Modeling Coherent Multidimensional Vibrational Spectroscopy

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GDRs EMIE-UP School: Multi-scale Dynamics in Molecular Systems

References

- S. Mukamel, *Principles of Nonlinear Optical Spectroscopy*. Oxford University Press, 1995.
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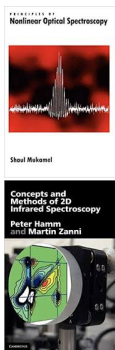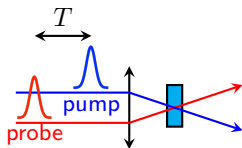
- Y. S. Kim and R. M. Hochstrasser, *Applications of 2D-IR spectroscopy to peptides, proteins, and hydrogen- bond dynamics*. J. Phys. Chem. B **113**, 8231 (2009).
- T. L. C. Jansen, S. Saito, J. Jeon, and M. Cho, *Theory of coherent two-dimensional vibrational spectroscopy*. J. Chem. Phys. **150**, 100901 (2019).
- A. Ghosh, J. S. Ostrander, and M. T. Zanni, *Watching proteins wiggle: Mapping structures with two-dimensional infrared spectroscopy*. Chem. Rev. **117**, 10726 (2017).

IR Pump-probe spectroscopy
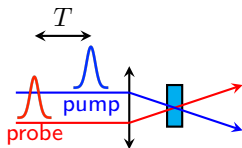
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- Pump-probe spectra $S(T, \omega)$, $\omega \equiv$ probe frequency, $T \equiv$ population time
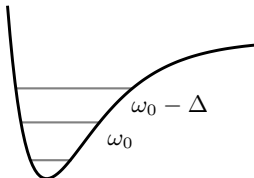
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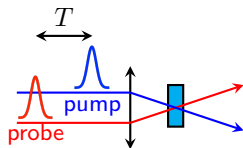
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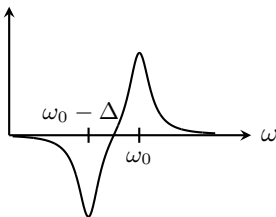
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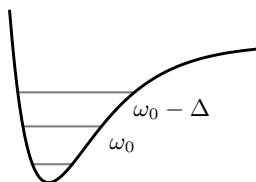
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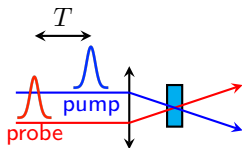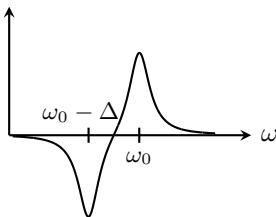
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Probe pulse induce three processes

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$\omega_0 - \Delta$

ω_0

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ω_0

ω

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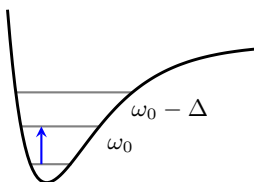
- ground-state bleaching
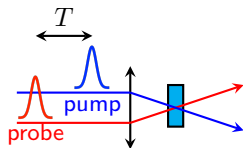
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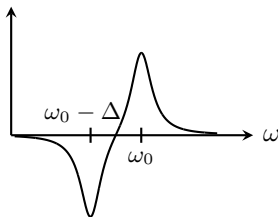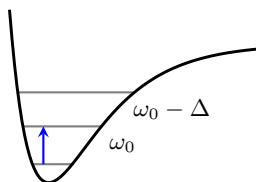- excited state emission
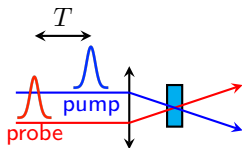
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- excited state absorption

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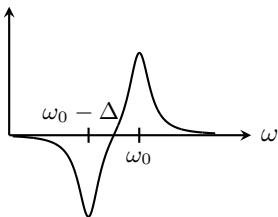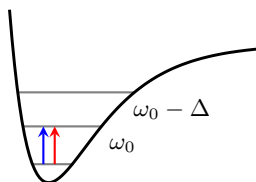
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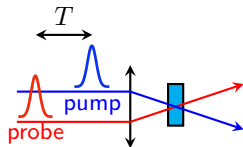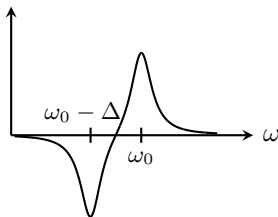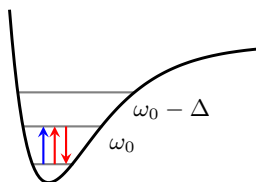
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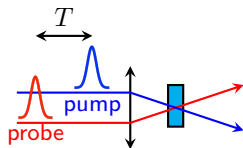

anharmonicity Δ

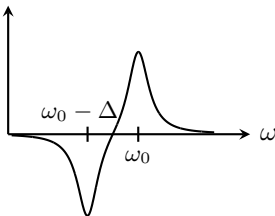$\omega_0 - \Delta$

ω_0

Probe pulse induce three processes

- ground-state bleaching
- excited state emission
- excited state absorption

- By varying time, we can measure the vibrational relaxation time

2D-IR spectroscopy in pump-probe geometry
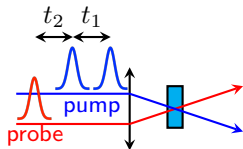
- 2D-IR spectroscopy in pump-probe geometry
- Use of two pump pulses
- Fourier transform along time t_1

$$S(t_1, t_2, \omega_3) \to S(\omega_1, t_2, \omega_3)$$

single anharmonic oscillator
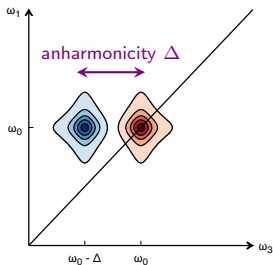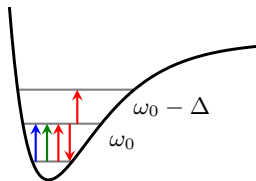
- $\omega_1 \equiv$ pump frequency
- $\omega_3 \equiv$ probe frequency
- $t_2 \equiv$ population time

Shim and Zanni PCCP **11** *748 (2009)*

2D-IR spectroscopy in BoxCARS
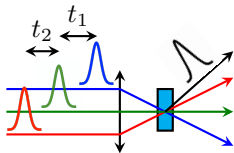
- Originally 2D-IR was developed in BoxCARS geometry
- Each pulse have a different direction $\mathbf{k}_1$, $\mathbf{k}_2$, $\mathbf{k}_3$
- Non-linear polarization resulting from the interaction with the pulses is measured using heterodyne detection in specific directions

$$\mathbf{k_I} = -\mathbf{k_1} + \mathbf{k_2} + \mathbf{k_3}, \quad \mathbf{k_{II}} = \mathbf{k_1} - \mathbf{k_2} + \mathbf{k_3}, \quad \mathbf{k_{III}} = \mathbf{k_1} + \mathbf{k_2} - \mathbf{k_3}$$
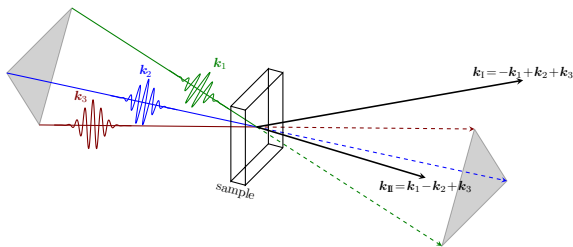
Asplund, Zanni, and R. M. Hochstrasser. PNAS **97**, 8219 (2000)

Spectral diffusion

set of molecules in different environments

ω

Hamm and Zanni, Concepts and Methods of 2D Infrared Spectroscopy (2011)

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homogeneous
linewidth

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$t_2 = 0$

pump frequency ω_{01}

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$\omega_{01}\text{-}\Delta$ ω_{01}

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spectral diffusion: dynamics of the bath on timescale τ_c
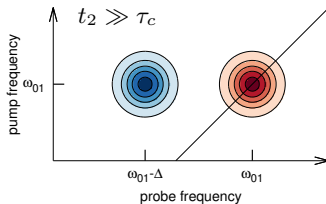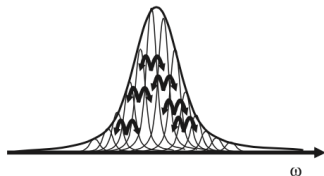
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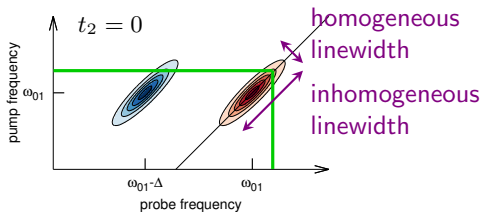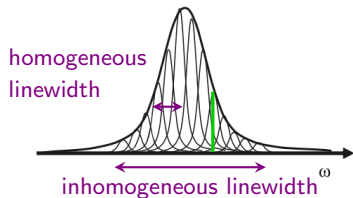
2D-IR spectroscopy is sensitive to the fluctuations of the environment
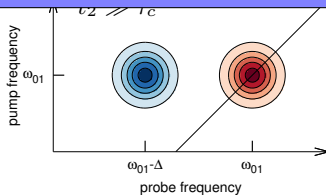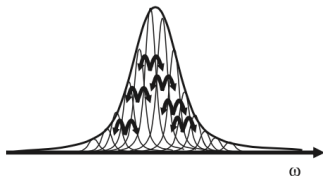
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Example: liquid water

- OH vibration of HOD in D_2O
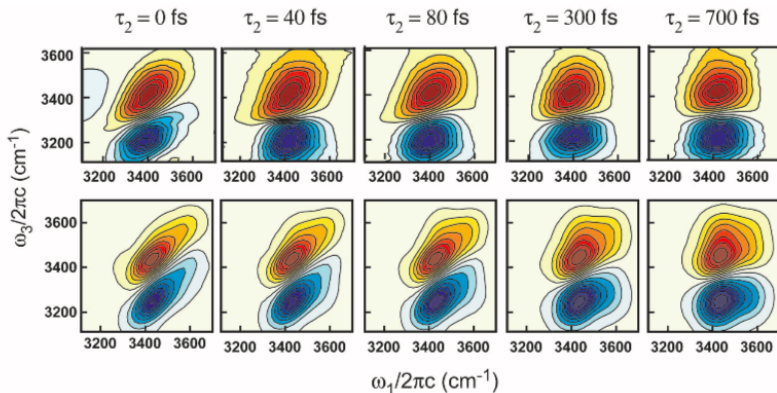
- 2D-IR probes the fluctuations of the hydrogen bond network

Loparo JCP **125** *194522 (2006)*

Example: carboxymyoglobin (MbCO)
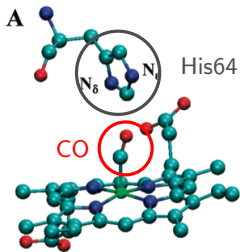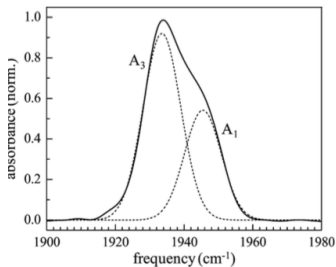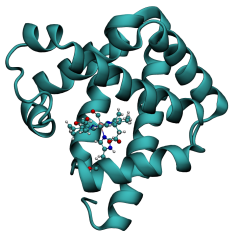
- In MbCO the CO band show two bands
- A_1 and A_3 states are connected to the orientation of the His64 side chain

Bagchi et al. JPCB 114, 17187 (2010)

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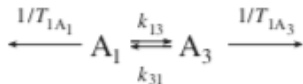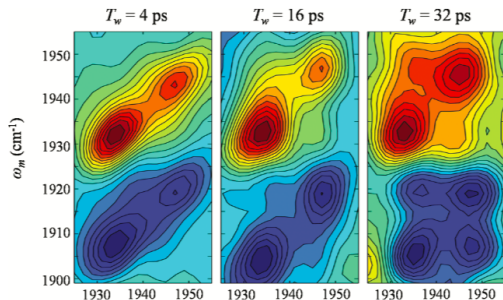
- The appearance of a cross-peak is the signature of the interconversion between the A_1 and A_3 states

Bagchi et al. JPCB 114, 17187 (2010)

Outline

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1. Theoretical foundation of 2D-IR spectroscopy
   - Response function formalism
   - Model systems

2. Molecular simulations
   - Classical dynamics
   - Mixed quantum-classical simulations

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- Semiclassical description of the system-field interaction
    - Molecular system is described quantum mechanically
    - The laser field is described classically

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  - Raman spectroscopy: $\hat{V}(t) = -\frac{1}{2}\hat{\boldsymbol{\alpha}} : \mathbf{E}(\mathbf{r}, t)\mathbf{E}(\mathbf{r}, t)$

Perturbation theory

- Interaction with the field creates a macroscopic polarization $\mathbf{P}(t) = \mathrm{Tr}\left[\hat{\boldsymbol{\mu}}\rho(t)\right]$
  $\rho(t) \equiv$ system density matrix <u>in interaction</u> with the field

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$$\rho^{(n)}(t) = (-i)^n \int_{-\infty}^{t} \mathrm{d}\tau_n \int_{-\infty}^{\tau_n} \mathrm{d}\tau_{n-1} \cdots \int_{-\infty}^{\tau_2} \mathrm{d}\tau_1 \, \mathscr{G}_0(t - \tau_n)\mathscr{V}(\tau_n)$$
$$\times \, \mathscr{G}_0(\tau_n - \tau_{n-1})\mathscr{V}(\tau_{n-1}) \cdots \mathscr{G}_0(\tau_2 - \tau_1)\mathscr{V}(\tau_1)\rho_{\mathsf{eq}}.$$

$\mathscr{G}_0(t) = \exp\left(-i\mathscr{L}_0 t\right)$ time-evolution operator <u>without</u> the field.
$\rho_{\mathsf{eq}} = \frac{1}{Z}e^{-\beta\hat{H}_0}$ equilibrium density matrix.

Linear response

- Linear polarization

$$P_\alpha^{(1)}(t) = \sum_\beta \int_0^\infty \mathrm{d}t' \ R_{\alpha\beta}^{(1)}(t') E_\beta(t - t')$$

- Linear response function

$$R_{\alpha\beta}^{(1)}(t) = \mathrm{i}\theta(t) \left\langle [\hat{\mu}_\alpha(t), \hat{\mu}_\beta] \right\rangle \qquad \hat{\mu}_\alpha(t) = e^{\mathrm{i}\hat{H}_0 t} \hat{\mu}_\alpha e^{-\mathrm{i}\hat{H}_0 t}$$

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$$P^{(1)}(\omega) = R^{(1)}(\omega)E(\omega) = \epsilon_0 \chi(\omega)E(\omega)$$

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$$\chi''(\omega) = \mathrm{Im}\,\chi(\omega) \propto \mathrm{Im}\,R^{(1)}(\omega) \rightarrow \text{absorption}$$

Linear response

- Example two-level system initially in the ground state: $\langle \hat{\mu}(t)\hat{\mu} \rangle = \mu_{01}^2 e^{-i\omega_0 t}$

$$S(\omega) \approx \mathrm{Re} \int_0^\infty e^{i\omega t} \langle \hat{\mu}(t)\hat{\mu} \rangle = \pi \mu_{01}^2 \delta(\omega - \omega_0)$$
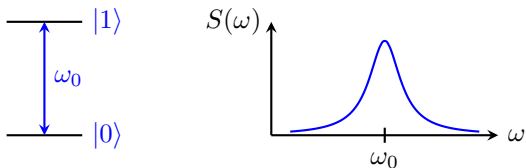
4-wave mixing experiment: Third-order response

- Third-order polarization

$$P_\alpha^{(3)}(t) = \sum_{\beta\gamma\delta} \int_0^\infty \mathrm{d}t_3 \int_0^\infty \mathrm{d}t_2 \int_0^\infty \mathrm{d}t_1 R_{\alpha\beta\gamma\delta}^{(3)}(t_1, t_2, t_3)$$
$$\times E_\beta(t - t_3) E_\gamma(t - t_3 - t_2) E_\delta(t - t_3 - t_2 - t_1)$$

- Third-order response function

$$R^{(3)}(t_1, t_2, t_3) = \mathrm{i}^3 \theta(t_1)\theta(t_2)\theta(t_3) \langle [[[\hat{\mu}(t_1 + t_2 + t_3), \hat{\mu}(t_1 + t_2)], \hat{\mu}(t_1)], \hat{\mu}] \rangle$$

- Third-order response function is composed of 8 different correlation functions.
- Using the **phase matching condition** and the **rotating wave approximation** we can show that they don't all contribute to the spectra

Phase matching condition
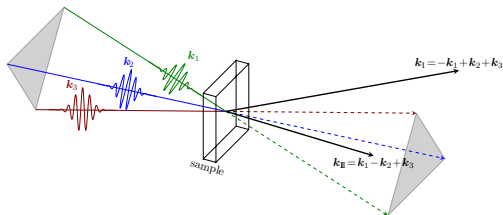
- Incoming field: sum of three laser pulses

$$E(\mathbf{r}, t) = \mathcal{E}(\mathbf{r}, t) + \mathcal{E}^*(\mathbf{r}, t) \qquad \mathcal{E}(\mathbf{r}, t) = \sum_{p=1}^{3} \mathscr{E}_p(t - \tau_p) e^{i\mathbf{k}_p \cdot \mathbf{r} - i\omega_p(t - \tau_p)}$$

- τ_p: center of the pulse, ω_p: pulse frequency, $\mathscr{E}_p$: pulse enveloppe and $\mathbf{k}_p$: pulse wavevector

$$P^{(3)}(t) = \sum_s \mathcal{P}_s^{(3)}(t) e^{i\mathbf{k}_s \cdot \mathbf{r}} \quad \mathbf{k}_s = m_1 \mathbf{k}_1 + m_2 \mathbf{k}_2 + m_3 \mathbf{k}_3$$

$$m_i = 0, \pm 1, \pm 2, \pm 3 \quad |m_1| + |m_2| + |m_3| = 3$$

Phase matching condition

- Maxwell's equations

$$\nabla \times \nabla \times \mathbf{E} + \frac{1}{c^2}\frac{\partial^2 \mathbf{E}}{\partial t^2} = -\frac{1}{\epsilon_0 c^2}\frac{\partial^2 \mathbf{P}^{(3)}}{\partial t^2}$$

- Third order polarisation generate a radiated field $\mathcal{E}_{\mathsf{rad}}(t) \propto i\mathcal{P}^{(3)}(t)\delta(\mathbf{k} - \mathbf{k}_s)$ **in the phase matching directions $\mathbf{k}_s = m_1\mathbf{k}_1 + m_2\mathbf{k}_2 + m_3\mathbf{k}_3$**
- In 2D-IR spectroscopy: the system interacts once with each laser pulse $\mathbf{k}_s = \pm\mathbf{k}_1 \pm \mathbf{k}_2 \pm \mathbf{k}_3$
  - Rephasing spectra $\mathbf{k}_\mathsf{I} = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$
  - Nonrephasing spectra $\mathbf{k}_\mathsf{II} = \mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3$
  - Double-quantum coherence spectra $\mathbf{k}_\mathsf{III} = \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3$

2D-IR signal

- Signal is given by the dispersed radiated field $\operatorname{Re} \mathcal{E}_{\mathsf{rad}}(\omega) = \operatorname{Im} \mathcal{P}^{(3)}(\omega)$
- We consider short pulses compared to the system dynamics $\mathcal{E}_p(t - \tau_p) \propto \delta(t - \tau_p)$

$$S(t_1, t_2, \omega_3) = \operatorname{Im} \int_0^\infty \mathrm{d}t \; e^{\mathrm{i}\omega_3 t_3} R^{(3)}(t_1, t_2, t_3)$$
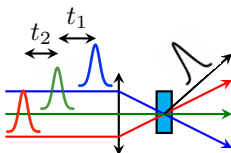
Rotating wave approximation

- Separation of upward transitions ($\hat{\mu}^+$) and downward transitions ($\hat{\mu}^-$)

$$\hat{\mu} = \hat{\mu}^+ + \hat{\mu}^-$$

$$\hat{\mu}^+(t) = e^{i\hat{H}_0 t}\hat{\mu}^+ e^{-i\hat{H}_0 t} \propto e^{+i\omega_0 t}$$

$$\hat{\mu}^-(t) = e^{i\hat{H}_0 t}\hat{\mu}^- e^{-i\hat{H}_0 t} \propto e^{-i\omega_0 t}$$

- Incoming field: $E(\mathbf{r}, t) = \mathcal{E}(\mathbf{r}, t) + \mathcal{E}^*(\mathbf{r}, t)$

$$\mathcal{E}(\mathbf{r}, t) \propto e^{-i\omega_0 t} \quad \mathcal{E}^*(\mathbf{r}, t) \propto e^{i\omega_0 t}$$

- Rotating wave approximation (RWA)

$$\hat{V}(t) = -\hat{\mu}E(\mathbf{r}, t) \approx -\hat{\mu}^+\mathcal{E}(\mathbf{r}, t) - \hat{\mu}^-\mathcal{E}^*(\mathbf{r}, t)$$

$|2\rangle$

$|1\rangle$ $\hat{\mu}^+$ $\hat{\mu}^-$

$\hat{\mu}^+$ $\hat{\mu}^-$

$|0\rangle$
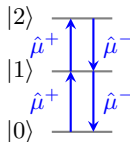
Rotating wave approximation

- Rotating wave approximation (RWA)

$$\hat{V}(t) \approx -\hat{\mu}^+ \mathcal{E}(\mathbf{r}, t) - \hat{\mu}^- \mathcal{E}^*(\mathbf{r}, t)$$

- Rephasing spectrum $\mathbf{k}_\mathsf{I} = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$

$$\mathcal{R}_{\mathbf{k}_\mathsf{I}} = \mathrm{i}^3 \theta(t_1)\theta(t_2)\theta(t_3)\langle[[[\hat{\mu}^-(t_1 + t_2 + t_3), \hat{\mu}^+(t_1 + t_2)], \hat{\mu}^+(t_1)], \hat{\mu}^-]\rangle$$

- Non rephasing spectrum $\mathbf{k}_\mathsf{II} = \mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3$

$$\mathcal{R}_{\mathbf{k}_\mathsf{II}} = \mathrm{i}^3 \theta(t_1)\theta(t_2)\theta(t_3)\langle[[[\hat{\mu}^-(t_1 + t_2 + t_3), \hat{\mu}^+(t_1 + t_2)], \hat{\mu}^-(t_1)], \hat{\mu}^+]\rangle$$

- Double quantum coherence $\mathbf{k}_\mathsf{III} = \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3$

$$\mathcal{R}_{\mathbf{k}_\mathsf{III}} = \mathrm{i}^3 \theta(t_1)\theta(t_2)\theta(t_3)\langle[[[\hat{\mu}^-(t_1 + t_2 + t_3), \hat{\mu}^-(t_1 + t_2)], \hat{\mu}^+(t_1)], \hat{\mu}^+]\rangle$$

Rephasing spectra $\mathbf{k}_I$

- System initially in the ground state $\rho_{\text{eq}} = |0\rangle\langle 0|$, with $\hat{\mu}^-|0\rangle = 0$.
- Only three terms contribute: Ground State bleaching (GSB), Excited State Emission (ESE) and Excited State Absorption (ESA)

$$\mathcal{R}_{\mathbf{k}_I} = i^3 \theta(t_1)\theta(t_2)\theta(t_3)\left(R_{\text{GSB}}^{\mathbf{k}_I} + R_{\text{ESE}}^{\mathbf{k}_I} - R_{\text{ESA}}^{\mathbf{k}_I}\right)$$

$$R_{\text{GSB}}^{\mathbf{k}_I}(t_1, t_2, t_3) = \langle \hat{\mu}^- \hat{\mu}^+(t_1)\hat{\mu}^-(t_1 + t_2 + t_3)\hat{\mu}^+(t_1 + t_2)\rangle$$

$$R_{\text{ESE}}^{\mathbf{k}_I}(t_1, t_2, t_3) = \langle \hat{\mu}^- \hat{\mu}^+(t_1 + t_2)\hat{\mu}^-(t_1 + t_2 + t_3)\hat{\mu}^+(t_1)\rangle$$

$$R_{\text{ESA}}^{\mathbf{k}_I}(t_1, t_2, t_3) = \langle \hat{\mu}^- \hat{\mu}^-(t_1 + t_2 + t_3)\hat{\mu}^+(t_1 + t_2)\hat{\mu}^+(t_1)\rangle$$

- We have something similar for the $\mathbf{k}_{II}$ non-rephasing spectrum

Double sided Feynman diagrams

- $\mathbf{k_l}$ ESE term

$$R_{\mathsf{ESE}}^{\mathbf{k_l}}(t_1, t_2, t_3) = \langle \hat{\mu}^- \hat{\mu}^+(t_1 + t_2) \hat{\mu}^-(t_1 + t_2 + t_3) \hat{\mu}^+(t_1) \rangle$$

Double sided Feynman diagrams

- $\mathbf{k}_I$ ESE term

$$R_{\mathsf{ESE}}^{\mathbf{k}_I}(t_1, t_2, t_3) = \langle \hat{\mu}^- \hat{\mu}^+(t_1 + t_2) \hat{\mu}^-(t_1 + t_2 + t_3) \hat{\mu}^+(t_1) \rangle$$

$$R_{\mathsf{ESE}}^{\mathbf{k}_I}(t_1, t_2, t_3) = \mathrm{Tr} \left[\rho_{\mathsf{eq}} \hat{\mu}^- \hat{\mu}^+(t_1 + t_2) \hat{\mu}^-(t_1 + t_2 + t_3) \hat{\mu}^+(t_1) \right]$$

Double sided Feynman diagrams

- $\mathbf{k_I}$ ESE term

$$R_{\mathsf{ESE}}^{\mathbf{k_I}}(t_1, t_2, t_3) = \langle \hat{\mu}^- \hat{\mu}^+(t_1 + t_2) \hat{\mu}^-(t_1 + t_2 + t_3) \hat{\mu}^+(t_1) \rangle$$

$$R_{\mathsf{ESE}}^{\mathbf{k_I}}(t_1, t_2, t_3) = \mathrm{Tr} \left[\rho_{\mathsf{eq}} \hat{\mu}^- \hat{\mu}^+(t_1 + t_2) \hat{\mu}^-(t_1 + t_2 + t_3) \hat{\mu}^+(t_1) \right]$$

$$R_{\mathsf{ESE}}^{\mathbf{k_I}}(t_1, t_2, t_3) = \mathrm{Tr} \left[\hat{\mu}^-(t_1 + t_2 + t_3) \hat{\mu}^+(t_1) \rho_{\mathsf{eq}} \hat{\mu}^- \hat{\mu}^+(t_1 + t_2) \right]$$

Double sided Feynman diagrams
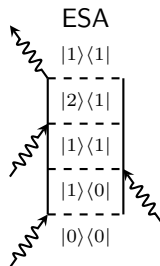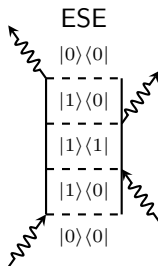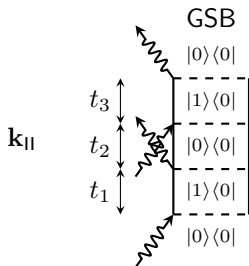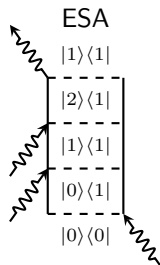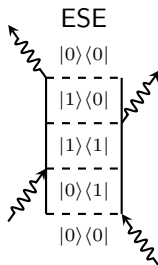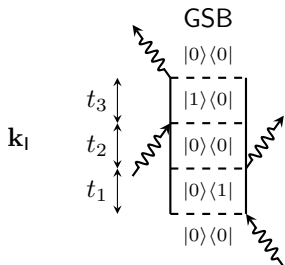
- $\mathbf{k}_I$ ESE term

$$R_{\mathsf{ESE}}^{\mathbf{k}_I}(t_1, t_2, t_3) = \langle \hat{\mu}^- \hat{\mu}^+(t_1 + t_2) \hat{\mu}^-(t_1 + t_2 + t_3) \hat{\mu}^+(t_1) \rangle$$

$$R_{\mathsf{ESE}}^{\mathbf{k}_I}(t_1, t_2, t_3) = \mathrm{Tr}\left[\rho_{\mathsf{eq}} \hat{\mu}^- \hat{\mu}^+(t_1 + t_2) \hat{\mu}^-(t_1 + t_2 + t_3) \hat{\mu}^+(t_1)\right]$$

$$R_{\mathsf{ESE}}^{\mathbf{k}_I}(t_1, t_2, t_3) = \mathrm{Tr}\left[\hat{\mu}^-(t_1 + t_2 + t_3) \hat{\mu}^+(t_1) \rho_{\mathsf{eq}} \hat{\mu}^- \hat{\mu}^+(t_1 + t_2)\right]$$

ESE

$|0\rangle\langle 0|$

t_3 $|1\rangle\langle 0|$

t_2 $|1\rangle\langle 1|$

t_1 $|0\rangle\langle 1|$

$|0\rangle\langle 0|$

Double sided Feynman diagrams

Outline

Model systems

- Anharmonic oscillator
- Two coupled anharmonic oscillators
- Anharmonic oscillator in a fluctuating environment

Anharmonic oscillator: Three level system

$$S_{\mathbf{k}_I}(t_1, t_2, \omega_3) = \mathrm{Re} \int_0^\infty \mathrm{d}t \, e^{i\omega_3 t_3} \Big(R_{\mathsf{GSB}}^{\mathbf{k}_I}(t_1, t_2, t_3) + R_{\mathsf{ESE}}^{\mathbf{k}_I}(t_1, t_2, t_3) - R_{\mathsf{ESA}}^{\mathbf{k}_I}(t_1, t_2, t_3) \Big)$$

$$R_{\mathsf{GSB}}^{\mathbf{k}_I}(t_1, t_2, t_3) = R_{\mathsf{ESE}}^{\mathbf{k}_I}(t_1, t_2, t_3) = \mu_{01}^4 e^{i\omega_0 t_1} e^{-i\omega_0 t_3}$$

$$R_{\mathsf{ESA}}^{\mathbf{k}_I}(t_1, t_2, t_3) = \mu_{01}^2 \mu_{12}^2 e^{i\omega_0 t_1} e^{-i(\omega_0 - \Delta)t_3}$$

$$R_{\mathsf{GSB}}^{\mathbf{k}_{II}}(t_1, t_2, t_3) = R_{\mathsf{ESE}}^{\mathbf{k}_{II}}(t_1, t_2, t_3) = \mu_{01}^4 e^{-i\omega_0 t_1} e^{-i\omega_0 t_3}$$

$$R_{\mathsf{ESA}}^{\mathbf{k}_{II}}(t_1, t_2, t_3) = \mu_{01}^2 \mu_{12}^2 e^{-i\omega_0 t_1} e^{-i(\omega_0 - \Delta)t_3}$$

$|2\rangle$ ———
$\omega_0 - \Delta$

$|1\rangle$ ———
ω_0

$|0\rangle$ ———

- 2D signals

$$S_{\mathbf{k}_I}(\omega_1, t_2, \omega_3) = \int_0^\infty \mathrm{d}\tau \, e^{-i\omega_1 t_1} S_{\mathbf{k}_I}(t_1, t_2, \omega_3)$$

$$S_{\mathbf{k}_{II}}(\omega_1, t_2, \omega_3) = \int_0^\infty \mathrm{d}\tau \, e^{i\omega_1 t_1} S_{\mathbf{k}_{II}}(t_1, t_2, \omega_3)$$

Anharmonic oscillator: Three level system

- To simplify we take $\omega_0 = 0$
- $\mathbf{k}_\mathrm{I}$ GSB term $S_{\mathrm{GSB}}^{\mathbf{k}_\mathrm{I}}(\omega_1, t_2, \omega_3) = \mu_{01}^4 \left(\pi^2 \delta(\omega_1)\delta(\omega_3) - \dfrac{1}{\omega_1\omega_3} \right)$
- $\mathbf{k}_\mathrm{II}$ GSB term $S_{\mathrm{GSB}}^{\mathbf{k}_\mathrm{II}}(\omega_1, t_2, \omega_3) = \mu_{01}^4 \left(\pi^2 \delta(\omega_1)\delta(\omega_3) + \dfrac{1}{\omega_1\omega_3} \right)$
- Purely absorptive spectra $S(\omega_1, t_2, \omega_3) = S^{\mathbf{k}_\mathrm{I}}(\omega_1, t_2, \omega_3) + S^{\mathbf{k}_\mathrm{II}}(\omega_1, t_2, \omega_3)$

$$S(\omega_1, t_2, \omega_3) = 2\mu_{01}^2\pi^2\delta(\omega_1)\left(2\mu_{01}^2\delta(\omega_3) - \mu_{12}^2\delta(\omega_3 + \Delta)\right)$$

$\mathbf{k}_\mathrm{I}$ $\mathbf{k}_\mathrm{II}$ $\mathbf{k}_\mathrm{I} + \mathbf{k}_\mathrm{II}$

Two uncoupled anharmonic oscillators
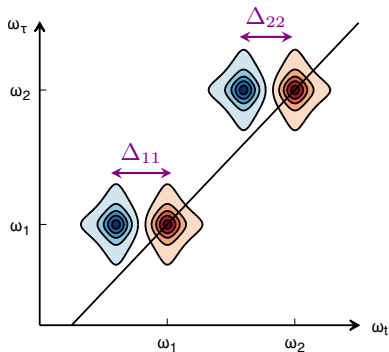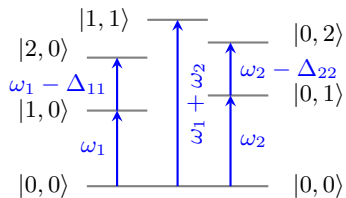
Two coupled anharmonic oscillators
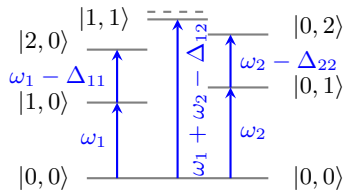
Two coupled anharmonic oscillators
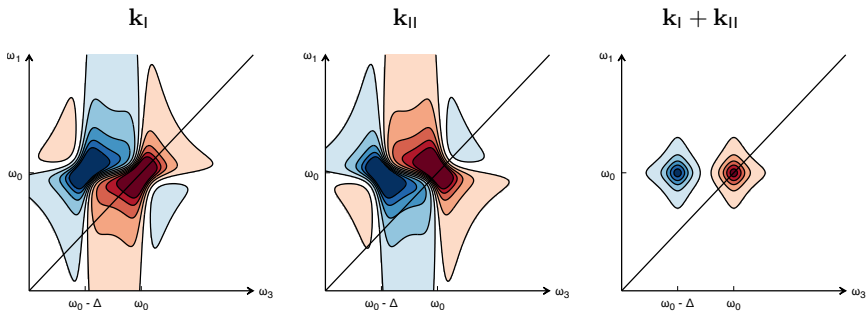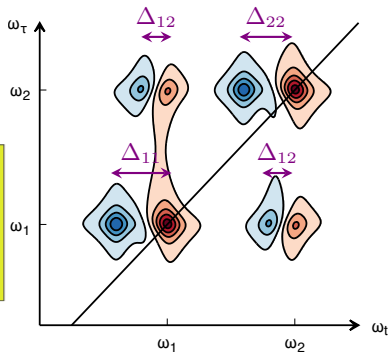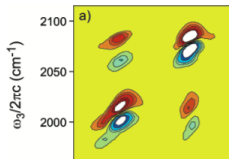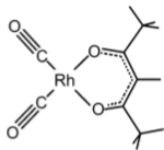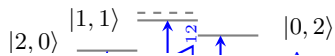
Two-level system in a fluctuating environnement

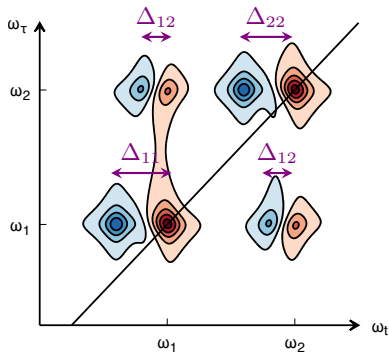- Simple description of the effect of the environment on a two level system (adiabatic approximation without back-reaction)
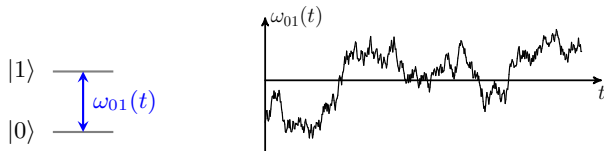
- $\omega_{01}(t)$ can often be described by a gaussian stationnary stochastic process
- $\hat{H}_0(t)$ is time-dependent
- Time-evolution operator $\hat{U}(t) = T_+ \exp\left(-\mathrm{i} \int_0^t \hat{H}_0(\tau)\mathrm{d}\tau\right)$
- Linear absorption $S(\omega) = \mathrm{Re} \int_0^\infty \mathrm{d}t \; e^{\mathrm{i}\omega t} J(t)$

$$J(t) = \langle \hat{\mu}(t)\hat{\mu} \rangle = \langle \hat{U}^\dagger(t)\hat{\mu}\hat{U}(t)\hat{\mu} \rangle = \mu_{01}^2 \langle e^{-\mathrm{i} \int_0^t \omega_{01}(\tau)\mathrm{d}\tau} \rangle$$

$\langle \dots \rangle \equiv$ average over the fluctuations

Two-level system in a fluctuating environnement

- For a gaussian stochastic process the second order cumulant expansion is exact

$$\langle e^\alpha \rangle = \exp\left(\langle \alpha \rangle + \frac{1}{2} \left(\langle \alpha^2 \rangle - \langle \alpha \rangle^2 \right) \right)$$

$$J(t) = \mu_{01}^2 e^{-i\overline{\omega}t - g(t)}, \quad \overline{\omega} = \langle \omega_{01} \rangle$$

- lineshape function $g(t)$

$$g(t) = \int_0^t \mathrm{d}\tau_1 \int_0^{\tau_1} \mathrm{d}\tau_2 \ \langle \delta\omega(\tau_1)\delta\omega(\tau_2) \rangle, \quad \delta\omega(t) = \omega_{01}(t) - \overline{\omega}$$

- Stationnary process $\langle \delta\omega(\tau_1)\delta\omega(\tau_2) \rangle = \langle \delta\omega(\tau_1 - \tau_2)\delta\omega(0) \rangle = C(\tau_1 - \tau_2)$
- Frequency fluctuations correlation function (FFCF) $C(t) = \langle \delta\omega(t)\delta\omega(0) \rangle$

$$g(t) = \int_0^t \mathrm{d}\tau \ (t - \tau)C(\tau)$$

Two-level system in a fluctuating environnement

- Simple exponential decay

$$C(t) = \langle \delta\omega(t)\delta\omega(0) \rangle = \Delta^2 e^{-\Lambda t}$$
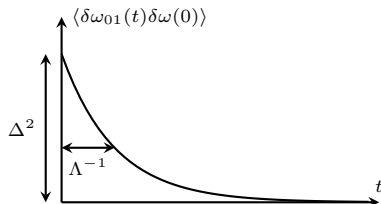
- Lineshape function $g(t) = \dfrac{\Delta^2}{\Lambda^2} \left(e^{-\Lambda t} + \Lambda t - 1 \right)$
- Slow fluctuations $\Lambda/\Delta \ll 1$, $g(t) \approx \frac{1}{2}\Delta^2 t^2$ Gaussian lineshape

$$S(\omega) = \sqrt{\frac{2\pi}{\Delta^2}} \mu_{01}^2 e^{-\frac{(\omega - \overline{\omega})^2}{2\Delta^2}}$$

- Fast fluctuations $\Lambda/\Delta \gg 1$, $g(t) \approx \frac{\Delta^2}{\Lambda} t = \Gamma t$ Lorentzian lineshape

$$S(\omega) = \frac{\Gamma \mu_{01}^2}{\Gamma^2 + (\omega - \overline{\omega})^2}$$

2D-IR spectrum

- GSB and ESE terms
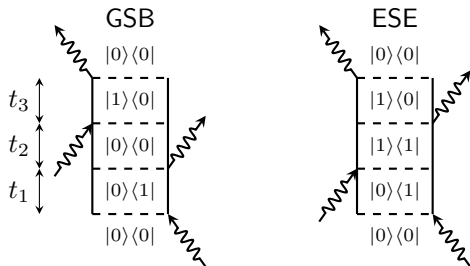
$$R_{\text{GSB}}^{\mathbf{k}_\text{I}}(t_1, t_2, t_3) = R_{\text{ESE}}^{\mathbf{k}_\text{I}}(t_3, t_2, t_1) = \left\langle e^{\text{i} \int_0^{t_1} \omega(\tau)\text{d}\tau - \text{i} \int_{t_1+t_2}^{t_1+t_2+t_3} \omega(\tau)\text{d}\tau} \right\rangle$$

$$= e^{\text{i}\overline{\omega}(t_1-t_3)} e^{-g(t_1)-g(t_3)+f(t_1,t_2,t_3)}$$

$$f(t_1, t_2, t_3) = g(t_2) + g(t_1 + t_2 + t_3) - g(t_1 + t_2) - g(t_2 + t_3)$$

- Similar equations for ESA term

2D-IR spectrum

$$C(t) = \langle \delta\omega(t)\delta\omega(0) \rangle = \Delta^2 e^{-\Lambda t}$$

- Spectral diffusion: time evolution show a loss of correlation between pump and probe frequencies due to a decaying FFCF
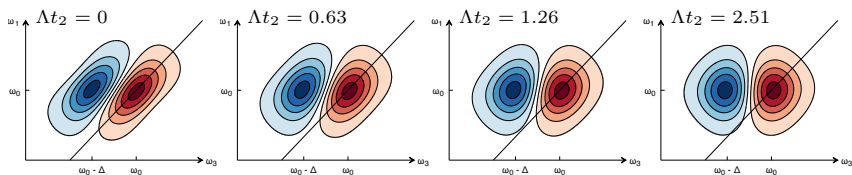
Quantifying spectral diffusion
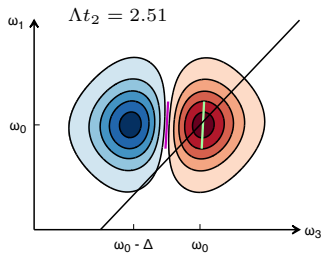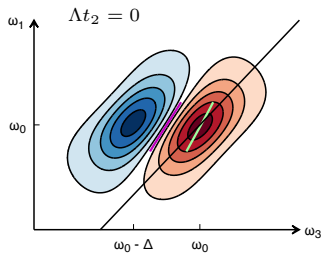
- Excentricity
  $$\epsilon(t_2) = \frac{\Delta_{\mathsf{d}}^2(t_2) - \Delta_{\mathsf{ad}}^2(t_2)}{\Delta_{\mathsf{d}}^2(t_2) + \Delta_{\mathsf{ad}}^2(t_2)}$$
- Nodal Line Slope (NLS)
- Center Line Slope (CLS)
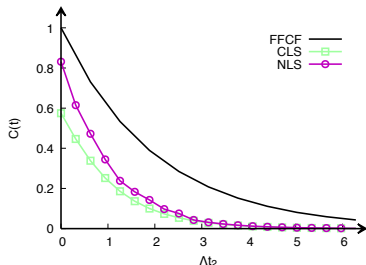
Center Line Slope (CLS)

- Slope of the line connecting the maxima of the GSB/ESE peak at each value of ω_1.

- Assuming slow fluctuations we can show that

$$C_{\mathsf{CLS}}(t_2) = \frac{C(t_2)}{C(0)}$$ *Kwak et al. JCP 127, 124503 (2007)*

- Combining this results and using the spectral width to obtain $C(0)$ we can in principle extract the FFCF from the CLS

- Taking into account fast fluctuations we can show that the CLS is given by the shifted and scaled FFCF

$$C_{\mathsf{CLS}}(t_2) = \alpha \frac{C(t_2 + \tau)}{C(0)}$$

Falvo, JCP 144, 234103 (2016)
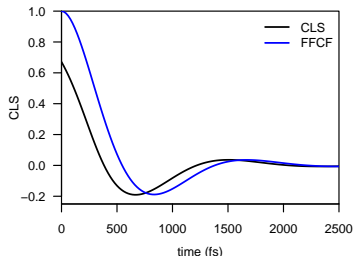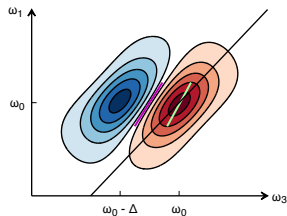
Outline

Outline

Classical simulations in IR spectroscpy

- Coherence is not uniquely a quantum effect
- Most spectroscopic observation can be explained by classical coherences.
- Classical dynamics is a powerful tool to model the spectroscopic response of complex molecular system

$$R^{(1)}(t) = i\theta(t) \operatorname{Tr} \{\hat{\mu}(t) [\hat{\mu}, \rho_{eq}]\}$$

- quantum-classical correspondance $\frac{1}{i\hbar}[\cdot, \cdot] \to \{\cdot, \cdot\}$
- Poisson brackets $\{A, B\} = \sum_i \dfrac{\partial A}{\partial q_i} \dfrac{\partial B}{\partial p_i} - \dfrac{\partial B}{\partial q_i} \dfrac{\partial A}{\partial p_i}$
- Classical response function $R_{cl}^{(1)}(t) = \theta(t)\beta \langle \dot{\mu}(0)\mu(t) \rangle$
- The classical response function can be easily computed from a classical equilibrium molecular dynamics simulations

Classical simulations in IR spectroscopy

Vibrational Dynamics of the Neutral Naphthalene Molecule from a Tight-Binding Approach

Nguyen-Thi Van-Oanh, Pascal Parneix,* and Philippe Bréchignac

*Laboratoire de Photophysique Moléculaire,[†] C.N.R.S. Bât 210, Université Paris-Sud,
F91405 Orsay Cedex, France*

The static and dynamical properties of the neutral naphthalene molecule in its ground electronic state have been investigated using a tight-binding potential. This semiempirical method has allowed us to obtain static information concerning geometry and normal-mode frequencies. Tight-binding molecular dynamics coupled with an adiabatic switching procedure has also given information on the anharmonicity of the potential energy surface of such neutral aromatic molecule. Finally, the absorption spectrum of the neutral naphthalene molecule, prepared in its ground vibrational state, has been calculated from the Fourier transform of the dipole autocorrelation function and compared with the experimental data.

Classical simulations in IR spectroscopy
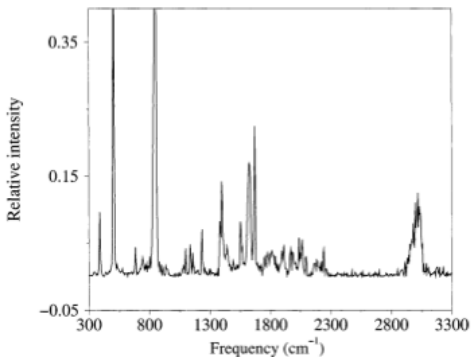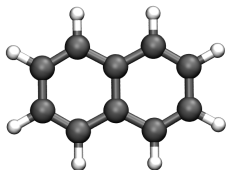
Figure 4. IR absorption spectrum calculated for the naphthalene molecule in its ground vibrational state.

Classical simulations in IR spectroscopy

FEATURE ARTICLE

Ab Initio Molecular Dynamics Computation of the Infrared Spectrum of Aqueous Uracil

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Classical simulations in IR spectroscopy
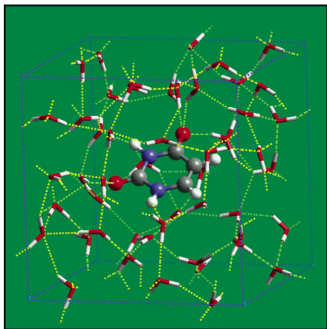
Figure 1. Instantaneous configuration of uracil surrounded by 49 water molecules sampled from the ab initio molecular dynamics simulation. The cubic box size is 11.5 Å. Periodic boundary conditions are applied.
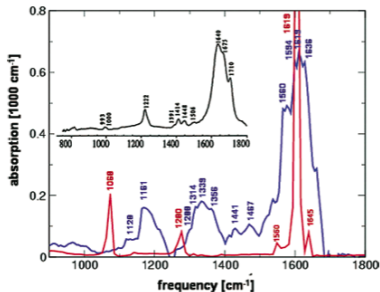
Figure 4. Infrared absorption spectrum of uracil in vacuo (red) and in aqueous solution (blue) as computed from Car–Parrinello trajectories at a temperature of 20 and 310 K, respectively. Displayed is the 2000–1000 cm^{-1} spectral domain of interest in biochemistry without any quantum corrections applied (see text and appendix for results on detailed balance corrections). The intensity of the 1619 cm^{-1} vacuum band is 6800 cm^{-1} and has been truncated in the graph. Inset shows the experimental infrared spectrum of aqueous uracil taken from ref 69.

Classical nonlinear response functions

- Classical nonlinear response functions are not so easy to compute
- They require the calculation of Poisson brackets of dipoles at different times
$$\{\mu(t), \mu(t')\} = \sum_{i,j} \frac{\partial \mu(t)}{\partial q_i(t)} \frac{\partial \mu(t')}{\partial q_j(t')} \frac{\partial q_j(t')}{\partial p_j(t)}.$$

- The stability matrix $J(t) = \begin{pmatrix} \frac{\partial q(t)}{\partial q(0)} & \frac{\partial p(t)}{\partial q(0)} \\ \frac{\partial q(t)}{\partial p(0)} & \frac{\partial p(t)}{\partial p(0)} \end{pmatrix}$ is usually difficult to compute and computationally demanding

Non equilibrium dynamics

- It is often easier to compute the classical nonlinear response function from non-equilibrium dynamics

$$R^{(1)}(t) = i \operatorname{Tr} \left\{ \mu(t) \left[\mu(0), \rho_{eq} \right] \right\} = \lim_{\epsilon \to 0} \frac{1}{\epsilon} \left\{ \langle \mu(t) \rangle_{\epsilon(0)} - \langle \mu \rangle \right\}$$

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- The nonlinear signal is then simply given by the contribution to the dipole proportional to all three pulses

$$R^{(3)}(t_1, t_2, t_3) = \lim_{\epsilon \to 0} \frac{1}{\epsilon^3} \left\{ S_{123} - S_{12} - S_{23} - S_{13} + S_1 + S_2 + S_3 - S_0 \right\}$$

$$S_{123} = \langle \mu(t_1 + t_2 + t_3) \rangle_{\epsilon(0), \epsilon(t_1), \epsilon(t_1 + t_2)} \quad S_{12} = \langle \mu(t_1 + t_2 + t_3) \rangle_{\epsilon(0), \epsilon(t_1)}$$

$$S_1 = \langle \mu(t_1 + t_2 + t_3) \rangle_{\epsilon(0)} \quad S_0 = \langle \mu \rangle$$

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$$S_1 = \langle\mu(t_1 + t_2 + t_3)\rangle_{\epsilon(0)} \quad S_0 = \langle\mu\rangle$$

- Mixed perturbative and non-equilibrium approaches have been introduced

Classical nonlinear response functions

- Classical nonlinear response functions have also conceptual issues

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- Example: quantum response function for a three level system

$$\mathcal{R}_{\mathbf{k}_l}(t_1, t_2, t_3) = i^3 \theta(t_1)\theta(t_2)\theta(t_3) 2e^{i\omega_0 t_1} \left(e^{-i\omega_0 t_3} - e^{-i(\omega_0 - \Delta)t_3} \right)$$
$$\approx \theta(t_1)\theta(t_2)\theta(t_3) 2e^{i\omega_0 t_1} e^{-i\omega_0 t_3} \Delta t_3$$

# Classical nonlinear response functions

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$$\approx \theta(t_1)\theta(t_2)\theta(t_3) 2 e^{\mathrm{i}\omega_0 t_1} e^{-\mathrm{i}\omega_0 t_3} \Delta t_3$$

- Similarly the classical response function will increase linearly in t_3 as it gives only the lowest order in the anharmonicity

Classical nonlinear response functions

- 2D spectrum of a Morse oscillator *Reppert and Brumer. JCP 148, 064101 (2018)*
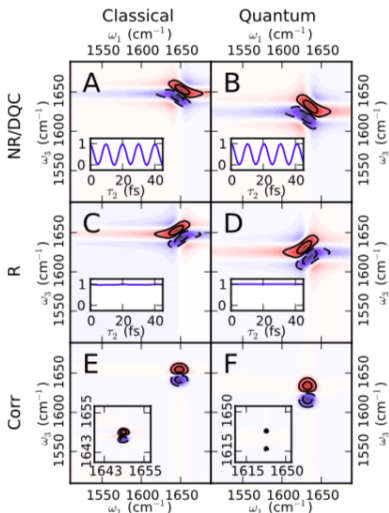
- In the quantum case, the anharmonic shift is independent of the time span
- In the classical case the anharmonic shift decreases with the time span.

Classical dynamics for nonlinear spectroscopy

- Classical dynamics can only be used for linear spectroscopy
- Use of classical dynamics to simulate nonlinear response function in the mid-IR is difficult and not reliable.
- This might still be useful for systems weakly anharmonic governed by large fluctuations.

Outline

1. Theoretical foundation of 2D-IR spectroscopy
   - Response function formalism
   - Model systems

2. Molecular simulations
   - Classical dynamics
   - Mixed quantum-classical simulations

System-Bath

- Classical dynamics can not describe properly the nonlinear response
- Full quantum dynamics can only be limited to very small system (up to ~ 10 atoms)
- We can treat with QM a limited number of degrees of freedom and treat the rest as a bath

System-Bath

$$\hat{H}_0 = \hat{H}_s + \hat{H}_b + \Delta\hat{H}$$

- To describe the system-bath dynamics several methods have been developed treating the dynamics of the reduced system's density matrix $\rho(t)$.
    - Perturbative treatment and markovian bath: Redfield master equation
    - Non perturbative and non markovian Gaussian (continuous) bath: Hierarchy Equation Of Motion (HEOM)
- We can also assume that the bath is classical and use mixed quantum-classical dynamics

Mixed quantum-classical simulations
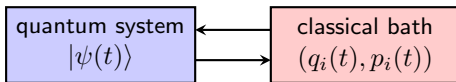
- The effect of the classical bath on the quantum system is easy to take into account: fluctuations

$$i\hbar\frac{d|\psi\rangle}{dt} = \left(\hat{H}_s + \Delta\hat{H}(\{q_i(t), p_i(t)\})\right)|\psi\rangle$$

Mixed quantum-classical simulations

Effect of the quantum system on the bath (back reaction) is less obvious

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- Ehrenfest *Billing The Quantum Classical Theory (2003)*

$$F_i = -\langle\Psi(t)|\frac{\partial}{\partial q_i}\left(H_b + \Delta\hat{H}\right)|\Psi(t)\rangle$$

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$$F_i = -\langle \Psi(t)| \frac{\partial}{\partial q_i} \left(H_b + \Delta \hat{H} \right) |\Psi(t)\rangle$$

- Surface-hopping *Tully JCP* **93** *1061 (1990)*, $|\phi_a(t)\rangle \equiv$ adiabatic eigenstates

$$F_i^{(a)} = -\langle \phi_a(t)| \frac{\partial}{\partial q_i} \left(H_b + \Delta \hat{H} \right) |\phi_a(t)\rangle, \quad P_{a \to b}$$

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- In many cases if the bath is "large" and at equilibrium we can neglect the system dissipation and only consider fluctuations

| quantum system $|\psi(t)\rangle$ | ← | classical bath $(q_i(t), p_i(t))$ |
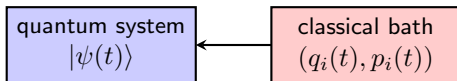
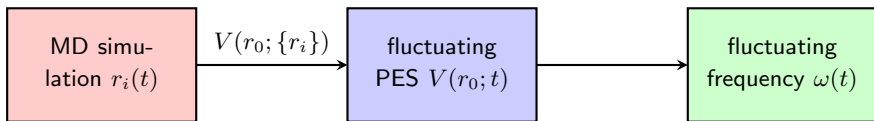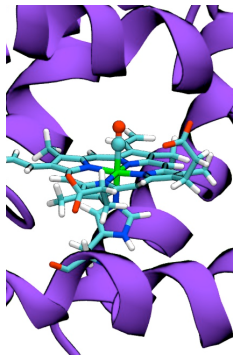# Simulation of 2D-IR spectroscopy
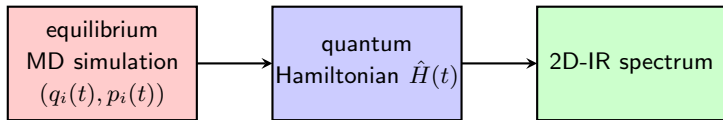
Carboxy-hemoglobin (HbCO)

- 4 globular proteins: 2α sub-units - 2 β subunits
- Each protein contains a heme group
- 1 single band CIII dominate the absorption
- Presence of a distal histidine as in MbCO
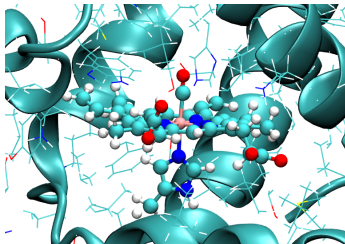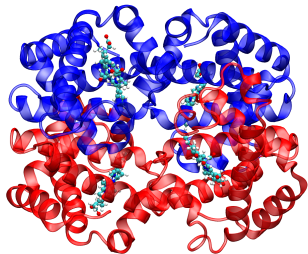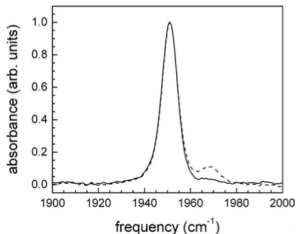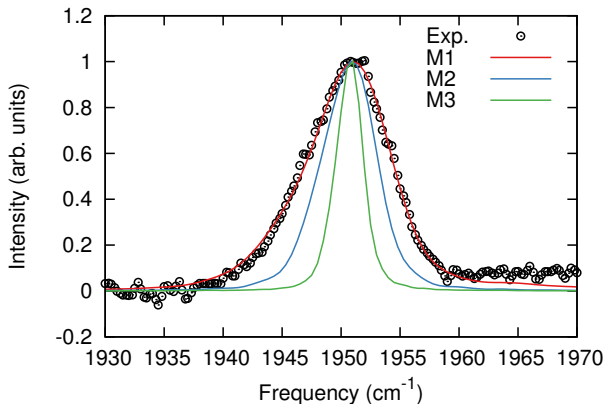

McClain JACS 126 15702 (2004)

Carboxy-hemoglobin (HbCO)

- Use of a parametrized potential energy surface $V(r_0; \{r\})$
  - $r_0 =$CO bond length
  - $r_i =$atomic coordinates of the protein and the solvent
- Parametrization performed using a set of dedicated electronic structure calculations (DFT)
- $V(r_0; \{r_i\})$ include effect of the heme vibration as well as the protein and solvent through electrostatic

| MD simulation $r_i(t)$ | $\xrightarrow{\ V(r_0; \{r_i\})\ }$ | fluctuating PES $V(r_0; t)$ | $\longrightarrow$ | fluctuating frequency $\omega(t)$ |

Carboxy-hemoglobin (HbCO)

- Linear absorption

M1 - full model
M2 - no His58
M3 - no protein

Falvo et al. JPCL **6**, *2216 (2015)*
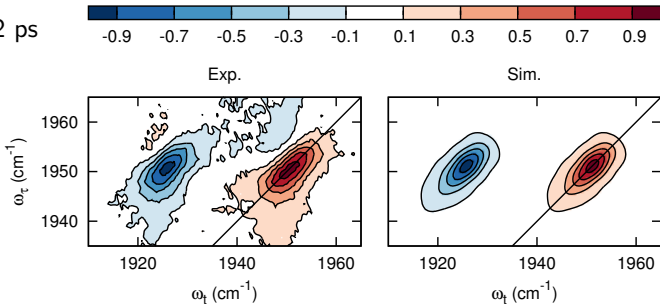
Carboxyhemoglobin (HbCO)

$t_2 = 0.5$ ps
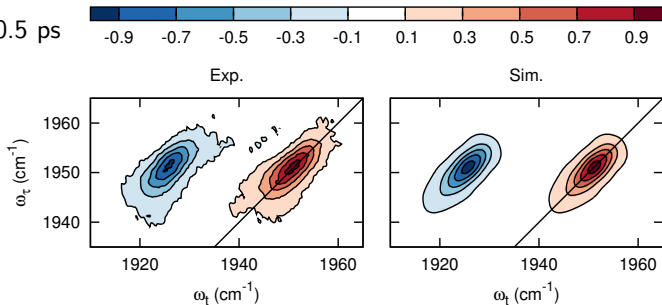
Falvo et al. JPCL **6**, 2216 (2015)

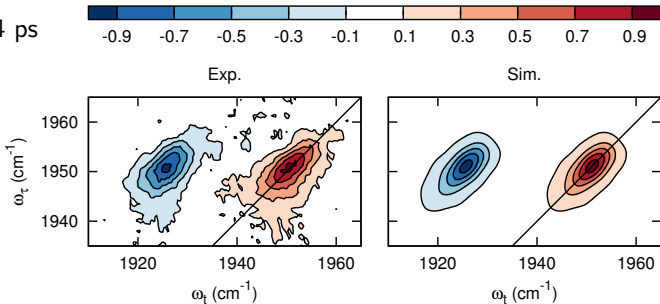# Carboxyhemoglobin (HbCO)

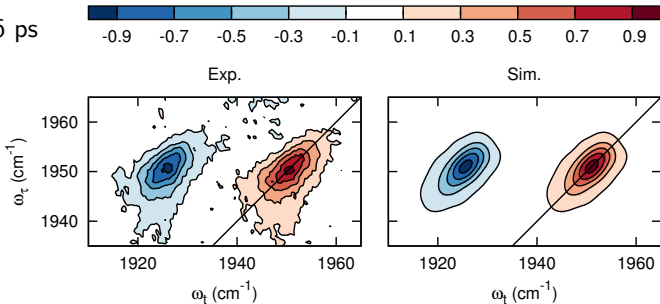$t_2 = 2$ ps

Falvo et al. JPCL **6**, 2216 (2015)

Carboxyhemoglobin (HbCO)

$t_2 = 4$ ps

Falvo et al. JPCL **6**, 2216 (2015)
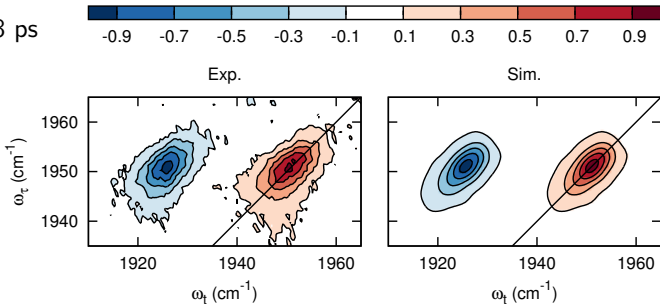
Carboxyhemoglobin (HbCO)

$t_2 = 6$ ps

Falvo et al. JPCL **6**, 2216 (2015)
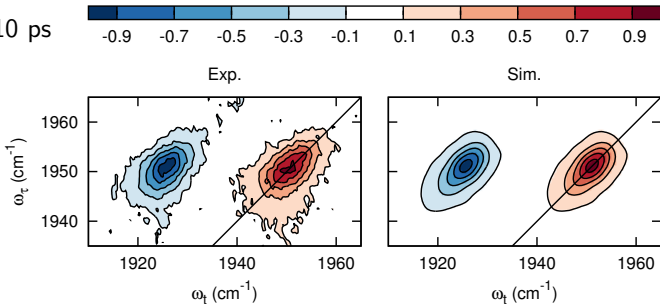
Carboxyhemoglobin (HbCO)

$t_2 = 8$ ps

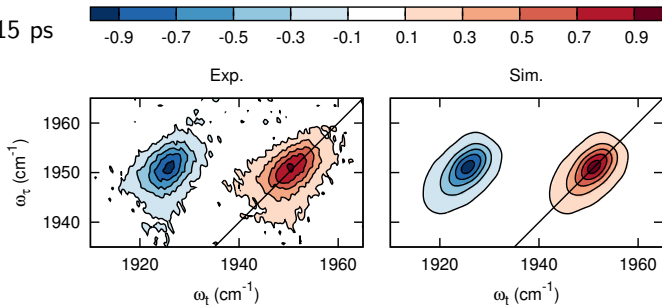Falvo et al. JPCL **6**, 2216 (2015)

Carboxyhemoglobin (HbCO)
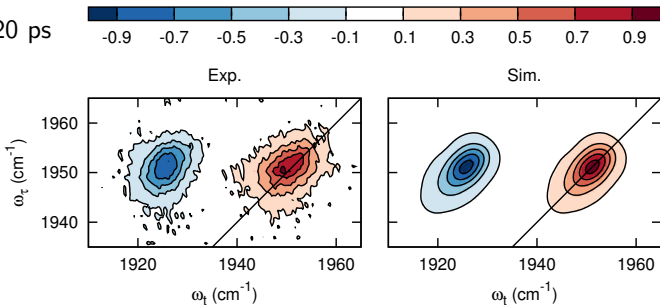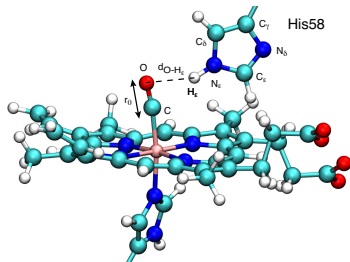

Falvo et al. JPCL **6**, 2216 (2015)

Carboxyhemoglobin (HbCO)

$t_2 = 15$ ps

Falvo et al. JPCL **6**, 2216 (2015)

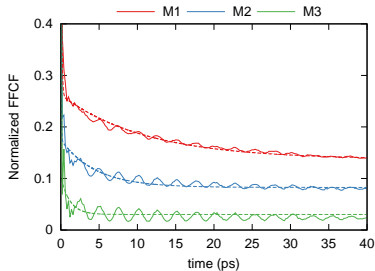# Carboxyhemoglobin (HbCO)

Falvo et al. JPCL **6**, 2216 (2015)

Carboxyhemoglobin (HbCO)

- The slow decay of the FFCF responsible for the change of shape of the 2D-IR spectrum is directly connected to the fluctuation of the hydrogen-bond between His58 and the CO molecule

Conclusions

- 2D-IR spectroscopy is a powerful technique to probe the fluctuations of the environment
- Classical dynamics can be used to simulate linear spectroscopy but in most cases cannot be used for nonlinear spectroscopy
- In many cases the environmental fluctuations can be taken into by a simple fluctuating Hamitonian

What's next ?

- Other approaches have been (are being) developed to simulate 2D spectroscopy
  - Quantum non-perturbative approaches (Gelin and Domcke)
  - Semi-classical approaches (Loring)
- I focused here on mid-IR 2D spectroscopy but other experimental technics are of interest
  - Surface specific methods e.g. 2D-SFG
  - 2D-Raman, IR-Visible methods, THz, . . .
- I only presented a simple treatment of the system-bath interaction (no back-reaction), we can use surface-hopping methods or HEOM,. . .

THANKS FOR YOUR ATTENTION