

Ultrafast Four-Dimensional Coherent Spectroscopy by Projection Reconstruction

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S Supporting Information

ABSTRACT: Multidimensional coherent spectroscopy provides insights into the vibronic structure and dynamics of complex systems. In general, the higher the dimensionality, the better the spectral discrimination and the more information that may be extracted about the system. A major impediment to widespread implementation of these methods, however, is that the acquisition time generally increases exponentially with dimensionality, prohibiting practical implementation. We demonstrate the use of nonuniform sampling based on the projection-slice theorem and inverse Radon transform within the context of a fifth-order, 4D technique (GAMERS) designed to correlate the vibrational contributions to different electronic states. Projection-reconstruction (PRO GAMERS) greatly reduces the data sampling requirements without sacrificing frequency resolution. The sensitivity of this technique is demonstrated to surpass conventional uniform sampling by orders



of magnitude. The incorporation of projection-reconstruction into multidimensional coherent spectroscopy opens up the possibility to study the structure of complex chemical, biological, and physical systems with unprecedented detail.

N onlinear optical spectroscopy has proven to be a powerful method to study the fundamental physics underlying a wide variety of complex chemical, biological, and materials systems.¹⁻⁴ Particular experimental and theoretical interest has been given to determining the physical significance of electronic and vibronic coherence to energy transfer, electron transfer, and conical intersections, just to name a few, in a variety of biological and synthetic molecular systems.⁵⁻⁷ Experimentally, assigning the origin of coherent optical signatures using pump-probe spectroscopic methods, where the third-order signal, $\chi^{(3)}$, is resolved over only one energy dimension can prove difficult because of significant spectral congestion.⁸ Therefore, the use of multidimensional coherent spectroscopy (MD-CS) methods has proliferated to investigate coherent optical signatures, techniques that spread the optical response across multiple correlated frequency dimensions.⁹ For instance, two-dimensional Fourier transform (2DFT) spectroscopy has been utilized to elucidate the electronic coupling between the constituents of dimers,^{13,14} mechanisms that underlie singlet-fission in TIPS-pentacene,¹⁵ and the nature of protein-protein binding in an insulin dimer.¹⁶ Technical improvements over the past two decades have dramatically increased the sensitivity and versatility of these methods by incorporating improved phase stability,¹⁷ balanced detec-tion,^{18,19} and pulse-shaping capabilities,²⁰ while utilizing improved light sources that span broad regions of the spectrum.²⁰⁻²³ However, despite the gains garnered from spreading the optical response over multiple dimensions and across expanded spectral regions, the lab time required to execute these experiments increases exponentially with the number of spectral dimensions. Therefore, despite the gains in resolution and information about the physical system under study, one of the major drawbacks of multidimensional spectroscopic techniques lies in the time required for sampling

these additional spectral dimensions, especially in the face of decreased signal strength. To overcome this limitation, inspiration may be taken from the field of nuclear magnetic resonance (NMR) spectroscopy, wherein techniques have been developed to greatly reduce the overall acquisition time without sacrificing signal strength or resolution.^{24,25} We report the adaptation of one such method to a fifth-order MD-CS technique, utilizing projection-reconstruction (PR) to reconstruct a 4D spectrum from radial slices of the fifth-order signal in time. We discuss the advantages of using PR for highdimensional coherent experiments, specifically, and the general advantages for any MD-CS method that requires scanning a space of correlated variables.

Recently, we developed a fifth-order coherent optical spectroscopy, gradient-assisted multidimensional electronic-Raman spectroscopy, or GAMERS, to resolve the origin of a coherence signatures between the ground and excited electronic states as well as to correlate electronic and vibrational degrees of freedom.^{26,27} The GAMERS sequence is shown in Figure 1A. In brief, GAMERS extends the dimensionality of 2D FT spectroscopy, which records the third-order signal, $\hat{S}^{(3)}$ $(\omega_{\tau}T,\omega_{\tau})$, by introducing two additional, temporally overlapped pulses (0 and 0'). These pulses are judiciously chosen to be preresonant with the absorption spectrum of the sample and appear prior to the traditional 4WM pulse sequence (i.e., before the time period τ between pulses 1 and 2). Experimentally, the GAMERS method is built upon a variant of traditional pointby-point 2D FT spectroscopy in which the signal is collected by spatially multiplexing τ_t directly detecting ω_t and scanning over

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Figure 1. (A) GAMERS pulse sequence showing resonant (blue) and nonresonant (red) pulses along with schematic of absorption spectrum. One of many possible coherence pathways is shown. (B) Simplified optical layout showing the generation of five pulses (0, 0', 1, 2, 3) used to generate the fifth-order signal, which interferes with a local oscillator (LO) after passing through an imaging spectrometer. Insets show phase-matching geometry and pulse front tilts at sample. BS = beam splitter, M = mirror, SM = spherical mirror, GM = GRAPES mirror assembly, CM = cylindrical mirror. Insets show beam geometry and phase fronts.

T. This spatial multiplexing scheme, known as gradient-assisted photon echo spectroscopy (GRAPES), relies on tilting the pulse fronts of the pulses so that each part of the sample experiences a different interpulse time delay.^{23,28–35} In GAMERS, the fifth-order signal, $\hat{S}^{(5)}$ ($\omega_{T_d} \omega_v \omega_T \omega_\tau$), is sampled in the same manner as GRAPES, but with the addition of a new time delay, T_0 , between the preresonant pulses. Figure 1B shows a simplified optical layout of the GAMERS apparatus, emphasizing the experimental control of the T and T_0 delay, and the generation of pulses 0 and 0' via a Sagnac interferometer. Details of the experimental and theoretical aspects of the GAMERS method can be found in previous work^{26,36} (also see the Supporting Information for additional details).

The 4D spectrum, $\hat{S}^{(5)}$ ($\omega_{T_0}\omega_{\nu}\omega_{T_0}\omega_t$), may be viewed in multiple ways in terms of lower dimensionality slices. For this work, one instructive way to view the data is as a 2D Ramanlike spectrum with respect to ($\omega_{T_0}\omega_T$) for each point in the 2D electronic spectrum ($\omega_{\nu}\omega_t$). The reason for this viewpoint will become apparent when we discuss the projection method. For a T_0 delay sampled at k points, the GAMERS signal requires k times the amount of time necessary to collect one entire 3D GRAPES data set. While the inherent multiplexing of GRAPES makes the extension to GAMERS feasible, the additional temporal scanning greatly limits the applicability of this method to very short scanning ranges (limiting the spectral resolution along T_0) and T and limited averaging (due to finite sample volume, accumulated photodamage, etc.). For instance, previous demonstrations of GAMERS were limited to a scanning range of ~ 1 ps along both T and T_{0} , which is significantly shorter than typical vibrational dephasing times of molecules in solution. Increasing the range by even a factor of three along each dimension would therefore require nearly an order of magnitude longer scan time, while, in practice, the scan time would likely extend by nearly two orders of magnitude or more because of noise introduced nonlinearly along the indirect dimensions (i.e., the slow scanning dimension). Therefore, extending the dimensionality of coherent spectroscopic methods necessarily creates an imperative for developing methods of fast data collection. Within this context, a possible avenue to decrease the experimental time relative to sampling uniformly on a rectangular grid is to judiciously choose the sampling schedule to take advantage of the signal's structure. Specifically, we borrow a powerful method routinely used in high-dimensional NMR experiments³⁷ that is based on PR, a type of nonuniform sampling (NUS) that takes advantage of the sparsity of the multidimensional (nD) NMR spectrum.³⁸

Conventionally, an *n*D NMR experiment requires uniform sampling (US) in the time domain according to the Nyquist criteria along *n* dimensions, each with *k* data points, resulting in a k^n -sized grid;³⁹ as *n* increases, the number of data points increases exponentially. However, the number of peaks in the spectrum generally remains nearly constant, resulting in an increasingly sparse spectrum within the total spectral volume.

PR-NMR (or other NUS NMR methods) capitalizes on this sparsity by sampling multiple dimensions in temporal space simultaneously, or, rather, taking a "slice" through multiple dimensions. As illustrated in Figure 2, for the case of two



Figure 2. (A) Conventional uniform scanning (US) on a Cartesian grid. (B) Projection reconstruction (PR) sampling on a polar grid. Insets shows 2D Fourier transform of each sampling pattern, which is equivalent to the point-spread function (PSF).

dimensions, each slice lies on a polar grid so that for each angle θ a slice corresponds to uniformly sampling along the radial direction, |r|. This slice, which is now along a coupled temporal dimension, $T_s \equiv [\cos(\theta)T + \sin(\theta)T_0]$, is then Fourier transformed, relating the slices in time to projections in frequency space by the projection-slice theorem. To reconstruct the spectrum, the signal is subjected to an inverse Radon transform that backprojects the signal by dispersing it in frequency space orthogonal to the slice direction. In regions where a true signal peak is present, back projection builds up amplitude and creates spectral features distinct from the background. In the limit of an infinite number of projections, the result is formally identical to linear sampling along each temporal domain and performing a Fourier transform (i.e., this just corresponds to a polar transformation of the Fourier integrals). When the number of projections is limited, the result is equivalent to the uniformly sampled Fourier transform convolved with the point-spread function (PSF) of the sampling method, which, in this case, appears as a spoke pattern (see insets of Figure 2). Although PR is widely used in nD NMR, prior to this work we were not aware of the utilization of this class of techniques to any coherent optical spectroscopy method. It is important to note that one reason that PR is an ideal method to combine with GAMERS is that the 2D Raman-like spectrum is sparse so that only a relatively small number of projections is needed for accurate reproduction of the full spectrum.

We demonstrate the use of PRO GAMERS on the molecular dye molecule Nile Blue A perchlorate (NB). This dye was chosen because, according to its Raman spectrum,⁴⁰ it exhibits a strong mode at 585 cm⁻¹, which lies within the bandwidth of both the resonant and preresonant pulses, making this beating signature's strength a prime candidate for comparing PR and US. The resonant pulses of GAMERS, generated from the output of a tunable third-harmonic noncollinear optical parametric amplifier (3H-NOPA) and pumped by an Yb laser amplifier, are sent into a passively phase-stabilized, four-arm interferometer, producing pulses 1, 2, 3, and LO (local oscillator). The preresonant pulses originate from a tunable second-harmonic NOPA (2H-NOPA), pumped by the same Yb laser system, from which are split two coincident, noncollinear pulses, 0 and 0', using a Sagnac interferometer. To finely control the timing between the pulse pair, pulse 0' passes through a set of beam wedges, where one beam wedge is affixed to a motorized delay stage, while beam 0 passes through a piece of compensating glass. The NOPA outputs are routed into the GAMERS setup such that the temporal delays between pulses 0/0' and pulse 1 (T₀) and pulses 2 and 3 (T) are precisely controlled on independent delay stages. Pulses 1-3 are arranged in a BOXCARS geometry on a cylindrical mirror, with pulses 0 and 0' arranged horizontally equidistant on either side of pulse 1, resulting in pulses 1, 0, and 0' having the same relative wavefront tilt at the sample (see Figure 1B). Pulse LO is arranged such that it overlaps with the emitted GAMERS signal. The pulses interact with the sample at the focus, and the fifth-order signal, $\hat{S}^{(5)}(\omega_{v}T,\omega_{v}T_{0})$, is emitted in the phasematched, background free direction, $\hat{k}_{6WM} = \hat{k}_{0'}(-\omega_0) + \hat{k}_{0'}(\omega_{0'})$ + $\hat{k}_1(-\omega_1)$ + \hat{k}_2 + $\hat{k}_3(\omega_3)$. The signal and LO are reimaged from the sample cuvette to the slit of a spectrograph and detected with an sCMOS camera.

The GAMERS signal is collected using a rapid scan and quasi-phase cycling technique. For US, T is rapid scanned over equally spaced time steps of 15 fs from 0 fs to 3 ps in the forward and reverse directions, while T_0 is stepped in between rapid scans over equally spaced time steps of 15 fs from 0 fs to 3 ps. Quasi-phase cycling is achieved by finely adjusting the 0' delay and rapid scanning along T for a given T_0 delay. The entire (T, T_0) grid is averaged 16 times. For radial sampling, the T_0 delay is "slaved" to the T delay, and both delays are rapid scanned over predefined time steps in the (T, T_0) plane determined by θ and |r|, that is, along T_s (see Figure 2). T_s is sampled in equal time steps of 15 fs from 0 fs to 3 ps for 32 equally spaced θ angles from 0.048 to 1.523 radians. The 32 T_s slices are sampled 100 times such that the total exposure time of the US Raster and PR scans is equivalent.

A 2D electronic spectrum may be generated at any point in the T/T_0 plane or by projecting along on or more of these axes. As shown in Figure 3A, the absolute value spectrum, shown



Figure 3. (A) Absolute value fifth-order 2D electronic spectrum projected along *T* and T_0 (only PR scan shown). (B–D) Scans along T_s at different slice angles in T/T_0 plane corresponding to points marked with "×" overlaid on 2D electronic spectrum in panel A.



Figure 4. 2D Raman-like spectrum at $\omega_t = 1.67 \times 10^4$ and -1.59×10^4 cm⁻¹. (A) Results of US with 192 indirect samplings of T₀. (B–D) Results of inverse Radon transform after $N_s = 8$, 16, and 32 slices. Horizontal and diagonal cuts shown for US and $N_s = 32$ slices. Right: Coherence pathways corresponding to diagonal ($\omega_{T_0} = \omega_{T_0}$ red)l and horizontal ($\omega_{T_0} = 0$, green) signals at location marked by an "×" in 2D electronic spectrum.

here as a projection along both T and T_{0} , is rather featureless, except for a pronounced Stokes shift along the emission axis (see the SI for details of the absolute accuracy of ω_{τ}). At each point along ω_{τ}/ω_{v} we may analyze the signal as a function of T, T_{0} , or T_{s} depending on the type of scan performed. Shown in Figure 3B–D are select polar scans at different angles in the T/T_{0} plane and at different points in the ω_{τ}/ω_{t} plane, as indicated by the colored "×" superimposed on the projected 2D electronic spectrum.

In general, the time dependence of the signal has contributions from both population and coherence dynamics, manifested by a low-frequency decay or growth superimposed on top of a high-frequency oscillatory beating signal. For points above the diagonal (Figure 3B,C), where uphill energy transfer is suppressed at room temperature, the oscillatory signal is typically easier to observe. Below the diagonal (Figure 3D), population dynamics typically dominate and the coherence signal may be fully or partially obscured. Notice that at different slice angles the frequency of the beating signal changes. This is simply a reflection of the fact that the 2D beating pattern in the T/T_0 plane is being "cut" at different angles, thereby showing different apparent frequencies. Another point of view is to consider the projection along heta in the $\omega_{
m T}/\omega_{T_0}$ plane, where the observed frequency is given by $\omega_{T_c} \equiv [\cos(\theta)\omega_T + \sin(\theta)\omega_{T_0}]$. Depending on the angle and combination of frequencies in the 2D Raman-like spectrum, the beating pattern projected on T_s may appear at higher or lower than the natural vibrational frequency. Note that while the apparent lifetime of the beating signal appears to change, in reality this is just a manifestation of the mixing of coherences and populations that occur at different polar angles. Because of the preresonant nature of the first pulse pair in GAMERS, population dynamics dominate along T so that projections close to the ω_T axis are heavily weighted by exponential-like dynamics in comparison with projections aligned with ω_{T_0} (see Figure 3B, for instance, comparing slices at small and large angles).

To isolate the coherences during T and T_{0} , it is critical to eliminate the low-frequency population dynamics from the signal. Otherwise, both PR and US methods yield 2D Ramanlike spectra dominated by zero-frequency components. In US, low-frequency noise has two sources: The first comes from the fact that one of the dimensions must be chosen (arbitrarily) to perform a 1D fit to the slowly decaying background (2D fits to the background are not well conditioned). This means that along the orthogonal direction, uncertainties in the fits are manifested as noise in the Fourier domain. The second noise source arises from the slow-scanning dimension (T_0) in this case), which is dominated by the noise spectrum at low frequency. The fast-scanning dimension (T, in this case) is mostly affected by the high-frequency component of the noise. Because most standard laboratory noise sources are relatively low frequency (e.g., < 1 kHz for 1/f noise), the slow-scanning dimension suffers. The end result is that the two orthogonal dimensions T and T_0 differ in their noise characteristics, as shown in Figure 4A, where the 2D Raman-like spectrum for US exhibits considerable noise along the ω_{T_0} dimension, especially near $\omega_T = 0$. In PR, the situation is different because the two dimensions are coupled during the acquisition, which proceeds along the slice dimension. In addition, the background subtraction is treated on a more equal footing when performing PR, and no Fourier transform occurs along the indirect dimension. This turns out to be a major advantage of PR beyond the reduction in indirect sampling points compared with US.

We process the raw PR data by first using a simple multiexponential fitting to subtract the slowly varying background at each slice angle, leaving just the coherence contributions to the signal. After Fourier transformation, the signal, $|S(\theta, \omega_{T_i})|$ is subjected to an inverse Radon transformation at each point along ω_{τ} and ω_{t} . The inverse Radon transform proceeds by two steps, interpolation and filtering, prior to backprojection. The interpolation step is needed so that the output of the reconstruction corresponds to the desired rectangular grid, while the filtering step is needed to remove high-frequency noise. Here a linear interpolation algorithm is used, while the window is set to a cosine function (other filters such as Hann and Hamming gave similar results). In Figure 4B-D, we compare PR for different numbers of projection angles ranging from $N_s = 8$ to the full 32 slices. As the number of slices increases, the accuracy of the reconstruction improves. With only eight slices, the position of the peaks in the ω_T/ω_T plane cannot be unambigiously assigned. Each true peak appears streaked across the 2D spectral plane, with more pronounced effects arising when the peaks are particularly narrow. As the number of slices increases, the true signal peaks are revealed, a consequence of amplitude building up as the projections overlap. By 32 slices, the spectrum appears wellresolved, and compared with full US, the signal-to-noise ratio (SNR) is dramatically improved. With this increased sensitivity, features such as the cross-peak patterns in the low-frequency (sub 50 cm⁻¹) region of the 2D Raman-like spectrum are resolved, while other more salient features such as the diagonal peak at (595 cm⁻¹, 595 cm⁻¹) or cross peaks near (0, 595 cm⁻¹) are in good agreement with the strongest features in the US spectra. A diagonal peak at (500 cm⁻¹, 500 cm⁻¹) in agreement with Raman studies⁴⁰ is also seen in PR, a feature absent in the US owing to the increased SNR. Both US and PR shown two nearby peaks at 590 and \sim 570 cm⁻¹, again in good agreement with previous Raman scattering experiments, as well as photon-echo peak-shift measurements.⁴

Each peak identified may be assigned to a specific coherence pathway, as shown in Figure 4. Both the diagonal and horizontal features arise from pathways in which positive frequencies evolve during the T and T_0 periods. Note that negative frequencies may also occur during these periods, but these signals are manifested in different regions of the 2D electronic spectrum. For instance, the diagonal features correspond to two interactions with the nonresonant Raman pulse that places the system into a ground-state coherence. Pulse 1 may then excite the system into any accessible vibronic state on the S₁ potential surface. Pulse 2 brings the system back to the ground-state creating another wave packet that evolves at the same frequency as during the T_0 period. The system interacts with pulse 3 before radiating back to the ground state. Therefore, a diagonal peak in the positive quadrant in the 2D Raman spectrum may arise from many regions of the 2D electronic spectrum depending on which excited states are accessed during the τ and t periods. Finally, note that many false peaks in the US spectra appear, especially along $\omega_T = 0$, and that such features are mostly eliminated in the PR spectra, even when only observing a relatively small number of slices. True peaks can only arise when all back projections intersect, which eliminates spurious features arising from noise or signal discontinuities. Interestingly, the PR spectra appear even better resolved than in US despite the severe undersampling ($\sim 15\%$), a consequence of the increased SNR. More detailed analysis of the 4D electronic-Raman spectrum of Nile Blue and related dyes will be the subject of future work.

We have demonstrated a method for the rapid collection of high-dimensionality nonlinear optical signal through a projection reconstruction procedure. We compare the results from uniform Nyquist sampling with that of PR to illustrate that the full (T, T_0) plane can be acquired with significantly higher sensitivity compared with conventional uniform sampling. The dramatically increased SNR reveals features buried in the noise of US spectra. While there are artifacts in the PR spectra, when the primary purpose is to isolate the peak positions, the benefits of PR greatly outweigh the costs. These artifacts include streaks in the spectrum that come from back projection and distortion in the line shape that arises from incomplete sampling of the full polar grid, imperfect background subtraction, and filtering prior to back projection. In the context of NMR, many of these issues have been addressed,⁴² but implementation of these more advanced methods is beyond the scope here.

We note that other works on speeding up 2D IR or ES spectroscopy using compressive sensing (CS) represent another class of nonuniform sampling schemes distinct from the approach used here.^{43,44} In CS, the sparsity of the spectrum is exploited, but the sampling is sub-Nyquist and the reconstruction occurs by a convex optimization procedure (minimizing the L1 norm of a linear problem). CS can reduce the sampling requirements dramatically in some instances where the spectrum is sparse.⁴⁵ Some notable drawbacks of CS are that artifacts in the line shape may be difficult to predict a priori and that extensive computational resources are required for the convex solver.^{46,47} In fact, CS cannot be used here because the memory requirements for such a large reconstruction are too steep for 4D spectra. In principle, CS and schemes using linear solvers could be combined with PR to decrease the sampling requirements even further because the data sets are significantly smaller. The main advantage of PR is that it is robust, artifacts are simple to simulate, no assumptions about the structure of the spectrum are needed, and the reconstruction is extremely fast. Possible improvements to further speed up the acquisition over radial sampling include using a priori information on the frequencies of the vibrational modes to judiciously select projections that locate cross peaks or other specific features of the 2D Raman-like spectrum. Other variants of nonuniform sampling are used in the field of multidimensional NMR, especially when the dimensionality exceeds three, including biased,⁴⁸ best-matched,⁴⁹ and Poisson gap sampling,⁵⁰ to name a few. These more sophisticated methods may require the use of pulse shapers that involve no moving parts and are straightforward to program with arbitrary delay patterns. Such methods have the advantage of sharper PSFs similar to those of Cartesian sampling compared with PR alone. Future efforts will be directed at exploring alternate sampling schemes and reconstruction methods to improve the sensitivity and minimize artifacts. We expect PRO GAMERS to have a dramatic impact on facilitating practical implementation of high-order and high-dimensionality nonlinear spectroscopies on increasingly complex molecular systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.8b00122.

Additional details regarding GAMERS, sample preparation, and data analysis. (PDF)

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Author Contributions

E.H. designed the experiment. A.P.S. and W.O.H. built and performed the experiment. E.H., W.O.H, and A.P.S. analyzed

the data. E.H., W.O.H., and A.P.S. prepared the manuscript. The data that support the findings of this study are available from the corresponding author upon reasonable request.

Notes

The authors declare no competing financial interest.

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