

The nonlinear susceptibility and quantum theory

Time-dependent Schrödinger equation

Semi-classical

Take for simplicity: $\hbar \rightarrow h$

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$$

Hamiltonian $\hat{H} = \hat{H}_0 + \hat{V}(t)$

$$\hat{V}(t) = -\hat{\mu} \cdot \mathbf{E}(t)$$

$$\mathbf{E}(t) = \sum_n \mathbf{E}(\omega_n) e^{-i\omega_n t}$$

Write for perturbation theory:

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}(t)$$

$$\Psi(\mathbf{r}, t) = \Psi^{(0)}(\mathbf{r}, t) + \lambda \Psi^{(1)}(\mathbf{r}, t) + \lambda^2 \Psi^{(2)}(\mathbf{r}, t) + \dots$$

Solutions to all powers in λ

$$i\hbar \frac{\partial \Psi^{(0)}}{\partial t} = \hat{H}_0 \Psi^{(0)}$$

$$i\hbar \frac{\partial \Psi^{(N)}}{\partial t} = \hat{H}_0 \Psi^{(N)} + \hat{V} \Psi^{(N-1)}$$

→ Calculate probability amplitudes of higher order Wave functions

→ Calculate higher order polarizations

$$P_k^{(3)}(\omega_p + \omega_q + \omega_r) = \sum_{hij} \sum_{pqr} \chi_{kjih}^{(3)}(\omega_\sigma, \omega_r, \omega_q, \omega_q) E_j(\omega_r) E_i(\omega_q) E_h(\omega_p)$$

→ Calculate susceptibilities (response of medium)

- Resonance denominators as in classical response (Lorentz model of an oscillator)

- $\chi^{(3)}$ is a tensor of 4th rank

Further improvement: density Matrix formalism

Third order susceptibility

$$\chi_{kjih}^{(3)}(\omega_\sigma, \omega_r, \omega_q, \omega_p) = \frac{N}{h^3} \mathcal{P} \sum_{mnv} \dots$$

→ Permutation operator → more terms

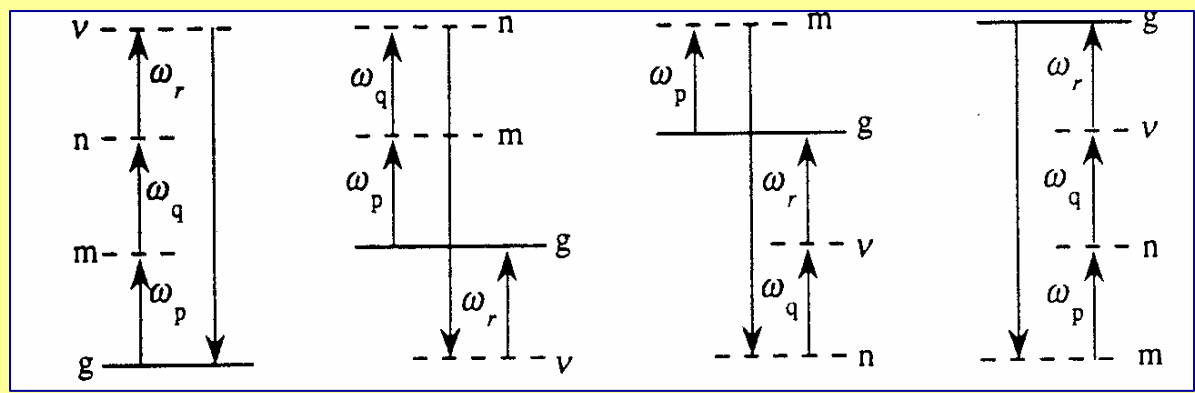
$$\times \left\{ \frac{\mu_{gv}^k \mu_{vn}^j \mu_{nm}^i \mu_{mg}^h}{(\omega_{vg} - \omega_r - \omega_q - \omega_p)(\omega_{ng} - \omega_q - \omega_p)(\omega_{mg} - \omega_p)} + \frac{\mu_{gv}^j \mu_{vn}^k \mu_{nm}^i \mu_{mg}^h}{(\omega_{vg}^* + \omega_r)(\omega_{ng} - \omega_q - \omega_p)(\omega_{mg} - \omega_p)} + \frac{\mu_{gv}^j \mu_{vn}^i \mu_{nm}^k \mu_{mg}^h}{(\omega_{vg}^* + \omega_r)(\omega_{ng}^* + \omega_r + \omega_q)(\omega_{mg} - \omega_p)} \right.$$

→ Summation over all combinations of levels

→ Product of 4 matrix dipole moments

$$\left. + \frac{\mu_{gv}^j \mu_{vn}^i \mu_{nm}^h \mu_{mg}^k}{(\omega_{vg} + \omega_r)(\omega_{ng}^* + \omega_r + \omega_q)(\omega_{mg}^* + \omega_r + \omega_q + \omega_p)} \right\}$$

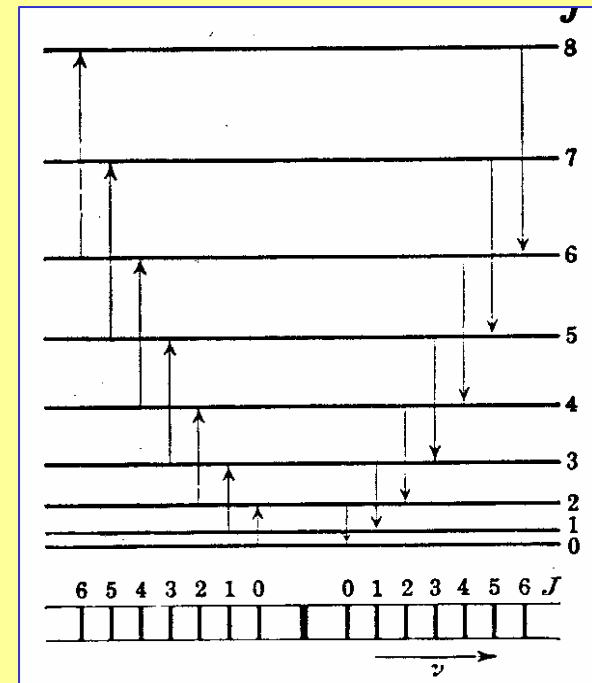
→ Resonance denominators - resonance enhancement
Damping should be included



Raman scattering in gases

Raman scattering:

- two-photon linear scattering of light
- inelastic light scattering (Rayleigh scattering is elastic)
- spontaneous Raman (all directions)
- Stokes and Anti-Stokes
- Two-photon selection rules
- Vibrational and rotational Raman (electronic Raman)



Selection rules for rotation:
 $\Delta J = -2, 0, +2$

Selection rules for vibration:
 $\Delta v = 1$

Pure rotational Raman possible with
 $\Delta v = 0$

Various forms of Stimulated Raman scattering in gases

Raman: resonance at $\omega_1 - \omega_2$

Non-linear gain processes

Direct coupling between waves, e.g. ω_1 and ω_2

One of the waves already present (pump)

→ One field is amplified with a gain factor
(starting from noise if needed)

Resonance structure of molecules determines
production of some frequencies

Phase matching property drops out:

Non-parametric process

Four-wave mixing

Input waves ω_1 and ω_2 and a wave at ω_4
produced

Novel wave at ω_3 not yet present

Polarization produced at:

$$\mathbf{P}^{NL} = \varepsilon_0 \chi^{(3)} \mathbf{E}_1 \mathbf{E}_2 \mathbf{E}_3$$

Maxwell equation with source term at ω_4
generates field at this frequency

$$\mathbf{E}_4 \propto \mathbf{P}^{NL}$$

Similar to OPO phase-matching plays a role
Intensity is proportional to:

$$I^{NL} = |\mathbf{E}_4|^2 \propto |\mathbf{P}^{NL}|^2 \propto |\chi^{(3)}|^2$$

Parametric process

Stimulated Raman; First Stokes production

Nonlinear polarization is source term in ME

$$\nabla^2 E_i - \epsilon_r \epsilon_0 \mu_0 \frac{\partial^2}{\partial t^2} E_i = \mu_0 \frac{\partial^2}{\partial t^2} P_i^{NL}$$

P^{NL} couples waves of different frequencies
Resonances due to Raman condition

Each frequency component:

$$\mathbf{E}(\mathbf{r}, t, \omega) = \mathbf{A}(\mathbf{r}, t) e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}$$

$$\nabla^2 \mathbf{E} = \left[\nabla^2 \mathbf{A} + 2i(\mathbf{k} \cdot \nabla) \mathbf{A} - k^2 \mathbf{A} \right] e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}$$

Slowly varying amplitude (space):

$$|\nabla^2 \mathbf{A}| \ll |(\mathbf{k} \cdot \nabla) \mathbf{A}|$$

Time derivative:

$$\frac{\partial^2}{\partial t^2} \mathbf{E} = \left[\frac{\partial^2}{\partial t^2} \mathbf{A} + 2i\omega \frac{\partial}{\partial t} \mathbf{A} - \omega^2 \mathbf{A} \right] e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}$$

Amplitude varies slower than ω

$$\left| \frac{\partial^2}{\partial t^2} \mathbf{A} \right| \ll \omega \left| \frac{\partial}{\partial t} \mathbf{A} \right|$$

Steady state approx: first two terms dropped

Take time derivative of P^{NL}

And imaginary part of $\epsilon_r \rightarrow \epsilon_r''$

$$2i(\mathbf{k} \cdot \nabla) \mathbf{A} + i\epsilon_r'' \epsilon_0 \mu_0 \omega^2 \mathbf{A} = -\mu_0 \omega^2 \mathbf{P}^{NL} e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)}$$

Derivative along direction r

→ Coupled amplitude equation for stimulated Raman

$$\frac{d}{dr} \mathbf{A}_s(\mathbf{r}) + \alpha \mathbf{A}_s(\mathbf{r}) = i\beta \mathbf{P}_s^{NL}(\mathbf{r}) e^{-i(\mathbf{k}_s \cdot \mathbf{r} - \omega_s t)}$$

with:

$$\alpha = \frac{\epsilon_r'' \epsilon_0 \mu_0 \omega^2}{2k} \quad \beta = \frac{\omega}{2\epsilon_0 n_\omega c}$$

First Stokes production

$$\frac{d}{dr} \mathbf{A}_S(\mathbf{r}) + \alpha \mathbf{A}_S(\mathbf{r}) = i\beta \mathbf{P}_S^{NL}(\mathbf{r}) e^{-i(\mathbf{k}_S \cdot \mathbf{r} - \omega_S t)}$$

Raman gain if $\text{Im } \chi^{(3)} < 0$

Nonlinear Raman Polarization

$$\varepsilon_0 \chi_1^{(3)}(\omega_{S1}; \omega_P, -\omega_P, \omega_{S1}) |\mathbf{A}_P|^2 \mathbf{A}_{S1} e^{i(k_P - k_P)z} e^{i\mathbf{k}_{S1} \cdot \mathbf{r}} e^{-i(\omega_P - \omega_P + \omega_{S1})t}$$



$$\frac{d}{dz} \mathbf{A}_S(r) + \alpha \mathbf{A}_S(r) = i\varepsilon_0 \beta \chi_1^{(3)} |\mathbf{A}_P|^2 \mathbf{A}_S$$

With cancelation of phase factors.
Integrate with boundary small input

$$\mathbf{A}_{S1}(\mathbf{r}) = \mathbf{A}_{S1}(0) e^{-\left[\varepsilon_0 \beta |\mathbf{A}_P|^2 \text{Im } \chi_1^{(3)} + \alpha \right] z} e^{i\varepsilon_0 \beta \left[|\mathbf{A}_P|^2 \text{Re } \chi_1^{(3)} \right] z}$$

$$g = -\varepsilon_0 \beta |\mathbf{A}_P|^2 \text{Im } \chi_1^{(3)}$$

First Stokes Raman gain:

- non-phase matched
- non parametric process
- produced on-axis

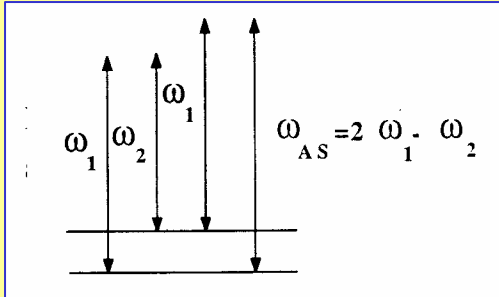
-This does not hold for Anti-Stokes (parametric process see below)

-Higher order Stokes processes via other mechanisms

Raman shifting in hydrogen:
Nearly all molecules in J=1 quantum state
4155 cm^{-1} shift

Coherent Anti-stokes Raman Spectroscopy; CARS

Four-wave mixing process with Raman resonance



$$\bar{P}_{CARS}(\omega_{AS}) = \chi^{(3)}(\omega_{AS} = 2\omega_1 - \omega_2) \bar{E}(\omega_1) \bar{E}(\omega_1) \bar{E}(\omega_2)^*$$

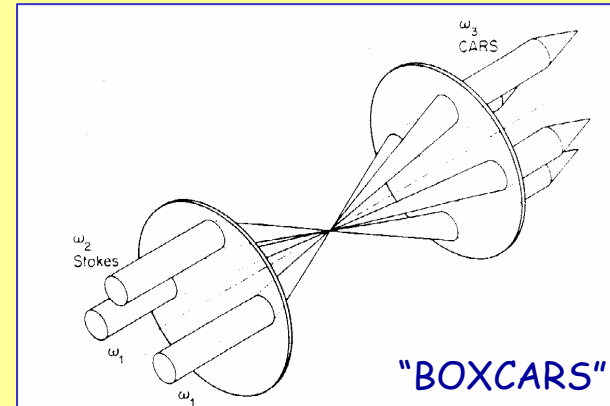
Generated intensity in medium:

$$I_{CARS} \propto \omega_{AS}^2 \left| \chi^{(3)}(\omega_{AS}) \right|^2 I_1^2 I_2 \text{sinc} \left[\frac{\Delta k L}{2} \right]$$

Again necessary condition of phase matching

$$\Delta \vec{k} = \vec{k}_{AS} - (2\vec{k}_1 - \vec{k}_2)$$

The process "phase-matches itself"
by choosing an angle



At any Raman condition:

$$\omega_{Raman} = \omega_1 - \omega_2$$

$$\omega_{AS} = 2\omega_1 - \omega_2$$

CARS susceptibility and CARS spectra

A single term in the $\chi^{(3)}$ produces a resonance

$$\chi^{(3)} = \sum N \rho_{gg} \frac{\mu_{gi} \mu_{iv} \mu_{vi} \mu_{ig}}{(\omega_1 \pm \omega_{i0}) (\omega_1 - \omega_2 - \omega_{v0} - i\Gamma_{v0}) (\omega \pm \omega_{i0})}$$

$$\omega_1 - \omega_2 = \omega_{v0}$$

Raman resonance and damping

Density of ground state population(s)

$$\chi^{(3)} \propto \frac{N_J S_{JJ}}{(\omega_1 - \omega_2 - \omega_{v0} - i\Gamma_{v0})} + \chi_{NR}$$

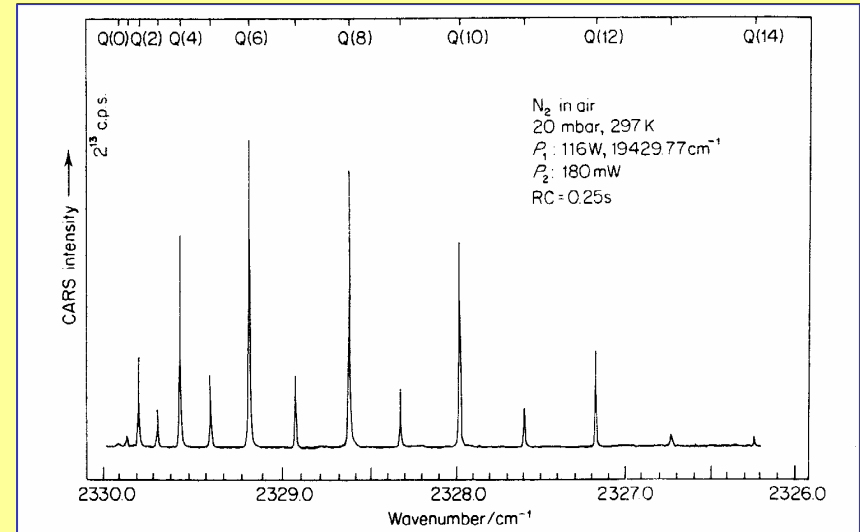
$$I_{CARS} \propto \left| \chi^{(3)} \right|^2 \propto \left| \frac{N_J S_{JJ}}{(\omega_1 - \omega_2 - \omega_{v0} - i\Gamma_{v0})} + \chi_{NR} \right|^2$$

Spectrum determined by:

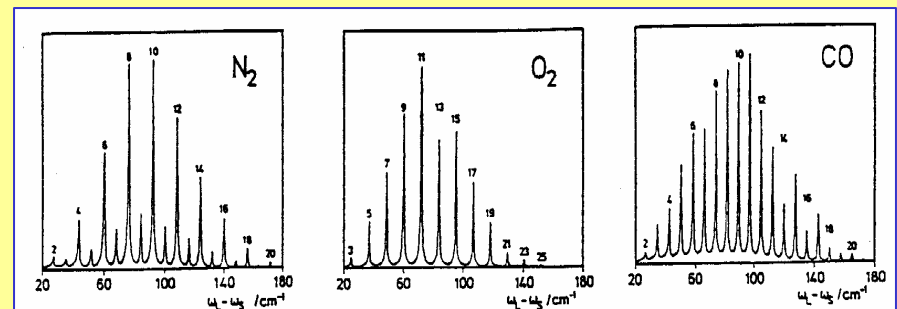
- Raman resonance condition (selection rules)
- proportional to density-squared
- interference effects due to background
- Boltzmann factor

$$N_J \propto (2J+1) \exp\left[-\frac{B_{rot} J(J+1)}{k_B T}\right]$$

Vibrational CARS in nitrogen



Rotational CARS



$$\chi^{(3)} \propto \frac{(N_J - N_{J'}) S_{JJ'}}{(\omega_1 - \omega_2 - \omega_{JJ'} - i\Gamma_{JJ'})} + \chi_{NR}$$