

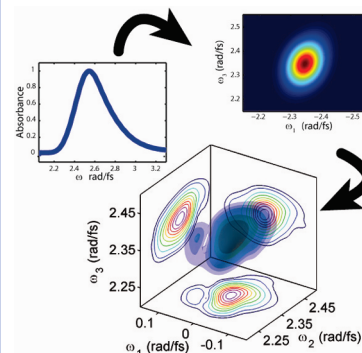
# Dissecting Hidden Couplings Using Fifth-Order Three-Dimensional Electronic Spectroscopy

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**ABSTRACT** We report the demonstration of single-quantum 3D electronic spectroscopy. Utilizing the recently introduced gradient assisted photon echo (GRAPE) methodology, the fifth-order nonlinear polarization of the solvatochromatic dye IR144 corresponding to evolution through three sequential single-quantum coherences is measured. GRAPE, which allows a 2D slice of data to be acquired in parallel, permits a practical implementation of 3D spectroscopy at optical frequencies in a matter of minutes instead of hours. By spreading frequencies into a third spectral dimension, we can resolve features in the spectra that are otherwise obscured. For IR144, a previously unresolved cross peak originating from high frequency vibronic modes is observed in the spectrum. Theoretical modeling based on the cumulant expansion truncated at second order reproduces the main features of the experimental results. This experimental approach will enable further high dimensional spectroscopic experiments.

**SECTION** Kinetics, Spectroscopy



Coherent multidimensional optical spectroscopy resolves spectral features hidden or obscured in lower dimensional spectroscopies to access detailed information about couplings, energy transport,<sup>1</sup> solvation dynamics,<sup>2</sup> and coherent dynamics.<sup>3–5</sup> Analogous to multidimensional NMR, multidimensional optical spectroscopy extracts electronic or vibrational molecular information by separating the polarization response into multiple spectral dimensions. The most common 2D implementation measures correlations among transition energies.<sup>6</sup> Coupled states can then be resolved using cross-peaks in distinct locations on the correlation diagram.

Two-dimensional optical spectroscopy is well-established in the infrared spectral region. Infrared wavelengths relax the technical requirements for phase stability enabling higher-order (with respect to the electric field) correlation experiments, for example, transient 2DIR, which performs 2D infrared spectroscopy of a nonequilibrium ensemble created by an actinic pulse and has been used to watch protein folding dynamics<sup>7</sup> and to probe higher-order correlation functions involved in solvation dynamics.<sup>8</sup> More recently, fifth-order 3D experiments have probed high-lying vibrational states to measure the anharmonicity in several model systems.<sup>9,10</sup> These spectroscopies offer superior spectral resolution by separating peaks that overlap in lower dimensional signals into a third spectral dimension, resolving individual contributions from overtones and combination bands.<sup>9</sup> The information accessed in these experiments cannot be obtained from lower-order measurements.

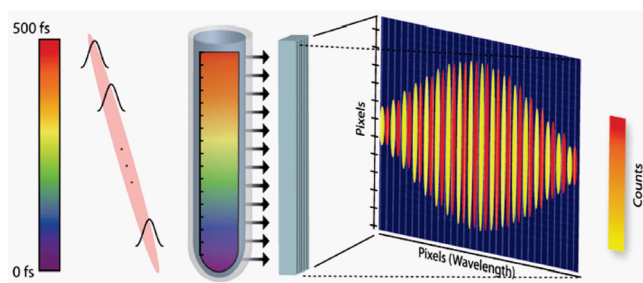
In the visible spectral regime, maintaining the required phase stability among all four pulses presents a challenge for 3D Fourier transform spectroscopies because of the long acquisition time. In 2D spectroscopy, phase stability must be

maintained only within the first and second pairs of pulses, thereby relaxing experimental constraints.<sup>11</sup> Many strategies have been developed to maintain phase stability experimentally for the duration of these experiments. Diffractive optics have been used to create pairs of phase-locked pulses in passively phase-stabilized systems,<sup>11,12</sup> and active phase stabilization strategies using piezoelectric-actuated mirrors and a reference beam to compensate for phase errors have been used.<sup>10</sup> More recently, a diffractive optic in conjunction with a pulse shaper was used to generate four coherent beams maintained for the duration of a 10 h experiment.<sup>13</sup> These point-by-point acquisition strategies increment the time delays among pulses and, for 3D experiments, require many hours of phase stability to collect the data.

We have developed a different approach to optical multidimensional spectroscopy by exploiting an optical analog of magnetic resonance imaging to greatly decrease the acquisition time of the experiment, which we call gradient assisted photon echo (GRAPE).<sup>14</sup> Shown in Figure 1 is a schematic of the GRAPE methodology. By tilting the pulse fronts of each beam relative to one another, we can spatially encode a time delay across a homogeneous sample and spectrally resolve the resulting line of emitted signal onto a 2D CCD array. We note that similar approaches using two pulses have been developed for pulse characterization in single-shot autocorrelators and single-shot frequency resolved optical gating.<sup>15</sup> Similar in spirit, our approach incorporates multiple pulse and heterodyne detection for phase-resolved measurements

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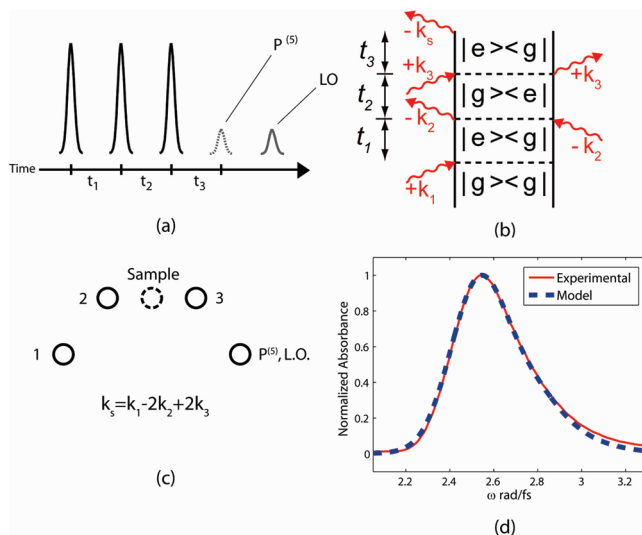


**Figure 1.** GRAPES methodology utilizes tilted pulse fronts to encode spatially a time delay on a homogeneous sample. The second and third pulses, with parallel beam fronts, then interact with the sample, and the signal radiated in the phase-matched direction is spectrally resolved onto a 2D CCD array. The 3D signal is then acquired by stepping the time delay between the second and third pulses.

in the Fourier domain. Other single-shot methods also exist that can provide complementary information on coherence and population dynamics using directional filtering.<sup>16</sup> The GRAPE method differs; it directly provides a means to acquire a fully phase-resolved 2D electronic spectrum in a single acquisition. For this experiment, the GRAPE method enables 2D slices of the signal to be acquired by averaging over a few laser shots. In our apparatus, the acquisition rate is limited by the frame rate of the camera rather than by the signal-to-noise of the data. A 3D experiment therefore requires only 8 min of phase stability to acquire an entire data set instead of roughly 16 h using a point-by-point acquisition scheme.

The optical spectroscopy presented here is directly analogous to 3D infrared methods but in the electronic regime. Following the work of Ding and Zanni,<sup>9</sup> a six-wave mixing experiment is conducted with only four pulses by exploiting multiple interactions with the pump beams. The first matter-field interaction promotes the system into a coherent superposition between the ground and excited states, which evolves for a time  $t_1$ . The second pulse directly converts the system to the conjugate superposition by interacting twice with the sample, which again evolves for a time  $t_2$ . The final pulse converts the system back to a third coherence, which radiates the fifth-order polarization in the phase-matched direction. Heterodyne-detection is used to measure the magnitude and phase of the emitted signal. Fourier transforming over the time delays results in a 3D spectrum that correlates the observed dipole oscillations during the three time delays. This process is succinctly represented by the double-sided Feynman diagram shown in Figure 2 for a two-state system. We note that Nelson and coworkers have developed a third-order 3D electronic spectroscopy, that correlates two one-quantum coherences with a double-quantum coherence to probe electron correlation in GSAs quantum wells.<sup>15</sup> Our spectroscopy involves only one-quantum coherences and is designed to observe couplings that are not evident in lower dimensional spectra.

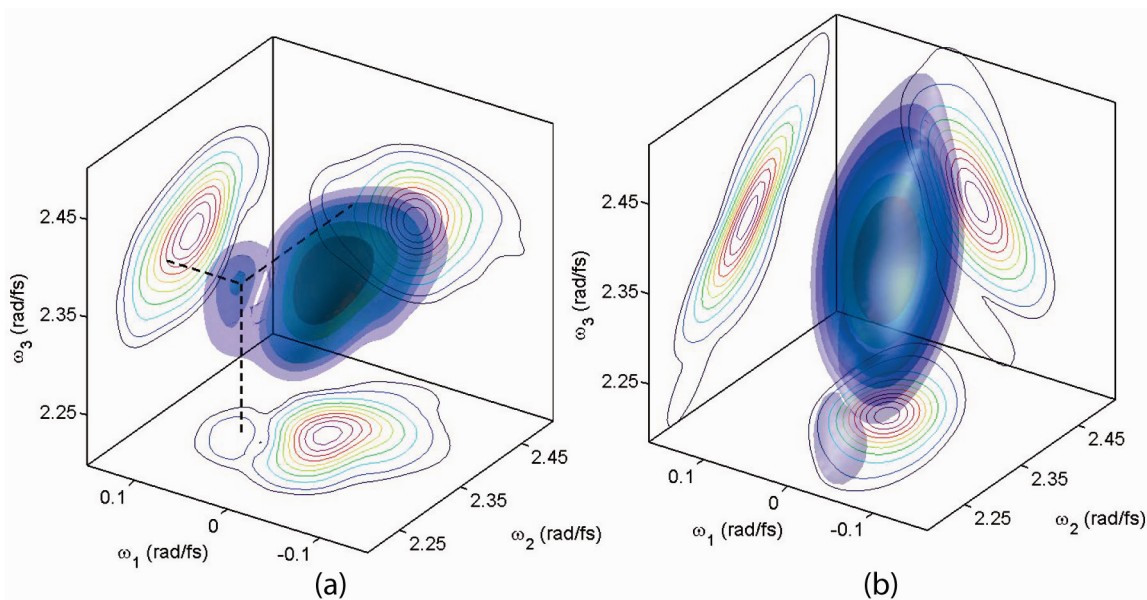
Experiments were conducted on the solvatochromic dye IR144 dissolved in methanol. The absorption spectrum of IR144 is shown in Figure 2. The broad tail on the blue side of the absorption spectrum results from coupling to high frequency intramolecular vibrational modes. The polar side



**Figure 2.** (a) Experimental pulse sequence used to detect the fifth-order polarization in the phase-matched direction  $k_s = k_1 - 2k_2 + 2k_3$ . (b) Double-sided Feynman diagram for a two-state system for the experimental pulse sequence, where the intermediate populations have been ignored. (c) Phase matching geometry and (d) absorbance spectra of the model system IR144 in methanol along with the model calculation of the absorbance spectra overlaid.

chains of IR144 make it a particularly sensitive probe of solvation dynamics. This system has been heavily studied with many third-order spectroscopies, including transient grating,<sup>17</sup> transient absorption,<sup>17</sup> photon echo peak shift,<sup>18</sup> and 2D spectroscopy.<sup>19</sup> These studies have yielded a rich understanding of the vibronic structure and spectral density of the solvent, making this sample ideal for developing a new approach to dissect nonlinear polarization responses.

Shown in Figure 3 are isosurfaces of the absolute value of the data. Phase-resolved data is necessary to enable the Fourier transform along the indirect dimensions, even though the absolute value of the fifth-order spectrum is presented here. Absolute phasing of the fifth-order signal to separate absorptive and refractive components of the spectra will be addressed in future publications. This signal falls mainly on the diagonal, which indicates a strong autocorrelation. The slight displacement of the maximum from the diagonal results from a dynamic Stokes shift. A vibronic cross-peak located below the diagonal at  $\sim 20\%$  of the maximum signal strength is fully resolved. This spectral feature, which was unresolved in lower dimensional spectra, indicates weak coupling of the electronic transition to high-frequency vibrational modes.<sup>20</sup> The cross peak arises when the system is in a vibrationally excited state during the first and second coherence times. Elongation of the signal along the diagonal indicates inhomogeneous broadening, signifying that the absorption and emission events are strongly correlated through all three coherence periods. Just as 2D spectroscopy is intimately related to pump probe through the projection slice theorem, a projection of a 3D spectrum along the  $\omega_2$  axis yields a zero population time fifth-order 2D spectrum correlating absorption and emission events.<sup>21</sup> We note that the vibrational cross peak is lost when integrating over the new dimension, appearing as a shoulder in the fifth-order 2D spectrum.

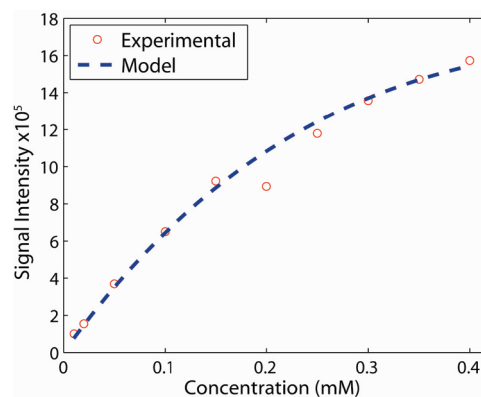


**Figure 3.** (a) Experimental and (b) simulated isosurfaces of the absolute value of the data. A vibronic cross-peak is resolved at 0.07, 2.32, and 2.35 rad/fs. Isosurfaces are shown at 10, 15, 20, 40, and 60% of the maximum of the absolute value of the signal. The model figure has an additional isosurfaces at 7%. Contour lines are drawn at 8, 13, and then in 10% increments of the maximum value of each projection. The  $\omega_1$  axis is detected in the rotating frame.<sup>14</sup>

Numerical simulations conducted based on Mukamel's response function formalism<sup>22</sup> recreate this vibronic feature. The energy gap correlation includes contributions from intramolecular vibrational modes taken from resonance Raman studies<sup>18</sup> as well as solvent contributions<sup>17</sup> and successfully reproduces the linear absorption spectrum. We use the energy gap correlation function, along with the transition frequency, to calculate the fifth-order response function via the cumulant expansion truncated at second order.<sup>22,25</sup> Whereas fifth-order spectroscopies are generally sensitive to three-point frequency correlation function,<sup>21</sup> the second-order cumulant expansion will be exact for systems displaying Gaussian statistics. We note that effects from anharmonic oscillators and higher-order correlations within the bath are not captured within this model. Inertial solvent dynamics are modeled as a Gaussian with a 160 fs time constant and coupling strength of 350  $\text{cm}^{-1}$ . Diffusive solvent modes are treated as two exponentials with time constants 1400 fs and 11 ps with coupling strengths of 290 and 280  $\text{cm}^{-1}$ , respectively. Previous resonance Raman studies are used for the intramolecular vibrational modes and coupling.<sup>18</sup> We adjust the coupling strengths of the two highest modes to be 210 and 195  $\text{cm}^{-1}$ . The vibronic contribution is altered to account for vibrational dephasing via the introduction of a phenomenological damping constant.<sup>24,25</sup> The fifth-order polarization is then calculated with eq 1, in which we have assumed no population evolution within the pulse.

$$p^{(5)}(t_1, t_2, t_3) = \int_0^\infty \int_0^\infty \int_0^\infty R^{(5)}(\tau_1, \tau_2, \tau_3) E(t_3 + t_2 + t_1 - \tau_1 - \tau_2 - \tau_3) E(t_3 + t_2 - \tau_2 - \tau_3)^2 E(t_3 - \tau_3)^2 \quad (1)$$

Shown in Figure 4 are isosurfaces of the absolute value of the model calculations. The vibronic cross-peak appearing in



**Figure 4.** Integrated signal strength versus concentration. Agreement between the measured signal and theory indicates that cascades do not contribute significantly to the signal. The two-parameter model takes into account the reabsorption of the signal as it propagates through the sample cell.

the signal is reproduced in the model, but the spectral location differs. We find that a single vibrational mode is required to produce the cross peak in our model. Physically, the cross peak arises when pathways involving three distinct coherence frequencies are observed, corresponding to an electronic state coupled to at least one vibrational state. Cross peaks corresponding to lower vibrational states are most likely present as well but are not separated sufficiently from the diagonal to be resolved. We attribute the disagreement between simulation and experiment to not having included the proper vibrational modes or having improper relative coupling strengths. We are working to calculate accurate coupling elements to improve the agreement between simulation and experiment. Future publications will address this issue.

With any higher-order experiment the possibility of competing cascades of lower-order processes must be addressed. In fifth-order experiments, cascades occur when a third-order polarization response acts as a pump for a second third-order polarization response, which is radiated in the same phase matched direction as the desired fifth-order signal. In some instances, these pathways can compete effectively with the signal such as in early fifth-order Raman experiments of neat liquids.<sup>26</sup> Several strategies have been developed for dealing with lower order cascades. Cascades appear in the same phase matched direction as the desired signal, but the relative magnitude of the process is controlled by the phase matching geometry<sup>26</sup> and optical density of the sample.<sup>27</sup> The cascade pathway requires interactions with two different chromophores; therefore, minimizing the optical density of the sample reduces the contributions from unwanted cascades. The concentration dependence also provides a definitive test for the relative contribution of lower-order cascades because cascades increase quadratically with sample concentration, whereas the desired fifth-order signal is linearly dependent on the concentration for a fixed path length. Our signal intensity as a function of concentration (Figure 4) definitively shows that cascades do not contribute significantly to the measured signal. Reabsorption of the nonlinear signal as it propagates through the sample causes the deviation from linearity at high concentrations. The plotted theoretical fit to the data<sup>19</sup> includes absorptive effects and provides a good agreement between the measurement and model. Whereas the cascades will be 180° out of phase with the fifth-order signal and thus destructively interfere with the signal, a simple calculation<sup>27</sup> shows that cascades will contribute <3% to the signal at the highest optical density of 0.3. We conclude that as in the case of resonant fifth-order IR experiments, in the limit of low optical densities, higher-order resonant polarizations in the electronic regime will not be significantly contaminated by lower-order cascades.<sup>10,27</sup>

Multidimensional optical spectroscopy provides a useful method for peering underneath featureless absorbance spectra to extract detailed dynamical and coupling information. This work shows that higher-order experiments can further increase spectral resolution by separating peaks that overlap in lower-order multidimensional spectra. Application of this technique to more complicated multichromophoric systems should reveal couplings between electronic states. For example, in photosynthetic light-harvesting complexes, high symmetry leads to many degenerate and near-degenerate states. This technique will improve resolution and permit detailed interrogation of patterns within the static and dynamic disorder. Combining imaging techniques with spectroscopic methods enables a practical implementation of more sophisticated experiments by greatly reducing the acquisition time. Extension of this method by the addition of two more pulses would allow for nonzero population times and extraction of kinetic data. This data will permit interrogation of pathway-specific energy transfer mechanisms.

**SUPPORTING INFORMATION AVAILABLE** Experimental details and model. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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