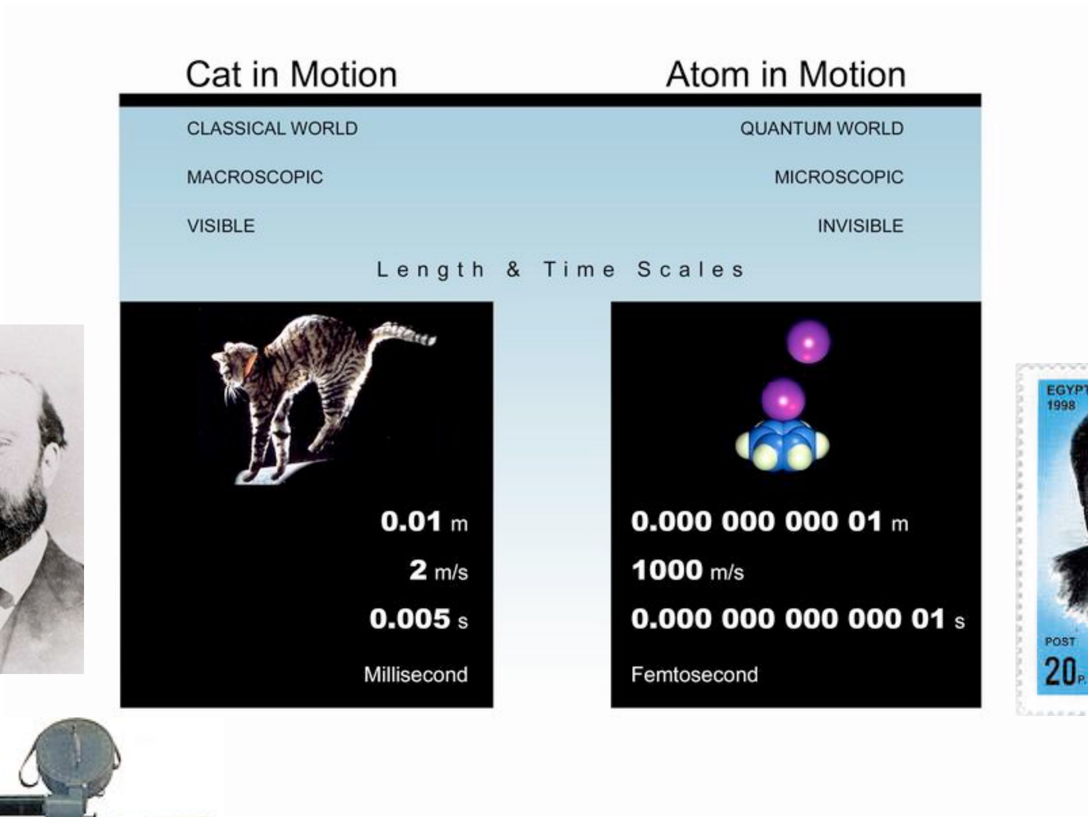
Universität Rostock
Traditio et Innovatio

INSTITUT FÜR PHYSIK

Lecture Two: Concepts of (Non-)linear Spectroscopy

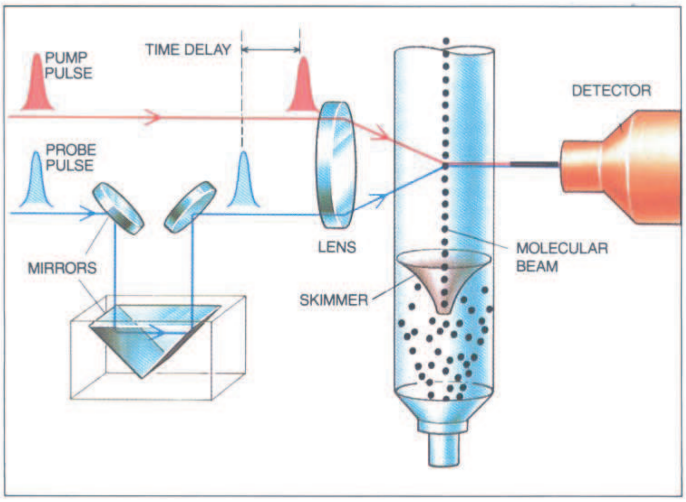
Oliver Kühn

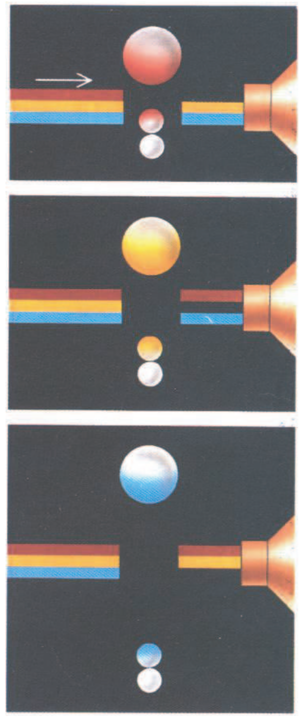


Etienne-Jules Marey
Wikipedia

A. H. Zewail,
http://www.bibalex.org/English/lectures/printable/zewail.htm)

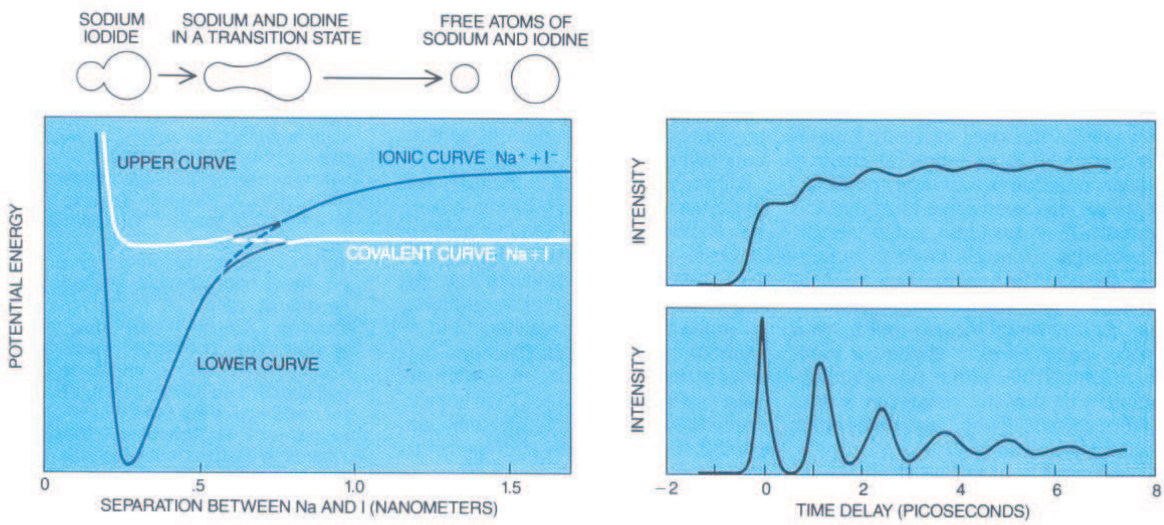
Pump-Probe Spectroscopy





A.H. Zewail
Femtochemistry—Ultrafast Dynamics of the Chemical Bond, Vols. I and II, World Scientific, New Jersey, Singapore (1994)

Predissociation



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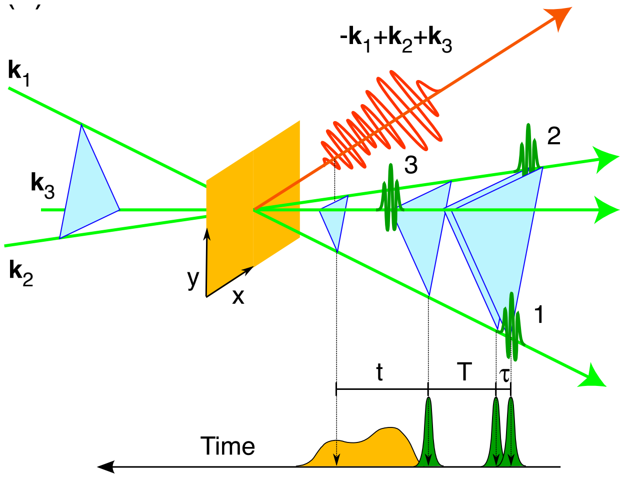
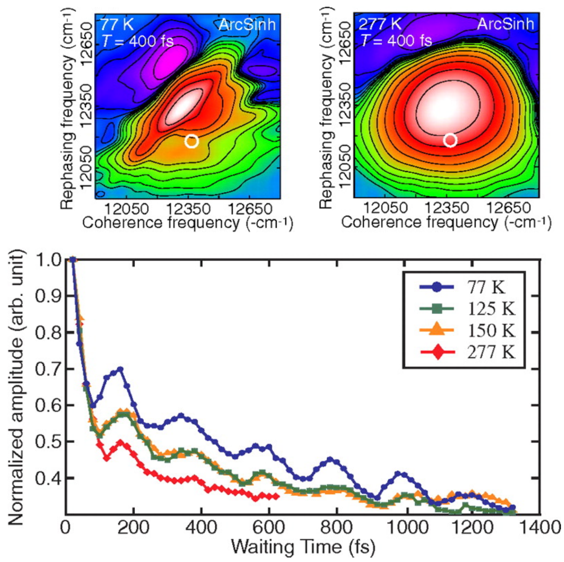
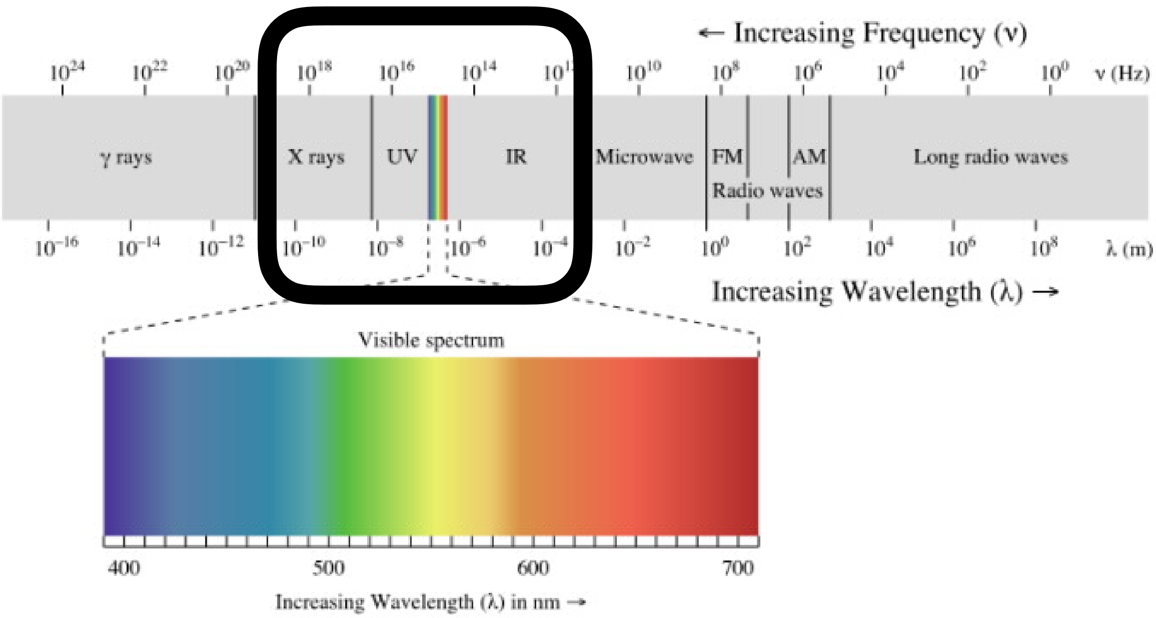
Two-Dimensional Spectroscopy





Source: Panitchayangkoon et al.

- multi-wave mixing
  - probes of coherent evolution of quantum system



Overview

- electrodynamics of dielectric media
- response function formalism
- example: two-level system
- pump-probe spectroscopy
- two-dimensional spectroscopy

Electrodynamics of Media

- wave equation for dielectric medium $\left(\frac{\partial^2}{\partial t^2} - c^2\Delta\right)\mathbf{E} = -\frac{1}{\varepsilon_0}\frac{\partial^2}{\partial t^2}\mathbf{P}[\mathbf{E}]$
  - incoming fields $\mathbf{E}(\mathbf{r},t) = \sum_{j=1}^{n}[\mathbf{E}_j(t)\exp(i\mathbf{k}_j\mathbf{r} - i\omega_j t) + \mathrm{c.c.}]$
  - signal field $\boldsymbol{E}_s$ is generated (n+1 wave mixing)
  - polarization field

$$\mathbf{P}(\mathbf{r},t) \;=\; \mathbf{P}^{(1)}(\mathbf{r},t) + \mathbf{P}_{\mathrm{NL}}(\mathbf{r},t)$$

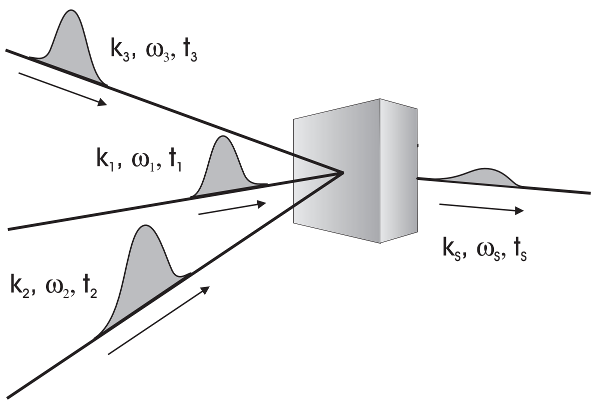
  - optically thin medium

$$\left(c^2\Delta - n_s^2\frac{\partial^2}{\partial t^2}\right)\mathbf{E}(\mathbf{r},t) = \frac{1}{\varepsilon_0}\frac{\partial^2}{\partial t^2}\mathbf{P}_{\mathrm{NL}}(\mathbf{r},t)$$

  - equations for fields coupled since

$$\mathbf{P}_{\mathrm{NL}}(\mathrm{r},t) = \mathbf{P}_{\mathrm{NL}}[\mathbf{E}]$$

  - linearization possible since $E_s \ll E_j$



- wave mixing due to $\mathbf{P}_{\rm NL}[\mathbf{E}] \propto \mathbf{E}^p$ yields combinations

$$\mathbf{k}_s = \pm\mathbf{k}_1 \pm \mathbf{k}_2 \pm \ldots \pm \mathbf{k}_n \qquad \omega_s = \pm\omega_1 \pm \omega_2 \pm \ldots \pm \omega_n$$

- general form of nonlinear polarization

$$\mathbf{P}_{\rm NL}(\mathbf{r},t) = \sum_{n=2,3,\ldots} \sum_s \mathbf{P}_s^{(n)}(t)\exp(i\mathbf{k}_s\mathbf{r} - i\omega_s t)$$

- consider one-dimensional case

$$\left(c^2\frac{\partial^2}{\partial x^2} - n_s^2\frac{\partial^2}{\partial t^2}\right)E(\mathbf{r},t) = \frac{1}{\varepsilon_0}\frac{\partial^2}{\partial t^2}P_{\rm NL}(\mathbf{r},t) \qquad \begin{aligned} k_s' &= \omega_s n_s/c \\ k_j &= \omega_j n_j/c \end{aligned}$$

- in general due to dispersion effects one has $k_s \neq k_s'$
- ansatz for fields

$$P_{\rm NL}(\mathbf{r},t) = P_s(t)\exp(ik_s x - i\omega_s t) \qquad E(\mathbf{r},t) = E_s(x,t)\exp(ik_s' x - i\omega_s t)$$

- within slowly varying envelope approximation

$$\left|\frac{\partial P_s}{\partial t}\right| \ll |\omega_s P_s(t)| \qquad \left|\frac{\partial E_s}{\partial t}\right| \ll |\omega_s E_s(x,t)| \qquad \left|\frac{\partial^2 E_s}{\partial x^2}\right| \ll \left|k_s\frac{\partial E_s}{\partial x}\right|$$

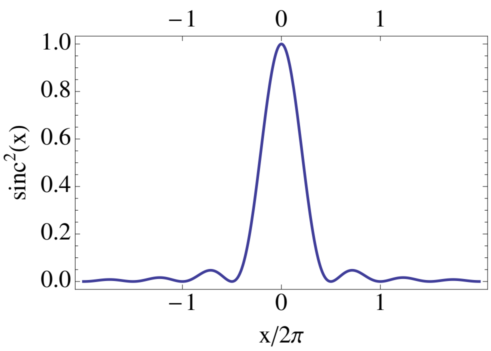
$$ik_s'\frac{\partial E_s(x,t)}{\partial x} = -\frac{\omega_s^2}{2c^2\varepsilon_0}P_s(t)\exp(i\Delta k x) \qquad \Delta k = |\mathbf{k}_s - \mathbf{k}_s'|$$

- integration for a slab [0:L]

$$E_s(L,t) = \frac{i\omega_s L}{2c\varepsilon_0 n_s}P_s(t)\mathrm{sinc}(\Delta k L/2)\exp(i\Delta k L/2) \qquad \mathrm{sinc}(x) = \frac{\sin x}{x} = \frac{1}{2}\int_{-\pi}^{\pi} dy\, e^{ixy}$$

- signal intensity

$$I_s(L,t) = \varepsilon_0 c n_s |E_s(L,t)|^2 = \frac{\omega_s^2 L^2}{4c\varepsilon_0 n_s}|P_s(t)|^2\mathrm{sinc}^2(\Delta k L/2)$$



- phase matching condition

$$\Delta k L \ll \pi$$

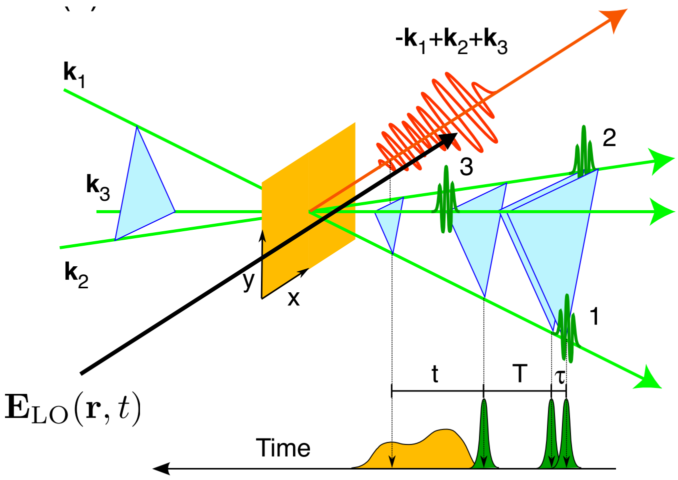
Summary

- linearization wave equation & slowly varying envelope approximation
  - incoming fields unaffected by medium
  - signal field proportional to nonlinear polarization
  - simple phase matching condition
- signals
  - homodyne detection

$$I_{\mathrm{H}}(t) \propto |E_s(t)|^2$$

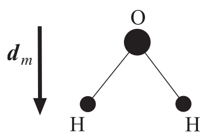
  - heterodyne detection

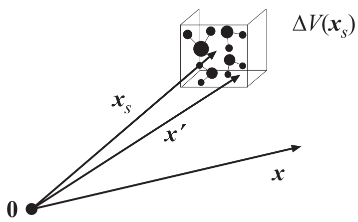
$$I_{\mathrm{HET}}(t) \propto \mathrm{Re}[E_{\mathrm{LO}}(t)^* E_s(t)]$$



- polarization=dipole density of medium

$$\mathbf{P}(\mathbf{r},t) = \frac{1}{\Delta V(\mathbf{r})} \sum_{m\in\Delta V} \mathbf{d}_m(t)$$





  - molecular dipole operator

$$\mathbf{d}_m(t) = \langle \vec{\mu}_m \rangle(t) = \mathrm{tr}\{\rho(t)\vec{\mu}_m\} \qquad \vec{\mu}_m = \sum_u q_u \mathbf{x}_u = -\sum_j e\mathbf{r}_j^{(m)} + \sum_n e z_n^{(m)} \mathbf{R}_n^{(m)}$$

  - limit of homogeneous medium

$$\boxed{\mathbf{P}(\mathbf{r};t) = n_{\mathrm{mol}} \mathbf{d}(\mathbf{r};t)}$$

- matter-field Hamiltonian for a system of charged particles
  - semiclassical dipole approximation

$$H(t) = \sum_u \frac{1}{2m_u}\mathbf{p}_u^2 + \frac{1}{8\pi\varepsilon_0} \sum_{u\neq v} \frac{q_u q_v}{|\mathbf{x}_u - \mathbf{x}_v|} - \vec{\mu}_m \mathbf{E}(\mathbf{X}_m, t) + H_{\mathrm{field}}(t)$$

Response Function Formalism

- time dependent perturbation theory
  - Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = H|\Psi(t)\rangle \qquad |\Psi(t)\rangle = U(t,t_0)|\Psi_0\rangle \qquad H = H_0 + V$$

  - time evolution operator

$$U(t,t_0) \equiv U(t-t_0) = e^{-iH(t-t_0)/\hbar} \quad \longrightarrow \quad U(t,t_0) = U_0(t,t_0)S(t,t_0)$$

  - free time evolution according to H_0

$$U_0(t,t_0) = e^{-iH_0(t-t_0)/\hbar}$$

  - *S*-operator

$$S(t,t_0) = \exp_+\left\{-\frac{i}{\hbar}\int_{t_0}^{t} d\tau V^{(\mathrm{I})}(\tau)\right\} \qquad V^{(\mathrm{I})}(t) = U_0^+(t,t_0)VU_0(t,t_0)$$

- perturbation expansion of polarization

$$\mathbf{P}(\mathbf{r};t) = n_{\mathrm{mol}}\mathbf{d}(\mathbf{r},t) = n_{\mathrm{mol}}\mathrm{tr}\{\rho(t)\vec{\mu}\} \longrightarrow \mathbf{P}(\mathbf{r},t) = \mathbf{P}^{(1)}(\mathbf{r},t) + \mathbf{P}^{(2)}(\mathbf{r},t) + \mathbf{P}^{(3)}(\mathbf{r},t)\dots$$

$$H = H_{\mathrm{mol}} + H_{\mathrm{int}}(t) \qquad H_{\mathrm{int}}(t) = -\mathbf{E}(\mathbf{r},t)\,\vec{\mu}$$

  - expansion of density operator

$$\rho(t) = U(t,t_0)\rho_{\mathrm{eq}}U^+(t,t_0) \quad \longrightarrow \quad \rho(t) = \rho^{(1)}(t) + \rho^{(2)}(t) + \rho^{(3)}(t) + \dots$$

$$U_0(t,t_0) = \exp(-iH_{\mathrm{mol}}(t-t_0)/\hbar) \qquad S(t,t_0) = \exp_+\left(-\frac{i}{\hbar}\int_{t_0}^{t} dt'\; H_{\mathrm{int}}^{(\mathrm{I})}(t')\right)$$

$$H_{\mathrm{int}}^{(\mathrm{I})}(t) = U_0^+(t-t_0)H_{\mathrm{int}}(t)U_0(t-t_0) = -\mathbf{E}(\mathbf{r},t)\,\vec{\mu}^{(\mathrm{I})}(t)$$

  - starting point

$$\mathbf{d}(\mathbf{r};t) = \mathrm{tr}\{\rho_{\mathrm{eq}}S^+(t,t_0)\vec{\mu}^{(\mathrm{I})}(t)S(t,t_0)\}$$

- first order term

$$\mathbf{d}(\mathbf{r};t) \approx \mathrm{tr}\{\rho_{\mathrm{eq}}\big[1+S^{(1)+}(t,t_0)\big]\vec{\mu}^{(I)}(t)\big[1+S^{(1)}(t,t_0)\big]\}$$

$$S^{(1)}(t,t_0) = \frac{i}{\hbar}\int\limits_{t_0}^{t} d\tau\ \mathbf{E}(\mathbf{r},\tau)\vec{\mu}^{(\mathrm{I})}(\tau)$$

$$\mathbf{d}^{(1)}(\mathbf{r};t) = \frac{i}{\hbar}\int\limits_{t_0}^{t} d\tau\ \mathbf{E}(\mathbf{r},\tau)\mathrm{tr}\{\rho_{\mathrm{eq}}[\vec{\mu}^{(I)}(t)\vec{\mu}^{(I)}(\tau) - \vec{\mu}^{(I)}(\tau)\vec{\mu}^{(I)}(t)]\}$$

- linear polarization

$$\mathbf{P}^{(1)}(\mathbf{r},t) = \int_0^\infty dt_1\, R^{(1)}(t_1)\mathbf{E}(\mathbf{r},t-t_1)$$

- linear response function

$$R^{(1)}(t) = \frac{i}{\hbar}\theta(t)n_{\mathrm{mol}}\mathrm{tr}\Big\{\rho_{\mathrm{eq}}\big[\vec{\mu}^{(\mathrm{I})}(t),\vec{\mu}^{(\mathrm{I})}(0)\big]_-\Big\} = \frac{i}{\hbar}\theta(t)n_{\mathrm{mol}}[J(t)-J^*(t)]$$

$$J(t) = \mathrm{tr}\Big\{\mu^{(\mathrm{I})}(t)\mu^{(\mathrm{I})}(0)\rho_{\mathrm{eq}}\Big\} \equiv \mathrm{tr}\Big\{\mu U_0(t)\mu\rho_{\mathrm{eq}}U_0^+(t)\Big\}$$

- third-order term

$$\begin{aligned}\mathbf{d}(\mathbf{r},t) &= \mathrm{tr}\{\rho_{\mathrm{eq}}\big[1+S^{(1)+}(t,t_0)+S^{(2)+}(t,t_0)+S^{(3)+}(t,t_0)\big]\vec{\mu}^{(I)}(t)\\ &\quad\times\big[1+S^{(1)}(t,t_0)+S^{(2)}(t,t_0)+S^{(3)}(t,t_0)\big]\}\ .\end{aligned}$$

$$\begin{aligned}S^{(3)}(t,t_0) &= \left(-\frac{i}{\hbar}\right)^3\int\limits_{t_0}^{t} d\tau_1\int\limits_{t_0}^{\tau_1} d\tau_2\int\limits_{t_0}^{\tau_2} d\tau_3\\ &\times\ \mathbf{E}(\mathbf{r},\tau_1)\vec{\mu}^{(\mathrm{I})}(\tau_1)\ \mathbf{E}(\mathbf{r},\tau_2)\vec{\mu}^{(\mathrm{I})}(\tau_2)\ \mathbf{E}(\mathbf{r},\tau_3)\vec{\mu}^{(\mathrm{I})}(\tau_3)\ .\end{aligned}$$

- third order polarization

$$\begin{aligned}\mathbf{P}^{(3)}(\mathbf{r};t) &= \int_0^\infty dt_3dt_2dt_1\, R^{(3)}(t_3,t_2,t_1)\\ &\times\ \mathbf{E}(\mathbf{r};t-t_3)\mathbf{E}(\mathbf{r};t-t_3-t_2)\mathbf{E}(\mathbf{r};t-t_3-t_2-t_1)\end{aligned}$$

- third order response function

$$R^{(3)}(t_3,t_2,t_1) = \left(\frac{i}{\hbar}\right)^3\theta(t_3)\theta(t_2)\theta(t_1)n_{\mathrm{mol}}$$

$$\times\mathrm{tr}\Big\{\rho_{\mathrm{eq}}\big[\big[\big[\vec{\mu}^{(\mathrm{I})}(t_3+t_2+t_1)\big],\vec{\mu}^{(\mathrm{I})}(t_2+t_1)\big],\vec{\mu}^{(\mathrm{I})}(t_1)\big],\vec{\mu}^{(\mathrm{I})}(0)\big]\Big\}$$

- eight multi-time dipole correlation functions

$$R^{(3)}(t_3,t_2,t_1) = n_{\mathrm{mol}} \left(\frac{i}{\hbar}\right)^3 \theta(t_3)\theta(t_2)\theta(t_1) \sum_{i=1}^{8} R_i(t_3,t_2,t_1)$$

$$\begin{aligned}
R_1(t_3,t_2,t_1) &= \mathrm{tr}\Big\{\rho_{\mathrm{eq}}\vec{\mu}^{(\mathrm{I})}(t_1)\vec{\mu}^{(\mathrm{I})}(t_2+t_1)\vec{\mu}^{(\mathrm{I})}(t_3+t_2+t_1)\vec{\mu}^{(\mathrm{I})}(0)\Big\} \\
R_2(t_3,t_2,t_1) &= \mathrm{tr}\Big\{\rho_{\mathrm{eq}}\vec{\mu}^{(\mathrm{I})}(0)\vec{\mu}^{(\mathrm{I})}(t_2+t_1)\vec{\mu}^{(\mathrm{I})}(t_3+t_2+t_1)\vec{\mu}^{(\mathrm{I})}(t_1)\Big\} \\
R_3(t_3,t_2,t_1) &= \mathrm{tr}\Big\{\rho_{\mathrm{eq}}\vec{\mu}^{(\mathrm{I})}(0)\vec{\mu}^{(\mathrm{I})}(t_1)\vec{\mu}^{(\mathrm{I})}(t_3+t_2+t_1)\vec{\mu}^{(\mathrm{I})}(t_2+t_1)\Big\} \\
R_4(t_3,t_2,t_1) &= \mathrm{tr}\Big\{\rho_{\mathrm{eq}}\vec{\mu}^{(\mathrm{I})}(t_3+t_2+t_1)\vec{\mu}^{(\mathrm{I})}(t_2+t_1)\vec{\mu}^{(\mathrm{I})}(t_1)\vec{\mu}^{(\mathrm{I})}(0)\Big\} \\
R_i(t_3,t_2,t_1) &= -R^*_{i-4}(t_3,t_2,t_1) \quad i=5,\ldots,8
\end{aligned}$$

- it's all in the Feynman diagrams!
  - model system

$$H|a\rangle = E_a|a\rangle \qquad \rho_{\mathrm{eq}} = |a\rangle\langle a| \qquad \mu = \sum_{a\neq b}\mu_{ab}|a\rangle\langle b|$$

$$E(\mathbf{r},t) = \sum_j [E_j(t)\exp(-i\omega_j t + i\mathbf{k}_j\mathbf{r}) + E_j^*(t)\exp(i\omega_j t - i\mathbf{k}_j\mathbf{r})]$$

  - linear response function

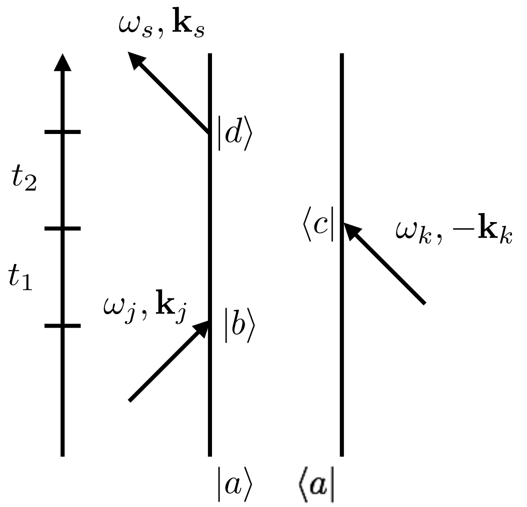
$$J(t_1) = \mathrm{tr}\Big\{\mu U_0(t_1)\mu\rho_{\mathrm{eq}}U_0^+(t_1)\Big\} = \sum_b |\mu_{ab}|^2 e^{-i\omega_{ba}t_1} = \sum_b |\mu_{ab}|^2 I_{ba}(t_1)$$

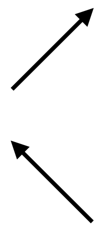
$$R^{(1)}(t_1) = \frac{i}{\hbar}\theta(t_1)n_{\mathrm{mol}}\sum_b |\mu_{ab}|^2(I_{ba}(t_1) - I^*_{ba}(t_1))$$

  - first order polarization

$$\begin{aligned}
P^{(1)}(\mathbf{r},t) &= \frac{i}{\hbar}n_{\mathrm{mol}}\sum_b |\mu_{ab}|^2 \int_0^\infty dt_1 \\
&\times \Big(e^{-i\omega_{ba}t_1} - e^{i\omega_{ba}t_1}\Big)\Big[E_1 e^{-i\omega_1(t-t_1)+i\mathbf{k}_1\mathbf{r}} + E_1^* e^{i\omega_1(t-t_1)-i\mathbf{k}_1\mathbf{r}}\Big]
\end{aligned}$$

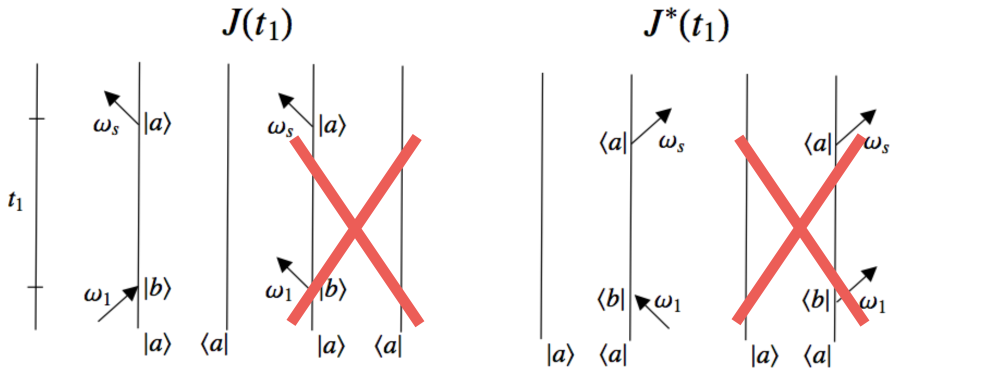
- rules for double-sided Feynman diagrams
  - density operator given by two vertical lines
  - time runs from bottom to top
  - interaction=arrow labeled by field frequency/wave vector
  - signal field to the left by convention
  - overall sign $(-1)^m$, m=number of interactions from right



$E_j \exp(-i\omega_j t + i\mathbf{k}_j \mathbf{r})$ 

$E_k^* \exp(i\omega_k t - i\mathbf{k}_k \mathbf{r})$

incoming/outgoing arrow = photon annihilation/creation

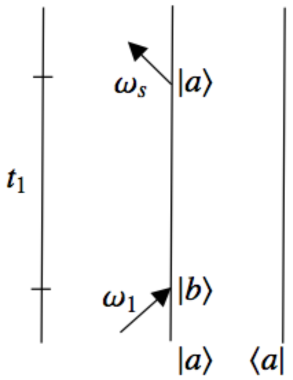


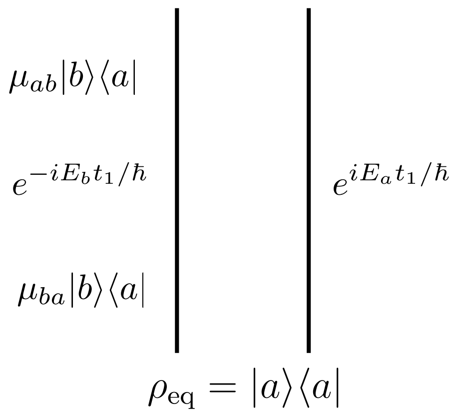
$$
\begin{aligned}
P^{(1)}(\mathbf{r}, t) &= \frac{i}{\hbar} n_{\mathrm{mol}} \sum_b |\mu_{ab}|^2 \int_0^\infty dt_1 \\
&\times \left(e^{-i\omega_{ba} t_1} - e^{i\omega_{ba} t_1}\right) \left[E_1 e^{-i\omega_1(t-t_1)+i\mathbf{k}_1\mathbf{r}} + E_1^* e^{i\omega_1(t-t_1)-i\mathbf{k}_1\mathbf{r}}\right]
\end{aligned}
$$

$\omega_1 \approx \omega_{ba} > 0$ ▶ rotating wave approximation (RWA)

- Feynman diagrams and correlation functions

$$J(t_1) = \mathrm{tr}\left\{\mu U_0(t_1)\mu\rho_{\mathrm{eq}}U_0^+(t_1)\right\}$$

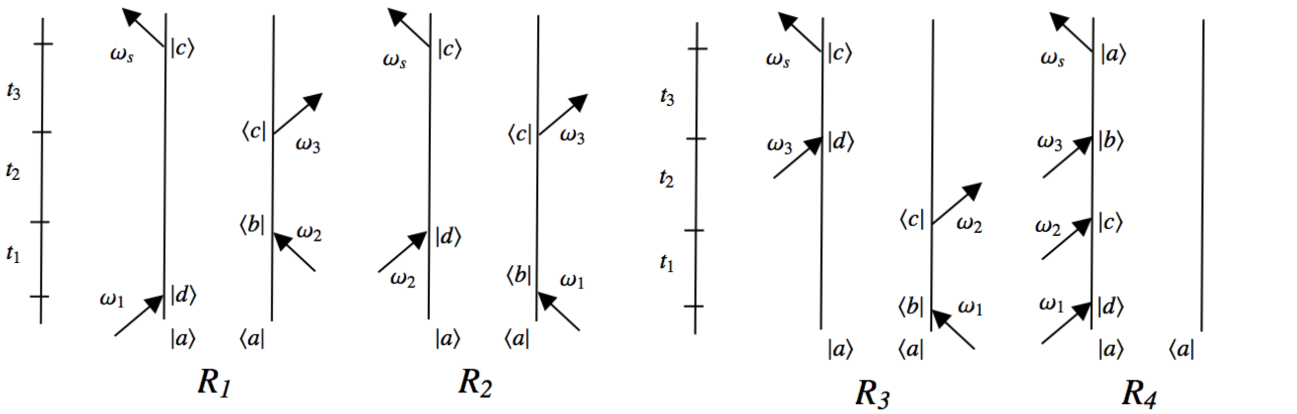




$$\rightarrow \sum_b |\mu_{ab}|^2 e^{-i\omega_{ba}t_1} = \sum_b |\mu_{ab}|^2 I_{ba}(t_1)$$

- third order response functions: diagramatic representation

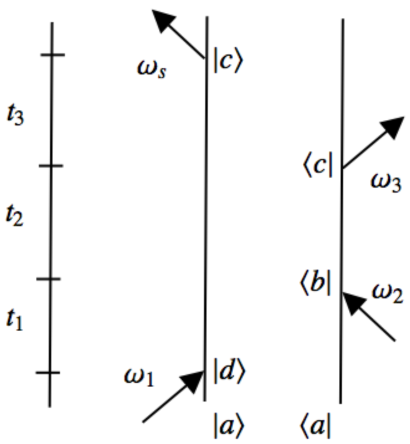
$$R^{(3)}(t_3,t_2,t_1) = n_{\mathrm{mol}}\left(\frac{i}{\hbar}\right)^3 \theta(t_3)\theta(t_2)\theta(t_1)\sum_{i=1}^{8} R_i(t_3,t_2,t_1)$$



$$R_i(t_3,t_2,t_1) = -R^*_{i-4}(t_3,t_2,t_1) \quad i = 5,\ldots,8$$

- time-ordering of fields can be different
- direction of arrows different depending on level structure
- in practice diagrams have to be drawn for the actual system

- for example R_1



phase matching

$$\mathbf{k}_s = \pm\mathbf{k}_1 \pm \mathbf{k}_2 \pm \mathbf{k}_3$$

in RWA only one possibility!

$$R_1\text{: } \mathbf{k}_s = \mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3$$

$$\begin{aligned}
R_1(t_3,t_2,t_1) &= \mathrm{tr}\{U_0^+(t_1)\mu U_0(t_1)U_0^+(t_1+t_2)\mu U_0(t_1+t_2)U_0^+(t_1+t_2+t_3)\mu U_0(t_1+t_2+t_3)\mu\rho_{\mathrm{eq}}\} \\
&= \mathrm{tr}\{U_0^+(t_1)\mu U_0^+(t_2)\mu U_0^+(t_3)\mu U_0(t_1+t_2+t_3)\mu\rho_{\mathrm{eq}}\} \\
&= \sum_{bcd}\mathrm{tr}\{U_0^+(t_1)|a\rangle\mu_{ad}\langle b|U_0^+(t_2)|b\rangle\mu_{bc}\langle c|U_0^+(t_3)|c\rangle\mu_{cd}\langle d|U_0(t_1+t_2+t_3)|d\rangle\mu_{da}\langle a|\} \\
&= \sum_{bcd}\mathrm{tr}\{|c\rangle\mu_{cd}\langle d|U_0(t_1+t_2+t_3)|d\rangle\mu_{da}\langle a|U_0^+(t_1)|a\rangle\mu_{ab}\langle b|U_0^+(t_2)|b\rangle\mu_{bc}\langle c|U_0^+(t_3)\} \\
&\approx \sum_{bcd}\mu_{ab}\mu_{bc}\mu_{cd}\mu_{da}I_{dc}(t_3)I_{db}(t_2)I_{da}(t_1)
\end{aligned}$$

Frequency Domain

- equivalent formulation, but more suitable for CW fields
  - linear response

$$P^{(1)}(\mathbf{r},t) = \int_0^\infty dt_1\, R^{(1)}(t_1)E(\mathbf{r},t-t_1)$$

$$P^{(1)}(\mathbf{r},\omega) = \chi^{(1)}(\omega)E(\mathbf{r},\omega)$$

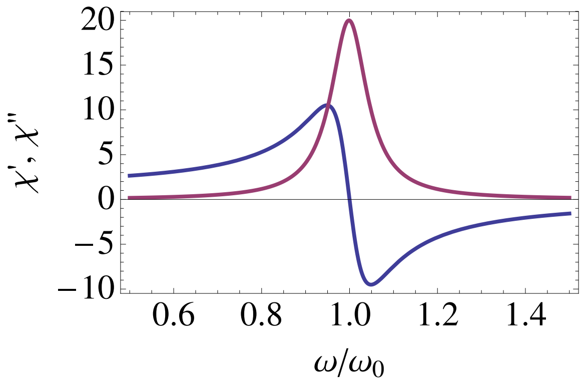
  - first order susceptibility

$$\chi^{(1)}(\omega) = \int dt\,\exp(i\omega t)R^{(1)}(t)$$

  - absorption coeffiecient

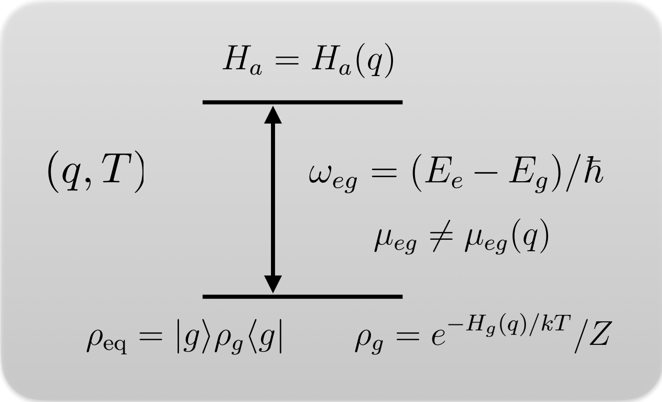
$$\alpha(\omega) = \frac{\omega}{cn(\omega)}\mathrm{Im}\chi(\omega)$$

$$\chi = \chi' + i\chi''$$



Two-Level System

- generic two level system coupled to some heat bath



  - QME like description
  - non-perturbative quantum description
  - semiclassical approach

- Quantum Master Equation approach

$$\frac{\partial}{\partial t}\rho_{ab} = (1-\delta_{ab})(-i\omega_{ab} - \gamma_{ab})\rho_{ab} - \delta_{ab}(k_{ab}\rho_{aa} - k_{ba}\rho_{bb})$$

  - two level system $\hbar\omega_{eg} \gg kT$

$$\rho_{ee}(t) = |c_e|^2 e^{-k_{eg}t} \qquad |c_e|^2 = \rho_{ee}(0)$$

$$\rho_{eg}(t) = c_e c_g^* e^{-i\omega_{eg}t - \gamma_{eg}t} \qquad c_e c_g^* = \rho_{eg}(0) \qquad \gamma_{eg} = k_{eg}/2 + \gamma_{eg}^{\mathrm{pd}}$$

  - Bloch model notation

$$\gamma_{eg} \equiv \frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*} \qquad k_{eg} \equiv \frac{1}{T_1}$$

  - response functions:

$$I_{eg}(t) \to e^{-i\omega_{eg}t - \gamma_{eg}t}$$

- non-perturbative quantum description
  - dipole correlation function for linear response

$$J(t) = \mathrm{tr}\Big\{\mu U_0(t)\mu\rho_{\mathrm{eq}}U_0^+(t)\Big\} \qquad U_0(t)|a\rangle = |a\rangle e^{-iH_a(q)t/\hbar}$$

$$J(t) = \mathrm{tr}\Big\{\mu_{ge}|g\rangle\langle e|e^{-iH_e t/\hbar}\mu_{eg}|e\rangle\langle g|\rho_g e^{iH_g t/\hbar}|g\rangle\langle g|\Big\}$$

  - take partial trace w.r.t. two-level system

$$J(t) = |\mu_{eg}|^2 \mathrm{tr}_q\Big\{e^{-iH_e t/\hbar}\rho_g e^{iH_g t/\hbar}\Big\}$$

  - general definition of S-operator

$$U(t,t_0) = U_0(t,t_0)S(t,t_0) \qquad S(t,t_0) = \exp_+\left\{-\frac{i}{\hbar}\int_{t_0}^{t} d\tau V^{(\mathrm{I})}(\tau)\right\}$$

  - introduce reference Hamiltonian

$$H_g = (H_g - H_g') + H_g' \qquad e^{iH_g t/\hbar} = \exp_-\left\{\frac{i}{\hbar}\int_0^t d\tau (H_g - H_g')^{(\mathrm{I})}(\tau)\right\} e^{iH_g' t/\hbar}$$

$$H_e = (H_e - H_e') + H_e' \qquad e^{-iH_e t/\hbar} = e^{-iH_e' t/\hbar}\exp_+\left\{-\frac{i}{\hbar}\int_0^t d\tau (H_e - H_e')^{(\mathrm{I})}(\tau)\right\}$$

- use ground state as reference $\quad H_g' = H_g \qquad H_e' = H_g + \hbar\omega_{eg}$
- correlation function

$$J(t) = |\mu_{eg}|^2 e^{-i\omega_{eg}t}\langle \exp_+\Big\{-\frac{i}{\hbar}\int_0^t d\tau U(\tau)\Big\}\rangle$$

- gap coordinate

$$U = H_e - H_g - \hbar\omega_{eg} \qquad U(t) \equiv U^{(\mathrm{I})}(t) = e^{iH_g t/\hbar} U e^{-iH_g t/\hbar}$$

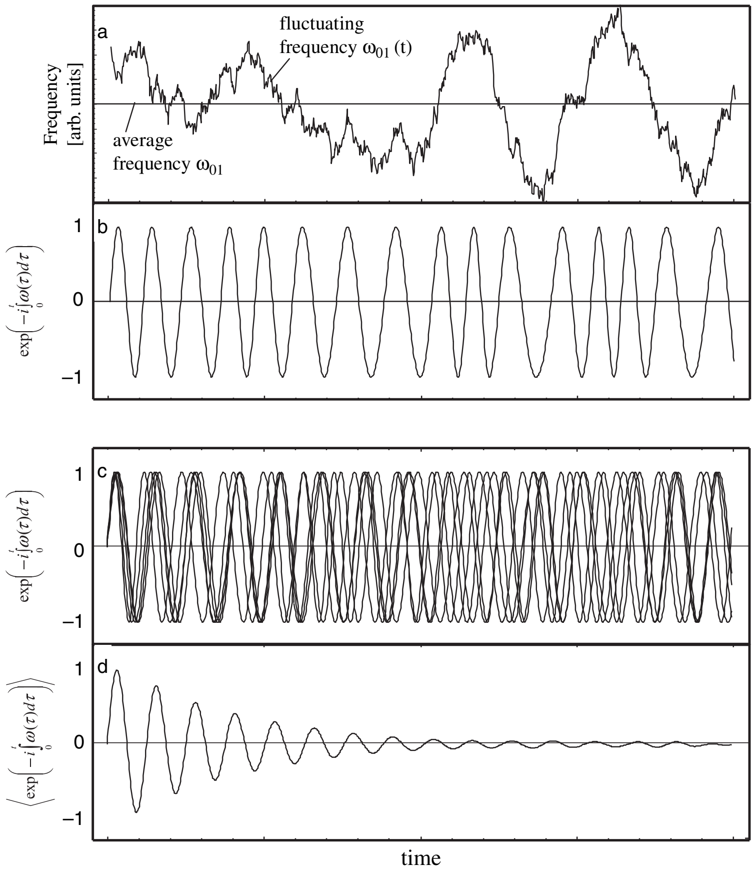
- choice of ω_{eg} arbitrary, often thermally averaged energy gap useful

$$\hbar\omega_{eg} = \langle H_e - H_g\rangle$$

- gap coordinate describes fluctuations of energy gap of two level system due to interaction with the thermally moving bath

$$U(t)/\hbar \equiv \delta\omega_{eg}(t) = \omega_{eg}(t) - \langle\omega_{eg}\rangle$$

- example: from gap fluctuations to correlation function



Source: Hamm&Zanni

- cumulant expansion
  - goal: approximate evaluation of time-ordered exponential

$$J(t) = |\mu_{eg}|^2 e^{-i\omega_{eg}t} \langle \exp_+ \{ -\frac{i}{\hbar} \int_0^t d\tau U(\tau) \} \rangle$$

  - cumulant expansion: resummation of perturbation series

$$A = A_0(1 + \lambda A_1 + \lambda^2 A_2 + \ldots) \quad \longrightarrow \quad A_0 e^{\lambda A_1 + \lambda^2 (A_2 - \frac{1}{2} A_1^2) + \ldots}$$

  - application to dipole correlation function

$$J(t) \approx |\mu_{eg}|^2 e^{-i\omega_{eg}t} \langle (1 - \frac{i}{\hbar} \int_0^t d\tau_1 U(\tau_1) + \left(-\frac{i}{\hbar}\right)^2 \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 U(\tau_2) U(\tau_1) + \ldots \rangle$$

$$\longrightarrow J(t) = |\mu_{eg}|^2 e^{-i\omega_{eg}t} e^{-g(t)}$$

  - lineshape function

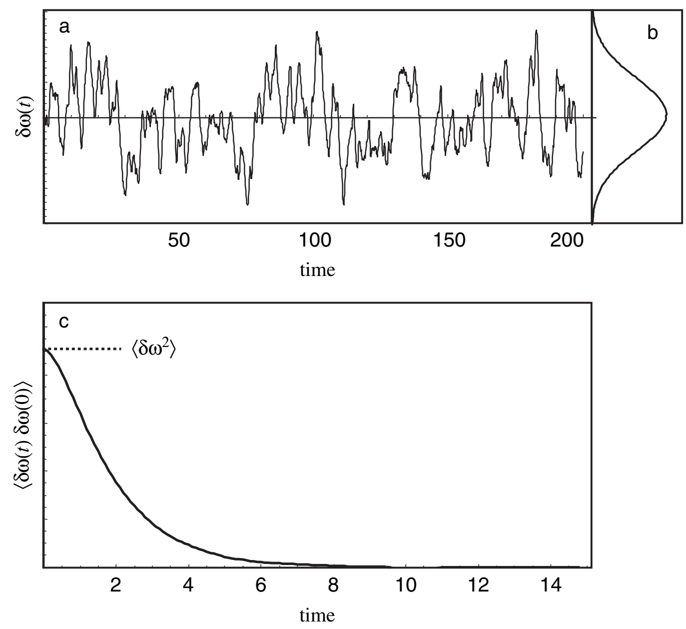
$$g(t) = \frac{1}{\hbar^2} \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \langle U(\tau_2) U(\tau_1) \rangle = \frac{1}{\hbar^2} \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \langle U(\tau_1) U(0) \rangle$$

- multi-time correlation functions

$$R_1(t_3,t_2,t_1) = \exp(-i\omega_{eg}t_1 - i\omega_{eg}t_3)\exp(-g^*(t_3) - g(t_1) - f_+(t_3,t_2,t_1))$$
$$R_2(t_3,t_2,t_1) = \exp(i\omega_{eg}t_1 - i\omega_{eg}t_3)\exp(-g^*(t_3) - g^*(t_1) - f_+^*(t_3,t_2,t_1))$$
$$R_3(t_3,t_2,t_1) = \exp(i\omega_{eg}t_1 - i\omega_{eg}t_3)\exp(-g(t_3) - g^*(t_1) - f_-^*(t_3,t_2,t_1))$$
$$R_4(t_3,t_2,t_1) = \exp(-i\omega_{eg}t_1 - i\omega_{eg}t_3)\exp(-g(t_3) - g(t_1) - f_-(t_3,t_2,t_1))$$
$$f_+(t_3,t_2,t_1) = g(t_2) - g(t_2+t_3) - g(t_1+t_2) + g(t_1+t_2+t_3)$$
$$f_-(t_3,t_2,t_1) = g^*(t_2) - g^*(t_2+t_3) - g(t_1+t_2) + g(t_1+t_2+t_3)$$

- within second order cumulant approximation, all response functions can be expressed by a single lineshape function!

- Kubo lineshape model



- Kubo ansatz $\langle \delta\omega_{eg}(t)\delta\omega_{eg}(0)\rangle = \Delta^2 e^{-|t|/\tau_c}$

Source: Hamm&Zanni

$$g(t) = \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \langle \delta\omega_{eg}(\tau_1)\delta\omega_{eg}(0)\rangle$$

- lineshape function in Kubo model

$$g(t) = \Delta^2 \tau_c^2 \left(e^{-t/\tau_c} + \frac{t}{\tau_c} - 1 \right)$$

- fast modulation/homogeneous limit: $\Delta\tau_c \ll 1$

$$t/\tau_c \gg 1 \quad \longrightarrow \quad \langle \delta\omega_{eg}(t)\delta\omega_{eg}(0)\rangle = \frac{\delta(t)}{T_2^*} \quad \rightarrow \quad g(t) = \Delta^2 \tau_c t = t/T_2^*$$

- Lorentzian absorption spectrum

$$\begin{aligned} \chi''(\omega) &\propto \mathrm{Re} \int_0^\infty dt\, e^{i\omega t} J(t) = |\mu_{eg}|^2 \mathrm{Re} \int_0^\infty dt\, e^{i\omega t} e^{-i\omega_{eg} t} e^{-g(t)} \\ &= |\mu_{eg}|^2 \frac{1/T_2^*}{(\omega - \omega_{eg})^2 + 1/T_2^{*\,2}} \end{aligned}$$

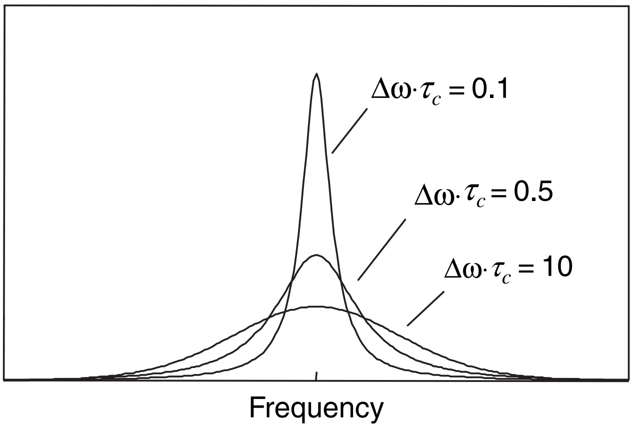
motional narrowing: $1/T_2^* \ll \Delta$

- slow modulation/inhomogenous limit: $\Delta\tau_c \gg 1$

$$t/\tau_c \ll 1 \quad \longrightarrow \quad \langle \delta\omega_{eg}(t)\delta\omega_{eg}(0)\rangle = \Delta^2 \quad \rightarrow \quad g(t) = \frac{\Delta^2}{2} t^2$$

- Gaussian absorption spectrum

$$\chi''(\omega) \propto |\mu_{eg}|^2 \exp\left(-\frac{(\omega - \omega_{eg})^2}{2\Delta^2} \right)$$



Source: Hamm&Zanni

- oscillator model
  - Caldeira-Leggett type description

$$H_{\rm R} = \sum_j \frac{\hbar\omega_j}{2}\Big(-\frac{\partial^2}{\partial Q_j^2} + Q_j^2\Big) \qquad H_{\rm S-R} = |e\rangle\langle e| \sum_j \hbar\omega_j g_j Q_j$$

  - shifted oscillator model!
  - gap fluctuation

$$\delta\omega_{eg}(t) = \sum_j \omega_j g_j Q_j(t)$$

$$C(t) = \sum_j \omega_j^2 S_j([(1+n(\omega_j)]e^{-i\omega_j t} + n(\omega_j)e^{i\omega_j t}) \qquad S_j = g_j^2/2$$

  - lineshape function

$$g(t) = \sum_j S_j[\coth(\hbar\omega_j/2k_{\rm B}T)(1-\cos(\omega_j t)) + i(\sin(\omega_j t) - \omega_j t)]$$

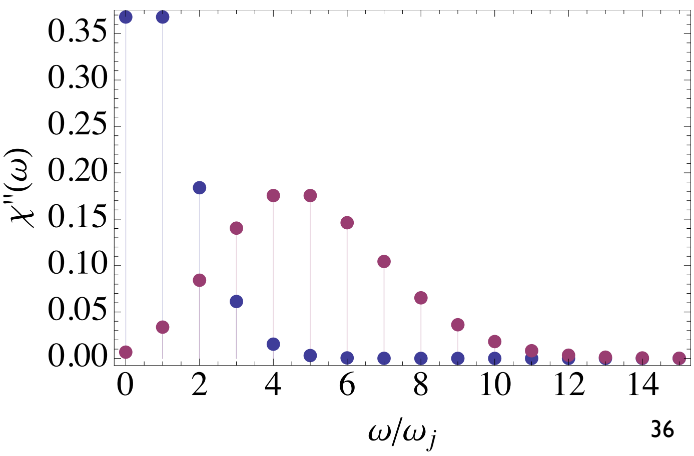
- absorption spectrum

$$\chi''(\omega) = \frac{n_{\rm mol}}{\hbar}{\rm Re}\int_0^\infty dt e^{i\omega t}[e^{-i\omega_{eg}t}e^{-g(t)} - e^{i\omega_{eg}t}e^{-g^*(t)}]$$

$$\chi''(\omega) = \frac{n_{\rm mol}}{\hbar}\exp(-S_j\coth(\hbar\omega_j/2k_{\rm B}T)) \times \sum_{n=-\infty}^{\infty}\exp(n\hbar\omega_j/2)I_n\left[S_j\sqrt{\coth^2(\hbar\omega_j/2k_{\rm B}T)-1}\right]\delta(\omega-\omega_{eg}^0-n\omega_j)$$

- at T=0K

$$\chi''(\omega) = \frac{n_{\rm mol}}{\hbar}\exp(-S_j)\sum_{n=0}^{\infty}\frac{S_j^n}{n!}\delta(\omega-\omega_{eg}^0-n\omega_j)$$



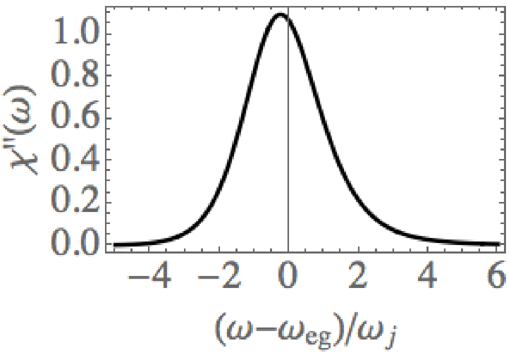
- Franck-Condon factors

- continuous distribution of oscillators (e.g. Debye)

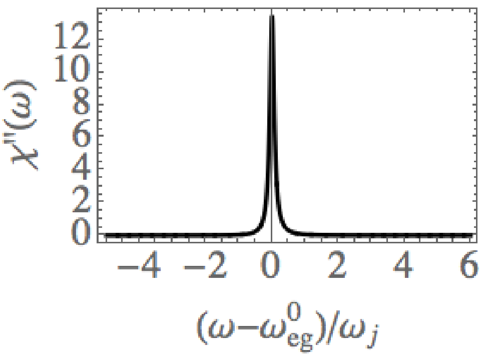
$$\omega^2 J(\omega) = \Theta(\omega)\Delta_{\mathrm{S}}\omega\frac{\gamma}{\omega^2+\gamma^2} \qquad C(t) = \frac{\Delta_{\mathrm{S}}\gamma}{2}\left[\frac{2k_{\mathrm{B}}T}{\hbar\gamma} - i\right]e^{-\gamma t}$$

$$g(t) = \frac{\Delta_{\mathrm{S}}}{2\gamma}\left[\frac{2k_{\mathrm{B}}T}{\hbar\gamma} - i\right]\left[e^{-\gamma t}+\gamma t - 1\right] \qquad T_{\mathrm{nuc}} = 1/\gamma \qquad T_{\mathrm{fluc}} = \hbar/\sqrt{k_{\mathrm{B}}T\Delta_{\mathrm{S}}}$$

$T_{\mathrm{nuc}} \ll T_{\mathrm{fluc}}$



$T_{\mathrm{nuc}} \gg T_{\mathrm{fluc}}$



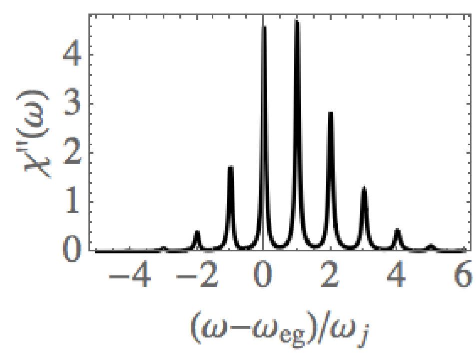
- Kubo model

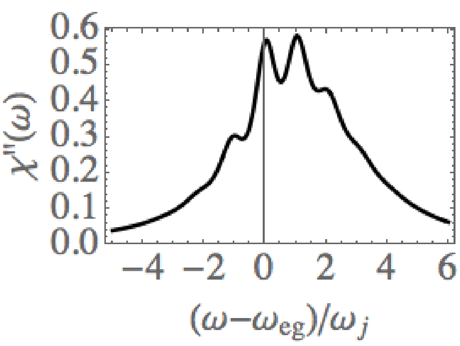
- multi-mode Brownian oscillator (MBO) model
  - coupling of discrete oscillators to secondary bath

$$H_{\mathrm{SB}} = \frac{1}{2}\sum_{\xi}\left[p_\xi^2 + \omega_\xi^2 x_\xi^2\right] + \sum_{\xi,j} c_{\xi j} Q_j x_\xi$$

  - MBO spectral density

$$\omega^2 J(\omega) = 2\sum_j S_j \omega_j^3 \frac{\omega\gamma_j}{(\omega_j^2-\omega^2)^2+\omega^2\gamma_j^2}$$





- classical bath

$$H(s,q) = H(s) + H(q) + V(s,q)$$

- quantize fast mode via eigenvalue problem for fixed bath

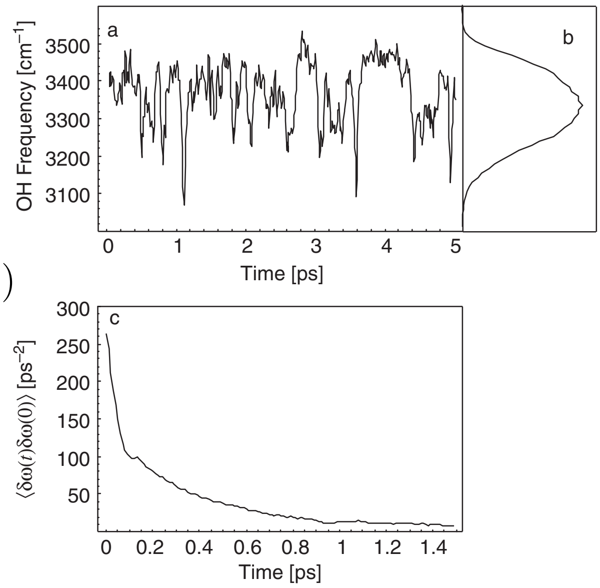
$$(H(s) + V(s,q))|\chi_A(s,q)\rangle = E_A(q)|\chi_A(s,q)\rangle \qquad A = 0,1,2\ldots$$

- Hellmann-Feynman force

$$F_\xi = -\int ds \chi_0^*(s,q(t)) \frac{\partial V(s,q(t))}{\partial q_\xi} \chi_0(s,q(t))$$

- time-dependent potential contribution

$$V(s,q) \approx \frac{\partial V}{\partial s}|_{s_0}(s - s_0) + \ldots = -F_s(s - s_0)$$

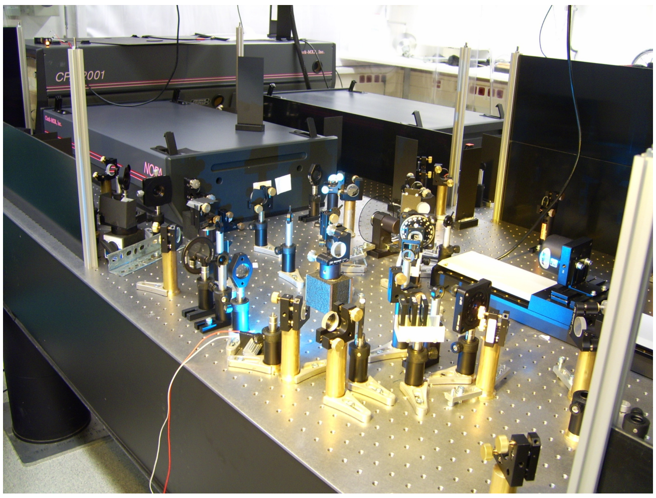


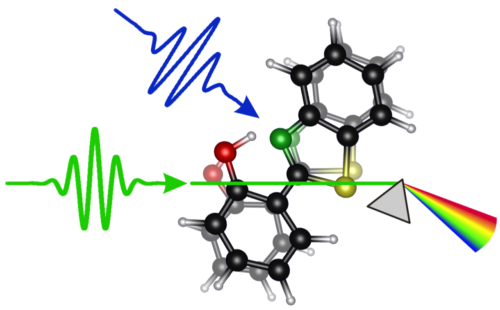
HOD in D_2O

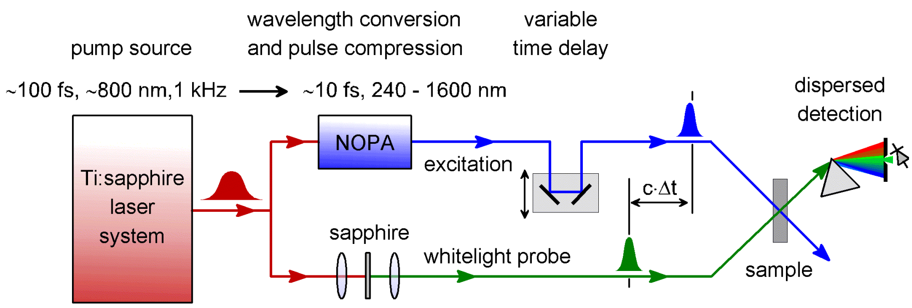
Source: Hamm&Zanni

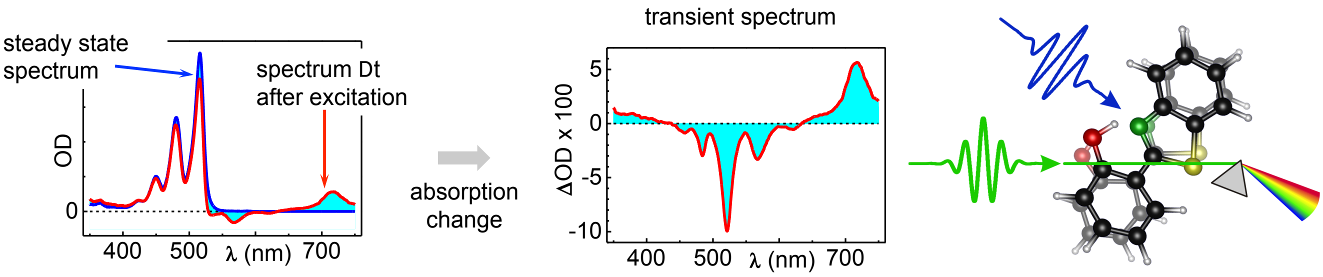
Pump-Probe Spectroscopy

S. Lochbrunner lab









$$E(t) = E_1(t)e^{-i\omega_1 t + i\mathbf{k}_1\mathbf{r}} + E_2(t-T)e^{-i\omega_2 t + i\mathbf{k}_2\mathbf{r}} + c.c.$$

- pump triggers dynamics
- probe observes transient spectral changes after delay *T*
- phase matching direction: $\mathbf{k}_s = \mathbf{k}_2 \quad (\omega_s = \omega_2)$
- probe acts like local oscillator (self-heterodyning)

$$I_{\mathrm{HET}}(t) = 2\varepsilon_0 c n_s \mathrm{Re}[E_2^*(t)E_s(t)] \propto 2\omega_2 \mathrm{Im}[E_2(t)P_s^*(t)]$$

- time-integrated & frequency-dispersed signal

$$S_{\mathrm{PP}}(\omega_2) = 2\omega_2 \int_{-\infty}^{\infty} dt \mathrm{Im}[E_2(t)P_s^*(t)] \qquad S_{\mathrm{disp}}(\omega) = 2\omega_2 \mathrm{Im}[E_2(\omega)P_s^*(\omega)]$$

Source: Lochbrunner

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- pump-probe signal

$$\begin{aligned} S_{\mathrm{PP}}(\omega_2) &= -2\omega_2 \int_{-\infty}^{\infty} dt \mathrm{Re}[iE_2^*(t)P_s(t)] \\ &= -\frac{2\omega_2 n_{\mathrm{mol}}\varepsilon_0}{\hbar^3} \mathrm{Re} \int_{-\infty}^{\infty} dt \int_0^{\infty} dt_3 dt_2 dt_1 e^{i\omega_2 t - i\mathbf{k}_2\mathbf{r}} E_2^*(t) \\ &\times \quad E(t-t_3)E(t-t_3-t_2)E(t-t_3-t_2-t_1) \sum_{i=1,8} R_i(t_3,t_2,t_1) \end{aligned}$$

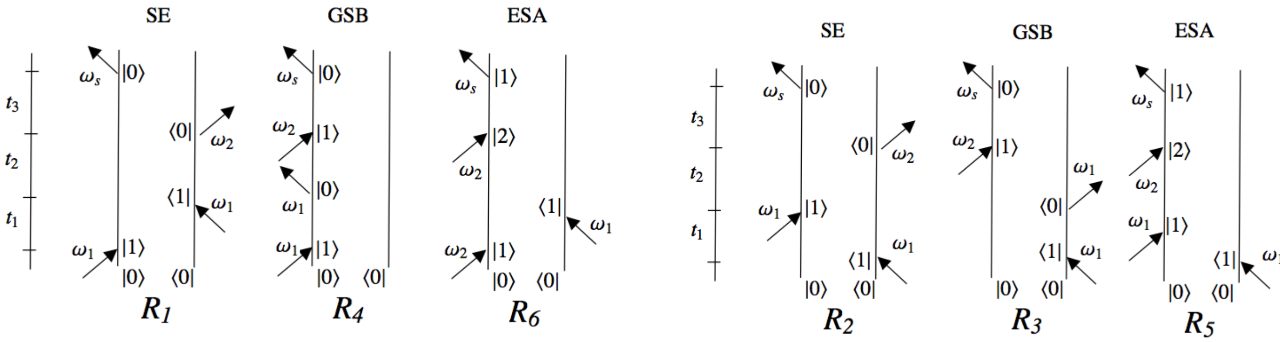
- semi-impulsive limit (pulses shorter than molecular motion, but longer than optical period)

$$E_i(t) \rightarrow \delta(t)$$

- note that one needs to keep the wave vector dependence to find proper phase matched contributions via

$$P_s = P \times \exp(i\omega_s t - i\mathbf{k}_s\mathbf{r})$$

- pump-probe signal for three level system (pure dephasing only)



$$R_1 = |\mu_{10}|^4 I_{10}(t_1) I_{11}(t_2) I_{10}(t_3) \approx |\mu_{10}|^4 I_{10}(t_3) = |\mu_{10}|^4 e^{-i\omega_{10}t_3 - \Gamma_{10}t_3}$$

$$R_2 = |\mu_{10}|^4 I_{01}(t_1) I_{11}(t_2) I_{10}(t_3) \approx |\mu_{10}|^4 I_{10}(t_3) = |\mu_{10}|^4 e^{-i\omega_{10}t_3 - \Gamma_{10}t_3}$$

$$R_3 = |\mu_{10}|^4 I_{01}(t_1) I_{00}(t_2) I_{10}(t_3) \approx |\mu_{10}|^4 I_{10}(t_3) = |\mu_{10}|^4 e^{-i\omega_{10}t_3 - \Gamma_{10}t_3}$$

$$R_4 = |\mu_{10}|^4 I_{10}(t_1) I_{11}(t_2) I_{10}(t_3) \approx |\mu_{10}|^4 I_{10}(t_3) = |\mu_{10}|^4 e^{-i\omega_{10}t_3 - \Gamma_{10}t_3}$$

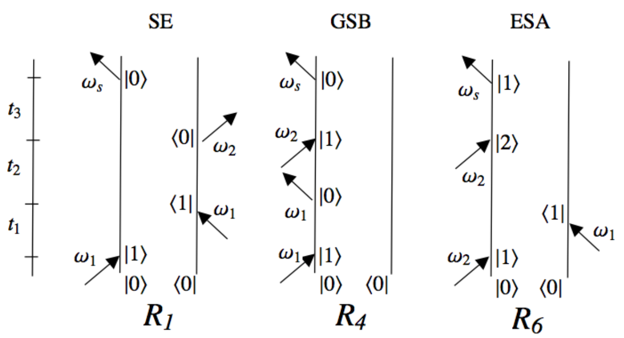
$$R_5 = -|\mu_{10}|^2 |\mu_{21}|^2 I_{10}(t_1) I_{11}(t_2) I_{21}(t_3) \approx -|\mu_{10}|^2 |\mu_{21}|^2 I_{21}(t_3) = -|\mu_{10}|^2 |\mu_{21}|^2 e^{-i\omega_{21}t_3 - \Gamma_{21}t_3}$$

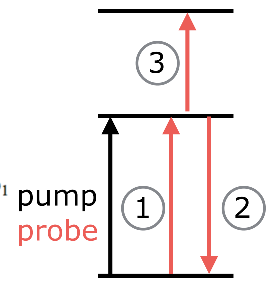
$$R_6 = -|\mu_{10}|^2 |\mu_{21}|^2 I_{01}(t_1) I_{11}(t_2) I_{21}(t_3) \approx -|\mu_{10}|^2 |\mu_{21}|^2 I_{21}(t_3) = -|\mu_{10}|^2 |\mu_{21}|^2 e^{-i\omega_{21}t_3 - \Gamma_{21}t_3}$$

$R_1 = R_2 = R_3 = R_4 \qquad R_5 = R_6$

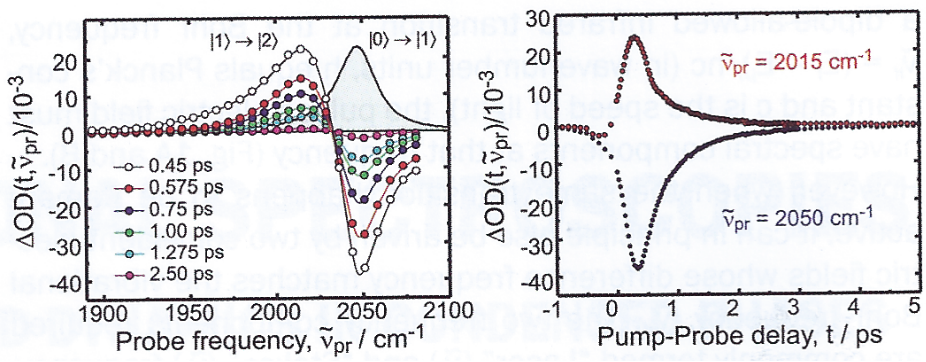
- contributions to the signal

$$S_{\mathrm{disp}}(\omega) \propto -\frac{4|\mu_{10}|^4 \Gamma_{10}}{(\omega - \omega_{10})^2 + \Gamma_{10}^2} + \frac{2|\mu_{10}|^2 |\mu_{21}|^2 \Gamma_{21}}{(\omega - \omega_{21})^2 + \Gamma_{21}^2}$$





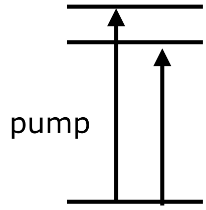
1: ground state bleach
2: stimulated emission
3: excited state absorption

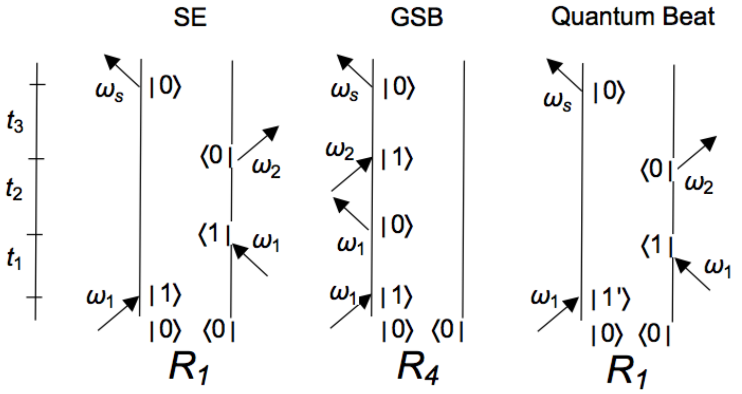


azide ion (N_3^-) in H_2O

Source: Vöhringer et al.

- quantum beat spectroscopy
  - three levels, but two can be coherently excited by the pump



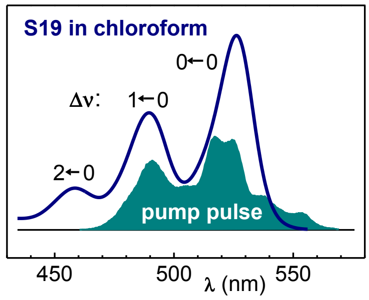


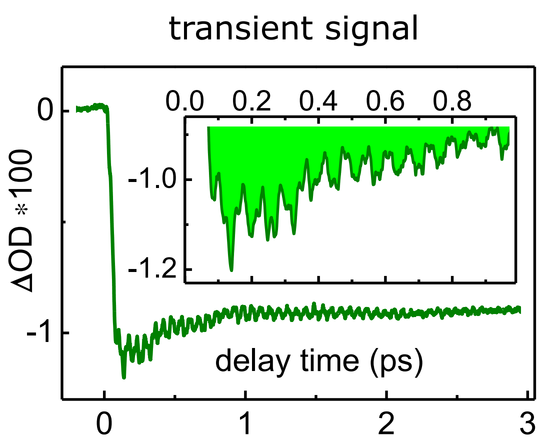
  - new type of R_1 diagram

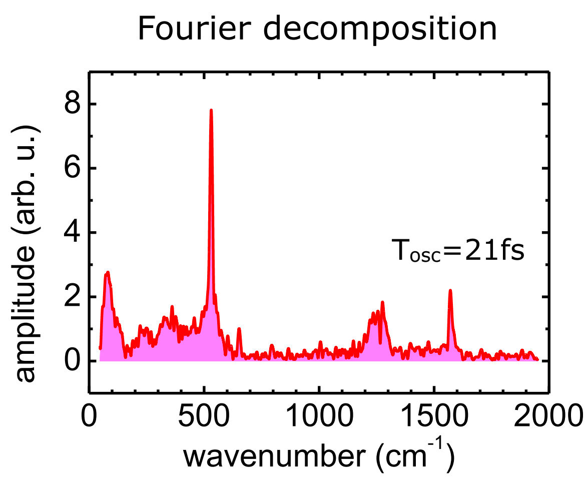
$$
\begin{aligned}
R_1 &= |\mu_{10}|^2|\mu_{1'0}|^2 I_{1'0}(t_1) I_{1'1}(t_2) I_{1'0}(t_3) \approx |\mu_{10}|^2|\mu_{1'0}|^2 I_{1'1}(T) I_{1'0}(t_3) \\
&= |\mu_{10}|^2|\mu_{1'0}|^2 e^{-i\omega_{1'1}T-\Gamma_{1'1}T} e^{-i\omega_{1'0}t_3-\Gamma_{1'0}t_3}
\end{aligned}
$$

  - oscillating signal as function of delay time

- Example: Wave packet dynamics of dye (S19) in chloroform
  - electronic excitation with 9 fs pump pulse
  - more info than in absorption spectrum







Source: Lochbrunner

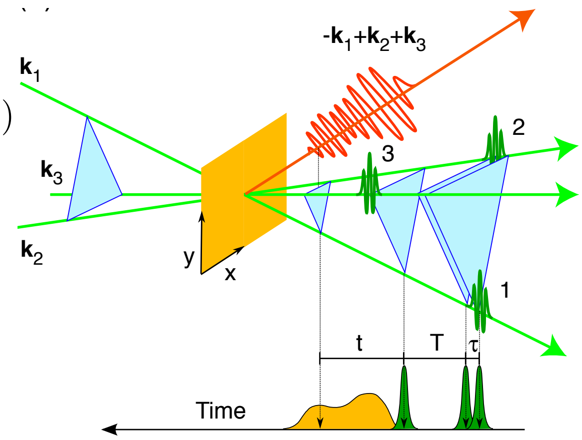
Two-Dimensional Spectroscopy

- goal: extract full information from $R^{(3)}(t_3,t_2,t_1)$
- inspired by multi-dimensional NMR spectroscopy

$$E(t) = E_1(t)e^{-i\omega_1 t + i\mathbf{k}_1\mathbf{r}} + E_2(t-t_1)e^{-i\omega_2 t + i\mathbf{k}_2\mathbf{r}} + E_3(t-t_1-T)e^{-i\omega_3 t + i\mathbf{k}_3\mathbf{r}} + c.c.$$

  - „clocking" of signal by LO field

$$S(t_{\mathrm{LO}},T,t_1) \propto \mathrm{Re}\int_0^\infty dt_3\, E_{\mathrm{LO}}(t_3-t_{\mathrm{LO}})E_s(t_3,T,t_1)$$



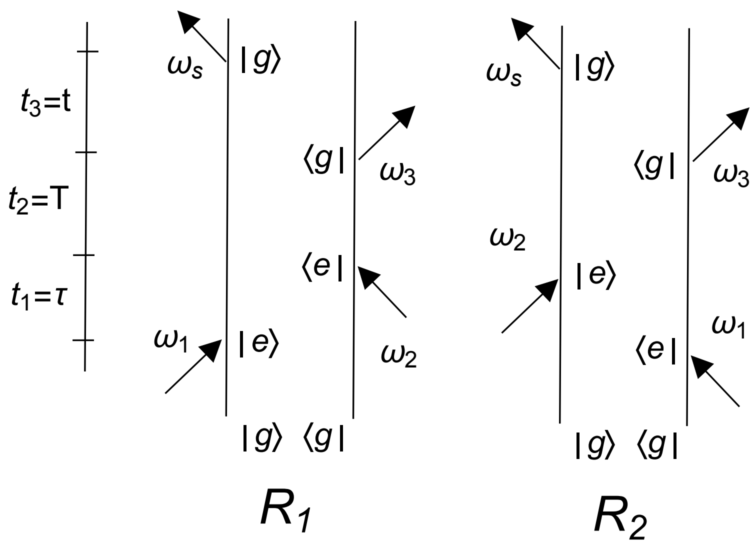
  - semi-impulsive limit

$$S(t_3,T,t_1) \propto E_s(t_3,T,t_1) = iR^{(3)}(t_3,T,t_1)$$

  - signal via double Fourier trafo

$$S(\omega_1,\omega_3,T) = \int_0^\infty dt_3 \int_0^\infty dt_1 e^{i\omega_1 t_1} e^{i\omega_3 t_3} S(t_3,T,t_1)$$

- phase matching
  - rephasing direction $\mathbf{k}_{\mathrm{R}} = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 \quad \to R_2, R_3, R_5$
  - non-rephasing direction $\mathbf{k}_{\mathrm{NR}} = +\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3 \quad \to R_1, R_4, R_6$



- rephasing vs. non-rephasing
  - example: two-level system with pure dephasing

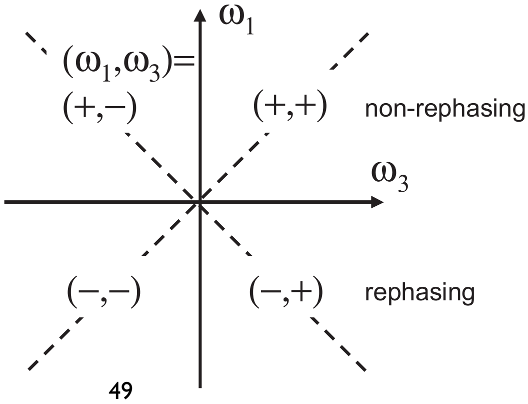
$$R_1 = |\mu_{10}|^4 I_{10}(t_1) I_{11}(t_2 = T) I_{10}(t_3) = |\mu_{10}|^4 e^{-i\omega_{10}t_1 - \Gamma_{10}t_1} e^{-i\omega_{10}t_3 - \Gamma_{10}t_3}$$

$$R_2 = |\mu_{10}|^4 I_{01}(t_1) I_{11}(t_2 = T) I_{10}(t_3) = |\mu_{10}|^4 e^{i\omega_{10}t_1 - \Gamma_{10}t_1} e^{-i\omega_{10}t_3 - \Gamma_{10}t_3}$$

  - phase of oscillation during t_1 different

$$S(\omega_1, \omega_3, 0) \propto \frac{1}{i(\omega_1 - \omega_{10}) - \Gamma_{10}} \frac{1}{i(\omega_3 - \omega_{10}) - \Gamma_{10}} + \frac{1}{i(\omega_1 + \omega_{10}) - \Gamma_{10}} \frac{1}{i(\omega_3 - \omega_{10}) - \Gamma_{10}}$$

  - signals in different parts of Fourier plane



Source: Hamm&Zanni

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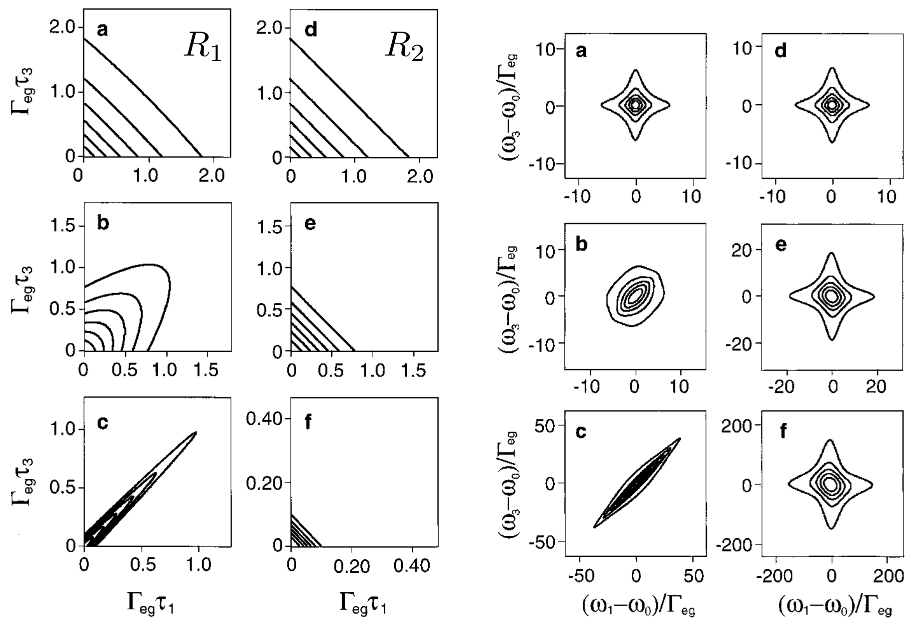
Example 1. Line-Broadening

- homogeneous vs. inhomogeneous broadening
- Kubo model $g(t) = \Gamma t + \frac{\Delta^2}{2} t^2$

$$R_1(t_3, 0, t_1) = |\mu_{10}|^4 e^{-i\omega_{10}(t_1+t_3) - \Gamma_{10}(t_1+t_3) - (t_1+t_3)^2 \Delta/2}$$

$$R_2(t_3, 0, t_1) = |\mu_{10}|^4 e^{-i\omega_{10}(t_3-t_1) - \Gamma_{10}(t_1+t_3) - (t_3-t_1)^2 \Delta/2}$$

(Δ/Γ =0.2 (a,d), 2 (b,e), 20 (c,f))



- only rephasing sensitive

Source: Tokmakoff et al

Example II: 3-level System

- Morse oscillator

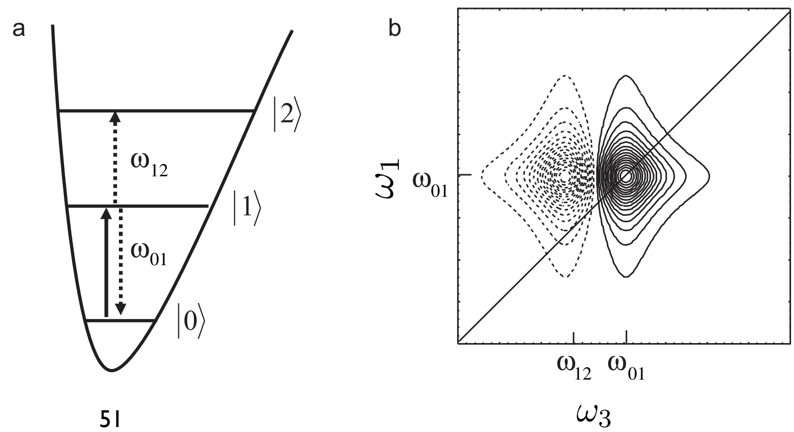
$$V(q) = D(1 - e^{-\alpha q})^2$$

  - eigenvalues

$$E_M = \hbar\omega(M + 0.5) - x(M + 0.5)^2$$

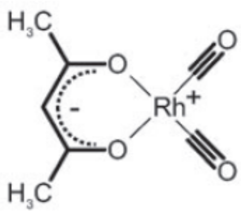
  - anharmonicity constant: $x = (\hbar\omega)^2/4D$
  - if dipole moment linear and x=0: no nonlinear signal

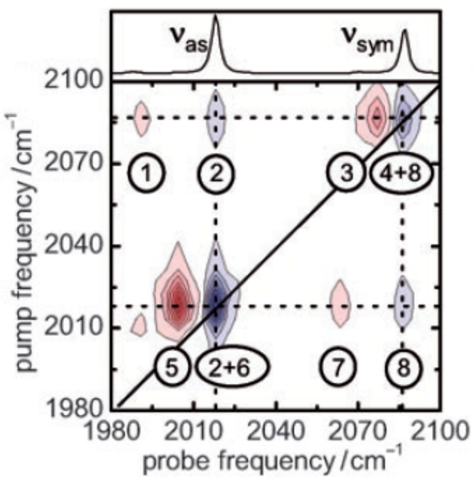
$\mu_{12}^2 = 2\mu_{10}^2$

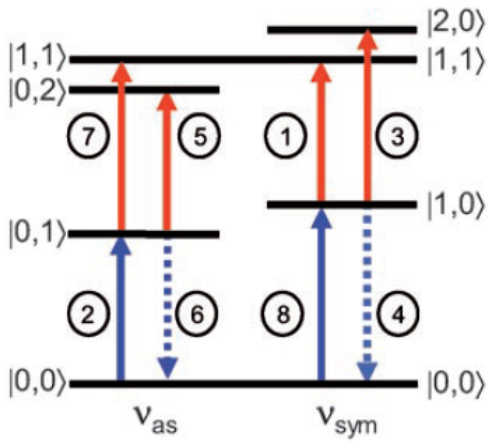


Source: Hamm&Zanni

Example II: Coupled Modes





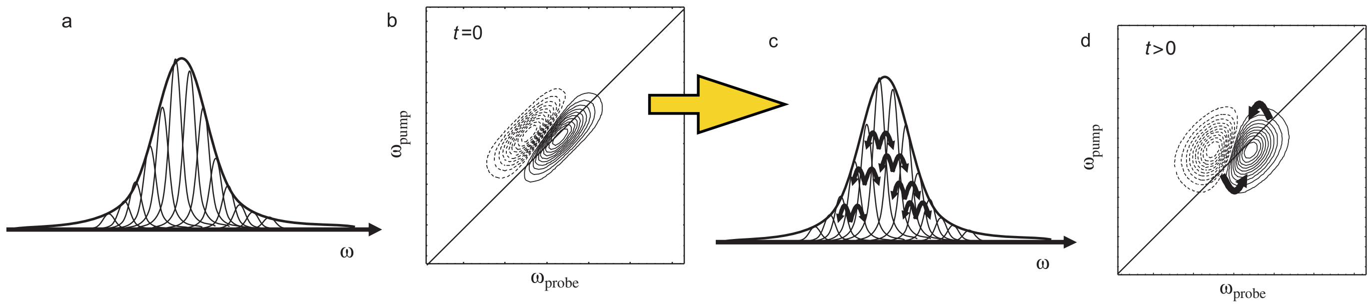


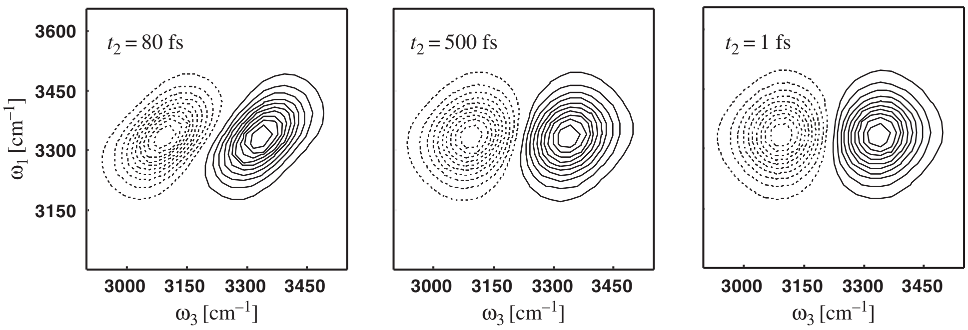
- power of 2D spectroscopy in unraveling mode couplings

Source: Bredenbeck et al

Example IV: Spectral Diffusion

- signature of inhomogeneity at T=0 disappears for T>0 if ensemble not completely frozen



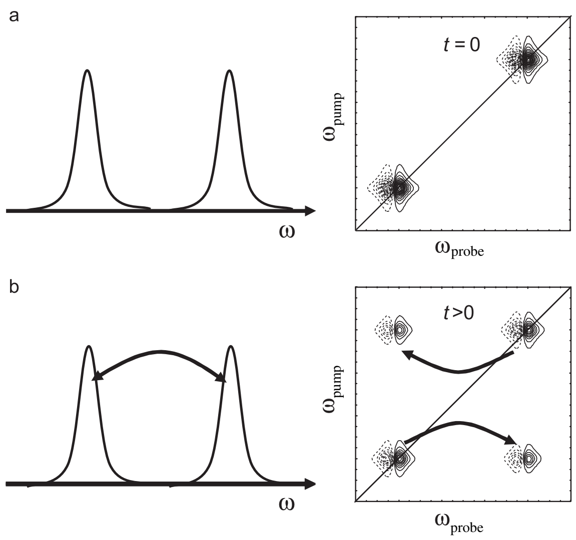


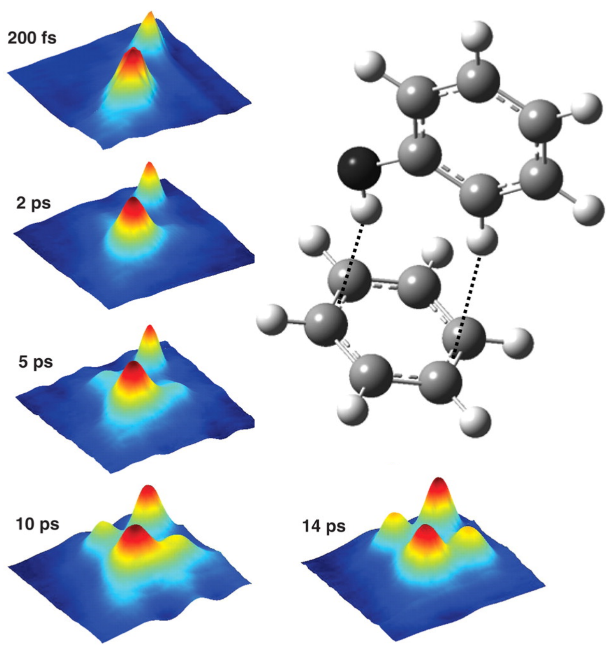
HOD in D_2O

Source: Hamm&Zanni

Example V: Chemical Exchange

- reaction dynamics can be monitored as function of T





HB dissociation of phenol-benzene complex

Sources: Hamm&Zanni. Zheng et al.