Raman Scattering

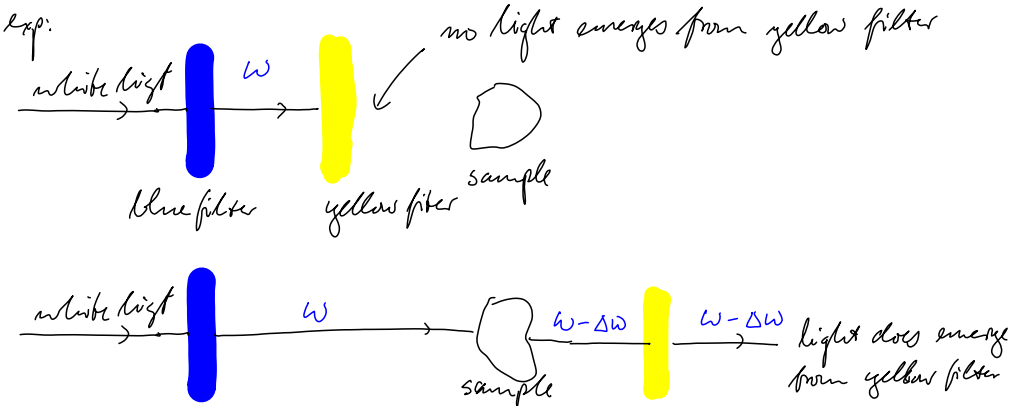
1.2.2010 R1

"Raman effect" = inelastic light scattering :

discovered 1928 by:

- Raman & Krishnan (Nobel prize for Raman: 1930)
- Landsberg & Mandelstam

Raman's exp:



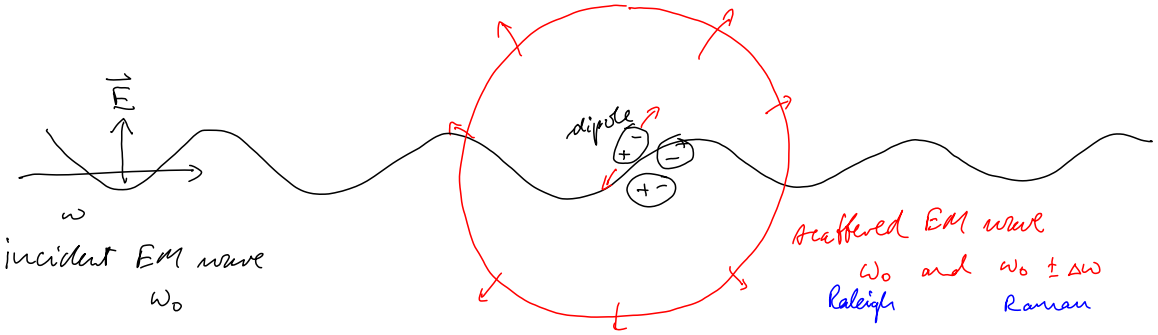
Classical picture

R2

for elastic scattering ("Rayleigh scattering"): light polarizes matter, creates oscillating dipoles, which reradiate at same frequency

$\omega_{out} = \omega_{in}$

for inelastic scattering ("Raman scattering"): same as above, but polarizability is modulated periodically due to internal vibrations of matter, producing frequency shift. $\omega_{out} = \omega_{in} \pm \Delta\omega$



R3

Induced dipole moment (say, of a molecule)

$p^a = \alpha^{ab} E^b$ ← polarizability

← sum over normal modes of molecule

$= \left(\alpha_0^{ab} + \sum_j \frac{\partial \alpha^{ab}}{\partial \vec{Q}_j} \cdot \vec{Q}_j(t) \right) E_0^b \cos \omega_0 t$

$\vec{Q}_j(t) = \Delta \vec{Q}_j^{(0)} \cos(\omega_j t + \Delta_j)$ ← phase shift; ← eigenfrequency of normal mode j

$\vec{d}(t) = \vec{d}_0 + \vec{Q}_j(t)$

$\cos A \cos B = \frac{1}{2}(\cos(A+B) + \cos(A-B))$

$= \left[\alpha_0^{ab} \cos \omega_0 t + \sum_j \frac{\partial \alpha^{ab}}{\partial \vec{Q}_j} \cdot \vec{Q}_j^{(0)} \left(\cos[(\omega_0 - \omega_j)t - \Delta_j] \right. \right.$ Stokes shift

$\left. \left. + \cos[(\omega_0 + \omega_j)t + \Delta_j] \right) E^b \right.$

↑ Rayleigh

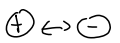
Anti-Stokes shift

Light is (re-) radiated at all frequencies of induced dipole moment: ω_0, $\omega_0 \pm \omega_j$ (ω_j runs over all normal modes ...)

R4

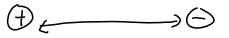
Why does polarizability depend on $\vec{Q}$?

consider three snapshots during normal mode vibration: $\vec{d}(t) = \vec{d}_0 + \vec{Q}_j(t)$

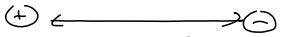


$\vec{d}_0 - \vec{Q}_j^0$

small polarizability since ⊕ and ⊖ are feel strong attraction



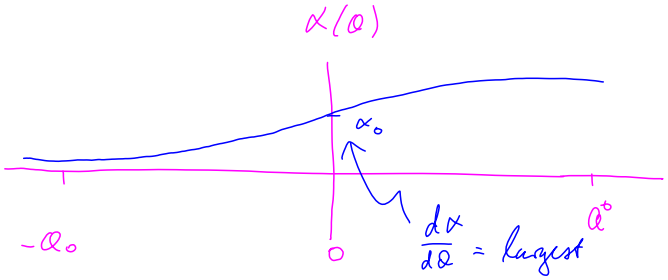
$\vec{d}_0$ = equilibrium spacing



$\vec{d}_0 + \vec{Q}_j^0$

large polarizability since ⊕ and ⊖ are feel weak attraction

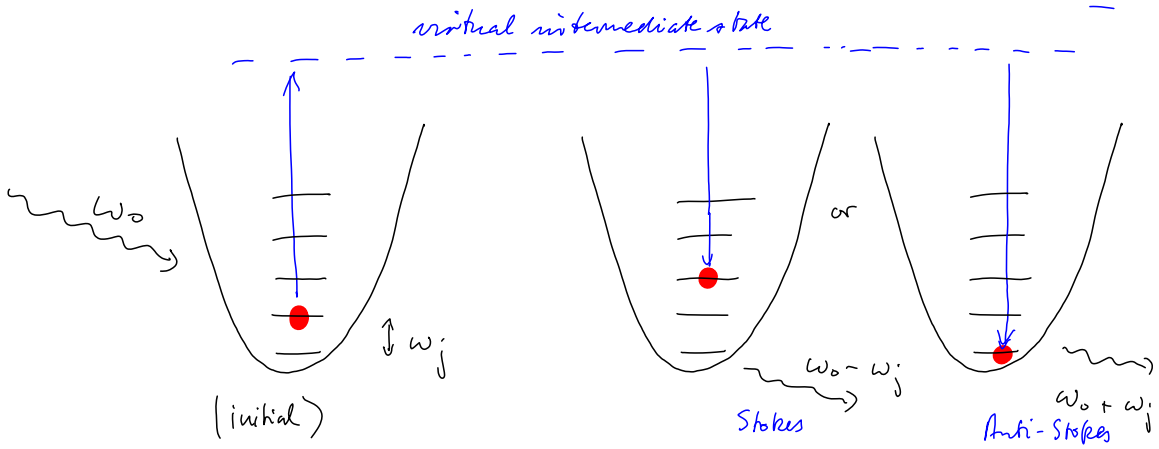
For example:



Simple QM picture:

R5

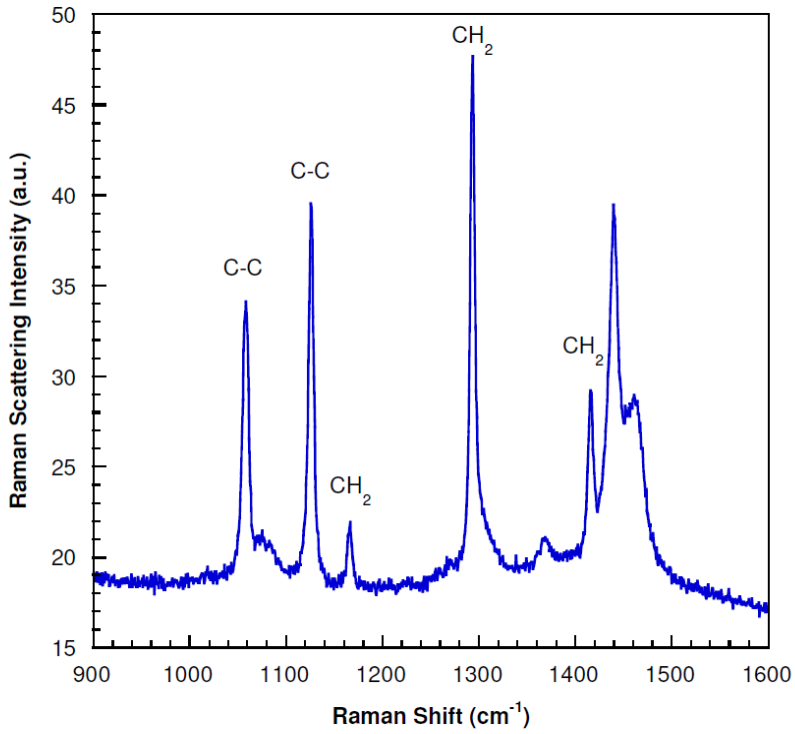
light initially excites a normal mode (= harmonic oscillator, ω_j) causing transition to a state different from initial state:



Probability for initial state $|n_j\rangle \sim e^{-n_j\omega_j/k_BT} \sim \frac{\text{intensity of Anti-Stokes}}{\text{intensity of Stokes}}$

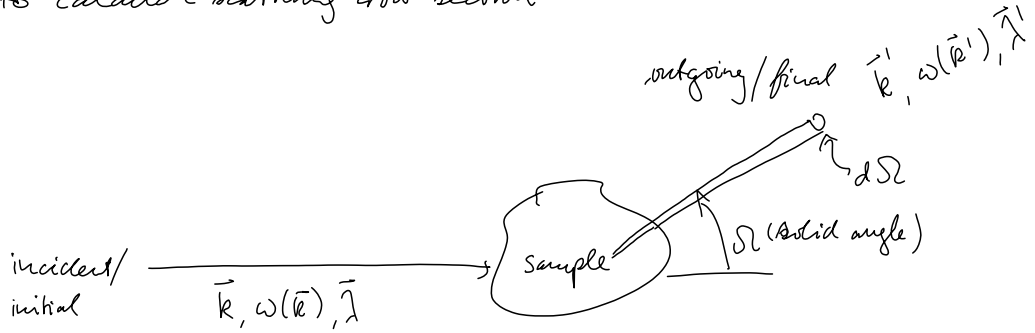
Example: Raman spectrum of Polyethylene

R6



For explicit QM treatment, we have to do perturbation theory in light-matter interaction, H_{int},

to calculate scattering cross section:



differential cross section: $\frac{\partial^2 \sigma}{\partial \Omega \, \partial \omega_f} = t_i \, r_0^2 \, \frac{\omega_f}{\omega_i} \, R$,

$r_0^2 = \frac{e^2}{mc^2}$ = "Thomson radius", R = transition rate.

transition rate R from golden rule:

$$R = \sum_f \sum \frac{e^{-\beta E_I}}{Z} |M_{f,I}|^2 \, \delta(E_f - E_i - t_i(\omega_i - \omega_f))$$

$\equiv \Delta\omega$

sum over all final states

average over initial states with Boltzmann distr.

We will find:

$M_{F,I} \equiv \langle F | M | I \rangle$ M: effective light-scattering operator

$= \langle F | H_{int} | I \rangle$ + terms in $\langle F | (H_{int})^2 | I \rangle$

we will find (later):

$H'_{int} \simeq -e \, \vec{R} \cdot \vec{E}(0,t)$, where $\vec{R} = \int d\vec{r} \; \vec{r} \, \rho(\vec{r})$ = dipole operator.

Raman scattering arises from $(H_{int})^2$. So, we need to learn how to do 2nd-order pert. theory with golden rule.

Reminder: golden rule :

(G. Baym, Lectures on QM, 1973)

[Notation in Schrödinger picture :
$|\psi(t)\rangle_S \equiv |\psi_t\rangle$, $\hat{O}_S(t) \equiv \hat{O}_t$]

$H = H_0 + V_t$ (here: V_t = light-matter interaction)

In interaction representation,

$|\psi_t\rangle = e^{-iH_0 t/\hbar} |\psi(t)\rangle$, $V(t) = e^{iH_0 t} V_t e^{-iH_0 t}$

then $-i\partial_t |\psi(t)\rangle = V(t) |\psi(t)\rangle$

Solution:

$$|\psi(t)\rangle = \mathcal{T}_t \, e^{-i \int_{t_0}^{t} dt' \, V(t')} |\psi(t_0)\rangle$$

$\mathcal{T}$ time-ordered product.

$$|\psi(t)\rangle = \underset{①}{|\psi(t_0)\rangle} - \frac{i}{\hbar} \int_{t_0}^{t} dt' \, \underset{①}{V(t')} |\psi(t_0)\rangle \equiv |\psi^{(1)}(t)\rangle$$

$$\left(-\frac{i}{\hbar}\right)^2 \underset{②}{\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''} \, V(t') \, V(t'') \, |\psi(t_0)\rangle \equiv |\psi^{(2)}(t)\rangle$$

(1)

Consider harmonic perturbation: "slowly turned on" from being 0 at $t_0 = -\infty$

$V_t = \hat{V} e^{\eta t} =: \hat{V} e^{\eta t}$ $(\eta = 0^+)$ (2)

transition amplitude from $|\psi(t_0)\rangle \equiv |i\rangle$ = |initial⟩ to $|f\rangle$ = |final⟩:

$$\langle f|\psi(t)\rangle \equiv \langle f|i\rangle + \langle f|i^{(1)}(t)\rangle + \langle f|i^{(2)}(t)\rangle \quad (3)$$

$$\equiv A_{fi}^{(0)} + A_{fi}^{(1)} + A_{fi}^{(2)} \quad (4)$$

$$A_{fi}^{(1)}(t) = \frac{-i}{\hbar}\int_{t_0}^{t} dt'\, e^{\eta t'} \underbrace{\langle f|\hat{V}(t)|i\rangle}_{e^{i(\varepsilon_f-\varepsilon_i)t'/\hbar}\underbrace{\langle f|\hat{V}|i\rangle}_{\equiv V_{fi}^{(1)}}} \xrightarrow[t_0\to-\infty]{} \frac{e^{\eta t}\, e^{i(\varepsilon_f-\varepsilon_i)t/\hbar}\, V_{fi}^{(1)}}{\varepsilon_i-\varepsilon_f+i\eta\hbar}$$

R11

transition probability:

$$P_{f\leftarrow i}^{(1)} = |A_{fi}^{(1)}(t)|^2 = e^{2\eta t}\,\frac{1}{(\varepsilon_f-\varepsilon_i)^2+(\eta\hbar)^2}\,|V_{fi}^{(1)}|^2$$

transition rate:

$$\Gamma_{f\leftarrow i} = \frac{d}{dt}P_{f\leftarrow i} = \frac{2\pi}{\hbar}|V_{fi}^{(1)}|^2\,\delta_\eta(\varepsilon_f-\varepsilon_i)$$

(usual) "golden rule"

where $\delta_\eta(E) = \dfrac{\eta\hbar}{E^2+(\hbar\eta)^2} \xrightarrow{\eta\to 0} \delta_{Dirac}(E)$

2nd-order transitions: (Raman is based on these...)

R12

insert $\mathbb{1} = |m\rangle\langle m|$

$$A_{fi}^{(2)} \overset{(10.1),(10.2)}{=} \langle f|i^{(2)}(t)\rangle = (-i/\hbar)^2\int_{t_0}^{t}dt'\int_{t_0}^{t'}dt''\,\underbrace{\langle f|V(t')V(t'')|i\rangle}$$

$$e^{\eta(t'+t'')}\sum_m e^{i(\varepsilon_f-\varepsilon_m)t'/\hbar}\underbrace{\langle f|\hat{V}|m\rangle}_{\equiv V_{fm}^{(1)}} e^{i(\varepsilon_m-\varepsilon_i)t''/\hbar}\underbrace{\langle m|\hat{V}|i\rangle}_{V_{mi}^{(1)}}$$

$$A_{fi}^{(2)} \overset{t_0\to-\infty}{=} \sum_m V_{fm}^{(1)}V_{mi}^{(1)}\left(\frac{-i}{\hbar}\right)\int_{t_0}^{t}dt'\,e^{i(\varepsilon_f-\varepsilon_m-i\eta\hbar)t'/\hbar}\underbrace{\left(\frac{-i}{\hbar}\right)\int_{t_0}^{t'}dt''\,e^{i(\varepsilon_m-\varepsilon_i-i\eta\hbar)t''/\hbar}}_{\frac{e^{i(\varepsilon_m-\varepsilon_i-i\eta\hbar)t'}}{\varepsilon_i-\varepsilon_m+i\eta\hbar}}$$

$$\frac{e^{i(\varepsilon_f-\varepsilon_i-2i\eta\hbar)t}}{(\varepsilon_i-\varepsilon_f+2i\eta\hbar)(\varepsilon_i-\varepsilon_m+i\eta\hbar)}$$

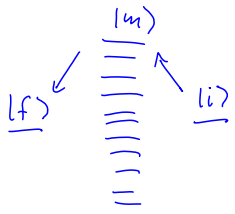
$$A_{fi}^{(2)} = \frac{e^{2\eta t}\; e^{+i(\varepsilon_f-\varepsilon_i)t/\hbar}}{(\varepsilon_i-\varepsilon_f+2i\eta\hbar)} \underbrace{\sum_m V_{fm}^{(1)} \frac{1}{\varepsilon_i-\varepsilon_m+i\eta\hbar} V_{mi}^{(1)}}_{\equiv V_{fi}^{(2)} = \text{"2nd-order matrix element"}}$$

If $A_{fi}^{(1)} = 0$, then

Transition prob: $P_{f\leftarrow i} = |A_{fi}^{(2)}|^2 = \frac{e^{4\eta t}}{(\varepsilon_i-\varepsilon_f)^2+(2\eta\hbar)^2} |V_{fi}^{(2)}|^2$

Transition rate for 2nd order transitions via all possible intermediate states:

$$\Gamma_{f\leftarrow i} = \frac{d}{dt} P_{f\leftarrow i} = \frac{2\pi}{\hbar} |V_{fi}^{(2)}|^2 \delta_{2\eta}(\varepsilon_i-\varepsilon_f)$$



intermediate states are called "virtual excitations".

If $V_{fi}^{(1)} \neq 0$, then use here $|V_{fi}^{(1)} + V_{fi}^{(2)}|^2$

Light-matter interaction of charged particles (charge e) in EM field:

$$H = \sum_i \frac{\left(\vec{p}_i - \frac{e}{c}\vec{A}(\vec{r}_i,t)\right)^2}{2m} + e\varphi(\vec{r}_i,t) + V(\vec{r}_i,t)$$

(minimal coupling; + other potentials)

$$= H_0 + H_{int} \qquad [\vec{r}_i, \vec{p}_j] = i\hbar\delta_{ij}$$

$$H_0 = \sum_i \frac{\vec{p}_i^{\,2}}{2m} + V(\vec{r}_i,t)$$

$$H_{int} = \sum_i -\frac{e}{2mc}\left(\vec{p}_i\cdot\vec{A}(\vec{r}_i,t) + \vec{A}(\hat{\vec{r}}_i,t)\cdot\vec{p}_i\right) + \frac{e^2}{2mc^2}A^2(\vec{r}_i,t) + e\varphi(\vec{r}_i,t)$$

write: $\sum_i e\varphi(\vec{r}_i,t) = \int d\vec{r}\;\varphi(\vec{r},t)\, e \sum_i \delta(\vec{r}-\vec{r}_i)$

$\equiv \hat{\rho}(\vec{r})$ = charge operator

similarly: $= -\frac{e}{c}\int d\vec{r}\;\vec{j}(\vec{r})\cdot\vec{A}$,

where $\vec{j}(\vec{r}) = \frac{1}{2}\sum_i\left(\frac{\vec{p}_i}{m}\delta(\vec{r}-\vec{r}_i) + \delta(\vec{r}-\vec{r}_i)\frac{\vec{p}_i}{m}\right)$

In this notation, we have

$$H_{int} = \int d^3r \left[-\frac{e}{c} \vec{j}(\vec{r}) \cdot \vec{A}(\vec{r},t) + \frac{e^2}{2mc^2} \rho(\vec{r}) A^2(\vec{r},t) + e\rho(\vec{r}) \varphi(\vec{r},t) \right]$$

Consider Raman scattering off localized charges (e.g. in molecules), localized around $\vec{r}_0 = 0$ (i.e. integrals have weight only for $\vec{r}$ near 0).

For later convenience, make gauge transformation, using gauge function: $\chi(\vec{r},t) = -\vec{r} \cdot \vec{A}(\vec{r},t)$

New gauge fields: $a,b \in \{x,y,z\}$

$$\Rightarrow \quad A'^a(\vec{r},t) = A^a + \nabla^a \chi = A^a - \nabla^a (r^b A^b) = -r^b \nabla^a A^b$$

(cancel)

$$\varphi'(\vec{r},t) = -\frac{1}{c} \partial_t \chi = \frac{1}{c} \vec{r} \cdot \frac{\partial \vec{A}}{\partial t} = -\vec{r} \cdot \vec{E}(\vec{r},t)$$

In new gauge, H_{int} becomes:

$$H'_{int} = \int d\vec{r} \left[-\frac{e}{c} j^a(\vec{r}) r^b \nabla^a A^b(\vec{r},t) \right] \quad (1) \quad \frac{j}{c} \sim \frac{v}{c} \ll 1$$

$$- \int d\vec{r} \; e \, \vec{r} \cdot \vec{E}(\vec{r},t) \rho(\vec{r}) \quad (2)$$

$$+ \frac{e^2}{2mc^2} \int d\vec{r} \; \rho(\vec{r}) \left[r^b \nabla^a A^b(\vec{r},t) \right]^2 \quad (3) \quad (\vec{\nabla} A)^2 \sim E^2$$

$(1) \sim \frac{v}{c} \sim \frac{v}{c} \ll 1$

in 2nd order, $(2)^2 \gg (3)$, due to $\frac{1}{mc^2}$ in (3).

For long wavelengths, ($\lambda \gg$ size of molecule) replace $\vec{E}(\vec{r},t) \to \vec{E}(0,t)$:

So: $H'_{int} \simeq -e \vec{R} \cdot \vec{E}(0,t)$, where $\vec{R} = \int d\vec{r} \; \vec{r} \rho(\vec{r})$ = dipole operator.