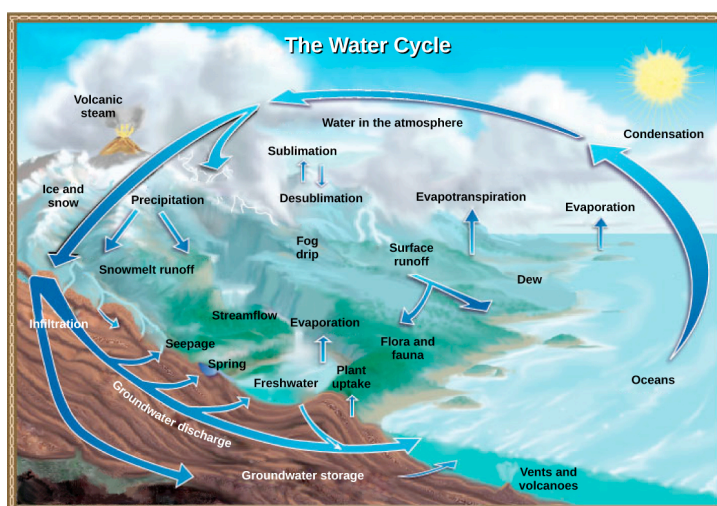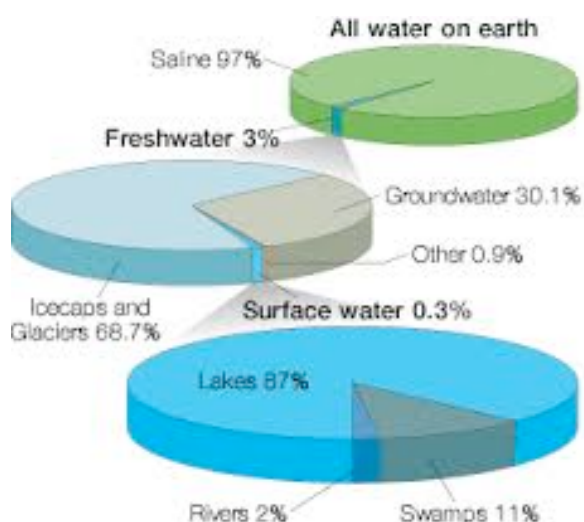
The residence time of water in the atmosphere is short compared to the mixing time, which itself is defined as the amount of water in atmosphere/amount entering (or leaving) and lasts for several years.

Some stats to justify this claim:
$7x10^{14}$ mol of H_2O in the atmosphere and approx. 9.5×10^{19} mol in seas/lakes
Rate of water evaporation: from the oceans 2.2×10^{16} mol y^{-1}; Lakes and rivers 3.5×10^{15} mol y^{-1}
Rate of precipitation: oceans 1.9×10^{16} mol y^{-1}; Land 5.5×10^{15} mol y^{-1}

So residence time = $7x10^{14}$ mol / (1.9×10^{16} + 5.5×10^{15}) mol y^{-1} = 0.03 y = **11 days,** which is short compared to mixing time

2.1.1 *THE ATMOSPHERE AS A RECYCLER OF ELEMENTS: CARBON CYCLE*

The Earth is composed of carbon-based life forms. The carbon-containing molecules possess embedded energy, which is released upon combustion. Much of this embedded energy in terms carbon reservoirs
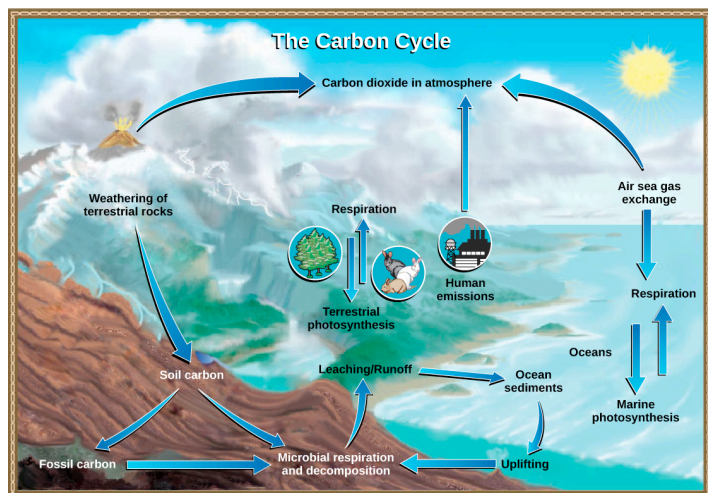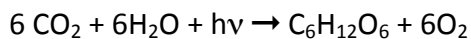
is the result of decomposition of dead animals and plants, and remains trapped as fossilized carbon, which humans use as fossil fuels. As a function of the use of these fossil fuels, the amount of carbon dioxide, which is an end product of combustion, in our atmosphere has increased as the fuels are burned. This increase in carbon dioxide has been associated with climate change and is a major environmental concern worldwide. Photosynthesis is an important biological process that converts atmospheric CO_2 into high-energy compounds such as glucose. The bonds within glucose are chemical stores of the energy from sunlight. The organisms that do this are called *autotrophs*. This energy is released by organisms in a process called respiration.

Most terrestrial autotrophs obtain their carbon dioxide directly from the atmosphere, while marine autotrophs acquire it in the dissolved form (HCO_3^-). No matter how the carbon dioxide is acquired, a byproduct of fixing carbon in organic compounds is oxygen. Photosynthetic organisms are responsible for maintaining approximately 21 percent of the oxygen content of the atmosphere that we observe today.

Plants
   Day time – photosynthesis to carbohydrates (sugars, starch)
   $6 CO_2 + 6H_2O + h\nu \rightarrow C_6H_{12}O_6 + 6O_2$
   Nighttime – respiration
 $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$
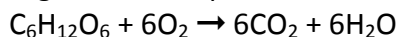
Animals – respiration only

The partners in biological carbon exchange are the *heterotrophs*. Heterotrophs acquire the high-energy carbon compounds from the autotrophs by consuming them (i.e. eating) and breaking them down by respiration to obtain cellular energy, such as ATP. The most efficient type of respiration, aerobic respiration, requires oxygen obtained from the atmosphere or dissolved in water. Thus, there is a constant exchange of oxygen and carbon dioxide between the autotrophs (which need the carbon) and the heterotrophs (which need the oxygen). Autotrophs also respire and consume the organic molecules they form: using oxygen and releasing carbon dioxide. They release more oxygen gas as a waste product of photosynthesis than they use for their own respiration; therefore, there is excess available for the respiration of other aerobic organisms. Gas exchange through the atmosphere and water is one way that the carbon cycle connects all living organisms on Earth.

Excrement and rotting dead organic plant and animal matter return nutrients to land (not via atmosphere). Note human sewage washed to sea – disrupts natural cycles for recycling nutrients. Human behaviour also disrupts the natural return of minerals and carbon content to the biosphere (e.g., the raising of livestock). In the atmosphere, carbon is stored primarily as $CO_2(g)$. The amount of atmospheric CO_2 is dependent on the amount of dissolved CO_2 in the oceans, which itself is reactive and

sensitive to pH and ion concentration in the oceans (e.g., $CaCO_3$). The largest carbon reservoirs on Earth are the limestone deposits. Carbon can also enter the atmosphere through volcanic eruption

2.1.2 *THE ATMOSPHERE AS A RECYCLER OF ELEMENTS: NITROGEN CYCLE*
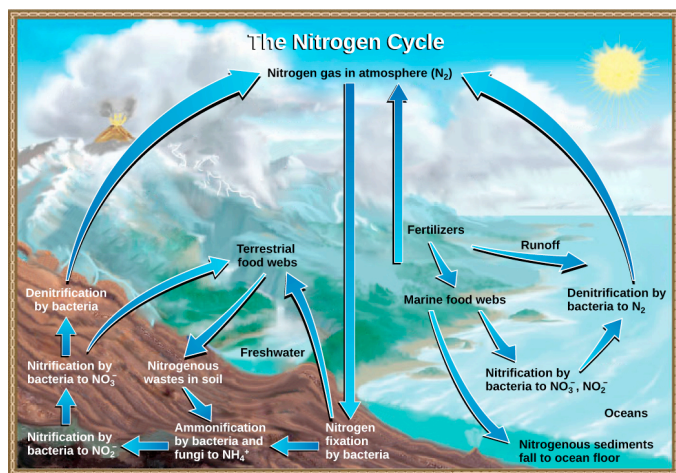
Getting nitrogen into living organisms is difficult. Plants and phytoplankton are not equipped to incorporate nitrogen from the atmosphere (where it exists as tightly bonded, triple covalent N_2) even though this molecule comprises approximately 78 percent of the atmosphere.

Nitrogen is incorporated into living organisms through nitrogen fixation processes mediated by bacteria wherein $N_2(g)$ is converted first into NH_4^+ (***ammonification***), which is then oxidized into NO_2^- (***nitrification***) and NO_3^-. The cycle is completed when nitrates are converted to N_2 (***denitrification***).

Ammonification: Cyanobacteria are able to "fix" nitrogen (from nitrogen gas) into ammonia (NH_3) that can be incorporated into the macromolecules of the organism. Rhizobium bacteria also fix nitrogen and live symbiotically in the root nodules of legumes (such as peas, beans, and peanuts) and provide them with the organic nitrogen they need. Free-living bacteria, such as Azotobacter, are also able to fix nitrogen.

Nitrification: Nitrifying bacteria such as Nitrosomonas are responsible for this step.

Denitrification: Bacteria, such as Pseudomonas and Clostridium, convert the nitrates into nitrogen gas, thus allowing it to re-enter the atmosphere.

Humans release nitrogen into the atmosphere through:
> ➢ Combustion of fossil fuels (nitrogen oxides)
> ➢ The use of fertilizers

Other sources of atmospheric nitrogen include acid rain (HNO_3) and greenhouse gases (N_2O). Nitric acid can be formed as a result of lighting discharges, which oxidize N_2.

2.1.3 *THE ATMOSPHERE AS A RECYCLER OF ELEMENTS: PHOSPHORUS CYCLE*

Phosphorus is essential for living processes and biomacromolecules such as DNA. It is naturally occurs as PO_4^{3-}. Phosphate runoff due to human activity (fertilizers and sewage) and weathering from rocks and minerals are two main sources of phosphorus in the environment. Volcanic ash is also high in phosphates as is ocean sediment. Average oceanic residence time for phosphate ranges from 20 000 to 100 000 y. An excess of phosphorus (and nitrogen) result in algae blooms, which deplete oxygen and lead to aquatic dead zones.
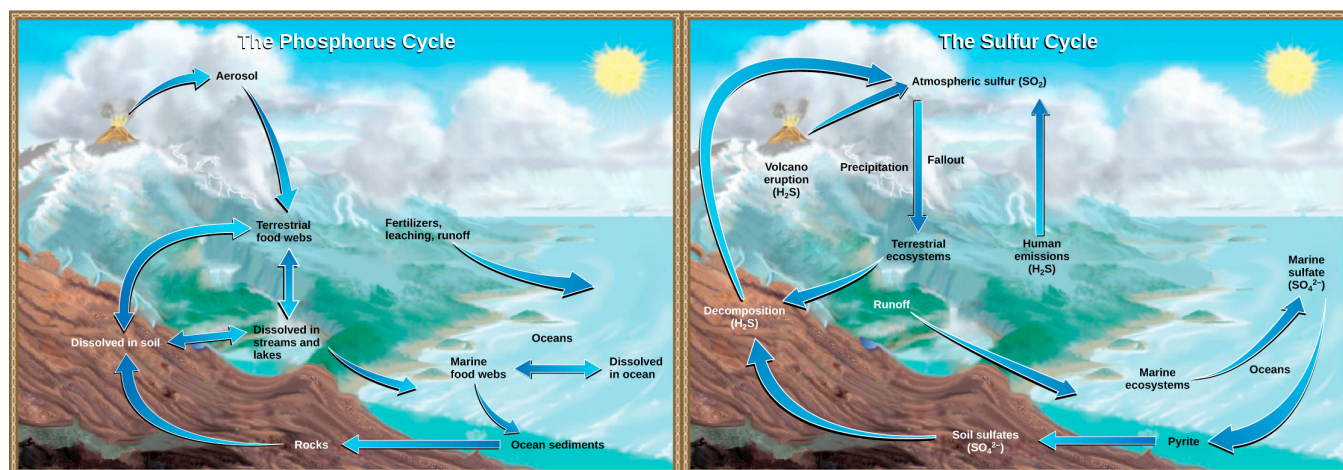
2.1.3 *THE ATMOSPHERE AS A RECYCLER OF ELEMENTS: SULFUR CYCLE*

Sulfur is also an essential element due to its presence in the amino acids cysteine and methionine. Atmospheric sulfur is found in the form of SO_2, which, after combined with rain, forms H_2SO_3. SO_2 can oxidize to SO_3, which wen combined with rain, forms H2SO4.

SO_2 enters the atmosphere through:
- ➤ Decomposition of organic matter (released at H_2S)
- ➤ Volcanic activity (fallout)
- ➤ Burning of fossil fuels (released as H_2S, especially coal)

2.1.4 *THE ATMOSPHERE AS A RECYCLER OF ELEMENTS: SUMMARY*

The elements listed above constitute some of the important elements for humans. Below is a table that summarizes the amount of each of these elements in the human body and whether the atmosphere plays a role in their recycling.
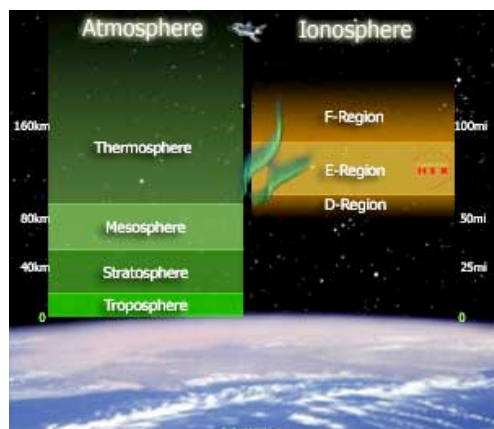
Element	Body level/ppm	Recycled by atmosphere?
O C	6.5×10^5 1.8×10^5	Respiration, photosynthesis, Rain
H	1×10^5	Rain
N	3×10^4	Nitrogen cycle
Ca	1.5×10^4	No
P	1.0×10^4	
S	2.5×10^3	Partly Me_2S, H_2S
K	2×10^3	No
Cl Na	1.5×10^3 1.5×10^3	Partly (wind-borne sea water)

Fe,Zn,Si,Cu,I,Mn,V,Co,Mo	Varies < 60	No

2.2 CHEMISTRY IN THE UPPER ATMOSPHERE: PHOTOCHEMISTRY

The atmosphere is composed of many distinct zones delineated by their altitude. The atmosphere extending from 550 km out to perhaps 10,000 km is known as the exosphere or outer thermosphere, which gradually merges into space. The upper atmosphere is composed of the thermosphere, the upper region of which is known as the ionosphere. Descending in altitude there is next the mesosphere followed by the stratosphere and finally the troposphere.

The international space station is located in the thermosphere.

There are two important photochemical processes in the upper ionosphere. They are **photodissociation** and **photoionization**.

Photodissociation: Energy to reach dissociation limit (homolytic bond cleavage)

e.g., $N_2 + h\nu \rightarrow 2N$ ΔH°: +945 kJ mol^{-1}

Molecules must be able to absorb light at these wavelengths (i.e. have an absorption band at the right energy) in order to photodissociate. N_2 does not have strong absorption bands in UVC and so it is difficult to photodissociate.

It is possible to determine the threshold energy required for photodissociation. This calculation is based on the conservation of energy. The energy of the photon used must be greater than the threshold energy, otherwise known as the bond dissociation energy (BDE). It is important to know that for photochemical processes only one photon is absorbed per molecule.

So for N_2, each photon must have energy ΔH° / N_A = 945,000 J·mol^{-1} / 6.02 x 10^{23} = 1.57 x 10^{-18} J
Now photons of wavelength λ have energy, E = hν = hc/ λ and so λ = hc/E

So in this case λ = hc/E = 6.6 x 10^{-34} m^2·kg·s^{-1} x 3x10^8 m·s^{-1}/ 1.57 x 10^{-18} J = **126 nm** – in the UVC region
For O_2 ΔH° =+498 kJ·mol^{-1}, which corresponds to **240 nm** in the UVC

The ultra-violet (UV) part of the electromagnetic spectrum is divided into three sub-zones, with UVC being the highest energy radiation.

UVA: 400 nm - 320 nm
UVB: 320 nm - 290 nm
UVC: 290 nm - 100 nm

Another possibility is **photoionization**, which involves the he ejection of electrons from atoms, ions or molecules:

e.g.,
Of the atoms O + hv → O$^+$ and N + hv → N$^+$
Of molecules: N$_2$ + hv → N$_2$$^+$ or O$_2$ + hv → O$_2$$^+$

A molecule does not need an absorption band in order to photoionize.

It is possible to determine the threshold energy required for photoionization. Photoionization mechanistically follows the following reaction:

e.g., A + hv →   A$^+$ + e-

This calculation is based on the Conservation of Energy So: E(A) + hv = E(A$^+$) + E (e$^-$)

Since the e$^-$ possesses only kinetic energy: KE = hv − [E(A$^+$) − E(A)] = hv − BE, where BE is the binding energy. This equation is known as the Einstein equation.

BE is usually measured in electron volts, eV. 1 eV is one electron moved through one volt = 1.6 x 10^{-19} J

The threshold energy occurs when <u>KE = 0 and hv = BE.</u>

For O$_2$ the BE of the highest orbital electron energy is 12 eV, So 12 eV x 1.6x10^{-19} J˙eV-^{1} = 1.92x 10^{-18} J,

So the max wavelength λ = hc/BE = 6.6 x 10^{-34} J˙s x 3x10^8 m˙s^{-1}/ 1.92x 10^{-18} J = **103 nm**

The thresholds for the O atom and the N$_2$ molecule are at **91.1 nm and 79.6 nm**, respectively.

Most O$_2$ photodissociates in upper atmosphere, so O$_2$$^+$ only is really formed by electron transfer reactions:
O$^+$ + O$_2$ → O + O$_2$$^+$ and N$_2$$^+$ + O$_2$ → N$_2$$^+$ + O$_2$$^+$

Photoionization is integral to Photoelectron spectroscopy (PES) where the KE is measured to determine the binding energies of the electrons in atoms and molecules.

Photoionization processes are also responsible for the ultimate formation of NO$^+$, which itelf can contribute to the destruction of the ozone layer lower down in the atmosphere.

O$^+$ + N$_2$ → NO$^+$ + O$_2$$^+$
N$_2$$^+$ + O → NO$^+$ + N
O$_2$$^+$ + N → NO$^+$ + O

Below are the amounts of heat absorbed as a consequence of common photoionization and photodissociation processes in the thermosphere. All oxygen in the thermosphere is atomic.

N$_2$+ hv → 2N   ΔHº: +945 kJ mol^{-1}
N + hv → N$^+$ + e   ΔHº: +1400 kJ mol^{-1}
O$_2$ + hv → O$_2$$^+$ + e   ΔHº: +1160 kJ mol^{-1}

$O_2 + h\nu \rightarrow 2O$ ΔH°: +498 kJ mol^{-1}

2.2.1 CHEMISTRY IN THE UPPER ATMOSPHERE: PHOTOELECTRON SPECTROSCOPY (PES)

Recall that photoionization is a measure of the energy necessary to eject an electron from an atom, ion or molecule and has an energy, $h\nu$. This energy corresponds to the energy of the orbital from which the electron was ejected.

The Franck-Condon principle states that electrons move faster than nuclei. Therefore, the nuclei do not move when the electron is ejected and changes in energy take place vertically on the energy-distance diagram (see red arrow in diagram).

For the example of the photoionization of H_2 on the right, as the H_2^+ ion is more weakly bound (BO: 0.5) and has therefore a longer equilibrium H-H bond length, its potential well is displaced and the ion is formed in **a vibrationally excited state**.

This gives rise to spacing between lines of emitted electron energies of the H-H frequency in H_2^+.

The H-H stretch in H_2^+ (2200 cm^{-1}) is lower than in H_2 (4000 cm^{-1}) as we have a weaker H-H bond.

If we now interpret the photoelectron spectroscopy of O_2 it has three sets of peaks corresponding to ionisation of the three most weakly bound electrons to give ions with electrons lost from σ_g, π_u, π_g orbitals (see figure below).
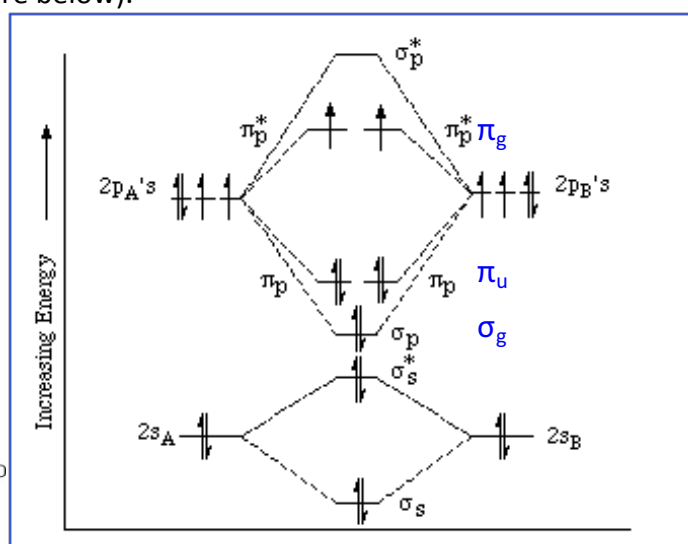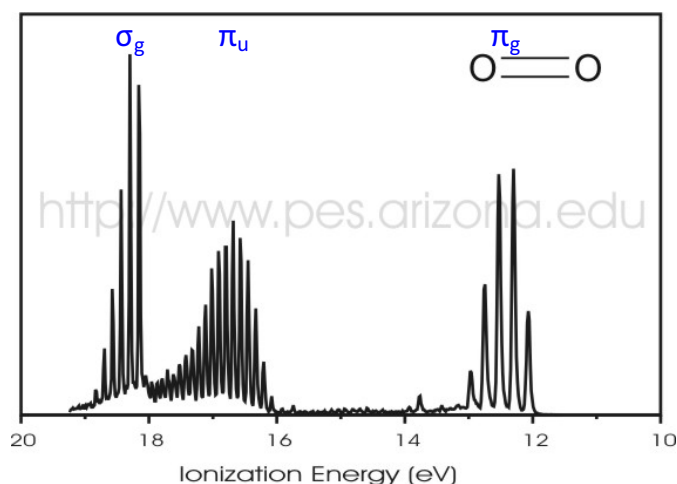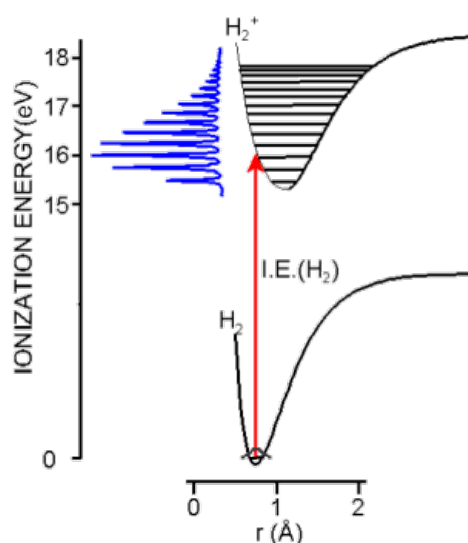
The lowest energy line shows vibrational fine structure with ν (O-O) (O-O stretching frequency 1868 cm^{-1}) higher (more widely spaced peaks) than that of neutral O_2 (1580 cm^{-1}), indicating bond is stronger in O_2^+ (BO=2.5 compared to 2.0 in O_2). The PES spectrum confirms that the HOMO in O_2 (and F_2) is anti-bonding (π_g) because removal of an electron from this orbital leads to a stronger bond.

2.2.2 CHEMISTRY IN THE UPPER ATMOSPHERE: THE AURORAS

The Auroras (both Borealis in the northern hemisphere and Australis in the southern hemisphere are caused when high-energy particles from Solar flares collide with O and N atoms or O_2 and N_2 molecules in the thermosphere, resulting in the formation of an electronic excited state in these.

O emits red (630 nm) in the upper atmosphere or yellow-green (558 nm) in the lower atmosphere. N_2 emits in the red (661-686 nm). N_2^+ emits in blue and purple (391-470 nm) in the lower atmosphere (60-90 Km)

St Andrews, **Nov. 20, 2003**

2.3. ANATOMY OF THE ATMOSPHERE

The sun is a black body radiation source with a temperature about 5900 ^{o}C. The energy of the sun hitting the outer atmosphere therefore shows a distribution as on the figure to the right. The sun radiates from high energy ultra-violet (short wavelength) to the infrared.
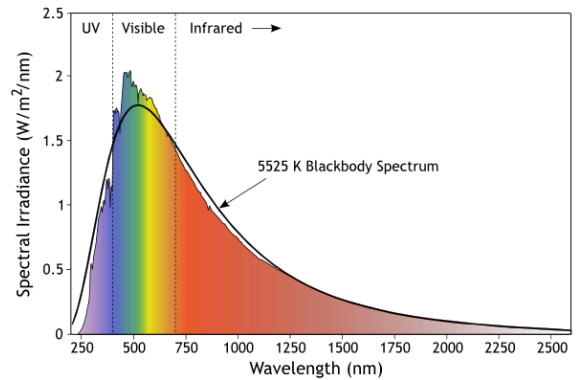

Based on the different photochemical processes occurring at different altitudes in the atmosphere, different parts of the electromagnetic spectrum get absorbed/reflected, resulting in gradients of temperature. Below, we will investigate in more detail what is the cause of the temperature gradients and associated weather phenomena.
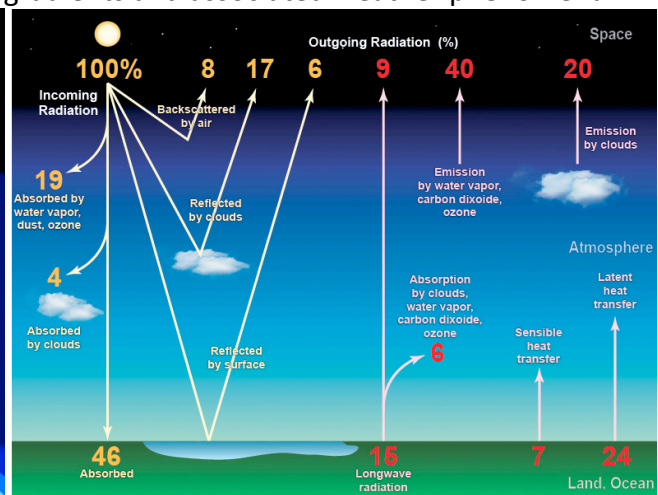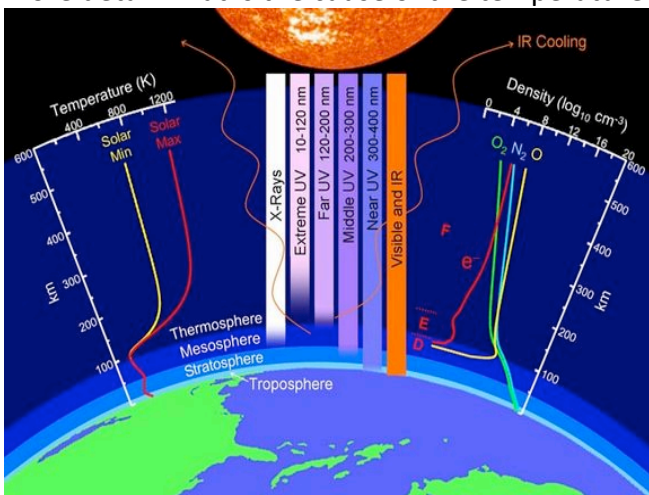
2.3.1 ANATOMY OF THE ATMOSPHERE: THERMOSPHERE

The upper boundary between the exosphere and the thermosphere is known as the thermopause. In exosphere, gases can escape into space if have escape velocity.

The large number of free electrons in the ionosphere (there is a long time between collisions so they have a long life) allows the propagation of electromagnetic waves. Radio signals - a form of electromagnetic radiation - can be "bounced" off the ionosphere allowing radio communication over long distances. Oliver Heaviside (1850-1925) along with Arthur Kennelly proposed the existence of the ionosphere, also known as the Kennelly-Heaviside layer. Guiglierlmo Marconi (1874-1937) was the first person to broadcast a radio transmission, which he did in 1901 from Poldhu, Cornwall to St John's Newfoundland, Canada using a kite antenna. Edward Appleton (1892-1965) proved the existence of the ionosphere and measured its altitude to be between 90-160 km. These measurements were adapted by Robert Watson-Watt (1892-1973), a St Andrews graduate of chemistry, towards the invention of Radar. Trans-Atlantic transmission is better at night as solar winds during the day press the ionosphere layer too close to the Earth to reflect for long distances.
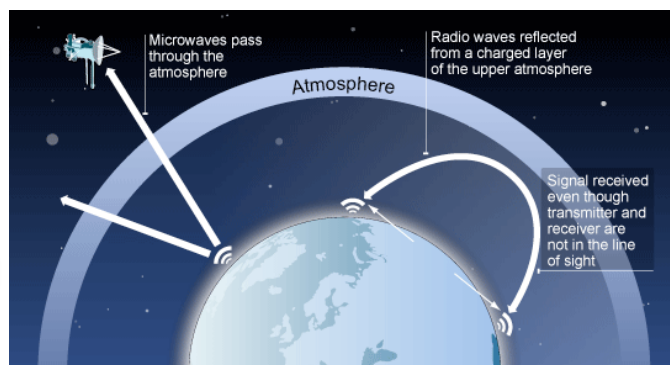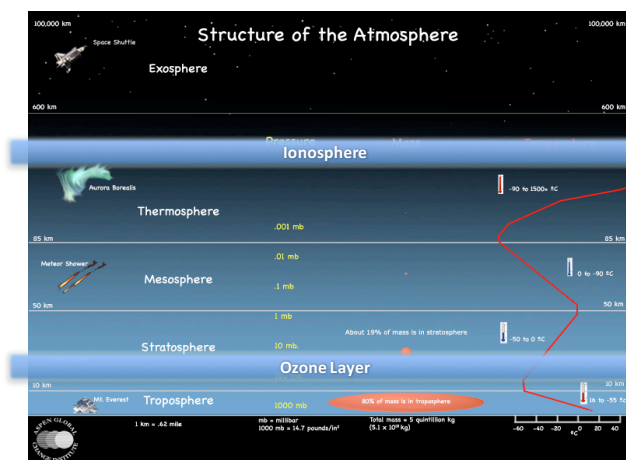
As a result of all the photodissociation and photoionization in the ionosphere, this region of the atmosphere is actually relatively "hotter" than the exosphere. This is because all photochemical processes are reversible and give off energy. However, hot is a relative term as the thermosphere has such low density that it is still very cold (though molecules are "hot" – it is a dilute heat). The temperature increases as we ascend the thermosphere as more solar energy absorbed. We can estimate T from KE, $KE = mv^2/2 = 3kT/2$ for ideal gas.
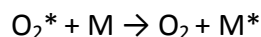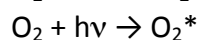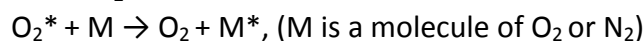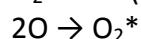
The temperature decreases as we descend as all the high-energy UV photons have now been absorbed, meaning that there is no longer enough energy in the photons for any of the reactions of N_2. A temperature minimum is reached at the mesopause, which marks the lower limit of the thermosphere at around 85 km. Here, the temperature is low enough that **noctilucent** clouds formed from ice crystals (rather than water droplets as for normal clouds) form. They are Earth's highest clouds and are 80.5 km high. The more common tropospheric clouds by contrast are a mere 1.6-4.8 km high.

### 2.3.2 ANATOMY OF THE ATMOSPHERE: MESOSPHERE & STRATOSPHERE
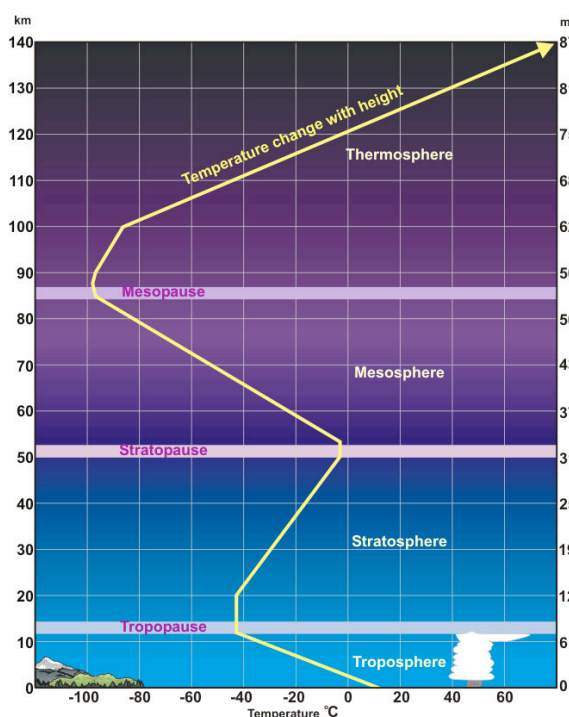
As one descends through the mesosphere to the stratopause there is an increase in the temperature of the atmosphere. Pressure and the absorption of light both increase as $[O_2]$ increases. The O_2 molecules can absorb only the very high energy UV light to give oxygen atoms or excited dioxygen (O_2*), also generating heat. Below the stratopause the UV energy < 240 nm (UVC) intensity has dropped off as this has all been absorbed by O_2 in the mesosphere and therefore the temperature drops anew.

The photochemistry in the mesosphere is described below. The star (i.e. M*) refers to molecules in their electronic excited states, which relax down to their ground state configuration and concomitantly release energy as heat.

$O_2 + h\nu$ (<240 nm) $\rightarrow$ 2O ΔH°: +495 – E(photon) kJ mol^{-1}
2O $\rightarrow O_2*$
$O_2* + M \rightarrow O_2 + M*$, (M is a molecule of O_2 or N_2)
$O_2 + h\nu \rightarrow O_2*$
$O_2* + M \rightarrow O_2 + M*$

2.3.4 *ANATOMY OF THE ATMOSPHERE: OZONE LAYER*

Ozone, O_3, an allotrope of O_2 is distributed through out the atmosphere but has a maximum concentration at around 30 km, which is within the stratosphere. This zone of high concentration of ozone is known as the ozone layer. As a function of its longer conjugation length, ozone absorbs mostly UVB radiation and also some UVC radiation (light between 240-320 nm).
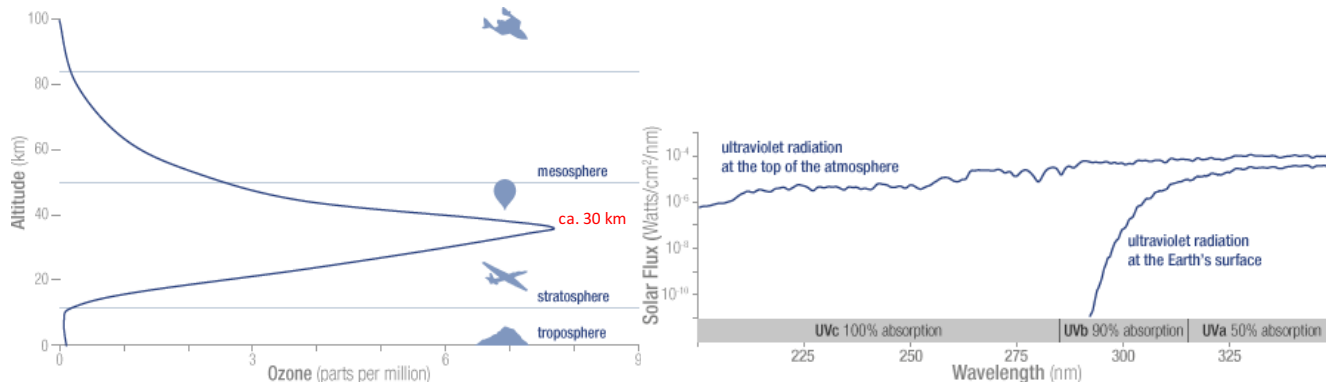
Recall that O_2 molecule can absorb only the very high energy UV light (UVC) to give oxygen atoms: $O_2 + h\nu$ (<240 nm) $\rightarrow$ 2O ΔH°: +495 – E(photon) kJ mol^{-1}

Now these O atoms can participate in chemistry. When they react with O_2 they give O_3
   - $O + O_2 \rightarrow O_3*$ (the O_3* molecule is in its excited state)
   - $O_3* + M \rightarrow O_3 + M*$ ΔH°: -105 kJ mol^{-1} $\therefore$ heat is evolved

Ozone destruction passes through one of two routes:
   - $O_3 + h\nu$ (<320 nm) $\rightarrow O + O_2$ ΔH°: +105 – E(photon) kJ mol^{-1}
   - $O + O_3 \rightarrow 2 O_2$ ΔH°: -389 kJ mol^{-1}

Ozone can reform, leading to a steady-state concentration of ozone, known as the ozone layer. This layer protects the Earth's surface from harmful UV radiation.
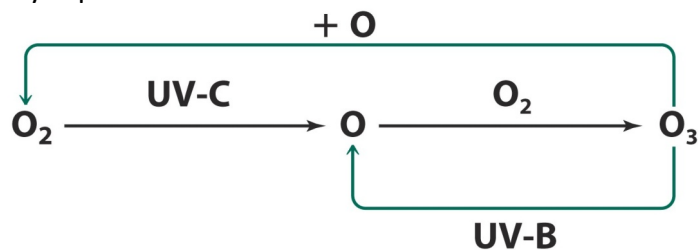
Sydney Chapman, a British scientist, in 1930 proposed a theory of the formation of ozone in the stratosphere, the details of which are shown to the left and above.

From the Chapman theory, As altitude increases then [M] (and [O_2]) decreases as the atmosphere because less and less dense (here M refers to other gaseous molecules or atoms). This translates to a decrease in the kinetics of formation of ozone, $k_1(O_3)$ decreases. As altitude increases then the incident photon flux of the sunlight [hv] increases as less has been absorbed. Therefore the rate of photodissociation of O_2 to form O increases, $k_2(O)$ increases. Both k_1 and k_2 contribute to decreasing the [O_3] in the mesosphere and upper stratosphere and this accounts for the falloff in ozone concentration at elevated altitude.
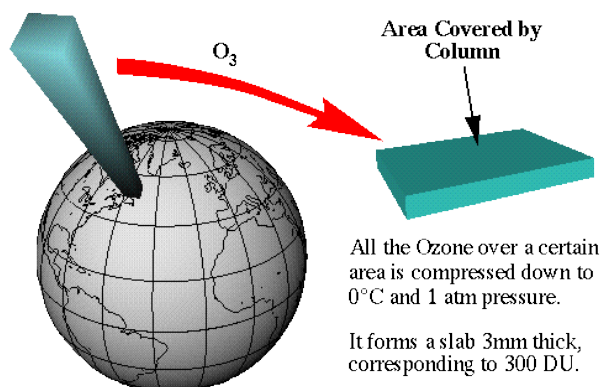
As altitude decreases then the [M] (and [O_2]) increases, resulting in an increase the kinetics of formation of ozone, $k_1(O_3)$ increases, assuming available oxygen atoms. However, as altitude decreases then the incident photon flux of sunlight [hv] decreases and therefore the rate of formation of oxygen atoms decreases, $k_2(O)$ decreases. Thus, k_1 and k_2 contribute to an overall decreases in [O_3] in the lower stratosphere, which explains the more shallow fall off in ozone concentrations at lower altitudes.

The Ozone layer found at roughly 30 km in altitude, which is only 3 mm thick, is also known as the "Chapman Layer". The steady state [O_x] = $(JO_2[O_2]/k_4)^{1/2}$, where X is 1 or 3, JO_2 is the photolysis rate constant. Each day 3.5×10^8 kg of O_3 is made by sunlight and destroyed.

The ozone layer resides much lower (25-30 km altitude) than the point of maximum O_3 production (at the temperature maximum, the stratopause, at 50 km). This is due to *Brewer-Dobson circulation*, which transports ozone-rich air from the area of the stratopause lying over the tropics to the lower levels of the atmosphere. The Brewer-Dobson circulation is also responsible for maximising the ozone concentration over mid-latitudes, rather than the tropics where light intensity is highest. Complex circulation also causes ozone peaking in **Spring** not summer and lowest in **Autumn** not winter at latitudes other than tropics.

The illustration to the right shows a column of air, 10 deg x 5 deg, over Labrador, Canada. The amount of ozone in this column (i.e. covering the 10 x 5 deg area) is conveniently measured in *Dobson Units*.

If all the ozone in this column were to be compressed to standard temperature and pressure (STP) (0 °C and 1 atmosphere pressure) and spread out evenly over the area, it would form a slab approximately 3mm thick.

All the Ozone over a certain area is compressed down to 0°C and 1 atm pressure.

It forms a slab 3mm thick, corresponding to 300 DU.

1 Dobson Unit (DU) is defined to be 0.01 mm thickness at STP; the ozone layer over Labrador then is 300 DU.

The unit is named after G.M.B. Dobson, one of the first scientists to investigate atmospheric ozone (~1920 - 1960). He designed the 'Dobson Spectrometer' - the standard instrument used to measure ozone from the ground. The Dobson spectrometer measures the intensity of solar UV radiation at four wavelengths, two of which are absorbed by ozone and two of which are not.

To summarize, UVC absorbed by atomic & molecular N_2 and O_2; UVB and some UVA absorbed by O_3.

### 2.3.4 ANATOMY OF THE ATMOSPHERE: STRATOSPHERE AND TROPOSPHERE

Below the stratopause the UV<240 nm (UVC) intensity drops off due to all the absorption that has already gone on at higher altitude. The temperature therefore starts to drop off. Air at the base of the stratosphere is cooler than the air above and so does not rise. This phenomenon is called a temperature inversion and leads to non-turbulent, stratified layers of air (hence the name stratosphere), except for high winds called the *jet stream* that are very well mixed horizontally but not vertically. The maximum altitude for clouds formed of water vapour corresponds to the minimum temperature in the troposphere. Most airplane jets fly above these clouds at 10 km (35k feet) in the jet stream, especially when going from west to east across the globe to take advantage of the prevailing high winds and consume less fuel. The temperature rises as one descends the troposphere due to the presence of natural (and non-natural) Greenhouse gases.

2.4 SUNSCREEN

Though essentially all of the UVC light is absorbed by the atmosphere, some of the UVB light, which is normally absorbed by the ozone layer, is transmitted all the way to the Earth's surface. This radiation is harmful as it is high enough to break chemical bonds.

Humans therefore apply sunscreens as additional protection against these harmful rays. In the past *para*-aminobenzoic acid, PABA, was used as a sunscreen as it absorbs UVB light (290-320 nm). However, as it discoloured clothing and was linked in some studies to cellular UV damage, it has been largely discontinued.
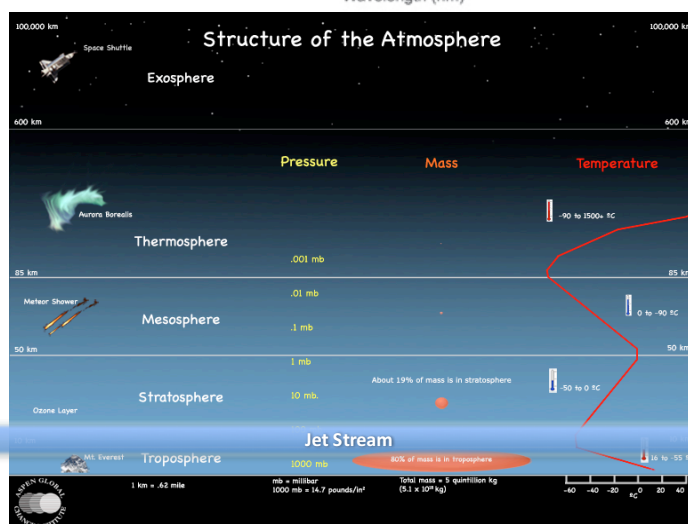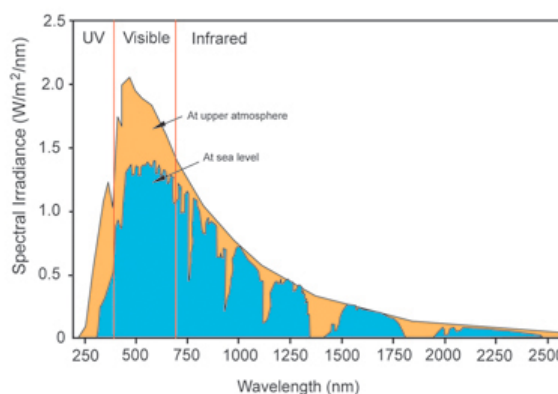
To protect against both UVA and UBC radiation mixtures of absorbing molecules are used in modern sunscreens. These include:

- Avobenzone (4-5%)
- Homosalate (9-11%)
- Octisalate (4-6%)
- Octocrylene (3-5%)
- Oxybenzone (4-6%)
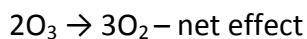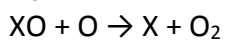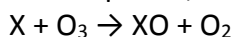- ZnO, TiO_2 used to reflect light
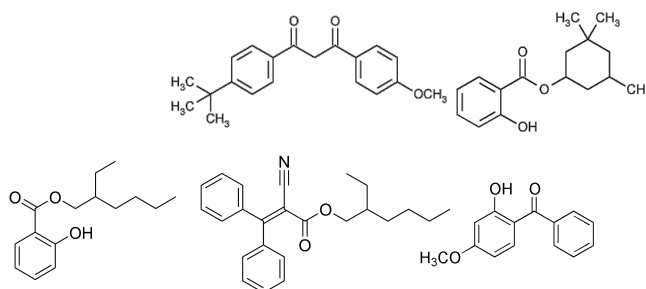
Sun **P**rotection **F**actor (SPF) is a measurement of UVB protection and figures prominently in sunscreen advertising. This number refers to the ratio of the amount of sunlight necessary to induce redness in skin protected by sunscreen compared to bare skin.

2.4 *OZONE DEPLETION*

There was a problem with the Chapman theory. In the 1960s it was realised that the loss of ozone given by:

$O + O_3 \rightarrow 2O_2$ was too slow and the Chapman theory was underestimating the rate of ozone depletion.

Other species, destroying O_3 faster, had to be responsible
$X + O_3 \rightarrow XO + O_2$
$O_3 + h\nu \rightarrow O + O_2$ to generate O for the next reaction
$XO + O \rightarrow X + O_2$
_____

$2O_3 \rightarrow 3O_2$ – net effect

Ozone was found to be depleted by both naturally occurring nitrogen monoxide; X = NO (from N_2O), OH and H are naturally occurring. However, ozone was also being depleted by the presence of Cl and Br in the atmosphere, whose sources are anthropogenic; X = Cl and Br are manmade!

2.4.1 *HUMAN SOURCES OF OZONE DEPLETION*

The 1920's saw the invention of chlorofluorocarbons, CFCs, as coolants in refrigerators by the American chemist Thomas Midgley. Previously, the main refrigerants used were ammonia and SO_2. Due to their noxious nature, they were only used in large installations. CFCs allowed fridges to be introduced into every home, allowing the longer term storage of many foods. CFCs are 10 900 fold worse than CO_2 as a Greenhouse gas and have a $t_{1/2}$ of ca. 100 years!
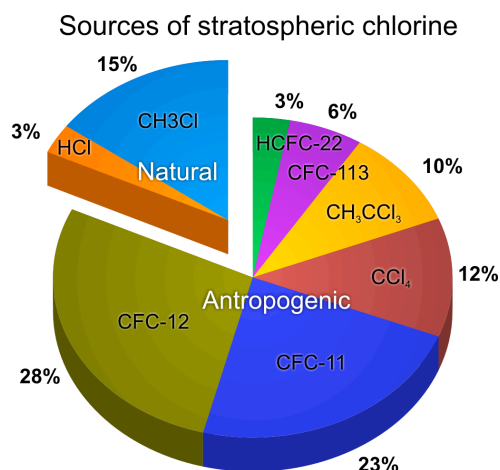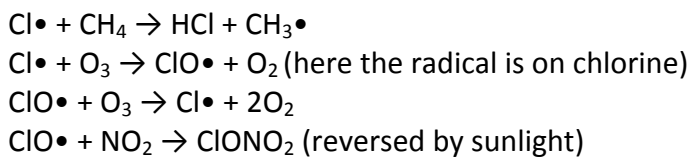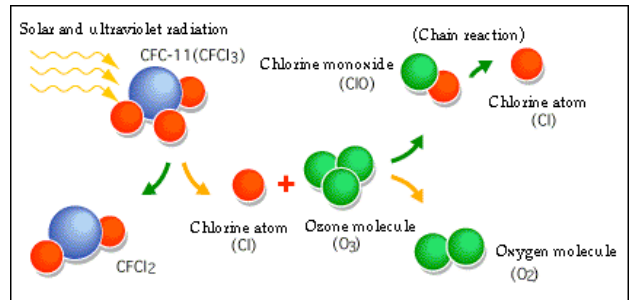
Human activities have caused a six-fold increase in the abundance of stratospheric chlorine, and a smaller increase in stratospheric bromine. These increases have been caused through the production and emission of CFCs (used as aerosol propellants, solvents, air-conditioning fluids, and refrigerants), halons (used as fire retardants), and methyl chloroform and carbon tetrachloride (used as solvents). We were extremely lucky that CFCs were widely

Sources of stratospheric chlorine

adopted rather than the very similar bromine-containing compounds. If they had chosen bromine, we would have had a catastrophic ozone hole everywhere and in all seasons by the 1970s

2.4.1.1 *CHEMISTRY OF OZONE DEPLETION*

Chlorine radicals are produced through homolytic cleavage of CFC molecules. Once chlorine radicals are in the atmosphere, they can react with methane to produce HCl and methyl radicals, which themselves can destroy ozone. Alternatively, the chlorine radicals can directly destroy ozone as shown below.


$Cl\bullet + CH_4 \rightarrow HCl + CH_3\bullet$
$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$ (here the radical is on chlorine)
$ClO\bullet + O_3 \rightarrow Cl\bullet + 2O_2$
$ClO\bullet + NO_2 \rightarrow ClONO_2$ (reversed by sunlight)

So HCl "stores" damaging $Cl\bullet$ and $ClONO_2$ "stores" damaging $ClO\bullet$
$Br\bullet$ is not stored as inactive forms, so causes more damage potentially than $Cl\bullet$

2.4.1.1.1 *CHEMISTRY OF OZONE DEPLETION: POLAR WEATHER*

From May-September during the winter polar night, sunlight does not reach the South Pole. A strong circumpolar wind develops in the middle to lower stratosphere (16 km altitude). These strong winds are known as the *'polar vortex'*. This has the effect of isolating the air over the polar region. Since there is no sunlight, the air within the polar vortex can get very cold. It is so cold that special clouds can form once the air temperature gets to below about -80 ^{o}C. These clouds are called ***Polar Stratospheric Clouds*** (or PSCs for short) but they are not the clouds that one is used to seeing in the sky, which are composed of water droplets. PSCs first form as nitric acid trihydrate. As the temperature gets colder however, larger droplets of water-ice with nitric acid dissolved in them can form. These PSCs are crucial for ozone loss to occur.
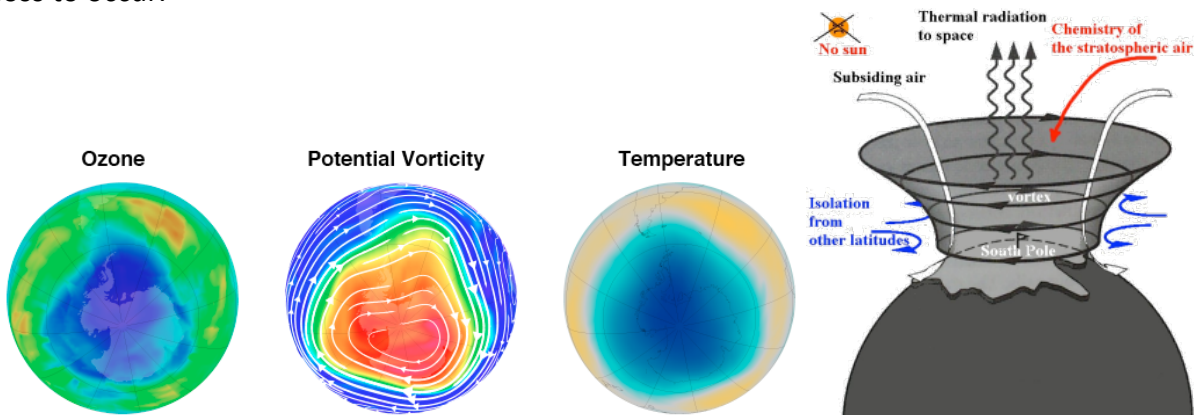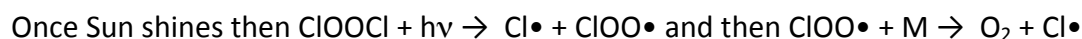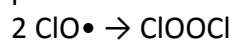
The vortex breaks up at the end of spring (December). At this point the ozone layer has diminished by 10% in NZ or South America in the spring (Oct-Dec). The chemistry underpinning the destruction of the ozone layer is shown below.

$ClONO_2 + H_2O \rightarrow HNO_3 + HOCl$

$HCl + HOCl \rightarrow H_2O + Cl_2$

_____

$HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$
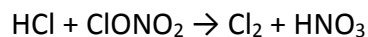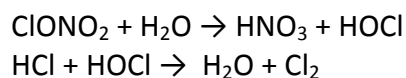
So Cl_g accumulates in the polar winter. As soon as spring arrives,

$Cl_2 + h\nu \rightarrow Cl\bullet$ and this attacks O_3

Moreover, at the low temperatures found within the polar vortex

$2 ClO\bullet \rightarrow ClOOCl$

Once Sun shines then $ClOOCl + h\nu \rightarrow Cl\bullet + ClOO\bullet$ and then $ClOO\bullet + M \rightarrow O_2 + Cl\bullet$

The result is that each Cl atom destroys up to 100 000 O_3 molecules!

The HNO_3 formed in the PSC accumulates over the winter and the $[NO_x]$ decreases. The result of this accumulation of HNO_3 in the PSCs is that the rate of removal of $ClO\bullet$ decreases ($ClO\bullet + NO_2 \rightarrow ClONO_2$), leading to an acceleration of ozone depletion.

AND

- $NO_2 + O_3 \rightarrow NO_3 + O_2$
- $NO_2 + NO_3 \rightarrow N_2O_5$

BUT

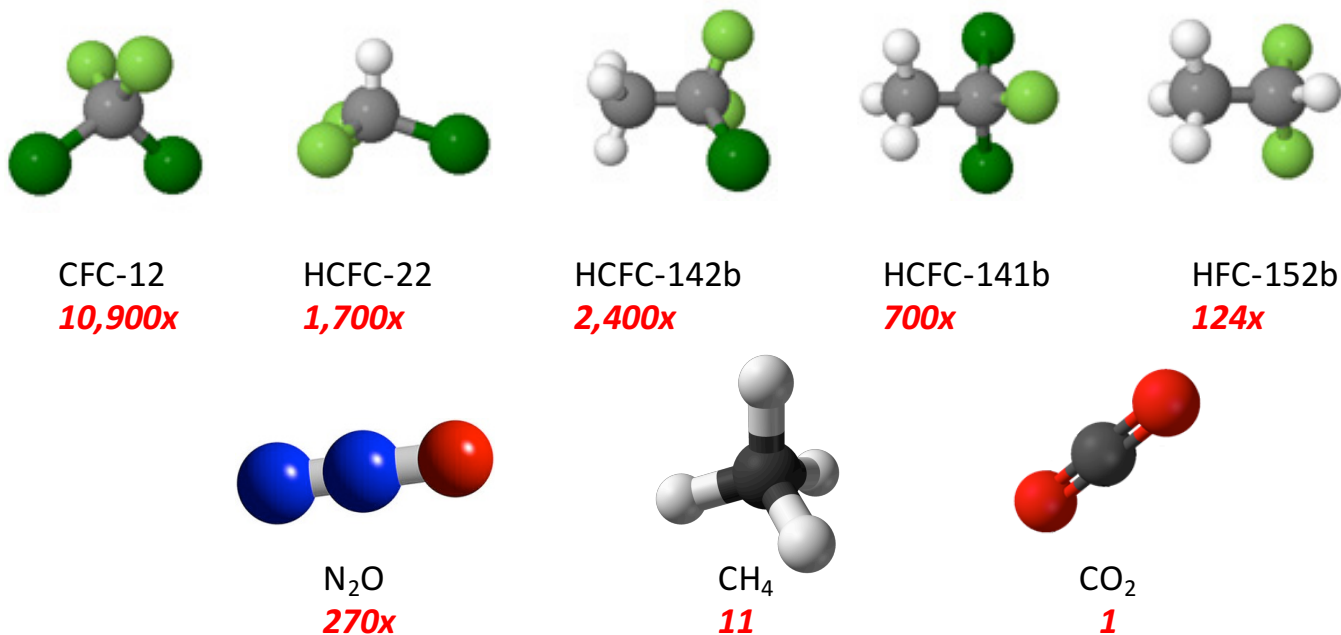- $N_2O_5 + H_2O$ (droplets) $\rightarrow 2HNO_3$

2.4.1.1.2 *CHEMISTRY OF OZONE DEPLETION: MID LATITUDE OZONE DEPLETION*

The poles are not the only region where the ozone layer is destroyed. In the mid latitudes, the atmosphere is not cold enough for the nitric acid-containing ice particles. However, it has been posited that cold liquid droplets of sulfuric acid (H_2SO_4) act in similar way. The sulfuric acid exists naturally in small natural amounts. Moreover, large amounts are ejected from volcanoes. The sulfuric acid droplets take up HCl and $ClONO_2$, playing a similar role to the PSC ice crystals to produce Cl_2 and hence damaging $Cl\bullet$ and $ClO\bullet$

2.4.1.2 *CFCs, HFCs AND HALONS*

As a consequence of the realization of the destructive nature of CFCs, the World came together to sign the Montreal Protocol in 1987. This agreement saw the ban all chlorofluorocarbons, carbon tetrachloride, methyl chloroform, and halons in developed countries as of January 1996 and in developing countries by 2010. Control measures for other halocarbons, such as methyl bromide and the transitional CFC replacement, hydrochlorofluorocarbons HCFCs were also put into place. The Montreal Protocol also declared that from 2013, there would be a freeze in the consumption and production of HCFCs and by 2015 this would see the start of the reduction and consumption and production of these compounds.

CFC-12	HCFC-22	HCFC-142b	HCFC-141b	HFC-152b
10,900x	*1,700x*	*2,400x*	*700x*	*124x*

N_2O	CH_4	CO_2
270x	*11*	*1*
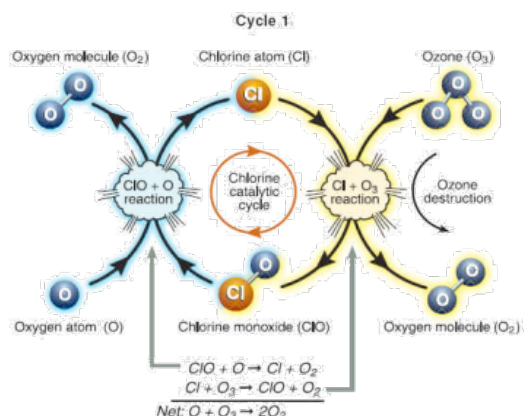
The World still required sources of refrigerants. However, these replacement chemicals should contain no Br or Cl in structure. C-F bonds are OK as they are stronger and do not photodissociate BUT their half-lives are extremely long and are greenhouse gasses. Hydrofluorocarbons, HFCs, were seen as a viable alternative but these too can be destroyed in the troposphere due to C-H bond.

e.g., $OH + CF_3CH_2F$ (HFC-134a) $\rightarrow H_2O + CF_3CHF$ which can be readily attacked by O_2

HFC-134a shows a good vapour pressure match with the most widely used refrigerant CFC-12 and also has a low toxicity.

Generally, HFCs are used mostly for refrigeration and air-conditioning but also as foaming agents, aerosols and fire-retardants and solvents.

Nomenclature used for CFCs and HFCs: Take number of the HFC or CFC (*e.g.*, CFC-12) and add 90. The number tells the molecular formula as digits C, H, F

e.g., 134+90 = 224 $\rightarrow C_2H_2F_4$ = HFC-134a;
11+90 = 101 $\rightarrow C_1H_0F_1Cl_3$ = CFC-11

Halons are bromine-containing chemicals that are used as fire retardants. C-Br bonds in halons and methyl bromide are weaker than C-Cl bonds and give Br radicals, which persist in the atmosphere and destroy ozone in a similar fashion to chlorine radicals.

Nomenclature used for Halons: Halon 1301 (H1301) = $C_1F_3Cl_0Br_1$

The goal of the Montreal Protocol is to return the chlorine radical concentrations to 2 ppbv and by doing so repair the ozone hole. Due to long-lived nature of CFCs, it would be only in 2050 for 2 ppbv levels to be attained even if we had stopped all production of these chemicals in 1995.

Is the Montreal Protocol working? The average size of the ozone hole in 2012 was 17.9×10^6 km^2, 2nd smallest in 20 year up until that point. The minimum value of total ozone in the ozone hole reached 124 DU (Dobson Units), the second highest in 20 years. **Recall:** When no ozone hole, total ozone ranges from 240-500 DU. But as the half-life of CFCs and other ozone-depleting chemicals are so long, a recovery is not likely to be noticeable until at least 2020. This past summer (2016), scientists for the first time reported that the ozone layer over the Antarctic was showing signs of healing!
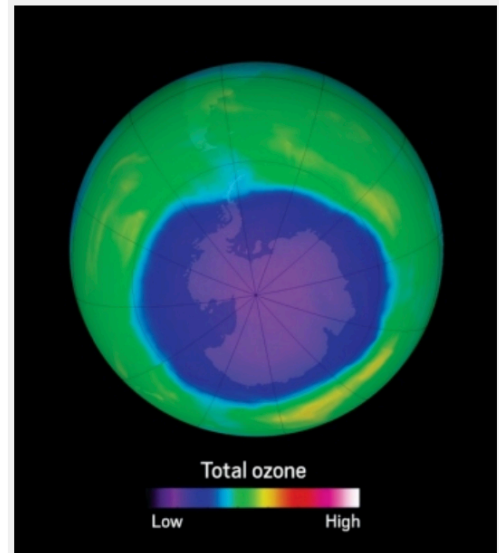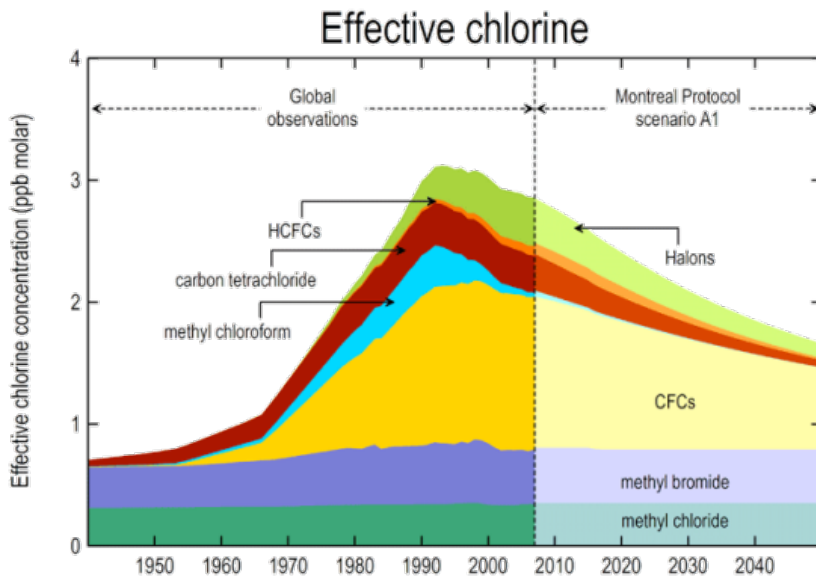
Closure
The seasonal Antarctic ozone hole, shown here in October 2015, is gradually shrinking.

Credit: NASA

2.5 *GLOBAL WARMING*

The temperature of the Earth is controlled through a careful balance of energy in from, mostly, the sun and energy being released.

Incoming energy:
- Total solar irradiation (TSI) output varies by approximately 0.1% or about 1.3 W/m² peak-to-trough of the 11-year sunspot cycle.
- The Earth collects TSI=1366 W m^{-2} from its projected disk area ($A=\pi R_e^2$) reduced to one-quarter (340 W m^{-2}) when averaged over the whole surface ($4\pi R_e^2$) over a day of Earth complete revolution
- 20% absorbed (UV by O_2 and IR by CO_2 and water)
- 30% reflected back to space (albedo)

Outgoing energy:
- If outgoing heat less than incoming heat the Earth gets warmer
- A warmer Earth will then emit more energy (it too is a black body radiation source, just a much cooler one than the sun)
- Only when the rate of warming (energy in) is equal to the rate of cooling will a steady temperature be achieved and the Energy Balance be maintained

We can calculate the wavelength of maximum intensity of the radiation and the amount of energy emitted from a blackbody radiation source Wien's Law and Boltzmann's law.

Wien's Law for "black body" radiation gives the peak wavelength:
$$\lambda_{max}=2897/T$$ - Sun (5800 K) emits visible light; Earth (300K) emits infra-red

Boltzmann's Law for "black body" radiation gives total energy:
$$E = \sigma T^4$$
where T is in Kelvin (T in °C = T in K + 273)
where σ is Boltzmann's constant at 5.67 x 10^{-8} W m^{-2}

The energy reaching the Earth is 340 W m^{-2}. Of this 100 W m^{-2} is reflected back out into space (albedo, 30%), which leaves 240 W m^{-2}.

For Earth to be at an energy balance 240 W m^{-2} = σT^4; $\therefore$ T = 255 K or -18 ^{o}C

To explain the discrepancy between this calculation and the fact that the average temperature of the Earth is considerably warmer, we invoke a Greenhouse effect (ε) that results in a rate of cooling on Earth that is lower than that for a black body (atmospheric insulation). So the Greenhouse cooling rate = $\varepsilon\sigma T^4$ and ε = 0.615 for the correct average temperature on Earth (T = 288 K = 15 ^{o}C).
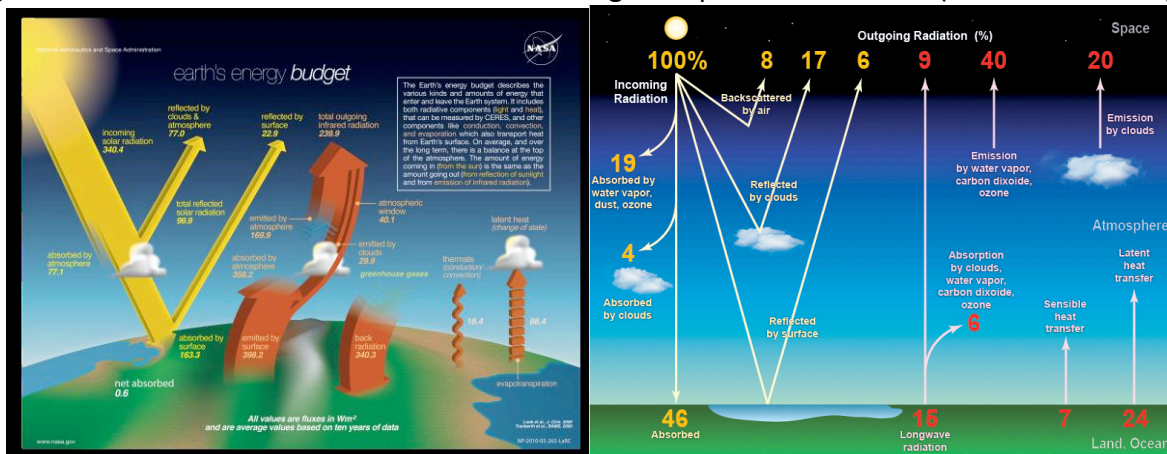
The energy reflected by the Earth gets reabsorbed by gases in the atmosphere and re-radiated back. Water vapour counts for about 2/3 of the effect (this is why deserts are so cold at night where there is little in the atmosphere to re-radiate the heat back); CO_2 counts for a 1/4 of the effect. This natural Greenhouse effect keeps Earth's average surface temperature near +15 ^{o}C. If absent then –18 ^{o}C!

2.5 *GLOBAL WARMING: THE PHYSICS BEHIND THE ABSORPTION OF LOW ENERGY BY GAS MOLECULES*

The total energy of a molecule is given by: $E_{total} = E_{electronic}+E_{vibrational}+E_{rotational}+E_{translational}$. E_{total} is quantized and molecules can only possess certain energy. Within a single electronic energy level there are many vibrational levels. We can think of a bond between two atoms in that molecule as two masses connected by a spring. Hooke's law gives the stretching frequency in a spring, where μ is the reduced mass.

$$v = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{m_1 \times m_2}{m_1 + m_2}$$

In a molecule these stretching frequencies are quantized and depend on the energy gap between the vibrational levels. The vibrational energy, $E_{vibrational}$ = (n+1/2) hv, so Zero Point Energy (1/2 hv), where v is reported in terms of wavenumbers (cm^{-1})
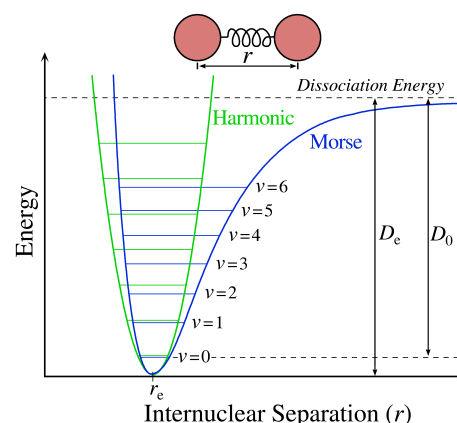
Recall: E = hv = hc/λ = $hc\omega$, $\therefore$ v = $c\omega$, where ω is the angular stretching frequency.

So the strength of the bond is related to the force constant, which is related to the stretching frequency.

For a molecule of N nuclei there are *3N* degrees of freedom (DOF) of which there are *3N-6* internal DOF (for non-linear molecules) or *3N-5* internal DOF (for linear molecules). These are called normal modes of vibration and have a stretching frequency, v, of same magnitude as IR radiation

Radiation interacts with matter through one of several processes: scattering, absorption & emission.

Absorption is a process whereby the energy of the photon is taken up by the matter
- UV radiation has enough energy to ionize electrons (i.e. ejects them from atoms)
- Visible radiation has enough energy to excite electrons (i.e. induces an electron transition)
- IR radiation has enough energy to excite vibrational and rotational states of a molecule

For a molecule to absorb IR radiation there must be a match between the change in dipole moment as a function of vibrations and rotations with the energy of the radiation. Upon absorption there will be a change in the amplitude of the molecular vibration. This is what is observed in an IR spectrum.

e.g., H_2O
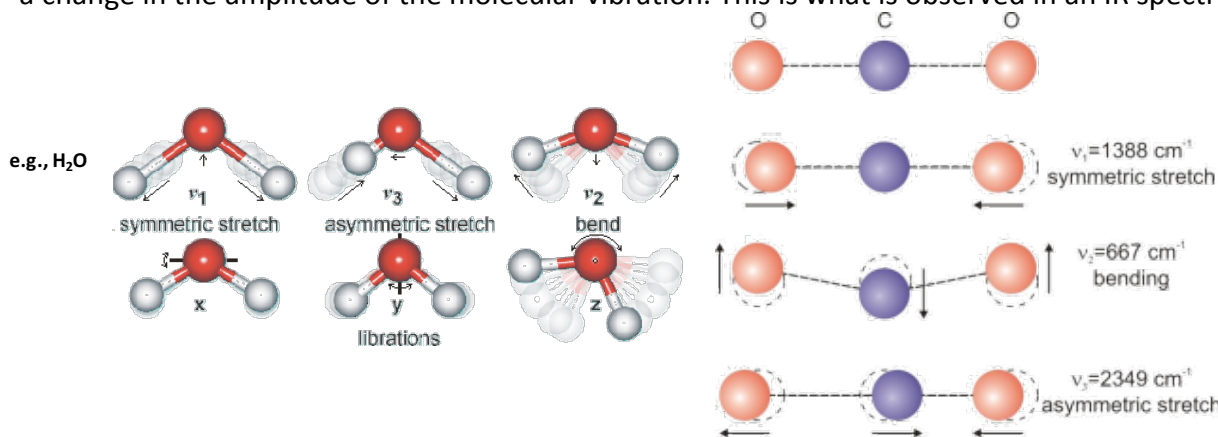
There are different possible vibrational modes. These are symmetric and asymmetric stretching modes and scissoring, wagging, rocking and twisting, all four of which are bending modes. For example, as shown above and to the left there are 3 different vibrational modes for water, all of which change the molecular dipole moment and so all of which are IR active. However, for CO_2 (above, right) there are 4 vibrational modes (3N-5 as it is a linear molecule) but only two of which are IR active. This is because two of the bending modes are degenerate which the symmetric stretch shows no net change in dipole

moment. We can see in the IR spectrum of CO_2 indeed only two bands. The band at 15 μm (670 cm^{-1}) is the one responsible for absorbing the IR energy emitted from the Earth's surface.
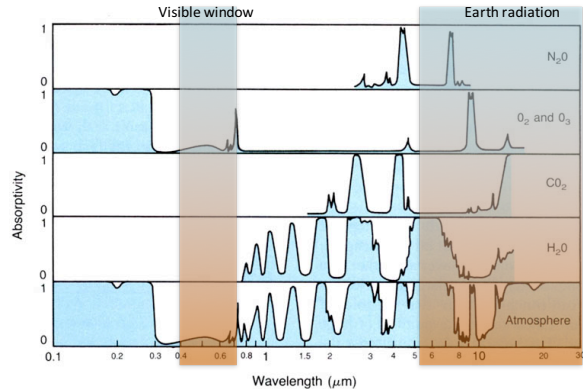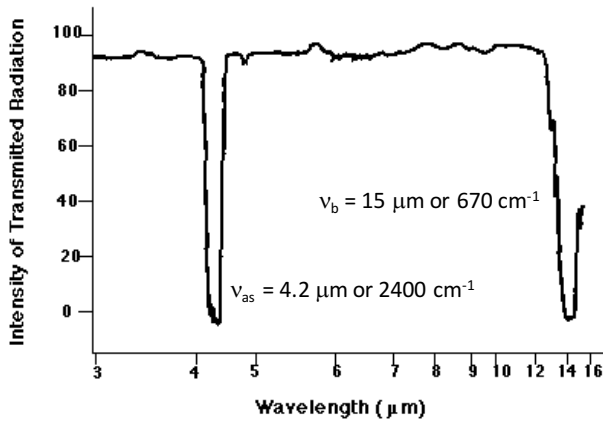

Figure 2•13   The absorptivity of selected gases of the atmosphere and the atmosphere as a whole.
(From R. G. Fleagle and J. A. Businger, An introduction to Atmospheric Physics. © 1963 by Academic Press; reprinted by permission of the publisher)

Water in atmosphere will increase exponentially with temperature, so will therefore increase the greenhouse effect. However, the increased water vapour will also give more clouds, which will reflect more sunlight away from the surface of the Earth, compensating somewhat.

2.5.1 GLOBAL WARMING: THE ANTHROPOCENE ERA

Since the start of the industrial revolution, CO_2 concentrations have steadily increased, and this unequivocally due to human activity. CO_2 concentrations cycle throughout the year and this cycling is due to vegetation content. CO_2 concentration falls during summer in the northern hemisphere and rises in the winter, with a minimum in October and a maximum in May. This summer decline is attributable to strong summertime uptake by photosynthesis of terrestrial vegetation (in the southern hemisphere, there is much less land and so a corresponding photosynthetic signal is not evident during the southern summer).
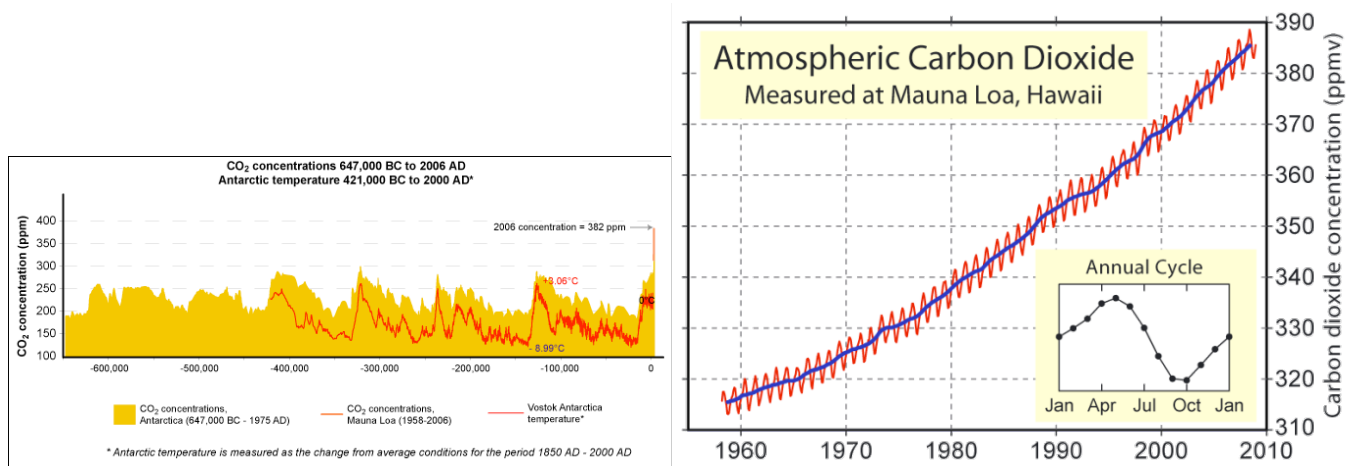
For the 650,000 years prior to 1950 CO_2 concentrations had never exceeded 300 ppm. The year 2016 is on track to be the first with an sustained CO_2 concentration in excess of 400 ppm!

The consequence of these elevated CO_2 levels are increased temperatures globally. The International Panel on Climate Change (IPCC) predicted an even worse scenario for CO_2 concentrations initially but this is not to say that the IPCC was wrong on the consequences of global warming.
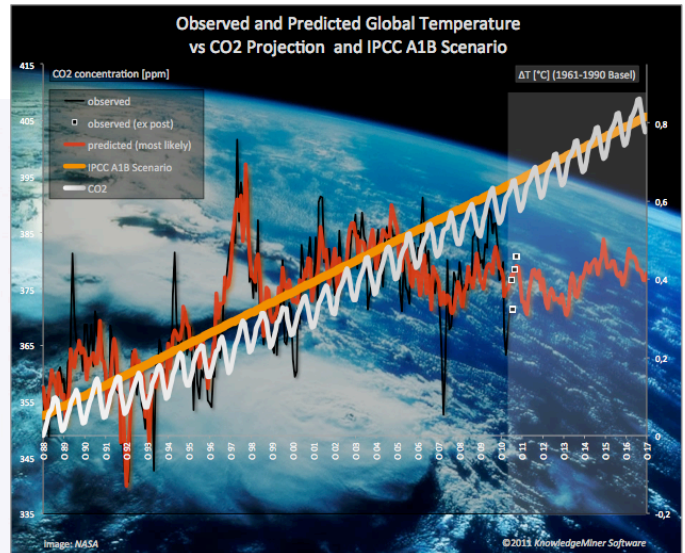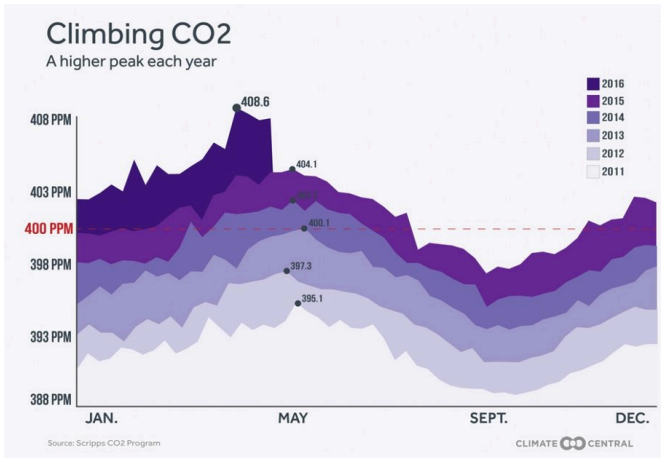
In addition to warmer temperatures, the IPCC concluded that sea levels would rise and Arctic and Antarctic ice cover would diminish. The predictions made by the IPCC on these last two points alarmingly under-represent the actual disappearance of sea and land ice and the increase in sea levels. Both these effects will have drastic negative consequences for humans, especially considering the large percentage of the human population that lives in coastal environments.

CO_2 represents the single largest contributor to global warming though halocarbons, N_2O, CH_4, micro-particulate matter emanating from the burning of fossil fuels (soot) all contribute as well.

As an example of the scale of greenhouse gas emissions, in 2010, the United States emitted over 6.8 billion metric tons of greenhouse gases, 84% of which were CO_2, followed by 10% CH_4, 4% N_2O and 2% HFCs and related fluorinated compounds. Different Greenhouse gases reside in the atmosphere for different periods of time. CO_2 can stay in the atmosphere for up to 200 years, exacerbating its effect.