



# Lower Atmosphere

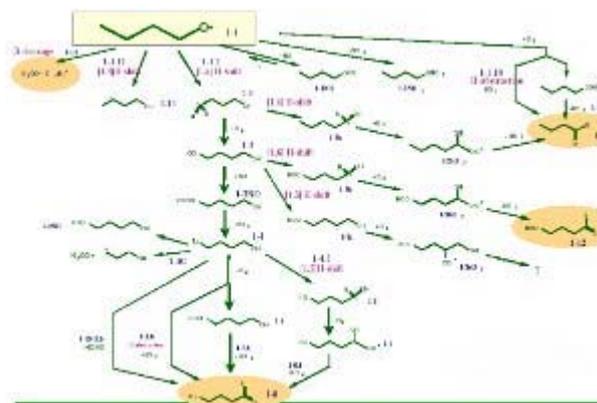
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## Unit 1

### The main oxidants in the troposphere and how we observe them

The troposphere is the most chemically reactive part of the atmosphere.

Most chemical reactions which occur in the troposphere involve oxidation. In this unit we look at the major oxidising species during the day and during the night and how we go about measuring them.



1. We will discuss only basic atmospheric chemistry in this unit. However the chemistry which goes on can be really complicated. Just have a look at the atmospheric chemistry of a simple organic molecule such as butane (which is used, for example, in camping stoves). From: lecture by Jim Smith at NCAR.



## Part 1: Oxidation and OH radicals

### Oxidation in the Atmosphere

Many chemical compounds are emitted into the atmosphere but removal processes prevent them accumulating in the air. Species are removed by dry deposition of gases or particles or can be incorporated into rain and removed by wet deposition. For gas phase organic chemicals, removal is easiest if they are first oxidised to a less volatile, water soluble form.



1. Hydroxyl radicals (OH) clean the air. Image: Elmar Uherek.

Oxidation in a chemical sense does not necessarily mean a reaction with oxygen containing compounds, it is rather the loss of electrons. However, in the air, oxidation does generally involve the reaction of a chemical species with an oxygen containing compound.

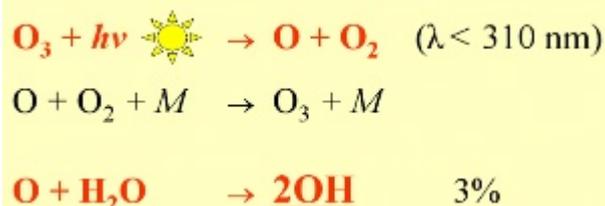
The three most important oxidising species in the air are:

the hydroxyl radical **OH**  
the nitrate radical **NO<sub>3</sub>**  
the ozone molecule **O<sub>3</sub>**

Hydroperoxy radicals (HO<sub>2</sub>) are also important and the sum of HO<sub>2</sub> and OH is sometimes referred to as HO<sub>x</sub>.

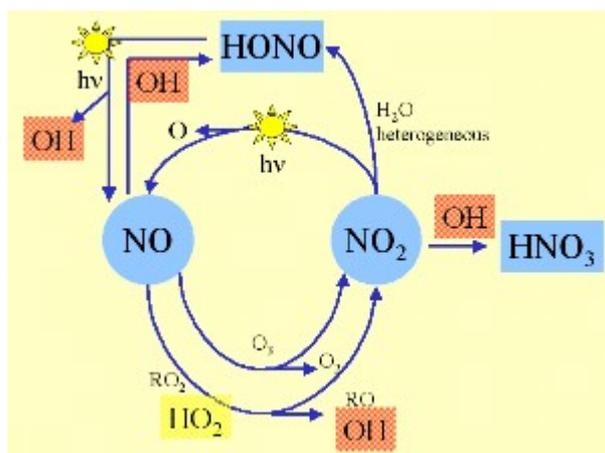
The most important oxidising species is the hydroxyl radical (OH). It is extremely reactive and able to oxidise most of the chemicals found in the troposphere. The hydroxyl radical is therefore known as the '**detergent of the atmosphere**'.

Only a few compounds in the troposphere do not react at all or react only very slowly with the hydroxyl radical. These include the chlorofluorocarbons (CFC's), nitrous oxide (N<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>). The rate of methane (CH<sub>4</sub>) oxidation by OH is also very slow, between 100 and 1000 times slower than other organic compounds. This is why methane concentrations in the atmosphere can reach around 1.7 ppm (1.7 μmol mol<sup>-1</sup>), a value significantly higher than the concentrations of other organic trace gas concentrations present which are generally below 1 ppb (1 nmol mol<sup>-1</sup>)\*.



2. Formation of OH: More than 97% of the O atoms which are formed by photolysis of ozone, react back again to ozone. Less than 3% start the formation of the most important radical in the atmosphere, OH. If two molecules or atoms collide to form a product, a third species M is needed to take away some excess energy. M (usually nitrogen N<sub>2</sub>) does not react itself.





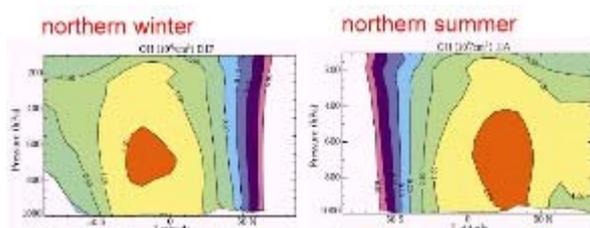
3. OH and the nitrogen oxide cycle  
Scheme by Elmar Uherek

### How is OH formed?

OH governs atmospheric chemistry during the day since its formation depends on radiation from the Sun. The initial reaction (shown above) involves the breakdown (photolysis) of ozone by solar radiation with wavelengths less than 310 nm. The oxygen atom (O) formed then reacts with water to form OH. This reaction mechanism is why a small amount of ozone is essential in the troposphere. Other sources of OH are: the photolysis of nitrous acid (HONO), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) or peroxy-methane (CH<sub>3</sub>OOH) the reaction of nitrogen monoxide (NO) with the hydroperoxy radical (HO<sub>2</sub>) or the reaction of alkenes with ozone. The scheme on the left shows how OH chemistry is fundamentally linked with the day-time reaction cycles of the nitrogen oxides.

### How much OH is formed?

Since OH is an extremely reactive radical it reacts as soon as it is formed. Its lifetime is less than a second. This means the concentration is extremely low, in the range of  $1 \times 10^5$  to  $2 \times 10^7$  molecules  $\text{cm}^{-3}$ . At sea level pressure this is equivalent to a mixing ratio of 0.01 - 1 ppt. Since its formation depends on water vapour, the concentration of OH tends to decrease with altitude as the air becomes cooler and drier.



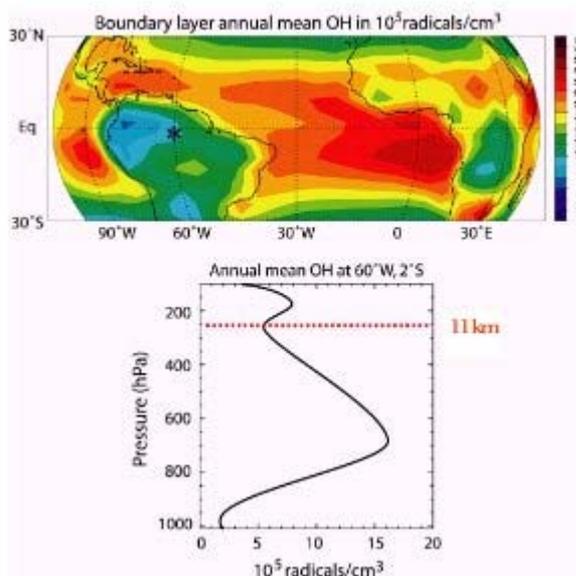
4. Zonal distribution of OH. A pressure of 250 hPa is reached at roughly 11 km altitude (the tropopause in the mid latitudes). Source: presentation by J. Lelieveld - MPI Mainz, 2003.



Hydroxyl radical concentrations not only decrease with altitude but also decrease with latitude since both the water vapour concentrations and sunlight intensity decrease as you move towards the poles.

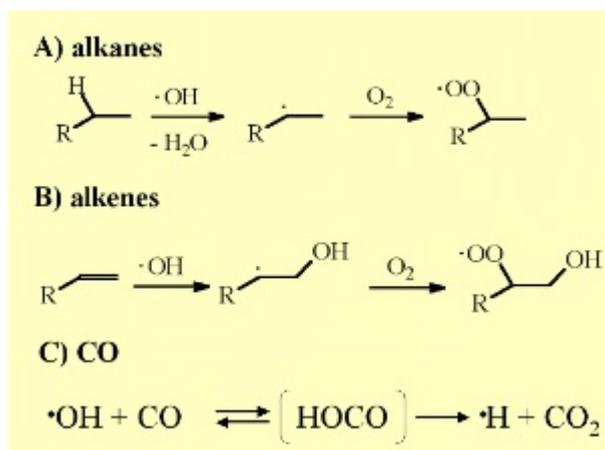
### How does OH react?

The figure on the right shows low levels of OH near the ground over the tropical rainforest. Why is this the case? Plants emit organic gases with isoprene being the most abundant. This isoprene reacts with OH, removing it from the air, and forming water and a reactive organic radical (R). OH has a strong tendency to remove (abstract) a hydrogen atom from organic species (RH) whenever possible. The organic radical (R) then reacts with oxygen (O<sub>2</sub>) to form organic peroxides (RO<sub>2</sub>). These compounds are an essential part of the ozone formation cycle.



5. OH distribution in the tropics. Top: the global distribution in tropical regions, below: profile over the Manaus rain forest station (Brazil). Source: presentation J. Lelieveld MPI Mainz, 2003.

On a global scale, OH reacts primarily with carbon monoxide (40%) to form carbon dioxide. Around 30% of the OH produced is removed from the atmosphere in reactions with organic compounds and 15% reacts with methane (CH<sub>4</sub>). The remaining 15% reacts with ozone (O<sub>3</sub>), hydroperoxy radicals (HO<sub>2</sub>) and hydrogen gas (H<sub>2</sub>).

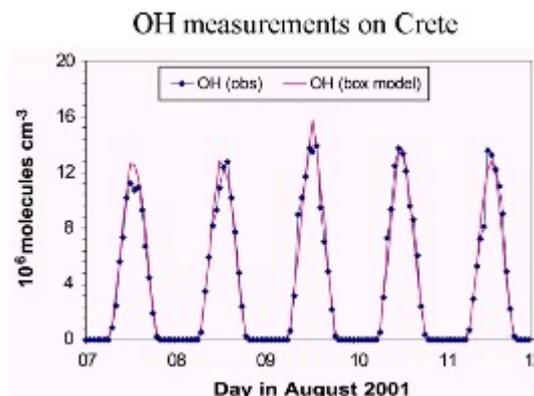


The oxidation of carbon monoxide and methane by OH are very important as they are the major ways by which OH is removed from the atmosphere. Reaction of OH with alkenes, a special class of organic compounds, is also very important as this reaction results in the formation of peroxides.

6. Important OH reactions in the troposphere.



OH is the most important oxidant in the atmosphere. However OH concentrations are close to zero during the night since sunlight is needed for its formation. So during dark periods and during night-time, ozone and nitrate radical ( $\text{NO}_3$ ) chemistry become important.



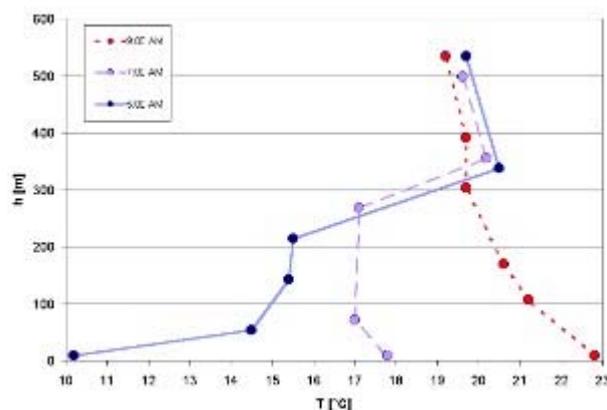
7. Time profile of OH concentrations over several days. Source: Presentation J. Lelieveld MPI Mainz, 2003.

\* The mixing ratio ppb (1 molecule in 1 billion molecules of air) or ppm (1 molecule in 1 million molecules of air) is often used in scientific publications as well as in other literature on the atmosphere and climate. Because of this we use it here in the Climate Encyclopaedia. However, the correct unit is  $1 \text{ nmol mol}^{-1}$  (equivalent to 1 ppb) or  $1 \mu\text{mol m}^{-3}$  (for 1 ppm) since mole is the standard unit of concentration.

## Part 2: Night and nitrate

### Night-time conditions and chemistry

The chemistry of the atmosphere depends not only on the chemical compounds present in the air but also on the physical conditions. These physical conditions depend, for example, on the season, whether it's day or night, what the temperature is and how humid the air is.



1. Collapsing temperature inversion on a July morning (Isar Valley / Germany). By Elmar Uherek and adapted from: Schirmer - Wetter und Klima - Wie funktioniert das?

### The diurnal cycle

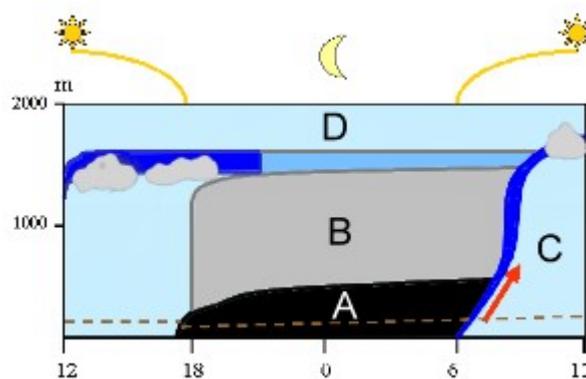
In the last section we saw that OH concentrations are highest during the day and approach zero at night when there is no sunlight present. Temperature and other physical properties also show a diurnal or daily cycle.

Conditions close to the ground in the planetary boundary layer vary and do not always follow the general rule (e.g. of decreasing temperature with increasing altitude) because of interactions with the Earth's surface. A very typical example is the night-time inversion layer which collapses in the morning.



## Night-time inversion in the planetary boundary layer

Everything below the free atmosphere (D) is part of our planetary boundary layer. Changes within the planetary boundary layer occur during the day and these are shown from the left to the right in the diagram. At noon the air is well mixed (light blue). After sunset a stable nocturnal layer forms (A) and residual air remains above it (B). Air from the surface layer (below the dotted brown line) cannot go up to high altitudes during the night as there is no energy from the Sun to drive this movement. Air movement starts again as the Sun rises. The ground warms, air starts rising (red arrow) and the stable layers formed during the night collapse. A so called 'entrainment zone' rises up from ground to the top of the boundary layer (dark blue) and mixes the air (C).



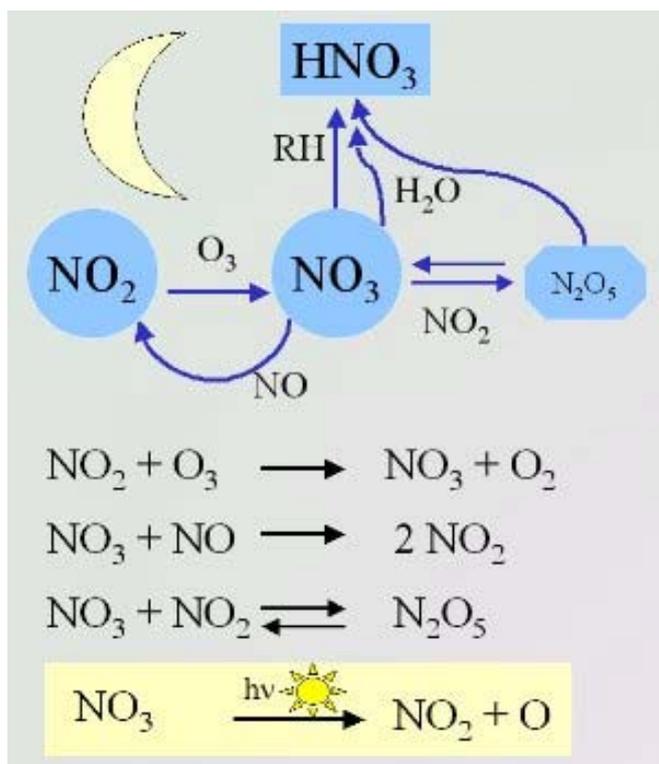
2. Model of the planetary boundary layer. The thickness of the planetary boundary layer may vary (see different altitudes at 12 o'clock).  
By Elmar Uherek, adapted from Stull, 1988.

In the winter the Sun's energy isn't always strong enough to breakdown the inversion layer in the morning and the layer exists for the whole day or even for several days. In these situations, pollution accumulates over the cities and leads to smog formation. Similarly in mountain valleys, the inversion layer can be trapped below the cloud layer



3. Inversion layer in winter in the mountains. © Institute for Geographical Education, University of Erlangen-Nurnberg, Germany.





4. Important night-time reactions of the nitrate radical. The radical is broken down by sunlight when the sun rises (shown in the yellow box). Scheme by Elmar Uherek.

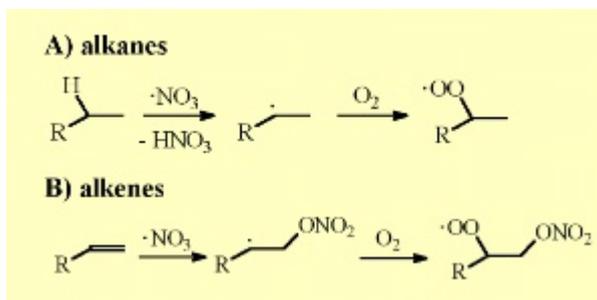
## Nitrate radical chemistry

The chemistry of the night-time atmosphere is dominated by the nitrate radical (NO<sub>3</sub>). These nitrate radicals are formed from the reaction of ozone (O<sub>3</sub>) with nitrogen dioxide (NO<sub>2</sub>). The reaction of NO<sub>3</sub> with NO<sub>2</sub> is the only way to form dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>) in the atmosphere. This N<sub>2</sub>O<sub>5</sub> acts as a store of NO<sub>3</sub>. It can either decompose back to NO<sub>3</sub> and NO<sub>2</sub> or react with water to form nitric acid (HNO<sub>3</sub>).

NO<sub>3</sub> reacts with organic molecules in the same way as OH does. It removes a hydrogen atom from alkanes to form an organic alkyl radical (R<sup>•</sup>) which then reacts with O<sub>2</sub> in the air to form peroxy radicals (RO<sub>2</sub><sup>•</sup>).

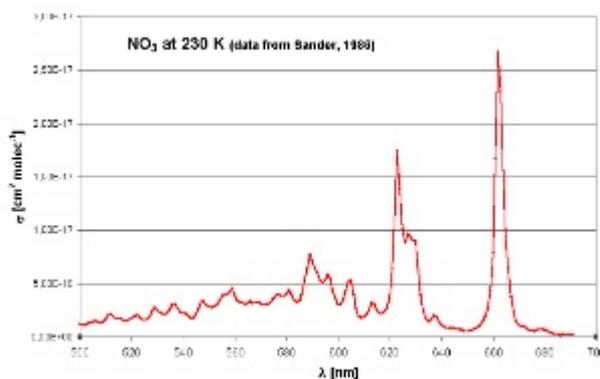
NO<sub>3</sub> adds also to the double bonds of unsaturated organic compounds and forms peroxy nitrates after addition of O<sub>2</sub>. The lifetime of NO<sub>3</sub> / N<sub>2</sub>O<sub>5</sub> decreases drastically as concentrations of water vapour increase. As water vapour levels increase, more of the NO<sub>3</sub> is converted to nitric acid (HNO<sub>3</sub>), in particular on liquid films on surfaces.

All peroxy species resulting from OH and NO<sub>3</sub> radicals or ozone reactions undergo rather complicated and numerous further reactions in the atmosphere leading to, for example, alcohols, aldehydes, nitrates and carboxylic acids.



5. Nitrate radical reactions with alkanes and alkenes.





6. Nitrate absorption spectrum in the visible range. Maximum absorption occurs in the red part of the spectrum (600-700 nm). Measurements were made at 230 K. Adapted from Sander (1986).

NO<sub>3</sub> radicals absorb light in the red part of the visible spectrum. As soon as the sun rises, the nitrate radical is photolysed mainly into NO<sub>2</sub> and O atoms and NO<sub>3</sub> concentrations fall to zero. Now hydroxyl radicals (OH) start to be produced and these become the most important oxidant in the atmosphere.

Ozone, the third most important oxidant in the atmosphere, does not react with alkanes but will react with alkenes (unsaturated hydrocarbons with a carbon to carbon double bond) if OH concentrations are low, particularly in the winter or the evening. We will look at the atmospheric chemistry of ozone later in this unit.

## Part 3: Observational spectroscopy

### Measurement techniques - spectroscopy

**Concentrations of trace gases in the atmosphere are very very low. In this section we look at the measurement techniques we use to determine the levels of trace gases in air.**

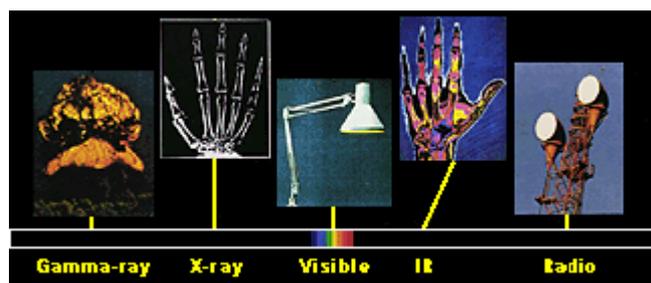
The two most common methods used for the analysis of air, either in the laboratory or outside, are:

- spectroscopy** - based on how different molecules interact with light
- chromatography** - based on how different molecules react with each other.

### The character of radiation

By using radios, microwaves, tanning salons and having X-Ray examinations we know that there are lots of different types of radiation in the air, all with different energies and only some of them visible as light. These different forms of radiation altogether form the electromagnetic spectrum. The least energetic form are the radiowaves, followed by microwaves, infra-red radiation, visible light, ultra-violet radiation and X-Rays with the most energetic being gamma rays. As the energy of the radiation increases, the frequency increases and the wavelength decreases. Nearly all these different forms of radiation interact with molecules and, from the way they do this, we can identify the chemical species present in the atmosphere.





1. The electromagnetic spectrum consist of different sorts of electromagnetic waves with different energies. We can use most of them to investigate the character and the concentrations of different molecules in the air. Source and further information about the electromagnetic spectrum: from NASA.

### Wavelength, frequency and energy of the different regions of the electromagnetic spectrum:

	Wavelength (m)	Frequency (Hz = s <sup>-1</sup> )	Energy (J)
<b>Radio</b>	$> 1 \times 10^{-1}$	$< 3 \times 10^9$	$< 2 \times 10^{-24}$
<b>Microwave</b>	$1 \times 10^{-3} - 1 \times 10^{-1}$	$3 \times 10^9 - 3 \times 10^{11}$	$2 \times 10^{-24} - 2 \times 10^{-22}$
<b>Infra-Red</b>	$7 \times 10^{-7} - 1 \times 10^{-3}$	$3 \times 10^{11} - 4 \times 10^{14}$	$2 \times 10^{-22} - 3 \times 10^{-19}$
<b>Optical</b>	$4 \times 10^{-7} - 7 \times 10^{-7}$	$4 \times 10^{14} - 7.5 \times 10^{14}$	$3 \times 10^{-19} - 5 \times 10^{-19}$
<b>Ultra-Violet</b>	$1 \times 10^{-8} - 4 \times 10^{-7}$	$7.5 \times 10^{14} - 3 \times 10^{16}$	$5 \times 10^{-19} - 2 \times 10^{-17}$
<b>X-Ray</b>	$1 \times 10^{-11} - 1 \times 10^{-8}$	$3 \times 10^{16} - 3 \times 10^{19}$	$2 \times 10^{-17} - 2 \times 10^{-14}$
<b>Gamma-Ray</b>	$< 1 \times 10^{-11}$	$> 3 \times 10^{19}$	$> 2 \times 10^{-14}$

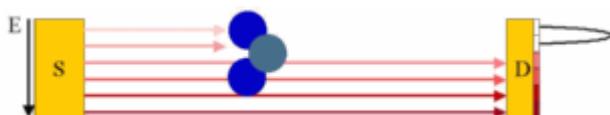
### Interaction of light and molecules

If a parcel of radiation meets a molecule in the air, it can transfer its energy and change the state of the molecule. Least energy is needed to make the molecule rotate, more to make the bonds move and even more to move the electrons present to higher energy levels.

The amount of energy transferred depends on the molecule, its size and how strongly the atoms of the molecule are bound together. Therefore, if we send radiation into the atmosphere and compare it before and after the air parcel we are looking at, we see that certain fractions of the radiation have been absorbed (consumed) by the molecules. From the character of the absorption we can determine the type and concentration of the molecules present.



So what happens if we emit infra-red radiation of different energies (E) from a source (S) through an air parcel and measure which fraction of the radiation reaches the detector (D)? The different energies (different wavelengths) are shown in different shades of red.



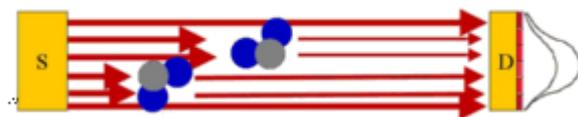
A molecule present in the air absorbs radiation of a particular energy from the source (here two of the six different energies emitted by the source are absorbed by the molecule)





2. a-c) Animations by Elmar Uherek.

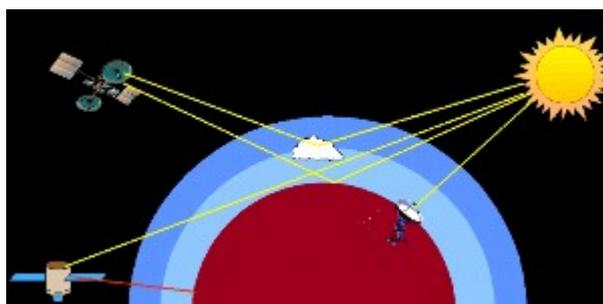
preventing it reaching the detector. If we subtract the original energy spectrum emitted from the source from that measured by the detector, we get an absorption peak which is shown on the right. This peak represents the radiation absorbed by the molecule. The more light absorbed, the higher the peak becomes. Another molecule in the air absorbs radiation as well. The bonds between the atoms in this molecule are, however, stronger so more energy is needed to make them move. As a result, the absorption peak appears at different energy (wavelength) of the spectrum.



2. d) In contrast to the three images before, we now zoom into a smaller energy range (all the arrows have very similar energies). The weakening of the colours tells us that less light arrives at the detector as the number of molecules present in the air increases. Since the absorption peak is the difference between the radiation emitted by the source and the radiation measured by the detector, the peak grows in size as the amount of radiation reaching the detector decreases.

From the position of the absorption band we get information on **which** molecules are present in the air. From the intensity of the absorption band, we can determine **how many** molecules there are in the air, because the amount of radiation absorbed is proportional to the number of molecules present.

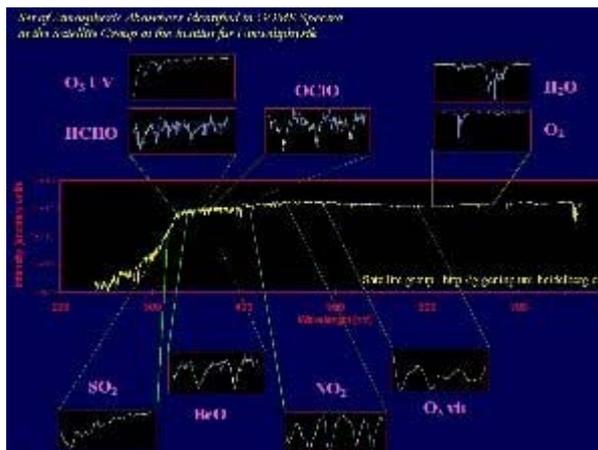
In the atmosphere there are several ways in which we can measure the absorption of radiation. On Earth, we can measure the absorption of ultra-violet and visible radiation from the Sun or reflected back from the Moon. We can also measure infra-red radiation emitted from the Earth's surface using satellites in space. We can also use satellites to measure the amount of solar radiation reflected directly back from the Earth's surface, by clouds or that which passes tangentially through the Earth's atmosphere.



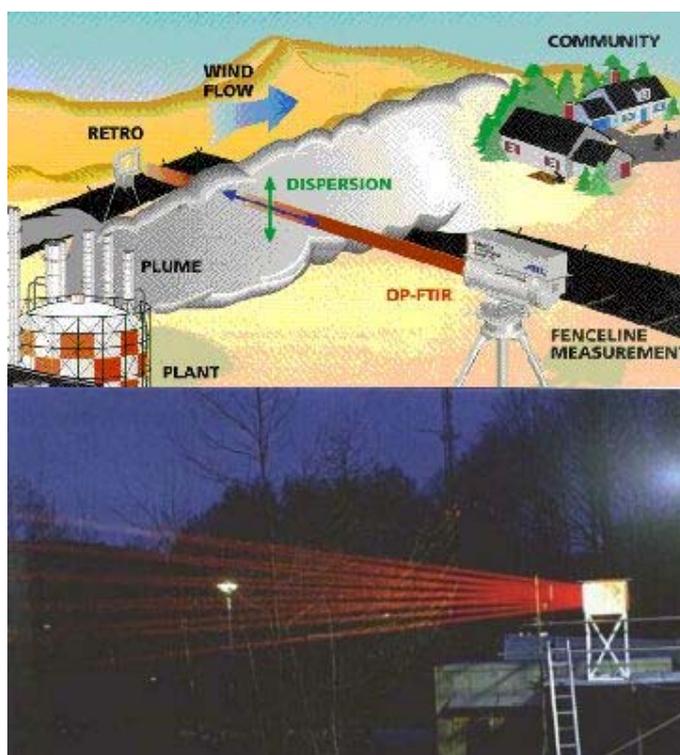
3. Satellite based measurements of absorption in the atmosphere. Image by Elmar Uherek.



It's not only infra-red radiation coming from the surface of the Earth which can be measured by satellites. It's also possible to measure the concentrations of important inorganic compounds such as ozone, nitrogen oxides and halogen oxides from space. One example is the Global Ozone Monitoring Experiment (GOME) which uses a spectrometer aboard the ERS-2 satellite to measure not only ozone but also nitrogen dioxide, water, sulphur dioxide and formaldehyde (HCHO) in the atmosphere at wavelengths from the ultra-violet, through the visible and into the infra-red (wavelengths from 240 to 790 nm).



4. Satellite based spectra of various inorganic compounds in the atmosphere, taken from the GOME instrument. Source: Satellite group, IUP Heidelberg.

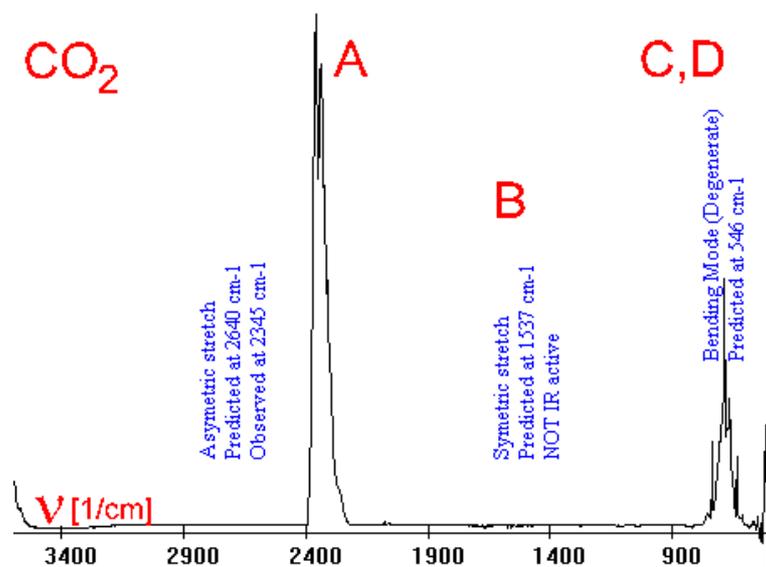


5. Please note: Infra-red radiation isn't visible to our eyes. In the photograph beams can be seen because the light source not only emits infra-red radiation but it also emits in the red part of the visible spectrum.

We can make similar measurements from the ground. As the concentrations of the chemicals we are interested in are really small, we use mirrors to reflect the radiation beam many times through the air before it reaches the detector. This means that the radiation passes through many kilometers of air and the concentrations of the chemical compounds are high enough for us to measure them.

The left hand side image shows such a set-up in theory (image from EPA Field Analytik Technology Encyclopaedia) and in practice (photo from FZ Jülich). Here infra-red spectroscopy is used and a simple example of the type of spectrum recorded is given below.

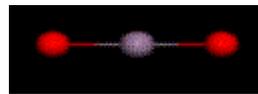




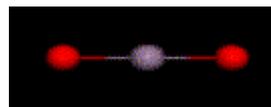
6. This simple example shows the infra-red spectrum of CO<sub>2</sub> together with the activated vibrations. Infra-red spectra can be rather complicated if the absorptions of different molecules overlap or if the molecules are complicated and many vibrations are possible. Spectrum and animations from Scott Van Bramer, Widner University.

Vibrations:

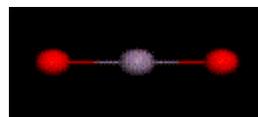
**A** asymmetrical stretch



**B** symmetrical stretch  
[not IR active]



**C** vertical bend



**D** horizontal bend

