



KTH Physics

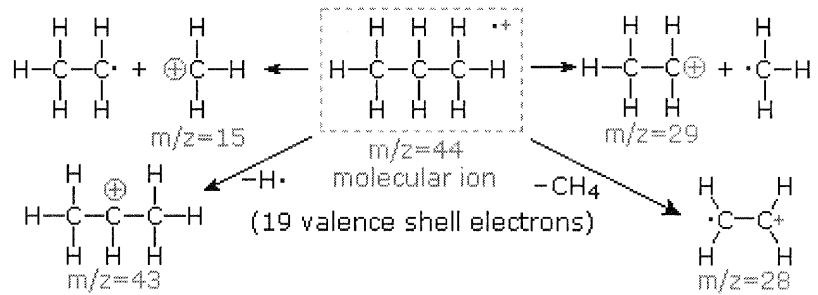
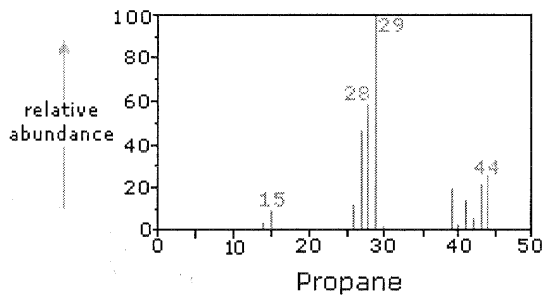
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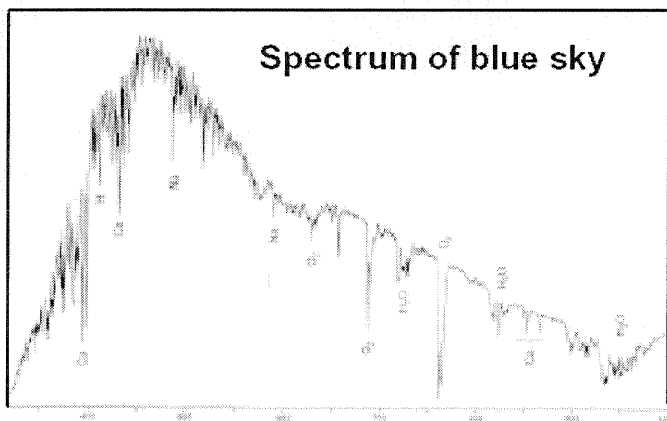
Laboration

The Mass Spectrometer and the Optical Grating Spectrometer

Mass Spectra of Propane



The Solar absorption Spectrum



Goals

There are several goals with this laboration. For the two main laborations:

A. The quadrupole mass spectrometer

The goal is, to understand that it's possible to get a useful spectrum through the process of fragmentation of the molecule and be able to interpret the most important mass fragments in air and in one other gas spectrum demonstrated by the assistant. Related goal is to learn that a pump system has to be used to lower the pressure in the system.

B. The optical grating spectrometer

One main goal is to use the spectrometer in environmental spectroscopy and look for and study pollutants and abundant molecules and atoms in the atmosphere. One specifically important goal is estimate the depth of the atmospheric ozone layer. A second goal is to study the solar curve and compare it to the Planck curve and measure the temperature of the surface of the sun. A third goal to do this is to use modern spectroscopic equipment, i.e. CCD cameras connected to a monochromator and a computer. Finally a fourth goal is to perform computer operations and data handling.

Performance

In this laboration **careful notes should be written by the student** which should be accepted by the assistant during the laboration.

The laboration consists of two main parts:

A. The quadrupole mass spectrometer

1. Demonstration of and measurements with a quadrupole mass spectrometer. The assistant teacher shows the instrument, and demonstrate how a) an air spectrum and b) an unknown gas, is measured.

B. The optical grating spectrometer

Demonstration and measurements with optical grating spectrometer.

1. The student detects and record a spectrum of a lamp choosed after discussion with the assistant. Assistant helps to calibrate the spectrometer.
2. The assistant demonstrates how the the solar curve can be measured and that it's possible to find absorption bands of ozone, O₃, O₂ and H₂O and other molecules. The temperature of the surface of the sun is determined.
2. If there are time, the assistant show how to estimate the depth of the ozone layer in the atmosphere. This will only give a rough estimate of ozone layer depth.

Steps in the laboration

A. The quadrupole mass spectrometer

The assistant demonstrates the main principles and record one air spectrum and one other gas spectrum and the spectra are analyzed together with the assistant.

B. The optical grating spectrometer

The laboration will be performed in three steps. Firstly, calibration of the monochromator has to be done by using standard calibration lamps and the mercury lamps in the experimental hall. Secondly, a registration of a thermal spectrum will be recorded from a glowing object to study the thermal intensity distribution as a function of wavelength, and thirdly the registration of the radiation from blue sky light (or in bad weather, the absorption of light in the laboratory, when white light passes, say 10 m of air.)

History of mass spectrometry

The foundation of mass spectrometry can be traced back to the pioneering work of J.J. Thomson and F.W. Aston from 1897 onwards at the Cavendish Laboratories, Cambridge University. The work carried out by Thomson and his co-workers received 7 Nobel prizes in Physics and Chemistry, including the unique occurrence of his son (one of his co-workers) also receiving one. The first practical mass spectrometers were made available in the early 1940s, and were principally used for low mass organic analysis, especially by the oil industry. These techniques made use of the electronic ionization (EI) technique to produce analyte ions. In 1948, Vickers, Manchester, U.K., marketed the MS-2 instrument - the World's first commercially produced mass spectrometer. This instrument had a very limited resolution and a maximum analyte mass range of around 300. Also at this time, the measurement of ion times-of-flight (TOF) as a mass analysis technique was discovered. In the early 1950's, the fragmentation pathways of ions were beginning to be understood; but instruments were still plagued by their limited mass range. In 1953 the quadrupole mass analyser was patented. These types of analyser along with the TOF systems have lead to the relatively cheap "benchtop" systems that are now currently available.

Gas Chromatography was the technique that, when used in conjunction with mass spectrometry (GC-MS), could be used for 'real' chemical analysis. It also made possible the analysis of the components and composition of mixtures. This triggered off a large development program in MS which is still going strong today. In 1956 the first biological samples (steroids) were successfully analysed. This sparked off interest in MS from synthetic chemists and biochemists in the drug and medical sciences.

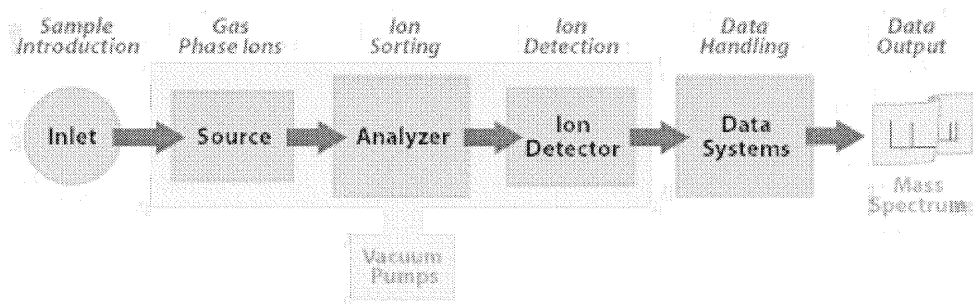
A. The quadrupole mass spectrometer

Mass spectrometry

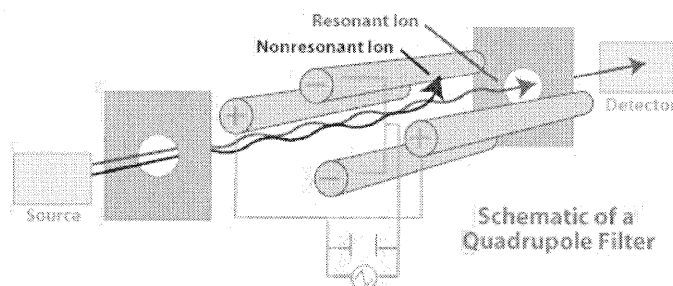
Mass spectrometry is a powerful analytical technique that is used to identify unknown compounds, to quantify known compounds, and to elucidate the structure and chemical properties of molecules. Detection of compounds can be accomplished with very small quantities (as little as 10^{-12} g, 10^{-15} moles for a compound of mass 1000 u). This means that compounds can be identified at very low concentrations (one part in 10^{12}) in chemically complex mixtures. Mass spectrometry provides valuable information to a wide range of professionals: physicians, astronomers, and biologists, to name a few. Mass Spectrometry (MS) is an analytical spectroscopic tool primarily concerned with the separation of molecular (and atomic) species according to their mass. MS can be used in the analysis of many types of sample from elemental to large proteins and polymers. In order to achieve a mass separation on a practical scale it is necessary to ionize the species under investigation so that you can take advantage of the basic principles of particle and ion physics for analysis. Accurate mass measurements can be used to match empirical formulae. Fragmentation fingerprints (specific to each compound) can be used to identify samples by comparison to fragment databases. Controlled fragmentation can be used for structural elucidation of novel compounds. Common peaks observed in a spectrum can give useful information regarding functional groups. Relative isotope abundance's are used to get information regarding the elements making up a compound.

The Quadrupole Mass Filter, working principle

The quadrupole mass filter is one of the most popular kinds of mass spectrometers. It's easy to detect and analyze gases with.



1. A sample of the gas to be analyzed is drawn into the system. All mass spectrometers analyze gases. If the substance to be analyzed isn't already a gas, it must be converted to a gas - usually by heating - before going through the rest of the procedure.
2. The gas is bombarded with electrons, which break the electrically neutral molecules apart and turn the fragments into positive ions.
3. The ions are guided into an area bordered by four parallel rods. The rods carry a varying, radiofrequency electrical potential (voltage) which creates a dynamic electric field that affects the paths of the ions. Ions of the correct charge-to-mass ratio are guided down the axis of the rods and strike the detector at the end, generating an electric current. All other ions - those whose masses are too high or too low relative to their charge - are deflected away and strike the rod surfaces or



the exit aperture.

4. The device's computer, knowing the precise charge and mass of the ions that reached the detector, can identify the fragments and calculate which kind of molecule they came from, thereby identifying the chemical. Then the electric field generated by the rods is changed, and ions of a different charge-to-mass ratio are guided to the detector. Eventually (after less than a sixth of a second) ions of all charge-to-mass ratios in the gas sample can be covered, and all the of corresponding chemicals identified.

Theory, the quadrupole mass analyser

At first the system will be pumped and working pressure is around 10^{-5} mbar $\approx 10^{-8}$ Pa. Then the molecules to investigate are ionized, then the ions go to the mass analyser. In a quadrupole mass analyser, only electric fields are used to separate ions according to their m/z values. A quadrupole consists of four parallel rods or poles through which the ions being separated are passed. The poles have a fixed DC and alternating RF voltages applied to them. Depending on the produced electric field, only ions of a particular m/z will be focused on the detector, all the other ions will be deflected into the rods. By varying the strengths and frequencies of electric fields, different ions will be detected thus making the mass spectrum. The trajectory of an ion through a quadrupole is very complex.

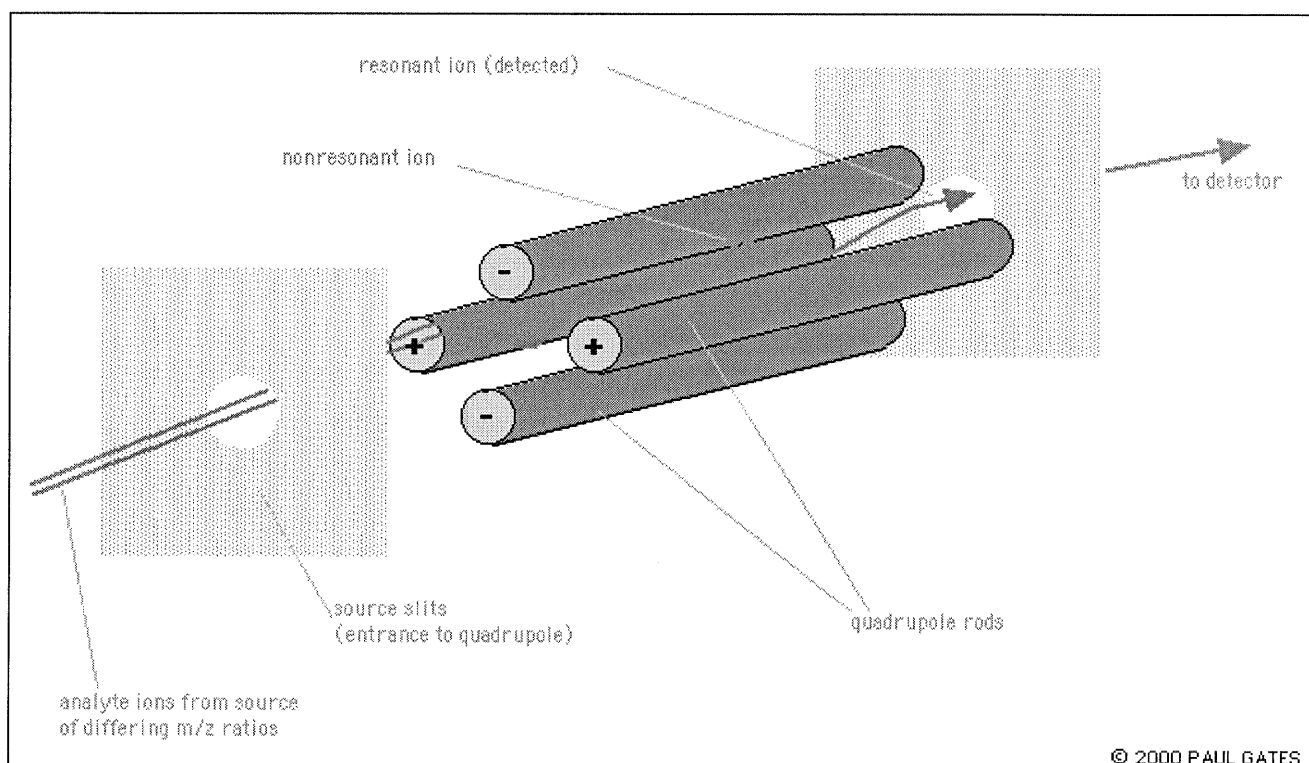


Figure: Schematic diagram of a quadrupole mass analyzer. The four rods are shown as being circular in the diagram but in practice they have a hyperbolic cross-section.

Two opposite rods will have a potential of $+(U+V\cos(\omega t))$ and the other two $-(U+V\cos(\omega t))$ where U is a fixed potential and $V\cos(\omega t)$ represents a radio frequency (RF) field of amplitude V and frequency ω . When $\cos(\omega t)$ cycles with time, t , the applied voltages on opposed pairs of rods will vary in a sinusoidal manner but in opposite polarity (due to them being offset). Along the central axis of the quadrupole assembly and also the axis between each adjoining rod the resultant electric field is zero. In the transverse direction of the quadrupoles, an ion will oscillate amongst the poles in a complex fashion, depending on its m/z , the voltages U and V and the frequency, ω , of the alternating RF potential. By suitable choices of U , V and ω , only ions of one m/z will oscillate stably through the quadrupole mass analyser to the detector. All other ions will

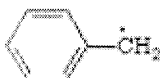
have greater amplitude of oscillation causing them to strike one of the rods. In practice, the frequency ω is fixed with typical values being 1-2 MHz. The length and diameter of the rods will determine the mass range and ultimate resolution that can be achieved by the quadrupole assembly. However, the maximum mass range that is normally achieved is around 4000 u with a resolution of around 2000.

Fragmentation

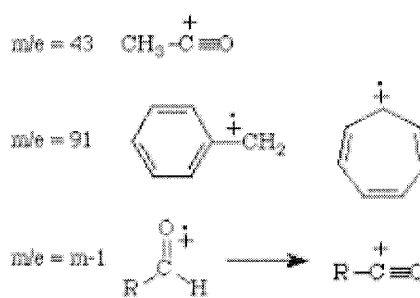
At the ionization the ionized molecules will crack into small fragment, and the fragments will create peaks in the mass spectrum.

Common Mass Spectrum Fragments

Commonly Lost Fragments

m-15	$\cdot\text{CH}_3$
m-17	$\cdot\text{OH}$
m-26	$\cdot\text{CN}$
m-28	$\text{H}_2\text{C}=\text{CH}_2$
m-29	$\cdot\text{CH}_2\text{CH}_3$ $\cdot\text{CHO}$
m-31	$\cdot\text{OCH}_3$
m-35	$\cdot\text{Cl}$
m-43	$\text{CH}_3\dot{\text{C}}=\text{O}$
m-45	$\cdot\text{OCH}_2\text{CH}_3$
m-91	

Common Stable Ions



The lists given above are by no means exhaustive and represents only the simplest and most common fragments seen in the mass spectrum.

Applications

- Detection and identification of steroids in athletes
- Monitoring the breath of patients by anesthesiologists during surgery
- Determination of the composition of molecular species found in space
- Determination whether honey is adulterated with corn syrup
- Location of oil deposits by measuring petroleum precursors in rock'
- Monitoring fermentation processes for the biotechnology industry
- Detection of dioxins in contaminated fish
- Determination of gene damage from environmental causes
- Establishment of the elemental composition of semiconductor materials

B. The optical grating spectrometer

1. Introduction.

Light from the sun reaching the earth is essential for life. The intensity and colors of the solar spectrum as it reaches the atmosphere is transmitted and arrives finally at the surface of the earth. The detailed balance between inflow and outflow of solar energy establishes the temperature of the earth's surface. It is well known that the abundance of ozone (O₃) in the atmosphere protects the earth from too intense UV radiation. Ozone absorbs radiation at wavelengths < 295 nm. Another important molecule in the atmosphere is CO₂ that is vital in regulating the energy balance of absorbed and emitted light of the earth. In this laboratory we will study the abundance of molecules and atoms in the atmosphere by recording the radiation from blue sky. We will also measure the blackbody radiation of the sun seen by studying the sky and try to determine the Temperature of the surface of the sun.

2. Thermal Radiation

2.1 Introduction

Electromagnetic radiation in the UV, visible and IR wavelength regions can be observed by using grating monochromators and detectors such as photomultiplier tubes, photodiodes and CCD-cameras. The silicon detectors can detect radiation between 285 nm and 1.23 μm.

2.2 Detection of Electromagnetic (E-M) Radiation

The most commonly used device, when detecting E-M radiation in the UV, visible and near IR wavelength regions, is the grating monochromator (Fig.1)

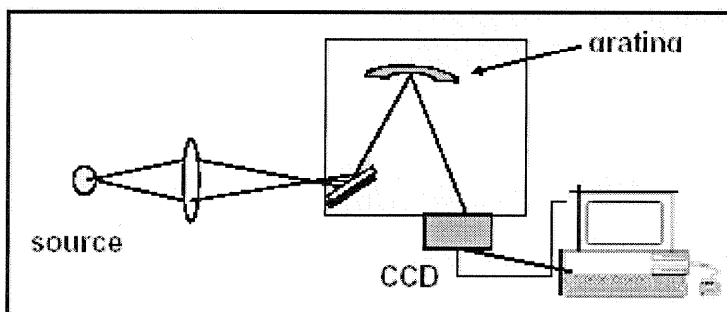


Fig.1 The experimental setup with the grating monochromator

Grating equation. The grating equation for light of wavelength λ incident perpendicular on the grating is

$$n\lambda = d \sin \theta \quad (1)$$

where n is the order number, d is the distance between the grooves of the grating and θ is the diffraction angle.

Overlapping orders. When one looks at the spectrum at a certain angle θ , one can in some cases, observe different wavelengths λ_1 and λ_2 in the same position of the spectrum, i.e. we have $n_1 \lambda_1 = n_2 \lambda_2 = d \sin \theta$. If we have $n_1 = 1$ and $n_2 = 2$ and $\lambda_1 = 500 \text{ nm}$ we get $\lambda_2 = 250 \text{ nm}$. Thus, one has to be very careful, when studying grating spectra due to the problem with overlapping orders. However, in this laboration, the grating is "blazed" why this is a minor problem. In this laboration we will study atomic spectral lines of different light source. We will use known spectral lines to calibrate the spectrometer.

Planck radiation. When observing the IR wavelength region, the spectrum is most often due to black body or thermal radiation that can be described by the Planck radiation law. The power distribution function of the Planck radiation law is given by the following expression:

$$F(\lambda) = \frac{\text{const}}{\lambda^5} \cdot \frac{1}{e^{\frac{hc}{\lambda kT}} - 1} \quad (2)$$

Where h is Planck's constant, k is the Boltzmann's constant, c is the speed of light and T is the absolute temperature. The function is shown in Fig.2 below.

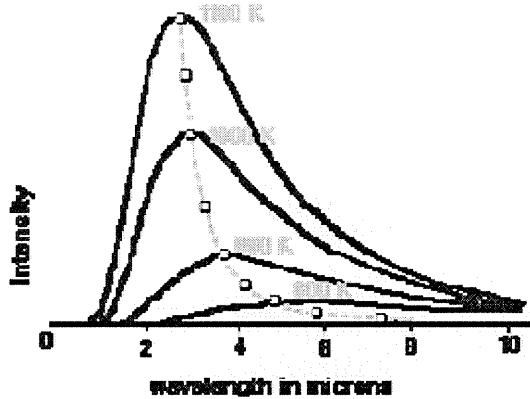


Fig.2 Planck radiation law. Power distribution function $F(\lambda, T)$. The intensity of the source as a function of wavelength at different temperatures.

This function agrees well with experiments and it also contains the Wien's displacement law where the value of λ_m is given as a function of the absolute temperature T :

$$\lambda = hc / (4.965kT) \quad (3)$$

This equation can be used to determine the temperature T , of a black body or a lamp, if the spectrum is recorded and the wavelength λ_m , where we have the maximum intensity is deduced. Here the monochromator equipped with the CCD-detector can be used. It consists of a linear array of 2048 silicon detectors of a total length of 25 mm.

2.3 Temperature of the sun

The recording of blue sky enables us to determine the temperature of the sun by measuring the wavelength where the intensity of the spectrum is at its maximum and to use Wien's law to deduce the temperature.

3. Atmospheric spectra

3.1 Introduction

Looking at the blue sky spectrum on the cover, we can observe several absorption bands belonging to both molecular and atomic species. The ozone molecule is responsible for many of the absorption bands. One sees a broad, but not deep dip in the intensity between 550 nm to 610 nm (The diffuse B-X Chappuis bands). However, the main absorbing region of light by the ozone molecule lies in the 220 nm – 300 nm wavelength region (The diffuse D-X Hartley bands). Other diffuse bands can be found in the IR region around 10 μm . The maximum concentration of ozone appears between 20 km to 26 km above the ground in the atmosphere. If one would collect all the ozone molecules in a layer at atmospheric pressure, the thickness of the layer would only be 0.3 – 0.4 cm!

At several other wavelengths than mentioned above, we see strong absorption due to water and of course also that is due to oxygen.

3.2 Absorption of radiation

If radiation is being absorbed by an absorbing gas one can deduce the so-called Lambert-Beer's law:

$$I(z) = I(0) e^{-Kz} \quad (4)$$

Where I is the intensity, K is the absorption coefficient and z is the distance of absorption. The coefficient K depends on several parameters, the number of molecules in the volume the light has passed, the refractive index, the Einstein coefficient for absorption and the light frequency. For ozone, the coefficient K has been measured to be of the order of 10^{-5} m^{-1} . This coefficient varies with altitude, why this value can be regarded as a rough mean value. Due to the fact that we use the sun as a light source for the experiment, and that the angle between the sun, the ozone layer and the observer, changes during the day, we have to use a constant that varies with the time of day according to the table below:

Time of day	constant
9,00	0.040 exp(-4)s
10,00	0.062 exp(-4)
11,00	0.068 exp(-4)
12,00	0.074 exp(-4)
13,00	0.080.exp(-4)
14,00	0.093.exp(-4)
15,00	0.101 exp(-4)
16,00	0.140 exp(-4)

Tasks during the laboration.

- Study the mercury spectrum and calibrate the spectrometer.
 - Use a white lamp and record its spectrum with the grating monochromator. Find the wavelength that gives the maximum intensity. Determine its color temperature using Wien's law.
 - Register the spectrum of blue sky and determine the temperature of the sun by applying Wien's law.
 - Study the solar spectrum and identify the absorption bands of ozone, O₃, O₂ H₂O and the abundant atoms. Make a table of these bands and their corresponding wavelength and compare with standard wavelength tables.
 - Try to calculate the ozone depth in the atmosphere by measuring the intensity variations of the he diffuse B-X Chappuis bands in the visible region. This will only give a rough estimation of the ozone layer depth.
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Appendix

CP200 Imaging spectrograph computer key words

In order to start the computer program after switch on:

Go to directory LAMDA

Then start the program by running: LS2000

C:<enter>

CD \LAMDA <enter>

LS2000 <enter>

Then the program starts and the readout on the last page in this paper is shown.

Exposure times can be varied from 0.005 s to 8 s.

Always start with short exposures, say 0.05 s for strong light sources.

A single scan will be obtained if the **ONE** mode has been chosen.

If you want to make a scan, just press **RUN**

If you already have made a recording and wants to clear the picture, then press **CLEAR**.

If you want to find the wavelength of a peak, just press **PEAK** and point at the peak and you will get the wavelength and intensity.

If you want to change **the intensity scale or the wavelength** scale, just click the number on the axes, i.e. 9999 on the intensity and a window will appear where you can choose the wanted intensity.

More details can be found in the manual. You will easily be making exposures after a couple of minutes.