2D Spectroscopy

Mike Reppert

October 9, 2019

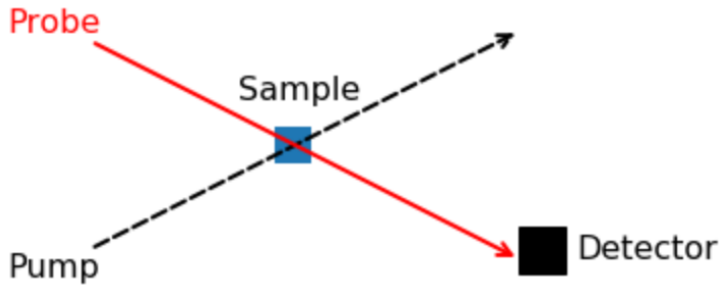
Previously on CHM676...

We learned about **pump-probe spectroscopy**:

Previously on CHM676...

We learned about **pump-probe spectroscopy**:

- Setup:

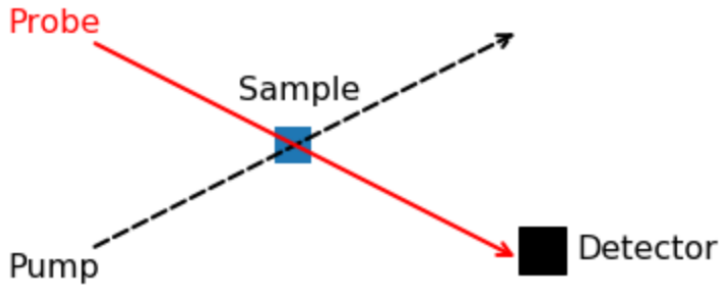


Today: 2D Spectroscopy!

Previously on CHM676...

We learned about **pump-probe spectroscopy**:

- Setup:
  - Two pulsed lasers cross in a sample

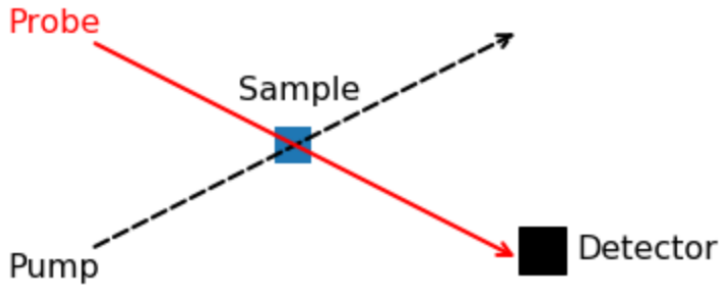


Today: 2D Spectroscopy!

Previously on CHM676...

We learned about **pump-probe spectroscopy**:

- Setup:
  - Two pulsed lasers cross in a sample
  - $\Delta OD =$ "pump on" $-$ "pump off"

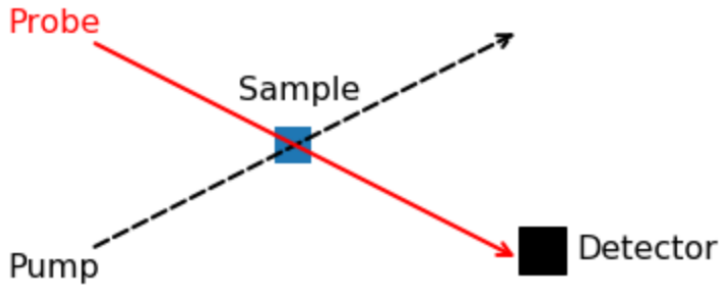


Today: 2D Spectroscopy!

Previously on CHM676...

We learned about **pump-probe spectroscopy**:

- Setup:
  - Two pulsed lasers cross in a sample
  - $\Delta OD =$ "pump on" $-$ "pump off"
- Third-order process

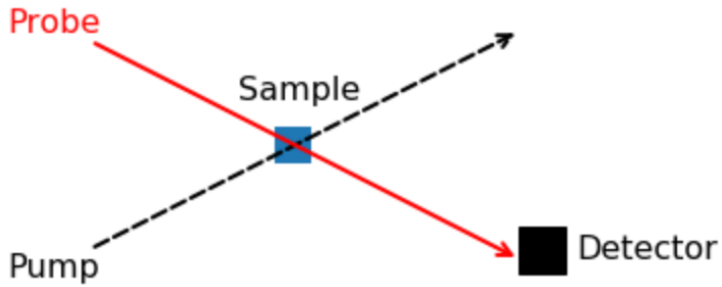


Today: 2D Spectroscopy!

Previously on CHM676...

We learned about **pump-probe spectroscopy**:

- Setup:
  - Two pulsed lasers cross in a sample
  - $\Delta OD =$ "pump on" $-$ "pump off"
- Third-order process
  - Two interactions with "pump" pulse

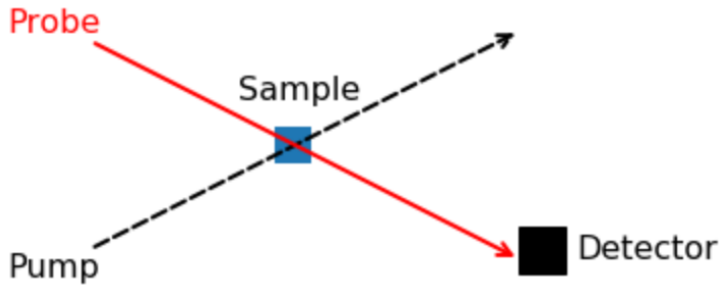


Today: 2D Spectroscopy!

Previously on CHM676...

We learned about **pump-probe spectroscopy**:

- Setup:
  - Two pulsed lasers cross in a sample
  - $\Delta OD =$ "pump on" $-$ "pump off"
- Third-order process
  - Two interactions with "pump" pulse
  - One interaction with "probe" pulse

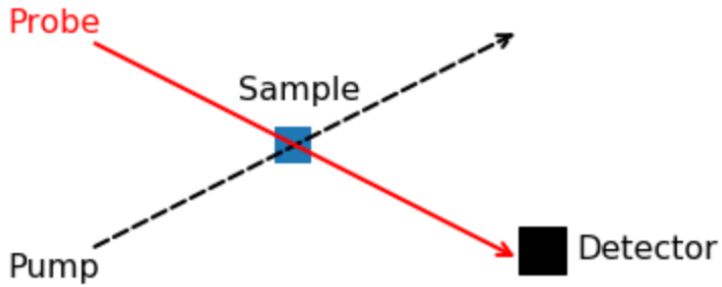


Today: 2D Spectroscopy!

Previously on CHM676...

We learned about **pump-probe spectroscopy**:

- Setup:
  - Two pulsed lasers cross in a sample
  - $\Delta OD =$ "pump on" $-$ "pump off"
- Third-order process
  - Two interactions with "pump" pulse
  - One interaction with "probe" pulse
- Two pathways:

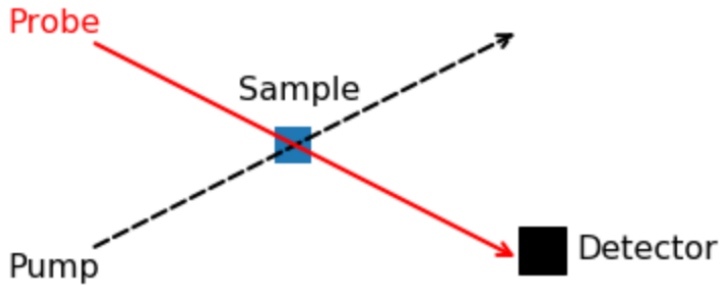


Today: 2D Spectroscopy!

Previously on CHM676...

We learned about **pump-probe spectroscopy**:

- Setup:
  - Two pulsed lasers cross in a sample
  - $\Delta OD =$ "pump on" $-$ "pump off"
- Third-order process
  - Two interactions with "pump" pulse
  - One interaction with "probe" pulse
- Two pathways:
  - **Rephasing:** $-\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3$

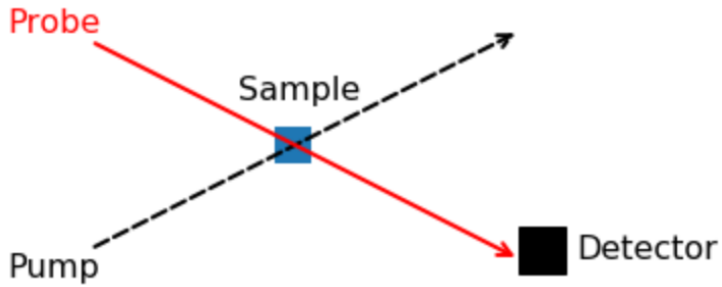


Today: 2D Spectroscopy!

Previously on CHM676...

We learned about **pump-probe spectroscopy**:

- Setup:
  - Two pulsed lasers cross in a sample
  - $\Delta OD =$ "pump on" $-$ "pump off"
- Third-order process
  - Two interactions with "pump" pulse
  - One interaction with "probe" pulse
- Two pathways:
  - **Rephasing:** $-\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3$
  - **Nonrephasing:** $\boldsymbol{k}_1 - \boldsymbol{k}_2 + \boldsymbol{k}_3$

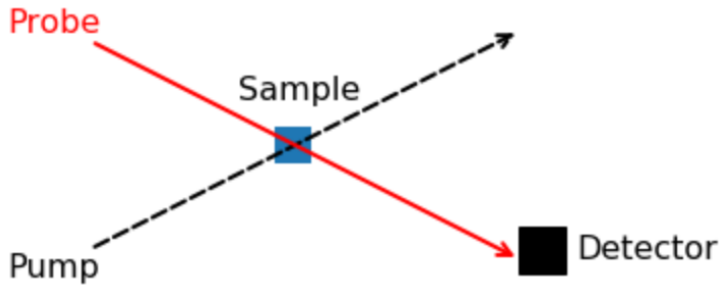


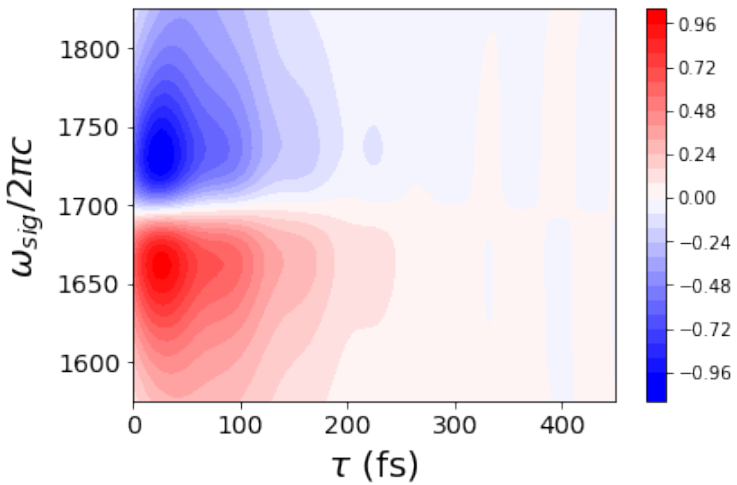
Today: 2D Spectroscopy!

Previously on CHM676...

We learned about **pump-probe spectroscopy**:

- Setup:
  - Two pulsed lasers cross in a sample
  - $\Delta OD =$ "pump on" $-$ "pump off"
- Third-order process
  - Two interactions with "pump" pulse
  - One interaction with "probe" pulse
- Two pathways:
  - **Rephasing:** $-\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3$
  - **Nonrephasing:** $\boldsymbol{k}_1 - \boldsymbol{k}_2 + \boldsymbol{k}_3$
- As a function of time-delay:



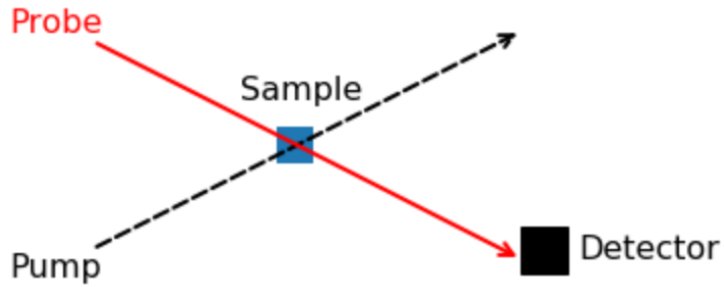


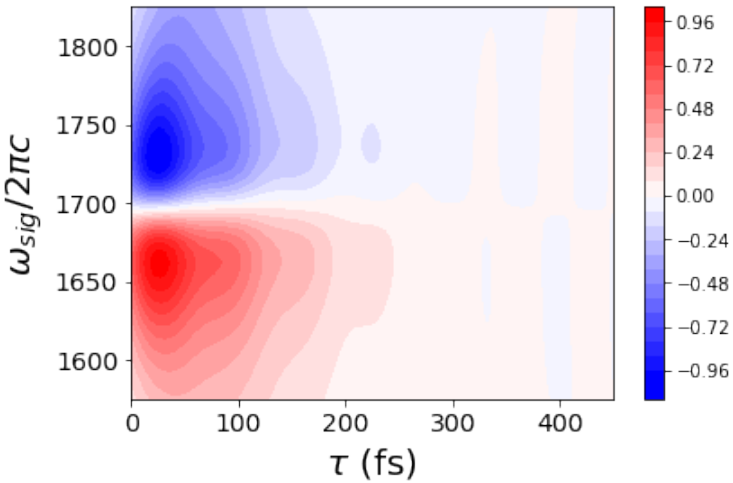
Today: 2D Spectroscopy!

Previously on CHM676...

We learned about **pump-probe spectroscopy**:

- Setup:
  - Two pulsed lasers cross in a sample
  - $\Delta OD =$ "pump on" $-$ "pump off"
- Third-order process
  - Two interactions with "pump" pulse
  - One interaction with "probe" pulse
- Two pathways:
  - **Rephasing:** $-\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3$
  - **Nonrephasing:** $\boldsymbol{k}_1 - \boldsymbol{k}_2 + \boldsymbol{k}_3$
- As a function of time-delay:
  - Does **not** oscillate at high frequencies



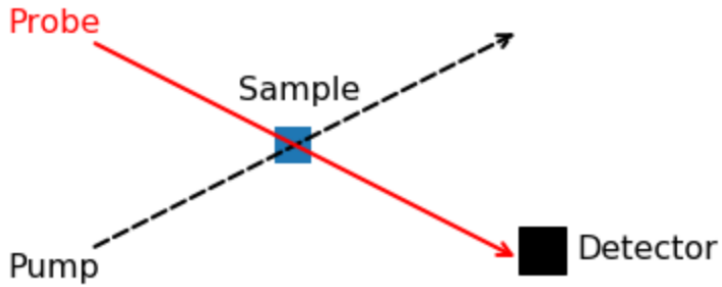


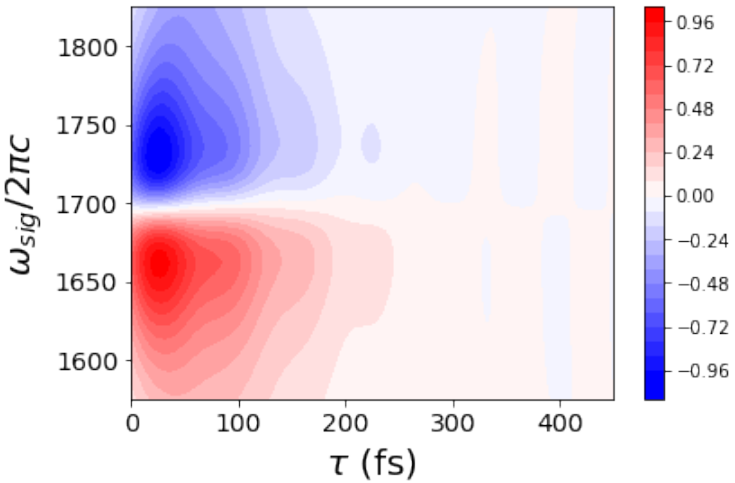
Today: 2D Spectroscopy!

Previously on CHM676...

We learned about **pump-probe spectroscopy**:

- Setup:
  - Two pulsed lasers cross in a sample
  - $\Delta OD =$ "pump on" $-$ "pump off"
- Third-order process
  - Two interactions with "pump" pulse
  - One interaction with "probe" pulse
- Two pathways:
  - **Rephasing:** $-\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3$
  - **Nonrephasing:** $\boldsymbol{k}_1 - \boldsymbol{k}_2 + \boldsymbol{k}_3$
- As a function of time-delay:
  - Does **not** oscillate at high frequencies
  - Monitors **dissipation**



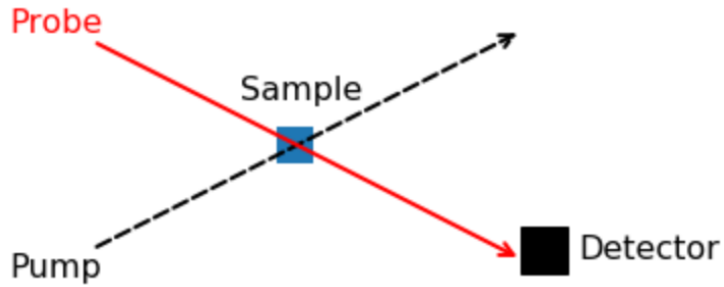


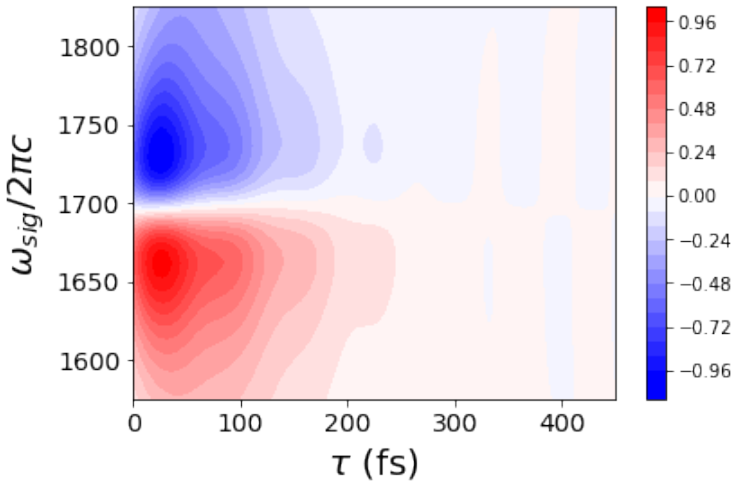
Today: 2D Spectroscopy!

Previously on CHM676...

We learned about **pump-probe spectroscopy**:

- Setup:
  - Two pulsed lasers cross in a sample
  - $\Delta OD =$ "pump on" $-$ "pump off"
- Third-order process
  - Two interactions with "pump" pulse
  - One interaction with "probe" pulse
- Two pathways:
  - **Rephasing:** $-\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3$
  - **Nonrephasing:** $\boldsymbol{k}_1 - \boldsymbol{k}_2 + \boldsymbol{k}_3$
- As a function of time-delay:
  - Does **not** oscillate at high frequencies
  - Monitors **dissipation**
  - **Not** sensitive to dephasing





Today: 2D Spectroscopy!

2D Spectroscopy: Big Idea

Pump-probe signal is determined by integrating $\mathbf{R}^{(3)}(\pm\omega_1, 0, \omega)$ over ω_1:

$$S^{(\mathsf{pp})}(\omega) \propto \varepsilon_{\mathsf{pump}}^2 \varepsilon_{\mathsf{probe}} \int d\omega_1 \left[\tilde{R}^{(3)}_{yyyy}(-\omega_1, 0, \omega) + \tilde{R}^{(3)}_{yyyy}(\omega_1, 0, \omega) \right].$$

2D Spectroscopy: Big Idea

Pump-probe signal is determined by integrating $\mathbf{R}^{(3)}(\pm\omega_1, 0, \omega)$ over ω_1:

$$S^{(\mathsf{pp})}(\omega) \propto \varepsilon^2_{\mathsf{pump}}\varepsilon_{\mathsf{probe}} \int d\omega_1 \left[\tilde{R}^{(3)}_{yyyy}(-\omega_1, 0, \omega) + \tilde{R}^{(3)}_{yyyy}(\omega_1, 0, \omega)\right].$$

Wouldn't it be great if we could measure $\mathbf{R}^{(3)}(\omega_1, 0, \omega)$ **without** integrating over the first interaction frequency?

2D Spectroscopy: Big Idea

Pump-probe signal is determined by integrating $\mathbf{R}^{(3)}(\pm\omega_1, 0, \omega)$ over ω_1:

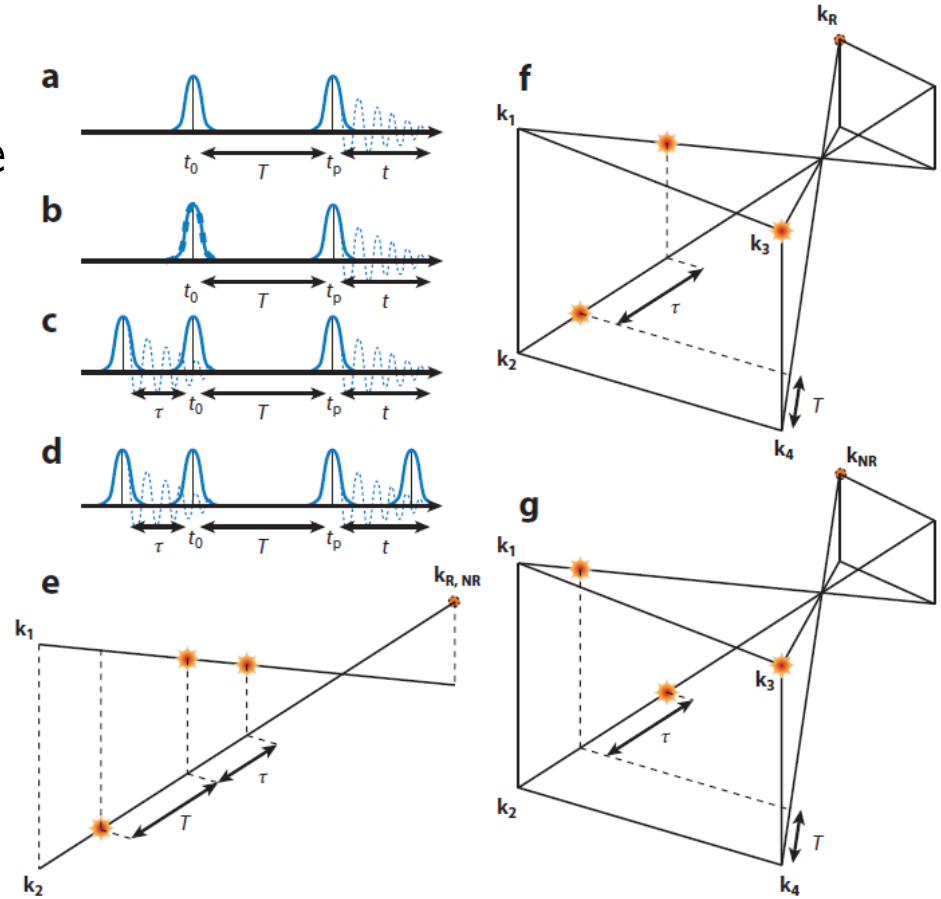
$$S^{(\mathsf{pp})}(\omega) \propto \varepsilon^2_{\mathsf{pump}}\varepsilon_{\mathsf{probe}} \int d\omega_1 \left[\tilde{R}^{(3)}_{yyyy}(-\omega_1, 0, \omega) + \tilde{R}^{(3)}_{yyyy}(\omega_1, 0, \omega)\right].$$

Wouldn't it be great if we could measure $\mathbf{R}^{(3)}(\omega_1, 0, \omega)$ **without** integrating over the first interaction frequency?

We can! 2D spectroscopy gives (in principle) the **full** third-order response tensor.

2D Spectroscopy: "Three-pulse pump-probe"

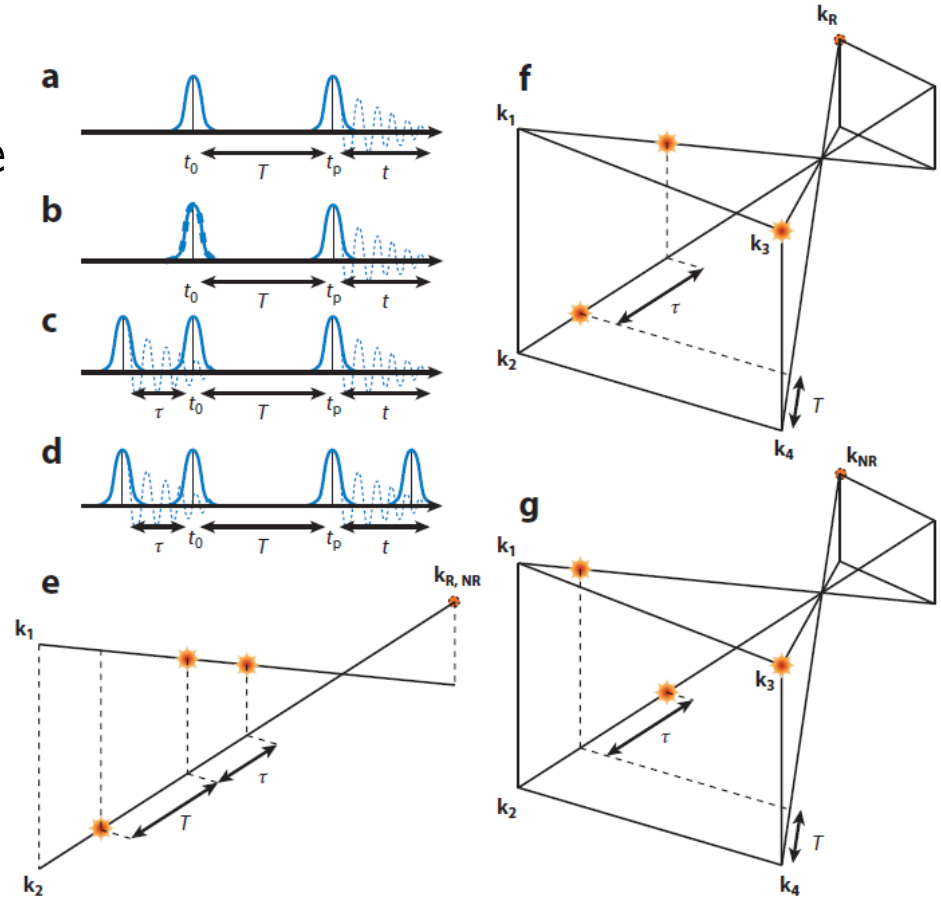
- **Key Idea:** By scanning the time delay *between* the first two interactions, we get **excitation** frequency information



Fuller and Ogilvie, *Ann. Rev. Phys. Chem.*, 2015 66, 667-690

2D Spectroscopy: "Three-pulse pump-probe"

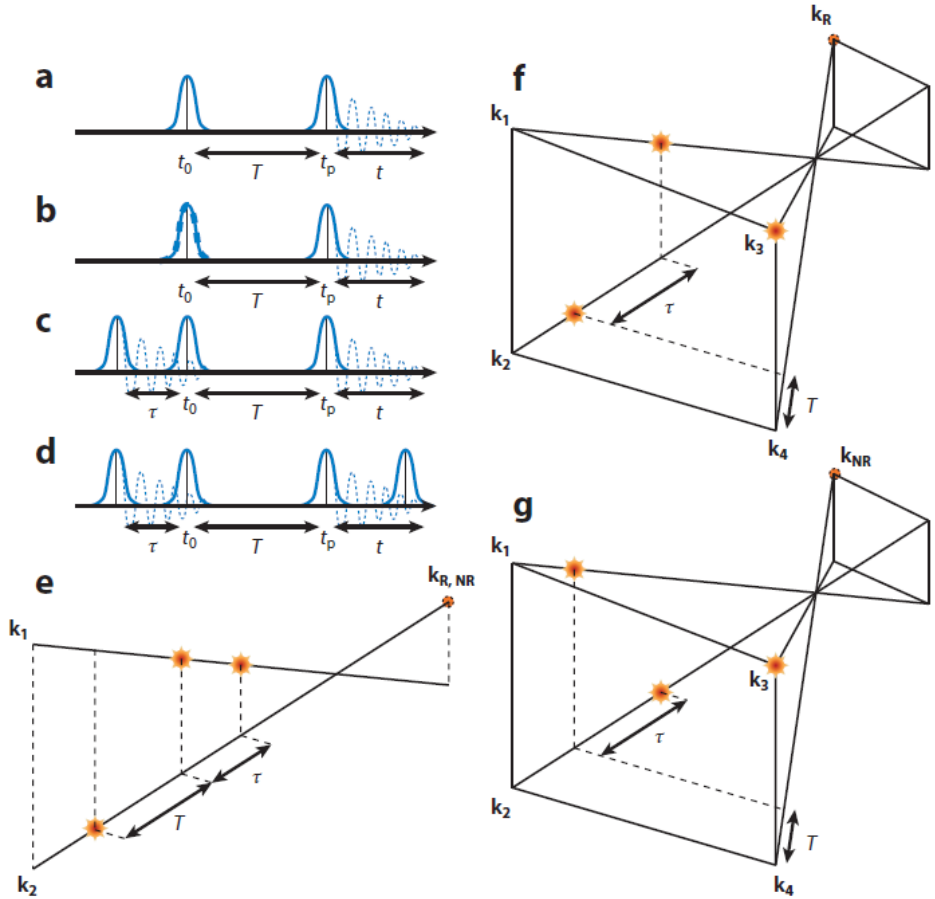
- **Key Idea:** By scanning the time delay *between* the first two interactions, we get **excitation** frequency information
- **Setup:** Two common geometries



Fuller and Ogilvie, *Ann. Rev. Phys. Chem.*, 2015 66, 667-690

2D Spectroscopy: "Three-pulse pump-probe"

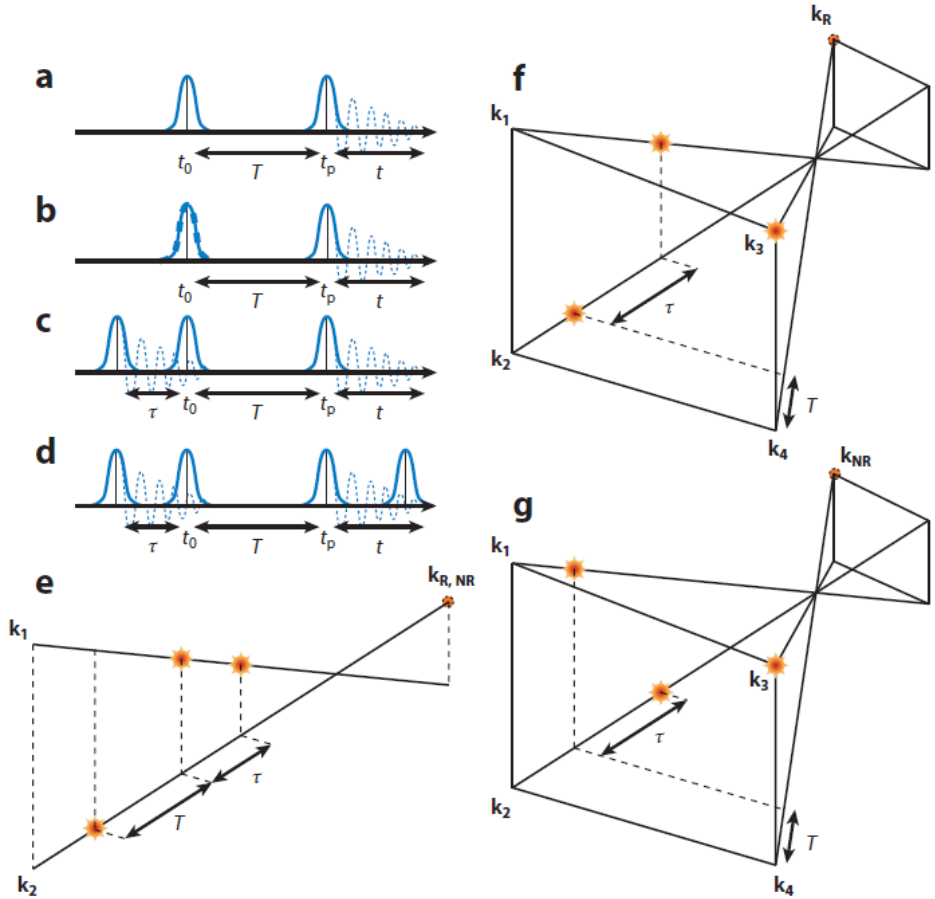
- **Key Idea:** By scanning the time delay *between* the first two interactions, we get **excitation** frequency information
- **Setup:** Two common geometries
  - Pump-probe



Fuller and Ogilvie, *Ann. Rev. Phys. Chem.*, 2015 66, 667-690

2D Spectroscopy: "Three-pulse pump-probe"

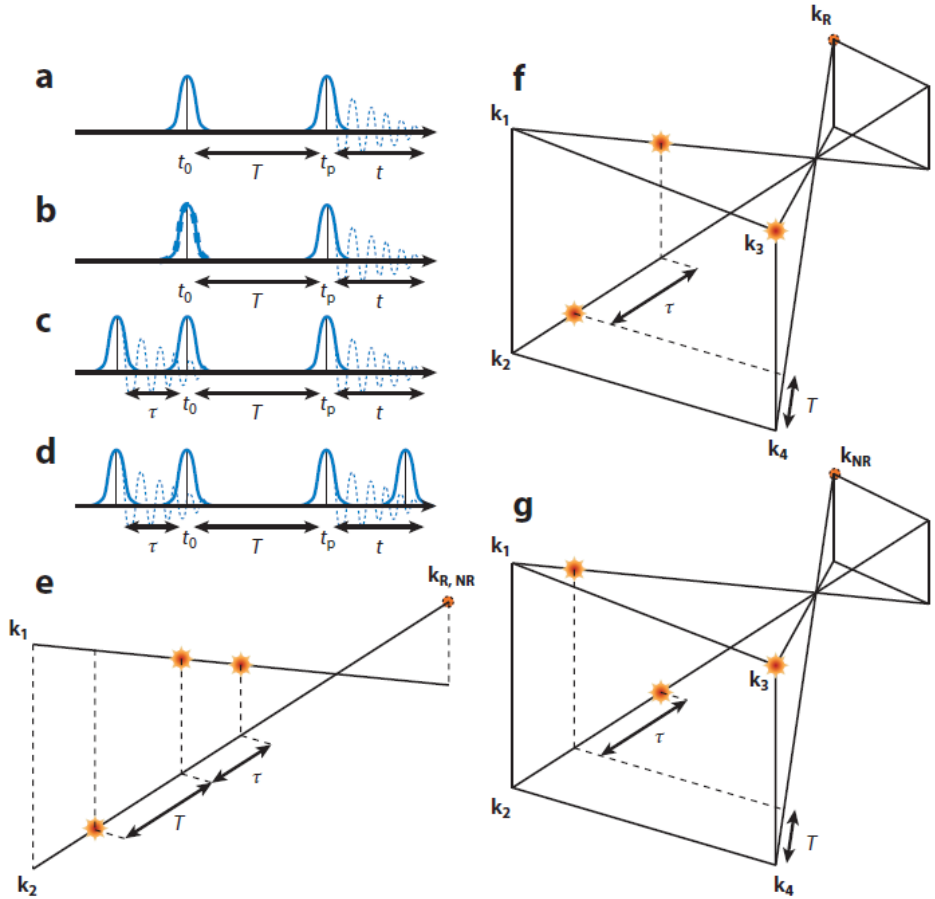
- **Key Idea:** By scanning the time delay *between* the first two interactions, we get **excitation** frequency information
- **Setup:** Two common geometries
  - Pump-probe
  - Box-CARS



Fuller and Ogilvie, *Ann. Rev. Phys. Chem.*, 2015 66, 667-690

2D Spectroscopy: "Three-pulse pump-probe"

- **Key Idea:** By scanning the time delay *between* the first two interactions, we get **excitation** frequency information
- **Setup:** Two common geometries
  - Pump-probe
  - Box-CARS
- **Applications:** By directly resolving **both** excitation **and** response, we can directly monitor energy-transfer dynamics



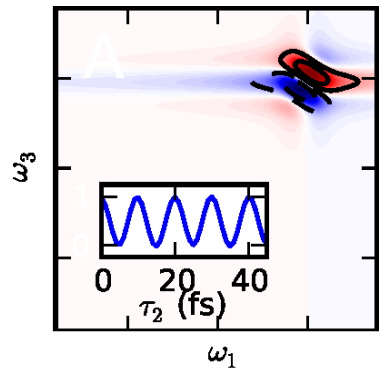
Fuller and Ogilvie, *Ann. Rev. Phys. Chem.*, 2015 66, 667-690

Flavors of 2D Spectroscopy

Double Quantum Coherence:

Beats at $2\omega_o$ in τ_2: sensitive to dephasing

$$\mathbf{k}_{\text{sig}} = \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3$$

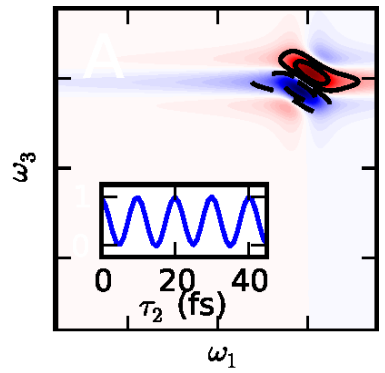


Flavors of 2D Spectroscopy

Double Quantum Coherence:

Beats at $2\omega_o$ in τ_2: sensitive to dephasing

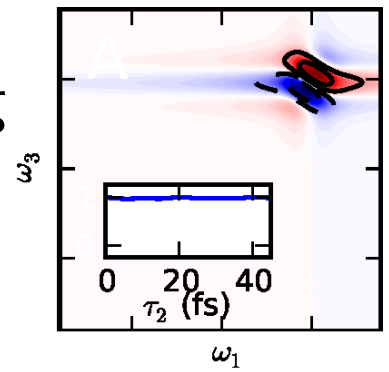
$$\mathbf{k}_{\text{sig}} = \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3$$



Nonrephasing:

Decays with *dissipation* in τ_2: insensitive to dephasing

$$\mathbf{k}_{\text{sig}} = \mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3$$

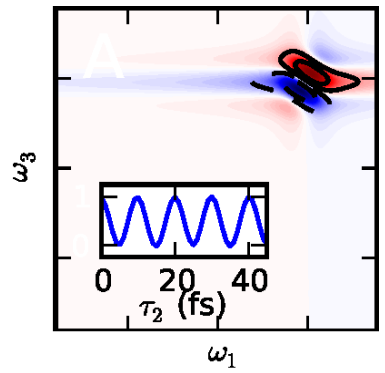


Flavors of 2D Spectroscopy

Double Quantum Coherence:

Beats at $2\omega_o$ in τ_2: sensitive to dephasing

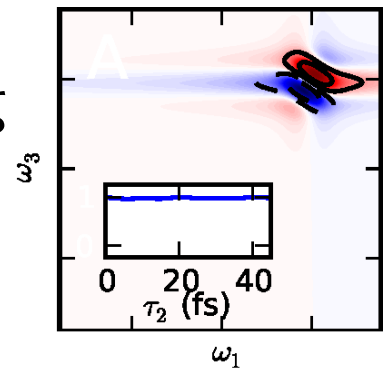
$$\mathbf{k}_{\text{sig}} = \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3$$



Nonrephasing:

Decays with *dissipation* in τ_2: insensitive to dephasing

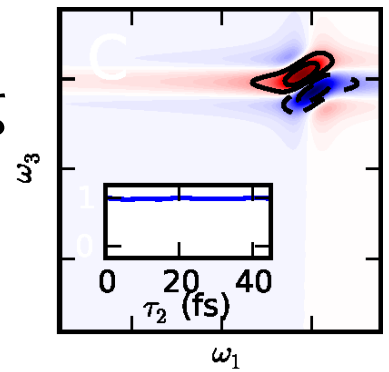
$$\mathbf{k}_{\text{sig}} = \mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3$$



Rephasing (photon echo):

Decays with *dissipation* in τ_2: insensitive to dephasing

$$\mathbf{k}_{\text{sig}} = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$$



2D Correlation Spectrum: One oscillator

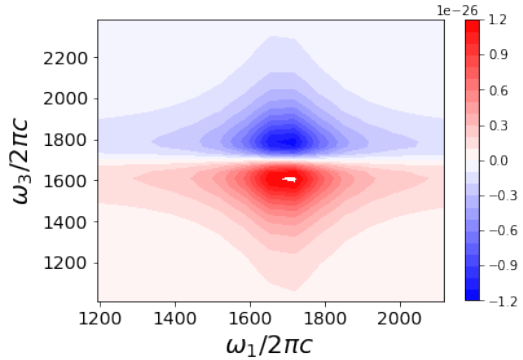
2D Correlation Spectrum = Rephasing + Nonrephasing surfaces. Directly measured in pump-probe geometry.

2D Correlation Spectrum: One oscillator

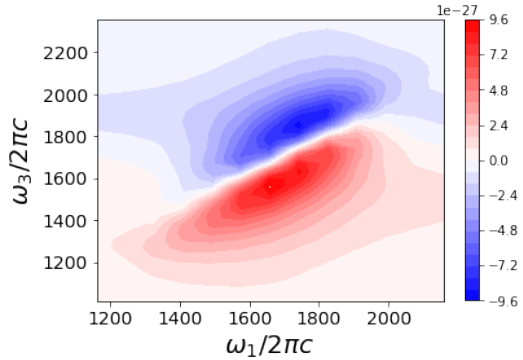
2D Correlation Spectrum = Rephasing + Nonrephasing surfaces. Directly measured in pump-probe geometry.

- (ω_1, ω_3) = (Excitation, Detection)
- **Diagonal width** feels *both* homogeneous *and* inhomogeneous broadening
- **Anti-diagonal width** feels only *homogeneous* broadening
- τ_2 feels dissipation **not** dephasing

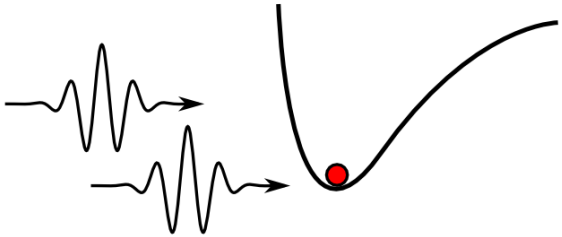
Homogeneous



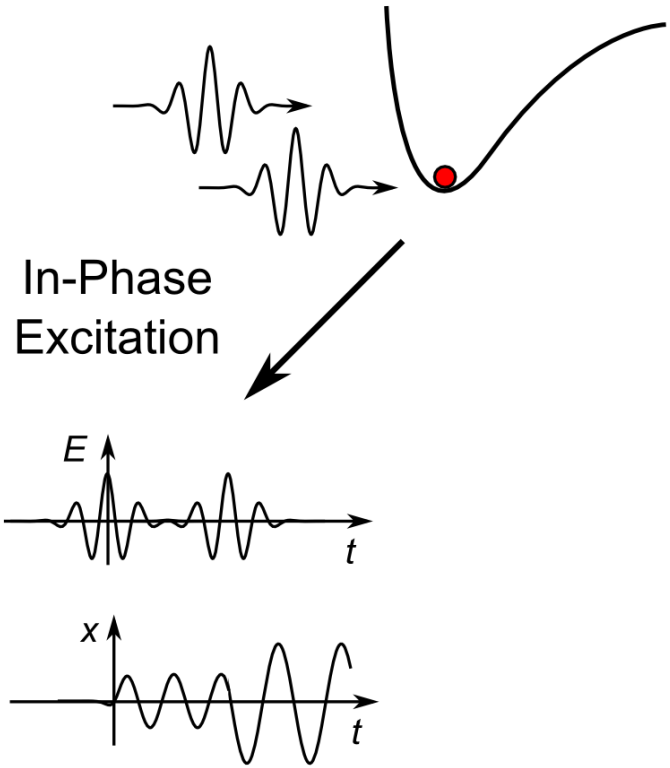
Inhomogeneous



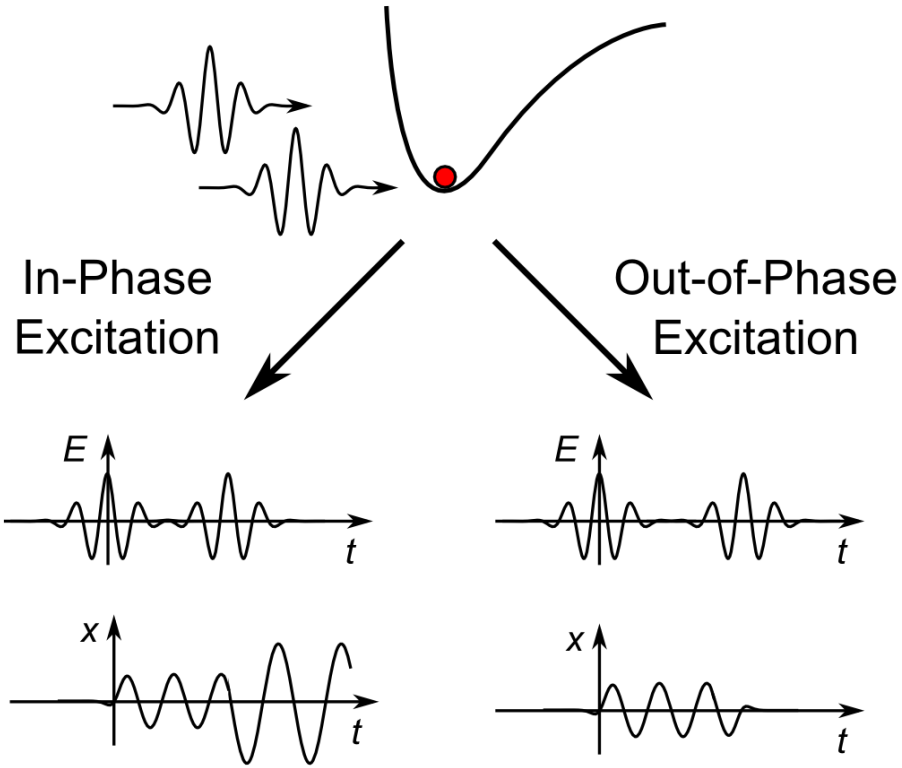
Classical Beats



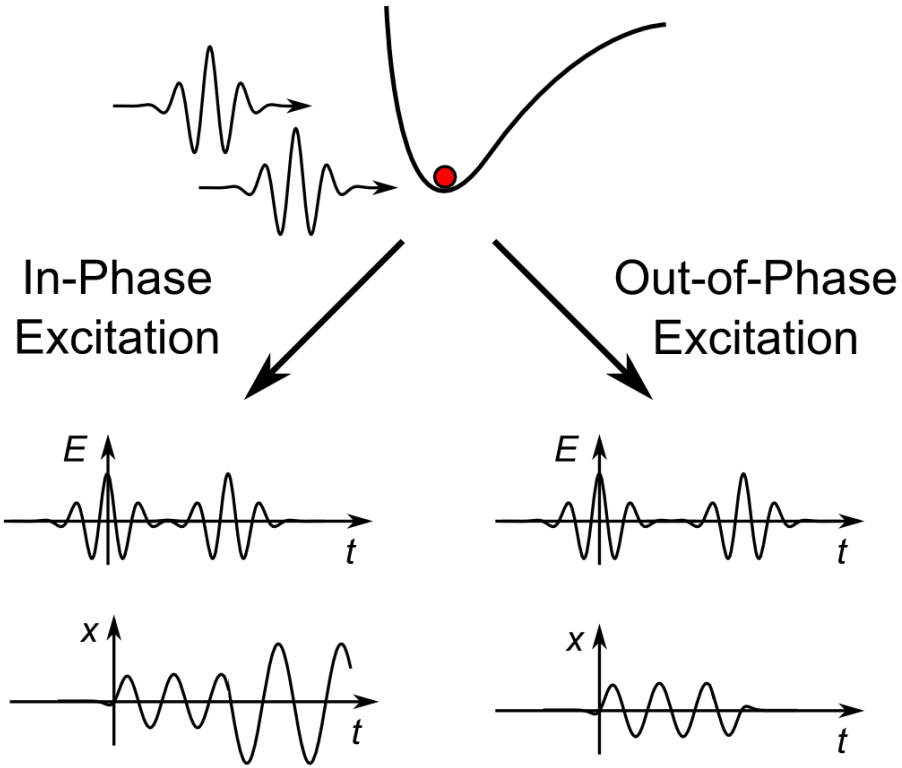
Classical Beats



Classical Beats

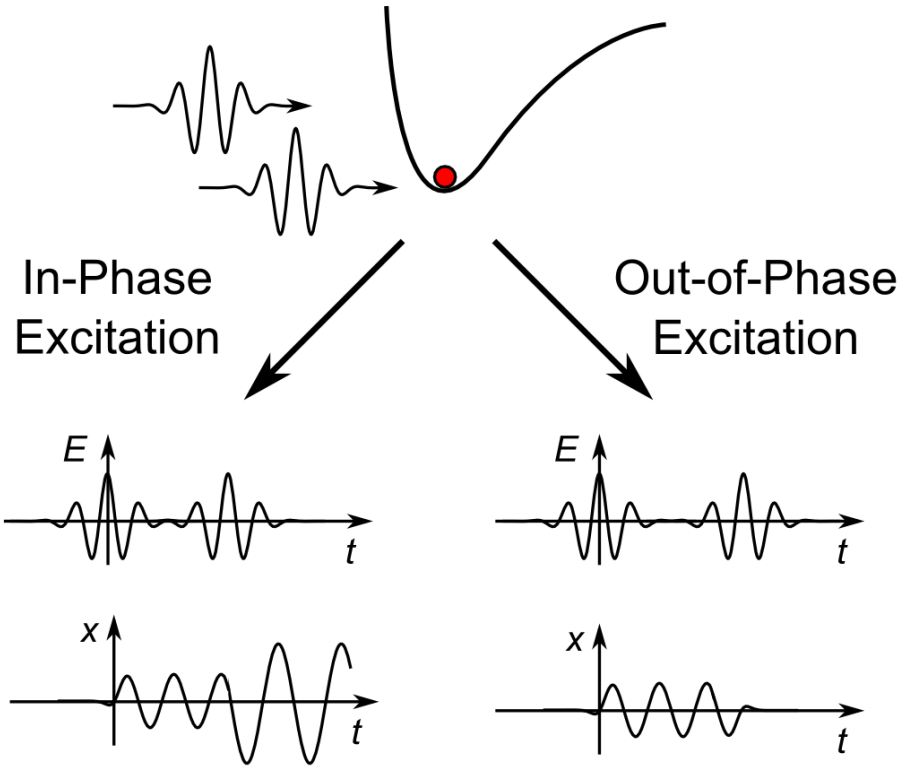


Classical Beats



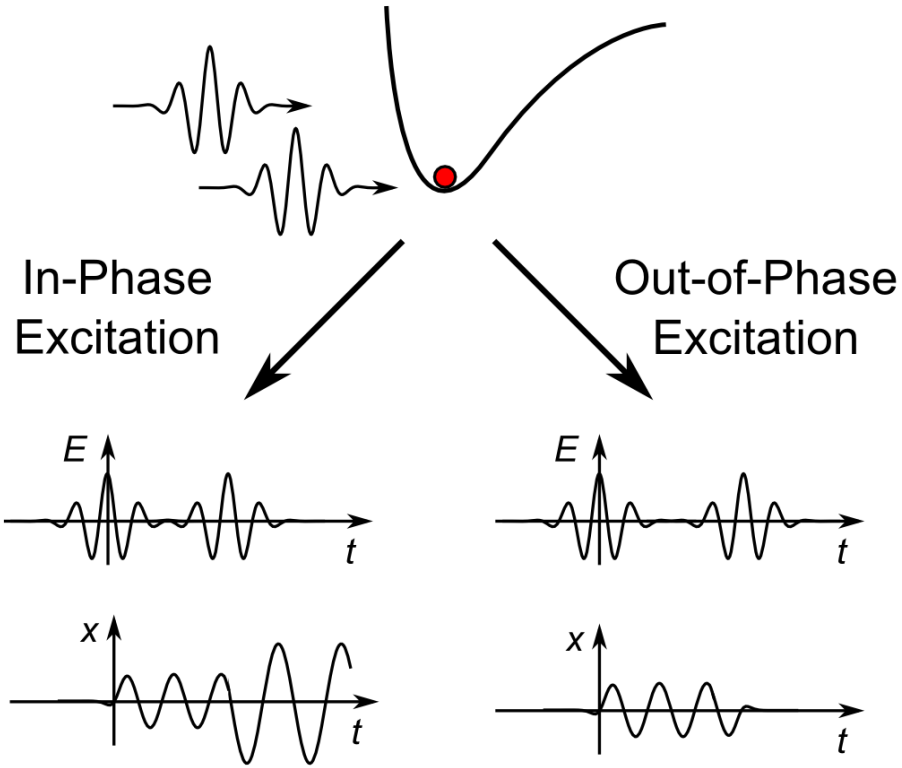
- *Frequency* probed by pulse 3 depends on *time delay* between 1 & 2 $\rightarrow$ Signal

Classical Beats



- *Frequency* probed by pulse 3 depends on *time delay* between 1 & 2 $\rightarrow$ Signal
- *Excitation* of one mode alters *frequencies* of coupled modes $\rightarrow$ Cross peaks

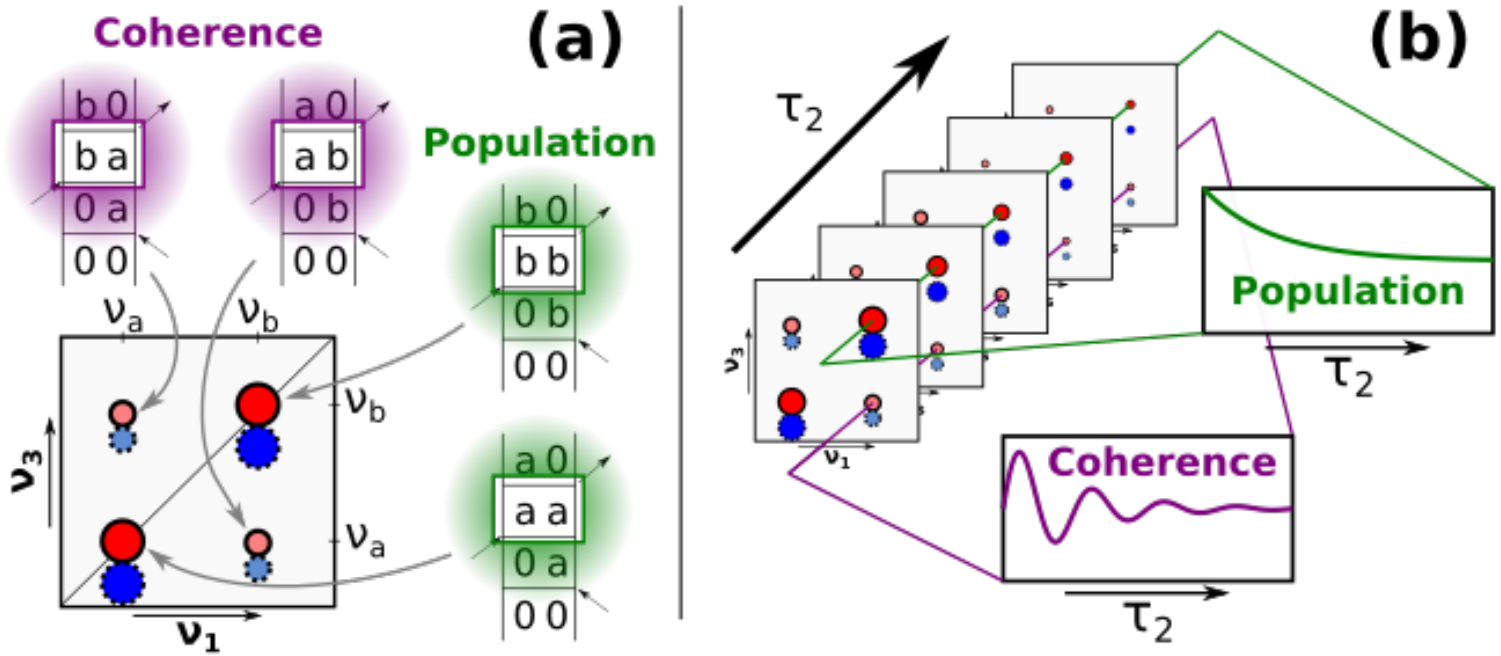
Classical Beats



- *Frequency* probed by pulse 3 depends on *time delay* between 1 & 2 $\rightarrow$ Signal
- *Excitation* of one mode alters *frequencies* of coupled modes $\rightarrow$ Cross peaks
- Interference between different modes $\rightarrow$ "Quantum" beats

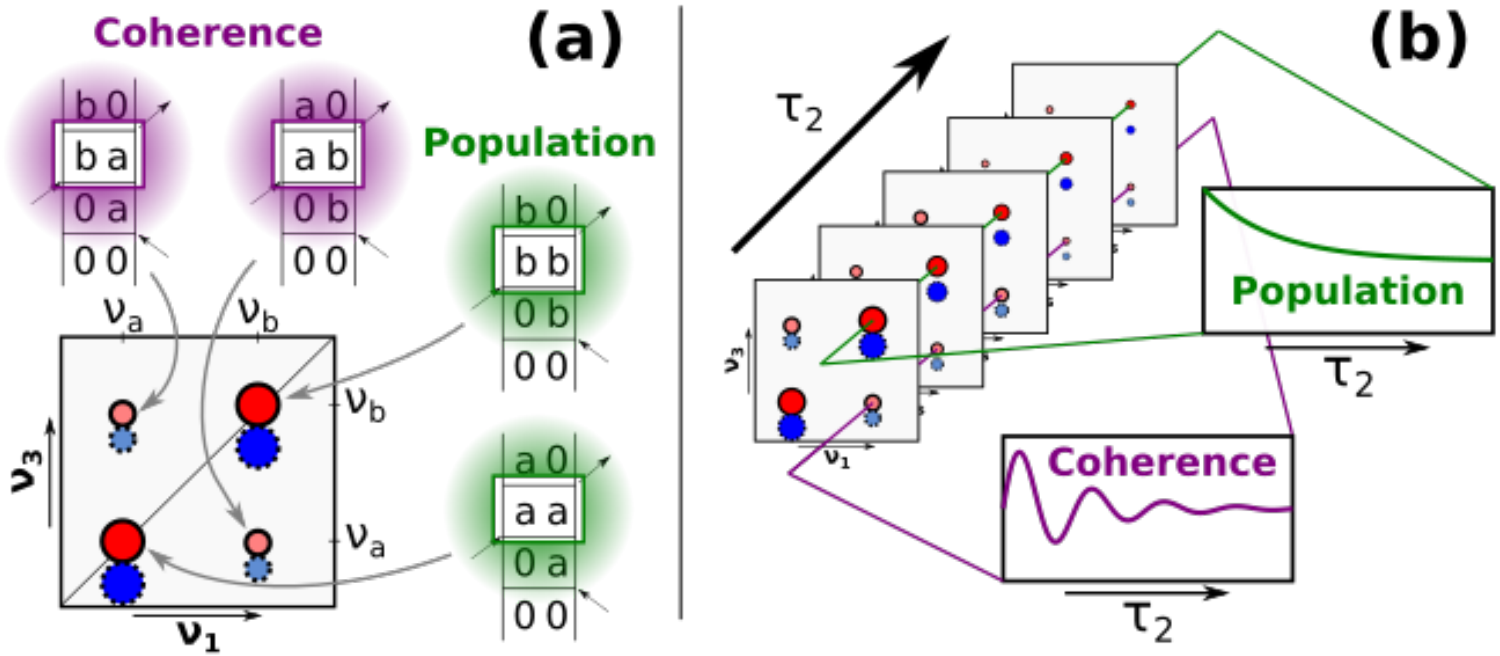
2D **Correlation** Spectra: Two Oscillators

Cross-peaks in 2D spectra indicate site-to-site **coupling** and **energy transfer**.



2D **Correlation** Spectra: Two Oscillators

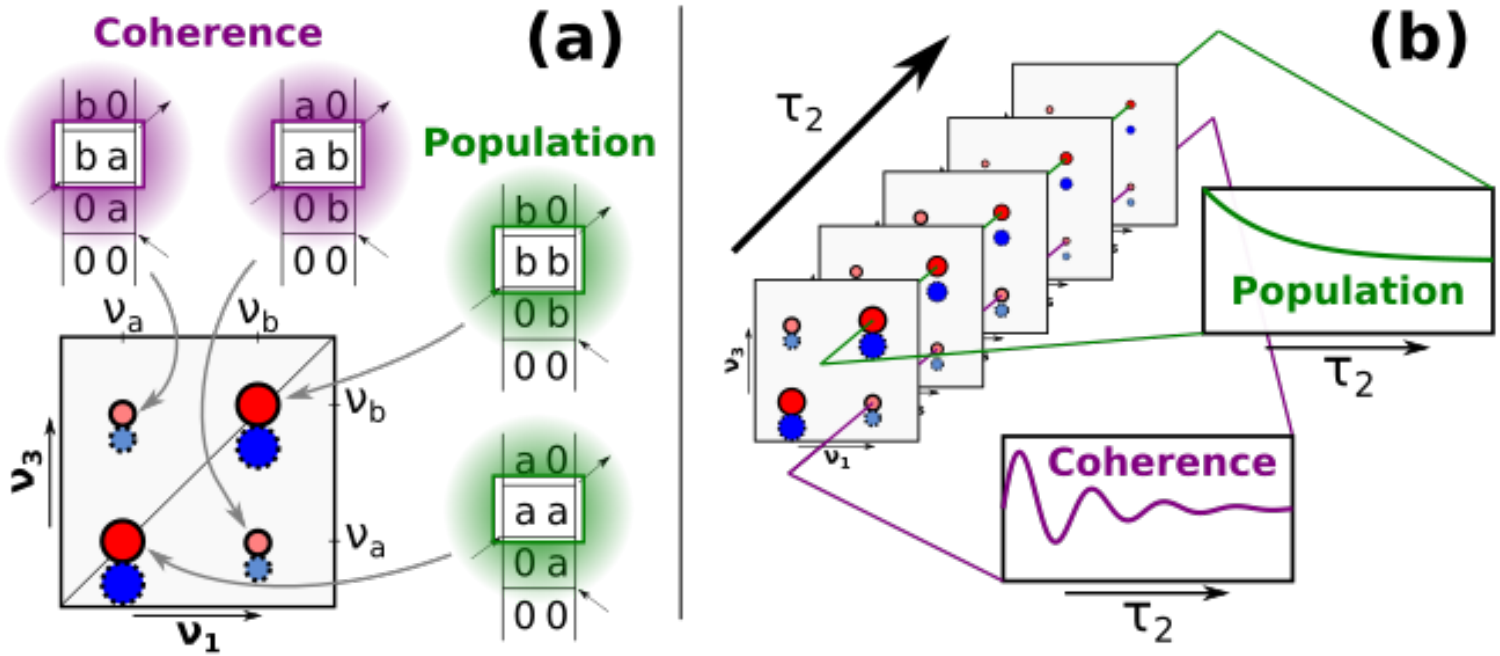
Cross-peaks in 2D spectra indicate site-to-site **coupling** and **energy transfer**.



Classical Interpretation:

2D **Correlation** Spectra: Two Oscillators

Cross-peaks in 2D spectra indicate site-to-site **coupling** and **energy transfer**.



Classical Interpretation: TBD

Take-Home Points

2D Spectroscopy is a generalization of pump-probe spectroscopy, where both **excitation** and **detection** frequencies are resolved.

Four basic types of 2D spectrum:

- Double-Quantum Coherence
- Nonrephasing
- Rephasing
- Correlation $=$ R $+$ NR

Diagonal vs. **Antidiagonal** linewidths distinguish homogeneous and inhomogeneous broadening

Cross-peaks indicate coupling and energy transfer