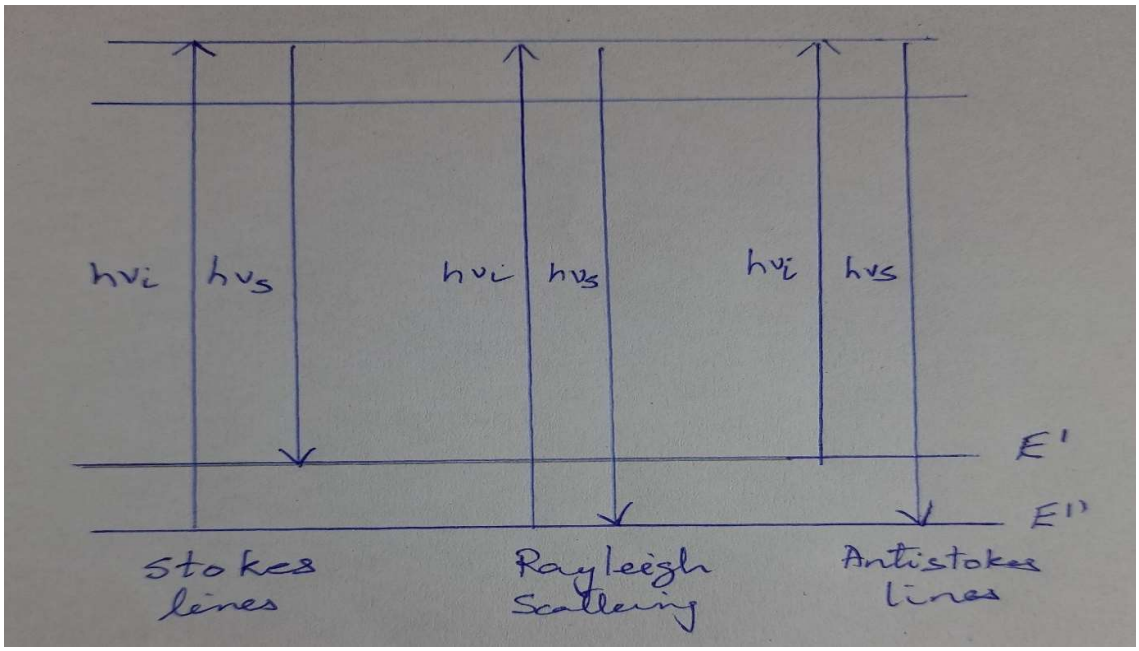
Raman Spectra:

Discovered by C.V.Raman

When a beam of monochromatic light is allowed to pass through organic substances such as benzene ,toluene etc, the scattered light contains additional frequencies which may be greater,lesser or equal to than that of the incident light.This effect is known as Raman Effect.

Stokes lines,antistokes lines



Rayleigh Scattering When the molecule collides with a photon,the collisions maybe elastic or non-elastic.If the collision is elastic,then the total energy of the molecules and the photons remain the same. Here the molecule will not get scattered without absorbing photon energy.The collision will merely induce forced oscillations in the molecule.This will give rise to Rayleigh Scattering.

Stokes lines and Anti-Stokes lines:

If the collision between the molecule and photon is inelastic,then there is a transfer of energy . Before collision the molecule is present in the lower energy level of the ground state after collision with the photon it reaches the higher level of the ground state.The frequency of the emitted photon is less.These are Stokes lines.

Before collision the molecule is present in the higher energy level of the ground state after collision with the photon it reaches the lower energy level of the ground state.The frequency of the emitted photon is more.These are Anti-Stokes lines.

If v_I --incident frequency v_s --Scattered frequency
Then Raman Shift $\Delta v = v_I - v_s$

For Stokes lines Raman Shift Δv is positive. $v_s < v_I$
Raman lines at lower frequencies are called Stokes lines.

For Anti Stokes lines Raman Shift Δv is negative. $v_s > v_I$
Raman lines at higher frequencies are called Anti Stokes lines

For Rayleigh Scattering Raman Shift Δv is zero.

Characteristics of Stokes lines and Antistokes lines :

The intensity of Stokes lines is always greater than the corresponding anti Stokes lines.
Raman frequencies are identified with Infra red vibrational frequencies.
Raman Lines are symmetrically displaced about the parent line.
When the temperature rises,their individual separations from the parent line decreases.
The frequency difference between the modified and parent line represents the frequency of the absorption band of the material.

Differences between Stokes and Antistokes lines

Stokes lines	Antistokes lines
1)Frequency of scattered lines is less than incident light.	1)Frequency of scattered lines is more than incident light.
2)Occurs by molecules at lower energy level,which are more populated.	2)Occurs by molecules at higher energy level,which are less populated.
3) These lines are more intense with high intensity of absorption.	3) These lines are less intense with low intensity of absorption.
4)At low temperature,these take place more frequently.	4)At high temperature,molecules are raised to higher energy state and the lines gradually increase.

INTENSITY DIFFERENCE

Scattering intensity is proportional to the square of induced dipole moment.If a vibration does not greatly change the polarizability,then the polarizability derivative will be near zero. The intensity of the Raman band will be low.

INTENSITY

The intensity of spectral transitions is determined by :

a)Boltzmann Population:

$N/N_0 = e^{-\Delta E/KT}$

N= Number of molecules in the excited state
N_0 = Number of molecules in the ground state.
ΔE = Difference in energy between the ground state and excited state.
K- Boltzmann constant
T =Temperature

If ΔE is large N/N_0 would be small i.e. number of molecules in the excited state would be less than the number of molecules in the ground state.

Hence transitions ,originating from ground state to higher energy state are more intense ,than transitions from first excited state to higher energy state.

b)Transition Probability: is the probability of transitions between two energy levels.

The molecule on absorption of a photon does not go anywhere it pleases ,it ends up in an energy level determined by the selection rule.

Transitions which obey selection rule are allowed transitions and those which do not obey selection rule are forbidden transitions.

Allowed transitions are having greater intensity than forbidden transitions.

The intensity of Stokes lines are proportional to the number of atoms in the ground state.The intensity of anti-Stokes lines are proportional to the number of atoms in the excited state.

Since the number of atoms in the ground state is more than the number of atoms in the excited state the intensity of Stokes lines is more than the intensity of anti Stokes lines.