THEORY OF RAMAN SCATTERING

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CLASSICAL THEORY

- An insight into the phenomenon of raman scattering is possible on the basis of classical considerations.
- When a molecule is placed in an electrical field, polarization of the medium takes place as the negatively charged electron cloud is being attracted towards the positive pole and the positively charged nuclei being attracted towards the negative pole.

- The polarization P so induced is proportional to the applied electric field E. That is,

$$P=\alpha E$$

- The constant of proportionality α is the polarizibilty of the molecule . In general it is a tensor with nine components.
- When radiation of frequency v0 is allowed to fall on molecules each molecule experiences a varying electric field

$$E= E0 \cos 2\Pi v0 t$$

- Q can be written as

  $Q = Q_0 \cos 2\Pi \nu_m t$

- The polarizability α can be expressed as a taylor series in the normal coordinate Q as

  $\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial Q}_0\right) Q + \ldots\ldots$

- Neglecting higher order terms and substituting we get,

$P = \alpha_o E_o \cos 2\Pi \nu_o t + \left(\frac{\partial \alpha}{\partial Q}_0\right) Q_o E_o \cos 2\Pi \nu_o t \cos 2\Pi \nu_m t$

- The polarization thus induced contains the three distinct frequency components

i. V= Vo Rayleigh line

ii. V= Vo-Vm Raman stokes line

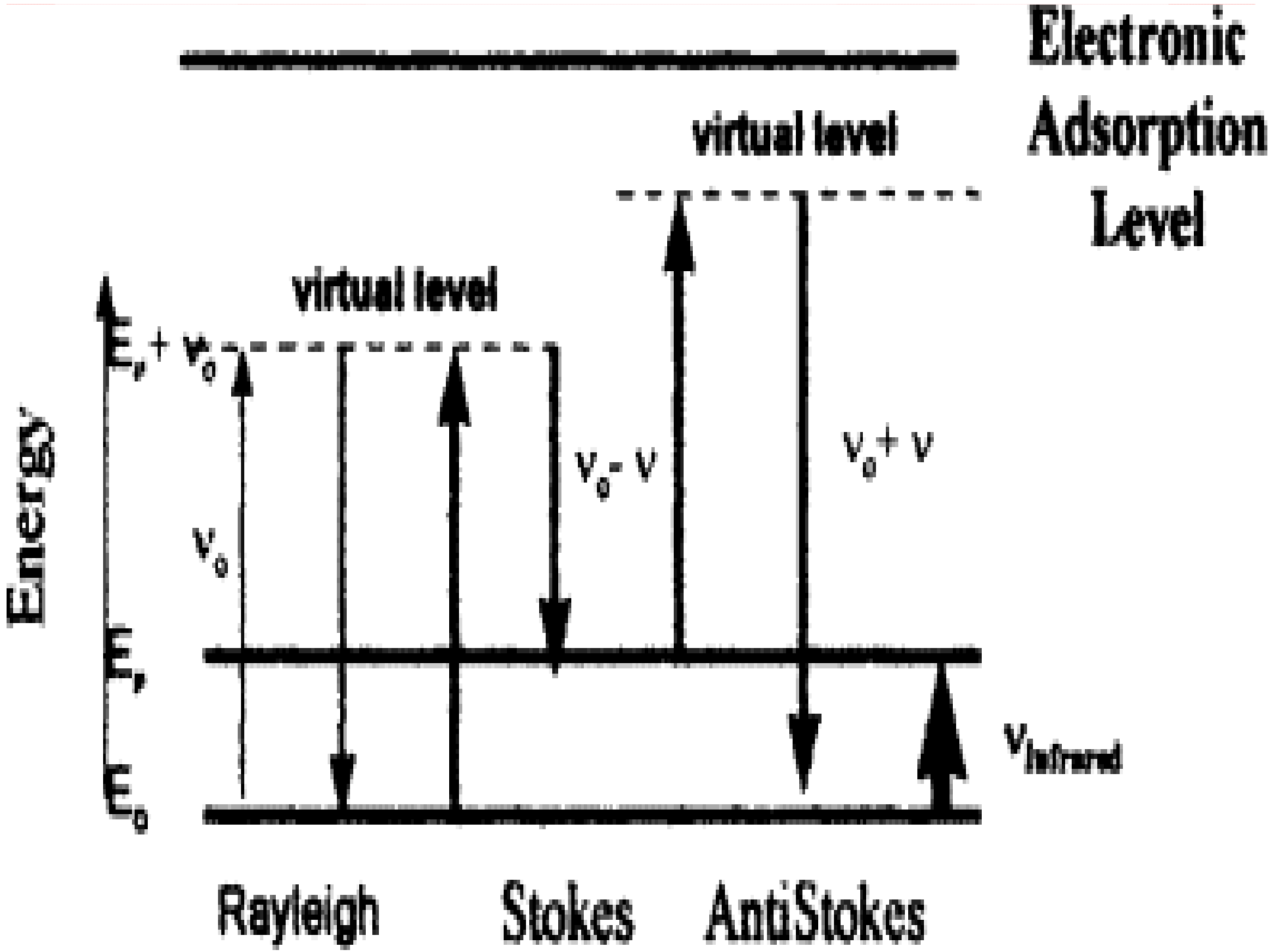
iii. V=Vo+Vm Raman anti stokes line

- It may be noted that if $\left(\frac{\partial \alpha}{\partial Q}\right)_0$ is zero, no raman line will be observed.
- A change in polarizability means a change either in magnitude or in direction.

- We can take the normal modes of the linear triatomic molecule CO2.
- The polarizability is plotted with respect to the displacement coordinate x.
- For the v1 and v3 modes, x is a measure of the extention or compression of the bond.
- For the v2 mode x measures the displacement of the bond angle from its equilibrium value.
- For small displacement from the equilibrium position, the curve is almost flat in both v2 and v3 modes leading to zero value for $\frac{\partial \propto}{\partial x}$
- Hence they are raman inactive

QUANTUM THEORY

- In the quantum picture, radiation has both particle and wave nature.
- In explaining raman scattering incident radiation of frequency vo is considered as a stream of particles undergoing collision with molecules.
- However there will be exchange of energy between the two if the collision is inelastic.
- The molecule can gain or lose energy equal to the energy difference between any two of its allowed states.


Electronic
Adsorption
Level
virtual level
virtual level
Energy
$E_n + v_0$
v_0
E_n
E_0
$v_0 - v$
$v_0 + v$
$v_{Infrared}$
Rayleigh
Stokes
AntiStokes

- When a system interacts with a radiation of frequency it may make an upward transition to a virtual state of a system.
- However a very small fraction returns to states of higher and lower energies giving rise to stokes and anti stokes line respectively.
- If the virtual state of the system coincides with a real state of the system it will lead to resonance raman effect.

- The intensity of a spectral line depends on number of factors the most important being the initial population of the state from which the transition originates.
- The intensity ratio of stokes to anti stokes is given by

  I s/ I a.s = exp hvm/kT

  K is boltzman constant and T is temperature in kelvin
- Taking other factors into account, gives

  I s/ I a.s = $\frac{(vo - vm)^4}{(vo + vm)^4}$ exp$\frac{hvm}{kT}$
- Anti stokes line have much less intensity than stokes line.