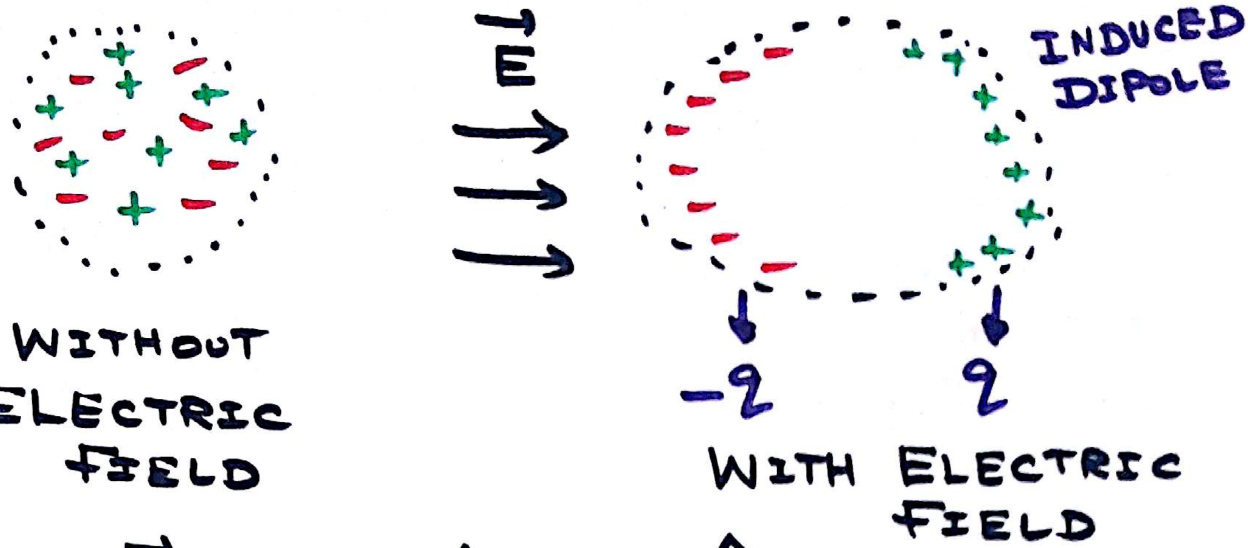
RAMAN SPECTROSCOPY

- POLARIZATION AND POLARIZABILITY



$$\vec{E} = E_x \hat{i} + E_y \hat{j} + E_z \hat{k}$$

INDUCED DIPOLE MOMENT:

$$\vec{\mu}_I = \bar{\bar{\alpha}} \vec{E}$$

↳ POLARIZABILITY

$$\mu_{I,x} = \alpha_{xx} E_x + \alpha_{xy} E_y + \alpha_{xz} E_z$$

$$\mu_{I,y} = \alpha_{yx} E_x + \alpha_{yy} E_y + \alpha_{yz} E_z$$

$$\mu_{I,z} = \alpha_{zx} E_x + \alpha_{zy} E_y + \alpha_{zz} E_z$$

$$\begin{pmatrix} \mu_{I,x} \\ \mu_{I,y} \\ \mu_{I,z} \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

IF $\vec{E}$ IS ALONG X-AXIS, $E_y = E_z = 0$

$$\Rightarrow \mu_{I,x} = \alpha_{xx} E_x \; ; \; \mu_{I,y} = \mu_{I,z} = 0$$

→ THINK ABOUT IT:

WHAT HAPPENS WHEN A HYDROGEN ATOM IN THE GROUND STATE IS PLACED IN AN UNIFORM EXTERNAL ELECTRIC FIELD? DOES IT POLARIZE? WHAT IS THE POLARIZABILITY OF THE HYDROGEN ATOM? DO YOU THINK THAT THE 1S ORBITAL OF THE HYDROGEN ATOM WILL BE SPHERICAL IN THE PRESENCE OF THE ELECTRIC FIELD?

- LIGHT $\Rightarrow$ OSCILLATING ELECTRIC FIELD

X-AXIS

$$E = E_0 \cos(\omega_0 t)$$ FREQUENCY OF THE INCIDENT LIGHT

$$E = E_0 \cos(2\pi \nu_0 t)$$

$$\mu_I = \alpha E = \alpha E_0 \cos(2\pi \nu_0 t)$$

- MOLECULES ARE NOT STATIC, BUT THEY ARE DYNAMIC

$$x = x_0 \cos(2\pi \nu_m t)$$

NORMAL MODE OR DISPLACEMENT FROM EQUILIBRIUM

FREQUENCY OF MOTION

$$\alpha(x) = \alpha(x_0) + \left.\frac{\partial \alpha}{\partial x}\right|_{x_0} x + \cdots$$

$$\alpha(x) = \alpha(x_0) + \left.\frac{\partial \alpha}{\partial x}\right|_{x_0} \left(x_0 \cos(2\pi \nu_m t)\right)$$

$$\Rightarrow \mu_I = \left[\alpha(x_0) + \left.\frac{\partial \alpha}{\partial x}\right|_{x_0} x_0 \cos(2\pi \nu_m t)\right] E_0 \cos(2\pi \nu_0 t)$$

$$= \alpha(x_0) E_0 \cos(2\pi \nu_0 t) + \left(\frac{\partial \alpha}{\partial x}\right)_{x_0} x_0 E_0 \cos(2\pi \nu_m t) \cos(2\pi \nu_0 t)$$

$$\cos A \cos B = \frac{1}{2}\left[\cos(A+B) + \cos(A-B)\right]$$

$$\mu_I = \alpha(x_0) E_0 \cos(2\pi\nu_0 t)$$ → ELASTIC (OR) RAYLEIGH SCATTERING

$$+ \left(\frac{\partial\alpha}{\partial x}\right)_{x_0} \frac{x_0 E_0}{2} \cos(2\pi(\nu_0 - \nu_m)t)$$

INELASTIC SCATTERING (OR) STOKES SCATTERING

$$+ \left(\frac{\partial\alpha}{\partial x}\right)_{x_0} \frac{x_0 E_0}{2} \cos(2\pi(\nu_0 + \nu_m)t)$$

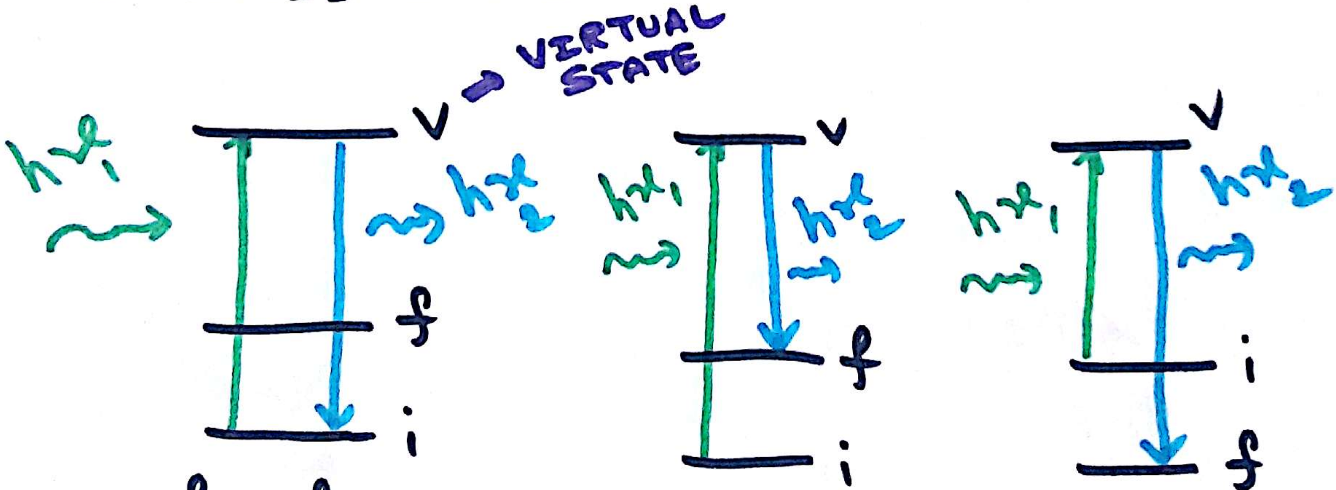
INELASTIC SCATTERING (OR) ANTI-STOKES

- CONDITION FOR RAMAN SCATTERING

$$\left(\frac{\partial\alpha}{\partial x}\right)_{x_0} \neq 0$$

- THE OSCILLATING DIPOLE HAS FREQUENCY COMPONENTS $\nu_0 \pm \nu_m$ AS WELL AS THE EXCITING FREQ. ν_0

- THREE-STATE MODEL :



$\nu_1 = \nu_1$ $\qquad$ $\nu_1 > \nu_2$ $\qquad$ $\nu_1 < \nu_2$

RAYLEIGH $\qquad$ STOKES $\qquad$ ANTI-STOKES

TRANSITION PROBABILITY $\propto \left| \langle f|\hat{\mu}|v\rangle \langle v|\hat{\mu}|i\rangle \right|^2$

ROTATIONAL RAMAN SPECTROSCOPY

→ SELECTION RULE $\Delta J = \pm 2$

- ROTATIONAL ENERGY OF A RIGID DIATOMIC MOLECULE

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \qquad J = 0, 1, 2, \ldots$$

J+2

$$E_J = B\,J(J+1)$$

J

$$\Delta E = E_{J+2} - E_J$$

$$= B(J+2)(J+3) - B\,J(J+1)$$

$$= B\left[\cancel{J^2} + 3J + 2J + 6 - \cancel{J^2} - J\right]$$

$$\boxed{\Delta E = 2B\left[2J+3\right]} \Rightarrow h\nu_m$$

$$\boxed{\nu_0 \pm \nu_m = \nu_0 \pm \frac{2B}{h}\left[2J+3\right]}$$

- SIMILAR APPROACH FOR VIBRATIONAL RAMAN SPECTROSCOPY

$$\Delta E = E_{V=1} - E_{V=0} = h\nu_m$$

WEAK OVERTONES CAN BE IGNORED

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