Raman Spectrometer :

(i) Source :

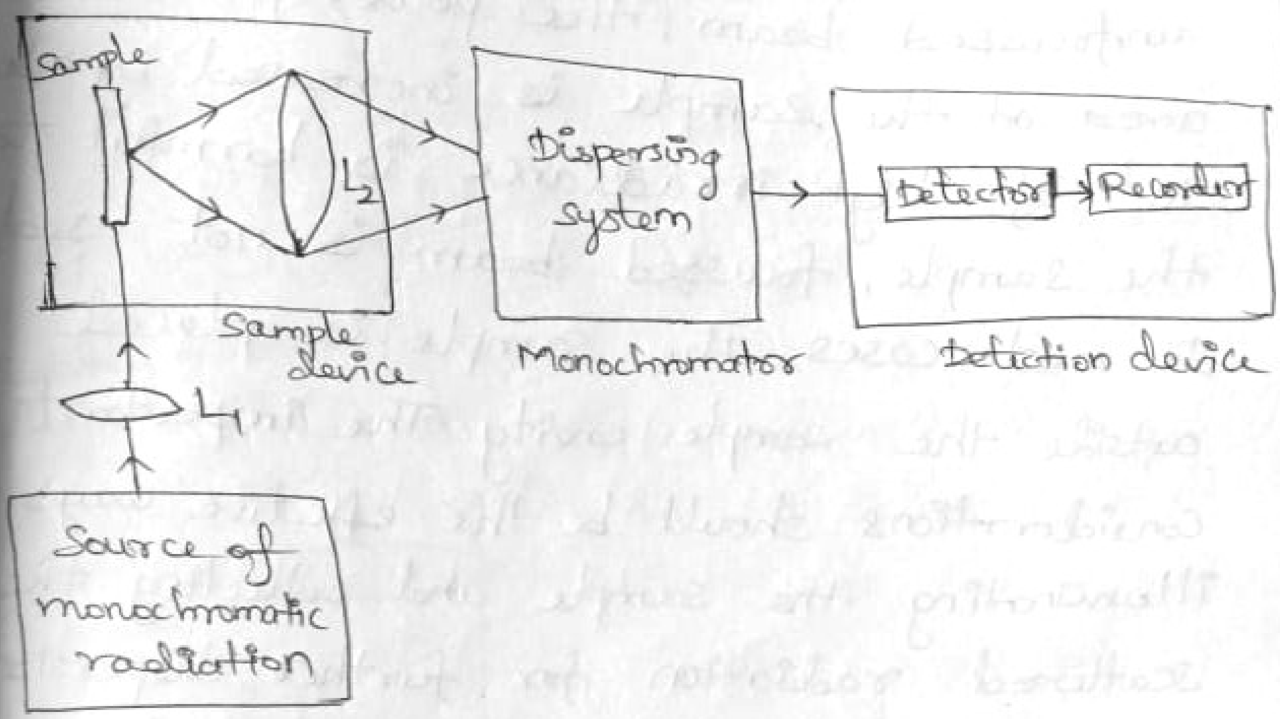
The first Raman spectrum of an organic compound was observed using sun as the source, a telescope as the receiver and human eye as the detector. As the scattering efficienc is proportional to the 4th power of frequency, one prefers to work with a high frequency source. However, to reduce fluorescence low frequency is preferred. In the prelaser days, the commonly used sources were the 435.8 nm (blue) and the 253.6 nm (uv) emission lines of mercury vapour. These have the following main disadvantages :

⇒ The source is an extended one and the brightness available per unit area is very small. This makes the sample very large and a good amount of the exciting radiation is scattered directly into the spectrometer. This makes recording of Raman lines fallin in the 10 - 125 cm^{-1} difficult.

⇒ The relatively high frequency of the mercury radiation often causes the sample to fluoresce, making the very weak Raman lines undetectable.

⇒ As coloured samples absorb in this high frequency region, it is not possible to record their spectra.

With the discovery of lasers, the situation changed considerably. The highly - directional and intense laser allows one to record the spectrum down up to 10 cm^{-1} from the exciting line. The fluorescence is also expected to be less, as most of the lasers operate at frequencies much lower than that of mercury source. If one laser makes the substance to fluorescence, one can select another one which gives a good Raman spectrum. The schematic of a Raman spectrometer with a laser source are shown in fig. The commonly used sources are He - Ne laser (632.8 nm), Argon ion laser (488 and 514.5 nm), Krypton laser (647.1, 568.2, 530.8, 520.8, 482.5, 476.2 nm) and Argon - Krypton mixed laser (488.0, 514.5, 647.1 nm). In certain cases, red radiation is preferred to reduce fluorescence and decomposition of the sample.



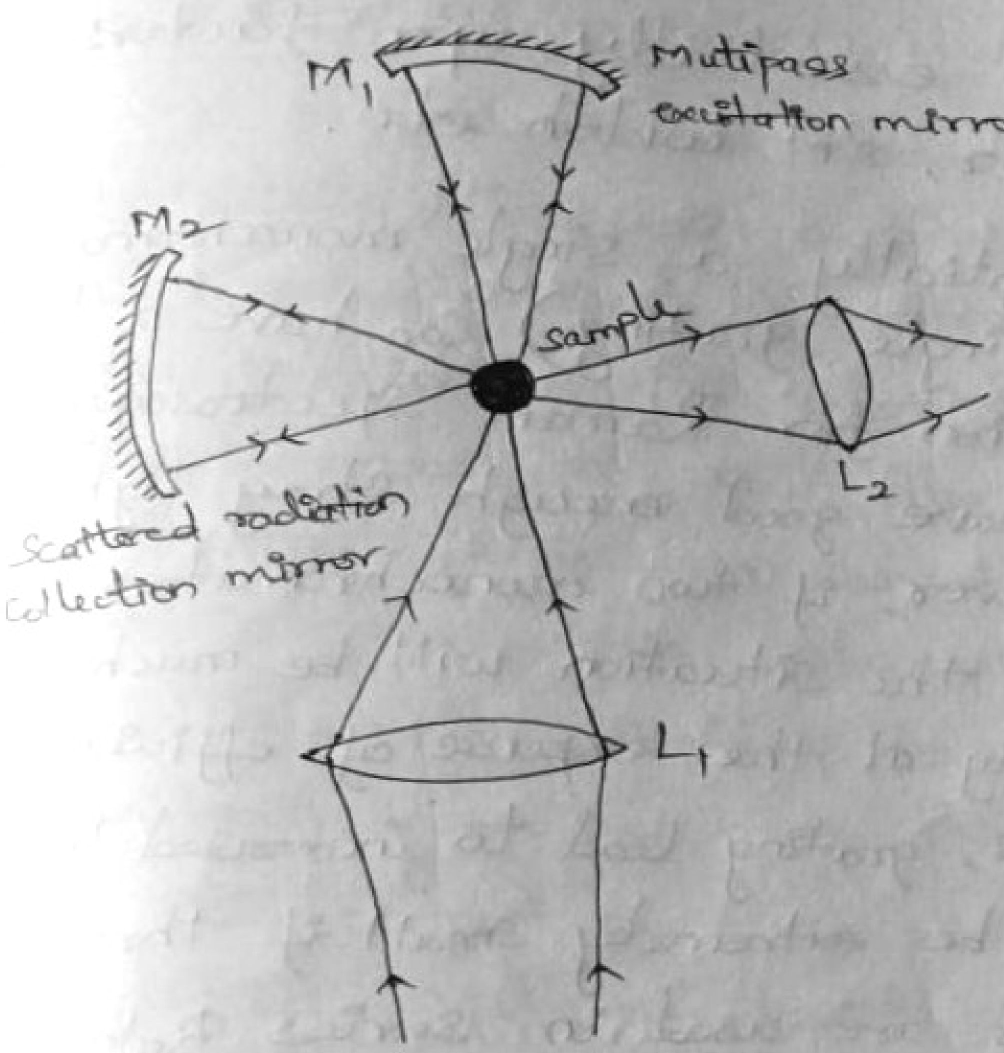
[Fig : The schematics of a Raman Spectrometer].

(ii) Sample device :

A laser beam may be focused to produce a beam of much smaller diameter using a lens. The small diameter beam extends over a short length before beginning to diverge again. The region in which the beam is most concentrated is called focal cylinder whose volume is of the order of $10^{-5} cm^3$. Hence, in principle the sample required is of this volume. As the area of the focussed beam ~~is about 10^3 times of high irradiance is~~

is about 10^3 times the area of the unfocussed beam, the power per unit area at the sample is increased by about 10^3. If high irradiance is harmful to the sample, focussed beam is not used. In most cases, the sample is placed outside the sample cavity. The important considerations should be the effective ways of illuminating the sample and collecting the scattered radiation for further dispersion. The sample illumination geometry is illustrat Two additional concave mirrors used in the illumination system increases the observed intensity of scattering by 8-10 times. Filte and optical devices such as polarizer, polarization analyser etc, may be inserted into the incident laser beam or into the scattered beam.

The figure : Sample illumination geometry is shown below.



(iii) Monochromator :

In a monochromator the different wavelengths of light are dispersed into beams travelling in slightly different directions and only a narrow wave number band is allowed to reach the detector at a time. It can either be based on diffraction grating or prism. The monochromato used often is the one based on grating. The most important property of any monochromator is its ability to distinguish lights of ~~nearby~~ wavelengths forming neighbouring line images.

This depends essentially upon factors resolving power, slit width etc.

Essentially a single monochromator (one with a single grating) can have a high enough resolution for Raman spectroscopy but it may not have good enough stray light rejection. However, if two monochromators are used in series the situation will be much better but only at the expense of efficiency (more mirrors, grating lead to increased losses Masking will be extremely small if three monochromators are used in series. Rotation of the gratings allows the successive bands to reach the detector. For the study of vibrational bands, a double monochromator is often sufficient. For high resolution work (rotation and rotation-vibration studies) a triple monochromator is preferred. In scanning spectrometers, a scale which translates the grating movements reads directly the wave number.

(iv) Detection device:

The dispersed radiation is detected photoelectrically. The exit slit allows only a narrow band to reach the photomultiplier tube and the rotation of the grating allows the successive bands to reach the detector. To reduce thermal emission contributing a noise element in the signal, the photomultiplier is cooled. The photomultiplier has a high efficiency and uniform response over the 4,000 to 8,000 Å range. The output of the photomultiplier tube is amplified and fed to the strip chart recorder which can be operated in the photon counting mode or direct current mode. The direct current mode is used for higher signal level.

(v) Modern Spectrometers:

Many developments have been made recently in the area of Raman spectrometers. This is partly due to the advent of (i) dispersive spectrometers with charge coupled device (CCD's) for detection, (ii) Fourier transform spectrometers with near infrared laser of excitation, (iii) fibre coupled

Raman Spectrometers, and (iv) Raman microscope. Though Raman effect is a wea phenomenon, it is now possible using the spectrograph - CCD combination to achieve unenhanced detection of material monolayers on dielectric substrates. The use of near infrared sources is most of the spectrometer helps one to get around the problem of fluorescence to a great extent. Fibre coupled spectrometers are also becoming very common since it can be used for on-line analysis in industry. In Raman microscopes the sample is simply presented to a microscope which is an integral part of the spectrometer. The major advantage of the microscope is that any sample or part of a sample that can be apertured optically can also have the Raman spectrum recorded.

A fascinating new development is the production of monochromators with simpler CCD detectors and with fibre optic coupled sensing. The size is approximately 4"×2"×2". It is truly portable and of much lower price than the lab-based instruments.