Supporting Information

A General Method for the Dimension Reduction of Adaptive Control Experiments

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General Laboratory Methods: The technique of adaptive femtosecond pulse shaping is a quantum control methodology[1] built around an adaptive learning loop.[2-5] In our laboratory this is comprised of (1) a computer controlled laser pulse shaper (2) measurement of molecular and material responses for feedback and (3) a computer-driven evolutionary algorithm. The input laser pulses for the pulse shaping device are derived from a broad-band Ti:Sapphire source consisting of a commercial multi-pass amplifier (Quantronix; Odin) seeded by a mode-locked Ti:Sapphire oscillator (K&M Labs). The oscillator is pumped by the second harmonic of a cw Nd:YVO_4 laser (Coherent; Verdi) while the amplifier is pumped by the second harmonic of a Nd:YLF laser (Quantronix; Darwin). The system produces a 1 KHz laser pulse train (~ 900 μJ/pulse) each with a temporal full-width half maximum (FWHM) of ~ 40 fs and a bandwidth of ~ 26 nm FWHM. The amplified laser pulses (~ 20% of total power) are coupled into a home-built pulse shaper constructed in the geometry of a zero-dispersion compressor.[6-9] A dual-layer computer-controlled spatial light modulator (SLM) (CRI Inc; SLM-640) is placed at the Fourier plane of the device. For any one pixel number across the Fourier plane, both SLM layers are fixed to the same phase retardation value thereby achieving phase shaping as opposed to phase and amplitude shaping. The SLM has 640 individually addressable pixels but only 208 of these are needed to cover our laser spectrum. The index of refraction at each pixel of the SLM is independently varied by application of a drive voltage ranging between 0 – 10 volts with 12-bit resolution. Index of refraction is converted to phase values using home-built calibration procedures and then phase is modulated modulo 2π ($0 - 2\pi$) over a drive voltage range spanning ~ 0 to ~ 2.3 V. The total parameter space that can be explored in the learning loop is based on the number of phase variables, the pixel-voltage range, and the voltage resolution. In our case it consists of $> 10^{620}$ shaped laser pulses. The background phase acquired from propagation through the optics and possible misalignment of the compressor in the amplifier is corrected for by measuring the phase necessary to maximize the second harmonic of the laser pulse. Adaptive searches are directed by an evolution strategy based on a genetic algorithm.[10, 11] The heuristic search methodology is based on metaphors common to evolutionary biology and is capable of accommodating the massive multidimensional parameter space. Adaptive experiments are initialized by randomly coding 60 numerical arrays (termed individuals) of 208 phase values to

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be applied to the pixels of the SLM. These individuals are thought of as having a genetic code made up of the array of applied phase values. For each generation the 60 pulses are ranked in terms of their *fitness* at achieving the user-defined optimization goal. To create a new generation, the algorithm renders a new population of 60 individuals by administering evolutionary operators which crossover, mutate, and clone the genetic material of a selection of fittest individuals in the previous generation. For each crossover operation, two individuals are chosen by tournament selection and yield two children; 30 new individuals are produced in this manner. For each mutation operation, an individual is randomly selected from among the ten fittest; 20 new individuals are produced in this manner. The 10 fittest individuals are also cloned to yield 10 new individuals. The population size of 60 individuals is held constant throughout the experiment.

Specific Laboratory Methods: The adaptive pulse shaping experiment undertaken for this work is similar to one previously pursued by the Gerber group.[12] The output of the pulse shaping device is split into two pulse trains, one of which (~ 12 mW) impinges on a 298K sample (~ 9×10^{-5}M; 1 cm path length) of $[Ru(dpb)_3](PF_6)_2$ in acetonitrile (where dpb = 4,4'-diphenyl-2,2'-bipyridine). The linear absorption spectrum of this molecule has negligible absorbance at the wavelengths contained in the laser pulse but electronic excitation occurs when the molecule absorbs two or more photons from the shaped field. The relative multi-photon excitation efficiency is monitored by collecting a spontaneous emission signal at 640±5 nm from the thermalized triplet ^{3}MLCT (metal-to-ligand charge transfer) state.[13] Wavelength selection is achieved using a bandpass filter (Thor Labs Inc.; FB640-10). A negatively biased PMT (Hamamatsu; H9305-02) records the emission signal with ~ 1.4 ns time resolution. We ensure that the signal results from the ^{3}MLCT state by box-car averaging (SRS) between ~ 0.1 μs and ~ 1.5 μs after the shaped excitation. This also guarantees that the recorded emission signal is not contaminated by any white light generated by the shaped fields passing through the sample cell or solvent. It is important to note, however, that we do not observe such white light generation with the pulse intensities we are using during this adaptive experiment. The output of the box car is sent to a digital lockin amplifier (SRS 810 DSP) locked to the frequency of a mechanical chopper (Thor Labs MC1000) that is modulating the output of the pulse shaper. The chopper is synched to the amplified laser and modulates the shaped excitation source at ω/2, where ω is the pulse-to-pulse frequency of the amplified pulse train. The second pulse train (~ 5mW) is transmitted through a 100 μm b-barium borate (BBO) crystal (Type I, 30º) to generate second harmonic (SHG) of the fundamental. This is passed through a glass prism to spatially separate the SHG from unconverted fundamental. The average intensity of the SHG signal is monitored using an amplified photodiode (Also Thor Labs PDA55), the output of which is fed into a second digital lockin amplifier (SRS 810 DSP) that is also locked at ω/2. This SHG signal is responsible for reporting the relative intensity of each laser pulse tested by the adaptive algorithm.

Maximizing either SHG or emission with the adaptive pulse shaping experiment results in the shortest laser pulse possible because each is an intensity-dependent phenomenon involving the interaction of the material or molecule with two photons.[12] Gerber's group has further shown that maximizing the *ratio* of these two signals (emission/SHG) removes the two-photon intensity dependence of either separate physical process allowing the adaptive algorithm to take advantage of molecule-specific information in order to discover optimal pulse shapes.[12] The optimization experiment analyzed for this manuscript was run for 195 generations (11700 total laser pulses explored) until convergence of the emission/SHG ratio was achieved.

PLS Regression Methodology: The salient features of PLS-regression as applied to adaptive control experiments is discussed here. The PLS-regression is implemented using *The Unscrambler®* (CAMO) software package.

In our analysis the spectral phase or phase function characterizing each laser pulse shape can be represented as a row vector, $\vec{\mathbf{P}}_i$, of a 11700-row matrix, $\mathbf{P} = p_{ij}$; where p_{ij} is a number corresponding to the applied phase (0 – 2π) at the jth pixel of the SLM for the ith laser pulse. As alluded to, the phase functions, $\vec{\mathbf{P}}_i$ are unwrapped by numerical algorithm to remove discontinuities. The resulting row vectors $\vec{\mathbf{P}}_i^u$ form a matrix $\mathbf{P}^u$. We note that at this point, one could numerically differentiate the unwrapped phase functions if it is desirable to consider only the relative phase of each pulse. $\mathbf{P}^u$ is autoscaled to center and normalize the variance along each column according to the following expression,

$$a_{ik} = (p_{ij}^u - p_{j-ave}^u) \Big/ \left[\sum_{i=0}^{N-1} (p_{ij}^u - p_{j-ave}^u)^2 \right]^{1/2} \qquad \textbf{\textit{Eq. S1}}$$

where p_{j-ave}^u is the numerical average of the jth column of $\mathbf{P}^u$ and N is the number of pixels. The covariance matrix $\mathbf{C} = c_{ij}$ is calculated by multiplying the autoscaled matrix by its transpose.

$$\mathbf{C} = \mathbf{A'A} \qquad \textbf{\textit{Eq. S2}}$$

The observed fitness for each pulse can be represented as a column vector, $\vec{\mathbf{F}} = f_i$, where f_i is the fitness of the ith pulse. The observed fitness is also autoscaled and the variance calculated in a manner analogous to **Eqs. S1** and **S2** to yield the vector $\vec{\mathbf{F}}^c$. The PLS-regression assumes a linear model relating the variance of the fitness to the covariance of the phase functions:

$$f_i^c = \sum_{j=0}^{N-1} \beta_j c_{ij} + \varepsilon_i \qquad \textbf{\textit{Eq. S3}}$$

In this expression the β_j are termed the regression coefficients and the ε_i is the residual not accounted for by the model. The covariance of the phase functions is described by the so-called outer relationship:

$$c_{ij} = \sum_{k=0}^{N'-1} u_{ik} b_{kj} + e_{ij} \qquad \textbf{\textit{Eq. S4}}$$

In this expression the u_{ik} are orthogonal basis functions that define a hyperplane which models the phase data, the b_{kj} are termed the loadings, N' is the dimensionality of the hyperplane, and e_{ij} is the residual error in c_{ij} not accounted for by the model. The variance of the fitness is described by the so-called inner relationship, which is also a linear combination of the basis functions u_{ik}:

$$f_i^c = \sum_{k=0}^{N'-1} \rho_k u_{ik} + \Delta_i \qquad \textbf{\textit{Eq. S5}}$$

Here, the ρ_k are termed the regression coefficients of orthogonal basis functions and Δ_i is the residual error in f_i^c not accounted for by the model. The β_j, u_{ik}, b_{kj}, and ρ_k, as well as, the residuals are iteratively calculated using the NIPALS algorithm developed by Wold which is described in detail elsewhere in the literature.[14, 15]

References Cited:

1. Rice, S. A.; Zhao, M., *Optical control of molecular dynamics.* Wiley: New York, 2000.
2. Baumert, T.; Brixner, T.; Seyfried, V.; Strehle, M.; Gerber, G., *Appl. Phys. B* **1997,** 65, 779-782.
3. Bardeen, C. J.; Yakovlev, V. V.; Wilson, K. R.; Carpenter, S. D.; Weber, P. M.; Warren, W. S., *Chem. Phys. Lett.* **1997,** 280, (1-2), 151-158.
4. Yelin, D.; Meshulach, D.; Silberberg, Y., *Opt. Lett.* **1997,** 22, 1793-1795.
5. Assion, A.; Baumert, T.; Bergt, M.; Brixner, T.; Kiefer, B.; Seyfried, V.; Strehle, M.; Gerber, G., *Science* **1998,** 282, (5390), 919-922.
6. Heritage, J. P.; Weiner, A. M.; Thurston, R. N., *Opt. Lett.* **1985,** 10, (4), 609-611.
7. Weiner, A. M.; Leaird, D. E.; Patel, J. S.; Wullert, J. R., *Opt. Lett.* **1990,** 15, 326-328.
8. Weiner, A. M., *Rev. Sci. Instrum.* **2000,** 71, 1929-1960.
9. Wefers, M. M.; Nelson, K. A., *Optics Letters* **1993,** 18, (23), 2032-2034.
10. Goldberg, D. E., *Genetic algorithms in search, optimization, and machine learning.* Addison-Wesley: Reading, 1993.
11. Schwefel, H. P., *Evolution and optimum seeking.* Wiley: New York, 1995.
12. Brixner, T.; Damrauer, N. H.; Kiefer, B.; Gerber, G., *J. Chem. Phys.* **2003,** 118, 3692-3701.
13. Damrauer, N. H.; Boussie, T. R.; Devenney, M.; McCusker, J. K., *J. Am. Chem. Soc.* **1997,** 119, (35), 8253-8268.
14. Wold, S.; Ruhe, A.; Wold, H.; Dunn, W. J., *Siam Journal on Scientific and Statistical Computing* **1984,** 5, (3), 735-743.
15. Wold, S.; Sjostrom, M.; Eriksson, L., *Chemometrics and Intelligent Laboratory Systems* **2001,** 58, (2), 109-130.