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14. ABSTRACT

The central premise of classical thermodynamics is that free energy gained by a system may not be larger than work done on it. However, in the presence of 'information-to-energy' feedback, energy may indeed move uphill in systems operating far from equilibrium. It remains an open question as to whether feedback itself is even necessary outside the confines of classical physics. In systems governed by quantum mechanics, energy can move reversibly between high and low energy states of the system, which, in the presence of relaxation, may result in energy trapping at a desired time and space. Many natural biological systems routinely achieve this energetic choreography

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Report Title

Final Report: Ultrabroadband Two-Dimensional Coherent Optical Spectrometer for Directed Energy Trapping in Quantum Dynamical Systems

ABSTRACT

The central premise of classical thermodynamics is that free energy gained by a system may not be larger than work done on it. However, in the presence of 'information-to-energy' feedback, energy may indeed move uphill in systems operating far from equilibrium. It remains an open question as to whether feedback itself is even necessary outside the confines of classical physics. In systems governed by quantum mechanics, energy can move reversibly between high and low energy states of the system, which, in the presence of relaxation, may result in energy trapping at a desired time and space. Many natural biological systems routinely achieve this energetic choreography with remarkable efficiency despite their exposure to "hot and wet" environmental conditions. This proposal seeks to develop instrumentation tailored to measure quantum transport processes in a new class of biomimetic quantum dynamical systems - colloidal nano-networks composed of organic-inorganic components – in order to achieve directed energy transport across a broad energy spectrum. These artificial molecules offer a unique platform with tailored electronic and vibrational structures to direct energy along controllable pathways in space. Specifically, we propose to develop a novel technique combining super-continuum generation with multi-dimensional coherent optical spectroscopy, which can realize simultaneous high spectral and temporal resolution across the entire visible region of the electromagnetic spectrum. The proposed instrument will serve to support current DoD funded efforts (ARO Grant W911NF-12-1-0290, PI: Elad Harel) for understanding how to exploit quantum mechanical effects in artificial PPCs operating in extreme environments.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
12/04/2015	1.00	Boris Spokoyny, Christine J. Koh, Elad Harel. Stable and high-power few cycle supercontinuum for 2D ultrabroadband electronic spectroscopy, Optics Letters, (03 2015): 0. doi: 10.1364/OL.40.001014
12/04/2015	2.00	Austin P. Spencer, Boris Spokoyny, Elad Harel. Enhanced-Resolution Single-Shot 2DFT Spectroscopy by Spatial Spectral Interferometry, The Journal of Physical Chemistry Letters, (03 2015): 0. doi: 10.1021/acs.jpclett.5b00273
TOTAL:	**2**	

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received		Paper
TOTAL:		

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Mapping Multidimensional Electronic Structure and Ultrafast Dynamics with Single Element Detection and Compressive Sensing

Number of Presentations: 1.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Post Doctorates

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Faculty Supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

Project Summary - Grant # W911NF1410551
(Reporting Period: October 2014 – November 2015)

Ultrabroadband Two-Dimensional Coherent Optical Spectrometer for Directed Energy Trapping in Quantum Dynamical Systems

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Objective

Here, we propose to build instrumentation that is uniquely suited to study transport in these nano-networks across all the relevant time and energy scale in which they operate. This instrument will augment our current research capabilities and enable new experiments in order to understand and exploit coherent and incoherent transport in coupled molecular networks. We propose to construct an ultrabroadband, phase-sensitive interferometer based on single-shot multi-dimensional optical spectroscopy, which will serve to support a **2013 Young Investigator Award (YIP): Controlling Energy Flow in Colloidal Nano-Networks**, awarded through the Army Research Office (Ref Award #: W911NF-12-1-0290, PI: Elad Harel). This instrumentation will serve as an important tool for understanding how to exploit quantum mechanical effects for enhanced energy trapping in artificial PPCs operating in extreme environments. In order to track the fate of energy as it moves through the network, we need to employ a measurement strategy that achieves

- high temporal resolution (< 10 fs) and high dynamic range (fs – ps).
- strong signals under extremely low pulse energy excitation conditions (10-100 nJ/cm^2)
- Fourier-limited spectral resolution limited by the system, not the instrument.
- sensitivity to wave function delocalization.
- signatures of quantum coherence between quantum states.
- a measurement of the dephasing caused by system-bath interactions.

These capabilities are critical for measuring the electronic and vibrational structure of the individual and system components of the network, and the influence of couplings to the phonon bath on energy transport.

Relevance to Army

1.1.1. Quantum Computing. The QD nano-networks envisioned here may serve as a scalable platform for room-temperature quantum information processing. At the timescales of energy transport, all microscopic motions are effectively "frozen" except for electronic and vibrational motion of the constituent atoms. In isolated molecules, the large number of degrees of freedom, imply that irreversible relaxation, most critically, dephasing is unavoidable at finite temperatures in which many states are populated. However, in networks, or in highly-coupled, nearly degenerate systems, certain coherences may be long-lived. Such prolonged coherences have been observed in photosynthetic proteins. The assemblies described here should exhibit long-lived coherences as well owing to the scaffolding molecules holding the QDs together. We envision that the proposed work will lead to design principles that prolong coherences to the picosecond regime. In this case, a large number of control pulses could conceivably be applied with the coherence time, similar to the way in which nuclear magnetic resonance (NMR) quantum

computing was implemented nearly a decade ago. Unlike NMR, however, optical signals are large, especially if converted to background-free fluorescence states. Furthermore, truly entangled, approximately-pure states may be created, leading to the possibility of a room-temperature, ensemble quantum computing device based on solution processing.

1.1.2. Autonomous Systems. The systems described here are incredibly robust to a host of environmental conditions, both static and dynamic. Since feedback can perturb the fragile quantum state of the system, a robust quantum dynamical system must avoid direct interactions with the outside world except at the terminating event. The approach outlined in this proposal may allow for truly autonomous systems that perform specific tasks dictated by the geometry, composition, and chemical modifications of nanostructured materials. These systems are incredibly cheap, possibly recyclable, and amenable to batch processing methods, instead of sophisticated and costly nano-lithographic techniques. Instead of isolating the system from its environment, our approach utilizes the environment in a productive manner.

1.1.3. Solar Energy Conversion. In most photovoltaic devices, an exciton created after photoexcitation, separates into charge carriers in the form of an electron and hole, which diffuse through a gel or film to their respective electrodes, producing a photocurrent. One of the major limitations of photovoltaic devices is the limited exciton diffusion length, which ultimately limits the thickness of the absorbing layer and the ability to efficiently produce electrical current. Photosynthetic systems can readily transport excitons across tens of nanometers, while the best photovoltaic devices are limited to 1-5 nm. Recent theoretical efforts suggest that the protein environment of the absorbing chromophores protects excitons from premature relaxation processes such as recombination, phonon-assisted relaxation, defect sites, and energy traps. The QD nano-networks described here will allow us to systematically test the limits of exciton migration in a platform with a high degree of synthetic control. This may lead to design principles supporting long-range energy transfer, an important requirement for more efficient solar energy conversion devices.

1.1.4. Environmental Impacts of Proposed Research. The intended research will not result in any environmental impacts outside the laboratory.

Accomplishments for Reporting Period

- Development of a high-power supercontinuum light source spanning 500-850 nm, 300 uJ/pulse, sub-6 fs, representing ~18 fold in temporal narrowing and ~25 fold in spectral broadening.
- Single-shot acquisition of a laser dye (IR-144) across the entire visible/NIR region, acquired in a single-laser shot (<1 ms acquisition) representing >100 fold larger spectral coverage than any previous single-shot method.
- Pulse shaping of sub-30 fs pulses from a Yb-doped solid-state laser system operating at 600 kHz, showing both amplitude and phase modulation capabilities with high throughput (>30 %).
- Demonstration of 5^{th}-order (6-wave mixing) spectroscopy, which will be used in the future to measure electron-phonon interactions in semi-conductors and dephasing in quantum networks.
- Use of compressive sensing, which allows signals to be efficiently captured by exploiting their inherent sparsity. We implemented sparse sampling to capture the electronic structure and ultrafast dynamics of molecular systems using phase-resolved 2D coherent spectroscopy. We report complete Hadamard reconstruction of the signals and

compression factors as high as 10, in good agreement with array-detected spectra. Single-Point Array Reconstruction by Spatial Encoding (SPARSE) Spectroscopy reduces acquisition times by about an order of magnitude, with further speed improvements enabled by fast scanning of a digital micromirror device. We envision unprecedented applications for coherent spectroscopy using frequency combs and super-continua in diverse spectral regions

Collaborations and Technology Transfer

- US Provisional Patent application filed: 'Two-Dimensional Single-Shot Ultrasensitive Spectrophotometer', E. Harel, Application # 62032696

Resulting Journal Publications During Reporting Period

- A. P. Spencer, B. Spokoyny, and E. Harel, Enhanced-Resolution Single-Shot 2DFT Spectroscopy by Spatial Spectral Interferometry, *J Phys Chem Lett***, 2015**, 6, 945-950
- B. Spokoyny, C. J. Koh, and E. Harel, Stable and high-power few cycle supercontinuum for 2D ultrabroadband electronic spectroscopy, Opt Lett, **2015**, 40 (6), 1014-1017
- A. P. Spencer, B. Spokoyny, S. Ray, F. Sarvari, and E. Harel, Mapping Multidimensional Electronic Structure and Ultrafast Dynamics with Single Element Detection and Compressive Sensing, *Nature Comm.***, 2015**, in press

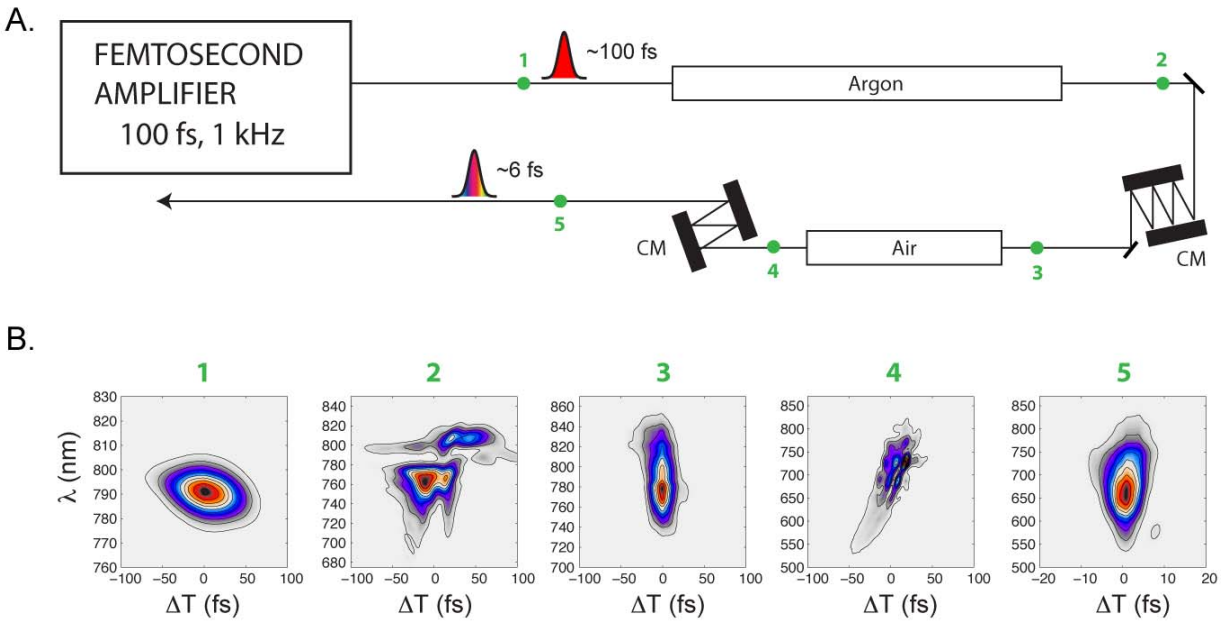


Figure 1. Supercontinuum generation. A. Output of an amplifier (100 fs, 1 kHz) is focused into a pressured cell of Ar gas to generate broadband light through filamentation. The broadened light is compressed using chirped mirrors (CM) and re-focused into air for further spectral broadening. After compression by CM, the output pulse is sub-6 fs in duration. B. Transient-grating frequency-resolved optical gating (TG-FROG) scans, which show the relationship between the spectral and temporal properties of the pulses at different points in A. The initial pulse (1) is ~100 fs and spans 775-805 nm, while the final output is sub-6 fs covering 500-850 nm.

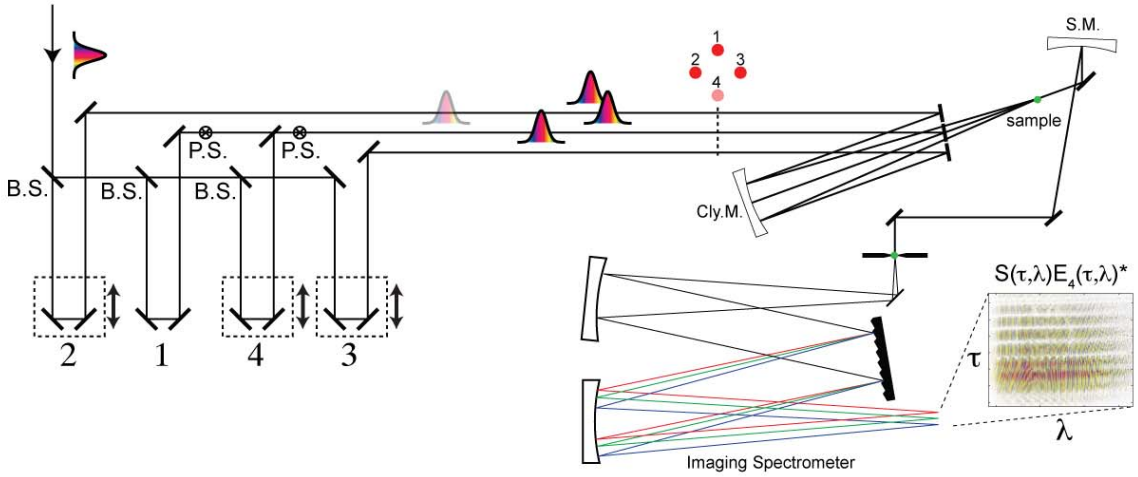


Figure 2. GRAPES instrument. Continuum pulse (Fig 1) is split into three pulses of near-equal intensity and one pulse of ~100 times lower intensity. All pulses are focused using a cylindrical mirror into the sample and the emitted signal is reimaged onto the slit of a high-resolution imaging spectrometer. The signal is detected on a fast frame-rate CMOS detector.

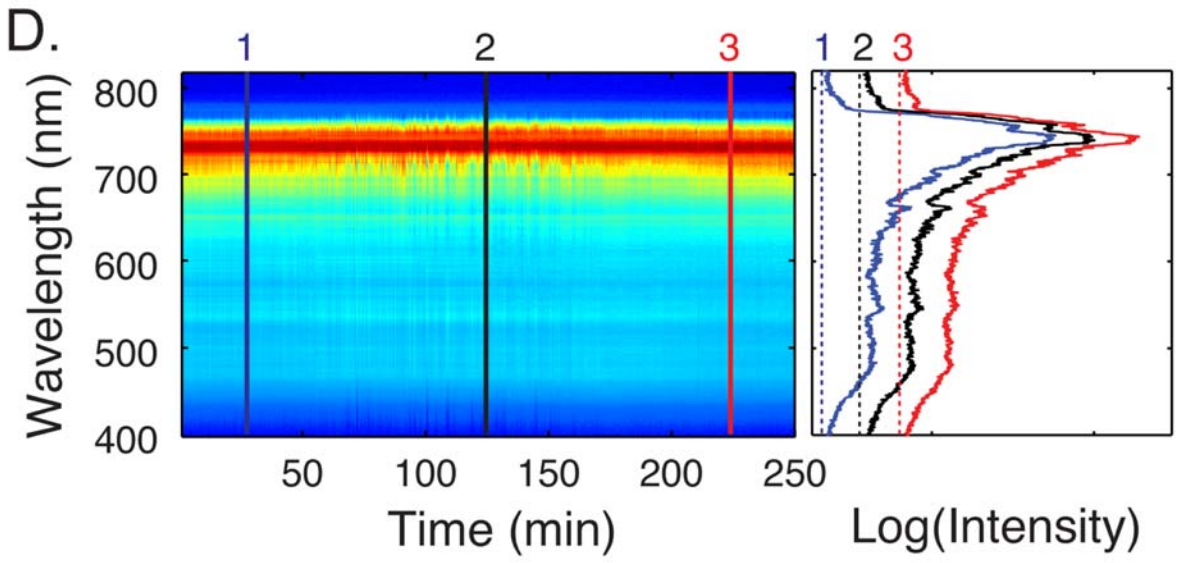


Figure 3. Stability of the supercontinuum spectrum in time. 3- 5% power fluctuations at each wavelength.

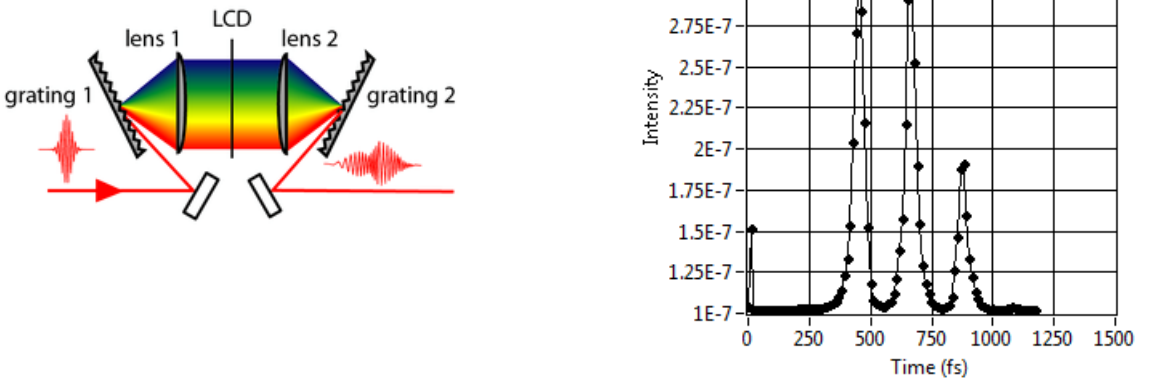


Figure 4. **Left:** 4f Pulse shaping scheme. **Right:** Experimentally measured auto-correlation scan showing the effects of applying third-order phase modulation to a transform-limited pulse.

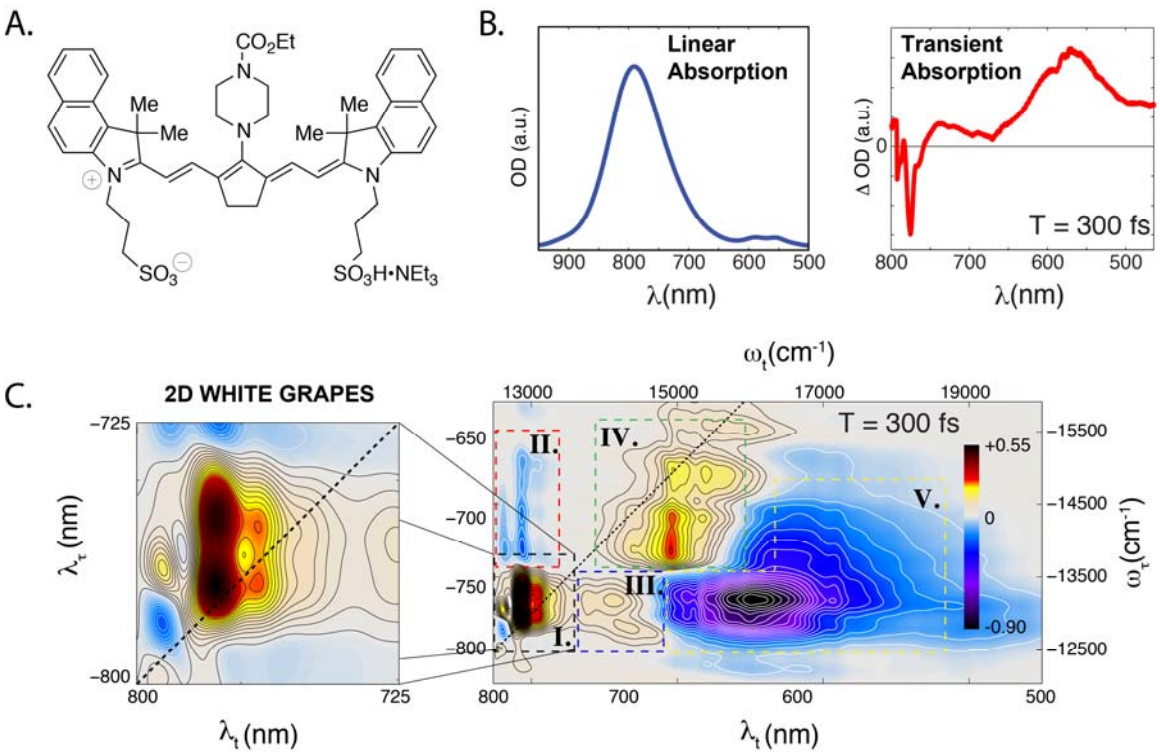


Figure 5. A. Molecular structure of IR-144. B. Linear absorption spectrum and transient absorption spectrum at 300 fs pump-probed delay. C. Real part of 2D WHITE GRAPE spectrum at T = 300 fs waiting time. Zoomed in 2D spectrum in 725-800 nm region. Spokoyny and Harel, *JPC Letters*, **2014**, 5, 2808-2814

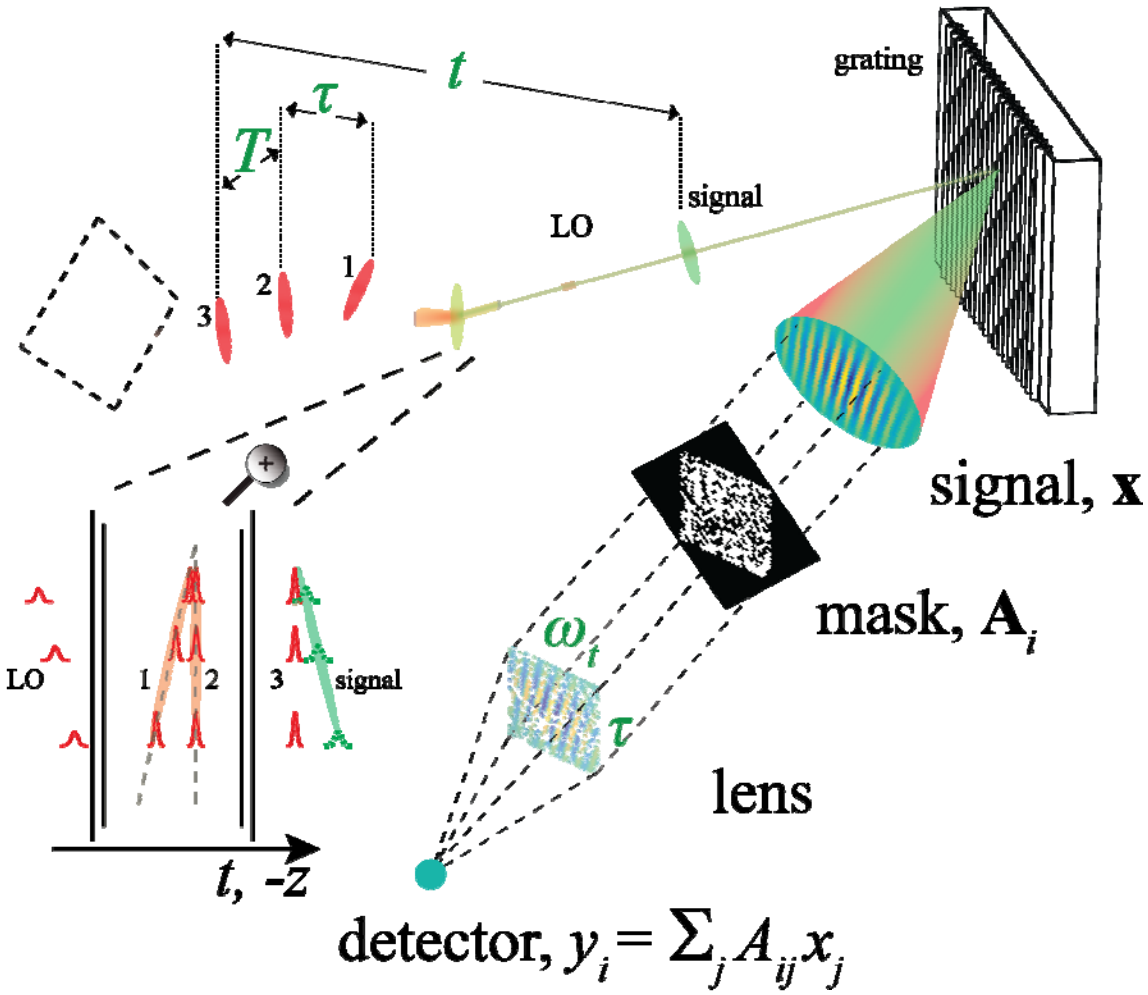


Figure 6. A simplified schematic of single-shot three-pulse photon echo SPARSE spectroscopy. Three pulses (1, 2, and 3) generate a polarization in the sample which subsequently radiates a signal field that spatially interferes with a reference pulse (or local oscillator, LO) at the exit image plane of a spectrometer. The two-dimensional signal–reference interferogram $\mathbf{x}$, which spatially encodes the coherence time τ (inset shows pulse front tilts of each beam at the sample) and detection frequency ω_t, is spatially masked by a DMD (shown as transmissive instead of reflective for simplicity) and then focused by a lens onto a single-element detector. Each mask yields one intensity value on the detector, and by measuring the intensities for a sequence of different masks, the signal–reference interferogram can be retrieved through Hadamard or compressive sensing methods.

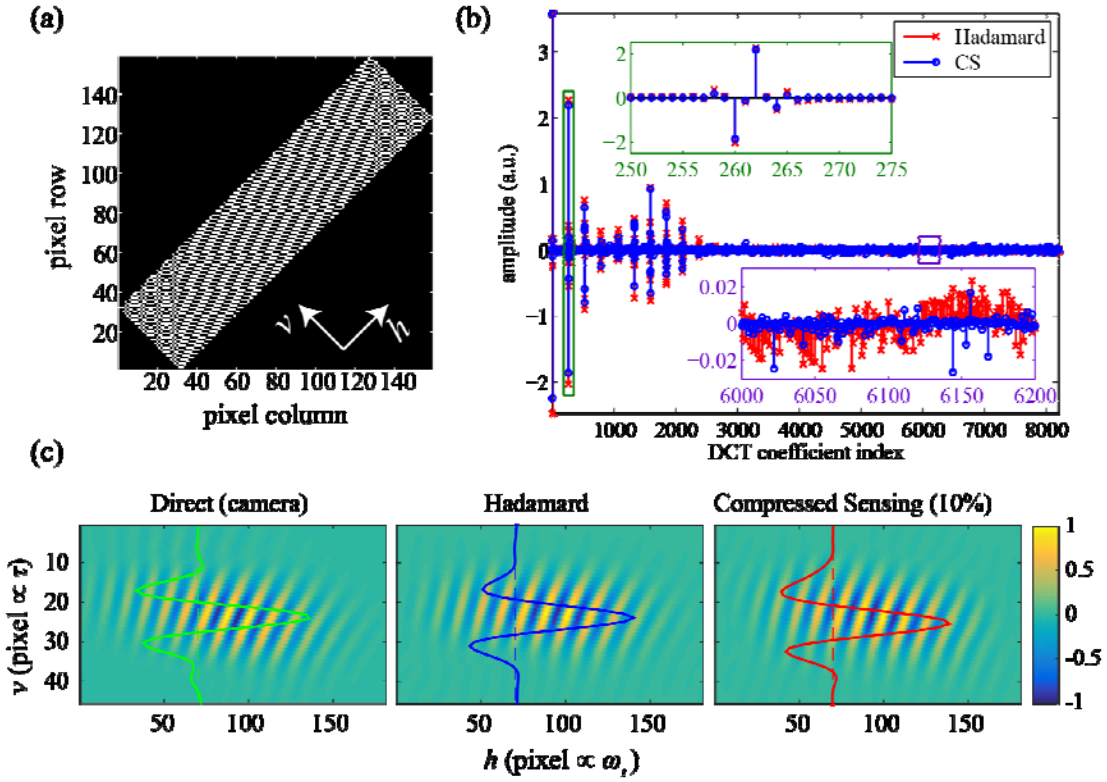


Figure 7. Hadamard encoding and 1D DCT sparsifying transform for the reconstruction of spatial spectral interferograms. (a) A single representative Hadamard spatial mask (without random inversions) tiled into the "active" region (see Methods) as it appears on the DMD. White arrows indicate horizontal (*h*) and vertical (*v*) lab coordinates. (b) Comparison of the 1D DCT of a Hadamard-retrieved flattened interferogram to that recovered by compressive sensing using convex optimization. Insets highlight two regions of the DCT interferogram: one at low spatial frequency (green, upper left) and one at high spatial frequency (purple, lower right). (c) Comparison of direct (camera), Hadamard, and CS (10× sub-Nyquist) detected interferograms after Fourier filtering, 45 degree rotation, and cropping. The *v* axis is proportional to the spatially encoded τ dimension and the *h* axis is proportional to the detection frequencies, ω_τ, in the 2DFT spectrum.

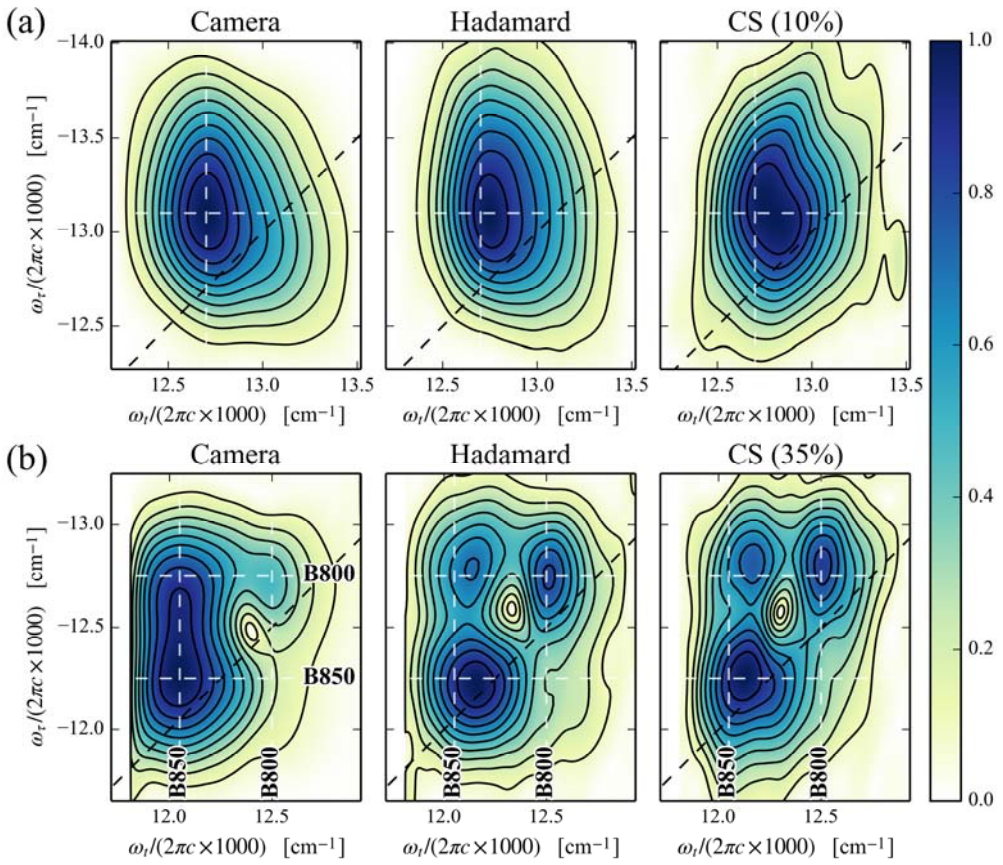


Figure 8. Comparison of 2DFT spectra. Absolute-value 2DFT spectra of (a) IR-144 cyanine dye (T 20 fs) and (b) LH2 (T 1 ps) detected directly by a camera versus SPARSE (DMD and PMT) detection using either the Hadamard transform (8192 spatial masks) or compressed sensing with a subset of the Hadamard-encoded measurements [10% (819 spatial masks) for IR-144 and 35% (2867 spatial masks) for LH2]. Diagonal peaks arise from B800 and B850 bands corresponding to the excitation of ring subunits of bacteriochlorophyll pigments in the protein. The upper cross peak results from energy transfer from B800 to B850 in about 1 ps. Approximate locations of band centers are marked with dashed white lines for comparison between figure panels.

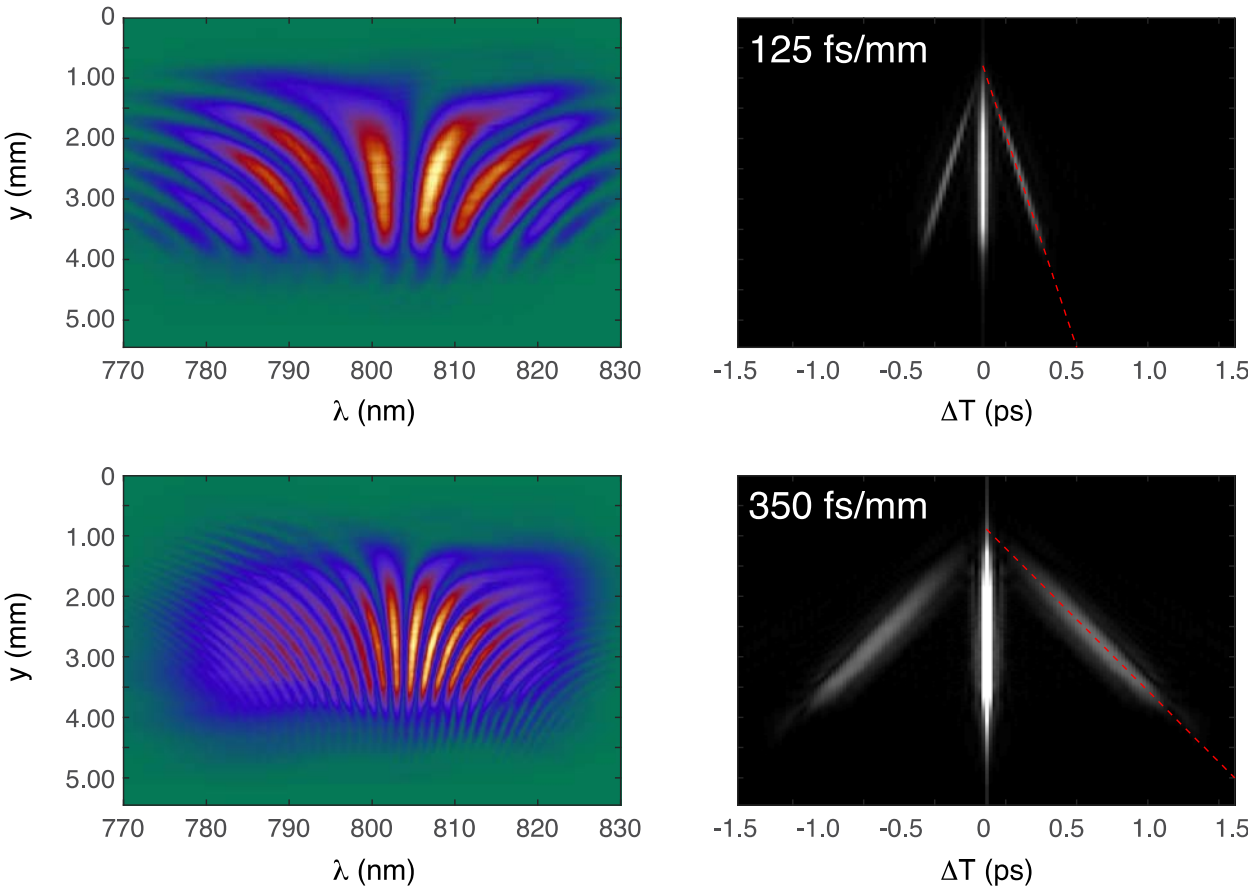
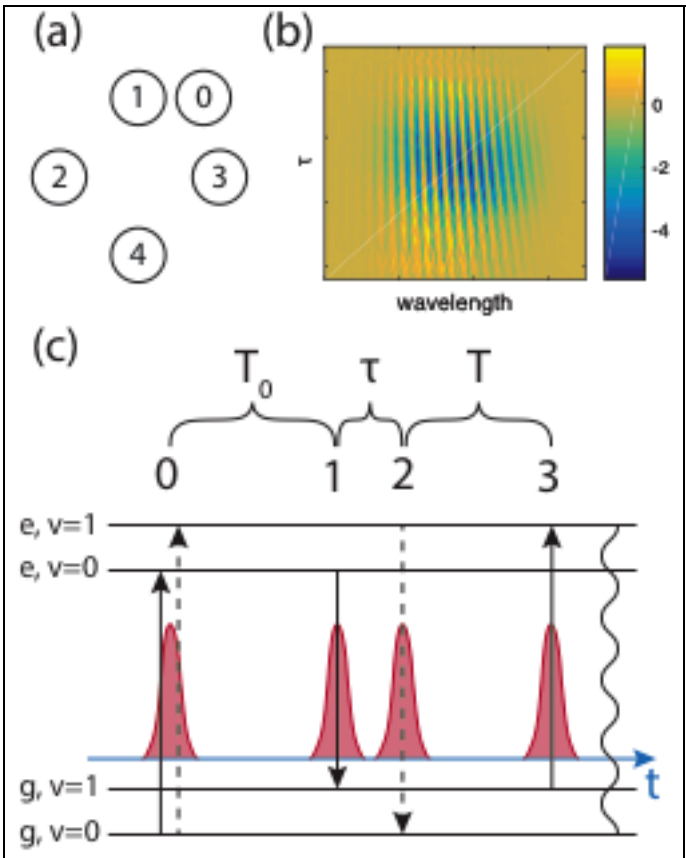


Figure 9. 2D Spatiotemporal pulse shaping. Experimental spatiospecral interferrograms showing two delayed pulses, with interpulse delays dependent on the vertical spatial coordinate. Fourier transform of left images yields the right traces, which show the interpulse delay gradient. Gradients are controlled solely by phase pattern uploaded to 2D spatial light modulator.



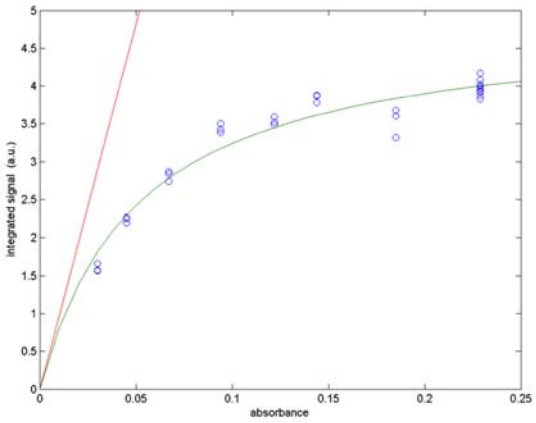


Figure 10. Left: 5th-order 6-wave mixing experiment. (a) pulse geometry, (b) raw 5-th order signal after proper subtraction routines. (c) pulse sequence and coherence pathways. Pulse 0 places the system into either a ground-state of excited-state vibrational coherence. The remaining pulses create an additional vibrational coherence during tau period. The correlation of these two coherences is a direct measure of vibrational relaxation, coupling, and the fate of reactants and products during a chemical reaction. Right. Signal as a function of concentration showing that it is indeed the desired 6-wave mixing and not cascade signal that dominates the response.