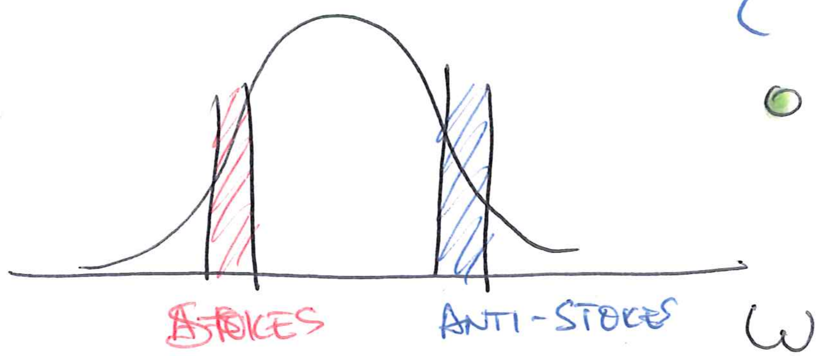
- IF WE INTEGRATE OVER ALL FREQUENCIES, THE SIGNAL = 0 (RAMAN SCATTERING CONSERVES # PHOTONS) — TRUE FOR PHOTON COUNTER

RESPONSE $\propto \frac{1}{\omega}$



- USE FILTERS (VARIOUS STRATEGIES)

$$\frac{dI}{dQ} \propto \cos(\Omega\delta)\,\frac{d|e_0|^2}{d\omega}$$

STOKES & A-STOKES ARE OUT-OF-PHASE (π)

- BOUNDARY EFFECTS

IMPORTANT IN ABSORBING MEDIA
THIN FILMS

CHECK 2006 NOTES P. 52

$$\frac{\Delta T}{T},\ \frac{\Delta R}{R} \propto \sin(\Omega\delta)$$

- PHASE MATCHING (WAVEVECTOR CONSERVATION)

$$Q \equiv Q(t - zn/c)$$

PUMP WITH ITSELF

$$Q_q = \frac{Q_0}{\sqrt{V}} \int \sin[\Omega(t - zn/c)]\, e^{iqz}\, dz\ \theta\!\left(t - \frac{zn}{c}\right)$$

$$\Rightarrow q \sim \frac{n\Omega}{c}$$

FORWARD SCATTERING

HOW LARGE IS THE PHONON AMPLITUDE?

$$\frac{\partial \chi}{\partial u} \sim \frac{10^{-1} - 10}{\text{Å}}$$ (RAMAN SUSCEPTIBILITY AWAY FROM RESONANCES)

ION DISPLACEMENT

AVERAGE POWER ~ 1 W

ENERGY/PULSE ~ $\frac{1\,W}{\text{REP. RATE}}$

80 MHz — 12.5 nJ

10 kHz — 100 μJ

THE SIZE OF FOCAL SPOT MATTERS

PUMP

$$Q = 2\pi \frac{\partial \chi}{\partial Q} \boxed{\frac{\text{ENERGY of PULSE}}{\text{AREA}}} \frac{1}{\Omega m c}$$

UNITS OF $(g/cm)^{1/2}$

$$u \sim \sqrt{\frac{V_{CELL}}{M_{ION}}}\, Q$$

$$\frac{u}{a_0} \sim \frac{\Delta I_{PROBE}}{I_{PROBE}} \sim 10^{-2} - 10^{-5}$$

LATTICE PARAMETER

HOW MANY PHONONS?

MACROSCOPIC $\frac{\text{VOLUME}}{\text{VOLUME CELL}}$

SELECTION RULES

SIGNAL IS PROPORTIONAL TO

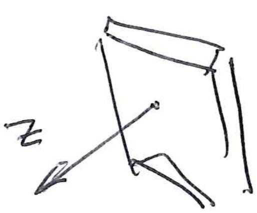
$$\underbrace{\left[\frac{\partial \chi_{mp}}{\partial Q_\alpha}\, \xi_{e_m}\, \xi_{e_p}\right]}_{\text{PUMP}} \otimes \underbrace{\left[\frac{\partial \chi_{st}}{\partial Q_\alpha}\, e_s\, e_t\right]}_{\text{PROBE}}$$

EXAMPLE

OPTICAL MODE OF GaAs

$$(Q_x, Q_y, Q_z) \Downarrow (R_x, R_y, R_z)$$

$$R_x : \begin{bmatrix} & & \\ & & c \\ & c & \end{bmatrix} \qquad R_y : \begin{bmatrix} & & c \\ & & \\ c & & \end{bmatrix} \qquad R_z : \begin{bmatrix} & c & \\ c & & \\ & & \end{bmatrix}$$



ONLY COUPLING IS THROUGH R_z

SIGNAL IS $\propto \left[\xi_{e_x}\, \xi_{e_y}\, e_x\, e_y\right]$

MORE WHEN WE DISCUSS SPECIFIC EXAMPLES

2.2. MICROSCOPIC THEORY

PRB 65, 144304 (2002)

Consider the following Hamiltonian

$$\hat{H} = H_0 + H_e + H_{e\text{-}ph} + H_{e\text{-}light}$$

$$H = \frac{1}{2}\left(P_q^2 + \Omega_0^2 Q_q^2\right)$$

{OMIT THE PHONON WAVEVECTOR

$$H_{e\text{-}ph} = -\hat{\Gamma}\, Q_q$$

$$\Gamma \equiv \frac{1}{\sqrt{V}} \sum_{\substack{bb' \\ kk'}} c^{+}_{bk} c_{b'k} \Gamma^{bb'}_{kk'} \longrightarrow \text{DEFORMATION POTENTIAL OR FROHLICH COUPLING}$$

$q = k - k'$

$$H_e = \sum_k \epsilon_k c^{+}_k c_k$$

$$H_{e\text{-}light} = -\underbrace{\hat{\Delta}}_{\text{dipole moment}} \cdot \vec{E}(t) \qquad (\text{or } \vec{A}\cdot\vec{P})$$

$\hat{\Delta}$, $\hat{\Gamma}$ DEPEND ON ELECTRON VARIABLES

$$\dot{Q} = \frac{i}{\hbar}[H,Q] = P$$

$$\ddot{Q} = \frac{i}{\hbar}[H,P] = -\Omega_0^2 Q - \frac{i}{\hbar}\hat{\Gamma}[Q,P]$$

$$= -\Omega_0^2 Q + \hat{\Gamma}$$

$$\Rightarrow \frac{d^2}{dt^2}\langle Q\rangle + \Omega_0^2\langle Q\rangle = \langle\hat{\Gamma}\rangle \equiv F(t)$$

EXACT !

SOLUTION IS

$$\langle Q\rangle = \int_{-\infty}^{t} \frac{\sin\Omega_0(t-\tau)}{\Omega_0} F(\tau)\,d\tau$$

$$= \left[\frac{e^{i\Omega_0 t}}{\Omega_0}\int_{-\infty}^{t} e^{-i\Omega_0\tau}F(\tau)\,d\tau\right.$$

$$\left. - \frac{e^{-i\Omega_0 t}}{\Omega_0}\int_{-\infty}^{t} e^{i\Omega_0\tau}F(\tau)\,dt\right]\Big/ 2i$$

THUS

$$\lim_{t\to\infty}\langle Q(t)\rangle = \frac{-i}{\sqrt{8\pi}\,\Omega_0}\left[e^{i\Omega_0 t}F(-\Omega_0) - e^{-i\Omega_0 t}F(\Omega_0)\right]$$

TWO EXTREME CASES

IF $F(\Omega)$ IS REAL

$\Rightarrow \langle \hat{Q}(t) \rangle \propto \sin \Omega_0 t$

IMPULSIVE EXCITATION (INCLUDES $F \propto \delta(t)$)

IF $F(\Omega)$ IS IMAGINARY

$\Rightarrow \langle \hat{Q}(t) \rangle \propto \cos \Omega_0 t$

DISPLACIVE EXCITATION

- CALCULATE $F(t) \equiv \langle \hat{\Pi} \rangle$

THIS EXPECTATION VALUE CAN BE CALCULATED USING PERTURBATION THEORY - THE LOWEST ORDER IS 2nd ORDER IN $\hat{\Delta}$ AND 1st ORDER IN Π

THE RESULT IS (FOUR TERMS)

SEE NOTES

$$F(t) = \frac{1}{2\pi\hbar^2} \underbrace{\sum}_{\text{INTERMEDIATE}} \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{+\infty} d\Omega\, e^{-i\Omega t}$$

MOST RESONANT TERM

$$\times \left\{ \frac{1}{2} \frac{\Pi_{mn} [\vec{\Delta}_{n0} \cdot \vec{E}(\omega)][\vec{\Delta}_{0m} \cdot \vec{E}^*(\omega-\Omega)]}{(\omega_m + i\gamma_m - \omega + \Omega)(\omega_n - i\gamma_n - \omega)} \right.$$

$$+ \frac{\Pi_{0m} [\vec{\Delta}_{mn} \cdot \vec{E}(\omega)][\vec{\Delta}_{n0} \cdot \vec{E}^*(\omega-\Omega)]}{(\omega_m - i\gamma_m - \Omega)(\omega_n - i\gamma_n + \omega - \Omega)}$$

$$\left. + \text{C.C.} \right\}$$

WE CAN WRITE $F(t)$ AS

$$F(t) = \frac{N v_c}{4\pi} \sum_{K\ell} \iint_{-\infty}^{+\infty} e^{-i\Omega t} E_\ell(\omega)\, \Pi_{K\ell}(\omega, \omega-\Omega)\, E_K(\omega-\Omega)\, d\omega\, d\Omega$$

WHERE

MOST RESONANT

$$\Pi_{K\ell} = \frac{2}{N \epsilon \hbar^2}\left[\sum_{\text{INTERMEDIATE}} \frac{1}{2} \frac{\Gamma_{mm}\, \Delta^{(K)}_{m0}\, \Delta^{(\ell)}_{0m}}{(\omega_m + i\gamma_m - \omega + \Omega)(\omega_m - i\gamma_m - \omega)} + \Gamma_{0m} \frac{\Delta^{(K)}_{mm}\, \Delta^{(\ell)}_{m0}}{(\omega_m - i\gamma_m - \Omega)(\omega_m - i\gamma_m + \omega - \Omega)} \right] + \text{c.c.}$$

SIGNS ARE CRUCIAL

IF $|\omega \pm \omega_m| \gg \gamma_m$

$$\Pi_{K\ell} \equiv R_{K\ell}(\omega, \omega - \Omega)$$

RAMAN TENSOR

CONSIDER MOST RESONANT TERMS (2 RES. DENOMINATORS) & TWO BAND PROCESSES &

$$\Gamma_{mm} \approx \Gamma_0 \equiv \text{CONSTANT}$$

$$\Pi_{kl} \approx \frac{\mathcal{E}_0}{N v_c \hbar^2} \sum \frac{|\Delta_{om}|^2}{(\omega_m + i\gamma_m - \omega + \Omega)(\omega_m - i\gamma_m - \omega)}$$

INTERMEDIATE STATES

$$\omega_m \approx \omega_m$$

$$\Delta_{om} \approx \Delta_{om}$$

WE CAN WRITE Π_{kl} AS

$$\Pi_{kl} \approx \frac{\mathcal{E}_0}{N v_c \hbar^2} \sum_m \frac{|\Delta_{om}|^2}{\Omega} \left[\frac{1}{\omega_m - i\gamma_m - \omega} - \frac{1}{\omega_m + i\gamma_m - \omega + \Omega} \right]$$

THE DIELECTRIC CONSTANT IS

$$\epsilon(\omega) = \frac{1}{V} \sum_j \frac{|\Delta_{oj}|^2}{\omega_j + i\gamma - \omega}$$

$$\Rightarrow \Pi_{kl} \approx \frac{\mathcal{E}_0}{4\pi\hbar\Omega} \left[\epsilon(\omega + \Omega) - \epsilon^*(\omega) \right] \quad !$$

$$\approx \frac{\mathcal{E}_0}{4\pi\hbar} \left[\frac{d\,\mathrm{Re}\,\epsilon}{d\omega} + 2i \frac{\mathrm{Im}\,\epsilon}{\Omega} \right]$$

VERY IMPORTANT RESULT

IF $\epsilon(\omega)$ VARIES SLOWLY OVER THE OPTICAL PULS WIDTH

$$F(\Omega) \propto \left[\frac{dR_e(\epsilon)}{d\omega} + 2i\,\frac{Im(\epsilon)}{\Omega} \right]$$

$$\times \int_{-\infty}^{\infty} e^{i\Omega t} \underbrace{|E(t)|^2}_{\text{PUMP PULSE}} dt$$

$\frac{dRe\epsilon}{d\omega} \Rightarrow$ IMPULSIVE • $F(t) \propto |E(t)|^2$

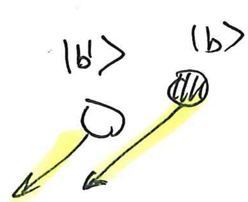
$\frac{Im\,\epsilon}{\Omega} \Rightarrow$ DISPLACIVE • $F(t) \propto \int_{-\infty}^{t} |E(t')|^2 dt'$

USUALLY ABOVE THE GAP $\left|\frac{dRe\epsilon}{d\omega}\right| \ll \frac{Im(\epsilon)}{\Omega}$

NOT FOR SHARP EXCITONIC FEATURES

COUPLING TO CHARGE-DENSITY FLUCTUATIONS INDUCED BY THE PUMP BEAM.

LIFETIME OF RAMAN COHERENCE $\gg$ CONDUCTION-VALENCE DEPHASING TIME



CLOSE IN ENERGY & WAVEVECTOR

$\langle c^\dagger_{b'} c_b \rangle$

I want to calculate

$$\langle O\rangle = \sum_{mn} O_{mn}\rho_{nm}^{(2)}$$

where [Boyd's Eq. (3.6.7), p. 135]

$$\rho_{nm}^{(2)} = \hbar^{-2}\sum_{v}\sum_{pq} \exp[-i(\omega_p+\omega_q)t]\times$$

$$\left\{\frac{[\rho_{mm}^{(0)}-\rho_{vv}^{(0)}][\boldsymbol{\mu}_{nv}.\mathbf{E}(\omega_q)][\boldsymbol{\mu}_{vm}.\mathbf{E}(\omega_p)]}{[(\omega_{nm}-\omega_q-\omega_p)-i\gamma_{nm}][(\omega_{vm}-\omega_p)-i\gamma_{vm}]} - \frac{[\rho_{vv}^{(0)}-\rho_{nn}^{(0)}][\boldsymbol{\mu}_{nv}.\mathbf{E}(\omega_p)][\boldsymbol{\mu}_{vm}.\mathbf{E}(\omega_q)]}{[(\omega_{nm}-\omega_q-\omega_p)-i\gamma_{nm}][(\omega_{nv}-\omega_p)-i\gamma_{nv}]}\right\}$$

Then

$$\langle O\rangle = \hbar^{-2}\sum_{vnm}\sum_{pq} \exp[-i(\omega_p+\omega_q)t]\times$$

$$\left\{\frac{O_{mn}[\rho_{mm}^{(0)}-\rho_{vv}^{(0)}][\boldsymbol{\mu}_{nv}.\mathbf{E}(\omega_q)][\boldsymbol{\mu}_{vm}.\mathbf{E}(\omega_p)]}{[(\omega_{nm}-\omega_q-\omega_p)-i\gamma_{nm}][(\omega_{vm}-\omega_p)-i\gamma_{vm}]} - \frac{O_{mn}[\rho_{vv}^{(0)}-\rho_{nn}^{(0)}][\boldsymbol{\mu}_{nv}.\mathbf{E}(\omega_p)][\boldsymbol{\mu}_{vm}.\mathbf{E}(\omega_q)]}{[(\omega_{nm}-\omega_q-\omega_p)-i\gamma_{nm}][(\omega_{nv}-\omega_p)-i\gamma_{nv}]}\right\}$$

Using $\rho_{kk}^{(0)} = \rho_0\delta_{k0}$, I get the following four terms

$$\langle O\rangle = \hbar^{-2}\sum_{vnm}\sum_{pq} \exp[-i(\omega_p+\omega_q)t]\times \rho_0$$

$$\frac{O_{0n}[\boldsymbol{\mu}_{nv}.\mathbf{E}(\omega_q)][\boldsymbol{\mu}_{v0}.\mathbf{E}(\omega_p)]}{[(\omega_{n0}-\omega_q-\omega_p)-i\gamma_{n0}][(\omega_{v0}-\omega_p)-i\gamma_{v0}]} - \frac{O_{mn}[\boldsymbol{\mu}_{n0}.\mathbf{E}(\omega_q)][\boldsymbol{\mu}_{0m}.\mathbf{E}(\omega_p)]}{[(\omega_{nm}-\omega_q-\omega_p)-i\gamma_{nm}][(\omega_{0m}-\omega_p)-i\gamma_{0m}]}$$

$$-\frac{O_{mn}[\boldsymbol{\mu}_{n0}.\mathbf{E}(\omega_p)][\boldsymbol{\mu}_{0m}.\mathbf{E}(\omega_q)]}{[(\omega_{nm}-\omega_q-\omega_p)-i\gamma_{nm}][(\omega_{n0}-\omega_p)-i\gamma_{n0}]} + \frac{O_{m0}[\boldsymbol{\mu}_{0v}.\mathbf{E}(\omega_p)][\boldsymbol{\mu}_{vm}.\mathbf{E}(\omega_q)]}{[(\omega_{0m}-\omega_q-\omega_p)-i\gamma_{0m}][(\omega_{0v}-\omega_p)-i\gamma_{0v}]}$$

In the following, I keep only the second and third (most resonant) terms and exchange (*p*,*q*) by (*q*,*p*) in the third term to obtain

$$\langle O\rangle_{\mathbf{RESONANT}} = -\hbar^{-2}\rho_0\sum_{vnm}\sum_{pq} \exp[-i(\omega_p+\omega_q)t]\times \frac{O_{mn}[\boldsymbol{\mu}_{n0}.\mathbf{E}(\omega_q)][\boldsymbol{\mu}_{0m}.\mathbf{E}(\omega_p)]}{[(\omega_{nm}-\omega_q-\omega_p)-i\gamma_{nm}]}\times$$

$$\left[\frac{1}{[(\omega_{0m}-\omega_p)-i\gamma_{0m}]} + \frac{1}{[(\omega_{n0}-\omega_q)-i\gamma_{n0}]}\right]$$

Assuming that $\gamma_{nm} = \gamma_{n0} + \gamma_{0m}$, we have

$$\langle O\rangle_{\mathbf{RESONANT}} = -\hbar^{-2}\rho_0\sum_{vnm}\sum_{pq} \exp[-i(\omega_p+\omega_q)t]\times \frac{O_{mn}[\boldsymbol{\mu}_{n0}.\mathbf{E}(\omega_q)][\boldsymbol{\mu}_{0m}.\mathbf{E}(\omega_p)]}{[(\omega_{0m}-\omega_p)-i\gamma_{0m}][(\omega_{n0}-\omega_q)-i\gamma_{n0}]}$$

Finally, the substitution $\omega_p \to -\omega_p$ gives the same result as Eqs. (4) and (5) of our PRL

$$\langle O\rangle_{\mathbf{RESONANT}} = \rho_0\sum_{vnm}\sum_{pq} \exp[i(\omega_p-\omega_q)t]\times \frac{O_{mn}[\boldsymbol{\mu}_{n0}.\mathbf{E}(\omega_q)][\boldsymbol{\mu}_{0m}.\mathbf{E}^*(\omega_p)]}{[(E_m+i\hbar\gamma_{0m}-\hbar\omega_p][(E_n-i\hbar\gamma_{n0}-\hbar\omega_q]}$$

This term can be written as

$$\langle O\rangle_{\mathbf{RESONANT}} \sim \sum_{nm} O_{mn} \times$$

$$\left\{\int_{-\infty}^{+\infty} \exp(i\omega_1 t)\times\frac{[\boldsymbol{\mu}_{0m}.\mathbf{E}^*(\omega_1)]}{[(E_m + i\hbar\Gamma_m/2-\hbar\omega_1]}d\omega_1\right\}\left\{\int_{-\infty}^{+\infty} \exp-(i\omega_2 t)\times\frac{[\boldsymbol{\mu}_{n0}.\mathbf{E}(\omega_2)]}{[(E_n - i\hbar\Gamma_n/2-\hbar\omega_2]}d\omega_2\right\}$$

where I use the fact that $\gamma_{nm} = (\Gamma_n + \Gamma_m)/2$ [Boyd's (3.3.25)].

The integrals satisfy causality in that, for $t<0$, $\langle O\rangle_{\mathbf{RESONANT}} \equiv 0$

while, for $t>0$, the poles associated with E_m and E_n give

$$-4\pi\sum_{nm} O_{mn}[\boldsymbol{\mu}_{0m}.\mathbf{E}^*(E_m/\hbar+i\Gamma_m/2)][\boldsymbol{\mu}_{n0}.\mathbf{E}(E_n/\hbar+i\Gamma_n/2)]\times\exp[i(E_m-E_n)t/\hbar]\times\exp[-(\Gamma_m+\Gamma_n)t/2]$$

which $\to 0$ when $t\to+\infty$

Now, I want to calculate the dipole moment

$$\langle\boldsymbol{\mu}\rangle = \sum_{mn}\boldsymbol{\mu}_{mn}\mathrm{P}_{nm}^{(2)}$$

where the second-order density matrix is

$$\mathrm{P}_{nm}^{(2)} = \hbar^{-2}\sum_{v}\sum_{\Omega,\omega}\exp[-i(\omega+\Omega)t]\times$$

$$\left\{\frac{[\rho_{mm}^{(0)}-\rho_{vv}^{(0)}][\boldsymbol{\mu}_{nv}.\mathbf{E}(\omega)][\Xi_{vm}(\Omega)]}{[(\omega_{nm}-\omega-\Omega)-i\gamma_{nm}][(\omega_{vm}-\Omega)-i\gamma_{vm}]}-\frac{[\rho_{vv}^{(0)}-\rho_{nn}^{(0)}][\boldsymbol{\mu}_{nv}.\mathbf{E}(\omega)][\Xi_{vm}(\Omega)]}{[(\omega_{nm}-\Omega-\omega)-i\gamma_{nm}][(\omega_{nv}-\omega)-i\gamma_{nv}]}\right\}$$

Here Ω and ω are the frequencies associated with the vibrational and electromagnetic field and $\Xi \propto Q$ is the time-dependent electron-phonon coupling. Then

$$\langle\boldsymbol{\mu}\rangle = \hbar^{-2}\sum_{vnm}\sum_{\Omega,\omega}\exp[-i(\omega+\Omega)t]\times$$

$$\left\{\frac{\boldsymbol{\mu}_{mn}[\rho_{mm}^{(0)}-\rho_{vv}^{(0)}][\boldsymbol{\mu}_{nv}.\mathbf{E}(\omega)][\Xi_{vm}(\Omega)]}{[(\omega_{nm}-\omega-\Omega)-i\gamma_{nm}][(\omega_{vm}-\Omega)-i\gamma_{vm}]}-\frac{\boldsymbol{\mu}_{mn}[\rho_{vv}^{(0)}-\rho_{nn}^{(0)}][\boldsymbol{\mu}_{nv}.\mathbf{E}(\omega)][\Xi_{vm}(\Omega)]}{[(\omega_{nm}-\Omega-\omega)-i\gamma_{nm}][(\omega_{nv}-\omega)-i\gamma_{nv}]}\right\}$$

Using $\rho_{kk}^{(0)} = \rho_0\delta_{k0}$, I get the following four terms

$$\langle \boldsymbol{\mu} \rangle = \rho_0 \hbar^{-2} \sum_{vnm} \sum_{\Omega,\omega} \exp[-i(\Omega+\omega)t] \times$$

$$\frac{\boldsymbol{\mu}_{0n}[\boldsymbol{\mu}_{nv}.\mathbf{E}(\omega)][\Xi_{v0}(\Omega)]}{[(\omega_{n0}-\omega-\Omega)-i\gamma_{n0}][(\omega_{v0}-\Omega)-i\gamma_{v0}]} - \frac{\boldsymbol{\mu}_{mn}[\boldsymbol{\mu}_{n0}.\mathbf{E}(\omega)][\Xi_{0m}(\Omega)]}{[(\omega_{nm}-\omega-\Omega)-i\gamma_{nm}][(\omega_{0m}-\Omega)-i\gamma_{0m}]}$$

$$-\frac{\boldsymbol{\mu}_{mn}[\boldsymbol{\mu}_{n0}.\mathbf{E}(\omega)][\Xi_{0m}(\Omega)]}{[(\omega_{nm}-\Omega-\omega)-i\gamma_{nm}][(\omega_{n0}-\omega)-i\gamma_{n0}]} + \frac{\boldsymbol{\mu}_{m0}[\boldsymbol{\mu}_{0v}.\mathbf{E}(\omega)][\Xi_{vm}(\Omega)]}{[(\omega_{0m}-\Omega-\omega)-i\gamma_{0m}][(\omega_{0v}-\omega)-i\gamma_{0v}]}$$

The most resonant term is the fourth term

$$\langle \boldsymbol{\mu} \rangle_{\mathbf{RESONANT}} = \rho_0 \hbar^{-2} \sum_{vm} \sum_{\Omega,\omega} \exp[-i(\Omega+\omega)t] \times \frac{\boldsymbol{\mu}_{m0}\Xi_{vm}(\Omega)[\boldsymbol{\mu}_{0v}.\mathbf{E}(\omega)]}{[(\omega_{0m}-\Omega-\omega)-i\gamma_{0m}][(\omega_{0v}-\omega)-i\gamma_{0v}]}$$

which has the expected pole structure of the Raman tensor.