RAMAN SPECTROSCOPY

Introduction:

A beam of electromagnetic radiation when made to incident on a sample, a part of the radiation is absorbed by the sample, a part of the radiation is transmitted by the sample and the remaining radiation is scattered by the sample.

Rayleigh observed that, if a substance is irradiated with a monochromatic light then the frequency of scattered radiation has been found to be same as the frequency of incident radiation.

Smekal in 1923, predicted that; if a substance is irradiated with a monochromatic light then the frequency of scattered light will be different from that of incident frequency.

Later in 1928, Sir C.V. Raman discovered Raman effect which is a beautiful confirmation of the Smekal prediction.

Raman Effect:

Sir C.V. Raman discovered that, if any substance (gaseous, liquid or solid) is exposed to radiation of definite frequency then the light scattered at right angles contains frequency different from the incident radiation. This is a characteristic property of a substance under examination. Thus the phenomenon due to which the scattering light has a slightly different frequency from that of the incident radiation and there is a change in the atomic oscillations with in the molecule is called Raman effect.

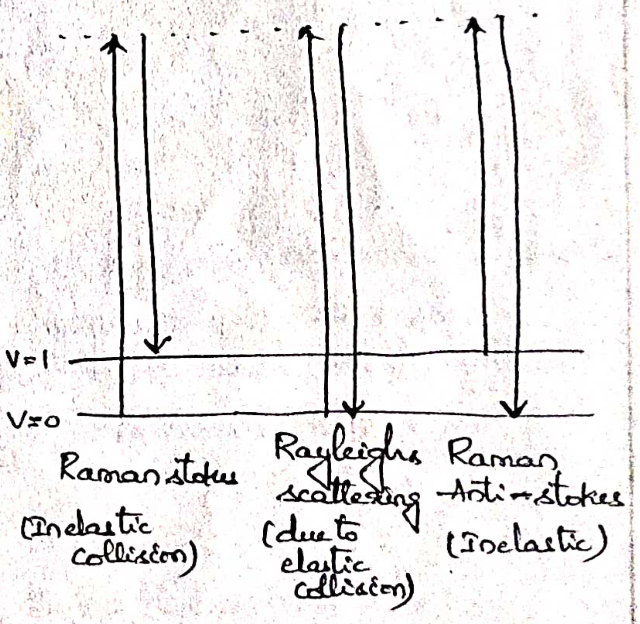
Molecules which do not absorb radiation will scatter radiation (eg Cl_2, N_2, O_2 etc). This scattered radiation can be studied by Raman Spectroscopy. Usually the scattered radiation constitutes one part in 10^6 of the incident light and hence it is necessary to use powerful light source inorder to detect this scattering. As lasers are powerful sources of monochromatic radiation, their development has greatly stimulated Raman spectroscopy.

If a radiation of frequency ν is sent over to molecules, the photons of the radiation may undergo two types of collisions with molecules of the sample.

(1) Elastic collisions : The photons will be scattered unchanged.

(2) Non-elastic & inelastic collisions: The energy is exchanged between photon and molecule during collision.

If the spectrum of the scattered radiation is examined, then two types of frequencies due to the above two types of collisions can be observed. In non-elastic collision the molecule can gain & lose amounts of energy only in accordance with quantal levels. This difference & change in the energy is due to vibrational & rotational energy & both in the molecule & energy between two of its allowed states (eg $V_0 \rightarrow V_1$). The photon can transfer its energy temporarily to molecules elevating the molecule to a 'virtual level'. This is not a stable position and therefore immediately falls back to its ground state. In falling back the molecule may end up in an excited vibrational state and in this case the photon will have less energy than the excitation by the amount characteristic of the particular vibrational level. (V_1).



If the molecule gains energy ΔE from the incident radiation, the photon will be scattered with an energy $h\nu - \Delta E$ & with a frequency $\nu - \frac{\Delta E}{h}$ and hence stoke's lines are ~~blue~~ observed.

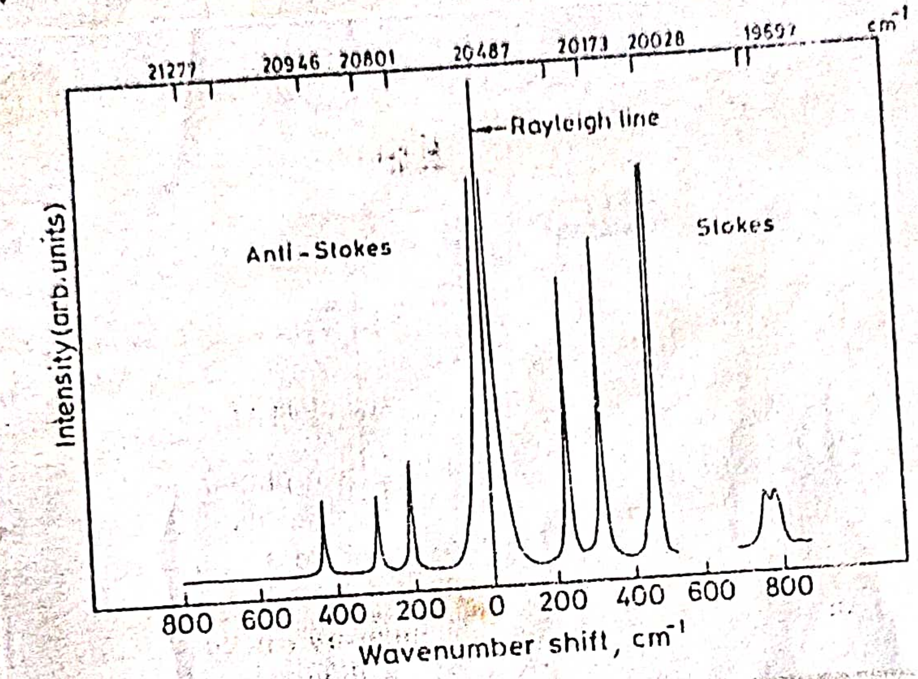
On the other hand some molecules may already been in the higher vibrational state before collision and the photon emitted will have slightly greater energy. In this the molecule loses energy ΔE and the scattered frequency will have $\nu + \frac{\Delta E}{h}$. So, the lines in the spectrum at higher frequency are called 'antistokes lines'. Antistokes lines are very weak to be observed since very few molecules exist in higher vibrational state (V_1) at normal temperatures.

So, in Raman spectrum we can observe a series of lines on either side of a central frequency i.e. Rayleigh line which arises due to elastic collision. The lines that are on the lower frequency side of central line are called stokes lines and those of higher frequency are antistokes.

Raman Spectra is reported as Raman shift, $\Delta\bar{\nu}$ given by the relation

$$\Delta\bar{\nu} = \pm(\bar{\nu}_0 - \bar{\nu}_{Raman}).$$

A typical Raman spectrum, is as shown in the figure, of carbon tetrachloride. If the wave number of exciting line is say, 20,487 cm⁻¹ then the Raman scattered light will have frequencies on either side of exciting line in the range ± 10 to 4000 cm⁻¹



So, Stokes lines correspond to positive sign and are more intense than antistokes lines. This shift in frequency is a measure of the difference in energy between two vibrational $(\nu_1 - \nu_0)$ or rotational levels. These shifts fall in the range of 100 to 4000 cm⁻¹ for vibrational changes, with small changes for rotational changes.

<u>Condition</u> or <u>essential</u> <u>criterion</u> for a molecule to be Raman active is:

The Raman spectrum is observed only when there is a change in the polarizability of a molecule due to its vibrational or rotational oscillations.

The mechanism of Raman effect is explained by classical theory and quantum theory.

Classical theory of the Raman Effect: classical theory gives a good explanation of Raman effect. In the presence of a static electric field, a molecule is polarized because it suffers some distortion, the positively charged nucleus is attracted towards the negative pole and the negatively charged electron cloud is attracted to the positive pole. This separation of charge centres cause an induced dipole moment, μ which is momentary and is due to elastic distortion of the electrons distributed around a bond in a molecule. The molecule is (temporarily) said to be polarized. The magnitude of the induced dipole, depends both on the magnitude of the applied field, E and the ease with which the molecule can be distorted.

$$\mu = \alpha E \text{ ——— } ①$$

Where E is applied field and α is the polarizability of the molecule.

The polarizability decreases as the electron density increases & as the length of the bond decreases. Hence Raman shift in scattering requires a change in the polarizability associated with the vibrational mode of the molecule.

If the electric field is produced by an electromagnetic radiation of frequency ν_0, then the electric field experienced by each molecule varies according to the equation

$$E = E_0 \sin 2\pi\nu_0 t \text{ ——— } ②$$

Here the electric component is not static but varies as the sine (or cosine) wave according to the above equation. Therefore, the induced dipole moment also undergoes oscillations of frequency ν_0

$$\therefore \ \mu = \alpha E = \alpha E_0 \sin 2\pi\nu_0 t \text{ ——— } ③$$

According to the electromagnetic theory, an oscillating dipole emits radiation of its own frequency. So μ oscillates with a frequency ν_0 and therefore Rayleigh scattering. The classical theory thus explains Rayleigh scattering as in equation (3) i.e. incident and scattered frequencies will be same. No consideration about vibrations & rotations is made in the molecule.

In addition, if the molecule undergoes some internal motion, such as vibration & rotation, the polarizability of the molecule (α) changes periodically then the oscillating dipole will have superimposed upon it, the vibrational & rotational oscillations.

Effect of vibration:

In a diatomic molecule, as the two nuclei vibrate along the line joining them, the polarizability of the molecule will change. If 'x' is the small displacement from the equilibrium position, the variation in the polarizability, α is given by

$$\alpha = \alpha_0 + \beta \frac{x}{A} \quad \text{———} ④$$

Where α_0 is known as equilibrium polarizability, β denotes the rate of variation ~~Vibration~~ of the polarizability with distance & change in polarizability during the vibration which is a function of time, and A is vibration amplitude. Suppose the molecule executes simple harmonic motion, then the displacement x can be put as

$$x = A \sin 2\pi \nu_{vib} t \quad \text{———} ⑤$$

Where ν_{vib} denotes the frequency of the vibration of the molecule. Substituting ⑤ in ③

$$\mu = (\alpha_0 + \beta \sin 2\pi\nu_{vib} t)\, E_0 \sin 2\pi \nu_0 t$$

$$\Rightarrow \mu = \alpha_0 E_0 \sin 2\pi\nu_0 t + \beta E_0 \sin 2\pi\nu_0 t \sin 2\pi\nu_{vib} t$$

$$= \alpha_0 E_0 \sin 2\pi\nu_0 t + \frac{1}{2}\beta E_0 \left[\cos 2\pi(\nu_0 - \nu_{vib})t - \cos 2\pi(\nu_0 + \nu_{vib})t\right] \quad ⑥$$

$$[\because 2 \sin A \sin B = \cos(A-B) - \cos(A+B)]$$

Thus the induced dipole oscillates with frequencies $(\nu_0 + \nu_{vib})$ and $(\nu_0 \cdot \nu_{vib})$ which are more and less than the frequency of incident radiation and predicts the existence of Raman scattering. So, the Terms in the equation provide the classical explanation for Rayleigh scattering (ν_0), antistokes lines $(\nu_0 + \nu_{vib})$ and stokes lines $(\nu_0 - \nu_{vib})$

$$\therefore \text{Raman Shift} = (\nu_0 + \nu_{vib}) - \nu_0 = \nu_{vib}$$

So, the shift will be equal to the frequency of vibration of the diatomic molecule.

Effect of rotation:

When a diatomic molecule rotates, the orientation of a molecule varies with respect to the electric field. If the molecule is not optically isotropic i.e. it exhibits different polarizabilities in different directions then its polarization will vary with time. The variation of α is given by the equation (identical to equation ⑤)

$$\alpha = \alpha_0 + \beta' \sin 2\pi (2\nu_r) t \quad \text{———} ⑦$$

ν_r is frequency of rotation. $2\nu_r$ is used instead of ν_r because a rotation through π angle will bring the diatomic molecule in a position in which its polarizability becomes same as it is initially.

On substituting ⑦ in ③, we get

$$\mu = \alpha_0 E_0 \sin 2\pi\nu_0 t + \beta' E_0 \sin 2\pi\nu_0 t \sin 2\pi (2\nu_r) t$$

$$= \alpha_0 E_0 \sin 2\pi\nu_0 t + \frac{1}{2}\beta' E_0 \left[\cos 2\pi(\nu_0 - 2\nu_r)t - \cos 2\pi(\nu_0 + 2\nu_r)t\right] \quad \text{———} ⑧$$

From this equation it follows that the frequency of Raman lines will be $(\nu_0 + 2\nu_r)$ and $(\nu_0 - 2\nu_r)$. In this case the Raman shift would be

$$\text{Raman Shift} = (\nu_0 + 2\nu_r) - \nu_0 = 2\nu_r \quad \text{———} ⑨$$

From equation ⑨ it follows that the Raman shift would be equal to twice the frequency of rotation of molecule.

Quantum mechanical treatment:

According to Quantum theory, Raman effect is due to the collisions between the light photons and molecule of the substance. If the collision between the photons and molecules is perfectly elastic then the photons will be deflected unchanged.

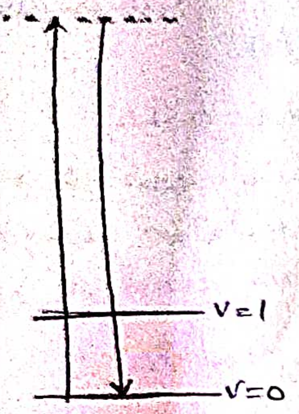
If the collision between photon and molecule is inelastic then there is exchange of energy between the photon and the molecule. The molecule can gain or lose energy after collision.

Let $h\nu$ be the energy of the photons incidenting on the molecules. Where h is planck's constant and ν is the frequency of incident radiation. Let ΔE be the energy change associated with the molecule due to change in the vibrational and rotational energy. If the molecule gains energy ΔE, then the photon will be scattered with energy $h\nu - \Delta E$. If the molecule loses energy ΔE, then the photon will be scattered with energy $h\nu + \Delta E$.

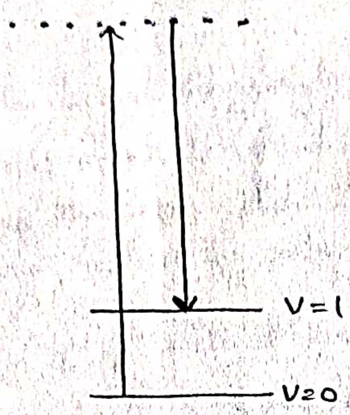
Radiation scattered with an energy lower than that of the incident beam is ~~[illegible]~~ referred to as stoke's radiation, while that at higher energy is called antistokes radiation. Stoke's lines are accompanied due to an increase in molecular energy while antistokes lines involve a decrease in molecular energy.

Stoke's radiation is generally more intense than anti-stokes radiation.

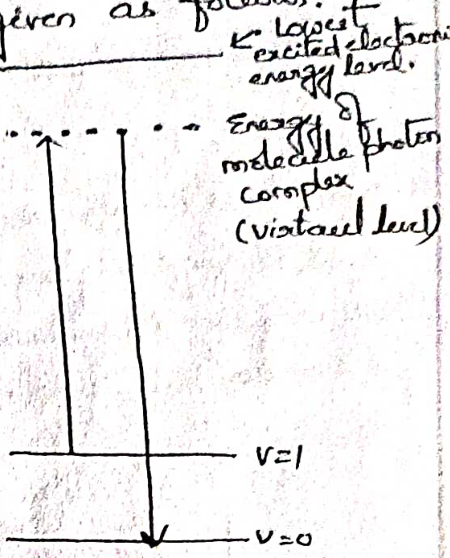
Diagram for Rayleigh scattering and Raman scattering can be given as follows.



Rayleigh scattering
$\Delta\bar{\nu} = 0$



Raman Scattering
with $\Delta\bar{\nu} > 0$



Raman scattering
with $\Delta\bar{\nu} < 0$.

If the molecule was initially in the lowest vibrational level (V=0), after interaction with a photon raised to virtual level. Being unstable at this level, it will reach the first excited vibrational & rotational level. In this case the photon will be scattered with a frequency less than that of incident frequency and will consequently be of lower frequency (stokes lines). There is a very small probability for the existence of a molecule in V=1 level. If this molecule interacts with a photon then it will be excited to a virtual level and being unstable reaches V=0 level. In this process the molecule loses energy and photon gains energy. As a result photon will be scattered with higher frequency. These two scattering are due to Raman effect.

At ordinary temperatures, only a small number of molecules can be in the V=1 level, while the majority of them exists in the V=0 level. Hence stokes lines appear with much intensity than the antistokes lines

Pure Rotational Raman Spectra:

Rotational energy changes in molecules can be studied with the help of Raman scattering. The rotational energy levels of a linear molecule can be written as

$$\epsilon_J = BJ(J+1)\ \text{cm}^{-1} \qquad J=0,1,2,3\ldots \text{———} ①$$

From quantum mechanical treatment, the selection rule has been deduced as

$$\Delta J = 0, \pm 2.$$

ΔJ=0 corresponds to trivial Rayleigh scattering. usually ΔJ is defined as J in the upper state minus J in the lower state. ΔJ = −2 may be ignored since for pure rotational changes, the upper state J must necessarily be greater ~~that~~ than the lower state J. Then restricting only to $\Delta J = J' - J'' = +2$ (S branch)

$$\therefore \Delta\bar{\nu} = \epsilon_{J'=J+2} \longrightarrow \epsilon_{J''=J} = BJ'(J'+1) - BJ''(J''+1)$$

$$= B(J+2)(J+3) - BJ(J+1)$$

$$= B(4J+6) \qquad J=0,1,2,\ldots$$

$$\text{———} ②$$

During collision, if the molecule gains rotational energy from the photon, it gives rise to a series of lines on the low frequency side of the exciting line. Such spectral lines are the stokes lines. Raman spectra deals with displacement of each line from the exciting line $\bar{\nu}_0$.

Hence Stokes lines can be written as

$$\bar{\nu} = \bar{\nu}_0 - B(4J+6)\ \text{cm}^{-1} \qquad J=0,1,2,3,\ldots$$

$$\text{———} ③$$

During collision, if the molecule gives energy to the photon, the lines appear on the high frequency side of the exciting line. These are antistokes lines and their frequencies are given by

$$\bar{\nu} = \bar{\nu}_0 + B(4J+6)\ \text{cm}^{-1} \qquad J=0,1,2,\ldots$$

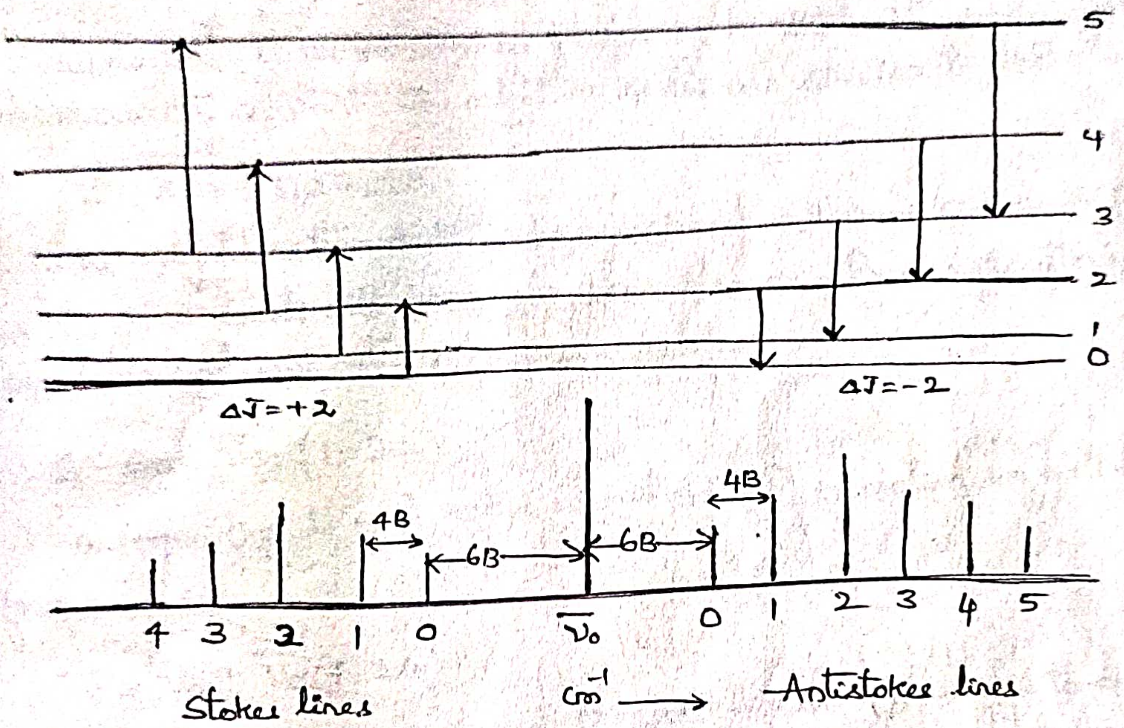
$$\text{———} ④$$

Combining equation ③ and ④ we get

$$\bar{\nu} = \bar{\nu}_0 \pm B(4J+6)\ \text{cm}^{-1} \qquad J=0,1,2,3,\ldots$$

Here, the positive sign refers to antistokes line and negative sign to Stokes's lines.

Schematically, the allowed transitions and the rotational Raman spectrum exhibited by a linear molecule can be given as follows.



The Raman shift of the first stokes and antistokes line from the exciting line is 6B cm⁻¹. The separation between successive lines on either side of the exciting line is 4B cm⁻¹. The stokes and antistokes lines appear with considerable intensity as all the rotational levels belong to V=0 vibrational state which makes all the levels reasonably populated. Molecules having larger moment of inertia may not give a well resolved rotational spectrum as B will be very small for such systems.

The rotational Raman spectrum of symmetric top molecules is some what different from that of the rotational Raman spectrum of a linear molecule. The rotational energy levels of a symmetric top molecule is given by

$$\epsilon_{J,K} = BJ(J+1) + (A-B)K^2 \text{ cm}^{-1} \quad J=0,1,2,\ldots \quad K=0,\pm1,\pm2\ldots\pm J$$

The selection rules are $\Delta K=0$, $\Delta J=0, \pm1, \pm2$
(except for K=0 states when $\Delta J=\pm2$)

Vibrational Raman Spectrum:

A molecule having n atoms has (3n-6) or (3n-5) [if linear] normal modes of vibrations. These different modes are anharmonic and the vibrational energy of an anharmonic oscillator is given by

$$\epsilon_V = \bar{\nu}'_{osc}\left(V+\frac{1}{2}\right)\left[1-a\left(V+\frac{1}{2}\right)\right] \text{cm}^{-1} \quad V=0,1,2,\ldots$$

Where $\bar{\nu}'_{osc}$ is the oscillation frequency of the anharmonic system and a is the anharmonicity constant. The selection rules are similar to those in IR.

$$\Delta V = \pm 1, \pm 2, \pm 3, \ldots$$

The only transition that can be considered is $V=0 \rightarrow V=1$, as the population in $V=1,2,3,\ldots$ levels will be negligible. Also, since Raman scattering is very weak, overtones and combinations appear seldom

$$\therefore \epsilon_1 - \epsilon_0 = \bar{\nu}'_{osc}(1-2a)$$

corresponding to each active normal mode of vibration we will have the Raman frequencies

$$\bar{\nu} = \bar{\nu}_0 \pm \bar{\nu}'_{osc}(1-2a)$$

The minus sign corresponds to stokes lines and plus sign to antistokes lines. As only very few molecules exist in the V=1 state the antistokes lines will be very weak in intensity.

Vibrational-Rotational Raman Spectra:

Theoretically, it can be predicted that vibrational and rotational transitions may occur simultaneously in Raman spectroscopy.

The vibration-rotation energy equation can be given as

$$\epsilon_{V,J} = \bar{\nu}'_{osc}\left(V+\frac{1}{2}\right)\left[1-a\left(V+\frac{1}{2}\right)\right] + BJ(J+1) \quad \text{cm}^{-1}$$

$$V=0,1,2,3,\ldots \qquad \Delta J = 0,1,2,3,\ldots$$

The rotational selection rule is $\Delta J = 0, \pm 2$.

$V=0 \rightarrow V=1$; $\Delta J = 0$ gives,

$$\Delta\epsilon_{V,J} = \bar{\nu}'_{osc}(1-2a)$$

This gives the Q branch stokes lines

$$\bar{\nu}_Q = \bar{\nu}_e - \bar{\nu}'_{osc}(1-2a)$$ where $\bar{\nu}_e$ is excitation frequency

for $V=0 \rightarrow V=1$, $\Delta J = +2$.

$$\Delta E_{V,J} = \bar{\nu}'_{osc}(1-2a) + B(4J+6)\ cm^{-1} \quad J=0,1,2,\ldots$$

This corresponds to energy gain by the molecule. Hence the frequency of the corresponding stokes line will be

$$\bar{\nu}_S = \bar{\nu}_e - \bar{\nu}'_{osc}(1-2a) - B(4J+6)\ cm^{-1} \quad J=0,1,2,\ldots$$

Where the subscript S stands for S branch ($\Delta J=+2$)

$V=0 \rightarrow V=1$ $\Delta J = -2$ gives.

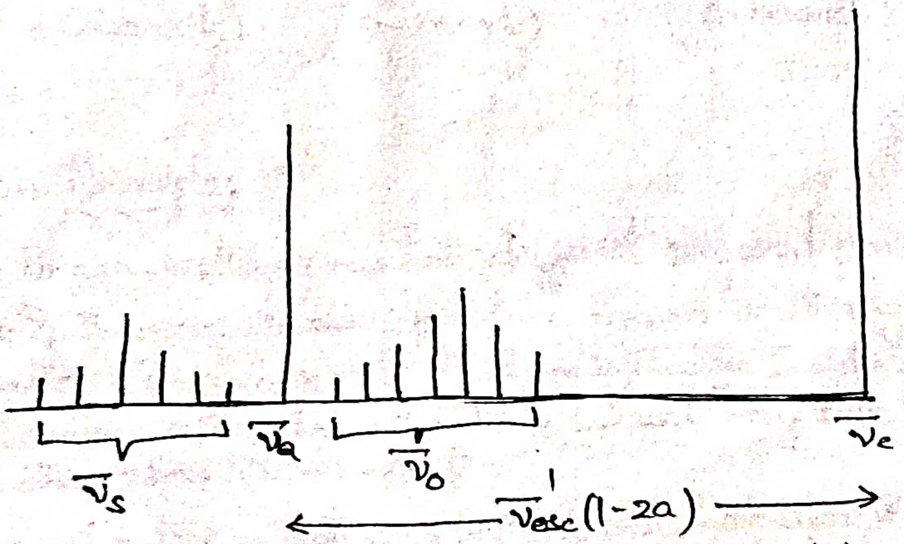
$$\Delta E_{J,V} = \bar{\nu}'_{osc}(1-2a) + B(J''-2)(J''-1) - BJ''(J''+1)$$

$$\Delta E_{J,V} = \bar{\nu}'_{osc}(1-2a) - B(4J''-2) \quad J''=2,3,\ldots$$

In this case also there is gain of energy by the molecule, since the second term is very small compared with the first term. This also gives rise to the stokes lines.

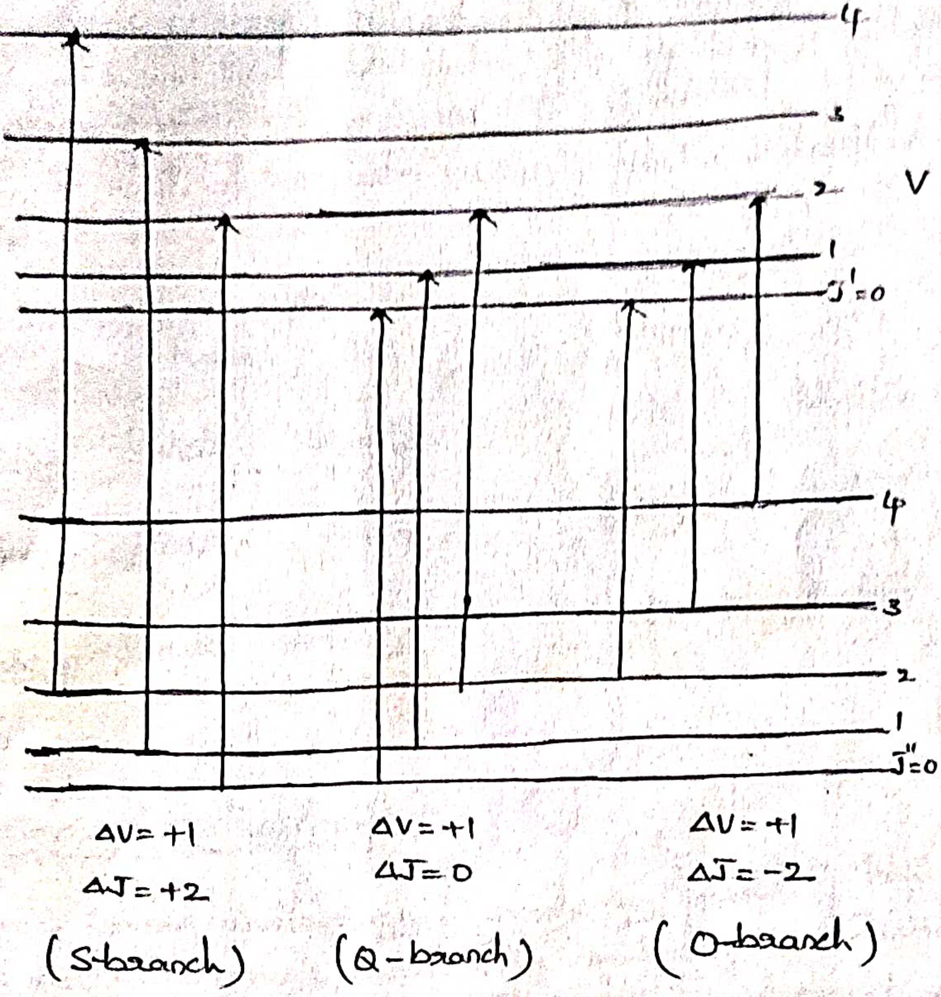
$$\bar{\nu}_O = \bar{\nu}_e - \bar{\nu}'_{osc}(1-2a) + B(4J-2)\ cm^{-1}. \quad J=2,3,4\ldots$$

Where the subscript O stands for 'O' branch. The resulting spectrum can be represented as.



Identification of O and S branch lines allow one to determine the B and from there the moment of inertia and bond length.

In the Raman spectrum, Q branch will be present where as it is absent in IR spectrum. Both S and O branches are some what similar to the R and P branches in IR spectroscopy



Mutual Exclusion Principle:

IR and Raman scattering are two different physical processes. A particular vibrational mode of the molecule may produce Raman scattering as well as absorb IR radiation. In such a case the same information is obtained from both the methods. But, certain molecular vibrations interact only with IR radiation where as certain others show Raman effect.

When a vibration is active in both, it may be easier to observe in one because of intensity considerations. In certain molecules which have centre of symmetry, the Raman active vibrations are IR inactive. If a molecule has centre of symmetry, those vibrations which are symmetric with respect to the centre of symmetry,

symmetry cannot produce a change in dipole moment. Hence they will be IR inactive. However, they will be Raman active as they produce a change in polarizability. The vibrations which are antisymmetric with respect to the centre of symmetry are IR active as they can produce a change in dipole moment and Raman inactive as they cannot produce a change in polarizability. Thus IR and Raman measurements complement each other and the complete picture of vibrational problem can only be obtained by using both the techniques. This is mutual exclusion principle. The significance of mutual exclusion principle can be understood from the following data.

	CO_2		H_2O	
Mode of vibration	Raman	IR	Raman	IR.
Symmetric stretching	Active	Inactive	Active	Active
Symmetric bending	Inactive	Active	Active	Active
Asymmetric stretching	Inactive -	Active	Active	Active.

RESONANCE RAMAN SPECTROSCOPY

The collision of photons of electromagnetic radiation with matter, results in either exchange or no exchange of energy and finally the photons are being scattered. Resonance Raman Spectroscopy (RRS) results, when a scattering system (matter) has an electronic absorption band close to the excitation frequency. Resonance Raman spectroscopy is simple modification of basic Raman effect (or Normal Raman Spectroscopy). The simple modification involves the use of an incident radiation that nearly coincides with the frequency of an electronic transition of the sample or material.

The intensity of 'Resonance Raman Scattering (RRS)' is many orders of the magnitude ($\sim 10^6$) greater than Normal Raman Scattering'. The resonance Raman spectrum is also different from that of the normal Raman Spectrum. In Resonance Raman Spectrum overtones may be observed with appreciable intensity and 'new bands' may appear. The availability of 'tunable laser sources' has resulted in the extensive use of RRS in application.

To record NRS, relatively high concentration samples (~ 0.1 M or greater) are required. This results in non-applicability of the method to biological problems. However, Resonance Raman Spectroscopy can be applied to biological problems to record the spectrum. It becomes possible to record the spectra of biological problems (whose concentrations are around 10^{-5} M) as the intensity of RRS is 10^6 times greater than the intensities of NRS

Resonance Raman Spectra arise only from the part of the molecule associated with electronic transitions. In case of a protein like hemoglobin which contains a chromophore (heme) that is orbitally separated from the bulk of the globin. In the Resonance Raman spectrum of oxy-hemoglobin, the vibrational bands associated with the chromophoric ~~group~~ centre are resonance enhanced but the vibrations of the surrounding protein molecule are attenuated (weakened). Even long overtone progressions of the vibrations associated with the chromophoric group, may be observed with appreciable intensity. This selective enhancement is a valuable aspect of RRS.

Resonance Raman Spectroscopy can be used to examine the metal ions in biological molecules (Eg: Iron in Hemoglobin and Cytochromes & Cobalt in vitamin B_{12}) which are present in very low concentrations that NRS cannot detect them. Usually in large biological molecules, the active site (generally a chromophore) is generally buried in & wrapped around by a large and complex protein back bone.

The scattered intensity is given by

$$I = \frac{I_0 A(\nu_0 - \nu)^4}{(\nu_{elc} - \nu_0)^2 + \delta^2}$$

ν_0 is the frequency of the lase radiation (ie. incident radiation)

ν is the frequency of the normal mode and the value of A depends on the particular vibrational mode involved.

ν_{elec} is frequency required to cause electronic transition in the sample.

δ is damping factor.

I_0 represents the intensity of the incident radiation.

The denominator becomes increasingly smaller as ν_0 approaches ν_{elec} and I becomes correspondingly larger. The presence of damping factor δ keeps I at a finite value when $\nu_0 = \nu_{elec}$.

The theory of Resonance Raman Spectroscopy is rather complex. The selection rules for the appearence of overtone progressions in the Resonance Raman Effect are such that only the totally symmetric fundamentals may show the effect.

By taking K_2CrO_4 as an example it is possible to explain the difference between the normal and resonance Raman Spectrum.

The normal Raman Spectrum of K_2CrO_4 shows four bands characteristic of the tetrahedral CrO_4^{-2} ion.

The Resonance Raman Spectrum of K_2CrO_4 shows a progression of several overtone bands of the fundamental symmetric stretching mode (ν_1) observed at 853 cm^{-1}. The nine peaks that are observed (identified) are the stokes lines that correspond to the excitation of the symmetric stretching mode of the tetrahedral CrO_4^{-2} ion.

so the resonance enhancement leads to selective observation of bands associated with the chromophore of a complex molecule. The magnitude of the resonance enhancement varies directly with the oscillator strength.

eg: For iodine molecule, progression of the overtone band upto $V=20$ has been observed.

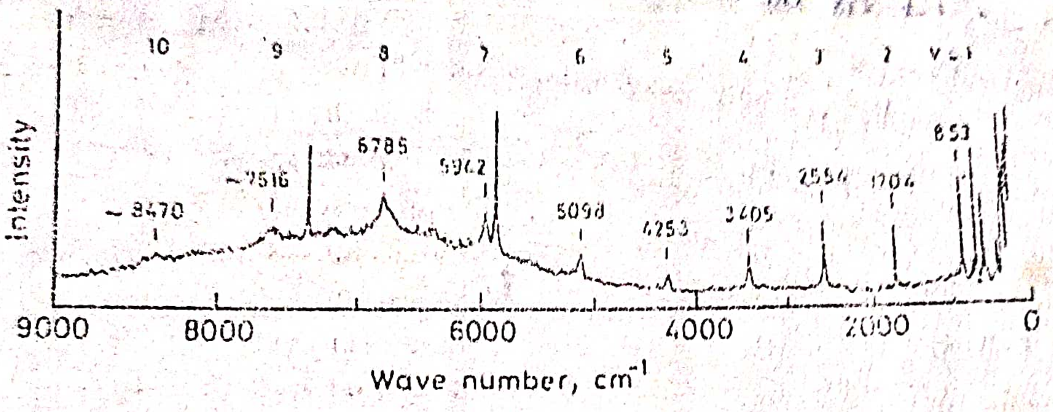


Fig. 7.14 Resonance Raman spectrum of K_2CrO_4

COHERENT ANTI-STOKES RAMAN SPECTROSCOPY (CARS) :

A number of new light scattering processes have come into existence by the development of high intensity laser systems. Very high electric field intensities are associated with monochromatic radiation produced particularly by giant-pulsed lasers. When the electric intensity of the incident radiation is very large, non-linear (second order) contributions to the ~~molecular~~ molecular polarizability become increasingly significant. For sufficiently intense exitation radiation, the polarizability of the scatterer is no longer adequately represented by the linear equation i.e.

$\mu = \alpha E$ [Linear relationship] and is represented by an equation consisting of higher order terms ~~[illegible]~~. i.e.

$$\mu = \alpha E + \frac{1}{2}\beta E^2 + \frac{1}{6}\gamma E^3 + \text{------}.$$

where $\beta, \gamma \ldots$ represent higher order polarizabilities

In general the electric field caused by an electromagnetic radiation can be given by

$E = A \sin 2\pi\nu t$ where ν is oscillating frequency.

If the response from the molecule is linear Then $\mu = \alpha E$

$\Rightarrow \mu = \alpha A \sin 2\pi\nu t$

If the ~~response~~ response is non linear then $\mu = \alpha E + \frac{1}{2}\beta E^2 + \frac{1}{6}\gamma E^3 + \ldots\ldots$

$$E = A\sin 2\pi\nu t \Rightarrow E^2 = A^2[\sin 2\pi\nu t]^2$$

$$= \frac{A^2}{2}\left[1 - \cos 2\pi\, 2\nu t\right]$$

$\therefore$ In E^2 equation there is 2ν term, which arises because of doubling of frequency [i.e. mixing of frequencies]. This phenomenon is called as the second harmonic generation or frequency doubling.

Coherent anti-stokes Raman Spectroscopy or CARS:

A non linear response of the system is said to mix the incident frequencies. When two coherent laser beams of sufficiently high irradiance and of frequencies ν_0 and ν_t where $\nu_0 > \nu_t$ coincide in space and time in a molecular medium, new frequencies of the type

$$\nu_a = \nu_0 + \nu_0 - \nu_t = 2\nu_0 - \nu_t$$ are generated.

$\mu = \alpha E$ (linear response)
$\mu = \alpha E + \frac{1}{2}\beta E^2 + \frac{\gamma E^3}{6} + \cdots$
(non linear response)

The intensity of Raman transitions particularly of anti stokes scattering may be enhanced by CARS. If the frequency ν_t is varied keeping ν_0, constant such that $\nu_0 - \nu_t = \nu_m$ where ν_m is the frequency of a Raman active vibrational or rotational transition of the molecule. The scattered radiation then occurs at $\nu_0 + \nu_M = \nu_a$. The scattered radiation frequency ν_a is at antistokes Raman radiation relative to ν_0 or is on high wave number side of ν_0 and ~~its~~ it is very intense and also coherent unlike normal Raman Scattering

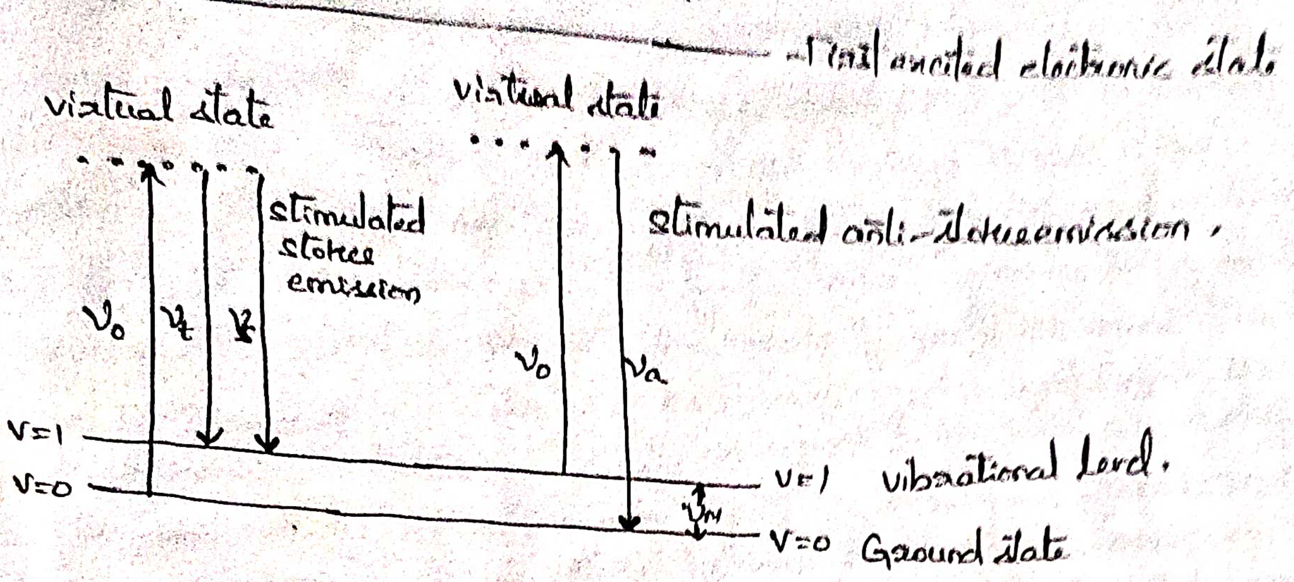
If ν_t is varied over a range of frequencies in the neighbourhood of ν_0, all Raman active frequencies say $\nu_{M1}, \nu_{M2}, \nu_{M3}$ etc can be observed, as the conditions $\nu_0 - \nu_t = \nu_{M1}$, $\nu_0 - \nu_t = \nu_{M2}$ etc are fulfilled successively with variation in ν_t. The complete CARS spectrum comprises of intense bands corresponding to Raman active vibrations. The CARS signals are stronger than ordinary Raman antistokes lines by 5 to 10 order of magnitude. The resolution is very high in CARS when compared with normal Raman spectroscopy

In addition to CARS phenomenon, the phenomenon Coherent Stokes Raman Spectroscopy (CSRS) ~~is~~ was also ~~discovered~~ discovered. In CSRS, a new frequency involves one photon of ν_0 and two of ν_t which corresponds to ν_s

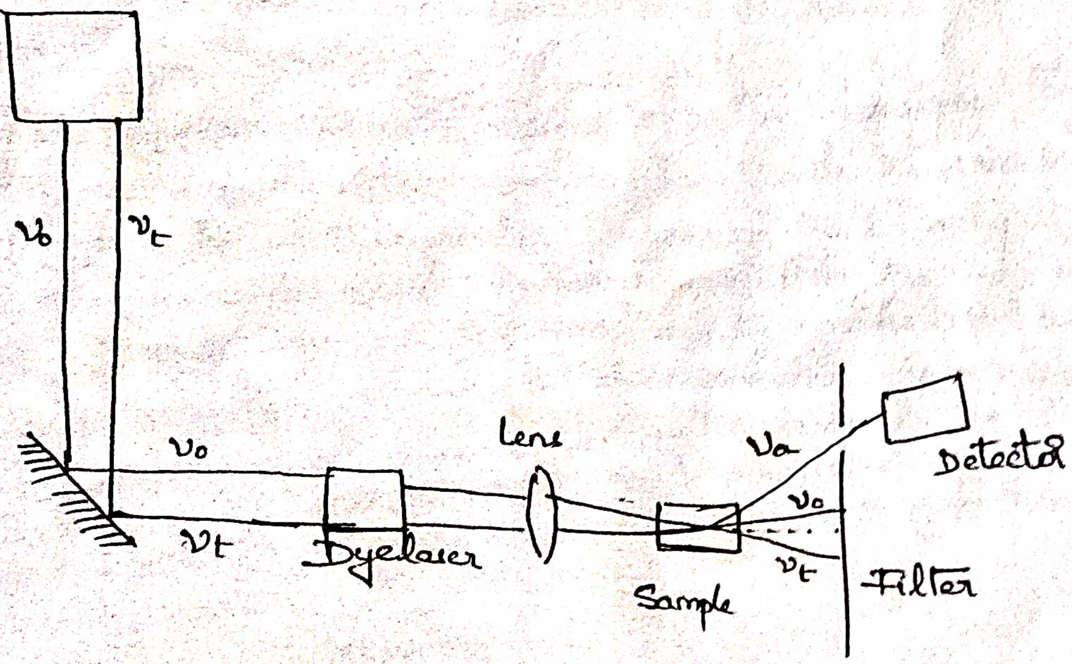
~~ν_t ν_0~~ $\nu_s = 2\nu_t - \nu_0 = \nu_t - (\nu_0 - \nu_t) = \nu_t - \nu_m$

This is achieved by keeping ν_t constant and varying ν_0 such that $\nu_0 - \nu_t = \nu_M$ where ν_M can bring about either vibrational or rotational transition. The CSRS signal is in principle weaker than CARS signal.

The transitions involved in CARS phenomenon and CSRS phenomena can be visualised as follows.



Experimental Set up for CARS



Fermi Resonance:

The phenomenon of Fermi Resonance is observed when an overtone & a combination band occurs with an unexpected high intensity in the IR & Raman spectrum. The phenomenon is named as Fermi resonance as it was first observed by Fermi in the Raman spectrum of CO_2. The overtone of the bending vibration (ν_2) of CO_2 at 667 cm^{-1} occurs in nearly the same region as the symmetric stretching frequency (ν_1) expected at 1334 cm^{-1}. Two bands of nearly the same intensity at 1285 (ν_1) and 1388 ($2\nu_2$) cm^{-1} are observed in the Raman spectrum of CO_2 in the region where the symmetrical stretching vibration is expected. The ν_1 of CO_2 is shifted downwards from 1334 cm^{-1} to 1285 cm^{-1}, whereas $2\nu_2$ of CO_2 is raised from 1324 cm^{-1} to 1388 cm^{-1}. The difference of about 100 cm^{-1} between the Fermi resonance doublets indicates strong Fermi resonance interaction. Although the fundamental ν_2 band (bending) of CO_2 is Raman inactive, the first overtone of ν_2 that is $2\nu_2$ is Raman active.

Fermi resonance usually occurs when two vibrational transitions, say a fundamental and a overtone (& combination) have nearly the same energy (frequency) and both belong to the same symmetry. In general the intensity of overtone band will be less, whereas under Fermi resonance condition, the overtone band steals intensity from the fundamental band and the overtone band instead of being weak may appear nearly as strong as the fundamental. As a result of Fermi resonance two nearly equal intense bands may be observed. The two energy levels involved repel one another so that both the levels are perturbed. The resonance interactions mixes the two original vibrational states to give two perturbed states whose energies are

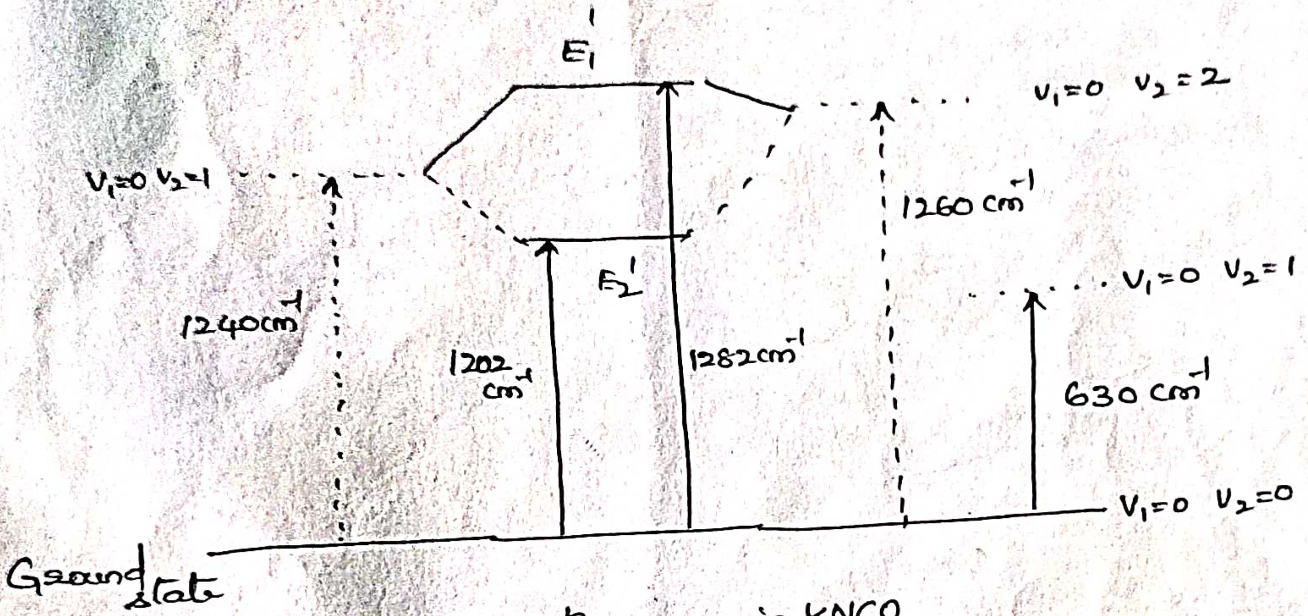
$$E_1 > E_2$$

$$E_1' = E_1 + E_{interaction}$$

$$E_2' = E_2 - E_{interaction}$$

The higher energy level (E_1) moves to still higher energy (E_1') and the lower level (E_2) to lower energy (E_2') after the interaction. Fermi resonance will be observed for two vibrational modes only when the two modes belong to the same symmetry and strong interaction is possible only when the energies of the two vibrational modes are closer.

The concept of Fermi Resonance is also observed in the spectrum of cyanate ion in KNCO. The overtone of the (NCO) bending frequency at 630 cm^{-1} appears in the region of the carbonyl stretching frequency expected at 1240 cm^{-1}. Due to Fermi resonance, two strongs bands at 1282 and 1202 cm^{-1} are observed in the IR spectrum instead of a single strong band for the C–O stretching frequency and a very weak overtone band of the bending mode as shown in the figure



Fermi Resonance in KNCO

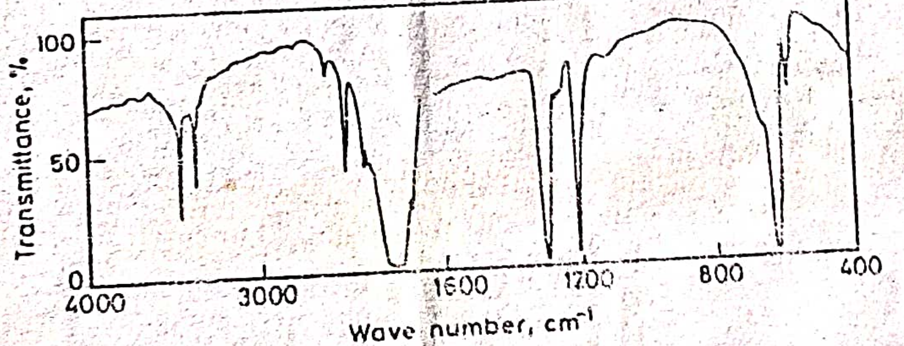


Fig. 1.27 Infrared spectrum of KNCO

Fermi resonance is observed in the IR spectrum of benzaldehyde. A doublet is observed in the region about 2800 cm^{-1}. Fermi resonance arises due to the closeness of frequencies of overtone of the inplane aldehyde CH bending and C-H stretching.

Overtone and combination frequencies:

The selection rule for a simple Harmonic oscillator is $\Delta V = \pm 1$ and the selection rule for anharmonic oscillator is $\Delta V = \pm 1, \pm 2, \pm 3, \dots$ i.e. in addition to ± 1, longer jumps pertaining $\pm 2, \pm 3, \dots$ are also allowed in case of anharmonic oscillator. These longer jumps results in the first, second etc overtones occurring at frequencies near $2\nu_1, 3\nu_1, \dots, 2\nu_2, 3\nu_2; \dots 2\nu_3 \dots$ etc, where each ν_i is a fundamental mode. In addition to the overtones, the selection rules now permit combination bands and difference bands. The former arise simply from the addition of two or more fundamental frequencies or overtones. Such combinations as $\nu_1+\nu_2$, $2\nu_1+\nu_2$, $\nu_1+\nu_2+\nu_3$ etc become allowed. The intensities are normally very small for these combination bands. Similarly the difference bands, for example $\nu_1-\nu_2$, $2\nu_1-\nu_2$, $\nu_1+\nu_2-\nu_3$ etc, have small intensities but are often to found in the complex spectrum.

Skeletal and Group frequencies:

For a molecule with N atoms either 3N-6 (if non linear) or 3N-5 (if linear) modes of vibrations are possible. usually complex molecules exhibit complex IR spectrum as large no of vibrations are possible for complex molecules. Each normal mode involves some displacement of all, or nearly all, the atoms in the molecule. In some other modes all atoms may undergo approximately the same displacement, ~~In some~~ while in some other modes the displacement of a small group of atoms may be much more vigorous than those of the remainder. Thus the normal modes of vibrations may be divided into two classes skeletal vibrations and Group vibrations. In skeletal vibrations, the displacement of many of the atoms occurs to the same extent. Group vibrations, involve only the vibration of a small portion of the molecule, the remainder being more or less stationary. Skeletal vibrations usually fall in the range 1400 – 700 cm^{-1}.

Group frequencies:

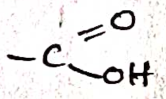
Group frequencies fall in the regions well above and well below that of the skeletal modes. In certain molecules, a particular group like $-CH_3$, $-OH$, $-C\equiv N$, $>C=O$ vibrate quite independent of the structure of the molecule as a whole. The group vibrations of light atoms in terminal groups (for example $-CH_3$, $-OH$, $-C\equiv N$, $>C=O$ etc) are of high frequency, while those of heavy atoms ($-C-Cl$, $-C-Br$, metal–metal etc) are low in frequency. These frequencies are highly characteristic of the group and can be used for analysis. For example, $-CH_3$, group gives rise to a symmetric C–H stretching absorption invariably falling between 2850 and 2890 cm^{-1}, an asymmetric stretching frequency at 2940 – 2980 cm^{-1}, a symmetric deformation at about 1375 cm^{-1}, and an asymmetric deformation at about 1470 cm^{-1}. Similarly $>C=O$ group shows a very sharp and intense absorption between 1600 and 1750 cm^{-1}.

The significance of group frequencies data can be ~~understood~~ identified from the following discussion.

In acetic acid, if one of the oxygen atom has been replaced by sulphur then immediate question which arises in the mind is that the thioacetic acid is either CH_3COSH or CH_3CSOH. The IR spectrum gives a very clear answer. The molecule shows a very sharp absorption at about 1730 cm^{-1}, and one at about 2600 cm^{-1}, and these are in accordance with the presence of $>C=O$ and $-SH$ groups respectively. Also the spectrum does not exhibit strong absorption at 1100 cm^{-1}, thus indicating the absence of $>C=S$.

Some important group frequencies

Group.	Approximate frequency (cm^{-1})	Assignment
$-OH$	3550–3650	ν_{OH} (free)
$-CH_3$	2940–2980	ν_{as}
	2850–2890	ν_s
	1445–1475	δ_{as}
	1365–1385	δ_s

Group	Approximate frequency (cm^{-1})	Assignment
$-CH_2-$	2910 – 2945 2835 – 2865 1455 – 1485	ν_{as} ν_s δ
$=CH_2$	3065 – 3095 2960 – 2990	ν_{as} ν_s
CH (aromatic)	3020 – 3050	ν
 $-C(=O)OH$	2800 – 3000 1600 – 1750 1220 – 1300	ν_{-OH} $\nu_{C=O}$ ν_{C-O} etc.