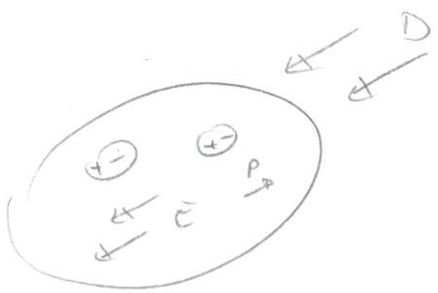
RAMAN ①

- BRIEFLY INTRODUCTION X-RAY, NEUTRON - SCATTERING TEM
- INFRARED AND RAMAN $q \Rightarrow 0$ OR VERY CLOSE TO 0
- INFRARED AND RAMAN VERY CHEAP
- DIFFERENCE NON-LINEAR VS PARAMETRIC

- CONSIDER A MEDIUM WITH DIELECTRIC SUSCEPTIBILITY χ

$\varepsilon = 1 + 4\pi\chi$



$P = \chi E$

- CONSIDER A PLANE-WAVE ELECTROMAGNETIC TRAVELLING IN THE MATERIAL

$$F(r, t) = F(k, \omega) \cdot \cos(k \cdot \vec{r} - \omega_1 t)$$

THIS WILL PRODUCE A POLARIZATION P

$$\vec{P}(r, \omega) = \hat{\chi}(k, \omega)\, \vec{F}(k, \omega) + \overbrace{\underbrace{\chi^2 F^2}_{\text{TWO-PHOTON RAMAN}} + \dots}^{\text{HYPER-RAMAN}}$$

IN GENERAL χ IS A TENSO (2)

$$\vec{P} = \begin{pmatrix} \chi_{11} & \chi_{12} & \chi_{13} \\ \chi_{21} & \cdots & \\ \chi_{31} & & \end{pmatrix} F \qquad (\text{Dopo})$$

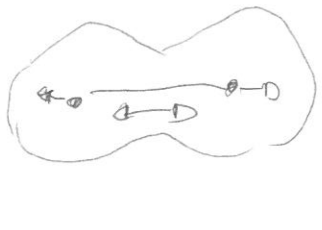
- FOR EACH SOLID WE CAN DEFINE THE PRINCIPES OPTICAL AXES

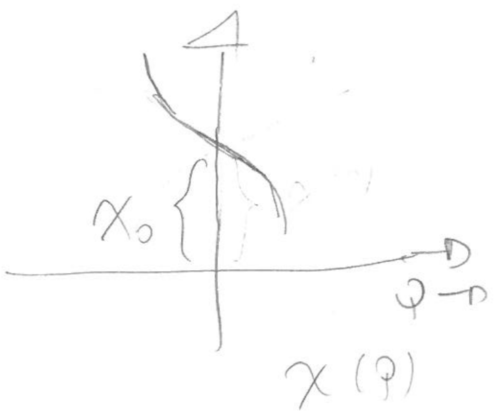
$$P' = \begin{pmatrix} \chi'_{xx} & 0 & 0 \\ 0 & \chi'_{yy} & 0 \\ 0 & 0 & \chi_{zz} \end{pmatrix} \begin{pmatrix} F'_x \\ F'_y \\ F'_z \end{pmatrix} \qquad \chi' = R^T \chi R$$

SIMPLE CASE CONSIDER ONE PHONON

$$\vec{\varphi}(R,t) = \vec{\varphi}(q,\omega_0) \cos(qR - \omega_0 t)$$

$$\chi_{ij}(\Omega) = \chi^{(0)}_{ij}(R_0) + \underbrace{[\partial\chi/\partial\varphi] \cdot \vec{\varphi}}_{\text{FIRST ORDER RAMAN}} + \underbrace{\tfrac{1}{2}[\partial^2\chi/\partial\varphi^2]\,\varphi^2}_{\text{SECOND ORDER RAMAN}}$$





$\chi(\varphi)$

$$\varphi = \sqrt{\mu}\,(u_2 - u_1)$$

3

$$\chi(k, \omega, \varphi) = \chi_0(k, \omega) + (\partial\chi/\partial\varphi)_0\, \varphi(r, t)$$

$$\Downarrow$$

$$P(r, t, \varphi) = P_0(r, t) + P_{IND}(r, t, \varphi)$$

$$\Downarrow$$

$$P_{IND}(r, t, \varphi) = (\partial\chi/\partial\varphi)_0\, \varphi(q, \omega_0) \cdot \cos(q r - \omega_0 t) \cdot F_i(k_i, \omega) \cdot \cos(k_i r - \omega_i t)$$

$$= \frac{1}{2}(\partial\chi/\partial\varphi)_0\, \varphi(q, \omega_0)\, F_i(k_i, \omega_i) \times \cos[(k+q) r - (\omega_1 + \omega_0) t] + \cos[(k_i - q) r - (\omega_1 - \omega_0) t]$$

STOKES $\rightarrow$ $K_S = K - q$ $\quad \omega_S = \omega_1 - \omega_0$

ANTI-STOKES $\rightarrow$ $K_{AS} = K + q$ $\quad \omega_{AS} = \omega_1 + \omega_0$

RAMAN FREQUENCY $= \omega_{S/AS} - \omega_1$

- <u>PARAMETRIC PROCESS</u> : PERIODICALLY CHANGES OF A PARAMETER OF THE MEDIUM

<u>FM-RADIO</u>

INCIDENT LIGHT = CARRIER WAVE

PHONONS = VOICE / SOUND

LIGHT	1-3 eV
PH	~ 60 meV
	15 THz
	1000 THz

SINCE WAVE-VECTOR OF LIGHT VERY SMALL RAMAN PROBES ONLY PHONONS $q \to 0$

$$q \sim 10^{6}\, cm^{-1} \simeq 1/100 \text{ BZ A SOLID}$$

b) SECOND ORDER RAMAN

$$q_1 + q_2 = 0$$

USE TO MEASURE PHONON DENSITY OF STATES

$\boxed{\text{LINE INTENSITY}}$

$$P(t) = \chi F_0 \cos(\omega_i t) + \frac{\partial \chi}{\partial \varphi} F_0 \left[\cos(\omega_i - \omega_0) + \cos(\omega_i + \omega$$

$\downarrow$ IRRADIATED LIGHT

$$I(t) \propto |\ddot{P}(t)|^2 = k_0^2 \cos^2(\omega_i t) + k_1^2 \cos^2(\omega_i - \omega_0 t)$$

$$+ k_2^2 \cos((\omega_i + \omega_0)t)^2$$

$\Rightarrow$ CROSS TERM CANCEL

$$\text{Power Spectrum}(\omega) = \lim_{\tau \to \infty} \frac{2}{\tau} \int_{-\tau/2}^{\tau/2} I(t)\, e^{-i\omega t}\, dt$$

$$PS(\omega) = k_0^2\, \delta(\omega - \omega_i) + k_1^2\, \delta(\omega - (\omega_i - \omega_0))$$

$$+ k_2^2\, \delta(\omega - (\omega_i + \omega_0))$$

$$\frac{I_{\text{STOKES}}}{I_{\text{ANTI-STOKES}}} = \frac{(\omega_i - \omega_0)^2}{(\omega_i + \omega_0)^2}$$ WRONG
WE NEED QM. 5

INTRODUCE χ TENSOR

$\chi^T = \chi$ SYMMETRIC TENSOR

$$\chi_{ij} = \chi_{ij}^{(0)} + \sum_{l=x,y,z} \delta\chi_{ij,l} \cdot \varphi_l + O(\varphi^2)$$

$$\chi_{ij,l} = \frac{\partial \chi_{ij}}{\partial \varphi_l}$$

$$\delta\chi_l = \begin{pmatrix} \delta\chi_{11,l} & \cdots & \\ \delta\chi_{21,l} & & \\ \cdots & & \delta\chi_{33,l} \end{pmatrix}$$

IN THE EQ FOR P

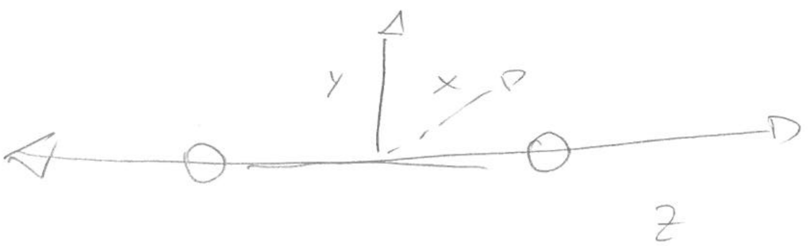
$$P_i = \chi_i E_{0_i} \cos(\omega_i t) + \sum_{l,i} \overbrace{\delta\chi_{ij,l}}^{\text{RAMAN TENSOR}} \varphi_l E_i$$

$$\cdot \left[\cos(\omega_l - \omega_0)t + \cos(\omega_l + \omega_0)t\right]$$

RAMAN AND SYMMETRIES

GENERAL RULE

- INFRARED ACTIVES MODES IF CHANGE DIPOLES !
- RAMAN ACTIVE MODES ONLY IF THEY CHANGE THE DIELECTRIC CONSTANT ! (AT LEAST ONE OF THE 6 COMPONENTS)



PRINCIPAL AXES X, Y, Z

$$\alpha = \begin{pmatrix} \alpha_{xx} & 0 & 0 \\ 0 & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{pmatrix}$$

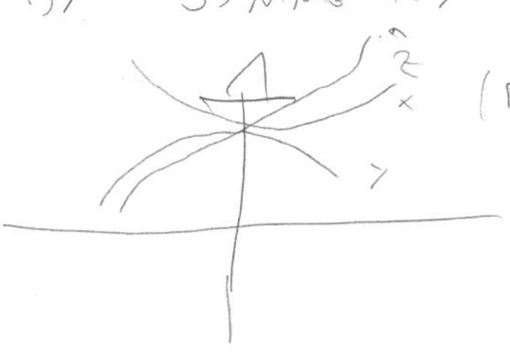
α IN PRINCIPLE

THE MODE $Q = \sqrt{\mu}\,(u_1 - u_2)$ DO NOT CHANGE SYMMETRY OF THE MOLECULE, WE WILL HAVE THE SAME ~~CRYST.~~ PRINCIPAL AXES

$$\alpha = \begin{pmatrix} \alpha_{xx} & 0 & 0 \\ 0 & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{pmatrix} \qquad \delta\alpha^{(1)} = \begin{pmatrix} \alpha_{xx,1} & 0 & 0 \\ 0 & \alpha_{xx2} & 0 \\ 0 & 0 & \alpha_{xx3} \end{pmatrix}$$

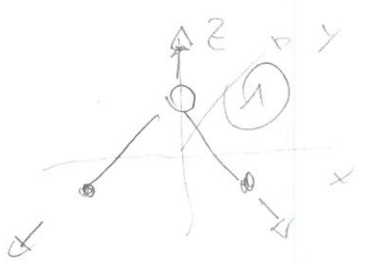
BY SYMMETRY $\longrightarrow \delta\alpha^{(1)} = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & c \end{pmatrix}$

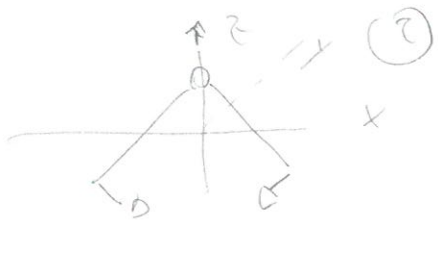
(FOR EXAMPLE II)

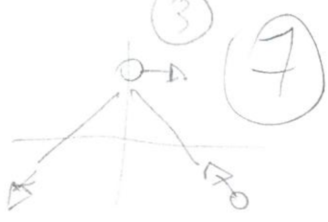


CHARGE DISTRIBUTION WILL BE DIFFERENT FOR OPPOSITE DISPLACEMENT !!

H_2O EXAMPLE $\boxed{\text{3 ACTIVE}}$





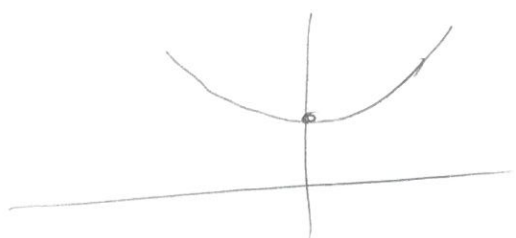


1 AND 2 DO NON CHANGE MOLECULE SYMMETRIES

$$\delta\alpha^{(s=1,2)} = \begin{pmatrix} \alpha_{xx,s} & 0 & 0 \\ 0 & \alpha_{yy,s} & 0 \\ 0 & 0 & \alpha_{zz,s} \end{pmatrix} = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}$$

MODE 3 WILL NO BE ACTIVE IS QUADRATIC !

$$\delta\alpha_{ii,3} = 0$$



BUT $x' \neq x$ $\quad z' \neq z$ $\quad y' = y$ $\quad$ SO OUT OF PLANE COMPONENTS $\alpha_{xz,3} \neq 0$

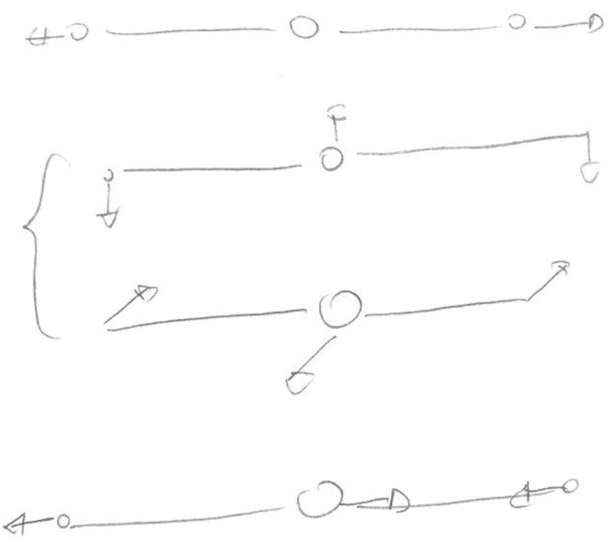
$$\delta\alpha^{(3)} = \begin{pmatrix} 0 & 0 & \alpha \\ 0 & 0 & 0 \\ \alpha & 0 & 0 \end{pmatrix}$$

ALL 3 MODES ARE ACTIVE

LINEAR MOLECULE

$\boxed{\text{1 ACTIVE}}$ 8

CO_2



Q_1 SYMM

Q_2 NOT

Q_3 SYMM

ALWAYS $x, y, z = x', y', z'$

$\alpha_{ij,s} = 0$ for $i \neq j$ $s = 1, 2, 3, 4$

Q_1 is RAMAN ACTIVE $\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & c \end{pmatrix}$

Q_2, Q_3 $\delta\alpha_{ii,s} = 0$ $\delta\alpha^{(2,3)} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$

Q_1 SYMMETRIC MODE g - MODE gerade

Q_2, Q_3 ANTI-SYMMETRIC MODE u - ungerade

IN GENERAL g ARE RAMAN ACTIVE

u MODE RAMAN INACTIVE

(OFTEN INFRARED ACTIVE)

MODE SYMMETRY

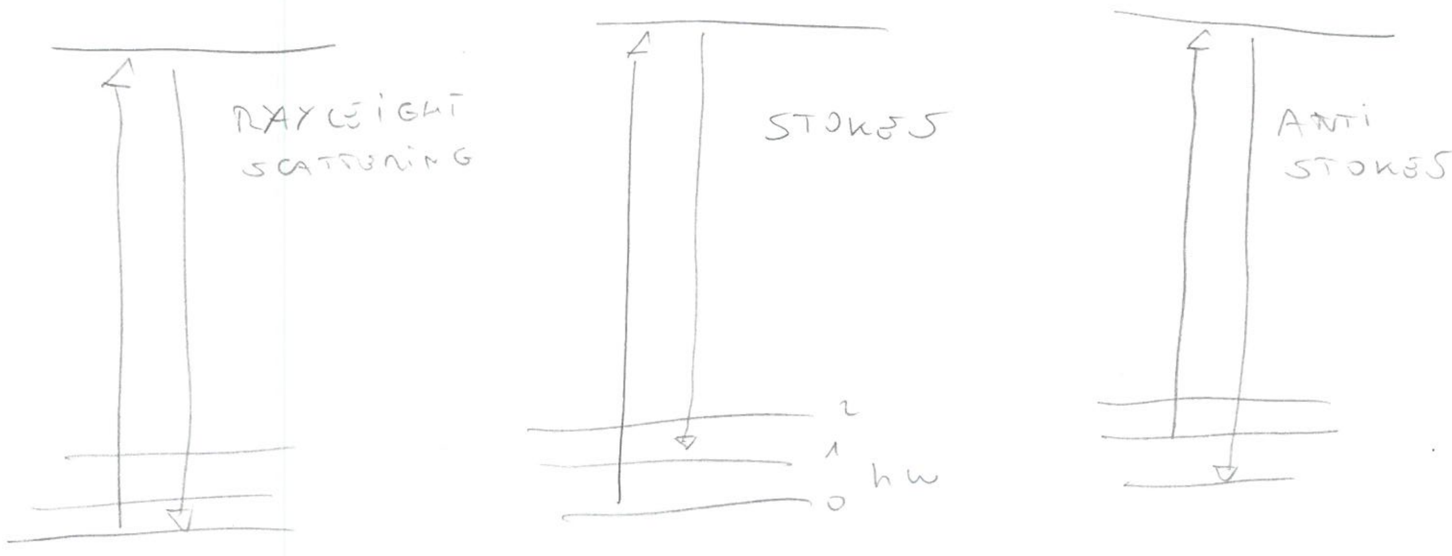
$$I(\varphi_1) = +\varphi_1 \quad g$$
$$I(\varphi_{2,3}) = -\varphi_2 \quad u$$

THIS CLASSIFICATION IS VALID ONLY IF THERE IS INVERSION SYMMETRY!

CRYSTAL

SEE SLIDES

QUANTUM THEORY



SINCE

$\omega_L \simeq \omega_S$

$k_L \simeq k_S$

$\to k_L = n(\omega_L)\dfrac{\omega_L}{c}$

IN REAL QM description of RAMAN (10)

PHOTON ⇝

VIRTUAL LEVEL

electronic + PHONON
(NOT REAL LEVEL)

↑
UNSTABLE

PHOTON →

→ RAMAN
LOW P

⇝ → RAYLEIGH
MUCH HIGHER
PROB

•) RESONANT RAMAN
RESONANCE WITH LEVELS REAL

•) RAMAN VS FLUORESCENCE
TIME SCALE
PHOTON REAL
ABSORBED

$$\left(\frac{\omega_L - \omega_S}{\omega_L + \omega_{SA}}\right)^4 e^{+\left(\frac{\hbar\omega_S}{kT}\right)} \gg 1$$

SHOW GRAPHENE