Chapter 6 Stimulated Light Scattering

6.1 Diagrammatic Density Matrix Analytical Method

To simplify the mathematical treatment of the third-order nonlinear optical processes, we will introduce a diagrammatic technique, which can

- clearly display the microscopic NLO processes,
- easily highlight the most important process amongst a host of others

The double-sided Feynman diagrammatic technique was developed to depict the overall effect of interaction sequences between external perturbations and an ensemble of molecules (or quantum objects in general).

To start with our presentation, let us consider a quantum system, which is influenced with various external perturbations. The dynamical evolution of the system can be described by the general time-dependent Hamiltonian $\boldsymbol{H}(t)$ via the dynamical equation

$$\frac{\partial \rho(t)}{\partial t} = \frac{1}{i\hbar}[H(t), \rho(t)] .$$

By using a formal integration technique, we can transform the differential equation into an integral equation $\rho(t) = \rho(0) + \frac{1}{i\hbar}\int_0^t [H(t'), \rho(t')]\, dt'$. Then, we can exploit an iteration procedure to solve the integral equation with an initial thermal equilibrium density matrix $\rho^{(0)} = \rho(t=0)$ of a ground state $|g>$

$$\rho(t) = \sum_{n=0}^{\infty} \rho^{(n)}(t) \quad \text{with}$$

$$\rho^{(1)}(t) = \frac{1}{(i\hbar)}\int_0^t [H(t_1), \rho(0)]\, dt_1$$

$$\rho^{(2)}(t) = \frac{1}{(i\hbar)^2}\int_0^t dt_2 \int_0^{t_2} dt_1 [H(t_2),[H(t_1), \rho(0)]] \quad ,\ldots.$$

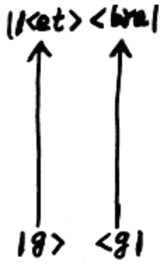
The solutions with successive perturbations can be represented in terms of double-sided Feynman diagrams, which can be done by noticing that

$$\begin{aligned}\rho^{(1)}(t) \propto [H(t_1), \rho(0)] &= H(t_1)\rho^{(0)} - \rho^{(0)} H(t_1) \\ &= H(t_1)|g><g| - |g><g| H(t_1)\end{aligned}$$

The first term depicts an interaction vertex on the left, and the second an interaction vertex on the right.

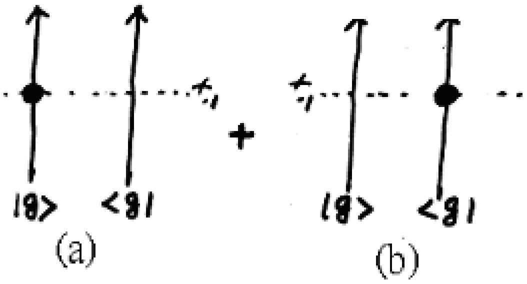
Based on the result, we can identify

(1) $\rho^{(0)}$: the initial state with zero-order iteration



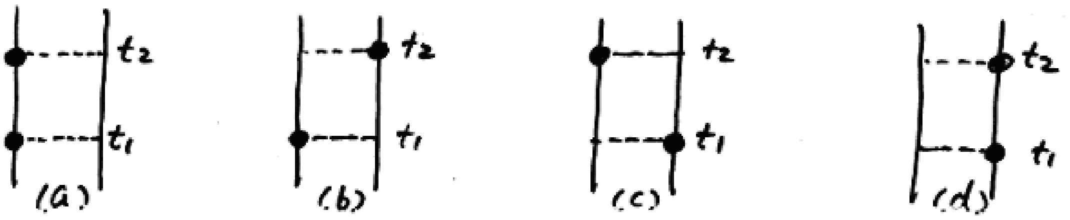
$$\Leftrightarrow \quad \rho^{(0)} = \underset{\text{ket}}{|g\rangle}\underset{\text{bra}}{\langle g|}\, e^{-\beta E_g}$$

(2) $\rho^{(1)}$: the first iteration result:



(a) (b)

(3) $\rho^{(2)}$: the second-order iteration result:



$$\rho^{(2)}(t) \propto [H(t_2),[H(t_1)\rho(0)]] = H(t_2)H(t_1)\rho^{(0)} - H(t_2)\rho^{(0)}H(t_1)$$
$$- H(t_1)\rho^{(0)}H(t_2) + \rho^{(0)}H(t_1)H(t_2)$$

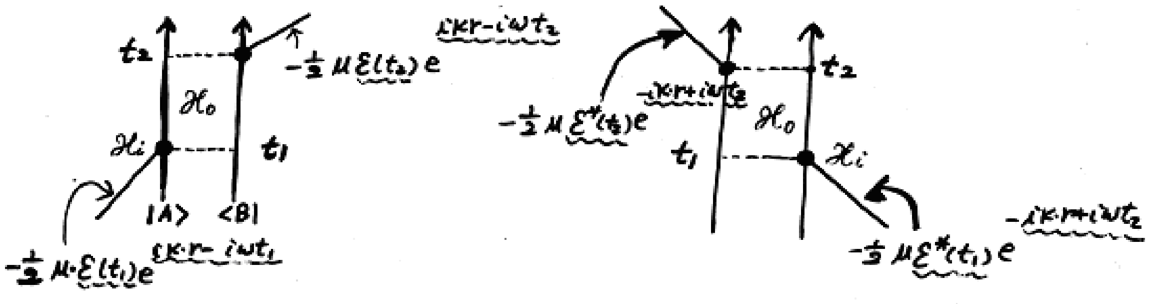
It is straightforward to note that the N*th*-order iteration yields a total of $\mathbf{2^n}$ distinct diagrams with each

- interaction vertex on the ket side $\Rightarrow$ $\boldsymbol{H(t)/(i\hbar)}$
- interaction vertex on the bra side $\Rightarrow$ $\boldsymbol{H(t)/(-i\hbar)}$.

We approximate the interaction Hamiltonian $H_i(t)$ of a light-matter interaction to be dipolar,

$$H_i(t) = \text{electron-photon} = -\mu\cdot\mathrm{Re}[E(t)] = -\frac{1}{2}\mu\cdot[E(t)+E^{+}(t)], \text{ indicating}$$

- only one single line to be attached to a single interaction vertex.



positive slope

negative slope

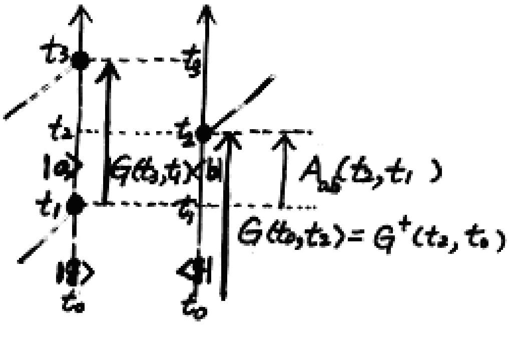
- From $\frac{\partial \rho(t)}{\partial t}=\frac{1}{i\hbar}[H(t),\rho(t)]$ with $\boldsymbol{H}(t)=\boldsymbol{H}_0+\boldsymbol{H}_i(t)$, the evolution stemming from $\boldsymbol{H}_0$ can be described with

$$\Rightarrow \quad \boldsymbol{\rho(t)=G(t,t_1)\rho(t_1)G(t_1,t)=G^{+}(t_1,t)\rho(t_1)G(t_1,t)}.$$

Here $\boldsymbol{G}(t_1, t_2)$ is the Green's function for the Schrodinger equation

$$G^{+}(t_2,t_1)=G(t_1,t_2)=\sum_i \left|i><i\right|e^{-i\frac{E_i}{\hbar}(t_2-t_1)};\quad t_1<t_2 \quad \text{if } \boldsymbol{H}_0 \text{ is independent of } t.$$

We introduce some useful notations for an expanded space formed by a direct product of ket vectors and bra vectors:



$|ab\rangle\rangle=|a><b|$

$\langle\langle ab|=|b><a|=|ket><bra|$

$\langle\langle ab|\hat{A}(t_1,t_2)|ab\rangle\rangle=|b><a|\hat{A}(t_1,t_2)|a><b|$

We can define a free propagator $\hat{A}(t_1,t_2)$ of the density matrix element to depict the field-free evolution between two neighboring interaction vertices, which can be expressed as

$$\boldsymbol{\langle \hat{A}_{ab}(t_1,t_2)\rangle\rangle=\langle\langle ab|\hat{A}(t_1,t_2)|ab\rangle\rangle=\langle a|G(t_2-t_1)|a\rangle\langle b|G^{+}(t_2-t_1)|b\rangle}$$

Note: $\boldsymbol{G(t_2-t_1)=\exp(\frac{1}{i\hbar}\int_{t_1}^{t_2}H_0\,dt')}$, and since $\boldsymbol{H}_0$ does not depend on t explicitly, the free propagator of $|\boldsymbol{ab}\rangle\rangle$ becomes

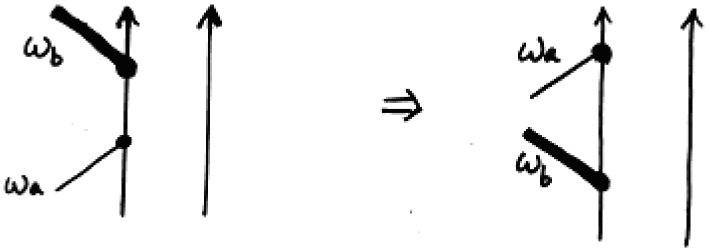
$$\boldsymbol{\mathrm{A}_{ab}(t_1,t_2)=\left\langle\hat{\mathrm{A}}_{ab}(t_1,t_2)\right\rangle=e^{-i(\Omega_{ab}-i\gamma_{ab})(t_2-t_1)}=e^{-i\Omega_{ab}(t_2-t_1)-\gamma_{ab}(t_2-t_1)}}.$$

We can obtain the complete solution $\rho(t)$ by integrating the product of propagation and interaction factors and **taking care of the time ordering**. The most important physical observable $P(t)$ of NLO can be calculated with

$$P(t) = Optical\ Polarization = N\ Tr[\mu\ \rho(t)].$$

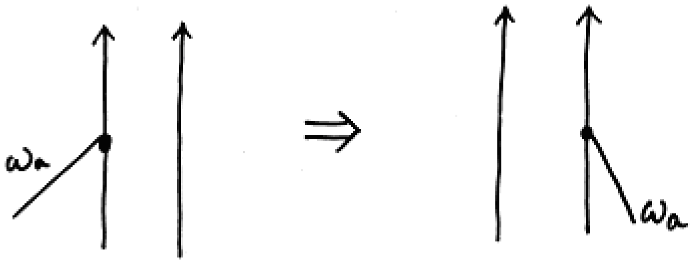
When one diagram is found to be important, four kinds of permutation can be invoked to generate other diagrams:

- **Time-ordering permutations of the vertices**



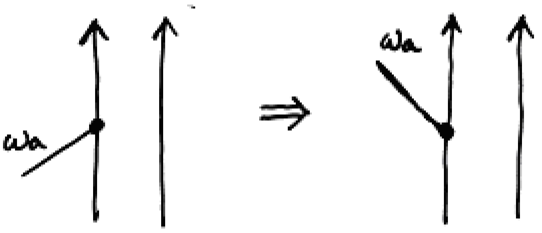
Although the initial and final states of the two diagrams remain the same, the time-permutated diagram may have **different probability of occurrence and resonance conditions** (*i.e.*, different energy denomination).

- **Bra-ket permutations**



This operation leads to completely different physical diagram and phase-matching condition.

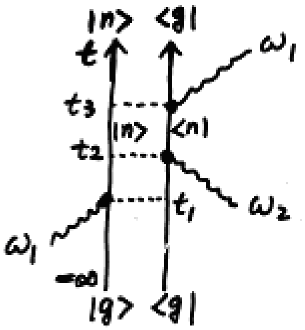
- **Absorption-Emission Permutation**



Similarly, this operation results in physically **different process** and different **phase-matching condition**.

- **Initial state permutation** ~ which may be not important when there is only one ground state to be populated, *i.e.*, $\rho_{gg}^{(0)}=1$.

For a case study, let us consider the following double-sided Feynman diagram with pulsed optical fields:



at vertex

$$\frac{\mathcal{H}_I(t_i)}{(\pm i\hbar)}=\frac{1}{(\pm i\hbar)}\left\{-\frac{1}{2}\mu\cdot\left[Ee^{-i\omega t}+E^{+}e^{+i\omega t}\right]\right\}$$

and $t_1 < t_2 < t_3 < t$

The corresponding third-order density matrix element becomes

$$\rho_{ng}^{(3)}(t)=\frac{-i}{(2\hbar)^3}\int_{-\infty}^{t}dt_3 e^{-i(\omega_{ng}-i\gamma_{ng})(t-t_3)}\ \mu_{ng}\cdot E_1(t_3)e^{-i\omega_1 t_3}$$

$$\int_{-\infty}^{t_3}dt_2 e^{-(t_3-t_2)/T_1}\ \mu_{gn}\cdot E_2^*(t_2)e^{i\omega_2 t_2}\int_{-\infty}^{t_2}dt_1\ e^{-i(\omega_{ng}-i\gamma_{ng})(t_2-t_1)}\ \mu_{ng}\cdot E_1(t_1)e^{i\omega_1 t_1}\rho_{gg}^{(0)}$$

When the optical fields are CW with

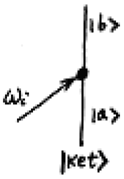
$$E(t)=E_0e^{-i\omega t}$$
$$E^{+}(t)=E_0^{*}e^{i\omega t},$$

then the density matrix element shown above can be rewritten to yield the steady-state form. From the example, we can also draw some general rules for the derivation of steady-state expression for any given diagram:

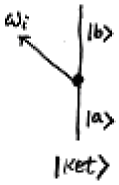
1. The system starts with $|\boldsymbol{g}\rangle\boldsymbol{\rho}_{gg}^{(0)}\langle\boldsymbol{g}|$

2. Ket propagation => multiplication factor on the left
Bra propagation => multiplication factor on the right

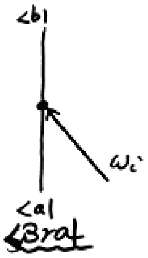
3



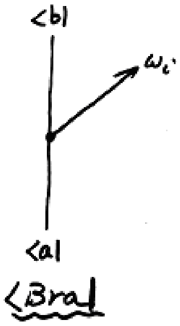
$$\Rightarrow \left(\frac{1}{i\hbar}\right)\langle b|H_{\text{int}}(\omega_i)|a\rangle$$ **Absorption**



$$\Rightarrow \left(\frac{1}{i\hbar}\right)\langle b|H^{+}_{\text{int}}(\omega_i)|a\rangle$$ **Emission**



$$\Rightarrow \left(-\frac{1}{i\hbar}\right)\langle a|H_{\text{int}}{}^{+}(\omega_i)|b\rangle$$ **Absorption**



$$\Rightarrow \left(-\frac{1}{i\hbar}\right)\langle a|H_{\text{int}}(\omega_i)|b\rangle$$ **Emission**

4. Propagation of $|j\rangle\langle k|$ from the ***l***-th vertex to the (***l+1***)-th vertex is described by

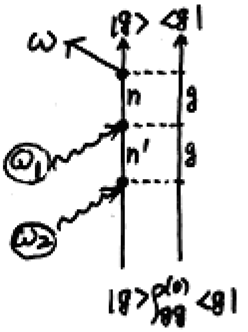
$$A_{l\rightarrow l+1} = \frac{\pm 1}{i\left[\left(\sum_{f=1}^{l} \pm\omega_f\right) - \omega_{jk} + i\gamma_{jk}\right]}\ .$$

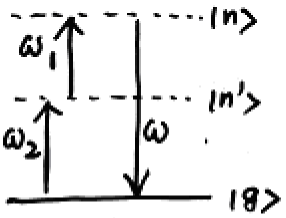
The positive sign implies a dipolar interaction with positive slope attached to a vertex

$$\underset{\text{(positive slope)}}{+\omega_f} = \begin{cases} \text{abs, on the left} \\ \text{or} \\ \text{emm, on the righ} \end{cases}$$

In the following, we will consider a steady-state SFG process as a case study.

(example)





$$\rho^{(2)}(\omega=\omega_1+\omega_2)=\sum|n\rangle\rho_{ng}{}^{(2)}\langle g|$$

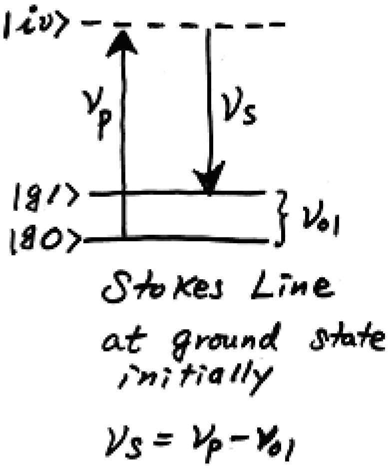
$$=\sum_{gnn'}|n\rangle\frac{1}{i\hbar}\langle n'|H_{\text{int}}(\omega_2)|g\rangle\rho_{gg}^{(0)}\langle g|\frac{1}{i(\omega_2-\omega_{n'g}+i\gamma_{n'g})}\cdot\frac{1}{i\hbar}\langle n|H_{\text{int}}(\omega_1)|n'\rangle\frac{1}{i(\omega_1+\omega_2-\omega_{ng}+i\gamma_{ng})}$$

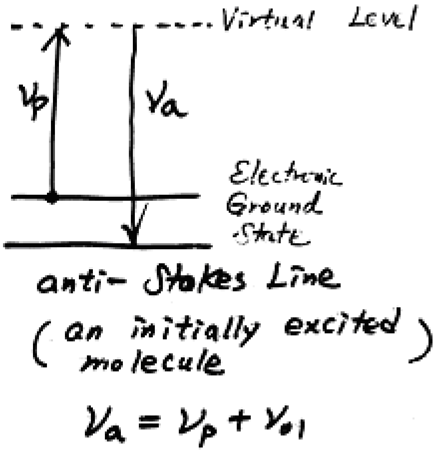
$$=\sum_{gnn'}|n\rangle\frac{1}{(2i\hbar)^2}E_{10}E_{20}e^{-i(\omega_1+\omega_2)t}\ \mu_{n'g}\mu_{nn'}\rho_{gg}^{(0)}\frac{1}{i(\omega_2-\omega_{n'g}+i\gamma_{n'g})}\frac{1}{i(\omega_1+\omega_2-\omega_{n'g}+i\gamma_{ng})}\langle g|$$

6.2 Stimulated Raman Scattering (SRS)

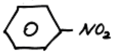
SRS is well known as a valuable tool to probing

- Structure of vibrational energy levels of a molecule
- Optical branch lattice vibrations in crystals





In 1962, Woodbury & Ng observed 1345-cm^{-1} down shifted from the laser frequency

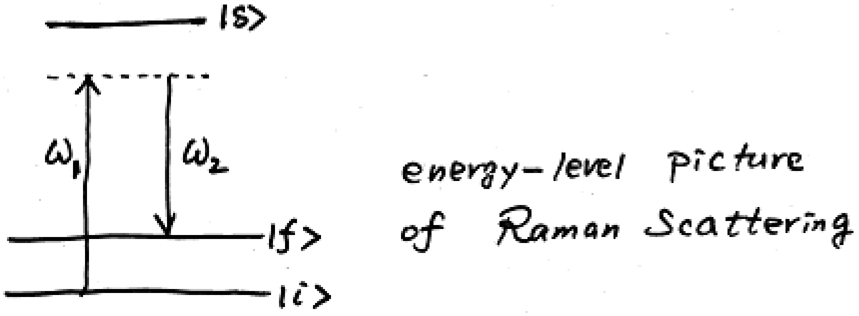
with a Raman cell containing nitrobenzene .

Afterward, SRS with some other gases or liquids had been observed, including

- ⇨ H_2-gas 4155 cm^{-1}
- ⇨ LN_2 2327 cm^{-1}

⇨ Benzene	992 cm^{-1}
⇨ CS_2	656 cm^{-1}
⇨ $LiNbO_3$	258 cm^{-1}

An energy-level diagram of Raman Scattering



To give some feeling on the SRS, let us first consider SRS as a light scattering process. The corresponding Raman transition rate W_{fi} (*i.e.*, the transition probability per unit time) per unit volume and per unit energy interval is found to be

$$\frac{d^2W_{fi}}{dV\,d(\hbar\omega_1)} = \frac{(2\pi)^3 N\,\omega_1\omega_2}{\varepsilon_1\varepsilon_2}\left|M_{fi}\right|^2 \left|\left\langle f\left|a_2^+a_1\right|i\right\rangle\right| g(\hbar\Delta\omega) \quad \textit{where}$$

$$g(\hbar\Delta\omega) = \frac{(\hbar\Gamma/\pi)}{\hbar^2(\Delta\omega)^2+\hbar^2\Gamma^2} = \textbf{ lineshape function}$$

Here ***M***= Raman transition matrix, which is given by

$$M = \sum_s \left[\frac{(\vec{\mu}\cdot\hat{e}_2)^*\left|s\right\rangle\left\langle s\right|(\vec{\mu}\cdot\hat{e}_1)}{\hbar(\omega_1-\omega_{si})} - \frac{(\vec{\mu}\cdot\hat{e}_1)\left|s\right\rangle\left\langle s\right|(\vec{\mu}\cdot\hat{e}_2)^*}{\hbar(\omega_2+\omega_{si})}\right].$$

The Raman photon number ***n***$_2$ at frequency ω_2 in a single mode shall meet the rate equation

$$\frac{dn_2}{dz} = (\overset{\text{create W2}}{\frac{dW_{fi}}{dw_2}}\rho_i - \overset{\substack{\text{annihilate W2}\\ \text{sec}^\wedge\text{-1}}}{\frac{dW_{if}}{dw_2}}\rho_f)\overset{\text{sec/cm}}{\frac{\sqrt{\varepsilon_2}}{c}} - \alpha_2 n_2$$

$$= G_R n_2 - \alpha_2\bar{n}_2 \ ,\text{cm}^{-1}$$

Here G_R = Stimulated Raman Gain and is defined to be

$$G_R = \frac{\frac{dW_{fi}}{d\omega_2}(\rho_i-\rho_f)}{\Phi_2} = \frac{dW_{fi}}{d\omega_2}(\rho_i-\rho_f)\frac{\sqrt{\varepsilon_2}}{c\bar{n}_2} = \frac{(2\pi)^3 N\,\bar{n}_1\hbar\omega_1\omega_2}{\varepsilon_1\sqrt{\varepsilon_2}c}\Delta\rho\left|M_{fi}\right|^2 g(\hbar\Delta\omega) \quad ,$$

where $\Phi_2 = \bar{n}_2 v_2 = \bar{n}_2 c\big/\sqrt{\varepsilon_2}$ = Raman photon flux.

For comparison, we can relate the above equation to Raman cross-section as

$$G_R = N\frac{4\pi^2 c^3 \varepsilon_1}{\omega_1 \omega_2{}^2 \varepsilon_2 \rho_i}(\rho_i - \rho_f)\frac{d\sigma}{d\Omega}\left|E_1\right|^2 g(\hbar\Delta\omega) \quad \text{with} \quad \frac{d\sigma}{d\Omega} = \frac{\omega_1 \omega_2{}^3 \sqrt{\varepsilon_2}}{c^4 \varepsilon_1} | M_{fi} |^2 \rho_i .$$

To find the Raman cross-section for a given normal mode of a molecule, note first that

The number density of radiation modes

$$\frac{d^2\sigma}{d(\hbar\omega_2)\,d\Omega} = \left[\frac{1}{(2\pi)^3} K_2^2 \frac{dK_2}{d\omega_2}\right] \frac{dW_{fi}}{d(\hbar\omega_2)} \frac{1}{N\bar{n}_1\bar{n}_2 c}$$

$$= \frac{\omega_1 \omega_2^3 \sqrt{\varepsilon_2}}{c^4 \varepsilon_1} \rho_i \left|M_{fi}\right|^2 g(\hbar\Delta\omega) = \frac{d\sigma}{d\Omega} g(\hbar\Delta\omega)$$

For the ring stretching mode of benzene at 992 cm^{-1}

$$\frac{d\sigma}{d\Omega} = 3.06\times10^{-8}\ cm^{-1}\cdot ster^{-1} \Rightarrow \frac{G_R}{I_1} = 2.8\times10^{-3}\ \text{cm/MW}$$

$$e^{G_R\cdot l} = e^{30} \Rightarrow \quad \mathrm{G_R}\cdot l = 30 \ \Rightarrow \ \mathrm{G_R} = \frac{30}{l} \ \Rightarrow \quad \mathrm{I} \approx 1\ \mathrm{GW/cm^2}$$

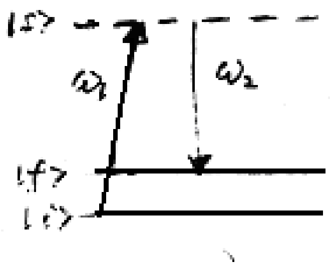
6.3 Coupled-Wave Description of SRS

From the wave-mixing picture, the stimulated Raman process in fact belongs to a third-order nonlinear optical process. This can be easily understood from the argument shown in the following: By using the detailed balance condition, the net transition rate from ***i*** to ***f*** is equal to the rate of generation of ω_2-photons

$$\frac{dW_{fi}}{d\omega_2}(\rho_i - \rho_f) = 2\,\mathrm{Re}\left[\frac{\partial P^{(3)}(\omega_2)}{\partial t} E_2^*(\omega_2)\right]/(\hbar\omega_2)$$

Since $\dfrac{dW_{fi}}{d\omega_2}(\rho_i - \rho_f) \propto \bar{n}_1\bar{n}_2 \propto \left|E_1\right|^2\left|E_2\right|^2$.

$$\Rightarrow \quad P^{(3)}(\omega_2) \propto \left|E_1\right|^2 E_2$$



Now let us start from the wave equations of

$$\begin{aligned} \nabla\times(\nabla\times E_1)-\tilde{\omega}_1^2\varepsilon_1 E_1 &= 4\pi\,\tilde{\omega}_1^2 P^{(3)}(\omega_1) \\ \nabla\times(\nabla\times E_2)-\tilde{\omega}_2^2\varepsilon_2 E_2 &= 4\pi\,\tilde{\omega}_2^2 P^{(3)}(\omega_2) \end{aligned}, \qquad (6.3.1)$$

where $P^{(3)}(\omega_1)=[\chi_1^{(3)}|E_1|^2+\chi_{R1}^{(3)}|E_2|^2]\,E_1$

$P^{(3)}(\omega_2)=[\chi_{R2}^{(3)}|E_1|^2+\chi_2^{(3)}|E_2|^2]\,E_2$

$\swarrow \qquad \searrow$

Two-wave coupling term   self-action

Since $\chi_1^{(3)},\chi_2^{(3)}$ have no effect on SRS, we will focus on $\chi_{R1}^{(3)},\chi_{R2}^{(3)}$,

which provide couplings between E_1 and E_2. Therefore,

$$\begin{aligned} \frac{dW_{fi}}{d\omega_2}(\rho_i-\rho_f) &= 2\,\mathrm{Re}[\frac{\partial P^{(3)}(\omega_2)}{\partial t}\,E^*(\omega_2)]/(\hbar\omega_2) \\ &= -\frac{2\,\mathrm{Im}\,\chi_{R2}^{(3)}|E_1|^2|E_2|^2}{\hbar}=G_R\,\bar{n}_2\,v_2=G_R\bar{n}_2\frac{c}{\sqrt{\varepsilon_2}} \end{aligned}.$$

Let $I_\omega=|E_\omega|^2\sqrt{\varepsilon_\omega}/2\pi=\hbar\omega\,\bar{n}$, we then obtain $|E_1|^2=2\pi\hbar\omega_1\bar{n}_1/\sqrt{\varepsilon_1}$.

Therefore, $G_\mathrm{R}=-\frac{4\pi\,\omega_2^2}{c^2k_2}(\mathrm{Im}\,\chi_{R2}^{(3)})|E_1|^2=\frac{(2\pi)^3N\hbar\omega_1\omega_2}{\varepsilon_1\sqrt{\varepsilon_2}c}|M_{fi}|^2\,\bar{n}_1\,(\rho_i-\rho_f)\,g(\hbar\Delta\omega)$

with

$$\begin{aligned} &\mathrm{Im}\,\chi_{R2}^{(3)}=-N|M_{fi}|^2(\rho_i-\rho_f)\pi g(\hbar\Delta\omega) \\ \Rightarrow\ &\chi_{R2}^{(3)}=\frac{N|M_{fi}|^2(\rho_i-\rho_f)}{\hbar[(\omega_1-\omega_2-\omega_{fi})-i\Gamma]}=\chi_{R1}^{(3)*} \end{aligned}.$$

The coupled -wave equations by invoking SVA on Eq. (6.3.1) become

$$\begin{aligned} (\frac{\partial}{\partial z}+\frac{\alpha_1}{2})E_1 &= i\frac{2\pi\,\tilde{\omega}_1^2}{k_1}\chi_{R1}^{(3)}|E_2|^2\,E_1 \\ (\frac{\partial}{\partial z}+\frac{\alpha_2}{2})E_2 &= i\frac{2\pi\,\tilde{\omega}_2^2}{k_2}\chi_{R2}^{(3)}|E_1|^2\,E_2 \end{aligned}. \qquad (6.3.2)$$

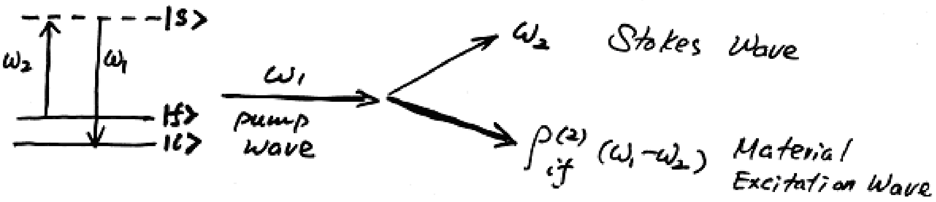
We can also express Eq. (6.3.2) in terms of beam intensities as

$$\begin{aligned} (\frac{\partial}{\partial z}+\alpha_1)|E_1|^2 &= -\frac{4\pi\,\tilde{\omega}_1^2}{k_1}\mathrm{Im}\,\chi_{R1}^{(3)}|E_1|^2|E_2|^2 \\ (\frac{\partial}{\partial z}+\alpha_2)|E_2|^2 &= -\frac{4\pi\,\tilde{\omega}_2^2}{k_2}\mathrm{Im}\,\chi_{R2}^{(3)}|E_1|^2|E_2|^2 \end{aligned}$$

These are the coupled-wave equations of SRS assuming that *the medium provides only the coupling effect without taking into account the propagation effect of material excitation.*

6.4 Parametric Coupling of Optical and Material Excitational Waves

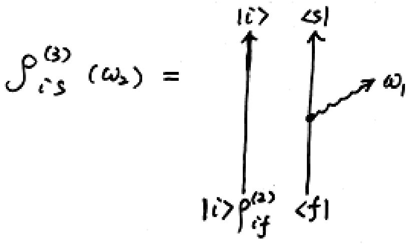
When the medium is excited to form a significant material excitation wave, we shall take the propagation effect of the material excitation wave into account.



Note

$$
\begin{aligned}
P_{res}^{(3)}(\omega_2) &= \chi_{R2}^{(3)}\left|E_1\right|^2 E_2 \\
&= N\ Tr(\mu\,\rho_{R2}^{(3)}) = N\sum_s[\mu\,\rho_{R2}^{(3)}]_{ss} + N[\mu\,\rho_{R2}^{(3)}]_{ff} \\
&= N\sum_s\langle s\left|e\vec{r}\cdot\hat{E}_2\right|i\rangle\,\rho_{is}^{(3)}(\omega_2) + N\sum_s\langle f\left|e\vec{r}\cdot\hat{E}_2\right|s\rangle\,\rho_{sf}^{(3)}(\omega_2) \\
&= I + II
\end{aligned}
\qquad . (6.4.1)
$$

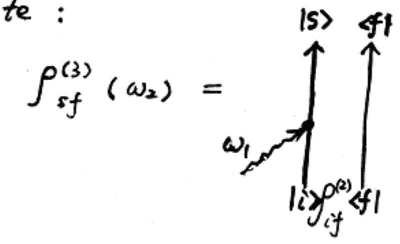
For **the first term *I***, $\rho_{is}^{(3)}(\omega_2)$ can be derived from



$$
= \frac{1}{i(\omega_1+\omega_2-\omega_1-\omega_{is})}\langle f\left|\frac{H(\omega_1)}{-i\hbar}\right|s\rangle\,\rho_{if}^{(2)}(\omega_2-\omega_1) = \frac{\langle f\left|er_1\right|s\rangle}{\hbar(\omega_2+\omega_{si})}E(\omega_1)\rho_{if}^{(2)}
$$
, and

for **the second term *II***,

Note :



Here the equality:

$\omega_1-\omega_{si}=\omega_2-\omega_{sf}$

$\Rightarrow \omega_1+\omega_{sf}=\omega_2+\omega_{si}$

$$\rho^{(3)}{}_{sf}(\omega_2)=\frac{1}{i(\omega_1+\omega_2-\omega_1-\omega_{sf})}\langle s|\frac{H(\omega_1)}{i\hbar}|i\rangle\rho^{(2)}_{if}(\omega_2-\omega_1)=\frac{-\langle s|er_1|i\rangle}{\hbar(\omega_2-\omega_{sf})}E(\omega_1)\rho^{(2)}_{if}.$$

Thus, Eq.(6.4.1) becomes

$$\begin{aligned}P^{(3)}_{res}(\omega_2)=N\sum_s[&\frac{\langle f|e\vec r\cdot\hat e_1|s\rangle\langle s|e\vec r\cdot\hat e_2|i\rangle}{\hbar(\omega_2+\omega_{si})}E(\omega_1)\rho^{(2)}_{if}(\omega_2-\omega_1)-\\&\frac{\langle f|e\vec r\cdot\hat e_2|s\rangle\langle s|e\vec r\cdot\hat e_1|i\rangle}{\hbar(\omega_2-\omega_{sf})}E(\omega_1)\rho^{(2)}_{if}(\omega_2-\omega_1)]\\=&-NM_{fi}E(\omega_1)\rho^{(2)}_{if}(\omega_2-\omega_1)\end{aligned}\qquad(6.4.2)$$

yielding an expression of the SRS polarization

$$\boxed{P^{(3)}_{res}(\omega_2)=-NM_{fi}E(\omega_1)\rho^{(2)}_{if}(\omega_2-\omega_1)}$$

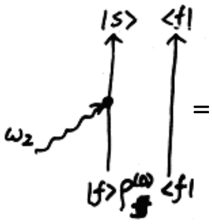
Here $\rho^{(2)}_{if}(\omega_2-\omega_1)$ denotes a material wave driven by a generalized force from optical mixing $E_1^*E_2$ and satisfies the dynamic equation

$$\left(\underset{\substack{\swarrow\\(\omega_i-\omega_f)}}{\frac{\partial}{\partial t}}+i\omega_{if}+\Gamma_{\mathrm{if}}\right)\underset{\substack{\downarrow\\\propto e^{-i(\omega_2-\omega_1)t}}}{\rho^{(2)}_{\mathrm{if}}}(\omega_2-\omega_1)=\frac{1}{i\hbar}\left\{\left[-e\vec r\cdot\hat e_1^+E_1^*,\ \rho^{(1)}(\omega_2)\right]+\left[-e\vec r\cdot\hat e_2E_2,\ \rho^{(1)}(-\omega_1)\right]\right\}_{if}\qquad(6.4.3).$$

The first commutator on the right-hand side implies

$$\left[-e\vec r\cdot\hat e_1^+E_1^*,\ \rho^{(1)}(\omega_2)\right]=E^*(\omega_1)\langle i|-er_1|s\rangle\rho^{(1)}_{sf}(\omega_2)-\rho^{(1)}_{is}(\omega_2)\langle s|-er_1|f\rangle E^*(\omega_1)$$

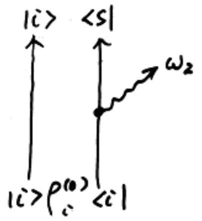
$\rho^{(1)}_{sf}(\omega_2)=$



$$=\frac{1}{i(\omega_2-\omega_{sf})}\langle s|\frac{H(\omega_2)}{i\hbar}|f\rangle\rho^{(0)}_f=\frac{-1}{\hbar}\langle s|-er_2|f\rangle\rho^{(0)}_fE(\omega_2)\frac{1}{\omega_2-\omega_{sf}}$$

And

$\rho^{(1)}_{is}(\omega_2)=$



$$=\frac{1}{i(\omega_2-\omega_{is})}\langle i|\frac{H(\omega_2)}{-i\hbar}|s\rangle\rho^{(0)}_i=\frac{1}{\hbar(\omega_2-\omega_{is})}\langle i|-er_2|s\rangle E_2\rho^{(0)}_i$$

By adding together the results, the first commutator of Eq. (6.4.3) becomes

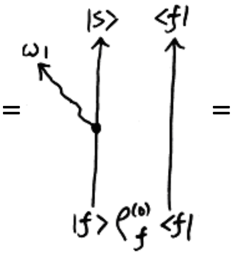
$$[-er_1,\rho^{(1)}(\omega_2)]_{if}\,E_1^*$$

$$= -\frac{\langle i|-er_1|s\rangle\langle s|er_2|f\rangle\rangle E_1^*E_2}{\hbar(\omega_2-\omega_{sf})}\rho_f^{(0)} - \rho_i^{(0)}\frac{\langle s|er_1|f\rangle\langle i|-er_2|s\rangle E_1^*E_2}{\hbar(\omega_2-\omega_{is})} \qquad \mathbf{(6.4.4)}$$

Similarly, for the second commutator of Eq. (6.4.3), we can obtain

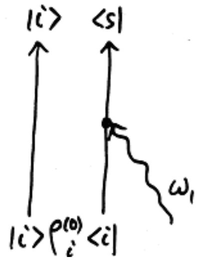
$$[-er_2E_2,\rho^{(1)}(-\omega_1)]_{if} = \langle i|-er_2|s\rangle\rho_{sf}^{(1)}(-\omega_1)E_2 - \rho_{is}^{(1)}(-\omega_1)\langle s|-er_2|f\rangle E_2$$

$$\rho_{sf}^{(1)} =$$



$$= \frac{1}{i(-\omega_1-\omega_{sf})}\langle s|\frac{H^+(\omega_1)}{i\hbar}|f\rangle\rho_f^{(0)} = \frac{1}{\hbar(\omega_1+\omega_{sf})}\langle f|-er_1|s\rangle E_1^*\rho_f^{(0)}$$

$$\rho_{is}^{(1)} =$$



$$= \frac{1}{i(-\omega_1-\omega_{is})}\langle i|\frac{H^+(\omega_1)}{-i\hbar}|s\rangle\rho_i^{(0)} = \frac{-\langle i|-er_1|s\rangle}{\hbar(\omega_1+\omega_{is})}\rho_i^{(0)}E_1^*$$

Thus, the second commutator becomes

$$[-er_2E_2,\ \rho^{(1)}(-\omega_1)]_{if}$$

$$= \frac{-\langle i|-er_2|s\rangle\langle s|-er_1|f\rangle E_1^*E_2}{\hbar(\omega_1+\omega_{sf})}\rho_f^{(0)} + \frac{\langle i|-er_1|s\rangle\langle s|-er_2|f\rangle E_1^*E_2}{\hbar(\omega_1+\omega_{is})}\rho_i^{(0)} \qquad \mathbf{(6.4.5)}$$

By combining Eqs. (6.4.4) and (6.4.5), we find

$$\boxed{[-er_1E_1^*,\rho^{(1)}(\omega_2)] + [-er_2E_2,\ \rho^{(1)}(-\omega_1)] = \mathrm{M}_{\mathrm{fi}}^*E_1^*E_2(\rho_i^{(0)}-\rho_f^{(0)})}$$

In steady state, Eq. (6.4.3) yields a solution

$$\rho_{if}^{(2)}(\omega_2-\omega_1) = \frac{M_{fi}^*(\rho_i-\rho_f)}{\hbar(\omega_2-\omega_1-\omega_{if}+i\Gamma_{if})}E_1^*E_2 .$$

Therefore, the SRS polarization becomes

$$P_{res}^{(3)}(\omega_2) = [\chi_{R2}^{(3)}]_R |E_1|^2 E_2 \quad \text{with} \quad \left[\chi_{\mathrm{R2}}^{(3)}\right]_R = \frac{N|M_{fi}|^2(\rho_i - \rho_f)}{\hbar[(\omega_1 - \omega_2 - \omega_{fi}) - i\Gamma_{fi}]} \cdot \qquad (6.4.6)$$

The stimulated Raman scattering can be viewed as a coupling among the three waves $\boldsymbol{E}_1(\boldsymbol{\omega}_1)$, $\mathbf{E}_2(\boldsymbol{\omega}_2)$ and $\boldsymbol{\rho}_{if}^{(2)}(\boldsymbol{\omega}_1 - \boldsymbol{\omega}_2)$ with the corresponding coupled-wave equations being

$$\begin{cases} [\nabla\times(\nabla\times\ ) + \frac{\varepsilon_1}{c^2}\frac{\partial^2}{\partial t^2}]E_1 = 4\pi\tilde{\omega}_1^2\,\hat{e}_1\{|E_1|^2 E_1\left[\chi^{(3)}\right]_{NR} + NM_{fi}^* E_2\rho_{fi}(\omega_1 - \omega_2)\} \\ [\nabla\times(\nabla\times\ ) + \frac{\varepsilon_1}{c^2}\frac{\partial^2}{\partial t^2}]E_2 = 4\pi\tilde{\omega}_2^2\,\hat{e}_2\{[\chi^{(3)}]_{NR}|E_2|^2 E_2 + NM_{fi}^* E_1(w_1)\rho_{fi}^*(\omega_1 - \omega_2)\} \\ \textit{and} \\ (\frac{\partial}{\partial t} - i\omega_{fi} + \Gamma_{fi})\rho_{fi}^*(\omega_1 - \omega_2) = -\frac{i}{\hbar}M_{fi}^*(\rho_i - \rho_f)E_1^* E_2 \end{cases} \qquad (6.4.7)$$

Under the weak excitation condition, the population difference $(\rho_i - \rho_f)$ can be approximated by its thermal equilibrium value $(\boldsymbol{\rho}_i^{(0)} - \boldsymbol{\rho}_f^{(0)})$. But in general, it should obey the relaxation equation

$$\begin{aligned} \frac{dW_{fi}}{Nd\omega_2}(\rho_i - \rho_f) &= \frac{1}{2}(\frac{\partial}{\partial t} + \frac{1}{T_1})[(\rho_i - \rho_f) - (\rho_i^{(0)} - \rho_f^{(0)})] \\ &= \frac{2}{\hbar\omega_2}\mathrm{Re}[\frac{\partial}{\partial t}P^{(3)*}(\omega_2)\,E_2] \\ &= \frac{i}{\hbar}[M_{fi}E_1E_2^*\rho_{fi}^* - M_{fi}^*E_1^*E_2\rho_{fi}] \end{aligned}$$

For the stimulated Raman scattering by molecular vibration, $\boldsymbol{\rho}_{fi}^{(2)}(\boldsymbol{\omega})$ relates to the excited normal mode coordinate Q as $\rho_{fi}^{(2)}(\omega) \to \sqrt{\frac{\hbar}{2M_Q}}Q$.

6.5 Experimental Observations

Stimulated Raman Scattering (SRS) in self-focusing media had been observed to have the following characteristic features:

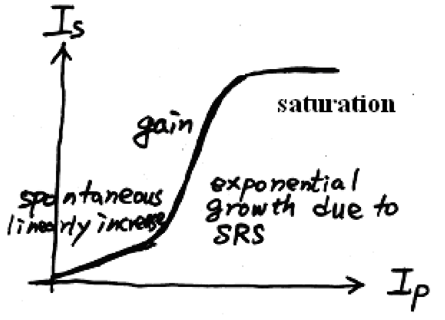
(a) **a sharp threshold:** This is due to an onset of self-focusing, which increases the actual pump intensity in the medium;

(b) **larger effective SRS gain than prediction by the theory:** This is due to generation of self-focused filaments which increases the pump intensity.

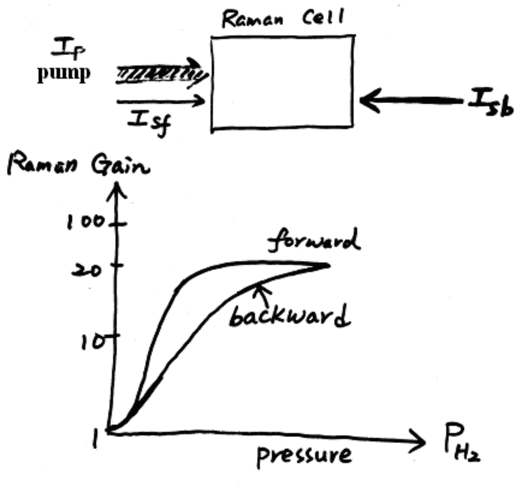
(c) **forward-backward asymmetry:** The forward-backward asymmetry can be understood as follows: In the forward direction, as a short Δt -section of the stokes wave propagates inside a medium, it always coherently interacts with the same Δt -section of pump wave. However, in the backward direction, a short section of the Stokes wave constantly encounters a new wavefront of the pump wave. Consequently, the backward Raman gain is reduced because an average over the amplitude and phase variation of the pump field, which leads to

$$G_{\mathrm{R}} \propto \begin{cases} \dfrac{1}{\Gamma}: & \text{forward} \quad 2\Gamma\text{=Raman Linewidth} \\ \dfrac{1}{\Gamma+\Gamma_L}: & \textit{backward} \quad 2\Gamma_L\text{=Linewidth of Pump Laser} \end{cases}.$$

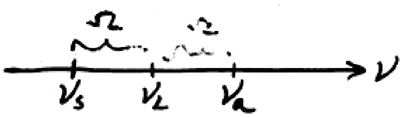
By carefully designing a SRS experiment without self-focusing, we shall see



By using a hydrogen cell, the resulting Raman Gain in forward and backward geometries was found to have



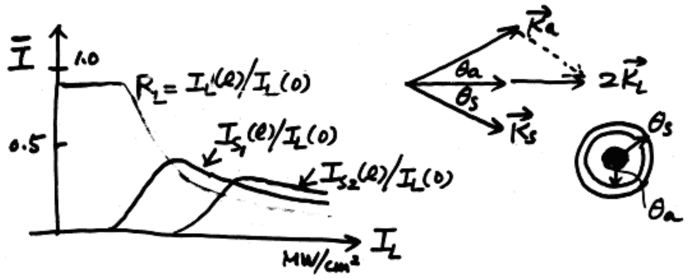
The anti-Stokes and higher-order Raman radiation can also be found



with the corresponding SRS wavevectors satisfying the momentum conservation law $\vec{K}_{a,n} = \vec{K}_{a,n-1} + (2\vec{K}_L - \vec{K}_{s,n})$.

Higher anti-Stokes and Stokes can be generated successively from the lower-order Stokes and anti-Stokes beams. They appear in the form of bright multi-colored rings (due to the axial symmetry of the experimental geometry) on a plane perpendicular to the laser beam with the emitted direction given by the phase-matching condition.

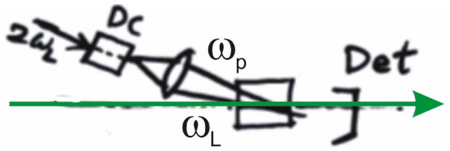
e.g., the 1st-order ring: $2\vec{K}_L = \vec{K}_a + \vec{K}_s$



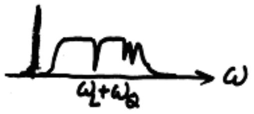
- **Competition between Raman Modes**

  Most effective modes are the ones with a large Raman cross section $d^2\sigma / d\omega_2 d\Omega$ and a narrow Raman linewidth Γ.

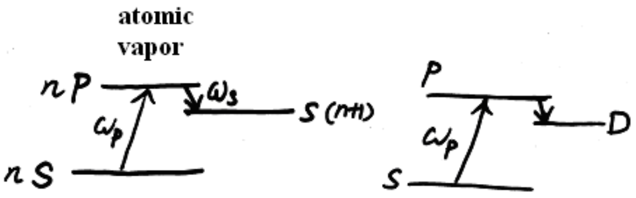
- Inverse Raman Effect ω_p



The attenuation of the pump radiation ω_p in a SRS with the gain of the Stokes Wave



- Tunable IR Sources from SRS

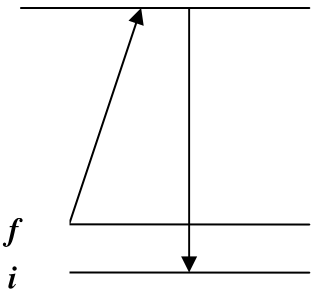


[$5S^2 5P^6$]

Cs: 2.5 → 4.75 um　　6S → 7S
5.67 → 8.65 um　　6S → 8S
11.65 → 15 um　　6S → 9S

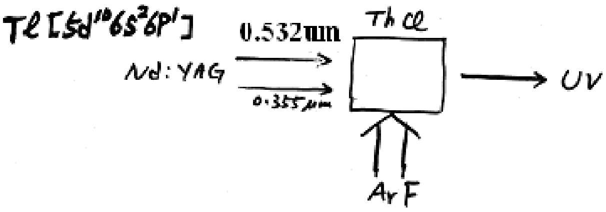
Peak photon conversion efficiency at multiply resonant condition can be as high as ~ 50%!

- Tunable UV from anti-Stokes scattering



if $\rho_f > \rho_i \Rightarrow$ *anti-Stokes* Raman gain , for example, population can be pumped into the metastable state by photo-dissociation such as

$$\mathbf{TlCl} \xrightarrow[\text{Laser}]{\text{ArF}} \mathbf{Tl}\,(6P\,{}^2P^{\circ}_{3/2}) + \mathbf{Cl}$$



- SRS as a high-resolution spectroscopic technique in both spectral and temporal domains

The basic concept is that an attenuation of pump beam can be associated with

Stokes-Raman gain $G_R(\omega_1-\omega_2)=\dfrac{8\pi^3 N\omega_1\omega_2\hbar}{\varepsilon_1\sqrt{\varepsilon_2}c}\left|M_{fi}\right|^2\tilde{n}_1 g(\hbar\Delta\omega)\Delta\rho_{fi}$ such

that $G_R(\omega_1-\omega_2)\ vs\ \ \omega_1-\omega_2$ can be exploited to yield a Raman spectrum of the medium.

For more recent application of SRS gain on optical microscopy, refer to

1. Label-Free Biomedical Imaging with High Sensitivity by Stimulated Raman Scattering Microscopy, *Science* **322**, 1857 (2008)
2. Video-Rate Molecular Imaging in Vivo with Stimulated Raman Scattering, *Science* **330**, 1368 (2010).

The advantages of coherent laser spectroscopy can be

(a) No spectrometer is needed, thus spectral resolution is limited only by the laser linewidth;
(b) Sensitive.

6.6 Transient Stimulated Raman Scattering

When pulsed lasers are used in stimulated Raman scattering experiment and the pulse width, τ_p, is shorter than

(1) the relaxation times of the Raman excitation, T_1 or T_2, or
(2) the time required for light to travel through the medium.

In this case, the transient effect is important.

From: $P_{res}^{(3)}(\omega_2) = -iNM_{fi}E(\omega_1)\underline{\rho_{if}^{(2)}(\omega_2-\omega_1)}$

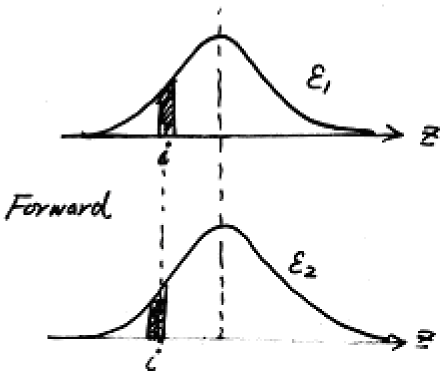
Material excitation, which can be the normal mode vibration of a molecular medium induced by $\boldsymbol{E}(\omega_1)$ and $\boldsymbol{E}(\omega_2)$.

$$\text{Let}\begin{cases}\rho_{fi}^{(2)}(\omega_1-\omega_2)=\rho_{if}^{*}(\omega_2-\omega_1)=A(z,t)e^{i(k_1-k_2)z-i(\omega_1-\omega_2)t} & \textbf{and} \\ E(\omega_i)=\varepsilon_i(z,t)e^{iK_i z-i\omega_i t}\end{cases},$$

First assuming the quasi-steady-state case and using the retarded time coordinates $v_1 = v_2$, $z' = z$, $t' = t - z/v$, we obtain

$$\begin{aligned}\frac{\partial}{\partial z'}\varepsilon_1 &= i\left(\frac{2\pi\tilde{\omega}_1^2}{K_1}\right)\chi_R^{(3)*}\left|\varepsilon_2\right|^2\varepsilon_1 \\ \frac{\partial}{\partial z'}\varepsilon_2 &= i\left(\frac{2\pi\tilde{\omega}_2^2}{K_2}\right)\chi_R^{(3)*}\left|\varepsilon_1\right|^2\varepsilon_2\end{aligned},$$

which become the steady-state equations in terms of *z*' and *t*'=*t*-*z*/*v*, implying that



the ***i***-th differential slice in the pump laser pulse always interacts with the same ***i***-th slice in the Stokes pulse in the quasi-steady-state case.

- **Transient Case**

(1) When laser pulse width $\tau_p < T_2 = \frac{1}{\Gamma_{fi}}$, the material excitation, ***A***, can not response instantaneously to the optical driving field.

(2) When $\tau_p \sim ps$, the backward Raman scattering is hardly detectable because of the very limited length of interaction between the backward Raman and the incoming pump pulse.

(3) Neglect the depletion of pump power and the induced population change

$$\left(\frac{\partial}{\partial z}+\frac{1}{v}\frac{\partial}{\partial t}\right)\varepsilon_2 = i\eta_1\varepsilon_1(t-z/v)A^* \qquad with \;\; \eta_1 = \frac{2\pi\tilde{\omega}_2^2}{K_2}NM_{fi}$$

$$\left(\frac{\partial}{\partial z}+\Gamma\right)A^* = -i\eta_2\varepsilon_1^*(t-z/v)\varepsilon_2 \qquad \eta_2 = M_{fi}^*\left(\rho_i-\rho_f\right)/\hbar \, .$$

Let t' = t - z/v and z' = z, then

$$\Rightarrow \;\; [\frac{\partial^2}{\partial t'\partial z'} - \eta_1\eta_2\left|\varepsilon(t')\right|^2]U = 0 \quad where \;\; U=Fe^{\Gamma t'}$$ F stands for ε_2 or A*.

We can eliminate $\left|\varepsilon_1(t'')\right|^2$ by replacing ***t'*** with $\tau = \int_{-\infty}^{t'}\left|\varepsilon_1(t'')\right|^2 dt''$

$$\Rightarrow \;\; \left(\frac{\partial^2}{\partial\tau\,\partial z'} - \eta_1\eta_2\right)U = 0 .$$

The equation is the standard form of a hyperbolic equation.

Ref. R.L. Carmen, F. Shimizu, C.S. Wang, and N. Bloembergen, *Phys. Rev.***A2**, 60 (1970)

For the general case of transient Raman scattering process, we shall start from the coupled wave equations in SVA

$$(\frac{\partial}{\partial z}+\frac{1}{V_1}\frac{\partial}{\partial t})\varepsilon_1(z,t)=i(\frac{2\pi\tilde{\omega}_1^2}{\mathrm{K}_1})NM_{fi}^*\varepsilon_2(z,t)A(z,t)$$

$$(\frac{\partial}{\partial z}+\frac{1}{V_2}\frac{\partial}{\partial t})\varepsilon_2(z,t)=i(\frac{2\pi\tilde{\omega}_2^2}{\mathrm{K}_2})NM_{fi}^*\varepsilon_1(z,t)A^*(z,t)\backslash$$

$$(\frac{\partial}{\partial t}+\Gamma_{fi})A^*(z,t)=-\frac{i}{\hbar}M_{fi}^*(\rho_i-\rho_f)\varepsilon_1^*\varepsilon_2$$

where v_1, v_2 are group velocities of the optical fields ε_1 and ε_2, all non resonant terms have been neglected.

- For the Quasi-Steady-State Case,

ε_1, ε_2 vary slowly ➔ $\left|\frac{\partial}{\partial t}A\right| << \Gamma A$ ➔ $A\ (z,t) = iM_{\mathrm{fi}}(\rho_i-\rho_f)\varepsilon_1\varepsilon_2^*/\left(\hbar\Gamma_{fi}\right)$

$$(\frac{\partial}{\partial z}+\frac{1}{v_1}\frac{\partial}{\partial t})\varepsilon_1=i^2(\frac{2\pi\tilde{\omega}_1^2}{K_1})NM_{fi}^*\varepsilon_2M_{fi}(\rho_i-\rho_f)\varepsilon_1\varepsilon_2^*/(\hbar\Gamma_{fi})$$

$$=(\frac{-2\pi\tilde{\omega}_1^2}{K_1\hbar\Gamma_{fi}})N\left|M_{fi}\right|^2\left|\varepsilon_2\right|^2\varepsilon_1(\rho_i-\rho_f)$$

Define $\chi_R^{(3)}=\frac{N\left|M_{fi}\right|^2(\rho_i-\rho_f)}{i\hbar\Gamma_{fi}}$ ➔ $\begin{array}{l}(\frac{\partial}{\partial z}+\frac{1}{v_1}\frac{\partial}{\partial t})\varepsilon_1=i\chi_R^{(3)*}\left|\varepsilon_2\right|^2\varepsilon_1\frac{2\pi\tilde{\omega}_1{}^2}{K_1}\\(\frac{\partial}{\partial z}+\frac{1}{v_2}\frac{\partial}{\partial t})\varepsilon_2=i\chi_R^{(3)*}\left|\varepsilon_1\right|^2\varepsilon_2\frac{2\pi\tilde{\omega}_2{}^2}{K_2}\end{array}$.

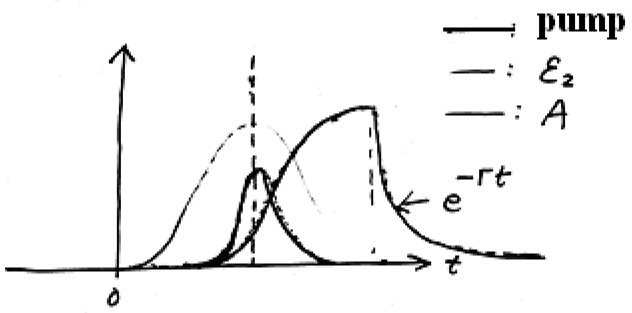
(a) When z <<1, $\varepsilon_2 \sim z$ in the beginning. Then in the limit of large amplification, ε_2 increase exponentially.

(b) For a long pump pulse, ε_2 takes on a quasi-steady-state exponential gain, *i.e.*,

if $\tau_p > (G_R\, l)\, T_2$ ➔ steady-state

(c) If $\tau_p < T_2$

ε_2 rapidly increases toward the middle part of the pump pulse, then drops off following the pump pulse at the tail. The material excitation amplitude ***A*** behaves in the similar behavior but has an exponential decay tail $e^{-\Gamma t}$ after the pump pulse is switched off.



(d) in the limit of large amplification

$$|\varepsilon_2|_{\max} \sim e^{G_T z/2}$$

$$\textit{where} \quad G_T = 4\sqrt{\frac{\eta_1\eta_2 <|\varepsilon|^2> \tau_p}{z}} = \textit{transient}\ \textbf{Raman gain}$$

$$\textbf{note:} \quad <|\varepsilon|^2> \tau_p = \int_{-\infty}^{\infty} |\varepsilon_1(z)|^2 dt$$

The transient Raman gain G_T is different from the steady-state gain G_R

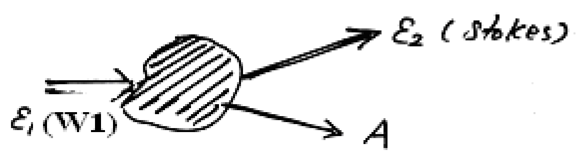
$$G_R = \frac{8\pi^3 N\omega_1\omega_2\hbar}{\varepsilon_1\sqrt{\varepsilon_2}c}|M_{fi}|^2\, \tilde{n}_1 g(\hbar\Delta\omega)\Delta\rho_{fi} = \frac{-4\pi\omega_2^2}{c^2 K_2}\operatorname{Im}\chi_{R2}^{(3)}|E_1|^2,$$

where $\operatorname{Im}\chi_{R2}^{(3)} = -N|M_{fi}|^2(\rho_i - \rho_f)\pi g(\hbar\Delta\omega)$ in the fact that the former (transient Raman gain) depends only on the Raman cross section ($\propto \eta_1\eta_2$), while the latter (steady-state gain) is also inversely proportional to the half-width Γ.

6.7 Measurements of the Relaxational Times of Material Excitaion

Relaxation of a material excitation can be measured directly by probing the decay of the excitation.

T$_2$ = transverse relaxation time (dephasing time of the excitational wave)
T$_1$=longitudinal relaxation time, decay of induced population change in the excited state
Transient stimulated Raman scattering yields a material excitaional wave A which decays exponentially as $e^{-\Gamma t} = e^{-t/T_2}$ even after the pump pulse is switched off.



$$(\frac{\partial}{\partial z}+\frac{1}{v}\frac{\partial}{\partial t})\varepsilon_2 = i\eta_1\varepsilon_1 A^* \qquad \eta_1=\frac{2\pi\tilde{\omega}_2^2}{K_2}NM_{fi}$$

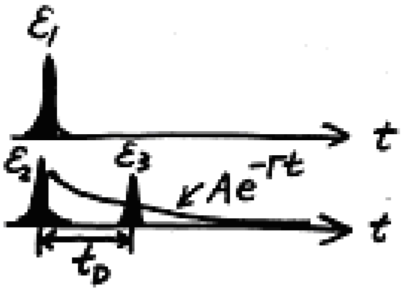
$$(\frac{\partial}{\partial z}+\Gamma)A^* = -i\eta_2\varepsilon_1^*\varepsilon_2 \qquad \eta_2 = M_{fi}^*(\rho_i-\rho_f)/\hbar$$

The material excitation wave at $\omega_1-\omega_2\cong\omega_Q$ can be probed by mixing A with a probe pulse E_3 at $\vec{k}_3$ and ω_3 to generate a coherent anti-Stoke wave $E_a=\varepsilon_a e^{i(k_1-k_2+k_3)z-i(\omega_1-\omega_2+\omega_3)t}$, which satisfies the wave equation

$$(\frac{\partial}{\partial z}+\frac{1}{v_a}\frac{\partial}{\partial t})\varepsilon_a = i\frac{2\pi\tilde{\omega}_a^2}{k_a}NM_{fi}^*[\varepsilon_3 A] \ .$$

First transform the equation with z'=z, t'=t-z/v_a

$$\varepsilon_a(\ell,t)\propto\int_0^\infty \varepsilon_3(z',t')A(z',t')dz'$$



$$S_{coh}\propto\int_{-\infty}^{\infty}\left|\varepsilon_a(l,t)\right|^2 dt$$

$$\propto\int_{-\infty}^{\infty}\left|\int_0^l \varepsilon_3(z',t')A(z',t')dz'\right|^2 dt$$

when A(z,t)=$e^{-\Gamma t}H(t)$

$\varepsilon_3(z,t)=\delta(t-z/v)$ **and** $t_D >> T_2 \geq \tau_p$

$t_D \equiv$ *time* **delay between the exciting the probing pulses**

$$\therefore \quad S_{coh} \propto \int_{-\infty}^{\infty} \left| \int_0^l \delta(t - z/v - t_D) e^{-\Gamma|t - z'/v|} H(t - z'/v) dz' \right|^2$$

$$= \int_{-\infty}^{\infty} \delta(t) \left| e^{-\Gamma t_D} H(t_D) \right|^2 dt = e^{-2t_D/T_2} H(t_D)$$

and

$$\left(\frac{\partial}{\partial t} + \frac{1}{T_1} \right) \Delta\rho = \frac{iN}{2\hbar} [M_{fi} \varepsilon_1 \varepsilon_2^* A^* - M_{fi}^* \varepsilon_1^* \varepsilon_2 A] \left(\rho_i^{(0)} - \rho_f^{(0)} \right) = 0$$

$$\frac{1}{2} \left[\rho_i - \rho_i^{(0)} - (\rho_f - \rho_f^{(0)} \right] = \Delta\rho << \left(\rho_i^{(0)} - \rho_f^{(0)} \right)$$

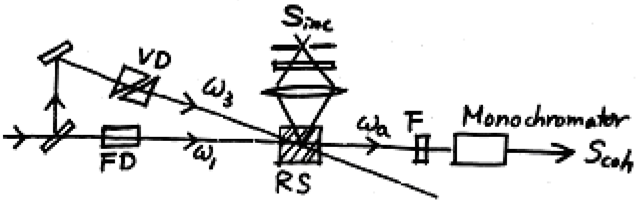
after pump pulse is over $(\varepsilon_1 = 0) \quad \Rightarrow \quad \Delta\rho \propto e^{-t/T_1}$

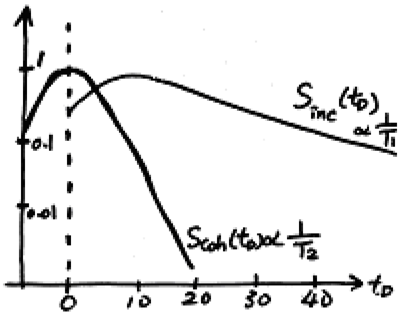
Spontaneous anti-Stokes scattering is proportional to $\Delta\rho$ and therefore can be used to probe the decay of $\Delta\rho$.

With a probe pulse E_2 at ω_2

$$S_{inc}(\omega_a = \omega_3 + \omega_1 - \omega_2) = \int_{-\infty}^{\infty} \int_0^l \left| \varepsilon_3(z,t) \right|^2 \cdot \Delta\rho(z,t)\, dz\, dt$$

$$\propto e^{-t_{D/T_1}} \quad when \quad t_D >> T_1 \geq \tau_p$$





A more sophisticated study with SRS on biomolecules can be found in the following:

1. Philipp Kukura, David W. McCamant, Sangwoon Yoon, Daniel B. Wandschneider, Richard A. Mathies, “Structural Observation of the Primary Isomerization in Vision with Femtosecond-Stimulated Raman ”, SCIENCE **310**, 1006-1009 (2005).