**Raman effect in solids, liquids and gases**

- ✓ The solid sample may be in the form of a single crystal or a pellet of compressed powder dispersed in KBr(similar to KBr technique used in IR)in concentration range of 10 to 100%.
- ✓ Raman lines obtained with crystals are sharp but they become diffuse as the temperature is raised.In calcite (CaCO3),two Raman lines are identified with oscillations of the crystal lattice,while the others are found to be due to vibrations of CO3 group present in calcite.
- ✓ A sharp line having a large frequency shift has also been obtained with diamond due to lattice oscillation.In case of gypsum(CaSO4.2H,0),Krishnan obtained three strong Raman lines at $\lambda$=2.8,2.9 and 3-0μ.In Raman spectra,the lower limit of detectability of solvents in pyridine is:water 0-07%,CH3OH 0-25%,C2H5OH 0.17%,HCOOH 0-09% and CCI4 0-15%.
- ✓ Raman spectra of gases are generally weaker than those of liquids or solids,hence require cells of larger path length.The gas may be filled in a glass or silica tube.If the molecule has sufficiently low moment of inertia, the rotational fine structure may be obtained on either side of the Rayleigh line.

**Applications in Inorganic Chemistry.**

- ✓ The vibrational Raman spectrum has been used to distinguish between linear $CS_2$,$HF_2$,$NO_2^+$,$N_3^-$,$BO_2^-$,$ZnCl_2$) and bent ($H_2O$,$H_2S$,$H_2Se$,$NO_2$,$OF_2$,$NO_2^-$) structures.
- ✓ ***Structure of $H_2O$:*** The three fundamental vibrations in a non-linear triatomic molecule are expected to be active both in IR and Raman. Since this prediction is true for $H_2O$, it has a bent structure like $SO_2$,$S_2O$ and $D_2O$.
- ✓ **Hydrogen cyanide:** In Raman spectrum HCN exhibits two lines at 2062 and 2094 $cm^{-1}$ which may be due to two isomers HCN and HNC in dynamic equilibrium.
- ✓ **Nature of Bonding in Complexes:** The IR spectra of symmetrical tetrahedral complexes ML4 (e.g. $ZnCI_4^{2-}$, $CdCl_4^{2-}$etc.) and octahedral complexes (e.g., $SiF_6^{2-}$, $SF_6$ etc.) exhibit no bands but the Raman spectra of such complexes exhibit strong lines. Thus, from the M-L bond stretching-force constant, useful information about the strength of the metal-ligand bond can be obtained. The oxy anions (e.g., $PO_4^{3-}$, $SO_4^{2-}$ etc.) have much larger force constants. This is considered as an evidence for the presence of $d\pi - P\pi$ bonding between the central atom and oxygen atom in addition to $\sigma$ bonding.

**Applications in organic Chemistry.**

- ✓ **Structure of Benzene:** Raman spectrum ofbenzene shows two strong Raman lines at 995 and 1050 cm-1 due to C-C and C=C bonds, respectively. This supports the Kekule structure of benzene.
- ✓ **Determination of Orientation:** Raman spectroscopy has been used to determine the relative positions of substituents on benzene ring. For example, all meta-disubstituted benzene derivatives exhibit an intense and strongly polarized Raman line at 995 cm-1 which is absent from the Raman spectra of ortho and para substituted derivatives. The Raman spectra of ortho-substituted compounds are richer in lines than their para isomers and the paraisomer shows a line at about 625 cm-1 which is absent in the case of ortho isomer.

**Applications in Physical Chemistry**

- ✓ The amorphous state of a substance gives rise to broad and diffused bands while crystalline state gives fine sharp lines.
- ✓ The degree of hydrolysis of a salt can be determined by measuring the relative intensities of a set of lines characteristic of the base, the acid or the salt.
- ✓ In case of phenomenon of electrolytic dissociation, the intensity of Raman lines enables us to determine the number and nature of ions produced. Thus we can decide whether the dissociation is complete or partial.

$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$$

Raman spectrum of anhydrous nitric acid shows a number of lines at about 1400 cm$^{-1}$ which is characteristic of –NO2 group. On dilution, this band gradually fades away and is replaced by a band near 1046 cm$^{-1}$ (which is characteristic of $NO_3^-$) with increasing intensity. This change in scattered radiation of $HNO_3$ is due to ionization. By monitoring the intensity of $NO_3^-$ and $HNO_3$ in Raman spectrum it is possible to obtain the dissociation of $H_2SO_4$.

**Applications in Polymer Chemistry**

- ✓ Raman spectra can be interpreted in terms of unit cells which may contain a few elements of different polymer chains. Stretched polymers may be examined with polarized radiation. Raman spectroscopy provides useful conclusions about the structural units of macromolecules, i.e., benzene nuclei (1000, 1600, 3060 cm-1), symmetrical Si-O-Si vibrations (490 cm-1) in silicones and C-S and S-S vibrations (650, 510 cm-1) in polysulphides. All these vibrations give intense Raman bands but are absent or weak in infrared spectra.

## RESONANCE RAMAN SPECTROSCOPY

Raman spectrum is generally obtained by irradiating the system in a region where the molecules do not absorb the incident beam. All Raman active modes of molecule will produce the spectrum. However, when the frequency of irradiating beam falls in the absorption region of the sample most of the vibrational bands are attenuated through self absorption. If, however, a powerful tunable dye laser is used and the frequency is brought nearly to coincide with the absorption maximum then intensity of a few scattered frequencies is greatly enhanced by several orders of magnitude ($10^2$ to $10^6$) than for normal Raman scattering. Overtone bands are also observed. The phenomenon is referred to as **resonance Raman effect** and the spectrum so obtained is called **Resonance Raman Spectrum** (RRS). Usually RRS is much simpler than the conventional Raman spectrum due to the fact that only vibrational modes are excited with the enhanced electronic transitions.

**How intensity is enhanced?** Raman intensity is proportional to an expression that has the energy difference $(\nu_e - \nu_o)$ in the denominator, where $\nu_e$ is the frequency of electronic transition of the molecule from the lowest to the first excited state and $\nu_0$ is the frequency of incident beam. The polarizability $\alpha$ has the denominator $1/(\nu_e - \nu_o)$. The extent of enhancement depends on the nearness of $\nu_0$ to $\nu_e$. Since the denominator also contains band width associated with the electronic transition, it does not go to zero. The very high intensity of resonance Raman effect makes it useful for the analysis of trace amounts of samples that is, solutions of $10^{-5}$ M could be examined.

**Theory.** The theory of resonance Raman effect is much complex. The polarizability theory completely fails under resonance conditions. The selection rules in the resonance Raman effect for the appearance of overtone progression are such that only totally symmetric fundamentals may show the effect.

**Technique.** The experimental set up for resonance Raman scattering is same as that used for normal Raman spectroscopy. Gas lasers or tunable dye lasers are used for excitation. The effect of local heating (which may decompose the sample) can be prevented by spinning the sample rapidly. Measurement of the depolarization ratios of the resonance Raman bands helps in their assignment.

**Difference Between Normal and Resonance Raman Spectrum.**

Difference can be illustrated by considering $K_2Cr_2O_4$. Normal Raman spectrum of $K_2CrO_4$ exhibits four bands characteristic of tetrahedral $CrO_4^{2-}$ ion. Resonance Raman spectrum of $K_2CrO_4$ shows several overtone bands (1704, 2554, 3405, 5947, .... 8470 $cm^{-1}$) of the fundamental symmetric stretching model ($v_1$) observed at 853 $cm^{-1}$.

The intensities of the overtones gradually decrease but the band width increases at higher frequencies. *Only those vibrations are enhanced which reflect the molecular distortion in the excited* electronic state. Thus resonance enhancement leads to selective absorption of bands associated with the chromophore of a complex molecule. The magnitude of resonance enhancement varies directly with the oscillator strength and inversely with its breadth. The resonance enhancement is maximum for sharp and strong bands and it is indicated by the extent of overtone progression. For instance in $I_2$, the progression of overtone band upto 20 vibrational levels has been seen.

## RESONANCE RAMAN EFFECT (RRE)

The enhanced intensity of few scattered frequencies gives rise to resonance Raman effect. Consider two situations in RRE.

1. The exciting frequency ($v_0$) approaching to that of an electronic absorption and of the scatterer resulting in **pre-resonance Raman effect** (pre-RRE).
2. The incident frequency coinciding with that of an allowed absorption band leading to rigorous **Resonance Raman Effect (RRE).**
   - When gaseous molecules are excited within an absorption band, two different resonance effects may occur that is, RRE and resonance fluorescence (RF). However, RRE occurs much faster than RF.
   - Resonance Raman intensity is the sum of the intensities of pre-RRE and RF. Thus resonance Raman spectrum is simpler than individual pre-RRE and RF.
   - RRE is generally treated as a single phenomenon for very broad absorption bands. For weak narrow bands the observed effect is either pre-resonance Raman scattering or RF. For example, the intensity of Stokes line of resonance Raman spectrum is much less than the intensity of corresponding RF band.
   - A resonance Raman spectrum can be observed under RF conditions only if the resonance fluorescence is quenched by the solvent or with an inert gas.

Forbidden electronic transitions such as *d-d* transitions in transition metal complexes show little *RR* enhancement.

**Exercise.** *Which type of bands occur in rubredoxin?*

**Solution.** Generally transition metal complexes exhibit charge transfer transitions from ligand to metal and vice versa. These are fully allowed transitions. Charge transfer bands are shown by rubredoxin. It exhibits an intense partially **polarised band** at 314 $cm^{-1}$ and a weak depolarised band at 368 $cm^{-1}$. These bands are assigned to totally symmetric and degenerate stretching modes of a distorted $FeS_4$ tetrahedron in rebredoxin.

**Exercise.** *Give an example of a compound showing resonance enhancement and allowed transitions.*

**Solution.** The compound $K_4Mo_2Cl_8$ has a strong absorption band at 517 nm in resonance Raman spectrum. Excitation of this species using argon ion laser (488 or 514 nm) shows a resonance enhanced fundamental band at 346 $cm^{-1}$ attributable to Mo–Mo stretching and a progression of its overtone up to $V = 5$. This supports the attribution of electronic absorption band at 517 nm to $\delta \rightarrow \delta^*$ transition (associated with Mo–Mo quadrupole bond) which is allowed and not to forbidden $\delta$–$\delta^*$ transition.

## APPLICATIONS OF RESONANCE RAMAN SPECTROSCOPY (RRS)

- RRS offers an accurate method for the determination of anharmonicity constants of resonance enhanced vibrational modes. Since anharmonicities and harmonic frequency can be accurately determined from the progression of overtone bands, solvent interactions with scattering solute molecules can be detected even at low concentrations.
- RRS is well suited for the study of free radicals and transient species.
- RRS is not affected by line broadening and other interferences which limit the applicability of electron spin resonance (ESR) spectroscopy.
- Excitation profiles of Raman bands show close relationship between Raman and electronic absorption spectroscopies. RRS can also help in the assignment of electronic transitions.
- RRS is highly specific to the absorbing species. Only those totally symmetric modes associated with the electronic chromophores are predicted to exhibit resonance enhancement. Although detailed structural informations cannot be obtained from such a spectrum but it represents a great simplification which is focussed directly on a specific part of the molecule.
- RRS is used for studying biostructural problems and complex biological materials.
- RRS obtained by using different lasers of wavelength coincident with different bands of electronic spectrum of the compound is more informative than normal Raman spectrum. Solute and solvent bands as well as buffers do not interfere.
- The availability of a range of excitation frequencies from laser sources and the development of tunable laser sources are particularly advantageous in RRS.

## NON-LINEAR RAMAN EFFECTS

Recent techniques in Raman spectroscopy employ giant pulsed lasers. When the electric field intensity of incident radiation is very large, non-linear (second order) contributions to molecular polarizability become significant. Several phenomenon arise as a consequence of non-linear interaction of a molecular system with an intense laser radiation. All phenomenon involve changes in the wave number of the laser exciting line as a result of its interaction with molecular system and thus are regarded as variants of the Raman effect *viz.*,

**(i)** Stimulated Raman effect, **(ii)** Hyper Raman effect, **(iii)** Inverse Raman effect.

Each of these effect provide new spectroscopic technique such as

(i) Inverse Raman spectroscopy, (ii) Coherent anti-Stokes Raman spectroscopy, (iii) Coherent Stokes Raman spectroscopy.

## COHERENT ANTI-STOKES RAMAN SCATTERING (CARS)

CARS is the non-linear analogue of spontaneous Raman scattering.

1. When two laser beams of sufficiently high intensity and of frequency $\nu_0$ and $\nu_t$ (where $\nu_0 > \nu_t$) coincide in space in a molecular medium, new frequencies of low intensity are generated of the following type $\nu_0 + \nu_0 - \nu_t = 2\nu_0 - \nu_t$.

2. If the frequency $\nu_t$ is varied such that $\nu_0 - \nu_t = \nu_M$, then the **scattered radiation** occurs at $\nu_0 + \nu_M = \nu_a$. ($\nu_M$ is the Raman active vibration of the molecular system).
3. Relative to $\nu_0$, the radiation frequency $\nu_a$ is anti-Stokes Raman radiation which is very intense and also coherent. It is known as coherent anti-Stokes Raman scattering or **CARS.**
4. All the Raman active frequencies (say $\nu_{M_1}, \nu_{M_2}, \nu_{M_3}$ etc.) can be observed, if $\nu_t$ is varied over a range of frequencies around $\nu_0$ and the conditions $\nu_0 - \nu_t = \nu_{M_1}$, $\nu_0 - \nu_t = \nu_{M_2}$ are fulfilled with variation in $\nu_t$. Hence CARS spectrum consists of intense bands corresponding to Raman active vibrations of the molecule superimposed on a weak background.
5. Other type of frequency is $2\nu_t - \nu_0$ which corresponds to $\nu_t - \nu_M$ when $\nu_0 - \nu_t = \nu_M$. It is Stokes radiation relative to $\nu_t$ and is referred to as **coherent Stokes Raman scattering, CSRS.** The CSRS spectrum may be studied by varying $\nu_0$ and keeping $\nu_t$ as fixed frequency radiation.

**CARS Process.** CARS process involves two coherent laser radiation beams $\nu_0$ and $\nu_t$ focussed nearly colinearly in a molecular medium. The mixing implies spatial and temporal coincidence of two beams. *When the frequency of one of the beam, $\nu_0$ is maintained constant and that of other beam is varied so that the frequency difference between the two beams is equal to* ***Raman shift*** *$\nu_M$ (the molecular vibrational frequency, for the gaseous molecular system, a third beam of frequency $\nu_a$ called* ***coherent anti-Stokes Raman scattering*** is produced which is almost parallel to the incident beams that is,

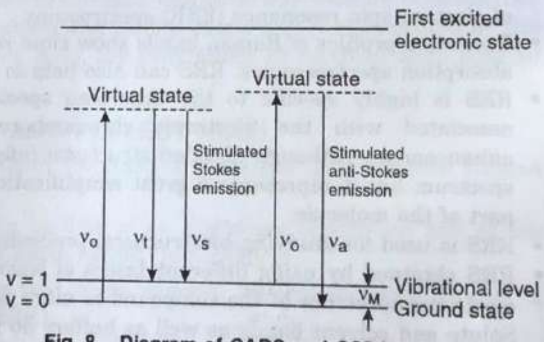

Fig. 8. Diagram of CARS and CSRS processes.

$$\nu_a = \nu_0 + (\nu_0 - \nu_t) = 2\nu_0 - \nu_t \text{ or } \nu_a = \nu_0 + \nu_M$$

The third beam $\nu_a$ can be separated from the incident beams by filtering. Fluorescence and thermal radiation from the hot samples can also be removed by filtration.

The CARS process depends on the square of the normal Raman scattering cross section and on the square of the number of molecules. Generally CARS signals are stronger than ordinary Raman lines by 8 to 10 orders of magnitude at standard temperature and pressure.

**Experimental Set up.** Experimental arrangement utilizes a tunable dye laser for the Stokes beam. The strong scattered light is collimated into a narrow beam to get CARS signal.

**Determination of Resolution.** Ultra high resolution like $0{\cdot}001\ \text{cm}^{-1}$ as against $0{\cdot}5\ \text{cm}^{-1}$ in high resolution Raman spectroscopy is obtained. The resolution in CARS spectrum is determined by the line width of the laser beams but not by Raman spectrometer.

The typical band width of lines in CARS is 1 to $0{\cdot}05\ \text{cm}^{-1}$ whereas in conventional Raman lines it is 1 to $10\ \text{cm}^{-1}$. The resolution is poor since the intensity of conventional Raman lines is low. However, accurate depolarization measurements can be made for CARS. Enhancement of CARS signals occurs if radiations $\nu_0$ and $\nu_t$ approach the electronic absorption frequencies of the system. The selection rules for CARS are similar to normal Raman effect.

**Scanning CARS.** It uses a narrow band tunable source which is scanned across a Raman resonance by changing the frequency difference $\nu_0 - \nu_t$. Other method uses a broad band source as the Stokes beam, which covers the entire Raman resonance. CARS spectrum is generated with each laser shot. The method gives good temporal resolution. In scanning CARS detection is usually carried out by photomultiplier tube while detection in the second method is made by optical multichannel analyser.

**Box CARS.** Here a three dimensional beam geometry is adopted to give a cylindrical interaction to generate the CARS signals.

### Advantages of CARS.

CARS signals are stronger than normal Raman lines by 8 to 10 orders of magnitude. Thus detection problem is much improved in CARS technique.

- CARS signals can be easily visualised compared to fluorescence.
- Because of non-linear nature of the technique, there is an enormous increase in scattering intensity as compared to conventional linear Raman scattering. CARS reveals a high resolution which is determined by line width of lasers.
- Microquantities ($10^{-5}$ to $10^{-7}$) can be detected by resonance CARS.

### Limitations of CARS.

- CARS requires complicated set up with difficult adjustment and costly equipment.
- Spectra evaluation is non-trivial.
- Band shapes are often distorted. Samples may decompose by high power laser beam focussing. Signal fluctuations are caused by frequent instabilities of the lasers.
- No quantitative conclusions can be drawn out of the signal intensity because of non-linear nature of the scattering process.

## APPLICATIONS OF CARS

- The CARS is an important tool for molecular structure determinations.
- CARS has been used for the study of rotational spectra of gases. Even differences between rotational and vibrational frequencies and deviations from Boltzmann distribution can be documented by CARS technique.
- CARS is well suited for single point temperature measurements. The signal strength is large and geometrical resolution is fair.
- CARS is one of the most widely used non-linear spectroscopic techniques for investigating gas phase combustion processes. The coherent nature of CARS provides a collimated signal beam with excellent immunity to background luminosity, high intensity and potentially high spectral resolution.
- Inspite of low absolute densities in free jet expansions, it is possible to obtain excellent CARS spectra of $N_2$, $O_2$, $C_2H_4$ etc. Several constituents of flames like $CO_2$, $CO$, $O_2$, $N_2$, $CH_4$, $H_2$, $H_2O$ have been studied using CARS technique, where $N_2$ spectra are used for temperature measurements.
- A particularly useful application of CARS spectroscopy is as a probe for species present in high temperature combustion source.
- CARS is an excellent technique for the study of biological samples in aqueous solution, which often produce strong fluorescence in the normal Raman scattering.
- Enhancement of the CARS signals occurs if radiations approach the electronic absorption frequencies of the system.

- Resonance enhancement of CARS signals in medicinal samples in aqueous solutions have been observed. By this method, ferrocytochrome and cyano cobalamin have been studied in dilute ($10^{-3}$ M) aqueous solutions.
- Numerous applications of CARS in molecular beam studies, energy transfer and plasma diagnostics are expected.

**Exercise.** *Express coherent and incoherent radiation.*

**Solution.** Radiation from the slits must be **coherent.** Important conditions for coherence are :

(i) Two sources of radiation must have identical frequencies, **(ii)** The phase relationship between the two beams must remain constant with time. **(iii)** With incoherent sources, light is emitted by individual atoms and the resulting beam is the sum of individual events, each of which lasts for $10^{-8}$ *s*. Hence a beam of radiation from this type of source is not continuous but is composed of a series of wave trains that are a few metres in length. Microwave sources, radiofrequency oscillators and optical lasers produce electromagnetic radiation in the form of trains with infinite length and constant frequency.

## SELECTED TIPS

- The exciting radiation must be monochromatic to get sharp Raman lines.
- A highly monochromatic source is essential to get **small Raman shifts.**
- In Raman spectrum, interaction of molecules takes place if the polarizability of the molecule is altered by vibration, *i.e.*, the shape of the molecule is changed without generating a dipole moment.
- Generally, in Raman spectroscopy Stoke's lines are more predominant than anti-Stoke's lines, while Rayleigh scattering is more pronounced than either Stoke's or anti-Stokes lines. Usually one has to measure weak Raman lines adjacent to Rayleigh lines.
- Raman technique is more useful for studying **metal bonding in coordination compounds** as it furnishes valueable information in the region 1000–700 $cm^{-1}$.
- In infrared, one can go upto a region of 200 $cm^{-1}$ while in Raman spectroscopy one can go down to about 20 $cm^{-1}$ giving access to low frequency vibrations.
- IR spectral characterisation of **diatomic molecules** ($O_2$, $H_2$, $CO_2$) **is cumbersome** but it is very simple with Raman spectroscopy.
- For **symmetrical molecules,** there is no better substitute for Raman spectroscopy. No overtones and combination bands appear in Raman spectra. But the spectra consists of weak bands with poor resolution.
- CO gives a Raman line at 2155 $cm^{-1}$ that closely resembles to $-C{\equiv}N$ of 2200 $cm^{-1}$.

## SHORT ANSWER QUESTIONS

1. *When will the Raman spectrum result?*

   **Ans.** Raman spectrum will result if the polarizability ellipsoid changes in size, shape or orientation due to molecular vibrations. Raman band intensity depend on the extent of this polarizability change.

2. *In which case alternate rotational level is absent?*

   **Ans.** If the molecule has a centre of symmetry (*e.g.*, $H_2$, $O_2$, $CO_2$), then the effects of nuclear spin will be observed in Raman as in IR. Since the spin of $O_2$ is zero, every rotational level with even $J$ values is missing and thus every transition labelled as $J = 0, 2, 4$ is completely missing from the spectrum. In case of $H_2$ and other molecules composed of nuclei with non-zero spin, the spectral lines show an alteration of intensity.