2D-IR Spectroscopy

pulse $\epsilon(t) = \epsilon'(t) \cdot \cos \omega t$

Interaction between field and dipole $\vec{\mu}$: $\hat{W} = -\mu\, \epsilon(t)$

Total Hamitonian : $\hat{H} = \hat{H}_0 + \hat{W}(t)$

Time independent schrödinger eq $\hat{H}_0 |n\rangle = \epsilon_n |n\rangle$

Time dep. of wavefunction $i\hbar \frac{\partial}{\partial t} |\psi\rangle = \hat{H} |\psi\rangle$

In absence of laserpulse $\hat{H} = \hat{H}_0$

$\Rightarrow |\psi\rangle = \sum_n c_n e^{-i\epsilon_n t/\hbar} |n\rangle$

In presence of laserpulse c_n time dependent

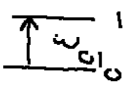
$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = \underbrace{i\hbar \sum \frac{\partial c_n}{\partial t} e^{-i\epsilon_n t/\hbar} |n\rangle}_{\hat{W}(t)|\psi\rangle} + \underbrace{\sum_n \epsilon_n c_n e^{-i\epsilon_n t/\hbar} |n\rangle}_{\hat{H}_0|\psi\rangle}$$

$$i\hbar \sum_n \frac{\partial c_n}{\partial t} e^{-i\epsilon_n t/\hbar} |n\rangle = \hat{W}(t) \cdot \sum_n c_n e^{-i\epsilon_n t/\hbar} |n\rangle$$ multiply with $\langle m|$

$$i\hbar \sum_n \frac{\partial c_n}{\partial t} e^{-i\epsilon_n t/\hbar} \langle m|n\rangle = \sum_n c_n e^{-i\epsilon_n t/\hbar} \langle m|\hat{W}(t)|n\rangle$$

$$i\hbar \frac{\partial c_m}{\partial t} e^{-i\epsilon_m t/\hbar} = \sum_n c_n(t) e^{-i\epsilon_n t/\hbar} \langle m|W|n\rangle$$ 2 level system

$$\frac{\partial c_m(t)}{\partial t} = -\frac{i}{\hbar} \sum_n c_n(t)\, e^{-i(\epsilon_n - \epsilon_m)t/\hbar} \langle \cdots \rangle$$



$\psi = c_0|0\rangle + c_1|1\rangle$

$$\frac{\partial}{\partial t} c_1(t) = \frac{i}{\hbar} c_0(t)\, e^{i\omega_{01}t} \langle 1|\hat{\mu}|0\rangle \epsilon(t) \quad + c_1$$

$$\frac{\partial}{\partial t} c_0(t) = \frac{i}{\hbar} c_1(t)\, e^{-i\omega_{01}t} \langle 0|\mu|1\rangle \epsilon(t)$$

$\langle 1|W|1\rangle = 0$

$\langle 0|W|0\rangle = 0$

$\hat{W} = -\mu_x \cdot \epsilon$

$c_1 \ll c_0$

$\Downarrow$

$c_0 \approx 1$

After laser pulse : $|\psi(t)\rangle = c_0 e^{-i\epsilon_0 t/\hbar} |0\rangle + i c_1 e^{-i\epsilon_1 t/\hbar} |1\rangle$

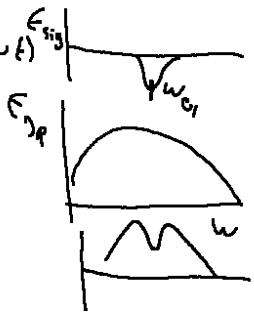
$P(t) = \langle \mu \rangle = \langle \Psi(t) | \hat{\mu} | \Psi(t) \rangle$ $\qquad \Psi = c_0 e^{\cdots} |0\rangle + i c_1 e^{\cdots} |1\rangle$

$(c_0 e^{i E_0 t/\hbar} \langle 0| - i c_1 e^{i E_1 t/\hbar} \langle 1|) \, \hat{\mu} \, (c_0 e^{-i E_0 t/\hbar} |0\rangle + i c_1 e^{-i E_1 t/\hbar} |1\rangle) =$

$c_0^2 \langle 0|\mu|0\rangle + c_1^2 \langle 1|\mu|1\rangle + \underbrace{c_0 c_1 \langle 0|\mu|1\rangle \sin(\omega_{01} t)}_{P(t)} = \mu_{01}^2 \sin(\omega_{01} t)$

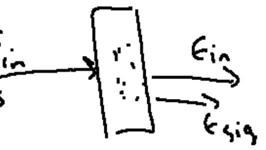
Emitted field has a 90° phase shift

$\Rightarrow E_{sig}(t) = -\mu_{01}^2 \cos(\omega_{01} t) \qquad E_{in} = E'(t) \cos(\omega t)$



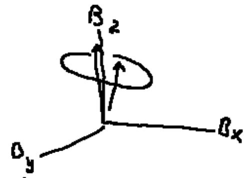
Mukamel for dummies

Hamm



} destructive interference = absorbtion

Bloch vectors



$c_0 e^{-i E_0 t/\hbar}$

single molecule $|\Psi\rangle = c_0(t)|0\rangle + i\, c_1(t)|1\rangle$

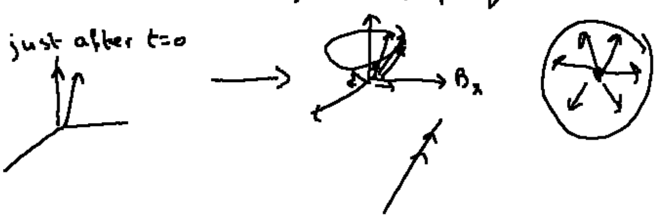
$B_z(t) = c_0(t) c_0^*(t) - c_1(t) c_1^*(t)$ population

$B_x(t) = i(\langle c_0 c_1^* \rangle - \langle c_0^* c_1 \rangle) = c_0 c_1 \sin(\omega_{01} t)$ polarisation

$B_y(t) = c_0 c_1^* + c_0 c_1 = c_0 c_1 \cos(\omega_{01} t)$

Ensemble of molecules with slightly diff. freq.

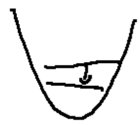
just after t=0



$kT \approx 200 \text{ cm}^{-1}$

$\frac{N_1}{N_0} = ?\, e^{\hbar \omega_i / kT}$

Density matrix $\qquad \psi = c_0|0\rangle + c_1|1\rangle$



Two level system

$$\rho = \begin{pmatrix} \rho_{00} & \rho_{01} \\ \rho_{10} & \rho_{11} \end{pmatrix} = \begin{pmatrix} \langle c_0(t) c_0^*(t)\rangle & -i\langle c_0(t) c_1^*(t)\rangle \\ i\langle c_1(t) c_0^*(t)\rangle & \langle c_1(t) c_1^*(t)\rangle \end{pmatrix}$$

Coherences $\qquad$ populations

$$\langle B_z\rangle = \rho_{00} - \rho_{11}$$
$$\langle B_x\rangle = -(\rho_{01} + \rho_{10})$$
$$\langle B_y\rangle = i(\rho_{01} - \rho_{10})$$

Homogeneous dephasing

$$\rho_{01}(t) = -i c_0 c_1 e^{i\omega_{01}t} e^{-t/T_2}$$
$$\rho_{10}(t) = i c_0 c_1 e^{-i\omega_{01}t} e^{-t/T_2}$$

$t=0$ just after laser pulse

Population relaxation

$$\rho_{11}(t) = \rho_{11}(0) e^{-t/T_1}$$
$$\rho_{00}(t) = 1 - \rho_{11}(t)$$

due to fluctuations of environment

pure dephasing

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*}$$

Calculation of response function of 2-level system $\qquad \mu_{01} = \mu_{10}$

ground state $\quad \rho(-\infty) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \qquad \hat{W}(t) = -\hat{\mu} E(t)$

at $t=0$ $\quad i\underline{\mu(0)}\cdot\rho(-\infty) = i\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ i & 0 \end{pmatrix} \qquad \mu = \begin{pmatrix} 0 & \mu_{01} \\ \mu_{01} & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

generated (10) coherence

$$i e^{-i\omega_{01}t_1} \mu(0)\rho(-\infty) = \begin{pmatrix} 0 & 0 \\ i e^{-i\omega_{01}t_1} & 0 \end{pmatrix}$$

$\psi = c_0|0\rangle + c_1|1\rangle$

to get light out $\quad i\underline{\mu(t_1)}\, e^{-i\omega_{01}t_1}\mu(0)\rho(-\infty) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & 0 \\ i e^{-i\omega_{01}t} & 0 \end{pmatrix} = \begin{pmatrix} i e^{-i\omega_{01}t_1} & 0 \\ 0 & 0 \end{pmatrix}$

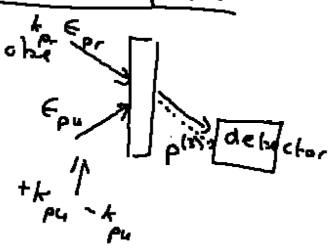
$$P = \langle\mu\rangle = \mathrm{Tr}(\rho\mu)$$

$$R^{(1)}(t_1) = i e^{-i\omega_{01}t_1} + cc$$
$$= \sin(\omega_{01}t_1) = \text{Polarisation}$$

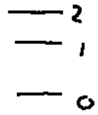
$-\cos(\omega_{01}t)$ ← field $90°$ phase shift

Third order response

pump - probe



3-level system



SE

$\rho_{10}(0) \propto \mu_{01}$ neglect pop. relaxation

$\downarrow$ pump 2

$\rho_{11}(0) \propto \mu_{01}^2$

$\downarrow$ probe

$\rho_{10}(t) \propto \mu_{10}^3 e^{-i\omega_{01}t_3} e^{-t_3/T_2}$

$\downarrow$ signal / outgoing

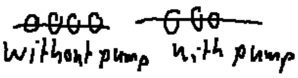
$\left(\frac{i}{\hbar}\right)^3 \xrightarrow[-\text{sign}]{\text{ignore}} S_{SE}^{(3)} \propto \frac{i}{\hbar^3}\mu_{10}^4 e^{-i\omega_{01}t_3} e^{-t_3/T_2}$

signal outgoing $\quad \overset{\shortparallel}{S_B^{(3)}}$

$\rho_{00} \xrightarrow{\text{pump pulse}} \rho_{10} \xrightarrow{2\text{-pump}} \rho_{00} \xrightarrow{\text{probe pulse}} \rho_{10} \longrightarrow \rho_{00}$ bleach B

$\rho_{10} \longrightarrow \rho_{11} \longrightarrow \rho_{10} \longrightarrow \rho_{00}$ stimulated emission = SE

$\rho_{11} \longrightarrow \rho_{12} \longrightarrow \rho_{11}$ excited state absorption ESA



Similar for ESA $\quad S_{ESA} \propto -\frac{i}{\hbar^3}\mu_{10}^2\mu_{12}^2 e^{-i\omega_{12}t_3} \underline{e^{-t_3/T_2}}$