VIBRATIONAL-ROTATIONAL RAMAN SPECTRA

Theoretically it is possible for vibrational and rotational transitions to occur simultaneously in a Raman transition. In such a case, the selection rules are identical with those for separate rotational and vibrational transitions, i.e.

$$\Delta J = +2, 0 \text{ or } -2 \text{ and } \Delta\vartheta = +1 \text{ or } -1$$

Since ΔJ may be zero, a Raman line representing Q branch will be observed. (In a nomenclature, spectral lines are designated O, P, Q, R and S branches corresponding to ΔJ values of -2, -1, 0, + 1 and +2, respectively.) The frequency of this line is referred to as $\Delta\vartheta o$ (it has same value for all 1) and is identical with that for the pure vibrational transition. If $\Delta\vartheta o$ is the frequency shift for the purely
vibrational transition (Q branch), the Raman shifts for the accompanying rotational transitions will be represented by

$$\Delta J = +2$$

$$\Delta\vartheta = \Delta\vartheta o + 2B(2J+3)$$

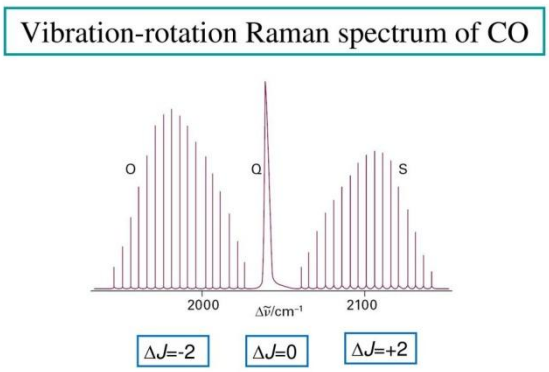
Where J=0,1,2,..... and

$$\Delta J = -2$$

$$\Delta\vartheta = \Delta\vartheta o - 2B(2J+3)$$

Where J=0,1,2,.....

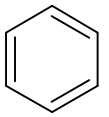
Thus, the central vibrational Raman lines (Q branch) will be accompanied by two wings or branches. The branch on the low frequency side for which ΔJ is -2 is known as O branch, and that on the high frequency side for which ΔJ is+2 is called S branch.

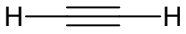


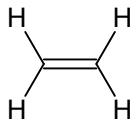
RULE OF MUTUAL EXCLUSION

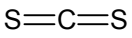
This rule states that 'if a molecule has a center of symmetry, then Raman active vibrations are IR inactive and IR active vibrations are Raman inactive. If there is no center of symmetry, then some (but not necessarily all) vibrations may be both Raman and IR active. Thus, the Raman and IR spectra having no common bands show that the molecule has a centre of symmetry but here caution is necessary because a vibration may be Raman active but too weak to be observed. If some of the bands are present in both the Raman and IR spectra, it is certain that the molecule has no center of symmetry.

Ex:







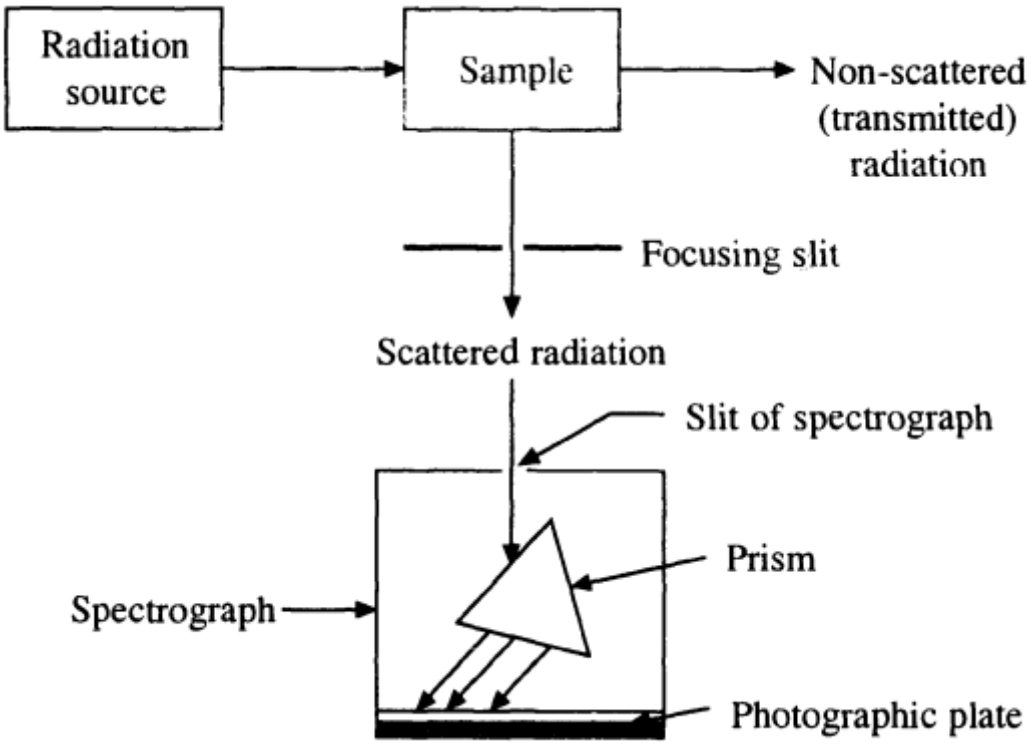


INSTRUMENTATION

Raman spectroscopy is essentially emission spectroscopy. The experimental arrangement for recording Raman spectra is quite simple in principle. An intense monochromatic radiation is passed through a sample and the light scattered at right angles to the incident (or exciting) beam is analyzed by a spectrophotometer.

The main components of a Raman spectrometer are:

- ✓ Radiation source
- ✓ Filters
- ✓ Sample (Raman) tube
- ✓ Spectrograph



Radiation Source

Since Raman lines are weak, it is essential to use a radiation of high intensity. The intensity of Raman lines is proportional to the fourth power of the frequency of incident (or exciting) radiation. Thus, the excitation frequency which is high enough, but not so much as to cause photodecomposition of the sample, is used. The mercury arc lamp is the most useful source of radiation. The most commonly used radiation in Raman spectroscopy is the line corresponding to 4358 Å which is obtained from the mercury arc lamp by use of suitable filters.

Nowadays laser is almost an ideal source of radiation for Raman spectroscopy and it is largely displacing the traditional mercury arc lamp. Helium-neon laser source has become very common; Laser beam of 6328 Å wavelength is generally employed. An argon-ion laser with lines at 4880 and 5145 Å are used, especially when higher intensity of Raman lines is required. Before the application of laser in Raman spectroscopy, it suffered from the following disadvantages:

- ✓ Samples had to be colourless, clear and non-fluorescent liquids.
- ✓ The low intensity of Raman lines required relatively concentrated solutions.
- ✓ Much larger volume of sample solutions were needed than that for IR spectroscopy.

These disadvantages were major factors in limiting the use of Raman spectroscopy. The scope of Raman spectroscopy is greatly widened with the application of laser as the exciting source because of its following advantages:

- ✓ It is a single, intense frequency source, hence no filtering is necessary.
- ✓ The line width of laser line is smaller than the mercury exciting line, hence it gives better resolution.
- ✓ Because of highly coherent character of laser radiation, it is easier to focus.
- ✓ A large number of exciting frequencies of laser are available, thus it is possible to study coloured substances without causing any electronic transitions. This is particularly useful in the study of solutions of inorganic salts which are generally coloured.

Filters

In case of non-monochromatic incident radiation, there will be overlapping of Raman shifts making the interpretation of the spectrum difficult. Thus, monochromatic incident radiations are necessary. Filters are used to obtain monochromatic radiation. They are generally made of nickel oxide or quartz. Sometimes, a coloured solution, e.g. aqueous solution of potassium ferricyanide or solution of iodine in carbon tetrachloride is used as a monochromator.

Sample (Raman) Tube

Various types of sample tubes are in use for Raman spectroscopy. The shape and size of the tube depends on the intensity of incident radiation, nature of the sample and its available amount. For gases, relatively bigger tubes are required.

Spectrograph

The spectrograph used in Raman spectroscopy should have large gathering power, hence, special prisms of high resolving power and short focus cameras are used. A lens directs the scattered radiation upon the slit of the spectrograph and Raman lines can be obtained on a photographic plate. Raman spectrographs with automatic reorders are also available. They use photographic emulsions or photomultiplier tubes. However, due to low intensity of Raman lines, photographic method is preferred because it is more sensitive. The intensity of Raman lines mainly depends on the polarizability of the molecules, intensity of the exiting radiation and concentration of Raman active species. Usually, Raman intensities are directly proportional to the concentration of Raman active species.

DIFFERENCE BETWEEN RAMAN AND IR SPECTRA

Although Raman shifts fall in the IR region of the electromagnetic spectrum, Raman spectra are quite different from infrared spectra.

	RAMAN SPECTRA	IR SPECTRA
1.	These originate from scattering of radiation by vibrating and rotating molecules.	These originate from absorption of radiation by vibrating and rotating molecules.
2.	Some change in molecular polarizability during the molecular vibration or rotation is essential for a molecule to exhibit Raman spectrum.	Some change in dipole moment during the molecular vibration or rotation is essential for a molecule to exhibit IR spectrum.
3.	Raman lines are weak in intensity, hence concentrated solutions are preferred as samples to give enough intensity.	Generally, dilute solutions are preferred.
4.	Water used as solvent	Water cannot be used
5.	Optical systems of Raman spectrometer made of glass or quartz.	Optical systems of IR spectrometer made of NaCl,NaBr,KCl,KBr etc.
6.	Sometimes photochemical reactions take place in the frequency regions of Raman lines and so create difficulties.	Photochemical reactions do not take place.
7.	These are recorded by using a beam of monochromatic radiation.	These are recorded by using a beam of radiation having a large number of frequencies in the IR region.
8.	Homonuclear diatomic molecules are Raman active.	Homonuclear diatomic molecules are IR inactive.
9.	Pure substances are required for studies by Raman spectra.	Studies by the IR spectra do not require a high degree of purity.