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General Method for Reducing Adaptive Laser Pulse-Shaping Experiments to a Single Control Variable

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Adaptive laser pulse shaping has proven to be expeditious for discovering laser pulse shapes capable of manipulating complex systems. However, if adaptive control is to be a valuable interrogative technique that informs physical and chemical research, methods that make it possible to infer mechanistic information from experimental results must be developed. Here, we demonstrate multivariate statistical analysis to extract a single control variable from results of a 137-parameter adaptive laser pulse-shaping optimization of multiphoton electronic excitation in a ruthenium(II) coordination complex in solution. We show that this single variable can be used to linearly manipulate the observed fitness, which is determined by the ratio of molecular emission to second harmonic generation of the laser pulse, over the range explored during the adaptive optimization. Further, manipulation of this variable reveals the latent control mechanism. For this system, that mechanism entails focusing the second harmonic power spectrum of the laser field in a spectral region where the probability of two-photon absorption by the molecule is also large. The statistical tools developed are general and will help elucidate control mechanisms in future adaptive pulse-shaping experiments.

Adaptive femtosecond laser pulse-shaping control experiments of the type first proposed by the Rabitz group[1] offer revolutionary possibilities in photophysics and photochemistry by providing a general methodology to manipulate physical observables in complex systems without a priori knowledge of the Hamiltonian. Their insight, that molecular systems can be used as analog computers to adaptively "teach" lasers how to achieve control, has been the basis of many intriguing results in chemistry and physics over the last 15 years, including, but not limited to, the references given here.[2−15] Yet, the ability of researchers to extract information about chemical systems from the results of adaptive control experiments has lagged behind the ability to demonstrate control. There are a few cases where optimal pulse shapes exhibit temporal features suggesting time-dependent manipulation of wavepacket motion[8,9,14] and others where theoretical considerations suggest suitable parametrizations of the electric field.[4,16−18] However, in the absence of obvious patterns or well-formed theory, it has proven difficult to infer control mechanisms. The control community is faced with an important challenge: if adaptive pulse-shaping methodologies are to become a useful tool for *interrogating* complex chemical systems as opposed to simply manipulating them, general procedures—both experimental[9] and theoretical[19]—must be developed that make it possible to extract information about control mechanisms directly from the results of optimization experiments.

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Toward this end, several groups have pursued statistical and algebraic methods that significantly reduce the dimensionality of the search space in adaptive control experiments.[20−22] In previous work, involving the control of a metal complex in solution,[22] we showed that it is important to include information about laser pulse fitness as an evaluative criterion during statistical dimension reduction procedures. We employed partial least squares regression (PLS) modeling[23] and demonstrated the dimension reduction of a 208-parameter adaptive optimization of intensity-normalized molecular emission to only seven statistically significant dimensions.[24] This procedure is effectively global fitting that treats laser pulse fitness as the dependent variable and finds the fewest number of orthogonal variables (i.e., a minimal dimension hyperplane) that best describe its variance. The orthogonal variables are linear combinations of the original control parameters, which in our case are the applied phases at each pixel of the spatial light modulator (SLM) in our pulse shaper. The orthogonal variables can be thought of as basis vectors that define the dimensionally reduced space. A cartoon of this in two independent dimensions is shown in Figure 1. The variables X_1 and X_2 are uncorrelated, and the gray surface is a linear fit (i.e., a plane) that models the control response (fitness) with respect to these variables. In other work, we showed that these fewer dimensions significantly reduce the time required for an adaptive optimization.[24] This technique has the distinct advantage of not arbitrarily biasing the search space (e.g., searching in orders of Taylor chirp) and thus maintains the complete generality of the adaptive methodology.

However, even as remarkable dimension reduction was shown, it remained unclear to us how these few dimensions could be used to understand a globally nonlinear control surface.

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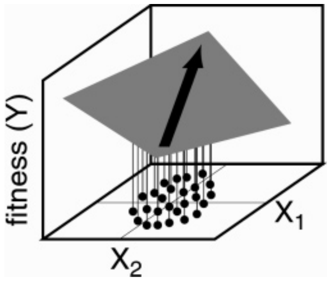

Figure 1. A response surface (dependent variable) in two orthogonal independent variables (X_1 and X_2) is illustrated in gray. The vector shows the regression solution chosen such that it is maximally correlated to the two independent variables.

Here, we address this question and show that a *single* linear control variable (aka, a single control knob) can be generally extracted from our statistical analyses following an adaptive optimization. Critically, this "control knob" allows for linear manipulation of the laser pulse fitness and can therefore be used to explore adaptive control mechanisms.

The ability to derive a single control variable from a linear fit of a globally nonlinear response surface requires that we modify the standard PLS procedure to reflect the fundamental nature of an adaptive optimization. To do this, we draw insight from important recent work by Rabitz et al.[25] who have demonstrated that the robustness of adaptive control stems from an absence of local extrema on control surfaces. Because of this, the "shape" of a control surface around a global maximum (whether or not it is unique) is actually simple. In practical terms, this means that, after some induction period, an adaptive optimization settles in a local region of the control surface near a particular global maximum where it ostensibly "climbs a hill" (i.e., the simple shape) toward the optimal solution. Consequently, a nonlinear control surface cannot be understood globally from the results of any single experiment because the information the results contain is inherently local. However, because the shape of the control surface around the global maximum is simple, the local region of the control surface should be amenable in a general fashion to a linear approximation. This is exactly what our modified implementation of PLS achieves.

In standard PLS, fitness as a function of position in the search space takes the generic form $Y = m_1X_1 + m_2X_2 + ... + m_nX_n + b$, which has a simple geometric interpretation as a vector that points in the direction that has the greatest correlation with variance in the observed fitness. Ostensibly, this vector characterizes the hyperplane, as shown schematically in Figure 1. However, because our model is meant only to reflect a local region of the control surface, care must be taken with respect to this interpretation. If the control surface were truly linear, the fitness could be improved at any suboptimal point by translation in the direction this vector points. However, because the model reflects only a small region of a globally nonlinear control surface, translation in this direction will only improve fitness if it is contained in the local region of the control surface on which the model is based. Thus, to make use of PLS analysis, it is imperative to properly situate the model of the simple shape in the local region around the optimal solution and not extrapolate to the global surface.

When the fit (hyperplane) from PLS modeling is expressed in the *original* variable space, it yields a predictive model for the observed fitness, f, as a function of the applied phase, x_j, at the jth pixel of the SLM at the Fourier plane of our pulse shaper:

$$f = f(x_1, ..., x_j) = \sum_{j=0}^{N-1} B_j x_j + b_0 \qquad (1)$$

The B_j's are termed the regression coefficients, and b_0 is an empirically determined constant. Geometrically, each B_j represents the slope of the minimum dimension hyperplane in the original j dimensions of the search space. Thus, the vector f points in the direction that has the best correlation with fitness and maps the search space to the fitness space. However, as alluded to before, one must be careful with the interpretation of f. First, the magnitude of b_0 depends on the numerical values of fitness, which can be scaled arbitrarily. Second, the direction of f is only physically meaningful in the local region of the search space on which the model is based. In short, while we expect eq 1 will be a good predictor of the fitness in a local region of the control surface, the model assumes global linearity and thus f contains no information whatsoever about where the local region of the control surface is located. In other words, the mathematics of PLS implicitly presume that the model is everywhere true.

To overcome these difficulties, we define a second equivalent vector, f', that allows us to specifically relate the PLS model to the local region of the control surface and thus remove the assumption of global linearity:

$$f' = \Phi \times [f(x_1, ..., x_j = 1) - b_0] + O(x_1, ..., x_j) \qquad (2)$$

In eq 2, Φ is a scalar that defines the magnitude of f'. Because only the direction of f is relevant, we need not consider the dependence of f on the independent coordinates, x_j, and for convenience we set each x_j to unity. Varying Φ allows for translation along the control surface in the direction that has the greatest correlation with fitness. $O(x_1, ..., x_j)$[26] is the origin in the search space which is chosen so that f' is explicitly situated in the local region of the control surface. If this criterion with respect to $O(x_1, ..., x_j)$ is satisfied, then we can vary the scalar, Φ, to affect translation along the local region of the control surface in the direction that has the greatest correlation with fitness. At any point along this translation, we expect that eq 1 will be a good predictor of fitness. The challenge then is to choose an appropriate value of $O(x_1, ..., x_j)$ and range for the scalar, Φ (which we make a discrete set of values $\{\phi_1, \phi_2, ..., \phi_n\}$), so that the calculated set of points $\{f'_1, f'_2, ..., f'_n\}$ are contained in the local region of the search space where the model is valid. This turns out to be quite simple. The origin can be chosen by inspection from any of a number of the pulse shapes tested during the experiment because the vast majority lie in the local region of the search space. We note that the range of Φ can take both positive and/or negative values depending on the choice of origin. Furthermore, because the model is linear, the variation of fitness with regard to varying Φ is implicitly independent of the choice of the origin. Therefore, as long as we are careful to restrict the model to the local region of the search space, we can interpret the variation of fitness around the global maximum in the context of a single variable and linearly manipulate the observed fitness with a single control knob.

The experimental setup used to test this idea has been described elsewhere.[10,22] The observable used as feedback during adaptive optimization is emission/SHG, where emission refers to the time-integrated phosphorescence signal from the ^{3}MLCT (metal-to-ligand charge transfer) excited state of the coordination complex $[Ru(dpb)_3](PF_6)_2$ in acetonitrile (where dpb = 4,4′-diphenyl-2,2′-bipyridine) following two-photon absorption. The denominator of the ratio (SHG) is the second harmonic

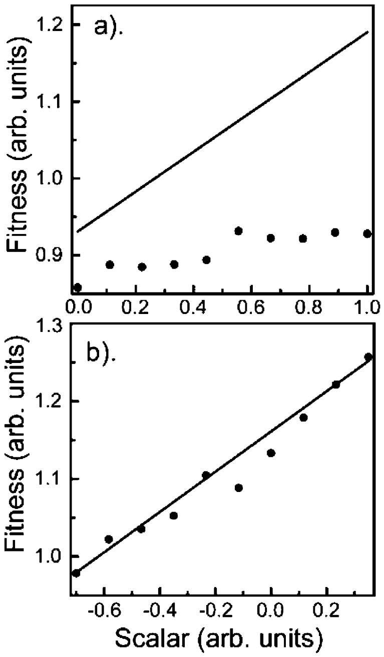

Figure 2. Predicted (solid line) and measured (dots) fitness as a function of the scalar when the origin of f' is set coincident with pulses 0 (a) and 4000 (b) of the data set. Only when the origin is set in the local region where the majority of the optimization has occurred is f a good predictor of fitness.

generated by the shaped laser field in a nonlinear medium. The ratio is conveniently thought of as intensity-normalized molecular emission.

Adaptive maximization of this ratio is a well-documented control problem.[10,22,24,27] We have used it as a prototype system for exploring dimension reduction methods in part because the adaptively discovered control pulses show complex field shapes with nontrivial time orderings of the constituent frequencies.[10,22,27] A second reason stems from the fact that we now understand the active control mechanism exploited by the adaptive algorithm during optimization, as has been recently reported using experimental and modeling evidence. Spectral phase shaping of a laser pulse centered at, for example, 800 nm alters how pairs of photons within this spectrum constructively or destructively interfere to produce a second harmonic (SH) power spectrum centered at 400 nm. Control is achieved when the algorithm manipulates this SH power spectrum (a property of the field) so that it is intense in spectral regions where the probability of two-photon absorption by the molecule is also large.[27]

Following the optimization, PLS modeling was performed on the total data set according to the prescriptions of our previous treatment.[22] Using the regression coefficients we specified f' with different choices of $O(x_1, ..., x_j)$ chosen randomly from the data set (pulses 0 and 4000 are shown here). For each f', we define a translation along the control surface by varying Φ over a specified range, $\{\phi_1, \phi_2, ..., \phi_n\}$, and experimentally test the fitness at these points. To assess the model, we compare the measured fitness at these points to the fitness predicted by eq 1. The results are shown in Figure 2.

As expected, we find (Figure 2a) that when $O(x_1, ..., x_j)$ is chosen such that the translation is *outside* the local region of the search space where the majority of the optimization occurred, eq 1 is a bad predictor of fitness. However, if the origin is chosen such that the translation is *contained* in the local region of the search space, eq 1 is a good predictor of the observed fitness (Figure 2b).

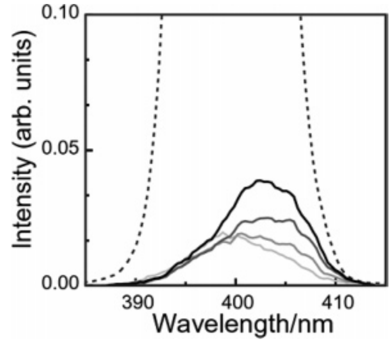

Figure 3. Measured second harmonic (SH) spectrum of points 1, 3, 6, and 10 (light to dark) from Figure 2b compared to the SH spectrum (off-scale) of a near-bandwidth limited pulse (dashed line). Varying the scalar corresponds directly to manipulation of the known control mechanism.

Having determined an appropriate origin, it is also possible to directly interrogate the control mechanism as a function of a single control variable. In this context, we have measured the SH spectrum for each of the laser pulse shapes explored in Figure 2b as we translate along the control surface. A number of these are shown in Figure 3. For comparison, a close-up of the SH spectrum of a near-bandwidth limited pulse (no phase modulation) is shown. The full-scale spectrum is near-Gaussian in shape, peaked at 400 nm, and has a maximum value of 1.0 in the arbitrary intensity units.

As can be seen, the modulation of Φ increases the integrated intensity of the SH spectrum while shifting the central wavelength toward the red edge of the near-bandwidth limited SH spectrum. As mentioned, we know from previous experiments and simulations that adaptive control of intensity-normalized emission for $[Ru(dpb)_3]^{2+}$ is achieved by focusing the SH power spectrum of the laser field into the red edge of the spectral region centered at 400 nm.[27] Thus, the control mechanism identified during linear manipulation of fitness is the same as the known adaptive control mechanism. Had we not previously identified the control mechanism, this set of measurements would have pointed us directly to it.

Our application of PLS modeling represents a powerful statistical tool that will allow researchers to directly interrogate control mechanisms from the results of adaptive optimizations in experimentally feasible times. The technique requires no arbitrary parametrization or other introduction of experimental bias, so it preserves the complete generality of the adaptive method. Furthermore, because PLS modeling should be valid in any local region around a global maximum, provided that the shape of the control surface is simple (a condition Rabitz et al.[25] have argued is an inherent property of control surfaces), this method should be generally applicable to a multitude of adaptive pulse-shaping experiments. Additionally, because the PLS model yields a linear relationship between position in the search space and the observed fitness, we have a powerful tool for relating subsequences of the applied spectral phase to the control mechanism. This is expected to provide a means of identifying salient pulse features and understanding them in the context of the underlying photophysics and photochemistry. We believe this technique will be useful in answering several outstanding questions regarding this (and other) adaptive control experiments. Namely, do the control pathways and mechanisms vary between individual experiments? Further, what is the physical significance of the variables derived by various statistical analyses?

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References and Notes

(1) Judson, R. S.; Rabitz, H. *Phys. Rev. Lett.* **1992**, *68*, 1500−1503.
(2) Bardeen, C. J.; Yakovlev, V. V.; Wilson, K. R.; Carpenter, S. D.; Weber, P. M.; Warren, W. S. *Chem. Phys. Lett.* **1997**, *280*, 151−158.
(3) Assion, A.; Baumert, T.; Bergt, M.; Brixner, T.; Kiefer, B.; Seyfried, V.; Strehle, M.; Gerber, G. *Science* **1998**, *282*, 919−922.
(4) Weinacht, T.; Ahn, J.; Bucksbaum, P. *Nature* **1999**, *397*, 233−235.
(5) Bartels, R.; Backus, S.; Zeek, E.; Misoguti, L.; Vdovin, G.; Christov, I. P.; Murnane, M. M.; Kapteyn, H. C. *Nature* **2000**, *406*, 164−166.
(6) Levis, R. J.; Menkir, G. M.; Rabitz, H. *Science* **2001**, *292*, 709−713.
(7) Brixner, T.; Damrauer, N. H.; Niklaus, P.; Gerber, G. *Nature* **2001**, *414*, 57−60.
(8) Herek, J. L.; Wohlleben, W.; Cogdell, R. J.; Zeidler, D.; Motzkus, M. *Nature* **2002**, *417*, 533−535.
(9) Daniel, C.; Full, J.; Gonzalez, L.; Lupulescu, C.; Manz, J.; Merli, A.; Vajda, S.; Woste, L. *Science* **2003**, *299*, 536−539.
(10) Brixner, T.; Damrauer, N. H.; Kiefer, B.; Gerber, G. *J. Chem. Phys.* **2003**, *118*, 3692−3701.
(11) Prokhorenko, V. I.; Nagy, A. M.; Miller, R. J. D. *J. Chem. Phys.* **2005**, *122*, 184502.
(12) Vogt, G.; Krampert, G.; Niklaus, P.; Nuernberger, P.; Gerber, G. *Phys. Rev. Lett.* **2005**, *94*, 068305.
(13) Bruggemann, B.; Organero, J. A.; Pascher, T.; Pullerits, T.; Yartsev, A. *Phys. Rev. Lett.* **2006**, *97*, 208301.
(14) Dietzek, B.; Bruggemann, B.; Pascher, T.; Yartsev, A. *Phys. Rev. Lett.* **2006**, *97*, 258301.
(15) Carroll, E. C.; Pearson, B. J.; Florean, A. C.; Bucksbaum, P. H.; Sension, R. J. *J. Chem. Phys.* **2006**, *124*, 114506.
(16) Hornung, T.; Meier, R.; Motzkus, M. *Chem. Phys. Lett.* **2000**, *326*, 445−453.
(17) Vogt, G.; Nuernberger, P.; Selle, R.; Dimler, F.; Brixner, T.; Gerber, G. *Phys. Rev. A* **2006**, *74*, 033413.
(18) Cao, J.; Bardeen, C. J.; Wilson, K. R. *Phys. Rev. Lett.* **1998**, *80*, 1406−1409.
(19) Pelzer, A.; Ramakrishna, S.; Seideman, T. *J. Chem. Phys.* **2007**, *126*, 034503.
(20) Cardoza, D.; Trallero-Herrero, C.; Langhojer, F.; Rabitz, H.; Weinacht, T. *J. Chem. Phys.* **2005**, *122*, 124306−124312.
(21) White, J. L.; Pearson, B. J.; Bucksbaum, P. H. *J. Phys. B: At. Mol. Opt. Phys.* **2004**, *37*, L399−L405.
(22) Montgomery, M. A.; Meglen, R. R.; Damrauer, N. H. *J. Phys. Chem. A* **2006**, *110*, 6391−6394.
(23) Wold, S.; Ruhe, A.; Wold, H.; Dunn, W. J. *Siam J. Sci. Stat. Comput.* **1984**, *5*, 735−743.
(24) Montgomery, M. A.; Meglen, R. R.; Damrauer, N. H. Robust basis functions for control from dimension reduction of adaptive pulse-shaping experiments. In *Ultrafast Phenomena XV*; Miller, R. J. D., Weiner, A. M., Corcum, P., Jonas, D. M., Eds.; Springer-Verlag: Berlin, 2006.
(25) Rabitz, H. A.; Hsieh, M. M.; Rosenthal, C. M. *Science* **2004**, *303*, 1998−2001.
(26) We stress for clarity that the origin $O(x_1, ..., x_j)$ is an explicit point in the search space (one particular pulse shape) which is set by specifying a phase value for each of the original x_j dimensions.
(27) Montgomery, M. A.; Damrauer, N. H. *J. Phys. Chem. A* **2007**, *111*, 1426−1433.