Chapter 9

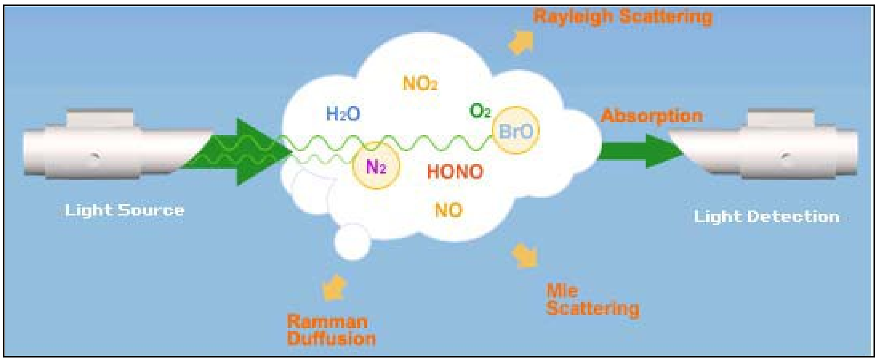
9. Environmental spectroscopy

9.1 Introduction

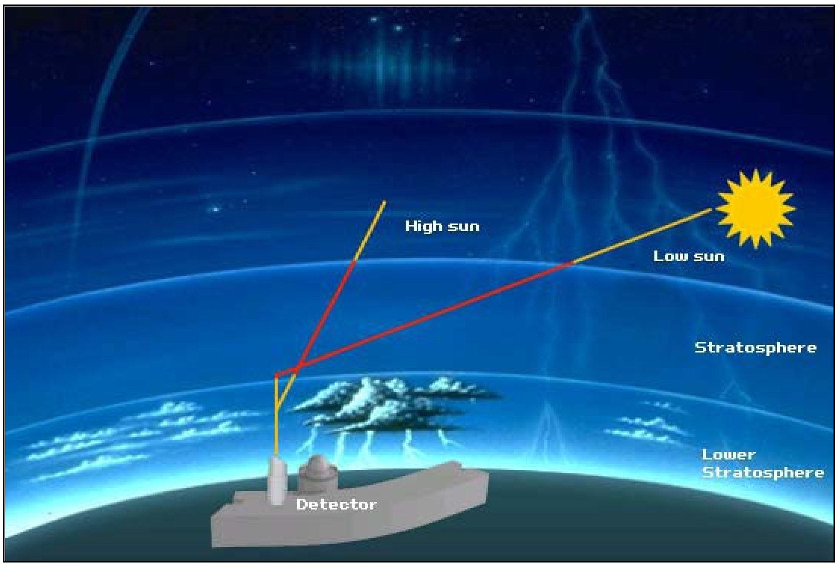
There are many areas in which laser technology is applied within environmental science as:

DOAS: Differential Optical Absorption Spectroscopy
LIDAR: Light Detection And Ranging
LIBS: Laser Induced Breakdown Spectroscopy
LDV:Laser Doppler Velocimetry
Laser – Aerosol measurements

9.2 DOAS

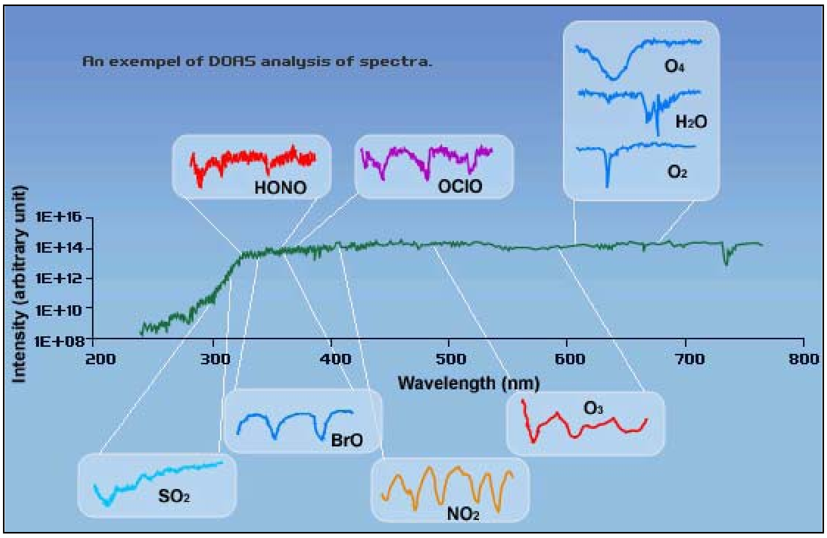


The DOAS system has basically three components, the emitter, the receiver and the analyser. The emitter sends a white light beam with a continuous spectrum (UV – IR) towards the receiver. A broadband laser can with modern technology be used as a emitter. Various pollutant molecules absorb at different wavelengths. The analyser, spectrometer and data handling system, measures the intensity against wavelength and converts the data to elemental contents.



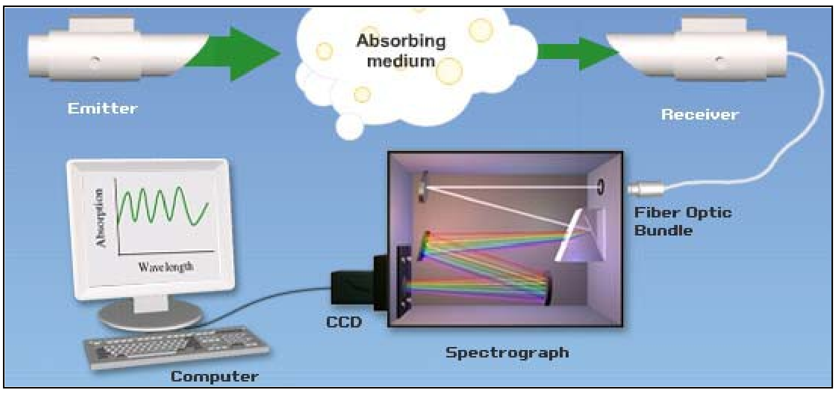
For stratospheric observations, one usually applies the zenith viewing direction, so called zenith-sky DOAS. Any viewing direction can be used; in fact measurements

towards the bright part of the sky especially, If the species of interest is known to be negligible in the troposphere. In some studies of e.g. OClO in Antarctica this method was shown to improve signal strength. At twilight, as a result of the long light path in the stratosphere, the sensitivity of this method is largest.
In the figure above this is illustrated, where simplified light paths are shown at both high and low sun. When a beam of light is passing through air or a gas, the DOAS principle relates the quantity of light absorbed to the number of gas molecules in the light path. It is just an example of applying the Lambert-Beer's absorption law.



This law just gives the relation between the amount of absorbed light and the number of molecules of the light path.
Since every molecule, and gas, has a unique absorption spectrum, it is possible to identify and determine the concentration of several different gases at the same time.

We can look in detail on the DOAS system. As described above, it has three major parts - an emitter, receiver and analyzer. A light source, or emitter (an ordinary light bulb, a so called globar irradiator, a xenon arc lamp or even a high frequency femtosecond laser beam) sends a beam of light to the receiver. The white light beam contains a range of wavelengths, from ultraviolet to the visible and to the infrared wavelength region. Different pollutant molecules absorb light at different wavelengths. The analyzer measure the intensity of the different wavelengths along the entire light path and converts this into concentrations for each of the gaseous pollutants.

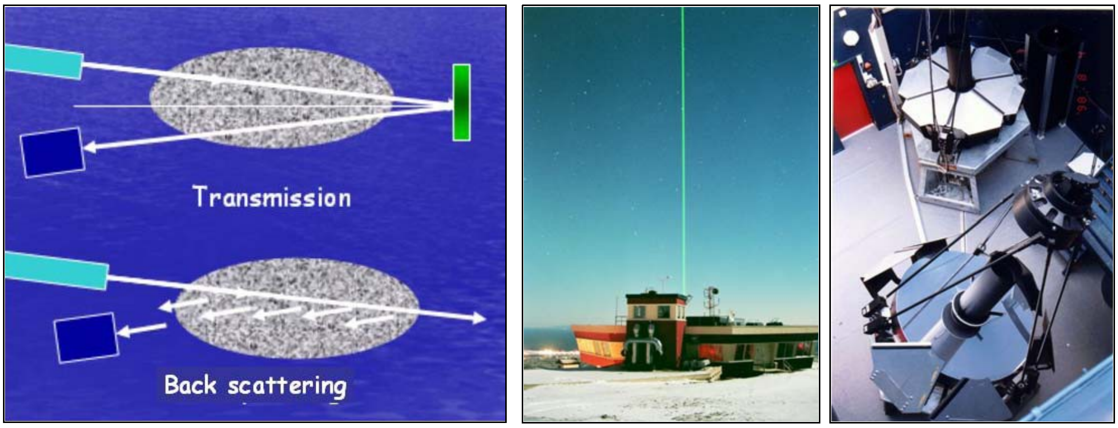


Details of the DOAS recording method

9.3 LIDAR

What you can do with LIDAR.
You can measure distances, velocities, rotation, chemical constituencies and concentrations.

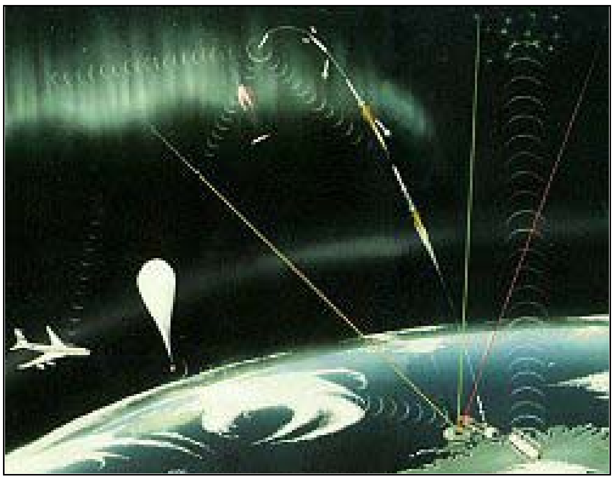
At the ALOMAR-laboratory in northern Norway, they study the ozone layer of the stratosphere at the height of 20-30 km. Two or three laser pulses are sent simultaneously towards the layer and a large telescope studies the back-scattered light.



One can use several methods based on either transmission or back-scattering when doing LIDAR experiments.

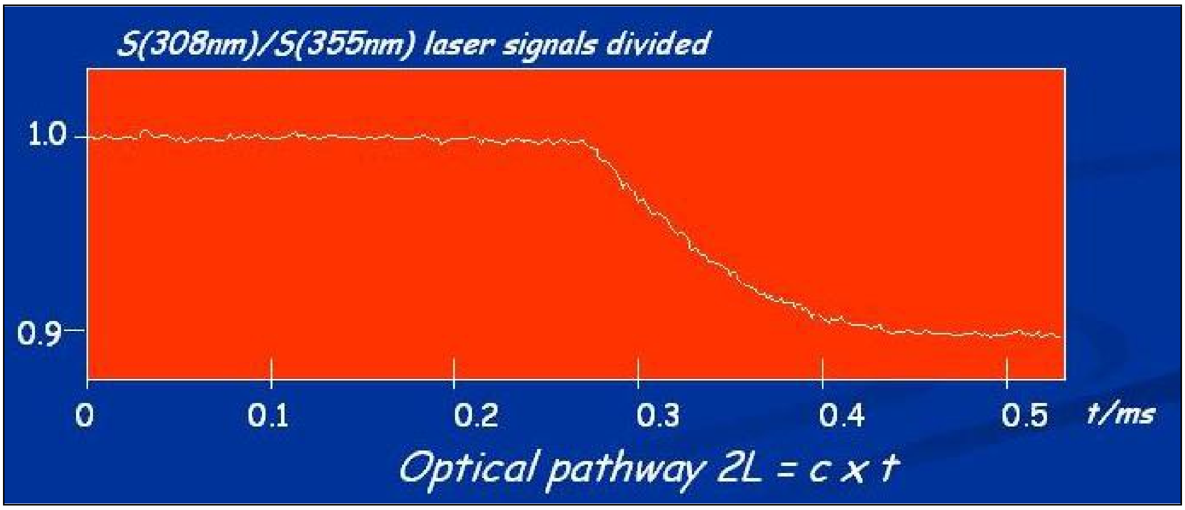
LIDAR-technology enables you to study the region between 2 and 100 km, e.g. that includes both the troposphere, the stratosphere (10-50 km), the mesosphere (50-90 km), the lower thermosphere (90-100 km), as well as the lower part of the ionosphere regarding clouds, chemical constituents etc.

One measures the atmospheric density, temperature, wind, impulse, concentrations and specific elements as ozone, water vapour, aerosols and particle content in the clouds.

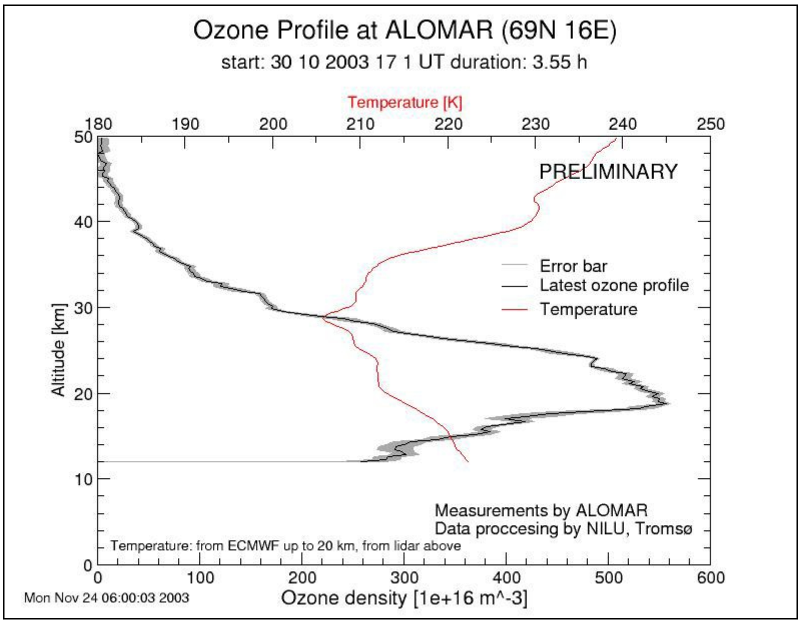


At the ALOMAR-laboratory in northern Norway, the ozone layer in the stratosphere at 20-30 km altitude is being studied. Two, or three laser pulses are shot simultaneously towards the ozone layer. Large telescopes detect the backscattered light.

A cw laser pumps two or three powerful pulsed lasers. There beams are made coaxial, parallel to the optical axis of the telescope, to the top of the telescope, where they are sent towards the ozone layer. By optical fibers, the backscattered light is transferred to the detection system.



The picture shows the result of ozone measurements by laser, where one have used two wavelengths, 308 nm partly absorbed by ozone, and 355 nm that is transparent to ozone without being absorbed. Backscattering is due to particles and aerosols in the atmosphere. At around 0,3 ms the intensity goes down for the response of one of the laser beams (308 nm), since the ozone layer starts to show. By studying the shape and changes of the curve, the number of ozone molecules per km can be determined at any height where we have a response. The thickness of the ozone layer can also be measured. In the figure below we see an intensity profile over the ozone layer as measured from the ALOMAR-laboratory.

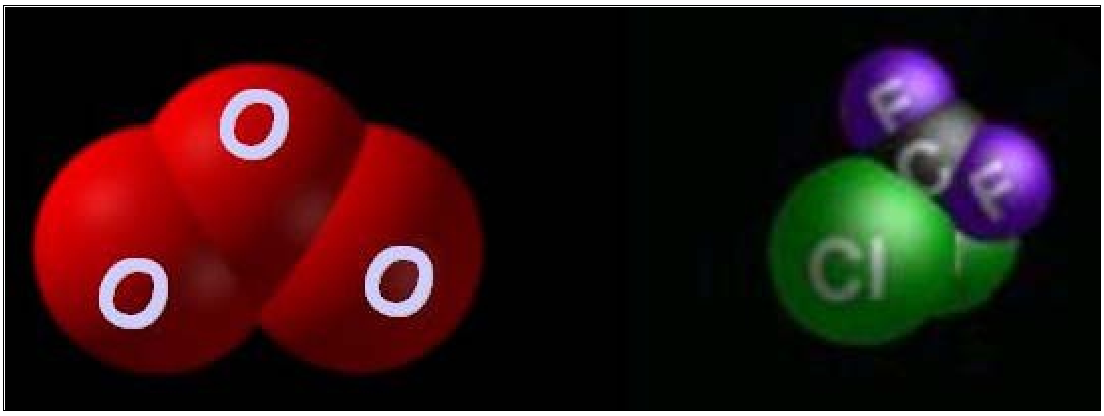


One sees that the density of ozone is at large at 20 km altitude and decreases up to 50 km. At the same time the temperature can be measured and we have a temperature minimum at 30 km altitude of around 210 K.

9.4 Dobson Unit

Let us hypothetically collect all ozone from the outer boarders of the atmosphere down to the ground, and create a layer of pure ozone with normal pressure and temperature. This will give a layer of thickness 2-5 mm. This whole amount of ozone is called *total ozone*, and has the unit *DU (Dobson Unit).* A more precise definition is: One DU is 2.69×10^{20} ozone molecules per m^2. The annual mean value lies around 350 DU over Sweden and corresponds to a thickness of 3.5 mm at STP, (Standard Temperature and Pressure). Globally the ozone layer is thinner closer to the Equator (ca 250 DU) and thicker at higher latitudes (300-400 DU). Nowadays, due to the annually appearing ozone hole over the Antarctic lead to a decrease in the annual mean value over the Antarctic as compared to the ozone layer over the Equatorial regions.

9.5 Ozone and the Ozone hole



ozone, three-atomic oxygen CFC

Ozone is a three-atomic oxygen molecule that is created in the atmosphere via the reaction:

O_2 + (UV-radiation < 240 nm) → 2 O
O + $O_2 \rightarrow O_3$

Interacting with atomic oxygen can destroy ozone:

O_3 + O → 2 O_2

This reaction can be catalyzed by certain free radicals, of which the most important are hydroxyl (OH), nitric oxide (NO) and atomic chlorine (Cl) and bromine (Br), that can be found in the atmosphere In recent decades the amount of ozone in the stratosphere has been declining mostly due to emissions of CFCs and similar chlorinated and brominated organic molecules.We can ask ourselves the question, why there is an ozone hole repeatedly appearing at the Antarctic region and not anywhere else? There shows to be several factors affecting the ozone:

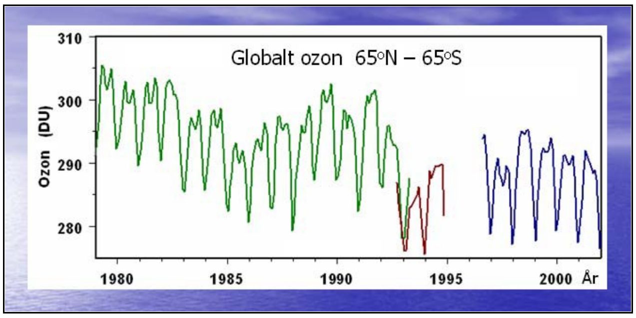
a) There are substances that dissociate the ozone molecule, i.e. oxides of chlorine, bromine and nitrogen. There are as described above, substances that dissociate the

O_3 molecule, as CFCs and airborne traffic at high altitudes. However, most often the

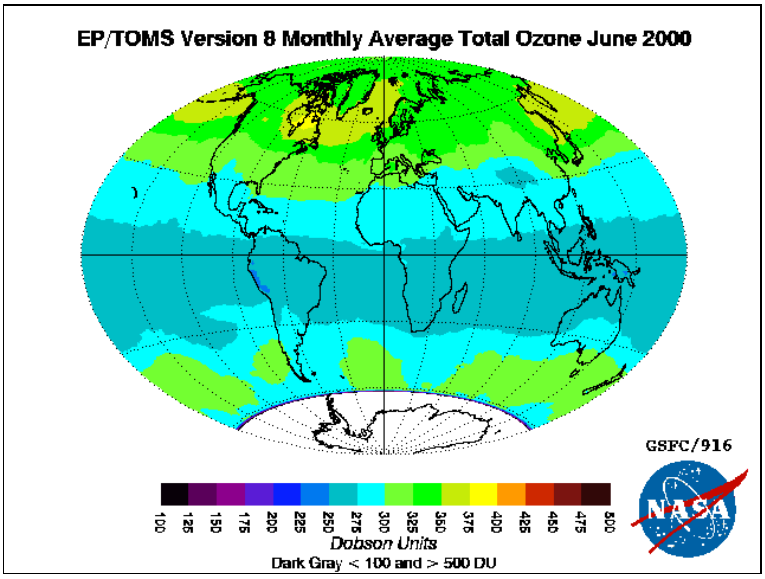
emission sources are close to the Earth. That is why it takes quite a long time for these pollutants to reach the altitude of 20-40 km where the ozone layer is situated. When these substances reach this altitude they will mix and distribute making the concentrations worldwide be the same.

b) During the Antarctic polar night over, a so-called polar whirl (Polar Vortex) is created. This is due to the dynamics of air and due to the cooling by radiation towards space. The polar whirl effectively separates the air within the whirl from the air outside. The temperature inside the whirl can decrease to -90 ^oC over large areas during the winter. When the temperature reaches -75 ^oC polar stratospheric clouds (PSC) can be created. They are a condition for rapid ozone depletion. These PSC lie higher up (20 km) than ordinary clouds (0-10 km). They consist of some water or ice, but also of SO_2 or *HCl*. They look very nice and are called mother-of-pearl clouds.

c) Another condition for ozone depletion is the sun activating chemical reactions destroying the ozone. This occurs when at last, the sun rises after the long polar night. However, it is a requirement for short wavelengths or higher photon energy to hit the ozone layer. When the sun reaches around 10 degrees above the horizon, this condition is fulfilled. That occurs in August over the Antarctic and the photochemical processes are activated resulting in a fast depletion of the ozone molecules.



In this picture we can study the annual ozone variation



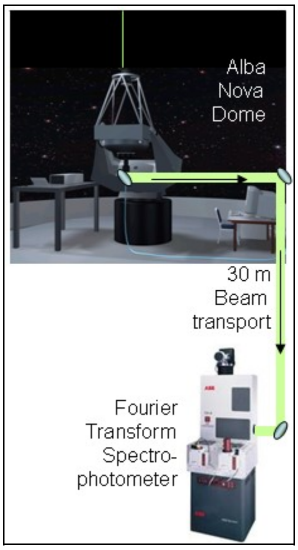
In this picture we can study how the ozone is spread around the World. On the x-axis we have the Dobson unit in colors. The picture is from NASA.

We summarize: Three factors are require for an ozone hole:

• Agents for ozone depletion like CFCs
• Low temperatures - PSC
• Radiation from the sun

9.6 Modern LIDAR-technology at KTH

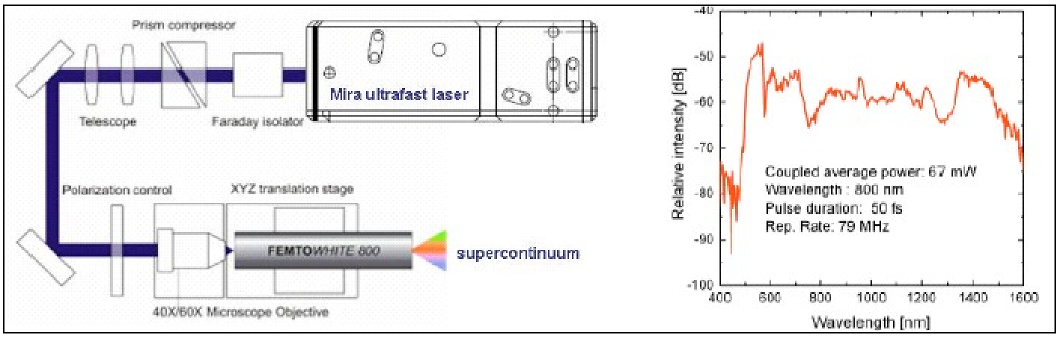
A*"state-of-the-art"* LIDAR-DOAS-laboratorium for the study of atmospheric atoms and molecules is under construction in Stockholm.
A 2.5 high telescope with an opening diameter of 1.1 m was placed in the AlbaNova dome at KTH during 2007.



A system for beam transport of the gathered light down to a high resolution Fourier Transform Spectrometer in the basement is under construction, where new technology will be used.

9.7 Supercontinuum-DOAS

Normal DOAS systems consist of three parts, emitter, receiver analyser. Here a *Super continuum* femtosecond laser, covering a large wavelength area depending on the femtosecond pump laser used, will replace the standard lamp.



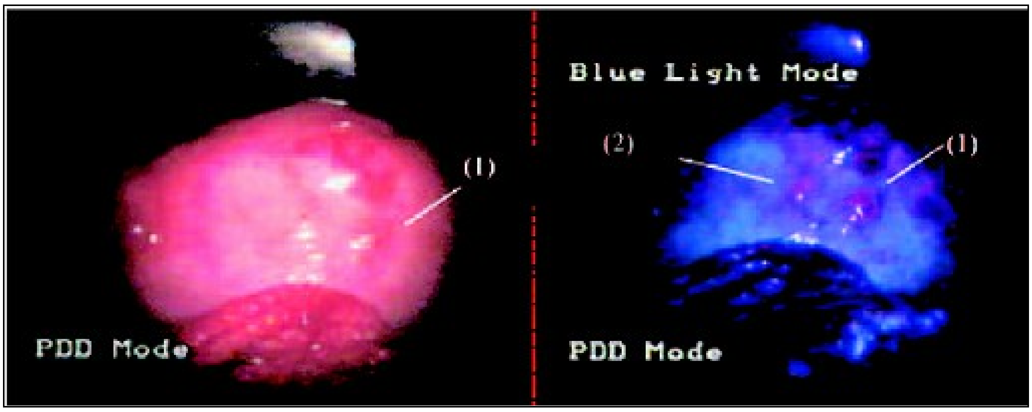
Super continuum-generation is the formation of a broad continuous spectrum by letting a high power laser propagate in a non-linear medium. Alfano and Shapiro observed the effect already in 1970. The spectral broadening of the laser light depends on the dispersion of the medium. This super continuum can be achieved by using fiber optic and will create wavelengths from the UV to the IR, making all kinds of molecules to be investigated.

9.8 Lasers within medicine

The use of laser technology has grown streadily within medicine since the 60-ies. Here are important milestines where the laser has become an important tool:

- Dentistry
- Skin therapy
- General surgery
- Ophthalmology
- Neurosurgery
- Photodynamic therapy
- Urology
- Veterinary medicine

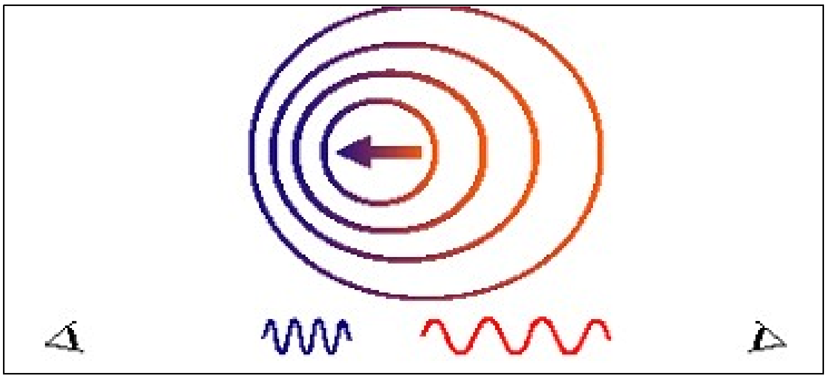
We will take an example within Skin therapy where the laser can be used in many fields, e.g. removal of large vessels in the face and on the legs (telangiectasias), when port wine toes are at hand, in removal of tattoos etc.
Lasers are also used to detect and remove tumours.



Detection of tumors with white ligt and remoal with blue light. Two fluorescent tumours can be seen.

Laser doppler velocimetry

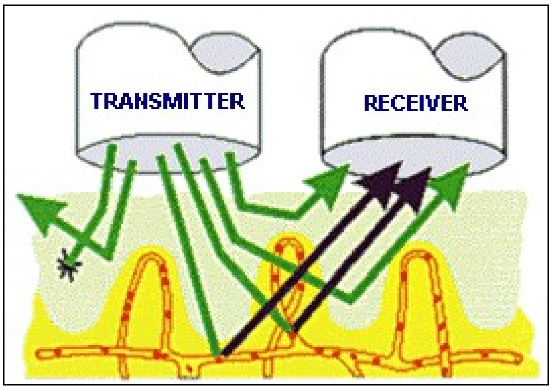
This is a field where one can study the flow in vessels where the velocity is low. One can use the method to study the flow in different tissues. A laser pulse is sent towards the vessel and the frequency shift between the reflected light from the moving blood particles and the surroundings is measured.



If the blood is moving towards the detector the received frequency increases. If the blood moves in the other direction the frequency decreases. By applying the Doppler effect (for small *v/c*) we get the following expression:

$$f = f'/(1-v/c) \rightarrow f' = f(1+v/c)$$

This expression directly gives the velocity of the blood.



Example:
Determine the frequency difference f – f´ if we have a blood flow in a capillary with speed 100 mm/s.
We use a He-Ne laser with wavelength $\lambda = 633$ nm
Solution
The Doppler expression gives $f' = f(1 + v/c)$ and the frequency difference:
$f' - f = fv/c$
With $c = f\lambda$ we get $f' - f = v/\lambda = 100 \times 10^{-3}\ ms^{-1}/633 \times 10^{-9}\ m = 158$ kHz.