# 2D Spectroscopy

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# Nonlinear Ultrafast Spectroscopy

**Key Idea:** If our total electric field is a sum of "delta functions":

$$E_\alpha(t) = \sum_j E_\alpha^{(j)}(t - t_j)\cos\left(\omega_j(t - t_j)\right)\delta(t - t_j),$$

then the *polarization*

$$\tilde{P}_\alpha^{(n)}\left[\tilde{\boldsymbol{E}}^{(\text{exc})}\right] = \sum_{\alpha_1,\ldots,\alpha_n}\int d\tau_n \ldots \int d\tau_1 R^{(n)}_{\alpha_1\ldots\alpha_n\alpha}(\tau_1,\ldots,\tau_n)$$

$$\times \int_V d\boldsymbol{x}\int dt\, \mathrm{e}^{\mathrm{i}(\omega t - \boldsymbol{k}\cdot\boldsymbol{x})} E^{(\text{exc})}_{\alpha_1}(\boldsymbol{x}, t - \tau_1 - \ldots - \tau_n)\ldots E^{(\text{exc})}_{\alpha_n}(\boldsymbol{x}, t - \tau_n)$$

$$\approx R^{(n)}_{\alpha_1\ldots\alpha_n\alpha}(T_1,\ldots,T_n)$$

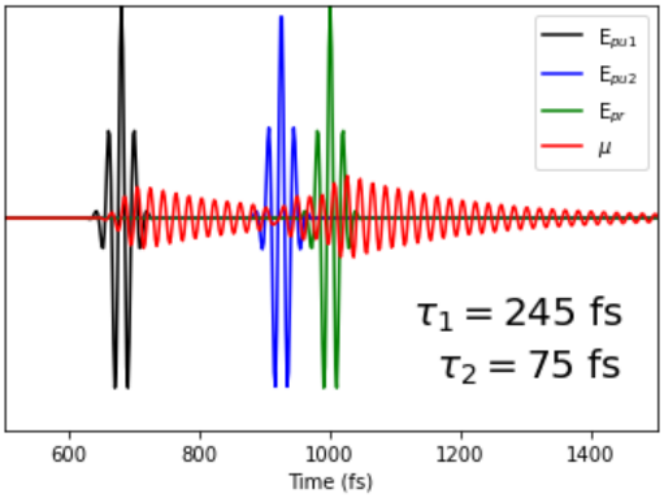
looks simply* like the response function evaluated at the time delays *between pulses* $T_n = t - t_n$, $T_{n-1} = t_n - t_{n-1}$, ....

* Note that here be multiple dragons that we're blindly ignoring.

# Note carefully!

In general, response functions depend on the time delay *between interactions*. Any number of interactions may occur within each pulse from the excitation source.

In most implementations of ultrafast spectroscopy, the experiment is *specifically constructed* to evaluate the response function as a function of time delays *between pulses*.

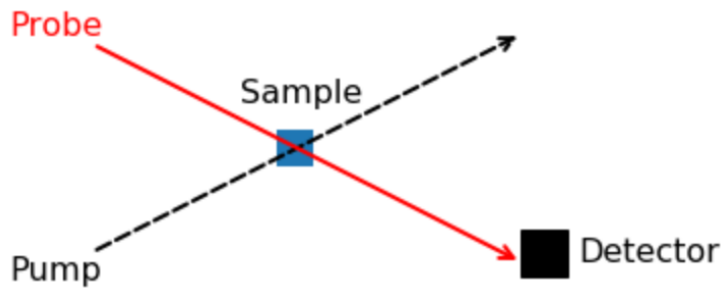


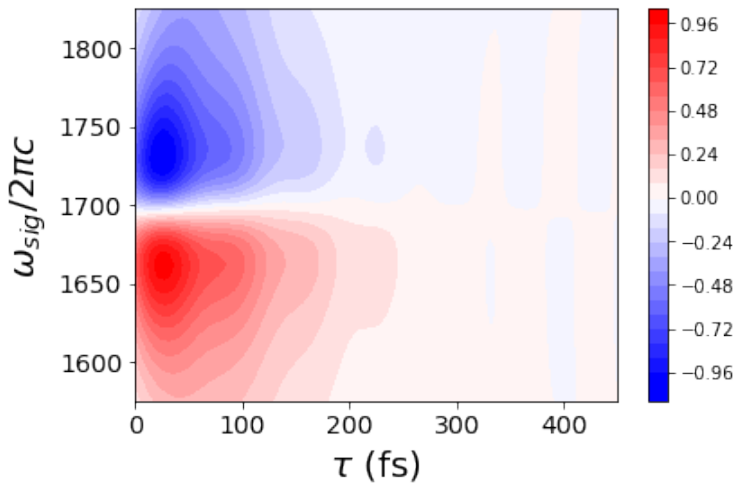

Several "tricks" needed to accomplish this:

- Very short pulses (to keep the range of possible interaction times small)
- Directional detection (to select signal only from specific pathways)
- Beam chopping (to eliminate signals coming from multiple interactions with the same pulse)
- Phase cycling (similar to beam chopping, but by applying specific phases to each pulse)

# Pump-probe Spectroscopy: "simple" four-wave-mixing

- "Tricks":
  - Directional detection
  - Beam chopping:
    $\Delta OD =$ "pump on" $-$ "pump off"




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

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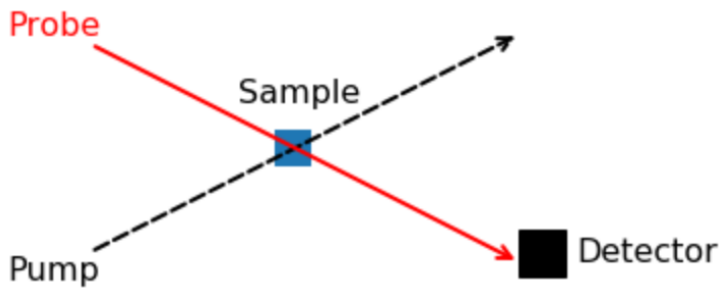


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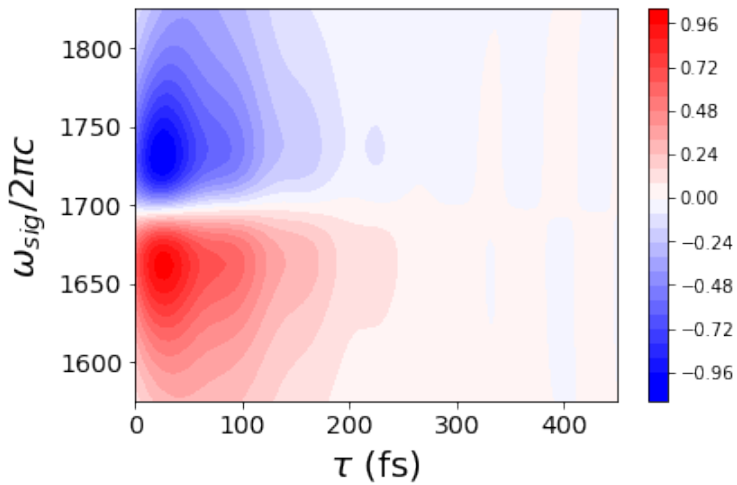


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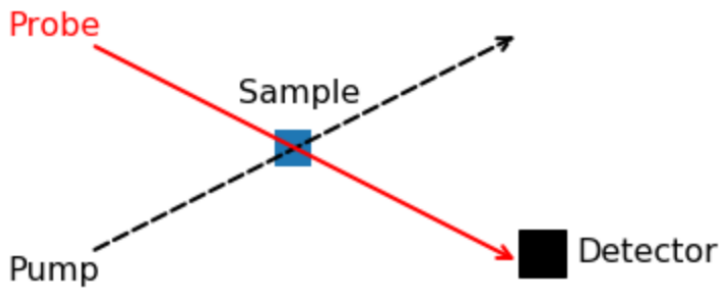


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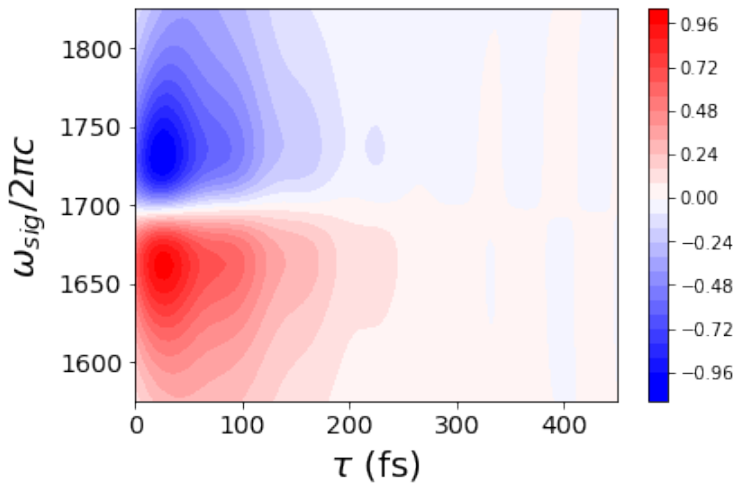


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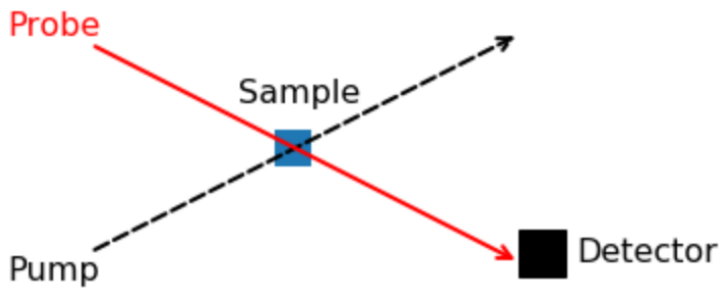


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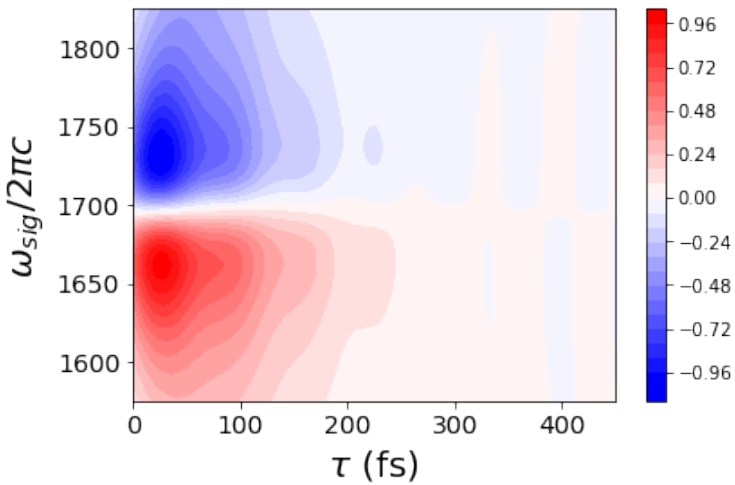


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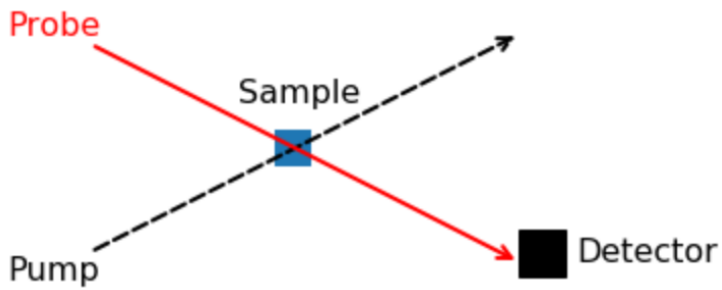


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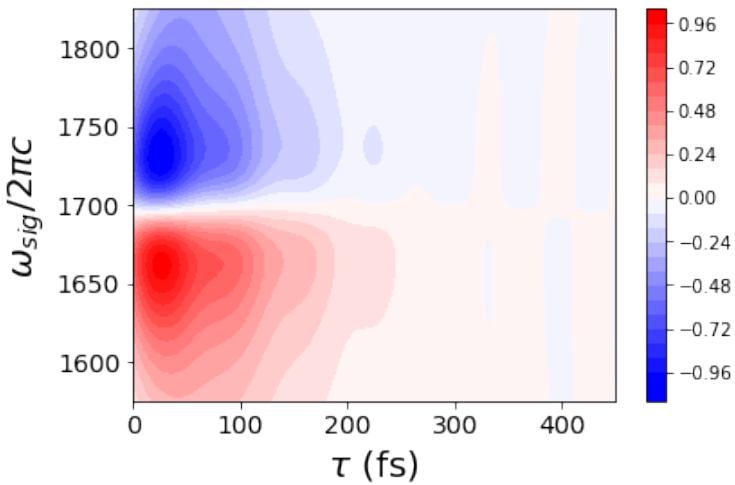
- As a function of time-delay:
  - Does **not** oscillate at high frequencies
  - Monitors **dissipation**
  - **Not** sensitive to dephasing

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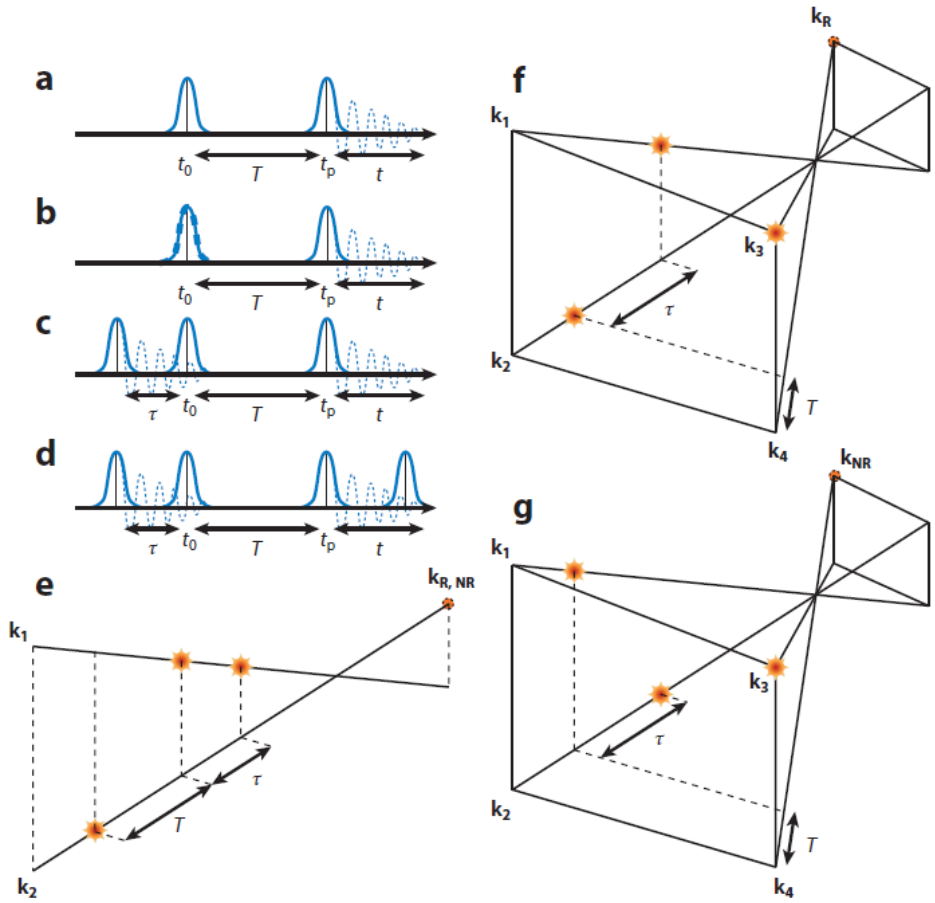
# 2D Spectroscopy: The full $R^{(3)}$ response tensor

- **Key Idea:** By scanning the time delay *between* the first two interactions, we get **excitation** frequency information
- Two common geometries
  - Pump-probe
  - Box-CARS
- **Why care?** By directly resolving *both* excitation *and* response, we can distinguish between homogeneous and inhomogeneous broadening.

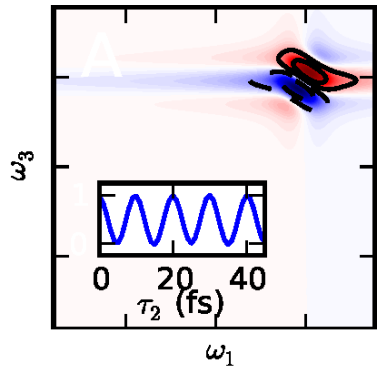



Fuller and Ogilvie, *Ann. Rev. Phys. Chem.*, 2015 66, 667-690

# Three different flavors

## Double Quantum Coherence:

Beats at $2\omega_o$ and decays with dissipation in $\tau_2$: sensitive to dephasing

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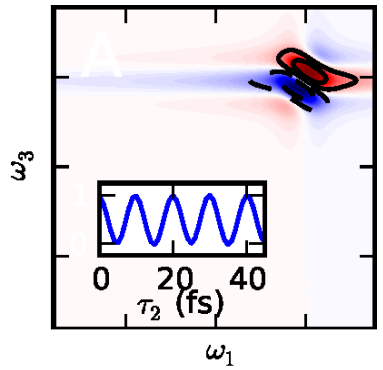


## Nonrephasing:

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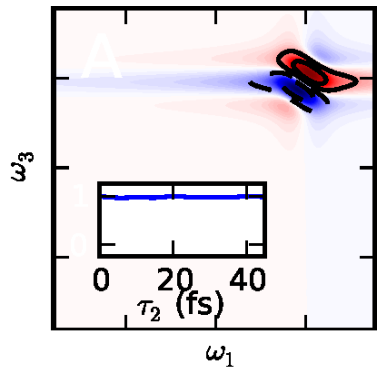

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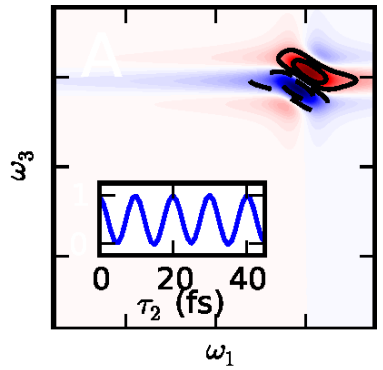


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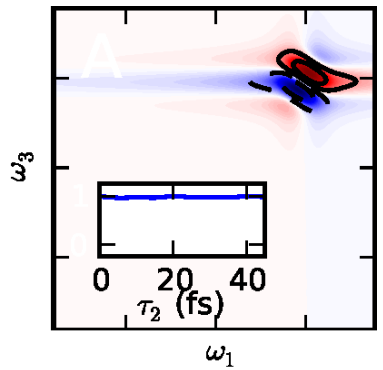


## Rephasing (photon echo):

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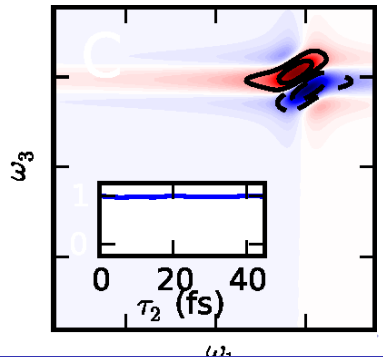

# 2D Correlation Spectrum: One oscillator

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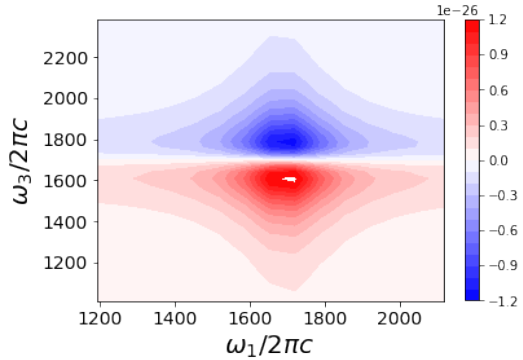
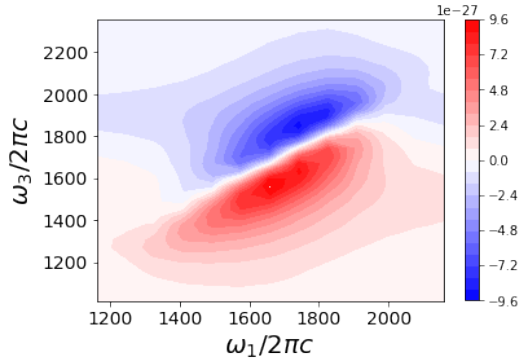
- $(\omega_1, \omega_3)$ = (Excitation, Detection)
- **Diagonal width** feels *both* homogeneous *and* inhomogeneous broadening
- **Anti-diagonal width** feels only *homogeneous* broadening
- $\tau_2$ feels dissipation **not** dephasing

**Homogeneous**




**Inhomogeneous**



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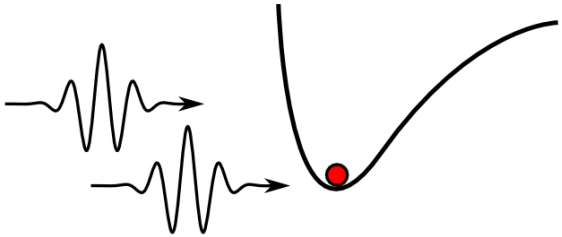

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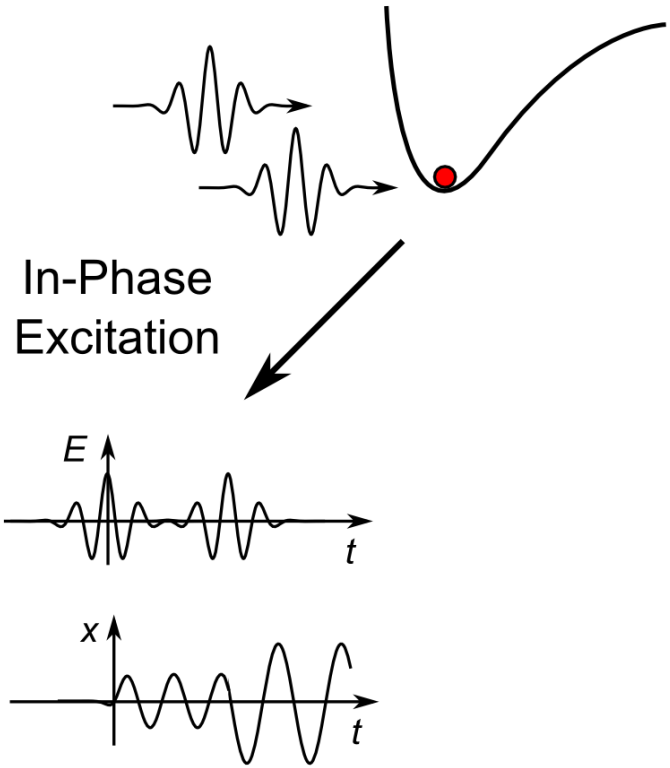

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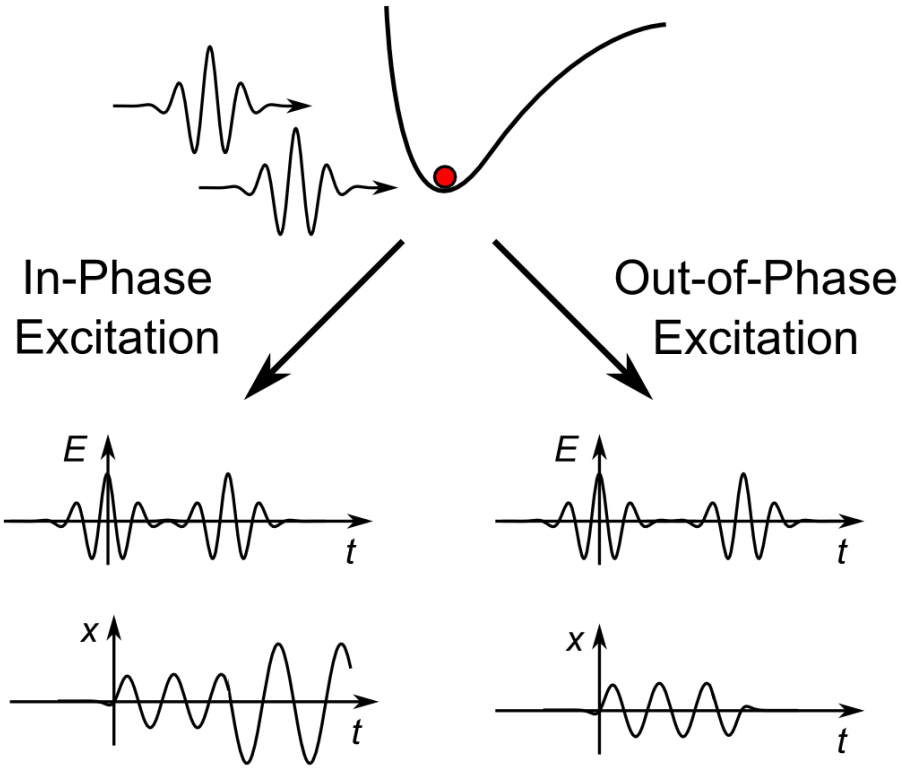

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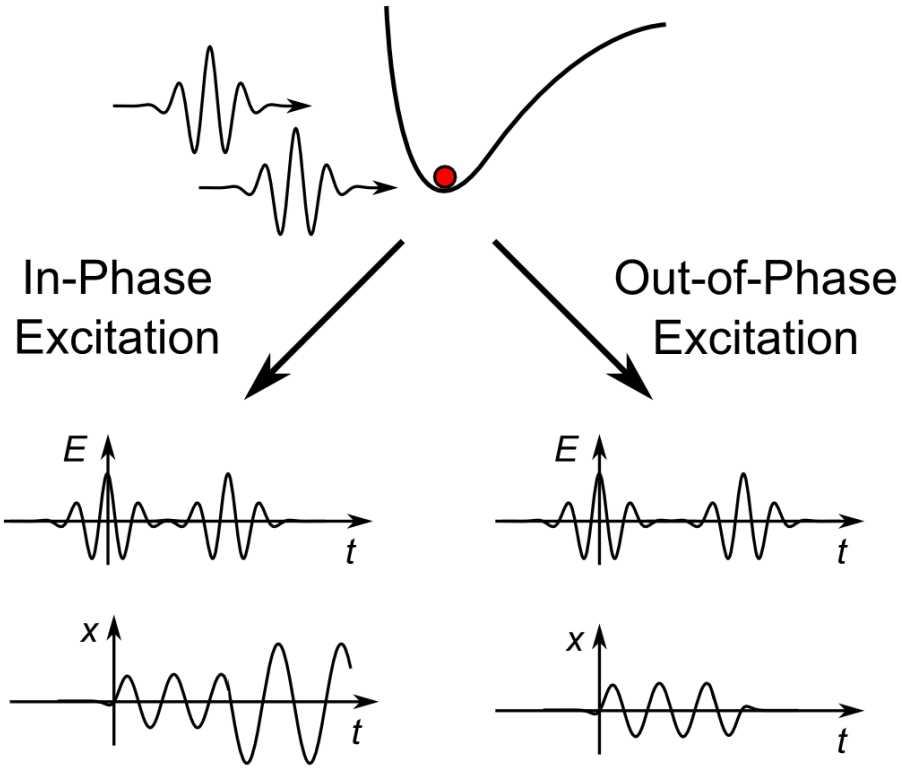


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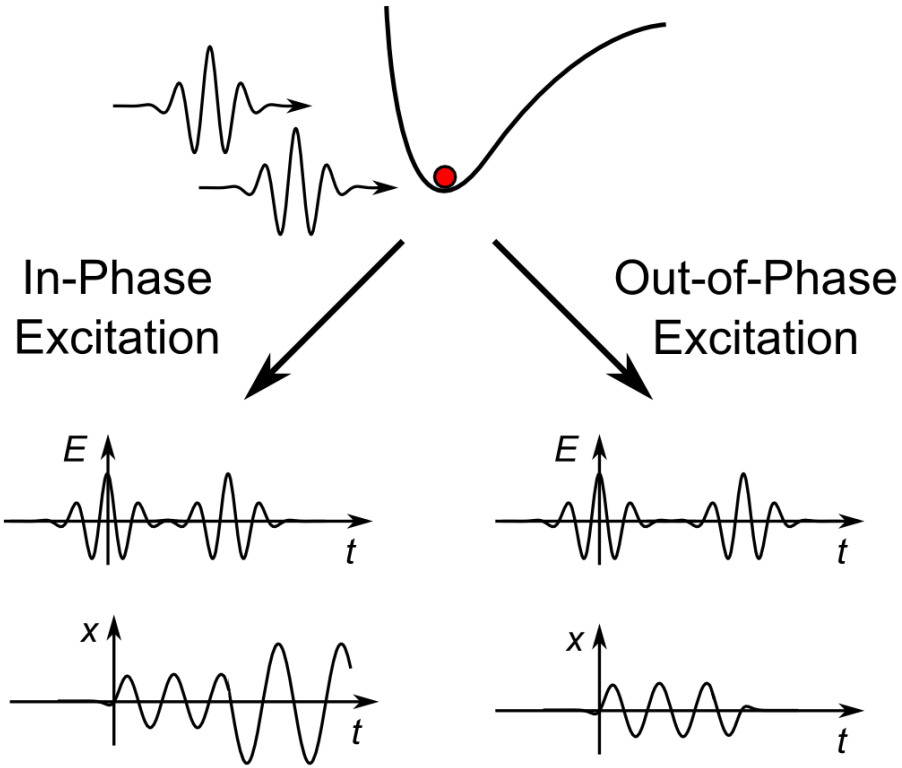


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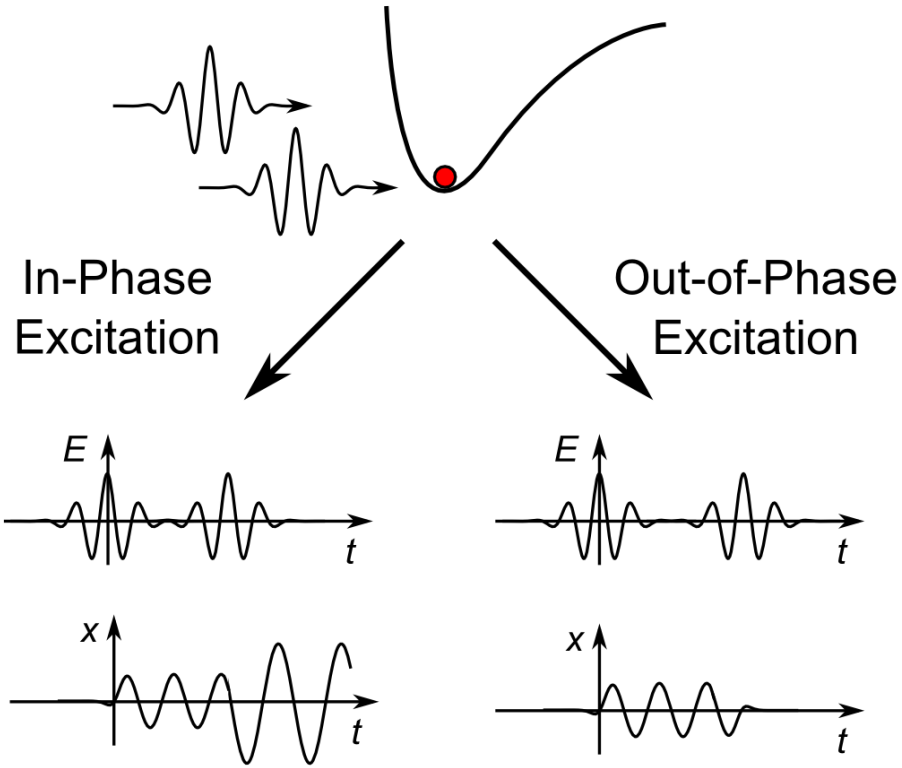
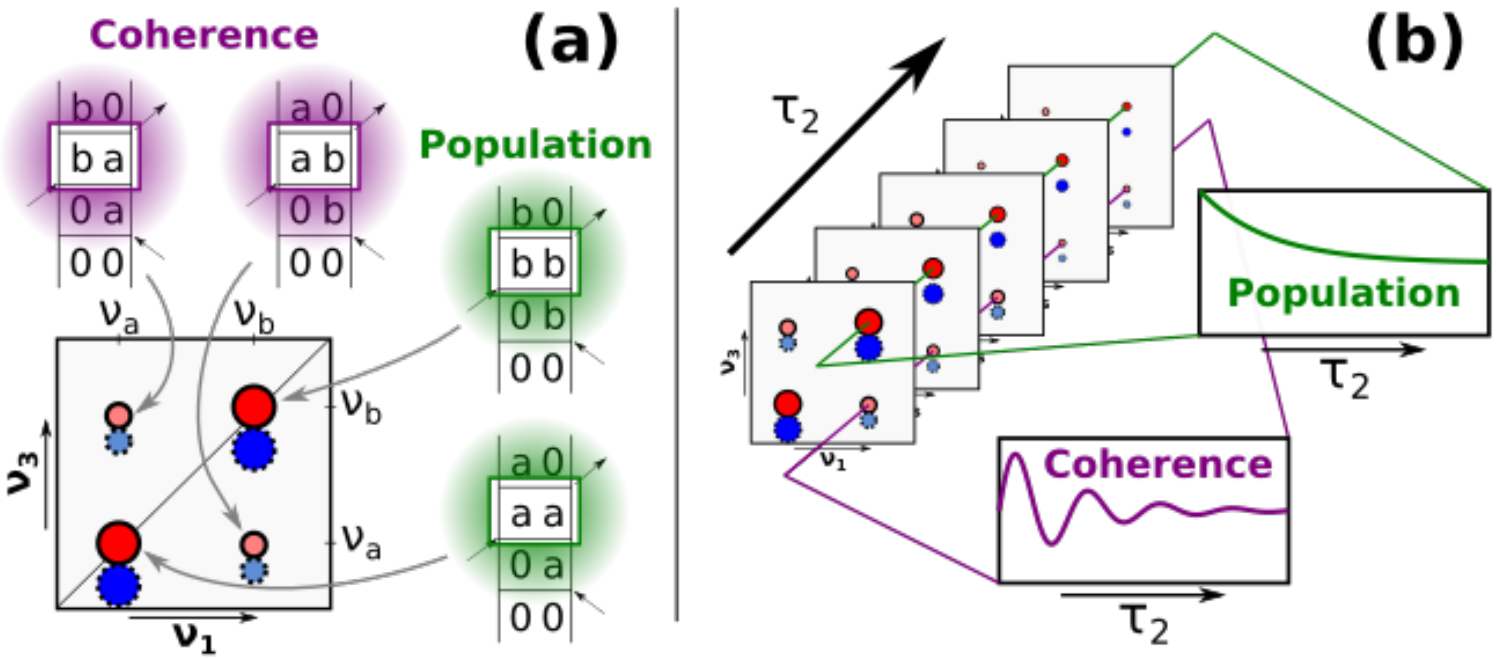



- *Frequency* probed by pulse 3 depends on *time delay* between 1 & 2 $\rightarrow$ Signal
- *Excitation* of one mode alters *frequencies* of coupled modes $\rightarrow$ Cross peaks
- Interference between different modes $\rightarrow$ "Quantum" beats

# 2D **Correlation** Spectra: Two Oscillators

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



# Take-Home Points

A well-designed ultrafast experiment can probe **specific response-tensor elements**.

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

Four basic "flavors" of 2D spectrum:

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

In correlation spectra, **Diagonal** vs. **Antidiagonal** linewidths distinguish homogeneous and inhomogeneous broadening.

**Cross-peaks** indicate coupling and energy transfer.