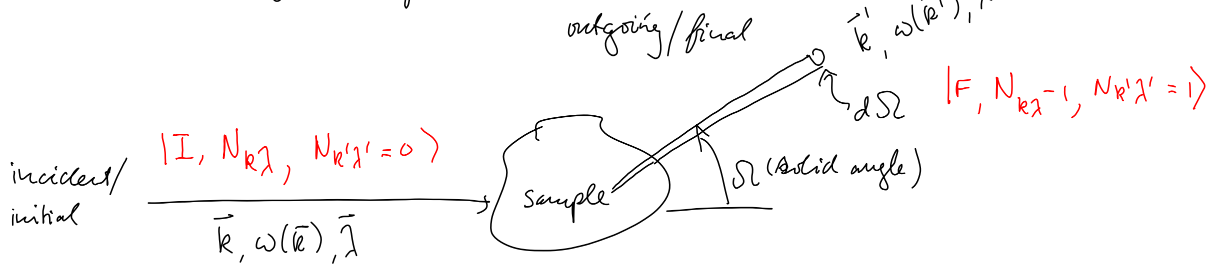
Raman scattering of light:

R17



Describe light field via vector potential : $\vec{E} = -\frac{1}{c}\frac{\partial \vec{A}}{\partial t}$, $\vec{H} = \vec{\nabla} \times \vec{A}$, (1)

$$\vec{A}(\vec{r},t) = \sum_{\vec{k},\vec{\lambda}} \left[A_{\vec{k},\vec{\lambda}}\, \vec{\lambda}\, \frac{e^{i\vec{k}\cdot\vec{r} - i\omega t}}{\sqrt{V\alpha}} + A^{*}_{\vec{k},\vec{\lambda}}\, \vec{\lambda}^{*}\, \frac{e^{-i\vec{k}\cdot\vec{r} + i\omega t}}{\sqrt{V\alpha}} \right] \quad (2)$$

wave vector   polarization vector

$$\omega_{\vec{k}} = c\,|\vec{k}|$$

$$E^{\text{radiation}} = \int d^3r \,\frac{1}{8\pi}\left[\vec{E}^2(\vec{r},t) + \vec{H}^2(\vec{r},t)\right] = \sum_{\vec{k},\vec{\lambda}} \frac{\omega_{\vec{k}}^2}{2\pi c^2}\, |A_{\vec{k},\vec{\lambda}}|^2 \quad (3)$$

Quantization of EM field :

R18

To scatter discrete amount of energy, one photon, $(\vec{k},\vec{\lambda},\omega) \to (\vec{k}',\vec{\lambda}',\omega')$ we will need quantized description of EM-field : treat amplitudes of $\vec{A}$-field as bosonic operators :

$$A_{\vec{k},\vec{\lambda}} \xrightarrow{\text{quantize}} \hat{A}_{\vec{k},\vec{\lambda}} \equiv n_{\vec{k}}\, \hat{a}_{\vec{k},\vec{\lambda}} \qquad A^{*}_{\vec{k},\vec{\lambda}} \xrightarrow{\text{quantize}} \hat{A}^{\dagger}_{\vec{k},\vec{\lambda}} \equiv n_{\vec{k}}\, \hat{a}^{\dagger}_{\vec{k},\vec{\lambda}} \quad (1)$$

with
$$\left[\hat{a}_{\vec{k},\vec{\lambda}}, \hat{a}^{\dagger}_{\vec{k}',\vec{\lambda}'}\right] = \delta_{\vec{k}\vec{k}'}\,\delta_{\vec{\lambda}\vec{\lambda}'} \quad (2)$$

Choose normalization $n_{\vec{k}}$ such that $E^{\text{radiation}} \longrightarrow \hat{H}^{\text{rad}} \equiv$ harmonic oscillators (3)

$$E^{\text{radiation}} \xrightarrow{\text{quantize}} \sum_{\vec{k},\lambda} \frac{\omega^2}{2\pi c^2}\, \hat{A}^{\dagger}_{\vec{k}\lambda} \hat{A}_{\vec{k},\lambda} = \sum_{\vec{k},\vec{\lambda}} \underbrace{\frac{\omega_{\vec{k}}^2}{2\pi c^2}\, n_{\vec{k}}^2}_{\equiv \hbar\omega_{\vec{k}} \text{ (by choice)}}\, \hat{a}^{\dagger}_{\vec{k},\vec{\lambda}}\, \hat{a}_{\vec{k},\vec{\lambda}} \equiv \hat{H}_0^{\text{rad}} \quad (4)$$

This fixes : $n_{\vec{k}} = \left[\frac{2\pi c^2 \hbar}{\omega_{\vec{k}}}\right]^{1/2}$ (5)

Choice (18.3) ensures that quantum time evolution, in interaction picture, R19

$$\text{gives}\quad \hat{a}_{\vec{k},\vec{\lambda}}(t) = e^{i\hat{H}_0^{rad}t/\hbar}\,\hat{a}_{\vec{k},\vec{\lambda}}\,e^{-i\hat{H}_0^{rad}t/\hbar} = e^{-i\omega_k t}\,\hat{a}_{\vec{k},\vec{\lambda}} \qquad (1)$$

$$\text{similarly}\quad \hat{a}^{\dagger}_{\vec{k},\vec{\lambda}}(t) = \quad '' \quad \hat{a}^{\dagger}_{\vec{k},\vec{\lambda}} \quad '' \quad = e^{+i\omega_k t}\,\hat{a}^{\dagger}_{\vec{k},\vec{\lambda}}\,, \qquad (2)$$

and therefore that the time evolution of

$$\hat{\vec{A}}(\vec{r},t) = e^{i\hat{H}_0^{rad}t/\hbar}\,\hat{\vec{A}}(\vec{r},0)\,e^{-i\hat{H}_0^{rad}t/\hbar}\,, \qquad (3)$$

produces the same phase factors $e^{\mp i\omega t}$, as in (17.2):

$$\boxed{\hat{\vec{A}}(\vec{r},t) = \sum_{\vec{k},\vec{\lambda}} \frac{n_k}{\sqrt{Vol}}\left[\hat{a}_{\vec{k},\vec{\lambda}}\,\vec{\lambda}\,e^{i\vec{k}\cdot\vec{r}-i\omega t} + \hat{a}^{\dagger}_{\vec{k},\vec{\lambda}}\,\vec{\lambda}^{*}\,e^{-i\vec{k}\cdot\vec{r}+i\omega t}\right] \qquad (4)}$$

So: R20

$$\hat{a}^{\dagger}_{\vec{k},\vec{\lambda}}\,|N\rangle_{\vec{k}\vec{\lambda}} = \sqrt{N+1}\,|N+1\rangle_{\vec{k}\vec{\lambda}} \qquad (1)$$

$$\hat{a}_{\vec{k},\vec{\lambda}}\,|N\rangle_{\vec{k}\vec{\lambda}} = \sqrt{N}\,|N-1\rangle_{\vec{k}\vec{\lambda}} \qquad (2)$$

raising and lowering operators for # photons with $\begin{cases}\text{momentum } \vec{k}, \\ \text{wave vector } \vec{\lambda}.\end{cases}$

Now, apply golden rule

$$\Gamma_{f\leftarrow i} = \frac{2\pi}{\hbar}\left|V_{fi}^{(1)} + \overbrace{\sum_m V_{fm}^{(1)}\frac{1}{\varepsilon_i-\varepsilon_m+i\eta\hbar}V_{mi}^{(1)}}^{V_{fi}^{(2)}}\right|^2\delta(\varepsilon_f-\varepsilon_i) \qquad (3)$$

to: $$H_0 = \overset{(14.3)}{H_0^{molecule}} + \overset{(17.2)}{H_0^{photons}} \qquad (4)$$

$$H'_{int} \overset{(16.5)}{\simeq} -e\,\vec{R}\cdot\vec{E}(0,t)\,, \qquad \text{where } \vec{R} = \int d\vec{r}\;\vec{r}\,\rho(\vec{r}) \qquad (5)$$

$$\vec{E}(0,t) = -\frac{1}{c}\frac{\partial\vec{A}(\vec{0},t)}{\partial t} = \sum_{\vec{k},\vec{\lambda}}\left[\hat{a}_{\vec{k},\vec{\lambda}}\,\vec{\lambda}\left(\frac{i\omega}{c}\right)\frac{e^{-i\omega t}}{\sqrt{Vol}} + \hat{a}^{\dagger}_{\vec{k},\vec{\lambda}}\,\vec{\lambda}^{*}\left(-\frac{i\omega}{c}\right)\frac{e^{i\omega t}}{\sqrt{Vol}}\right] \qquad (6)$$

R21

Eigenstates : $H_0|m\rangle = \varepsilon_m|m\rangle$

eigenstates of H_0 molecule — H_0 photons — molecule, $\vec k\vec\lambda$, $\vec k'\vec\lambda'$

$$|i\rangle = |I\rangle \otimes |N\rangle_{\vec k\vec\lambda} \otimes |0\rangle_{\vec k'\vec\lambda'} \equiv |I, N, 0\rangle$$

$$|f\rangle = |F\rangle \otimes |N-1\rangle_{\vec k\vec\lambda} \otimes |1\rangle_{\vec k'\vec\lambda'} \equiv |F, N-1, 1\rangle$$

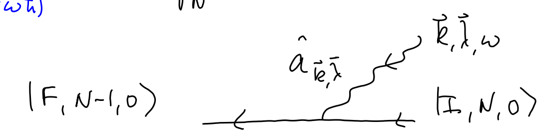
$|i\rangle$ and $|f\rangle$ differ by $\hat a^\dagger_{\vec k'\vec\lambda'}\hat a_{\vec k\vec\lambda}$ (two-photon operators involved!)

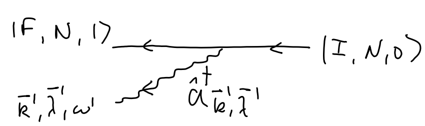
Hence, 1-st order matrix elements $V^{(1)}_{fi}$ vanish for Raman scattering

[they do contribute for absorptive scattering]

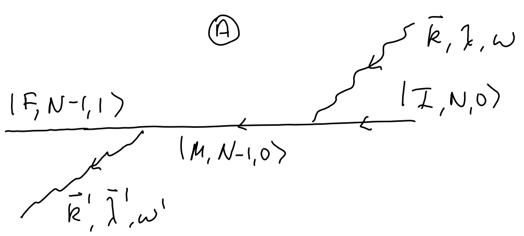
$$V^{(1)}_{fi} = \langle f|(-e)\vec R\cdot\vec E(0,t)|i\rangle = -e\langle F|\vec R|I\rangle \times$$

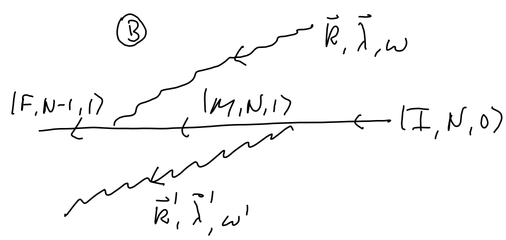
$$\frac{1}{\sqrt{Vol}}\Big[i\underbrace{\left(\frac{\omega n_{\vec k}}{c}\right)}_{(2\pi\omega\hbar)^{1/2}}\vec\lambda\,\underbrace{\langle N-1|\hat a_{\vec k\vec\lambda}|N\rangle}_{\sqrt N}\underbrace{\langle 1|0\rangle}_{=0} - i\underbrace{\left(\frac{\omega' n_{\vec k'}}{c}\right)}_{(2\pi\omega'\hbar)^{1/2}}\vec\lambda'^*\underbrace{\langle N-1|N\rangle}_{=0}\underbrace{\langle 1|\hat a^\dagger_{\vec k'\vec\lambda'}|0\rangle}_{=1}\Big]$$





R22





$$V^{(2)}_{fi} = \sum_m V^{(1)}_{fm}\frac{1}{\varepsilon_i - \varepsilon_m + i\eta\hbar}V^{(1)}_{mi}$$

$$\varepsilon_i = \varepsilon_I + \hbar(N\omega) \qquad (1)$$

$$\varepsilon_f = \varepsilon_F + \hbar[(N-1)\omega + \omega']$$

$$\varepsilon_m = \varepsilon_M + \begin{cases}\hbar(N-1)\omega & (A)\\ \hbar(N\omega+\omega') & (B)\end{cases}$$

$$= e^2\frac{\sqrt N}{Vol}2\pi\hbar\sqrt{\omega\omega'}\sum_M\Big[\overset{(A)}{\frac{\langle F|\vec R\cdot\vec\lambda'^*|M\rangle\langle M|\vec R\cdot\vec\lambda|I\rangle}{\varepsilon_I - \varepsilon_M + \hbar\omega + i\eta\hbar}} + \overset{(B)}{\frac{\langle F|\vec R\cdot\vec\lambda|M\rangle\langle M|\vec R\cdot\vec\lambda'^*|I\rangle}{\varepsilon_I - \varepsilon_M - \hbar\omega' + i\eta\hbar}}\Big] \qquad (2)$$

Energy-conserving δ-function ensures $\varepsilon_i = \varepsilon_f$

$\Rightarrow$ energy loss by photon $= \omega - \omega' = \varepsilon_F - \varepsilon_I =$ energy gained by molecule

Comments:

If molecular states have definite parity, then

$\langle M | \vec{R} | I \rangle \neq 0$ only if $|M\rangle$ and $|I\rangle$ have opposite parity.

$\langle F | \vec{R} | M \rangle \neq 0$ " " $|M\rangle$ and $|F\rangle$ " " "

$\Longrightarrow$ $|F\rangle$ and $|I\rangle$ must have same parity.

For molecules, Raman scattering can be used to analyze the symmetries of vibrational states (from analyzing which transitions contribute to the Raman spectrum).