Survey
on
Laser Spectroscopic Techniques for Condensed Matter

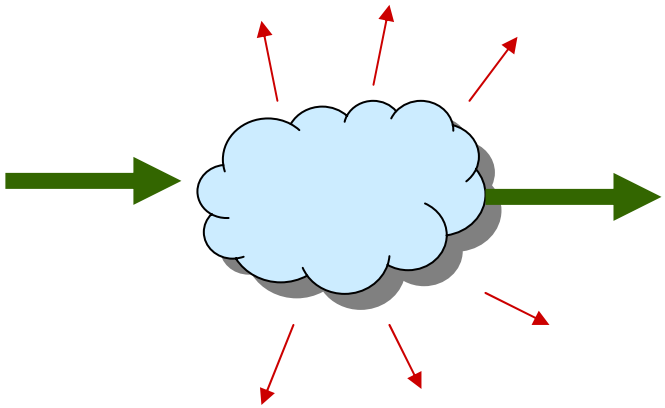
Coherent Radiation Sources for Small Laboratories

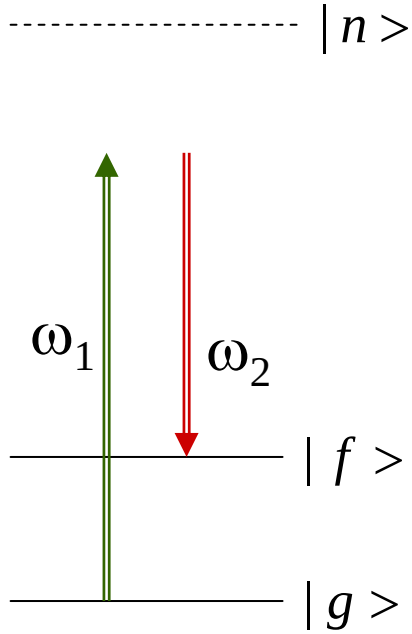
CW: Tunability: IR—Visible
Linewidth: 1 Hz
Power: μW—10W

Pulsed: Tunabality: THz — Soft X-ray
Pulse width: ns, ps, fs
Linewidth: Transform limited
Power: up to TW for fs pulses

Quasi-cw: ~100 MHz mode-locked pulses
Tunability: IR — Visible
Frequency Comb: Periodic fs pulses
Spectral components with~100 MHz spacing
and <KHz linewidth
Stable carrier/envelope phase relation

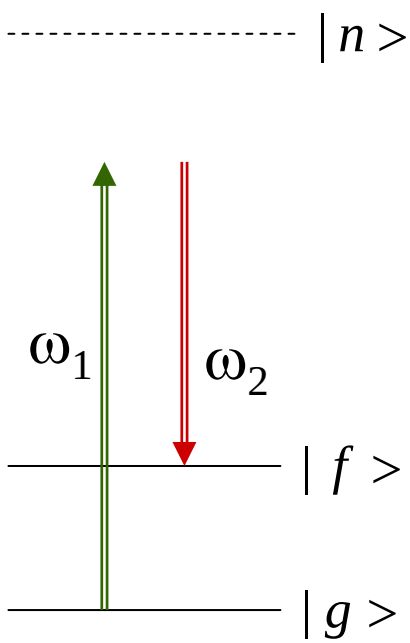
Light Scattering



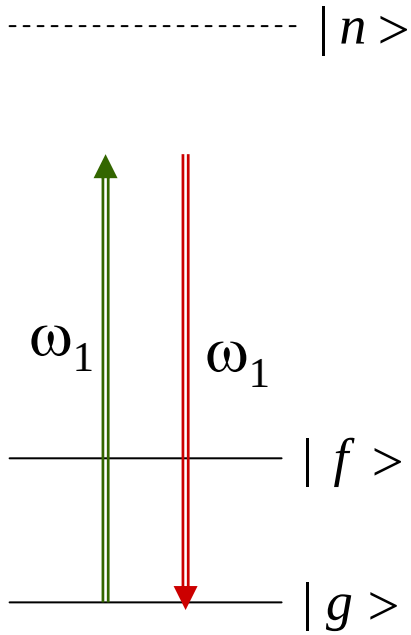


$$\frac{d\sigma}{d\Omega} \propto \frac{\omega_1 \omega_2^3}{c^4} \left| \sum_n \left[\frac{< f \mid e\vec{r} \cdot \hat{e}_1 \mid n >< n \mid e\vec{r} \cdot e_2 \mid g >}{\omega_1 - \omega_{ng}} - \frac{< f \mid e\vec{r} \cdot \hat{e}_1 \mid n >< n \mid e\vec{r} \cdot e_2 \mid g >}{\omega_2 + \omega_{ng}} \right] \right|^2$$

Raman Scattering



Rayleigh Scattering



$$S = N \frac{d\sigma}{d\Omega} \Delta\Omega (I / \hbar\omega) V \quad \text{photons/sec}$$

Estimates of Signal Strength

$$\frac{d\sigma}{d\Omega} \equiv \frac{\text{Scattered \#photons in d}\Omega\text{ per sec}}{\text{Incoming photon intensity}}$$

$$N\left(\frac{d\sigma}{d\Omega}\right)_{Raman} \sim 10^{-8}\ \text{cm}^{-1}$$

$$N\left(\frac{d\sigma}{d\Omega}\right)_{Rayleigh} \sim 10^{-6}\ \text{cm}^{-1}$$

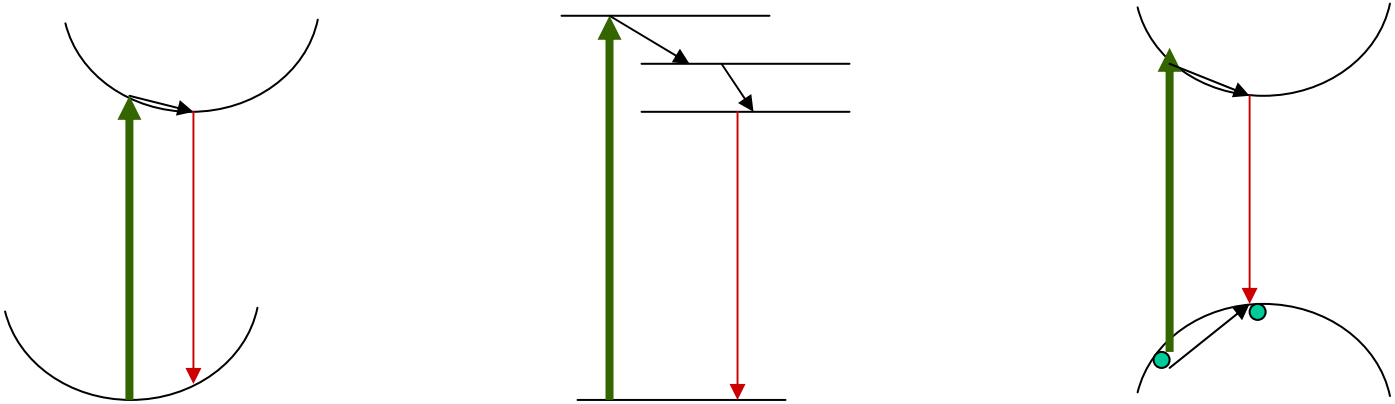
For a 1-mW beam focused to a spot of 10x10x10 μm^3,

$$(I/\hbar\omega)V \sim 10^{15}\ \text{photons/sec}$$

$$S_{Raman} \sim 10^{7}\,\Delta\Omega\ \text{photons/sec}$$

$$S_{Rayleigh} \sim 10^{9}\,\Delta\Omega\ \text{photons/sec}$$

Luminescence/Fluorescence



$$\sigma_L = \sigma_{abs}\eta_R \frac{\text{Rate of lum. trans.}}{\text{Total decay rate}} = \sigma_{abs}\eta_R R_L T_1$$

$$\beta = \text{absorption coefficient} = N\sigma_{abs}$$

$$\frac{\#\text{Photons emitted}}{\#\text{Photons absorbed}} = \eta_R R_L T_1$$

Luminescence >> Rayleigh Scattering

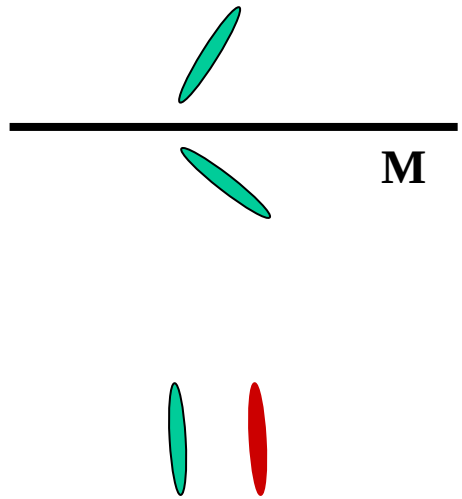
(Single Molecule Detection)

Fluorescence Quenching

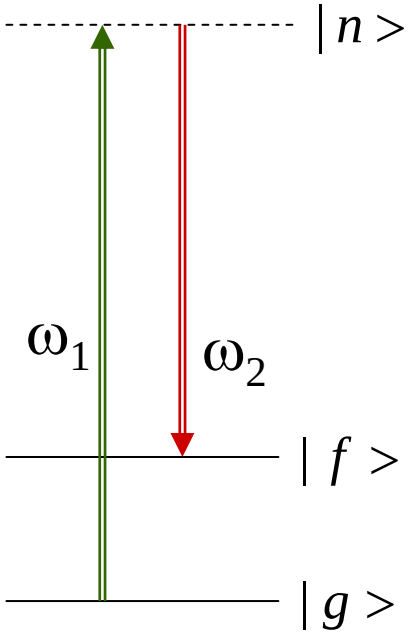
$$\text{Intermolecular Interaction} = C / R^6$$

Excitation energy transferred to neighbors through interactions:

- Fluorescence quenching of molecules on metals
- Fluorescence resonance energy transfer (FRET) between molecules



Resonant Light Scattering & Hot Luminescence



$$\left(\frac{d\sigma}{d\Omega}\right)_{Raman} \propto \frac{\omega_1 \omega_2^3}{c^4} \left| \sum_n \frac{< f \,|\, e\vec{r}\cdot\vec{e}_1 \,|\, n >< n \,|\, e\vec{r}\cdot e_2 \,|\, g >}{\omega_1 - \omega_{ng} + i/T_2} \right|^2$$

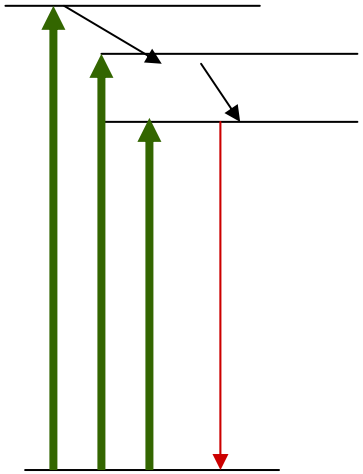
$$\sigma_L = \sigma_{abs} \frac{\text{emission rate}}{\text{total decay rate}}$$

$$\propto \; |< n \,|\, e\vec{r}\cdot\vec{e}_1 \,|\, g >|^2 \, T_2 \, |< f \,|\, e\vec{r}\cdot e_2 \,|\, n >|^2 \, T_1$$

Resonant enhancement of scattering:

$$\eta_{sc} \sim \left| \frac{1/T_2}{\omega - \omega_{ng}} \right|^2 \sim 100 \quad \text{if} \quad 1/T_2 \sim 10^3 \text{ cm}^{-1}, \quad \omega - \omega_{ng} \sim 10^4 \text{ cm}^{-1}$$

Excitation Spectrum



$$\sigma_L = \sigma_{abs}\eta_R \frac{\text{emission rate}}{\text{Total decay rate}}$$

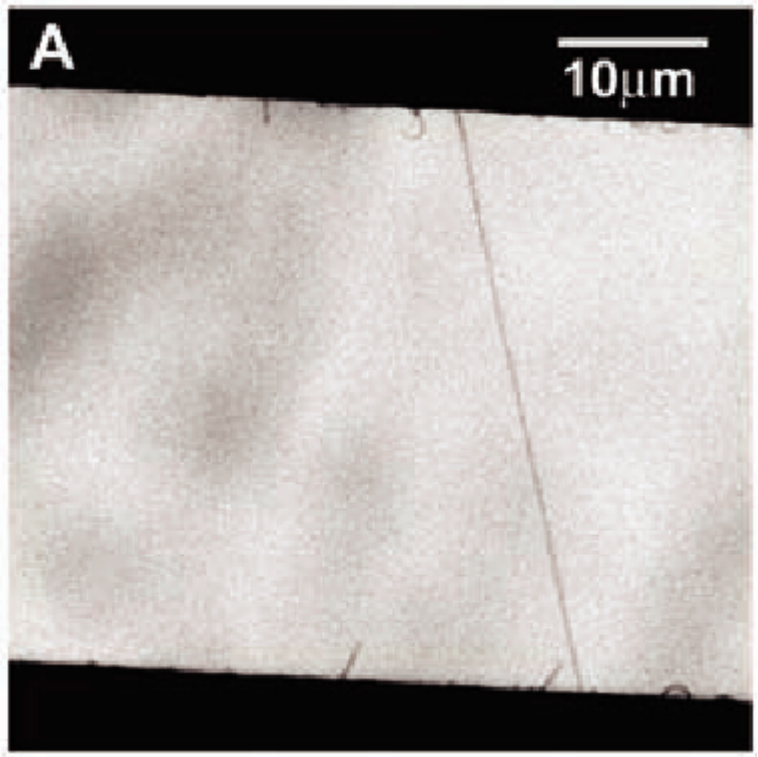
$$\propto \sigma_{abs}$$

$$\sigma_{Rayleigh} \propto \left| \sum_n \frac{< f \mid e\vec{r} \cdot \hat{e}_1 \mid n >< n \mid e\vec{r} \cdot e_2 \mid g >}{\omega_1 - \omega_{ng} + i/T_{2,ng}} \right|^2$$

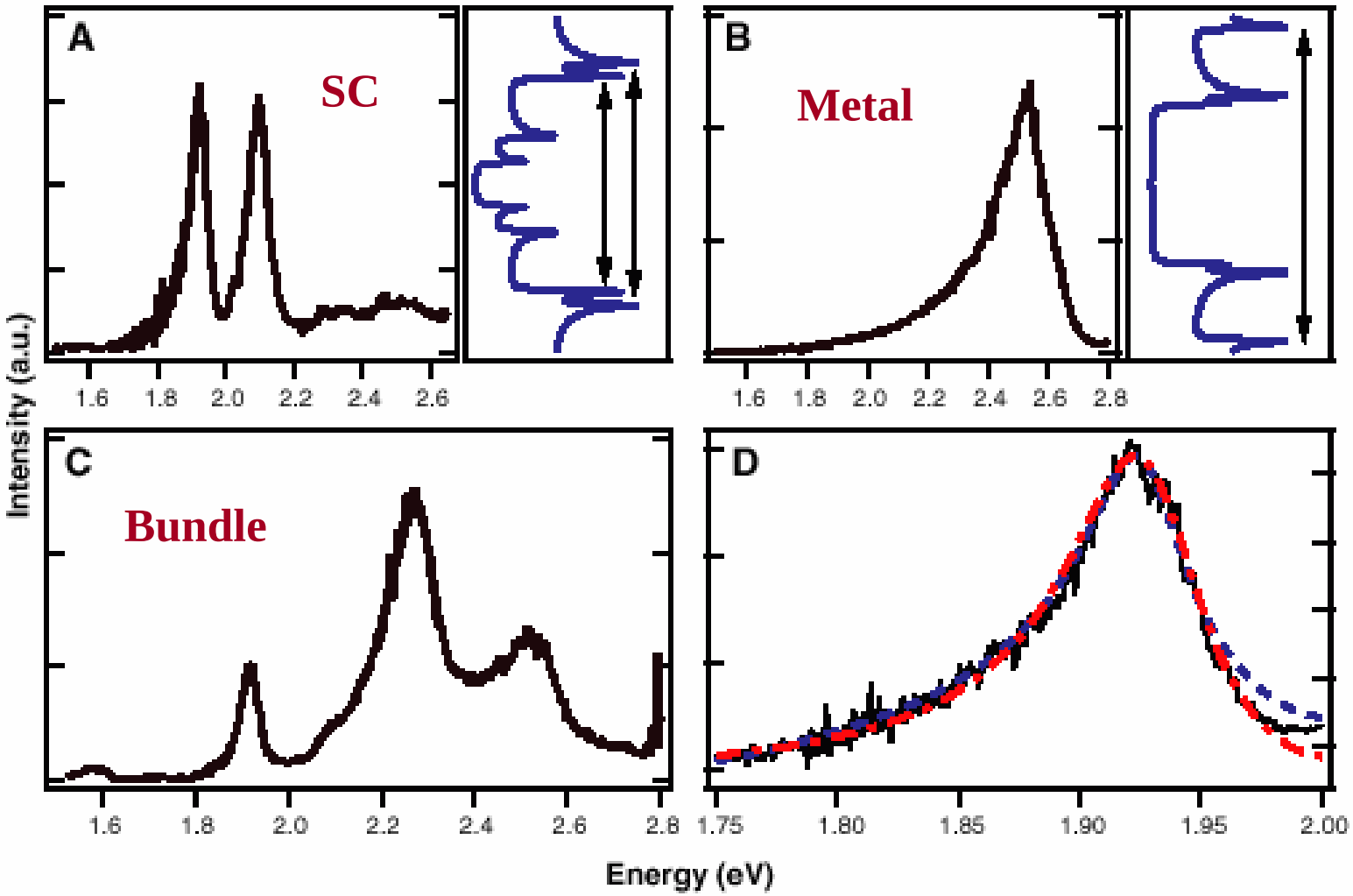
Resonant enhancement in σ_L or $\sigma_{Rayleigh}$ yields the excitation spectrum

$\Rightarrow\Rightarrow$ A sensitive method to obtain absorption spectrum

A Single Carbon Nanotube

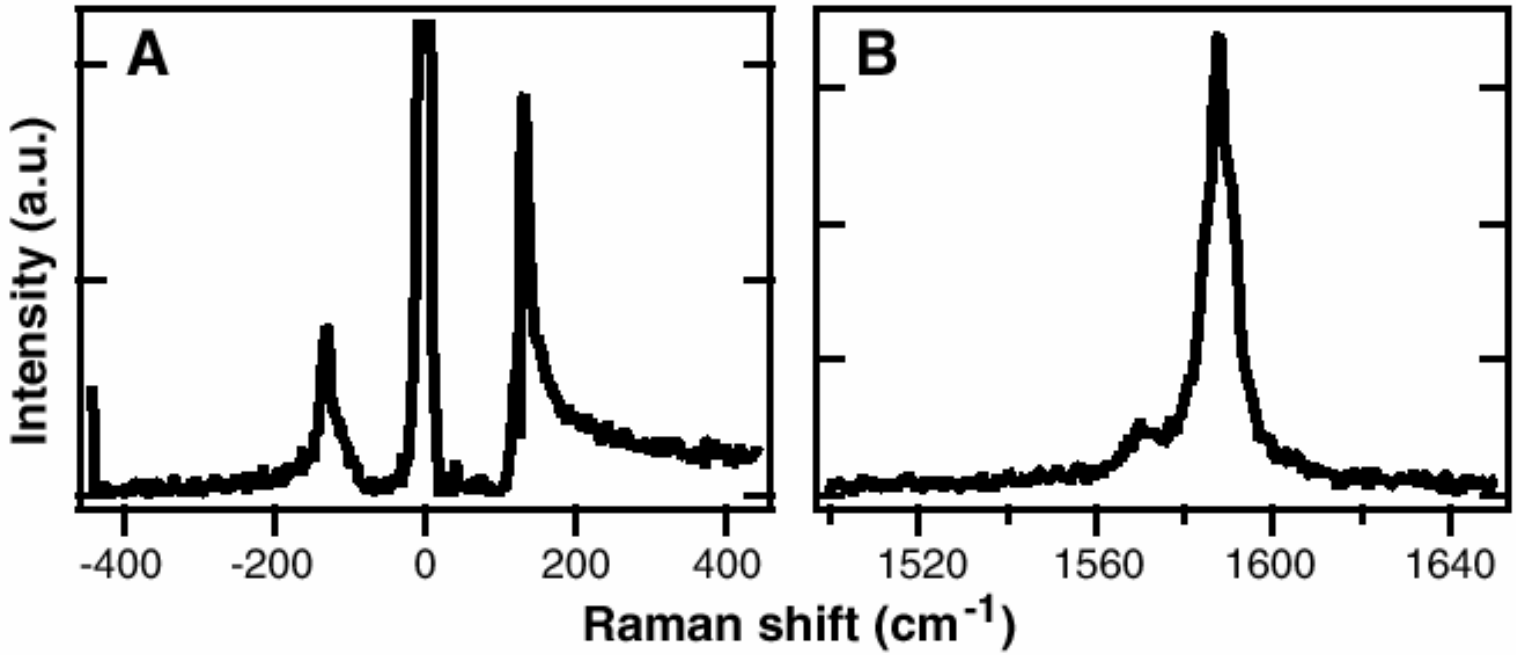


Excitation Spectra of Rayleigh Scattering of Carbon Nanotubes



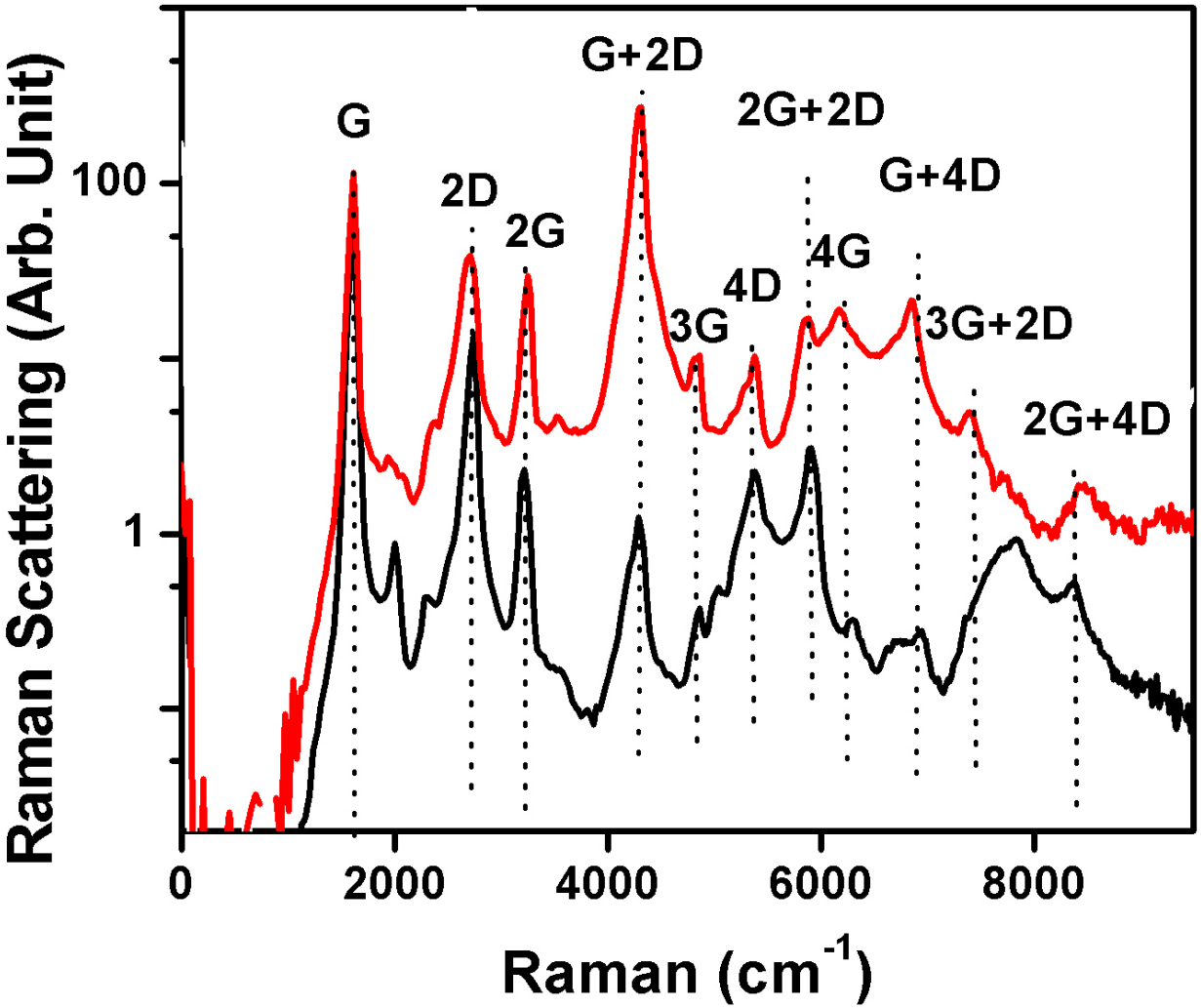
M.Y. Sfeir et al, Science **306**, 1540 (2004)

Resonance Raman Scattering from Single-Wall Carbon Nanotubes



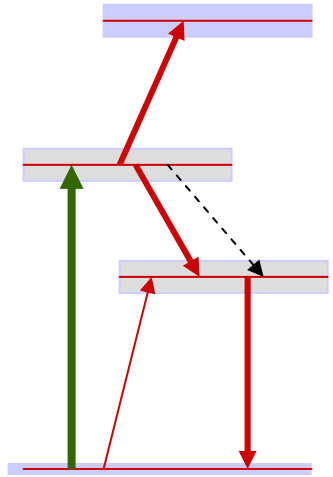
M.Y. Sfeir et al, Science **306**, 1540 (2004)

Multi-Phonon Raman Scattering from Single SW Carbon Nonotubes



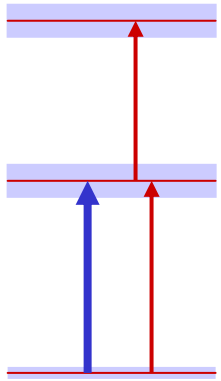
Labeling Spectroscopy

- **Elimination or reduction of inhomogeneous broadening**
- **Selective detection or probe of species in an ensemble**
- **Studies of interactions and energy transfer between neighbors**

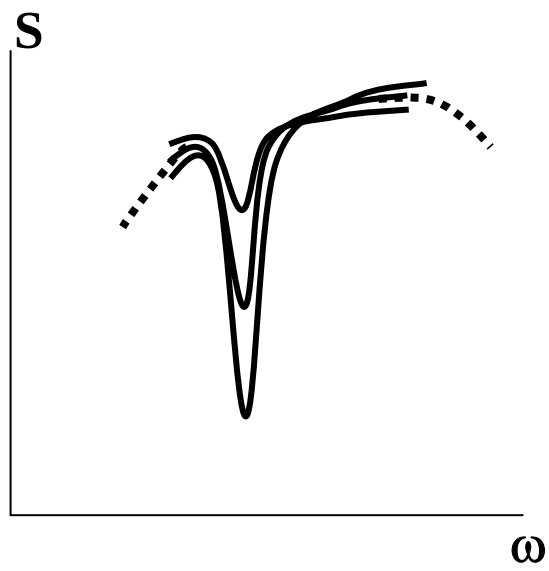


Examples: Carbon nanotubes
Semiconductor nanoparticles

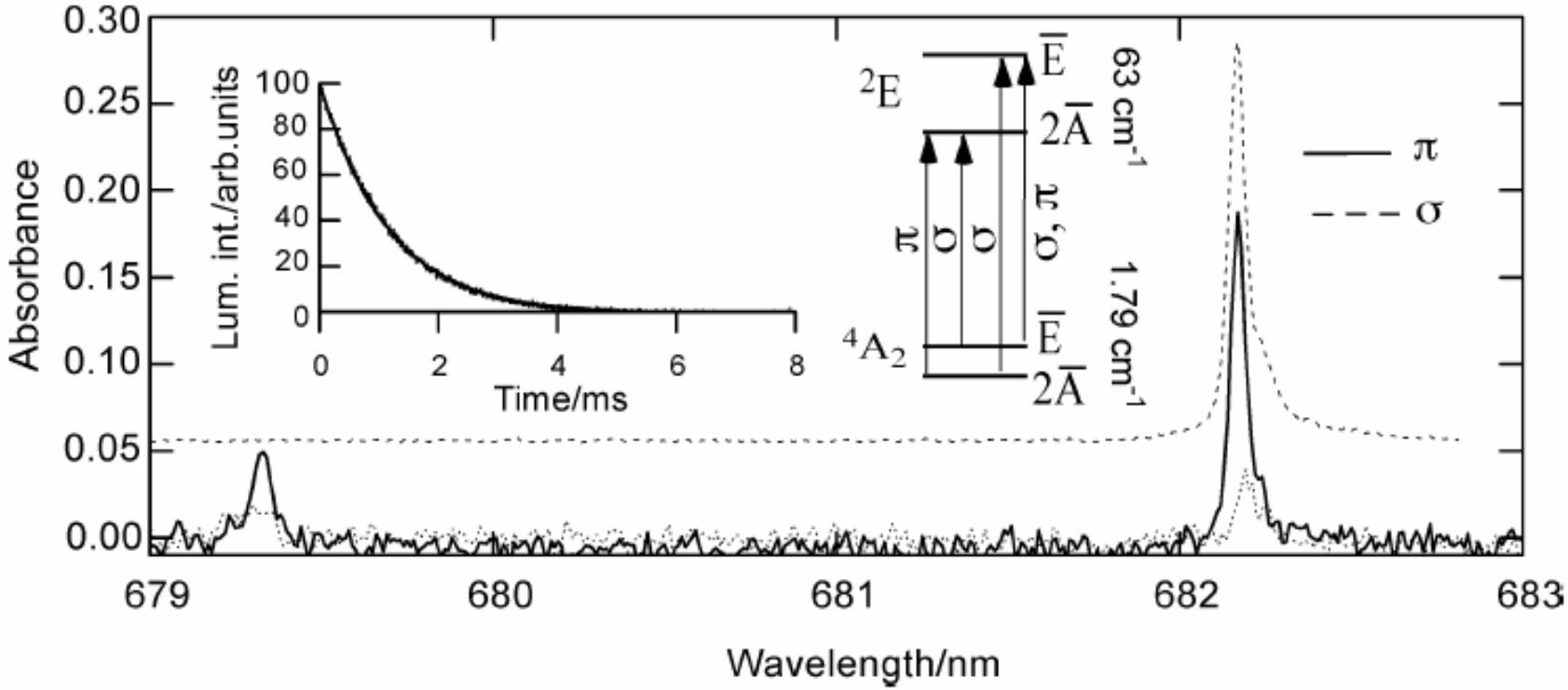
Spectral Hole Burning

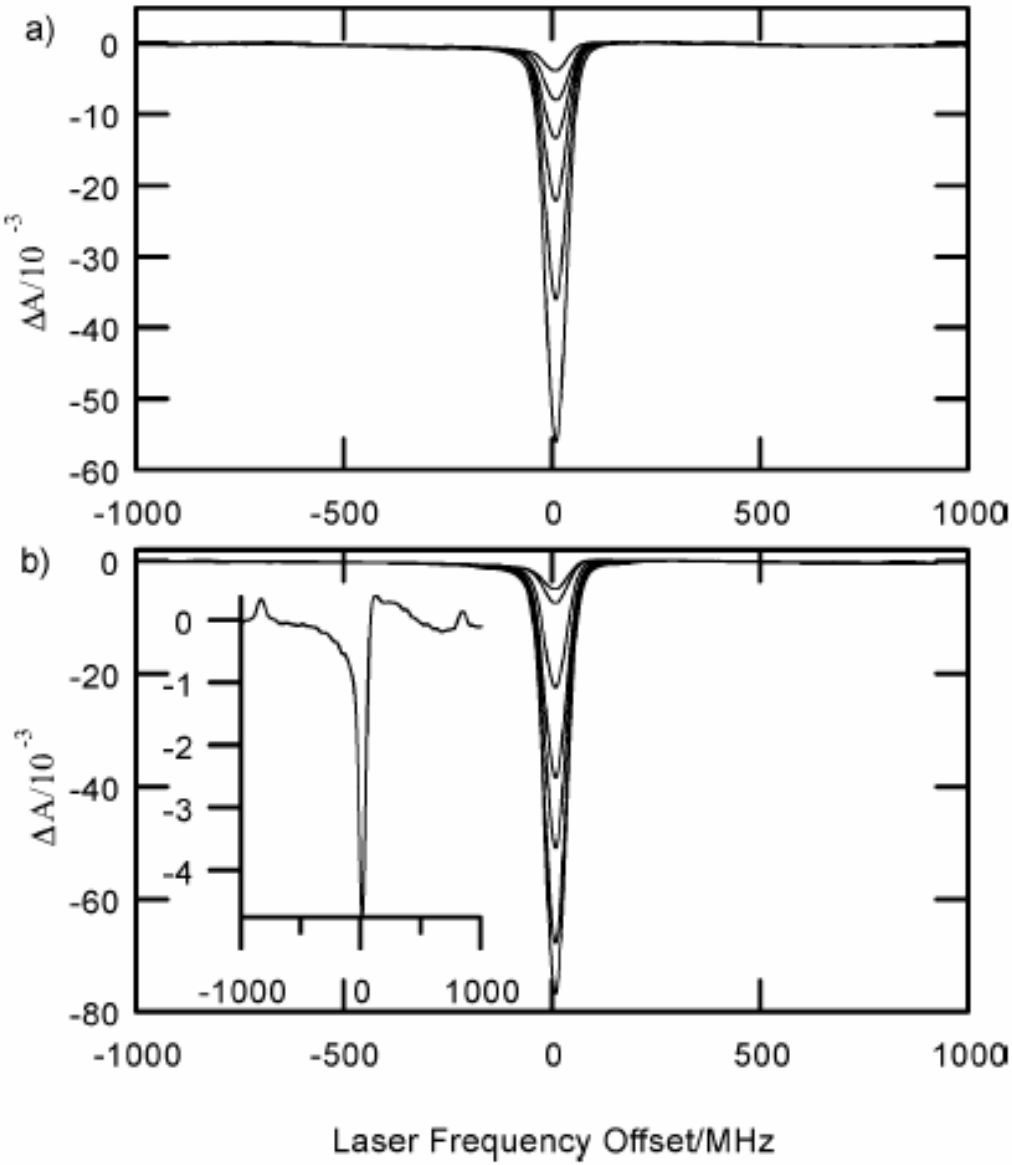


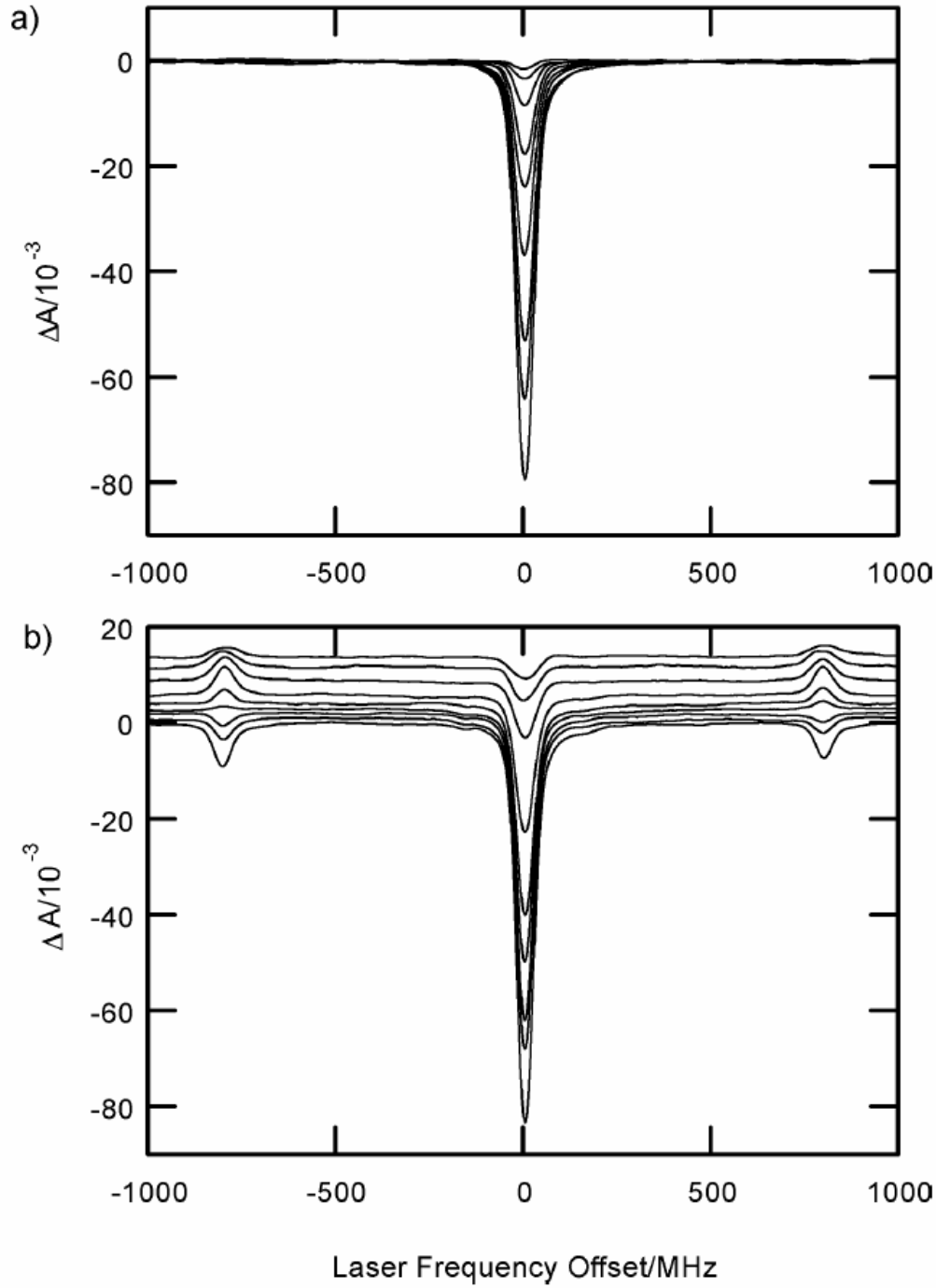
- hole width ~ homogeneous linewidth
  = 1/dephasing time
- hole recovery time
  ~ population relaxation time
- hole broadening with time
  ~ excitation transfer to neighbors
  (spectral diffusion)



Absorption Spectra of $Be_3Al_2Si_6O_{18}$:Cr (Emrald) at 2.5K



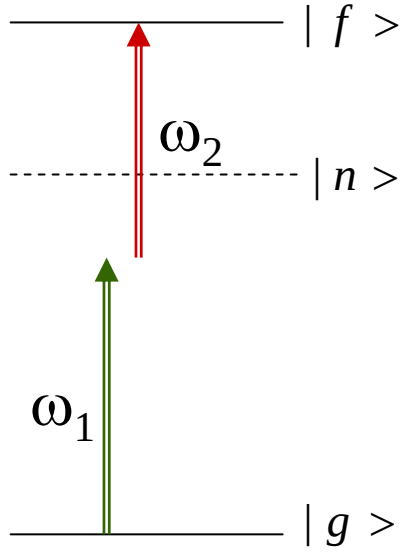

a)
b)
0
-10
-20
-30
-40
-50
-60
-80
ΔA/10^-3
-1000
-500
0
500
1000
-1
-2
-3
-4
Laser Frequency Offset/MHz


a)
0
-20
-40
-60
-80
ΔA/10-3
-1000
-500
0
500
1000
b)
20
0
-20
-40
-60
-80
ΔA/10-3
-1000
-500
0
500
1000
Laser Frequency Offset/MHz

Multi-Photon Excitation

Multi-photon absorption

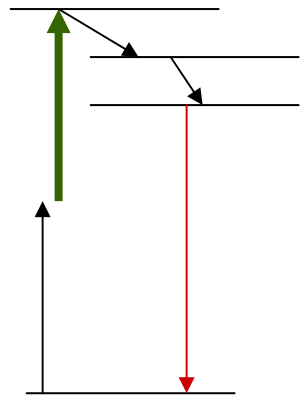
$$\sigma_{abs}^{(2)} \propto \left| \sum_{n} \left[\frac{< f | e\vec{r} \cdot \hat{e}_1 | n >< n | e\vec{r} \cdot e_2 | g >}{\omega_1 - \omega_{ng}} + \frac{< f | e\vec{r} \cdot \hat{e}_1 | n >< n | e\vec{r} \cdot e_2 | g >}{\omega_2 - \omega_{ng}} \right] \right|^2$$



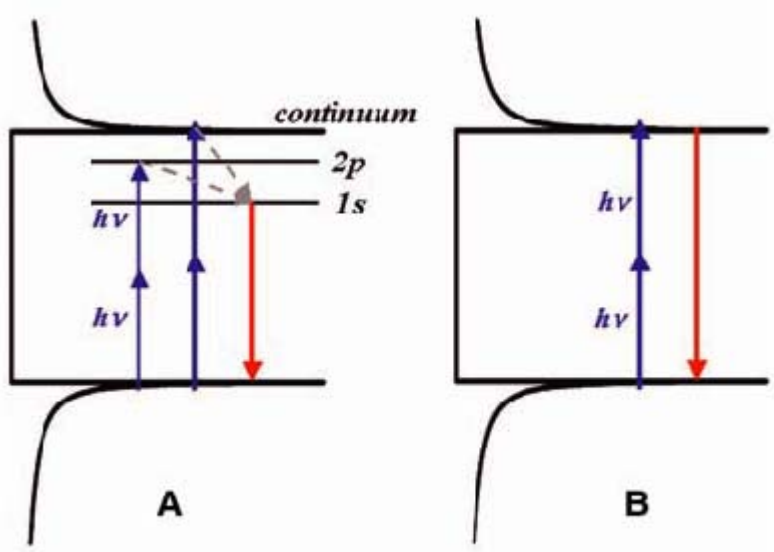
Multi-photon-excited Luminescence

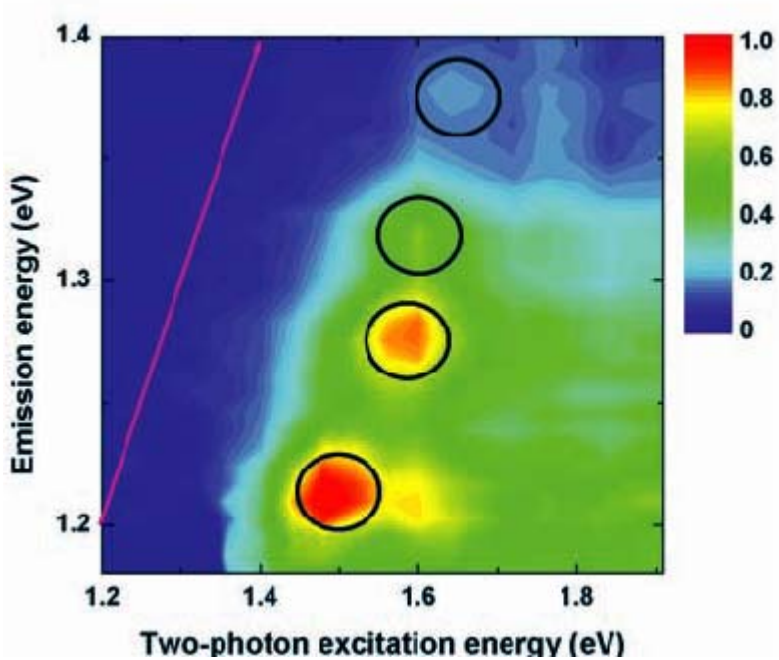
$$\sigma_{L}^{(2)} = \sigma_{abs}^{(2)} \eta_R \frac{\text{Rate of lum. trans.}}{\text{Total decay rate}} = \sigma_{abs}^{(2)} \eta_R R_L T_1$$

$$\frac{\#\text{Photons emitted}}{\#\text{Photons absorbed}} = \eta_R R_L T_1$$

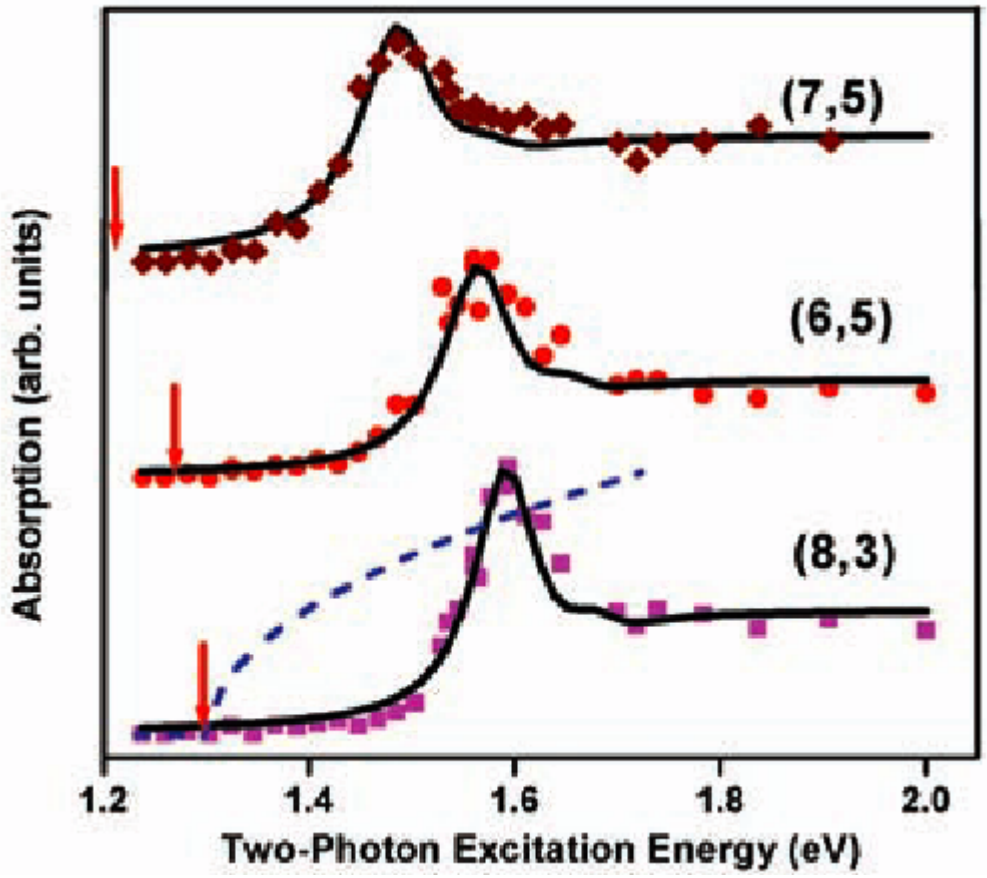


Two-Photon Excitation Spectra of Single-Wall Carbon Nanotubes



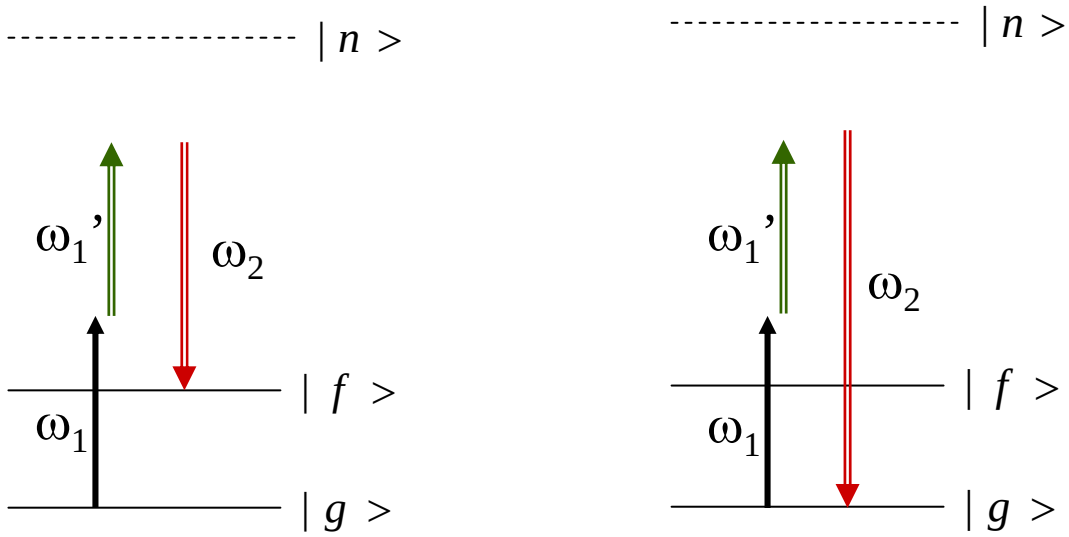


F. Wang et al, Science **308**. 838 (2005)



F. Wang et al, Science **308**. 838

Hyper-Light Scattering



$$\frac{d\sigma}{d\Omega} \propto \left| \sum_{n,n'} \left[\frac{< f | e\vec{r} \cdot \hat{e}_2 | n' >< n' | e\vec{r} \cdot e_1' | n >< n | e\vec{r} \cdot e_1 | g >}{(\omega_1 - \omega_{ng})(\omega_1 + \omega_1' - \omega_{ng})} + - - - \right] \right|^2$$

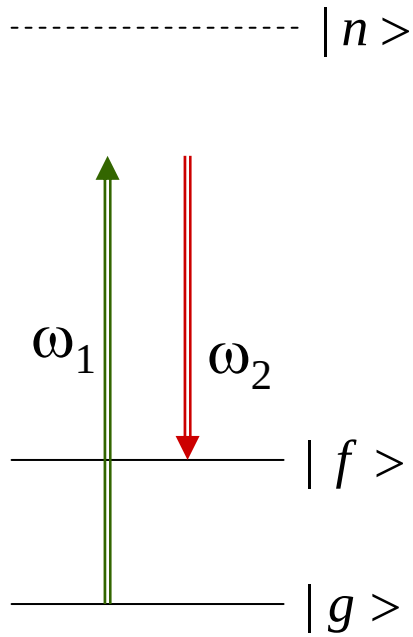
Stimulated Raman Spectroscopy

$$\frac{dn_2}{dz} = -\frac{dn_1}{dz} = \gamma n_1 (n_2 + 1)$$

$$\approx \gamma n_1 n_2$$

$$n_2 = n_{20} e^{\gamma n_1 z} \approx n_{20}(1 + \gamma n_1 z)$$

$$\text{Raman Gain} = \gamma n_1 \propto N \frac{d\sigma}{d\Omega} \frac{1}{\Gamma} n_1$$



For $N \frac{d\sigma}{d\Omega} \sim 10^{-8}$ / cm and $\Gamma \sim 1\ \text{cm}^{-1}$,

$\gamma \sim 10^{-3}$ cm/MW

Gain $\sim 1\ \text{cm}^{-1}$ for $I_1 = n_1 \hbar \omega_1 c \sim 1\ \text{GW/cm}^2$

Estimate of Detection Limit

Consider a 100-fs input pulse at ω_1 with 0.1 μJ/pulse, focused to a 10 μm spot: $I \sim 10^{12}$ W/cm^2

$$\frac{\Delta n_2}{n_{20}} = \frac{\Delta I_2}{I_{20}} \approx (Gain)z, \qquad \text{Gain} = \gamma n_1 \propto [N(d\sigma/d\Omega)/\Gamma]n_1$$

$$\text{detectable } [(Gain)z]_{\min} \sim 10^{-6}.$$

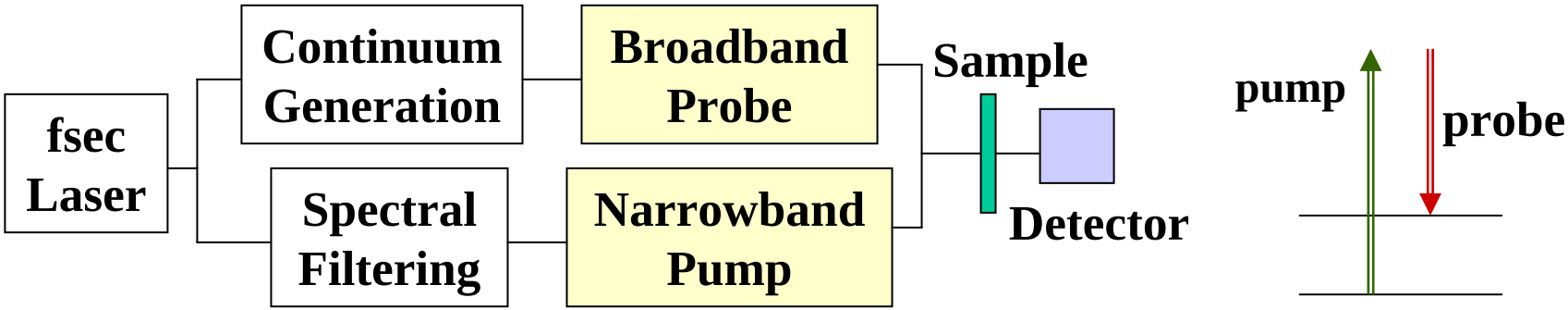
With $z \sim 1$ mm and $I \sim 10^{12}$ W/cm^2,

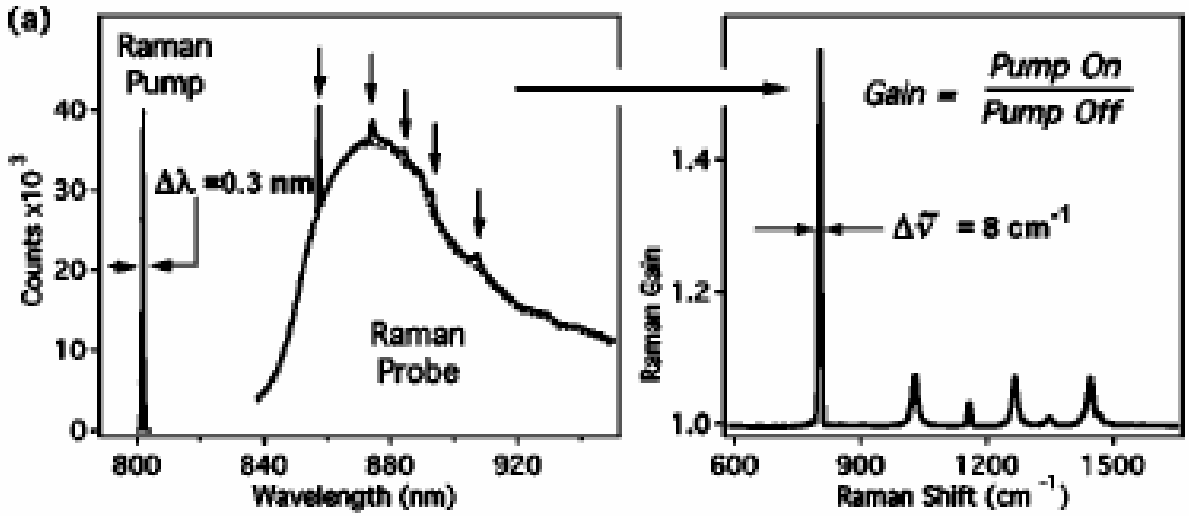
detectable $\gamma_{\min} \sim 10^{-11}$ cm/MW

or $[N(d\sigma/d\Omega)/\Gamma]_{\min} \sim 10^{-16}/\text{cm}$

as compared to typical $N(d\sigma/d\Omega)/\Gamma \sim 10^{-8}/\text{cm}$

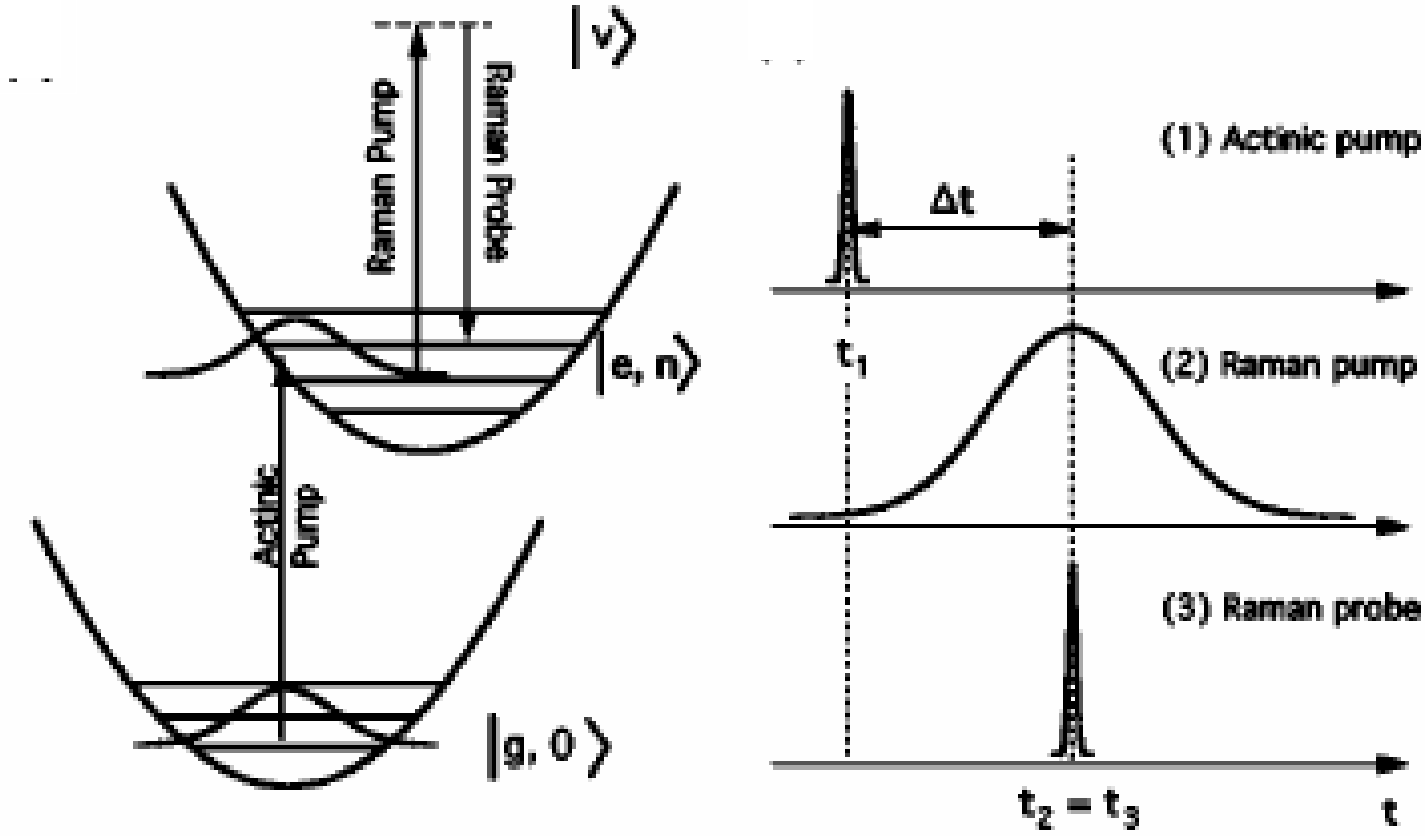
Experimentals





McCamant et al, Rev. Sci. Inst. 75, 4971(2004)

Probing Vibrations in Excited Electronic Configurations

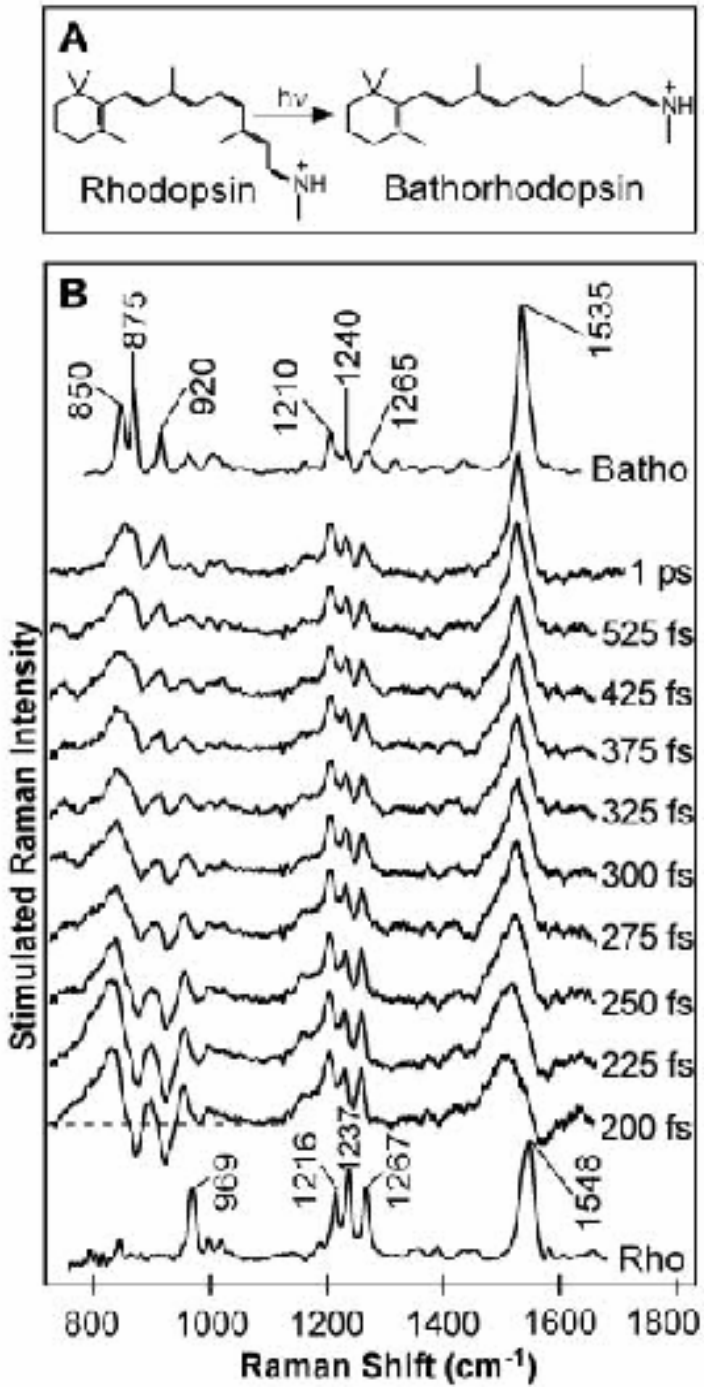


Merits:

- **Background elimination**
- **Fluorescence rejection (making resonant Raman studies possible)**
- **Fast data collection (pump intensity, ~1 GW/cm^2; path length, ~3 mm; SNR ~ 2 with single shot)**
- **Ultrafast time resolution (~ 100 fs)**
- **Reasonable spectral resolution (< 10 cm^{-1})**
- **Capable of probing transient vibrational modes in the excited electronic configurations**

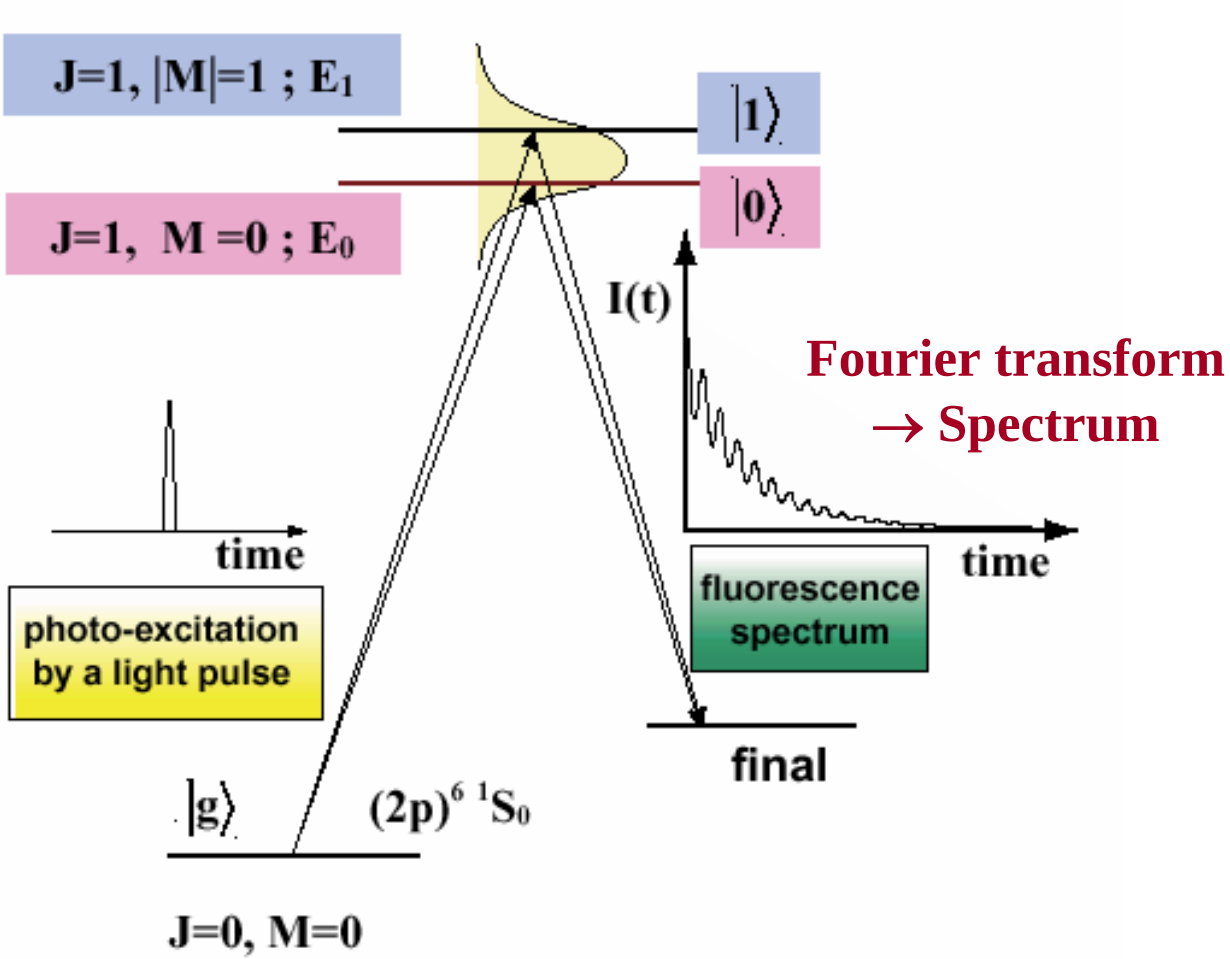
Example:

Light-Induced cis-trans Isomerization of Retinal in Rhodopsin



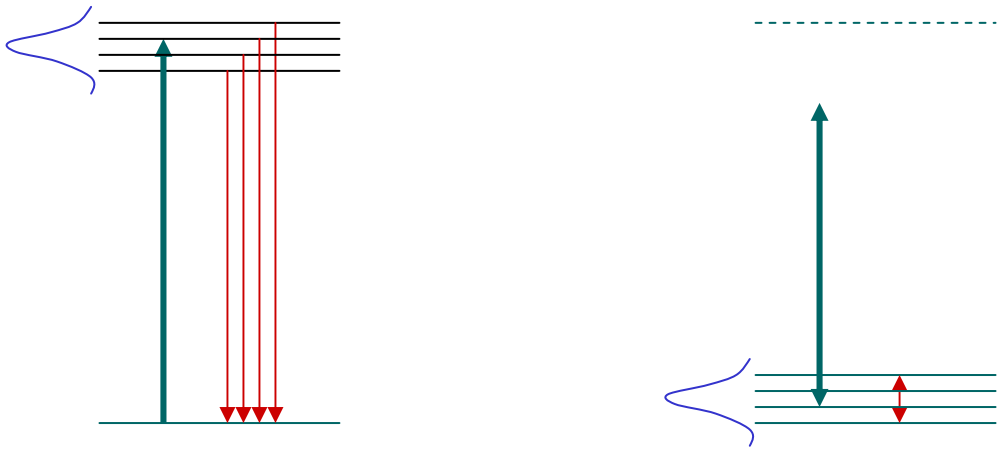
Kukura et al, Science *310*, 1006 (2005)

Quantum Beats
(resulting from pulse excitation)



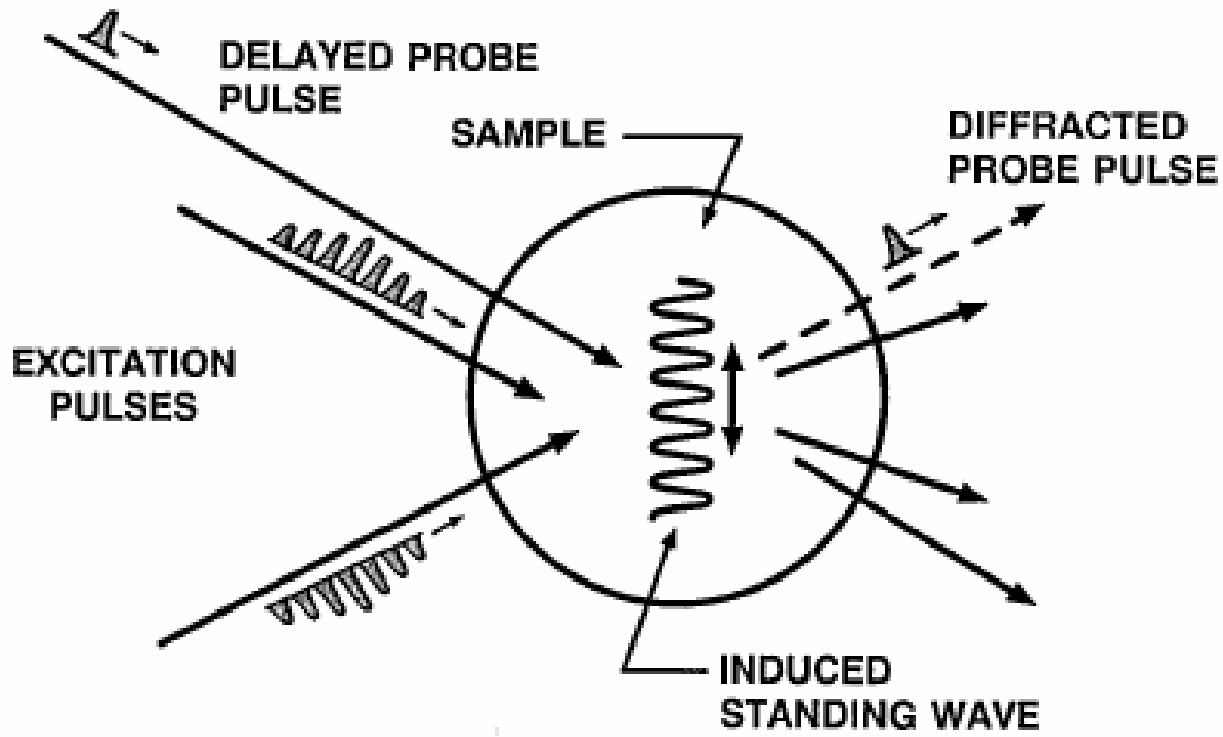
Impulsive Excitations

100-fs pulse $\Longleftrightarrow$ ~ 300 cm^{-1} spectral width

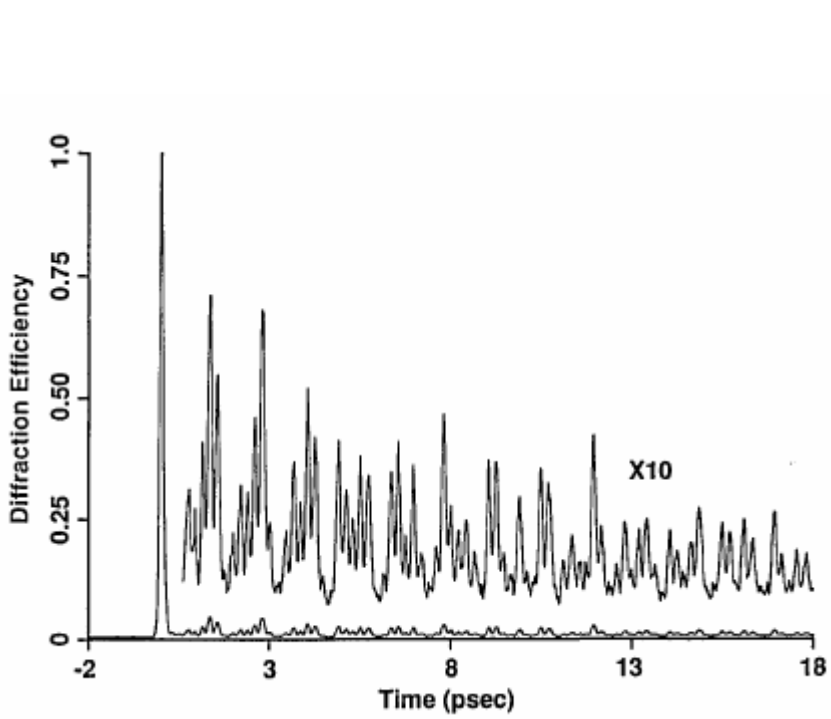


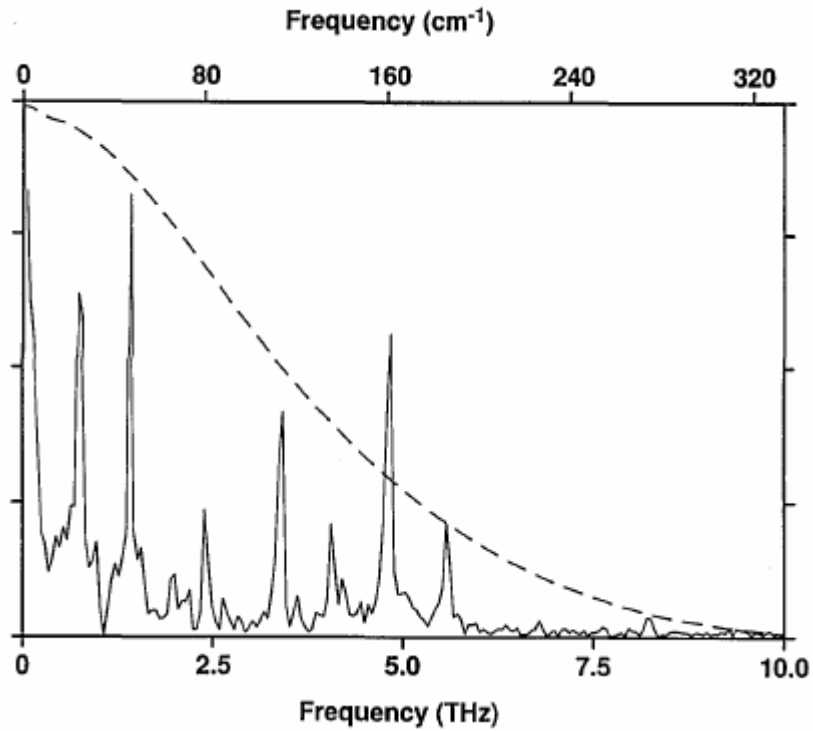
fs pulse sets up coherent excitations in a set of excited states. Signal appears as oscillation on the fs time scale. Fourier transform of the time-dependent signal yields the spectrum.

Time-Resolved Impulsive Raman Spectroscopy



Impulsive Stimulated Raman Spectroscopy: Perylene Crystal



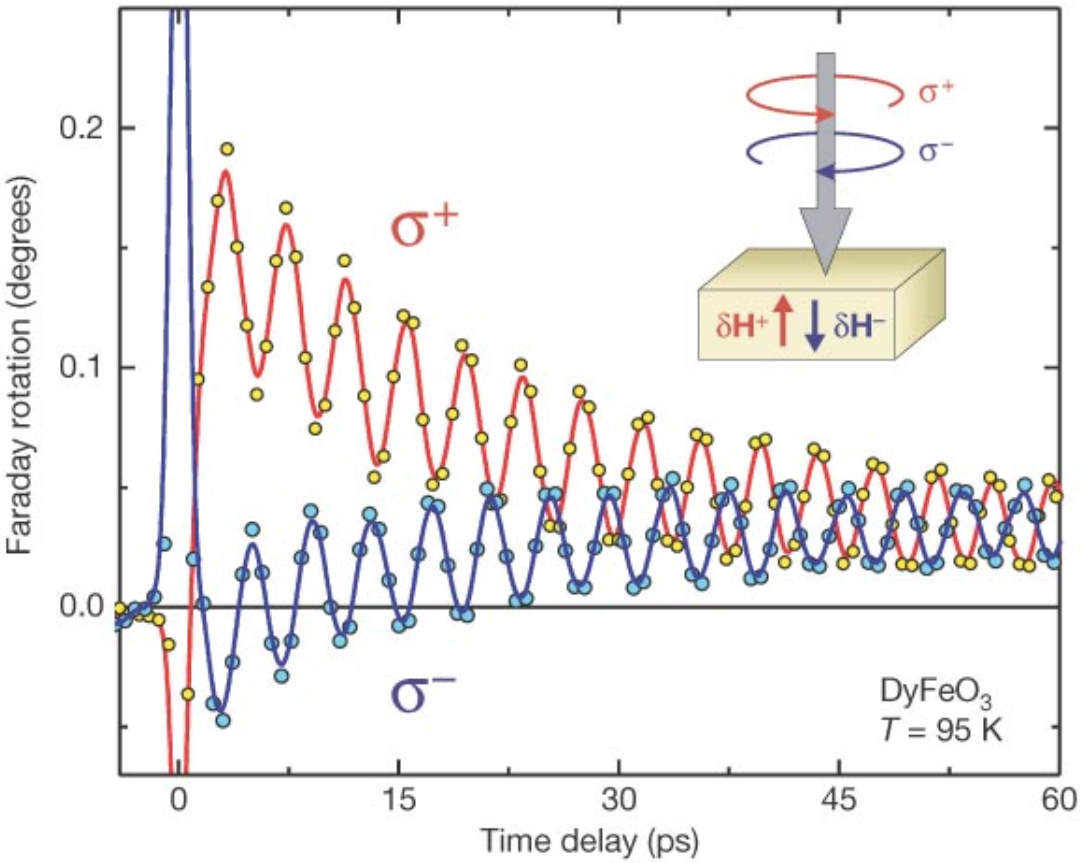


Weiner et al JOSA B8, 1264 (1991)

Time-Resolved Impulsive Spectroscopy

- **Molecular vibrations**
- **Phonons**
- **Plasmons**
- **Phonon-plasmons**
- **Magnons (spin waves)**
- **Other elementary excitations**

Impulsive Spin Excitations in $DyFeO_3$



Detection by Faraday Rotation

$$\theta_F \propto M_z = Ae^{-\gamma t} + Be^{-\gamma' t}\cos\omega t$$

Kimel et al, Nature 435, 655(2005)

Optical field induces magnetization?

Optical Rectification & Opical-Field-Induced Magnetization

Time-averaged Free Energy:

$$F = F_0(H_{dc}) - \sum_{i,j} \chi^{(1)}_{ij}(H_{dc}) E^*_i(\omega) E_j(\omega)$$

$$[\approx -(\gamma_{+0} - \gamma_{-0}) H_{dc,z} (|E_+(\omega)|^2 - |E_-(\omega)|^2)/2]$$

$$- \sum_{i,j,k} \chi^{(2)}_{ijk} E_{dc,i} E^*_j(\omega) E_k(\omega) + - -$$

Induced dc polarization:

$$P_{dc,i} = -\frac{\partial F}{\partial E_{dc,i}} = \sum_{j,k} \chi^{(2)}_{ijk} E^*_j(\omega) E_k(\omega)$$

Induced dc magnetization:

$$\Delta M_{dc,z} = -\frac{\partial F}{\partial H_{dc,z}} = (\gamma_{+0} - \gamma_{-0})(|E_+(\omega)|^2 - |E_-(\omega)|^2)/2$$

Optical-Field-Induced Magnetization

$$\Delta F = -(\gamma_{+0} - \gamma_{-0}) H_{dc,z} (|E_+(\omega)|^2 - |E_-(\omega)|^2)/2 = -\Delta M_z H_{dc,z}$$

$$\Delta M_{+z} = (\gamma_{+0} - \gamma_{-0}) |E_+(\omega)|^2 = \chi_H H_{eff}$$

$$H_{eff} = [(\gamma_{+0} - \gamma_{-0})/\chi_H] |E_+(\omega)|^2$$

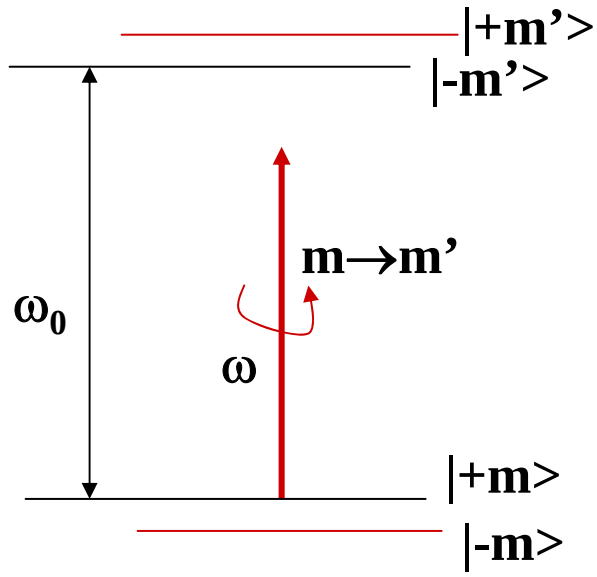
For $|E_+(\omega)|^2 \sim 10^8$ esu $(2.5x10^{10}$ W/cm$^2)$,

$(\gamma_{+0} - \gamma_{-0}) \sim 10^{-8}$/gauss $(\sim 0.1^0$ / gauss-cm),

and $\chi_H \sim 10^{-4}$ emu (at $T = 30K$),

$H_{eff} \sim 10^4$ gauss (fs pulse of magnetic field)

Physical Interpretation (AC Stark Effect)



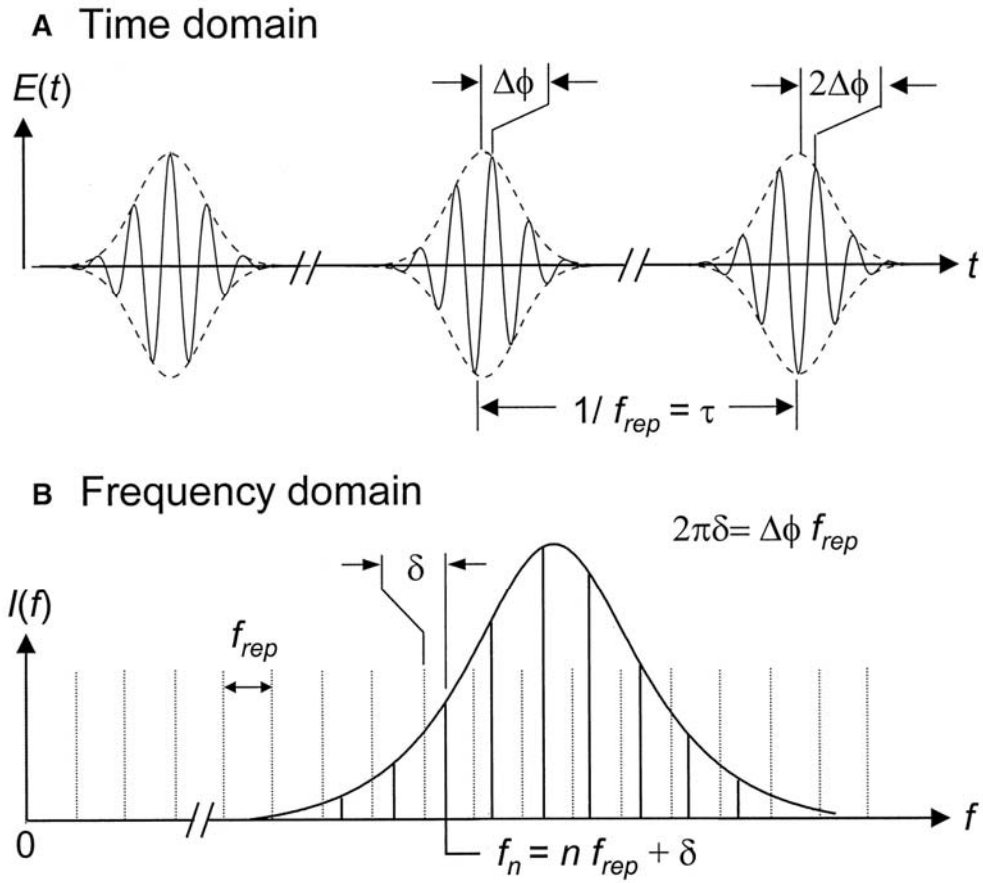
$$\Delta E_{g,\pm m} = \sum_n \left[\frac{|< n | e\vec{r} \cdot \vec{E}(\omega) | g, \pm m >|^2}{\hbar(\omega - \omega_{ng,\pm m})} - \frac{|< n | e\vec{r} \cdot \vec{E}^*(\omega) | g, \pm m >|^2}{\hbar(\omega + \omega_{ng,\pm m})} \right]$$

$$M = -Ng_J \beta < J_z >$$

$$= -Ng_J \beta [< m | J_z | m > \rho_m + < -m | J_z | -m > \rho_{-m}]$$

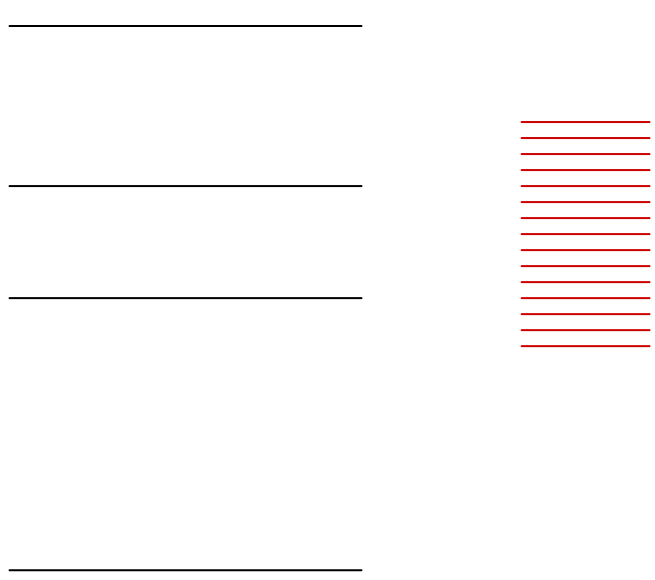
Frequency Comb

$$E(t) = A(t)\cos[2\pi ft + (\Delta\phi/\tau)t]$$
$$A(t) = A(t+\tau)$$



$$2\pi\delta = \omega_0 = \frac{\partial}{\partial t}[(\Delta\phi/\tau)t]$$
$$= (\Delta\phi)/\tau$$

Feedback Control can yield $\Delta\phi < 10^{-3}$ rad.

Characteristics of Frequency Comb

- **Well defined optical field: $E(t)=A(t)\cos\omega t$**
- **Femtosecond periodic pulses: $A(t)=A(t+T)$**
- **Thousands of equally spaced spectral lines with KHz linewidth**