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H_2O - solvent

CaF_2, NaBr

R
↓
Vibrational freq. of large molecules can be measured
↓
Photochem. react. taken place
↓ calculus.

1930 Nobel prize

1923 - Smekel
1928 by Sir C.V. Raman
1871 - Rayleigh

Raman spectroscopy

In contrast with other conventional branches of spectroscopy, Raman spectroscopy deals with the scattering of light and not with absorption. Homonuclear diatomic molecules such as H_2, N_2 O_2 etc which do not show IR spectra since they do not posses a permanent dipole moment do show Raman spectra since their vibration is accompanied by a change in polarisability of the molecules

Polarisability of the molecule

In a molecule the positive charges act at some specific point - the centre of gravity of the +ve charge. Similarly the -ve charge due to electrons in orbits may be considered to act at a point - centre of gravity of the negative charge. When these two centres of gravity coincide then the molecule has no resultant charge and zero dipole moment. Such a molecule is said to be nonpolar

On the other hand when the two centres of gravity are separated from each other by a short distance then the molecule as a whole possesses polarity and has a permanent dipole moment.

When either of these types of molecule is placed in an external e.field, the small displacements of the orbital electrons will cause distance between the centres of gravity to alter. Thus non polar molecules become induced dipoles whereas polar molecules which are already dipoles, will be oriented by the field and may have resall and dipole moment modified

The orientation of the induced dipoles or the permanent dipoles in external field will be such as to set or tend to set the axis of dipole along the line of forces. This phenomenon is known as electric polarization

As a consequence of the change in polarisability there occurs a change in the induced dipole moment at the vibrational frequency

All modes are either IR active or Raman active. Many molecules have modes that are IR active and other modes that are Raman active

A unique feature of Raman scattering is that each line has a characteristic polarisation and polarisation data provide additional information related to molecular structure. It has been observed that Raman spectroscopy is most effective when used in conjunction with IR data.

Raman spectroscopy

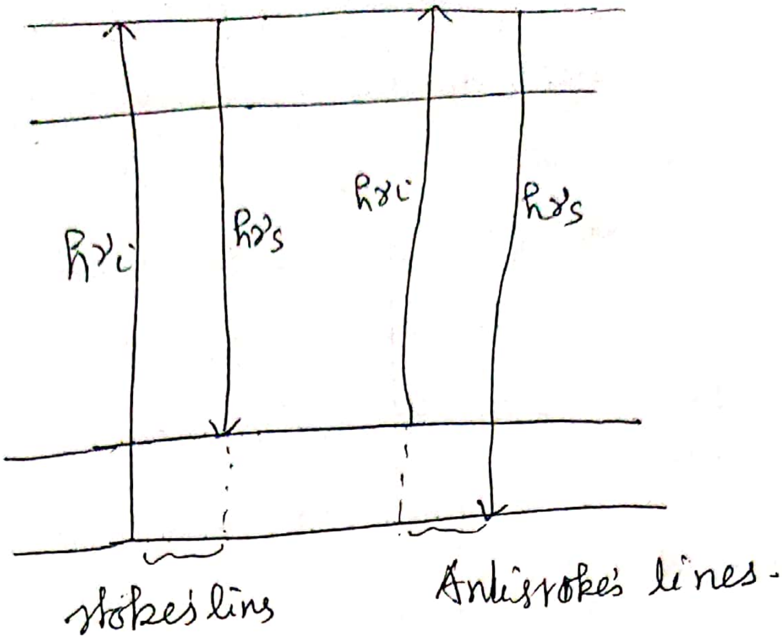
Raman discovered that when a beam of monochromatic light was allowed to pass through a substance in solid liquid or gaseous state, the scattered light contains some additional frequencies over and above that of incident frequency. This is known as Raman effect.

The lines whose wavelengths have been modified in Raman effect is called Raman lines. The lines having wavelengths greater than that of the incident wavelength are called stoke's lines and those having shorter wavelengths Anti-stokes lines.

If ν_i is the frequency of incident radiation ν_s the radiation scattered by the given molecular species, then the Raman shift $\Delta\nu$ is defined by the following relation

$$\Delta\nu = \nu_i - \nu_s$$

The Raman shift does not depend upon the frequency of the incident light but it is regarded as a characteristic of a substance causing Raman effect. For stoke's lines $\Delta\nu$ is positive and for Antistoke's lines $\Delta\nu$ is negative



Characteristic properties of Raman lines

i) The intensity of stokes lines is always greater than the corresponding Anti-stoke's lines.

ii) Raman shift Δν, ~~generally~~ generalley lies within the far and near infrared regions of the spectrum. It means that frequencies are generalley identical with the infrared vibrational frequencies. It is not necessary that all Raman lines will have their corresponding infrared bands and similarly all infrared bands may not have the corresponding Raman lines.

(iii) The frequency difference between the modified and parent lines represents the frequency of the absorption band of the material.

(iv) Raman lines are symmetrically displaced about the parent lines. When the temperature rises, their individual separations from the parent lines decrease.

Mechanism of Raman effect

The classical theory is able to explain the existence of the Raman effect whereas the quantum theory is needed to predict selection rules and intensities correctly.

Thus inorder to be Raman active a molecular rotation or vibration must cause some change in a component of the molecular polarizability.

—x—

The Quantum theory of Raman effect

The occurrence of Raman scattering may be most easily understood in terms of the quantum theory of radiation. According to this theory, the Raman effect may be regarded as the outcome of the collisions between the light photons and the molecules of the substance. [There are two types of collisions; elastic and inelastic. If energy is exchanged between photon and molecule during the collision such collisions are called inelastic. If no energy is exchanged between light photons and molecules then such a collision is said to be perfectly elastic and the molecule just deflects the photon].

$\lambda' < \lambda$

(ii) If $E_p > E_q$ then $\nu' > \nu$ which refers to the anti-stoke's lines. It means that the molecule was previously in the excited state and it handed over some of its intrinsic energy to the incident photon. Thus the scattered photon has greater energy.

(iii) If $E_p < E_q$ then $\nu' < \nu$. This corresponds to stoke's lines. The molecule has absorbed some energy from the photon and consequently the scattered photon will have lower energy.

As the change in the intrinsic energy of the molecule is governed by the quantum rules

$\frac{E_p - E_q}{h} = \nu' - \nu$

$h(\nu' - \nu) = \pm n h\nu_c$

$\nu' = \nu \pm \nu_c$

$$E_p - E_q = \pm n h \nu_c \quad \text{———} \quad ③$$

If $n = 1, 2, 3 \ldots$ and ν_c is the characteristic frequency of the molecule. If $n = 1$ eqn ③ becomes

$$\nu' = \nu \pm \nu_c \quad \text{———} \quad ④$$

From the above eqn it follows that the frequency $(\nu - \nu')$ between the incident and scattered photon in the Raman effect corresponds to the characteristic freq ν_c of the molecule.

Suppose a molecule of mass m in the energy state Ep is moving with a velocity v and is colliding with a light photon $h\nu$. Suppose this molecule undergoes a change in its energy state as well as in its velocity. After collision the new energy state be Eq and the velocity be v'. If we apply the energy of conservation

$$E_p + \frac{1}{2}mv^2 + h\nu = E_q + \frac{1}{2}mv'^2 + h\nu' \quad — ①$$

It can be easily proved that the change in velocity is practically neglible. Thus eqn ① may be written as

$$E_p + h\nu = E_q + h\nu'$$

$$h\nu' = h\nu + E_p - E_q$$

$$\nu' = \nu + \frac{E_p - E_q}{h}$$

$$\nu' = \nu \pm \Delta\nu \quad — ②$$

From eqn ② three cases may arise.

i) If $E_p = E_q$ the the frequency difference $\Delta\nu$ i.e $\left(\frac{E_p - E_q}{h}\right)$ is zero. It means that $\nu' = \nu$ and this refers to unmodified line where the molecule simply deflects the photon without receiving any energy from it. (elastic)

The Raman lines are equidistant
om the unmodified parent line on the
ither side, at distances equal to the
haracteristic frequency of the molecule and
they refer to the infrared absorption lines
of the scatterer.

$h\nu$

$$h(\nu' - \nu) = E_p - E_q$$

$$\frac{E_p - E_q}{\ } = \nu' - \nu$$