Non linear Raman Spectroscopy. 10/3/24.

For normal raman spectroscopy:

$$p_i(t) = \mu_i + \sum_j \alpha_{ij} E_j + \sum_{jk} \beta_{ijk} E_j E_k + \sum_{jkl} \gamma_{ijkl} E_j E_k E_l .$$

$$\text{Polarization}[P_i(E)] = \epsilon_0 \left(\chi_i + \sum_k \chi_{ik} E_k + \sum_{k,j} \chi_{ijk} E_k E_j \ldots \right)$$

χ_i has 2 definitions: $\chi_i = N \mu_i / \epsilon_0$ // $\chi_{ik} = N \alpha_{ik} / \epsilon_0$.

For sufficiently small electric fields Non-linear terms can be neglected.

Stimulated Raman scattering

$$E = E_L \exp(i[\omega_L t - k_L z]) + E_s \exp(i[\omega_s t - k_s z]).$$

Potential energy: $V_{pol} = p.E$
$= -\alpha |E|^2.$

$$\text{Force} = -\left(\frac{\partial \alpha_{ij}}{\partial q}\right) \cdot |E|^2 .$$

$q \longrightarrow$ displacement for a particular mode;

we refer to the oscillator model (AGAIN):

$$\ddot{q} + \gamma \dot{q} + \omega_v q = \frac{f}{m}\left(\frac{\partial \alpha}{\partial q}\right) |E|^2 \longrightarrow (1)$$

$$\longrightarrow |E|^2 = \left[E_L e^{-i(\omega_L t - k_L z)} + E_s e^{-i(\omega_s t - k_s z)}\right]\left[E_L e^{i(\omega_L t - k_L z)} + E_s e^{i(\omega_s t - k_s z)}\right]$$

$$= E_L^2 + E_s^2 + E_L E_s e^{i[(\omega_L - \omega_s)t - (k_L - k_s)z]} + E_L E_s e^{i[(\omega_L - \omega_s)t + (k_L - k_s)z]}$$

Sample solution: $\frac{1}{2}\left(q_{\mu} e^{i\omega t} + q_{\nu} e^{-i\omega t}\right)$. $\quad \omega \rightarrow (\omega_L - \omega_S)$

Polarization: $N\mu + N(\alpha E)$. $N\mu$ → magnetic moment; αE → dielectric absorption.

$$q_\nu = \frac{\left(\frac{d\alpha}{dq}\right) E_L E_S e^{-i(k_L - k_S)z}}{2m\left[\omega_\nu^2 - (\omega_L - \omega_S)^2 + i\gamma(\omega_L - \omega_S)\right]}$$

induced pol (P): $\boxed{\frac{1}{2}\left(\frac{\partial\alpha}{\partial q}\right) q E}$

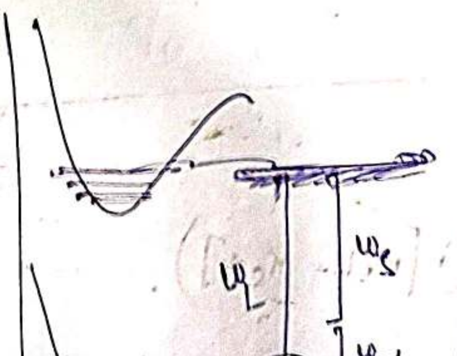
$$P_{NL} = \frac{\left(\frac{\partial\alpha}{\partial q}\right)^2 E_L^2 E_S e^{i(\omega_S t - k_S z)}}{4m[\quad]}$$

(1) Strong Raman signal
(2) Less background.

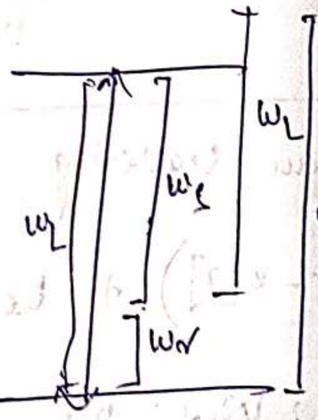
General principle.

$\omega_L = \omega_S + \omega_\nu$.
ω_ν → incident
ω_L → laser
ω_S → Stoke's

COHERENT Anti stokes law. (CARS)



Spontaneous RS
Raman scattering.



ω_A: Anti stokes.

$$\boxed{\begin{aligned}\omega_S &= \omega_L - \omega_\nu \\ \omega_A &= \omega_L + \omega_\nu\end{aligned}}$$

For coherent condition –

$$\boxed{2\vec{K}_L = \vec{K}_A + \vec{K}_S}.$$