

# Rayleigh scattering by gas molecules: why is the sky blue?

## Objectives

After completing this experiment:

- You will be familiar with using a photomultiplier tube) as a means of measuring low intensities of light;
- You will have had experience of working safely with a medium power laser producing visible wavelength radiation;
- You will have had an opportunity to use the concept of solid angle in connection with scattering experiments;
- You will have had the opportunity to experimentally examine the phenomenon of polarization;
- You should understand how the scattering of light from molecules varies according to the direction of polarization of the light and the scattering angle relative to it;
- You should have a good understanding of what is meant by cross-section and differential cross section.
- You should be able to describe why the daytime sky appears to be blue and why light from the sky is polarized.

**Note the total time for data-taking in this experiment is about one hour. There are a lot of useful physics concepts to absorb in the background material. You should read the manual bearing in mind that you need to thoroughly understand how you will calculate your results from your measurements BEFORE your final lab session. This is an exercise in time management.**

## Safety

A medium power Argon ion laser is used in this experiment. The light from it is potentially dangerous to you and other people in the room. You must read the safety notes in Section 3 (Method) before opening the laser beam shutter.

The photomultiplier tube is easily damaged and you should read the instructions in Sections 2 and 3 (Apparatus and Method) before operating this device.

# 1 Background Physics

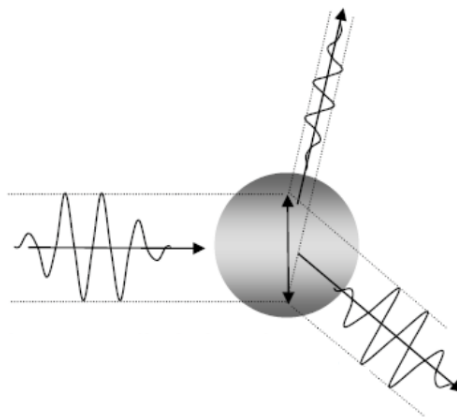
## 1.1 Rayleigh Scattering

The scattering of radiation by particles that are small compared with the wavelength of the incident radiation is known as Rayleigh Scattering.

- *The laser used in this experiment emits mostly green light of wavelength 488 nm. Estimate the ratio of the wavelength of this radiation to the size of a gas molecule in the air.*

In this regime the photons cannot resolve the constituents of a gas molecule, the electrons and nuclei, and interact coherently with the ensemble. In addition the molecule is sufficiently massive that its recoil energy is negligible compared with that of the photon and the scattering process is said to be elastic, resulting in the scattered photon having the same frequency as the incoming light.

It is useful to think of a classical model of Rayleigh scattering, as illustrated in Figure 1. The incident laser beam can be considered to be a continuous electromagnetic wave



**Figure 1** – Interaction of an electromagnetic wave with a spherically symmetric molecule

comprising an oscillating electric field and an associated magnetic field. In our case, as we will see, the incoming wave is polarized and therefore has an electric field in a

defined direction. The incident electric field forces the electrons associated with the molecule to oscillate at the frequency and in the direction of its electric field whereas the heavier nucleus remains essentially stationary.

The molecule is therefore an oscillating charge dipole and, if it is spherically symmetric, we expect the amplitude of oscillation of the electrons to be independent of the direction of the incoming electric field. According to electromagnetic theory, the oscillating dipole must itself radiate light. However, as suggested in Figure 1, the amplitude of the reradiated light is expected to depend on the angle between its direction of propagation and the direction of the driving electric field of the incoming radiation. Notice that although the molecules in this model are spherically symmetric with respect to their interaction with electromagnetic radiation, if the incoming radiation is *polarized* the intensity of reradiated light is not isotropic (i.e. it depends on the viewing angle).

- *Imagine the incoming wave is in a horizontal beam, with its E field vertical. Would you expect the scattered light to be stronger when viewed from above the beam, or from the side? Consider: (i) the E field of the scattered light must be perpendicular to its direction of travel (light is a transverse wave); (ii) the E field of the scattered light is generated by the electric polarisation of the molecules; (iii) the polarisation is proportional to, and aligned with, the incoming E field.*

From the above discussion a reasonable hypothesis is to assume that the intensity of light scattered would vary as given by

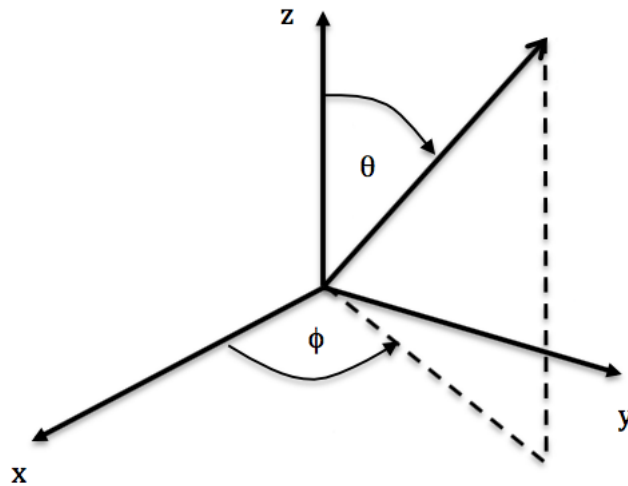
$$\delta I(\theta) \propto \sin^2 \theta, \quad (1)$$

where  $\delta I(\theta)$  is the light intensity or power collected by our detector at an angle  $\theta$  to the electric field of the incoming laser beam, see Figure 2.

- *Using the geometrical arguments discussed above, show that equation 1 is indeed reasonable.*

Notice that in this equation we have to assume that the detector is small enough or far enough away that we can assign a single value of  $\theta$  to the measurement. We will return to this point in the next section. Surely the total power collected depends on the size of the detector and its distance from the scattering volume and also, in some way, on the number of molecules in the scattering volume?

- *Suggest another parameter that you would expect the intensity of the scattered light to depend upon.*



**Figure 2** – Spherical polar geometry. The incident radiation is traveling along the negative  $x$  direction with its electric field oscillating in the  $x$ - $z$  plane. Scattered light is viewed at an angle  $\theta$  to the  $z$  axis, and  $\phi$  is  $90^\circ$  in our apparatus.

## 1.2 Solid Angle

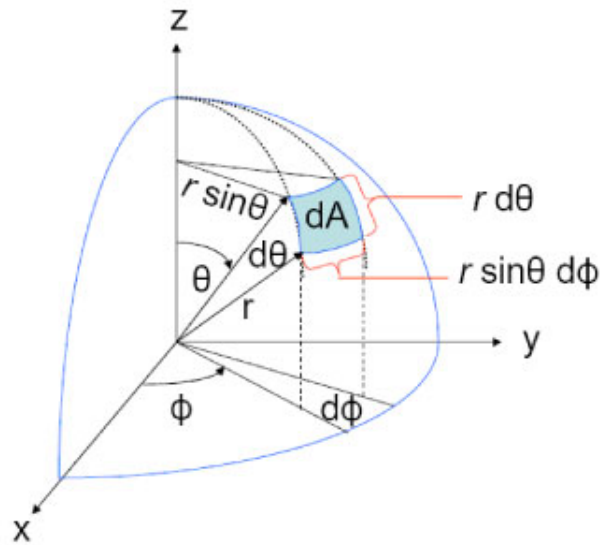
In order to compare our measurements of scattered light power at different angles with theory, we need to use the concept of solid angle to quantify how much light our detector will detect given its distance from the source and its area. You will probably have come across solid angles in other contexts such as electricity and magnetism, so this may be revision for you.

Angle, in radians, is simply the length of an arc of a circle divided by its radius and clearly the largest angle subtended by such an arc is  $2\pi$ . We can use the same idea in two dimensions and state that the solid angle  $d\Omega$  is the area of a selected patch on a spherical shell,  $\delta A_S$  divided by the square of the radius of the shell,  $R$ ,

$$d\Omega = \frac{\delta A_S}{R^2}. \quad (2)$$

- *Suppose that the scattering takes place with equal intensities over all angles from a small volume of gas. If our detector was a distance  $d$  away and had an area  $\delta A_S$ , what fraction of the total scattered light would it detect?*

We know that we can express the area of the patch in terms of spherical polar coordinates:  $\theta$ , the polar angle, with  $\theta = 0$  at the 'North pole', and  $\phi$ , the angle of azimuth



**Figure 3** – Illustrating solid angle  $dA/r^2 = \sin\theta d\phi d\theta$  ( $r$  is the same as  $R$  in our equations, and  $dA$  is  $\delta A_S$ )

[http://www.oceanopticsbook.info/view/light\\_and\\_radiometry/geometry](http://www.oceanopticsbook.info/view/light_and_radiometry/geometry)

measured in the equator (longitude), see Figure 3. If the patch is defined by the angular widths  $d\theta$  and  $d\phi$  centered about the angles  $\theta$  and  $\phi$ , then

$$\delta A_S = R \sin\theta d\phi \cdot R d\theta. \quad (3)$$

or using equation 2 we can define

$$d\Omega = \sin\theta d\phi d\theta \quad (4)$$

- Integrate equation 4 over the surface of a sphere and show that it comes to  $4\pi$ .
- What are the units of solid angle?

The geometry of the collimator attached to the photomultiplier tube is sketched in the appendix, and the parameters required to calculate the solid angle that the detector subtends at the laser beam are given.

### 1.3 Scattering cross-sections

Now we need to think about how the physics of the interaction and the details of the reradiating volume of gas contribute to our measurement of scattered power. Cross-sections are widely used in physics to describe scattering phenomena. In the simplest

case of billiard ball-type collisions between a point like projectile and a target of radius,  $r$ , the cross-section  $\sigma$  would be defined as an area of the target as seen by the projectile. This would simply be  $\sigma = \pi r^2$ . Now imagine that the incoming particle travels in a direction perpendicular to a slab of material of area  $A$ , containing a total of  $\nu$  particles. If the particle is free to enter the block anywhere on its surface, the probability of its hitting one of the particles is simply

$$P = \nu \frac{\pi r^2}{A}. \quad (5)$$

If there are  $N$  scatterers per unit volume and the thickness of the block is  $t$  we know that  $\nu = Nat$ , so that equation 5 can be written,

$$P = \sigma Nt. \quad (6)$$

and we use this as the definition of  $\sigma$  even when the simple mechanical model of the collisions does not apply.

We extend this idea by expressing the probability of a scattering event to be given by the fraction of the intensity of incident radiation that is scattered from the beam,

$$\delta I = I_0 \sigma Nt. \quad (6a)$$

If the scattering is completely isotropic, this light is scattered uniformly over  $4\pi$  steradians (sr). On the other hand, for anisotropic scattering, we need to know the component of the total cross section that is responsible for scattering light at angle  $\theta$ ,

$$\delta I(\theta) = \delta \sigma(\theta) I_0 Nt \quad (6b)$$

If we then write this equation in terms of the scattering cross section per unit solid angle

$$\delta I(\theta) = \left( \frac{d\sigma}{d\Omega} \right)_{\theta} \delta \Omega_d \cdot I_0 Nt, \quad (6c)$$

where now  $\delta \Omega_d$  is the solid angle subtended by the detector and  $\left( \frac{d\sigma}{d\Omega} \right)_{\theta}$  is referred to as the differential cross-section for scattering into an angle  $\theta$ .

- Write down a definition of differential cross-section.

Given the reasoning behind equation 1 on page 3, we can rewrite equation 6c on the preceding page as

$$\frac{\delta I(\theta)}{\delta \Omega_d I_0 N t} = \left( \frac{d\sigma}{d\Omega} \right)_\theta \approx K \sin^2 \theta \quad (7)$$

where  $K$  is a constant. The aim of the experiment is to measure  $K$  and hence, with the information given in the next section, compare it with the expected value of the total cross section for Rayleigh scattering. Equation 7 sets out the parameters that need to be determined experimentally in order to measure the Rayleigh cross-section. The Appendix shows the geometry required to calculate  $\delta \Omega_d$ .

## 1.4 The Rayleigh cross-section

The Rayleigh differential cross-section for the scattering of polarised light from spherically symmetrical molecules is

$$\left( \frac{d\sigma}{d\Omega} \right)_\theta = \frac{4\pi^2 (n-1)^2 \sin^2 \theta}{N^2 \lambda^4} \quad (8)$$

where  $N$  is the number of molecules per unit volume,  $n$  the refractive index of the medium and  $\lambda$  the wavelength of the light. Given this functional form, an integral of it over the full solid angle will give the total cross-section. Thus the total cross-section can be obtained as

$$\sigma = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \left( \frac{d\sigma}{d\Omega} \right)_\theta \sin \theta d\theta d\phi. \quad (9)$$

Note that as the gas pressure increases  $N$  increases but so does the refractive index  $n$ . These two effects cancel to leave the Rayleigh cross-section independent of pressure.

- Evaluate the integral in eqn. 9 to obtain an expression for the total Rayleigh scattering cross-section, in terms of  $K$  from eqn. 7, and hence the experimental observables.
- Can you derive, from the statements given above, a relationship between the refractive index of a gas and its pressure? Why is there a relationship between scattering and refractive index?
- How accurately do you need to know the refractive index of air to enable you to calculate the Rayleigh scattering to make a determination of  $\left( \frac{d\sigma}{d\Omega} \right)_\theta$  to 10%?

In reality the gas molecules in the air are not spherical. In this case the scattering is modified slightly to give,

$$\frac{d\sigma}{d\Omega} = \frac{4\pi^2 (n-1)^2}{N^2 \lambda^4} \left( \frac{2\rho_v}{1-\rho_v} + \sin^2 \theta \right), \quad (10)$$

where  $\rho_v$  is the depolarisation factor, which for air is approximately 0.015. When  $\theta = 90^\circ$  the depolarisation factor can be considered to be negligible.

- Evaluate algebraically the ratio of the differential cross-section in equation 10 for  $\theta = 0^\circ$  to that for  $\theta = 90^\circ$ .
- How would the angular dependence of the differential cross section, and a non-zero depolarisation factor show up in a plot of scattered intensity as a function of angle  $\theta$ ? Use eqns. 7 and 10 to decide what function you will need to fit to the data to get  $K$ ,  $\sigma$  and  $\rho_v$ .

## 2 Apparatus

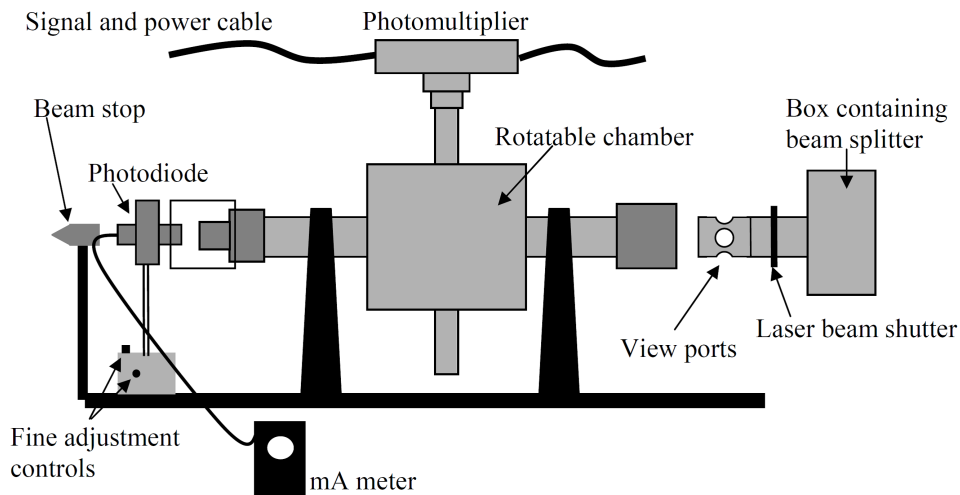
A schematic of the experimental apparatus is shown in Figure 4. The laser beam is incident on a beam splitter which is housed in the locked aluminium box at the end of each beam line. Immediately after the box containing the beam splitter is a shutter which can be closed to isolate the laser from the rest of the beam line. Do not open the shutter until you have read the rest of this section and the sections on experimental method and safety. After the shutter there is a section of the beam pipe with four viewing ports to enable you to observe the scattering of the laser beam by the air.

These ports allow observation both from above and from the side of the laser beam. Just after the section of pipe with the viewing ports there is a gap in the laser beam line which would normally be covered with a sliding light guard. This gap is used to allow a polaroid to be inserted into the laser beam to check its polarization. The main body of the apparatus comprises a sealed vacuum chamber that can be rotated about an axis coaxial with the laser beam. On the side of the chamber there is a collimator system and a photomultiplier tube. Details of the collimator are shown in the Appendix. An angle scale is fixed to the chamber so that the angle of rotation can be measured. Note that the angle has an arbitrary zero.

The beam line ends with an oblique exit window followed by a photodiode. It should not be possible to view light from the laser beam between the photodiode and cover for the exit window.

- Why is the exit window mounted at an oblique angle to the laser beam?





**Figure 4** – Scattering chamber, laser beam line, photodiode and photomultiplier

A fixed beam stop is mounted at the end of the optical bench to ensure no laser light can escape the beam line and be a danger to people working in the laboratory.

### **On no account must the beamstop be removed!**

A photodiode and a mA meter are provided to monitor the power of the laser at the end of the beam line.

The photomultiplier is connected to a unit which provides both the necessary high voltage to give the gain in the photomultiplier and an amplifier to detect the photocurrent. The photocurrent is given on the larger display in relative units. The smaller display shows the photomultiplier bias voltage in kilovolts.

You are also supplied with a neutral density filter mounted in a brass tube. There are two attenuators (one for each set of apparatus) that are labelled 3 and 4. Filter 3 has an attenuation coefficient of  $6.3 \times 10^{-11}$ , while filter 4 has attenuation factor of approximately  $7.6 \times 10^{-12}$ . There is also a sheet polarizer for shared use. You may need to ask a demonstrator to show you how to identify the direction of polarization (plane of the electric field) of the laser beam.

On the bench is a vacuum manifold. The centre tap of the manifold is not used and should be kept closed. The tap on the left is an air admittance valve and the right hand tap connects to the vacuum line. The vacuum pump is situated under the stone bench at the back of the laboratory and is common to all experiments. When you have evacuated your apparatus, close the vacuum valve to prevent air being let into the system by other users evacuating their vacuum systems.

### 3 Method

#### Safety Check

**Before starting, check that the laser beam shutter is closed: that is, pushed down. If you see a blue green glow coming from the apparatus then there is laser light getting through and the shutter is open. Close the shutter.**

**Check that the photodiode is mounted at the end of the laser beam line and the angled mount of the diode is closely positioned against the end window of the beam line. Ensure the sliding safety guards are in place just after the view ports and by the end window and photodiode. Check that the photomultiplier is mounted on the side of the scattering chamber and the coupling between the chamber and phototube is bound with black tape.**

- *Have you observed the safety procedures?*

#### 3.1 Align the detection optics

Open the beam shutter and observe the change in the reading of the current from the photodiode detecting the intensity of the light transmitted straight through the apparatus. You may have to adjust the position of the diode with the horizontal and vertical translation adjustments on the mount to maximise the signal on the meter.

#### 3.2 View scattering through ports

You should also observe a faint blue/green light through the view ports. This will be caused by the scattering of the light from the air, which is a very faint continuous light, as well as scattering from dust that is seen as specks of light that vary slowly in intensity. Note the relative intensity of the Rayleigh scattered light from the air and ignore the scattering from the dust specks.

- *Is the Rayleigh scattered light stronger when viewed from the side or from the top of the view port?*

### 3.3 Determine the polarization of the laser

Slide the light guard away from the gap in the laser beam line. With your hand shielding the sheet polarizer, so that no laser light can scatter from it into your eyes, insert the polarizer into the laser beam. Rotate it and note the intensity variation of the laser light as registered by the photodiode at the end of the laser line. Remove the polariser and slide the guard over the gap in the laser beam line. This measurement reveals the polarization axis of the laser beam, so long as you know the polarisation axis of the polariser. The latter can be determined using daylight reflected from the polished floor, using a trick based on figure 1; ask a demonstrator to show you.

### 3.4 Check that the chamber is at atmospheric pressure

Look at the mechanical pressure gauge to check that the chamber is not evacuated. If it is, open the air admittance valve and let the pressure rise slowly, taking about a minute to go from fully evacuated up to atmospheric pressure. If you let air in to the chamber too quickly it can stir up dust. As you have seen in Section 3.2, scattering from the dust is much stronger than that from the the air, so the presence of dust in the chamber can adversely affect your results.

### 3.5 Align the photomultiplier

Rotate the chamber so that the photomultiplier is viewing light scattered in the horizontal plane. When rotating the chamber use two hands to apply a torque while minimising lateral forces that may misalign your beam line. Check that the photodiode current does not vary by more than a few percent. If it does, this is an indication that the beam line has been misaligned. If this is the case you should seek the help of a demonstrator.

### 3.6 Power up the photomultiplier

Turn on the photomultiplier bias and current readout electronics. Adjust the potentiometer on the photomultiplier case to apply about 850 V to the photomultiplier (0.85 kV on the small display). You can try different values of bias voltage without damaging the photomultiplier tube: a large current should be more accurate but perhaps more unstable. Note the setting, because it has a strong effect on the photomultiplier gain. You must keep it the same in the later straight-through measurement.

### 3.7 Make measurements of scattered intensity vs angle

Measure the photomultiplier signal as a function of the angle over an angular range that covers at least  $120^\circ$ . The expected intensity distribution is a  $\sin^2 \theta$  function, so ensure your measurements go somewhat beyond the vertical and horizontal positions.

- *Why do you only need to cover a little over  $90^\circ$  and include the vertical and horizontal positions in the measurements?*

The readings will fluctuate due to photon counting statistics, thermal noise in the photomultiplier, and occasional dust particles intercepting the laser beam. Hence you should take several readings at each angle setting.

### 3.8 Determine the background

You need to take measurements with air in the chamber and with the chamber evacuated. The readings in vacuum will give you a measure of the background intensity. Although you will not need to use a background reading taken with the shutter closed it would be useful for you to make one such measurement.

- *What causes the background?*
- *Why is it sufficient to take readings with air in the chamber and with the air removed?*
- *What is the best method of determining the mean intensity and the uncertainty on this mean at each angle?*

As evacuation and refilling the chamber with air takes time and also risks disturbing dust you should think carefully about the order in which you do the measurements. You also need to think about the uncertainties and the number of angle settings you will make.

### 3.9 Data Checking

Subtract the readings taken with the chamber evacuated from those made with the chamber full of air to obtain the background corrected intensity. Plot this as a function of angle. You will later use a version of this plot to determine the Rayleigh cross section. See Section 1.4 on page 7 for details.

- *Why is it a good idea to plot the data points as they are being taken?*

### 3.10 Determine the signal as a function of pressure

Set the photomultiplier to the angle at which the maximum intensity was measured and take intensity readings as a function of pressure in the chamber. Again you need to think about the uncertainties on these readings as you take the data.

### 3.11 Calibrating the photomultiplier tube

So far you have made relative intensity readings of the scattered light with a photomultiplier and readings of the direct laser beam with a photodiode. In order to extract a cross-section (normalised intensity for scattering see equation 7 on page 7), you need to use the same device to measure both the beam and the scattered light. To do this you need to observe some safety precautions. These precautions are essential to protect the sensitive photomultiplier from light. Excessive light can destroy a photomultiplier tube, especially while it is powered. Even a small exposure can adversely affect the background count rate and short-term sensitivity of the tube, which will adversely affect your results. **Please read through the following procedure carefully PRIOR to making the adjustment.**

1. Ensure that the room is dark and illuminated only by the red safety lights. Ask others working in the room to turn off or shield intense sources of light.
2. Note the voltage set on the high voltage power supply then turn it off (no need to turn it down).
3. Close the beam shutter.
4. Remove the black tape acting as a light seal from the coupling between the photomultiplier and the scattering chamber.
5. While shielding the photomultiplier from stray light uncouple it from scattering chamber and attach it to the housing of the neutral density filter. Once this has been done, you can relax the precautions taken against stray light.
6. Mount the photomultiplier with the neutral density filter in place of the photodiode at the end of the beam line.
7. Open the laser beam shutter. Turn on the photomultiplier supply and check it is exactly the same value as was used for the measurements of the scattered light. Adjust the position of the photomultiplier until the signal is maximised. You should **NOT** look at the laser spot on the end window at any point. Always make sure that the sliding light guard is in place when the beam shutter is open.

8. Once you have made a set of readings of the laser intensity with the photomultiplier you should turn off the photomultiplier supply, shut off the laser beam and return the photomultiplier to its original position on the scattering chamber **WHILE OBSERVING ALL THE PREVIOUS STATED PRECAUTIONS.**
- *How can you check if the repositioning of the photomultiplier affected the background count rate, also known as the dark current of the tube?*

## 4 Results and analysis

You should have:

- Tables of data for the intensity as a function of chamber angle. These should include background readings and intensity after background subtraction. You should be able to work out the uncertainty on each of the results.
- A plot of the background corrected intensity as a function of angle.
- The intensity of the laser beam measured with the photomultiplier and attenuator.
- The attenuation coefficient for the neutral density filter.

By fitting a suitable function to your data, using a nonlinear fitting program such as Qtiplot, Scidavis, ..., you should determine experimental values for the Rayleigh cross section and the depolarisation factor.

For comparison, you should calculate the expected cross section from eqns. 8 and 9 by looking up the refractive index  $n$  of air.

Figure 5 summarises the flow of data described in this manual.

You should also investigate whether the scattering has the expected pressure dependence.

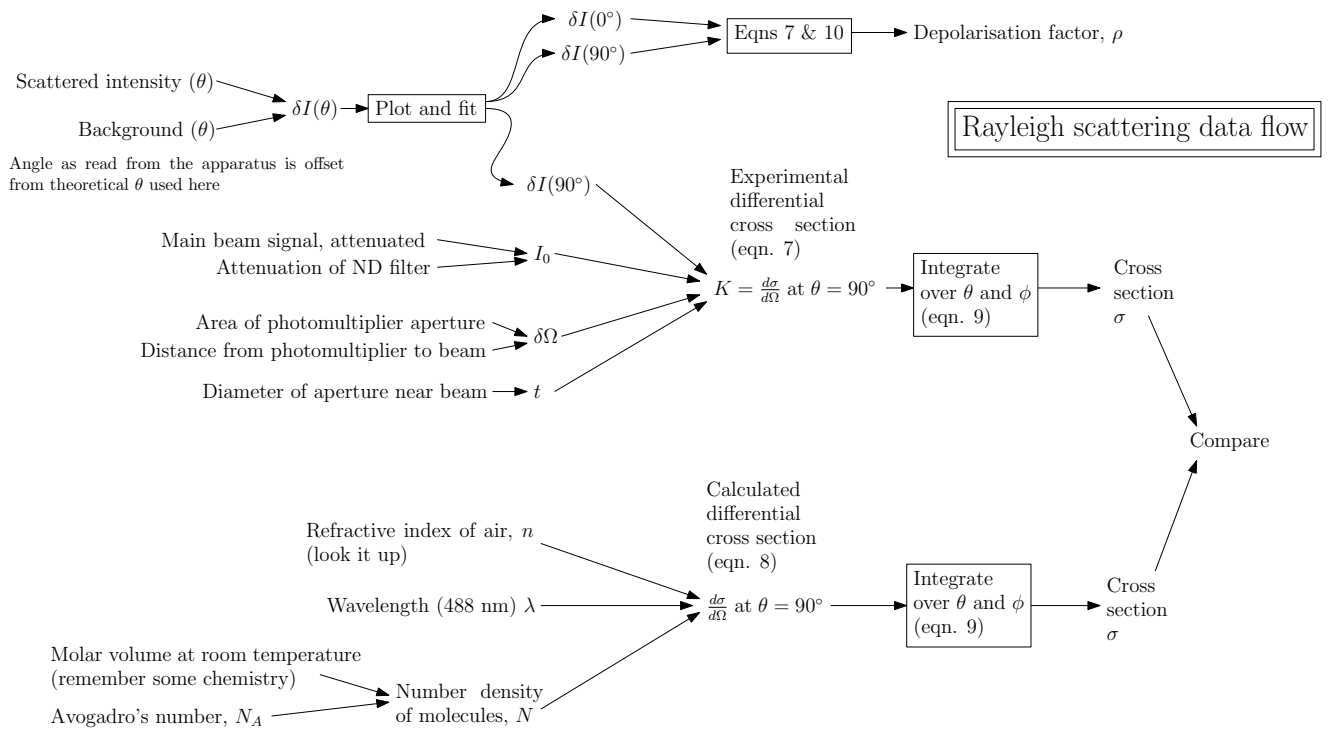


Figure 5 – Flow of data in the experiment

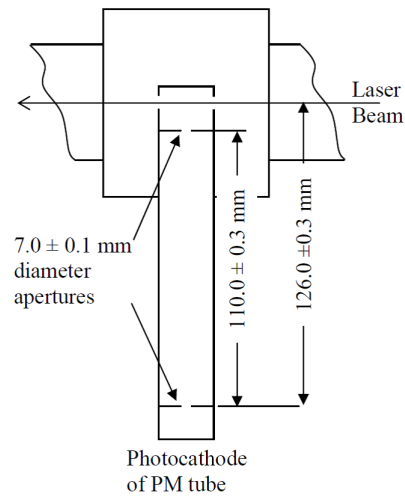
## Appendix: Geometry of the photomultiplier tube collimator

To obtain the solid angle required for the interpretation of your results (see equation 7 on page 7) it is sufficient to divide the area of the aperture nearest the photomultiplier tube by the square of the distance from the laser beam. In a more detailed treatment one would have to determine the effective solid angle by averaging the solid angle over all the points illuminated by the laser on the photomultiplier with both apertures taken into consideration.

- *Why is the aperture nearest the laser beam so small?*

## Bibliography

More than you ever wanted to know about the refractive index of air:  
<https://aty.sdsu.edu/explain/optics/disp.html>



**Figure 6** – Section through the scattering chamber showing aperture geometry

Recent measurement of  $\sigma$  in air:

<https://doi.org/10.1016/j.jqsrt.2014.05.030>

*Rayleigh scattering cross-section measurements of nitrogen, argon, oxygen and air,*

R. Thalman et al., *Journal of quantitative spectroscopy and radiative transfer* 147 (2014) 171-177, and (important) Erratum 189 (2017) 281-282.

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