11/08/2017

RAMAN EFFECT

Introduction :

If beam of monochromatic light passes through a transparent medium (solid, liquid, gases) then it gets scattered. The scattered radiation can be observed at right angles to the incident radiation. Generally the freqⁿ of scattered radiation is same as that of incident radiation & is known as Rayleigh's scattering. But Smekel in 1923 & Kramers and Heisenberg theoretically shows that scattered radition should contain radiation at different freqⁿ from the incident.

Raman & Krishan conducted a series of experimental work on scattering of light (visible radiation) by a various transparent substance & should in 1928 that the scattered radiation do contain faint radiation with freqⁿ grater as well as less than incident freqⁿ

This scattering effect is known as Raman effect. The spectral line in the scattered light with modified freqⁿ are known as Raman lines.

When the photon of energy $h\nu_i$ is incident on atom / molecule of scattering medium the state of energy of atom / molecule of the medium changes from E_1 to E_2. Hence the energy of scattered photon is given by,

$$h\nu_s = h\nu_i - (E_2 - E_1)$$

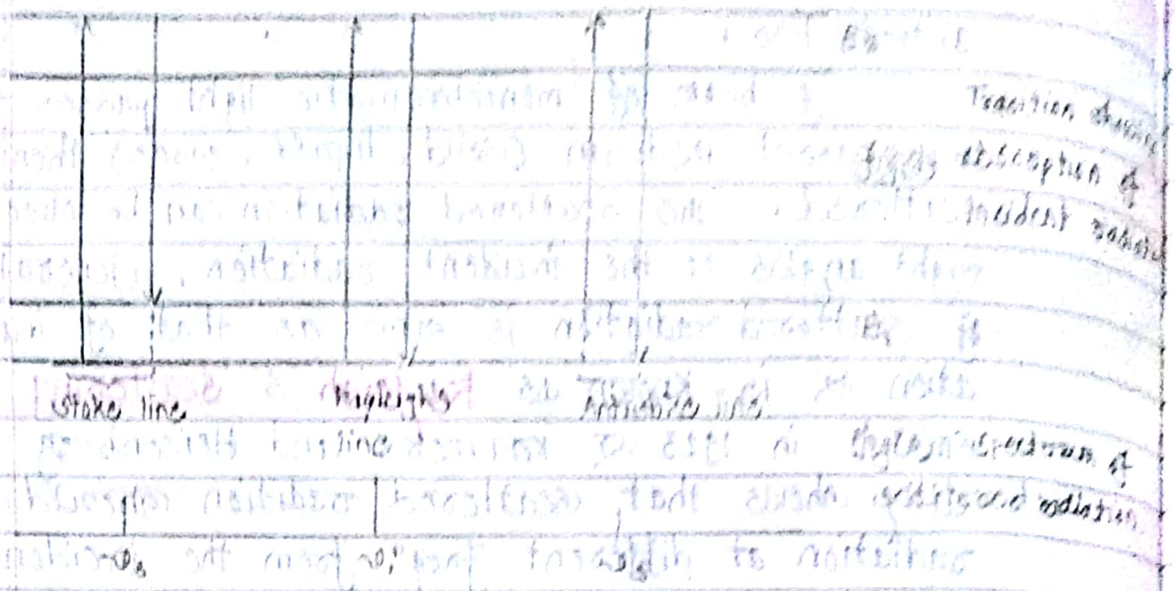
$h\nu_i$ = energy of
[illegible] incident

$$\nu_s = \nu_i - \frac{(E_2 - E_1)}{h}$$

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

where, $\Delta\nu$ is Raman shift and

$$\boxed{\Delta\nu = \nu_i - \nu_s}$$



It should be noted that Raman shift ($\Delta\nu$) does not depends upon the freq^n of incident radiation but the depends on nature of scatterer. Depending upon the value of $\Delta\nu$, Raman lines are classified as,

i) $\Delta\nu > 0$, i.e. if $\Delta\nu$ is +ve then
$\nu_i > \nu_s$
and the scattered lines are called stoke line.

ii) $\Delta\nu < 0$, i.e. if $\Delta\nu$ is −ve then
$\nu_i < \nu_s$
and the scattered lines are called antistoke line.

As shown if fig :

electric field = F
dipole moment - μ - magnetic moment
induced

12/08/2017

* Characteristics of Raman line.

1) Raman lines are very weak in intensity as compair to Rayleigh's line

2) Stokes line are more intens as compair to corr antistokes line

3) Raman lines are symmetrically displaced about the undisplaced parent line (Rayleigh's scattered line)

4) Raman shift $\Delta\nu$ generally lies in infra-red region of the spectrum

5) The $\Delta\nu$ represent the freqⁿ of infrared vibrational freqⁿ of the absorption band of the scattering material

6) Even though $\Delta\nu$ corr. to infrared region the Raman line (ν_s) appeares in visible region.

14/08/2017

* Classical Theory of Raman Effect.

When atom or molecules are placed in external electric field $\bar{F}$, The e⁻ & nuclei i.e ± ve charge centers gets displaced. consequently small electric dipoles are created, when medium is said to polarised, as these dipoles align along the field direction. The dipole moment (μ) of induced dipole is propotional to strength of electric field (F)

$$\mu \propto F$$

$$\mu = \alpha F \quad ①$$

where propotionality const. α is called $\boxed{\text{polarisability}}$ of molecule.

When light is incident on transparent scattering medium, The mol. of medium are subjected to the electric field of electromagnetic radiation of freqⁿ ν_i which is given by,

$$F = F_0 \sin 2\pi\nu_i t \quad \text{———} (2)$$

$$\therefore \quad \mu = \alpha F = \alpha F_0 \sin 2\pi\nu_i t \quad \text{———} (3)$$

Thus induced dipole moment oscillates with freqⁿ ν_i equal to freqⁿ of incident radiation.

Let us now consider the vibrational & rotational interaction with incident radiation.

i) Vibrational (Rotational) interaction (ν_v)

If the molecule undergoes vibrational motion with freqⁿ ν_v then it introduces the periodical change in the polarisability of the mol. which is given as,

$$\alpha = \alpha_0 + \beta \sin 2\pi\nu_v t \quad \text{———} (4)$$

where α_0 = equilibrium polarisability.

β = rate of chang of polarisability with vibration..

Now substituting for α from eqⁿ (4) in eqⁿ (3)

$$\mu = (\alpha_0 + \beta \sin 2\pi\nu_v t)\, F_0 \sin 2\pi\nu_i t.$$

$$\mu = \alpha_0 F_0 \sin 2\pi\nu_i t + \beta F_0 \sin 2\pi\nu_i t \,.\, \sin 2\pi\nu_v t.$$

Using : $\sin A.\sin B = \frac{1}{2}(\cos(A-B) - \cos(A+B))$

IR-infrared

H2 N2 freq^n $2\nu_r$

$$\mu = \alpha_0 F_0 \sin 2\pi\nu_i t + \frac{1}{2}\beta F_0 \left[\cos 2\pi(\nu_i - \nu_v)t - \cos 2\pi(\nu_i + \nu_v)t\right] \quad \text{—— (5)}$$

eq^n (5) shows that the indused dipole moment oscillate with freq^n ν_i, $(\nu_i - \nu_v)$ & $(\nu_i + \nu_v)$

And hence freq^n of emitted radiation called the scattered radiation are ν_i, $(\nu_i - \nu_v)$ & $(\nu_i + \nu_v)$. [The scattered freq^n ν_s is equal to ν_i corr. to Rayleigh's scattering, while the scattered freq^n corr. to Raman lines $\nu_s = (\nu_i \pm \nu_s)$]

Thus Raman shift $\Delta\nu = \nu_v$ —— (6)
i.e Raman shift corr. to freq^n of IR-vibrational band. Raman shift represent the freq^n of IR vibrational freq^n

2) Rotational interaction (ν_r)

∵ The mole. is not optically isotropic. ∴ when the mole. rotate in the direction of electric field of incident radi. then polarisability of mole. varies periodically. [In case of diatomic mole., the rotation through π^c brings the mole. in the same situation as in original. Hence the polarisability changes with freq^n double that of rotational freq^n (ν_r) of the mole. ∴ we can express the polarisability α as

$$\alpha = \alpha_0 + \beta' \sin(2\nu_r) 2\pi t$$

Now put for α from eq^n (7) in eq^n (3).

$$\mu = (\alpha_0 + \beta' \sin 2\pi(2\nu_r)t) F_0 \sin 2\pi\nu_i t$$

$$\mu = \alpha_0 F_0 \sin 2\pi\nu_i t + \beta' F_0 \sin 2\pi(2\nu_r)t \cdot \sin 2\pi\nu_i t.$$

$$\mu = \alpha_0 F_0 \sin 2\pi\nu_i t + \frac{1}{2}\beta' F_0 \left[\cos 2\pi(\nu_i - 2\nu_r)t - \cos 2\pi(\nu_i + 2\nu_r)t\right] \quad \text{—— (8)}$$

From eqⁿ (8) it is clear that the Raman lines have freqⁿ $\nu_s = \nu_i \pm 2\nu_r$
Hence $\Delta\nu$ in the freqⁿ is given by,

$$\Delta\nu = 2\nu_r$$

Thus the raman shift is the freqⁿ equal to twice the rotational freqⁿ of mole.

16/08/2017

	Raman Spectra	IR - Spectra.
1)	It arised due to scattering of light by vibrating mole.	1) It arised due to absorption of light by vibrating mole.
2)	The observation of Raman Spectra depends upon polarising of the mole.	2) IR spectra are produced only is the mole possess permanent electric dipole moment.
3)	Raman line weak in intensity & sample with conc. solⁿ are prepared	3) Generally dil. solⁿ are prefered.
4)	Water can be used as a solvent to prepare solⁿ	4) Water being opaque to IR It is can't be used as solvent.
5)	optical system are made up of glass as Raman spectra observed in visible	5) optical system are made upto CaF_2 & NaBr which are transparent to IR.

permenent.

6) Substance under investigusing must be pure & colourless	6) These condition is not rigid.
7) vibrational freq^{n}s of large mole can be measured.	7) vibrational freq^{n} of large mole. can't be measure.
8) Even homonuclear diatomic mole. like H_2, N_2 etc produces Raman spectra	8) Homonuclear diatomic mole. can't produce IR spectra as did not possess parmenent dipole moment
9) Raman lines being very weak, the excitation source must have high intensity	9) It is not so