2D Spectroscopy

Mike Reppert

October 21, 2020

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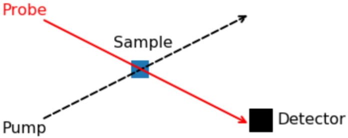

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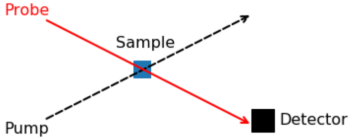

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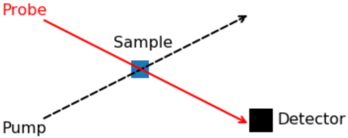

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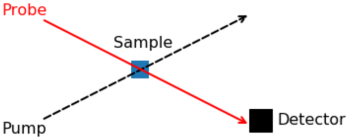

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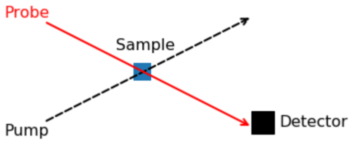

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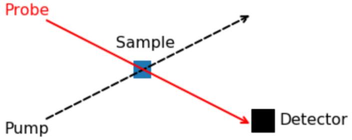

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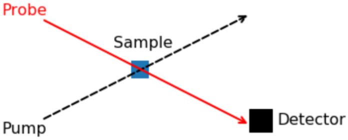

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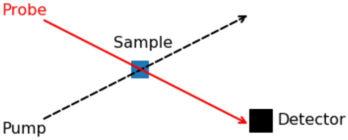

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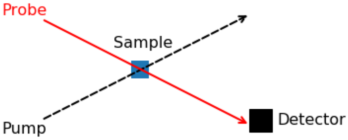

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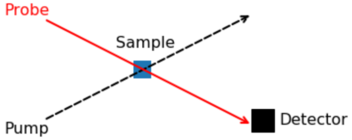

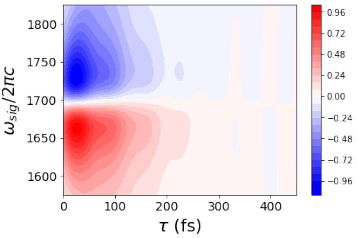

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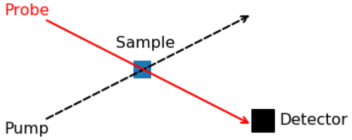

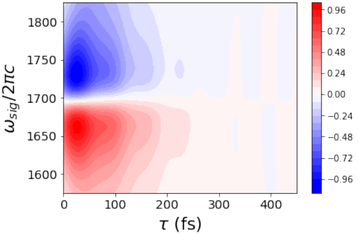

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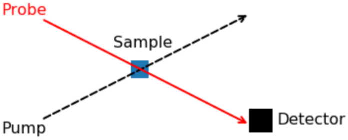

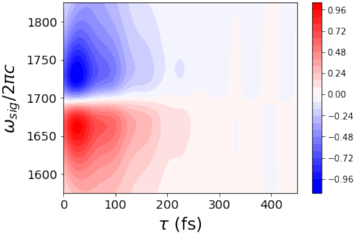

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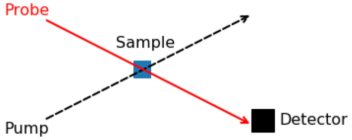

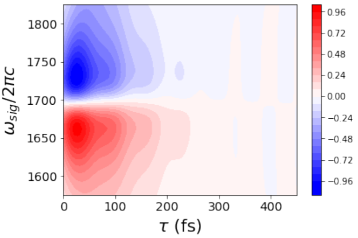

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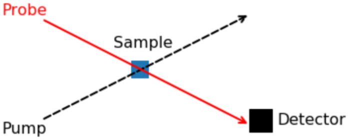

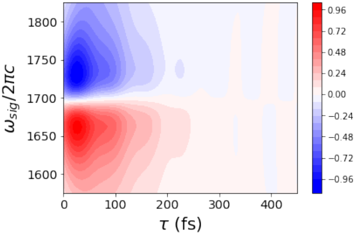

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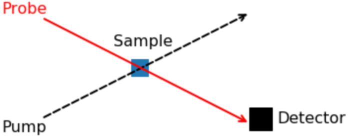

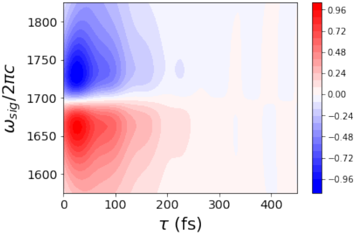

Today: 2D Spectroscopy!

2D Spectroscopy: Big Idea

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

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

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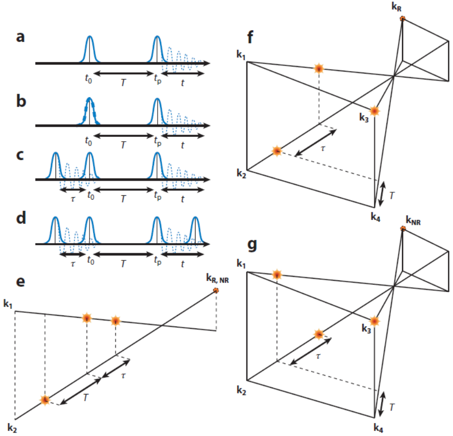
We can! 2D spectroscopy gives (in principle) the **full** third-order response tensor.

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

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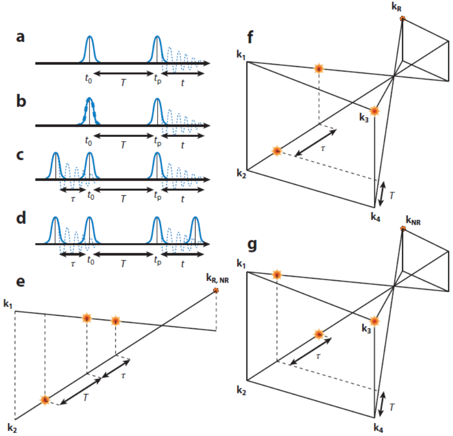

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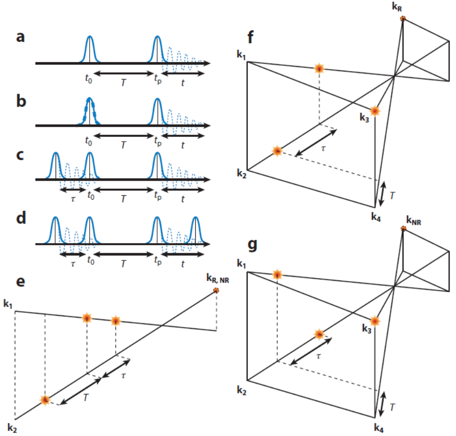

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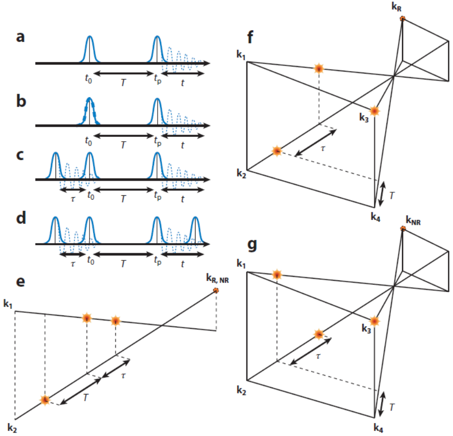

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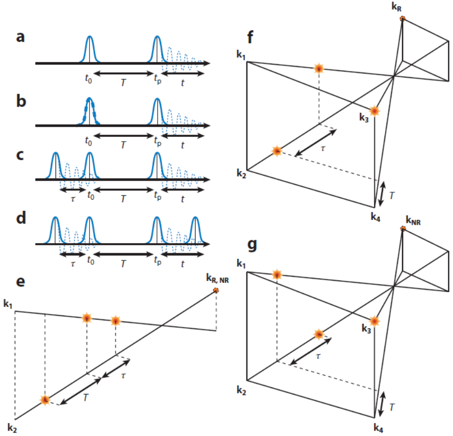
- **Applications:** By directly resolving **both** excitation **and** response, we can directly monitor energy-transfer dynamics



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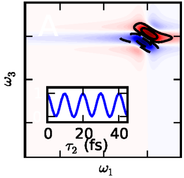
Flavors of 2D Spectroscopy

Double Quantum Coherence:

Beats at $2\omega_o$ and decays with dissipation in τ_2: sensitive to dephasing



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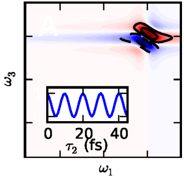

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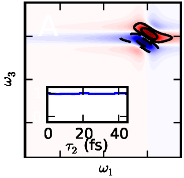

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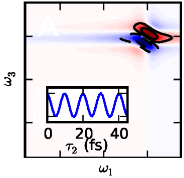

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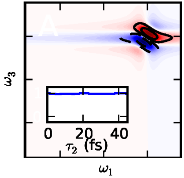

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Rephasing (photon echo):

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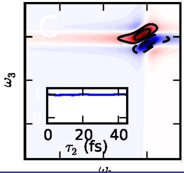

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2D Correlation Spectrum: One oscillator

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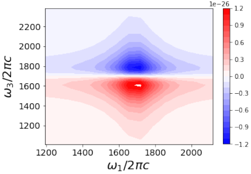
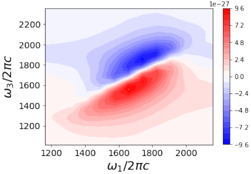
- (ω_1, ω_3) = (Excitation, Detection)
- **Diagonal width** feels *both* homogeneous *and* inhomogeneous broadening
- **Anti-diagonal width** feels only *homogeneous* broadening
- τ_2 feels dissipation **not** dephasing

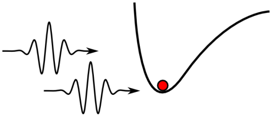
Homogeneous



Inhomogeneous



Classical Beats



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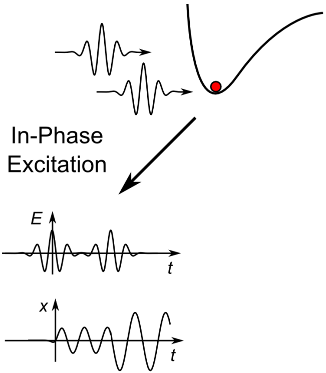

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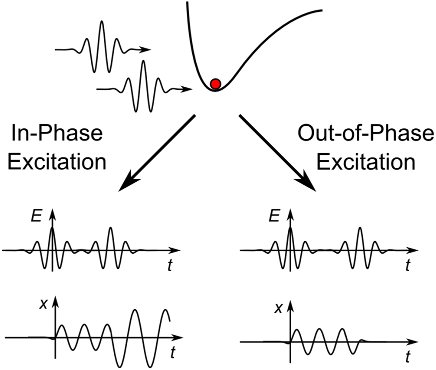

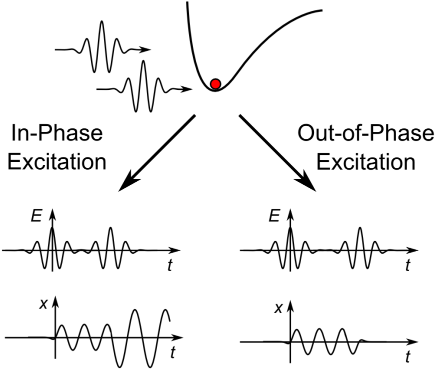

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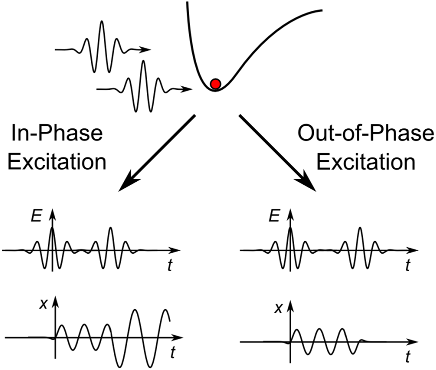

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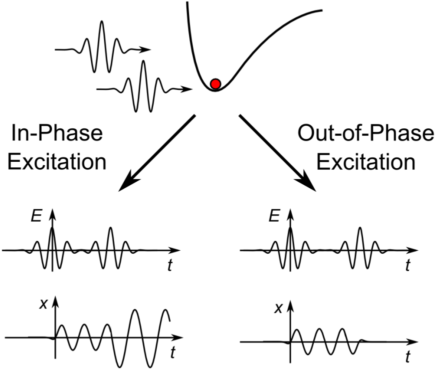

- *Frequency* probed by pulse 3 depends on *time delay* between 1 & 2 $\rightarrow$ Signal
- *Excitation* of one mode alters *frequencies* of coupled modes $\rightarrow$ Cross peaks
- Interference between different modes $\rightarrow$ "Quantum" beats

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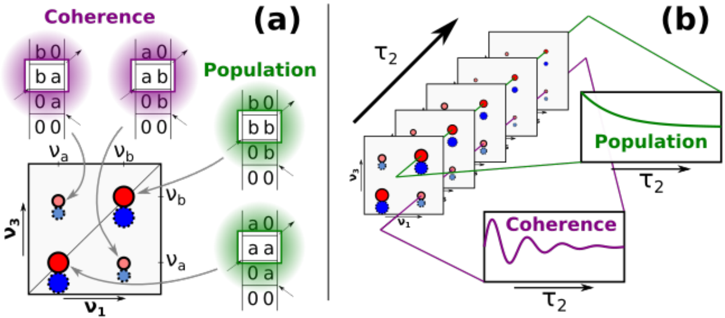

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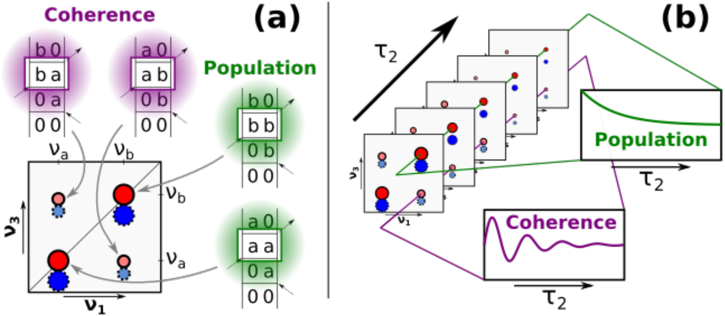

Classical Interpretation:

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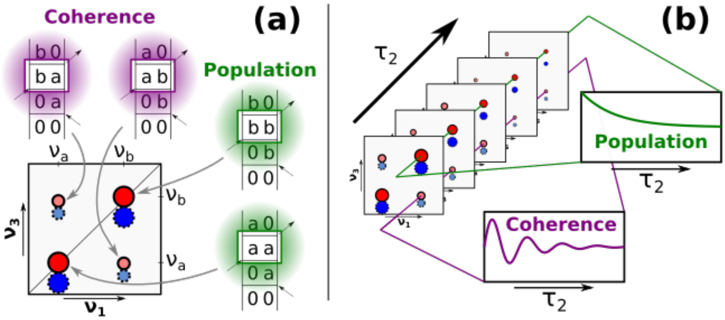

Classical Interpretation: TBD

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