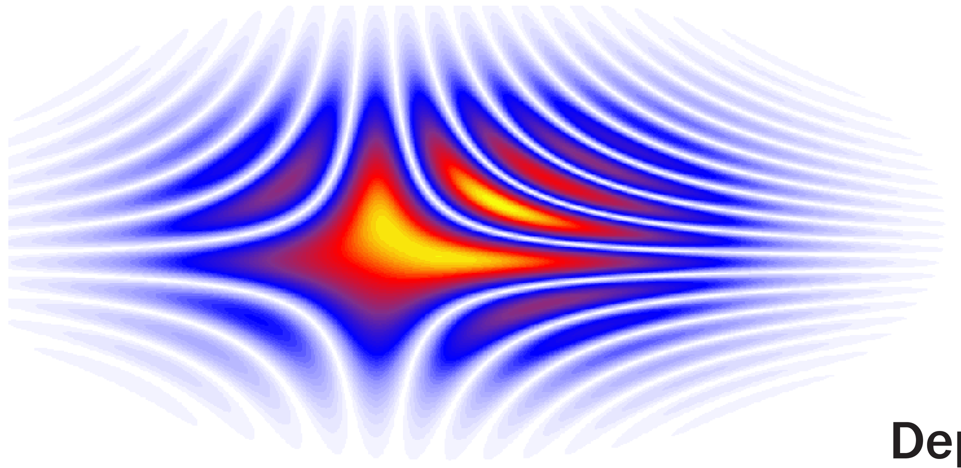

Electronic–vibrational coupling probed by 4D Raman–electronic spectroscopy

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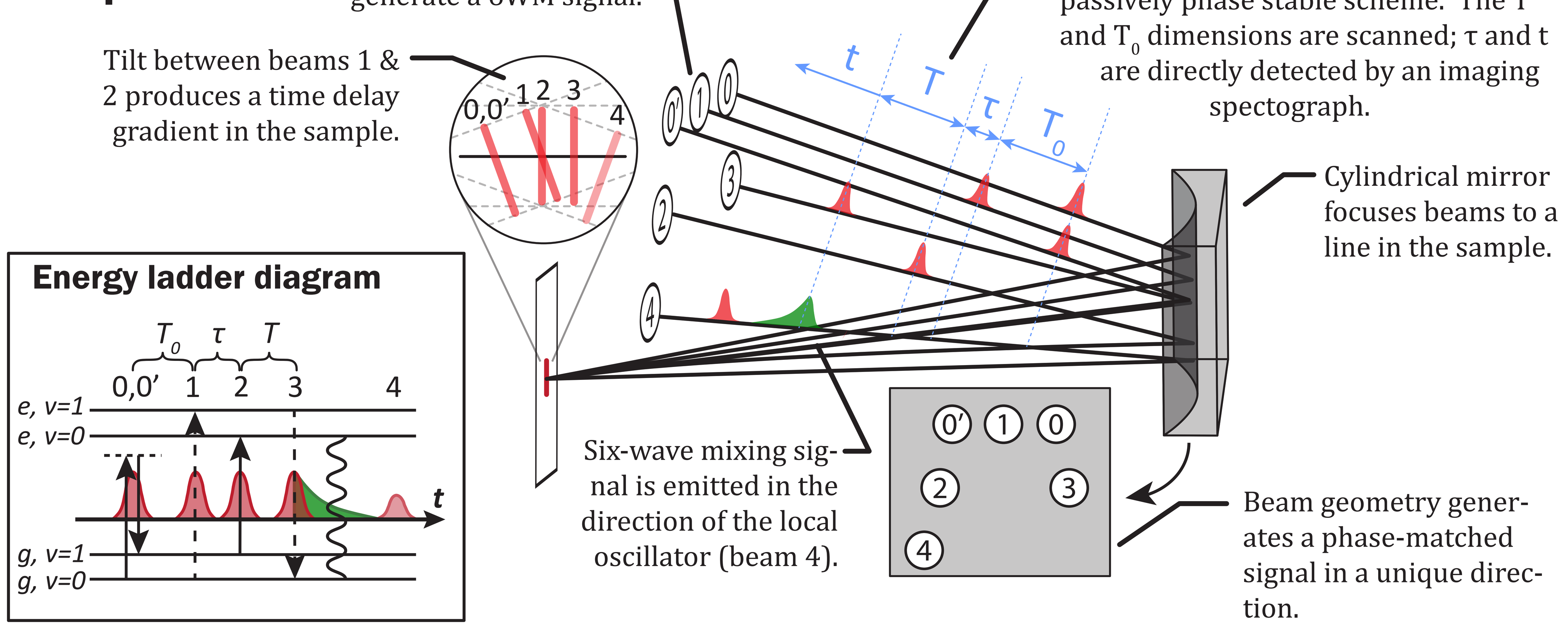
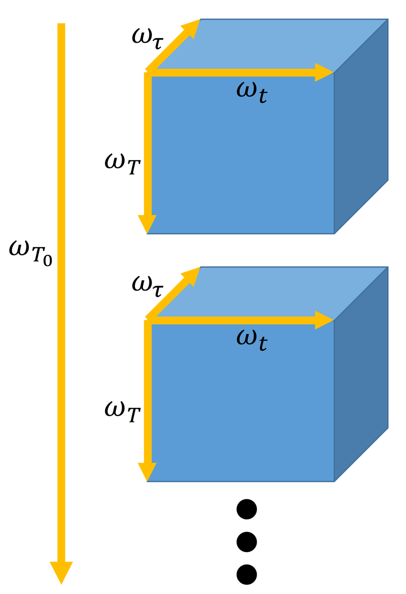
Multidimensional Electronic–Raman Spectroscopy*

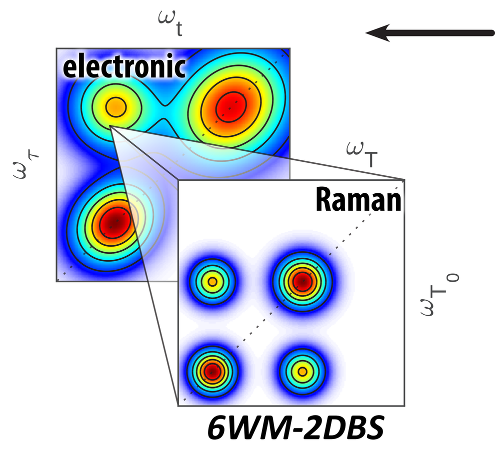
Abstract Electronic-vibrational coupling is the driving force behind many fundamental photochemical processes, ranging from phonon-assisted carrier cooling in semiconductors to photoisomerization in proteins and molecular chromophores. Correlations between electronic and vibrational transitions are sensitive reporters of the structural dynamics underlying these processes, yet they have proved challenging to study. Gradient assisted multidimensional electronic–Raman spectroscopy (GAMERS) is a powerful new technique for correlating such interactions across two electronic and two Raman (vibrational) dimensions, enabling functional group-level specificity. Its ability to resolve coherence pathway-specific signatures in a cyanine dye is demonstrated. Additionally, we show that GAMERS enables two structurally similar chromophores with nearly identical electronic spectra to be distinguished based on differences in their 2D electronic–2D Raman spectra. Finally, GAMERS is applied to colloidal CdSe quantum dots, exposing the coupling of excitons to both optical and acoustic phonons.

Experiment



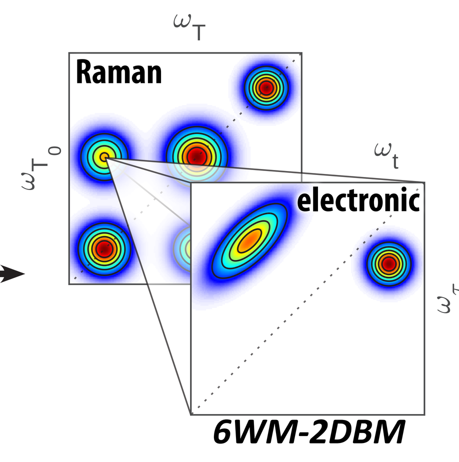
Slices of the 4D GAMERS spectrum





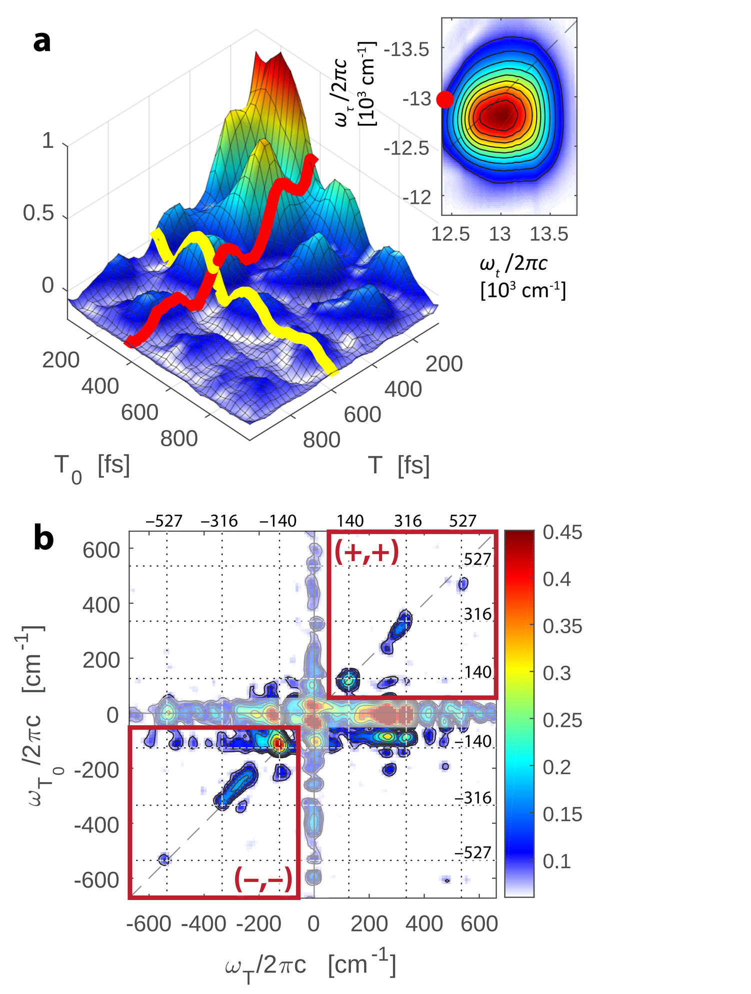
2D Beating *Slice*
2D Raman-like spectrum at each point in the 2D electronic spectrum.

2D Beating *Map*
2D electronic spectrum associated with a specific beating frequency in the 2D Raman spectrum.



GAMERS spectra of IR-140, a cyanine dye

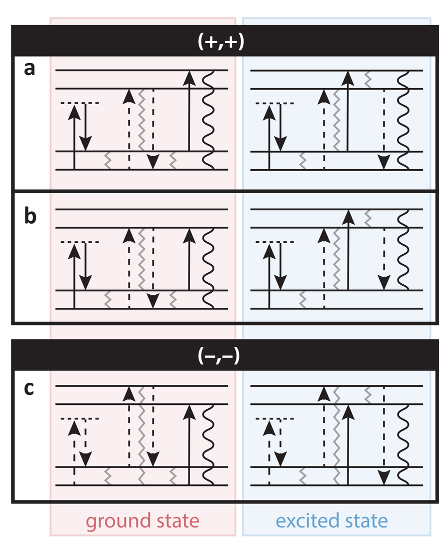
Raman vibrations are observed along both the T and T_0 dimensions.



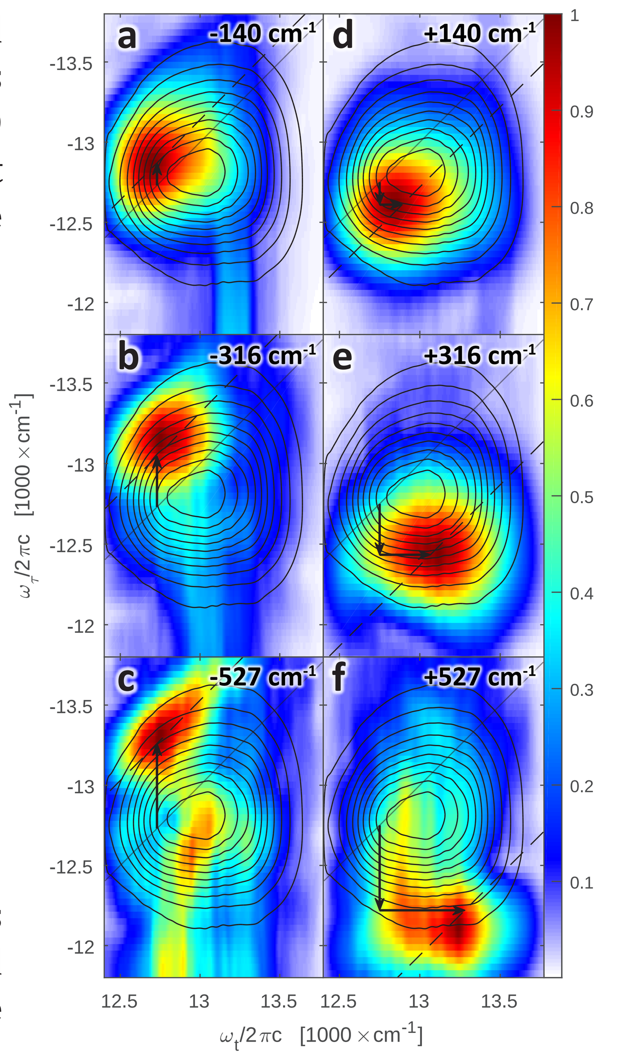
The Fourier transform of the 2D transient contains features primarily along the diagonal in the (+,+) and (-,-) quadrants.

2D Beating Maps

Beating maps constructed from frequencies of peaks along the diagonal of the 2D Raman spectrum exhibit peak shifts related to the vibrational frequency.



The observed peak shifts can be explained based on the above coherence pathways.

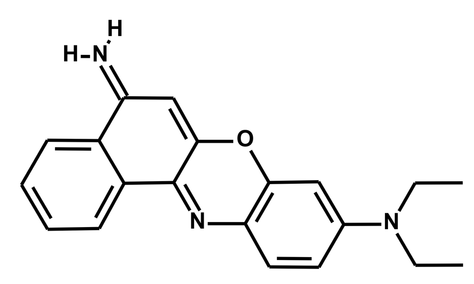


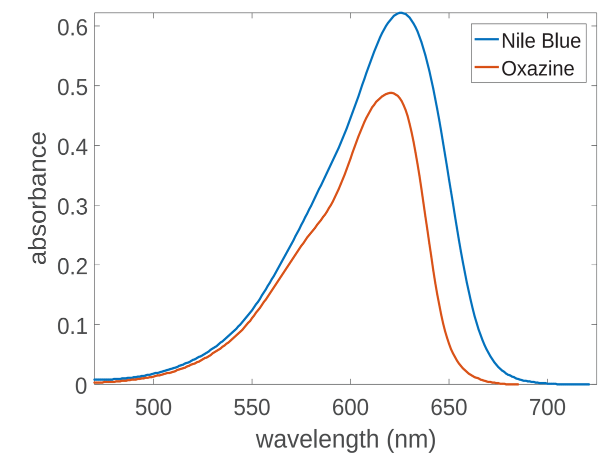
*Spencer, A. P., Hutson, W. O. & Harel, E. Quantum coherence selective 2D Raman–2D electronic spectroscopy. *Nat Commun* 8, 14732 (2017).
Hutson, W. O., Spencer, A. P. & Harel, E. Isolated Ground-State Vibrational Coherence Measured by Fifth-Order Single-Shot Two-Dimensional Electronic Spectroscopy. *J. Phys. Chem. Lett.* 3636–3640 (2016).

GAMERS Applications†

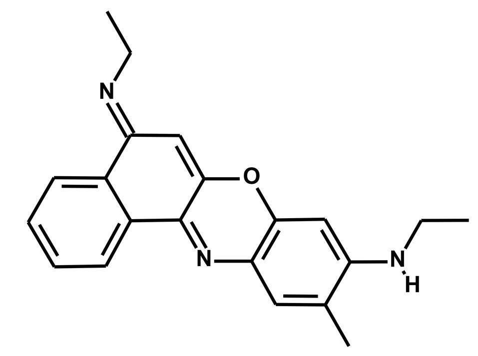
Distinguishing related chromophores

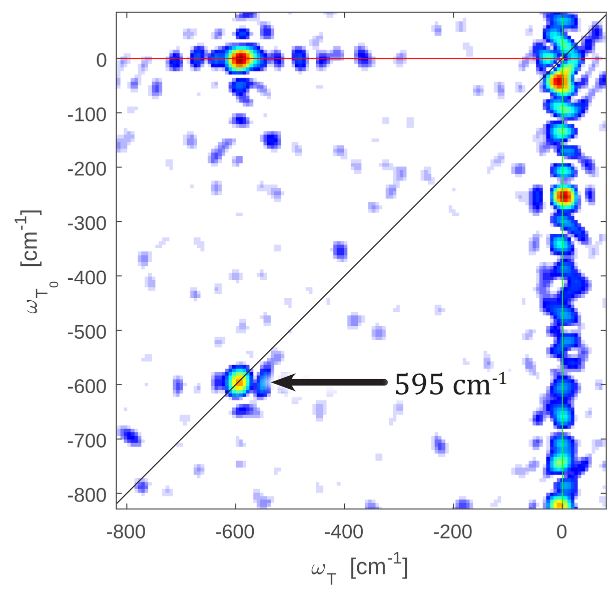
Nile Blue



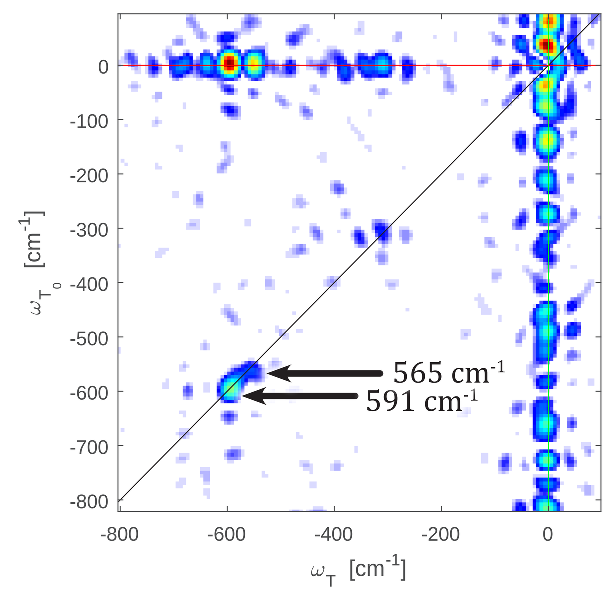


Oxazine 170



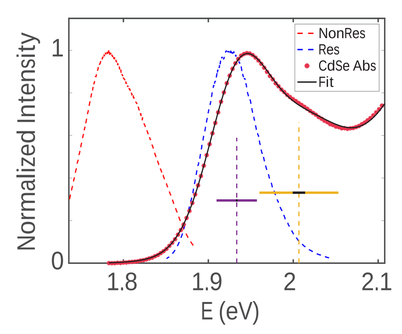


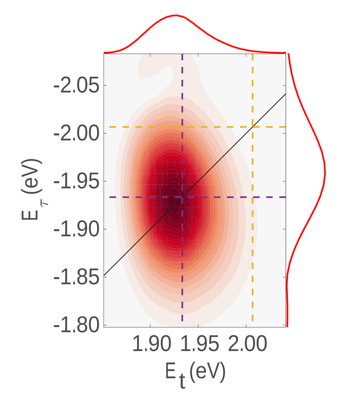
Nile Blue and Oxazine 170 are structurally related cyanine dyes that have nearly identical linear absorption spectra in the visible region. However, differences in their 4D GAMERS spectra enable the two molecules to be distinguished based on their Raman vibrational frequencies. While Nile Blue has a single vibration at 595 cm^{-1}, Oxazine has two modes: 591 cm^{-1} and 565 cm^{-1}.

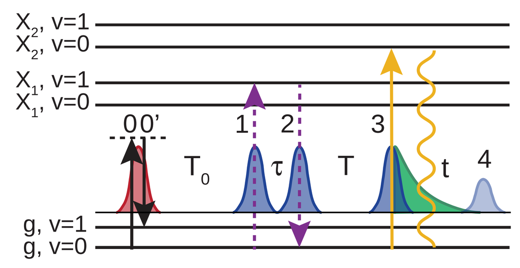


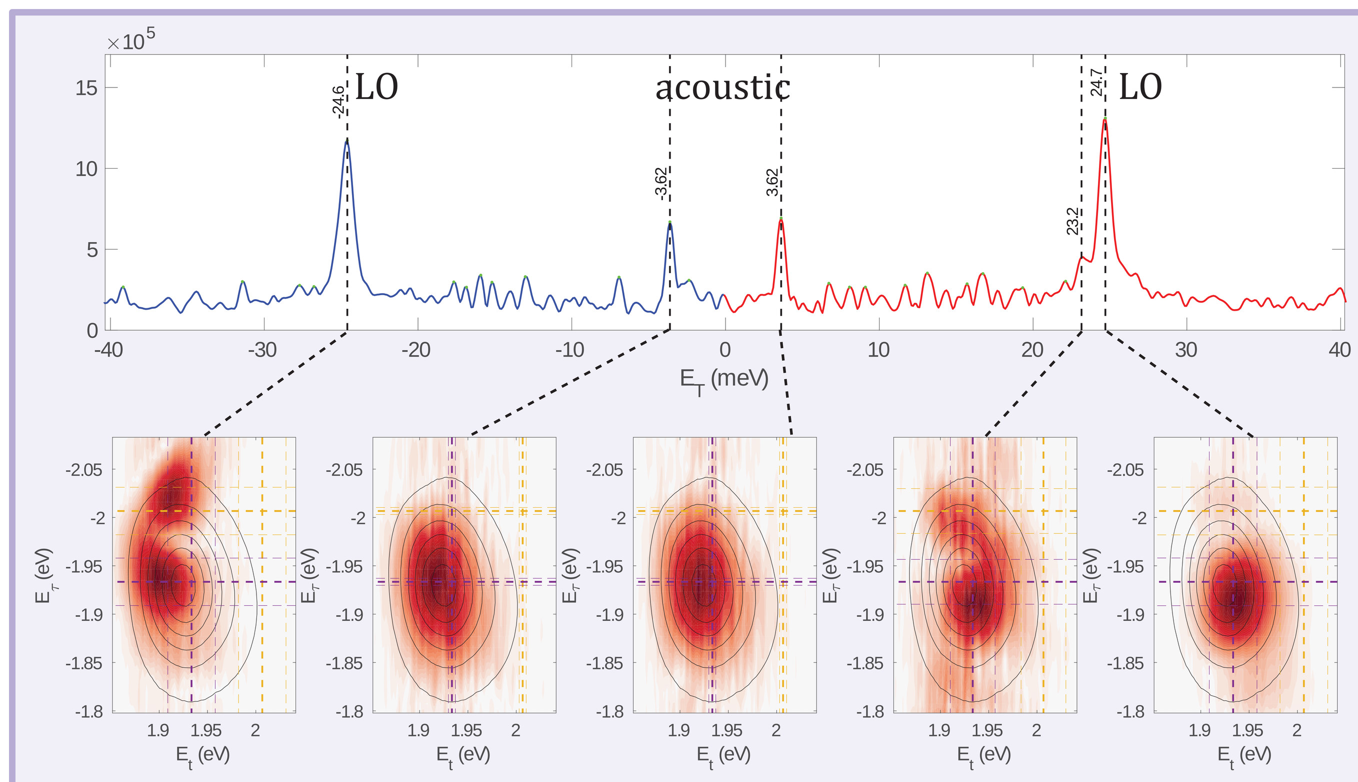
Electron-phonon coupling in CdSe quantum dots

Exciton–phonon interactions play a key role in the relaxation and energy transfer dynamics of colloidal quantum dots. Characterizing how phonons intermediate such processes as carrier cooling and exciton–exciton interaction is critical for understanding their photophysical properties.





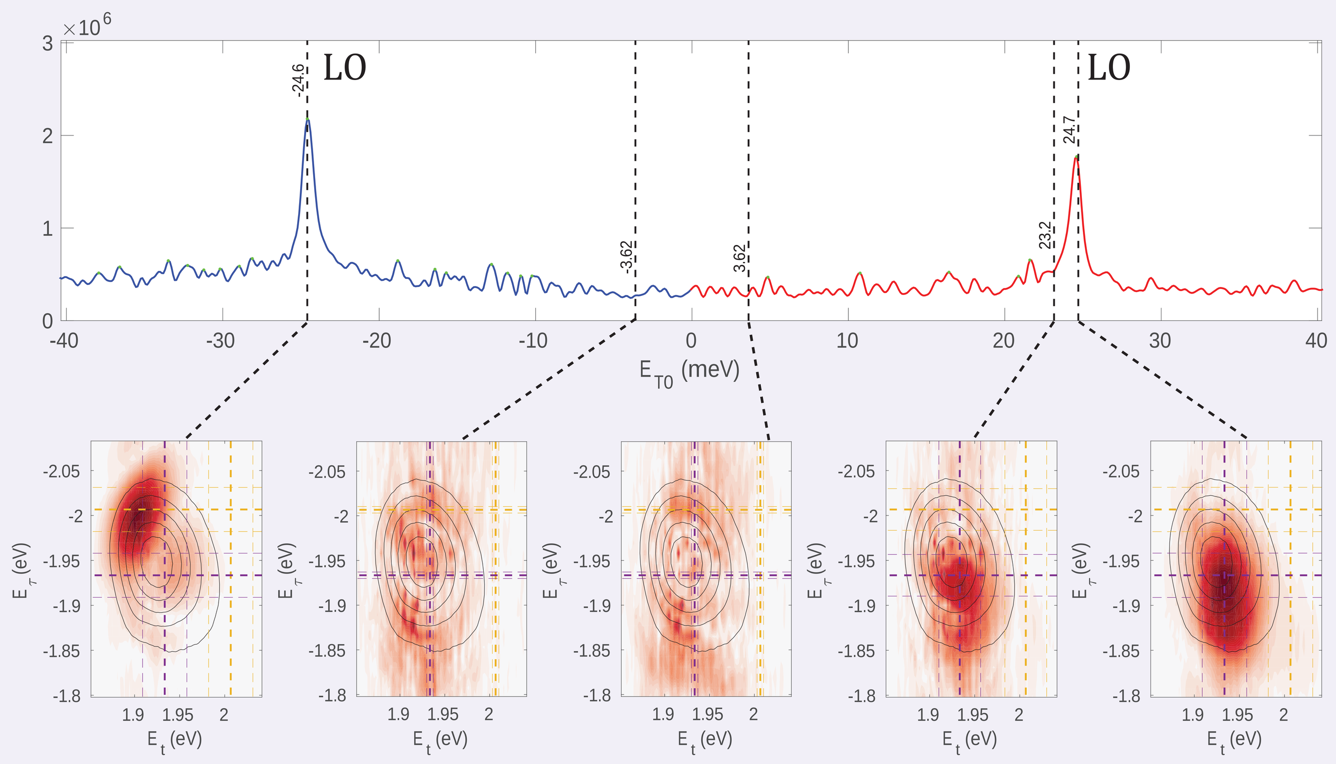




T (resonant)

The Raman-like spectrum along T exhibits vibrational modes at ±24.6 meV (≈ ±200 cm^{-1}) and ±3.62 meV (≈ ±29 cm^{-1}). These are attributed to longitudinal optical (LO) phonons and acoustic phonons, respectively.

Beating maps for LO phonon modes show two peaks, corresponding to the X_1 and X_2 exciton transitions.



T_0 (nonresonant)

The Raman-like spectrum along T_0 contains only the LO phonon modes.

The beating maps for nonresonantly excited phonons (T_0 dimension) are clearly distinct from resonantly excited phonons (T dimension).

†Spencer, A. P., Hutson, W. O. & Harel, E., in preparation.

Conclusions

GAMERS is a powerful method for probing electronic–vibrational coupling in a wide range of chemical systems. The added dimensionality of the technique uncovers structure that is hidden in lower-order methods under the broad lineshapes of congested electronic spectra. In addition, control over resonance within the experiment helps in parsing the electronic character of coherent oscillations during each time interval between pulses, enabling pathway-specific assignment of features within the 4D GAMERS spectrum.