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Elucidation of Control Mechanisms Discovered during Adaptive Manipulation of $[Ru(dpb)_3](PF_6)_2$ Emission in the Solution Phase

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To design methodologies that will allow researchers to directly correlate the results of adaptive control experiments with physiochemical control pathways in arbitrary complex molecular systems it is imperative that prototype systems are developed and that exigent control pathways are understood. We have been interested in the results of adaptive control experiments in our laboratory involving the maximization of a ratio of two experimental observables: (1) the thermalized emission from the solution-phase coordination complex $[Ru(dpb)_3](PF_6)_2$ and (2) the second harmonic signal (a purely intensity-dependent phenomenon) of the shaped laser fields. Using a rational pulse shaping strategy, we have made a measurement of the ratio spectrum (in essence the two-photon absorption cross section) for the molecule $[Ru(dpb)_3](PF_6)_2$ in a room temperature solution of acetonitrile. This spectrum is highly varied across the accessible two-photon power spectrum of our broad-band laser pulses and demonstrates the existence of a control pathway wherein a shaped laser field can manipulate excited-state population (with respect to SHG) by conforming to the second-order spectral response of the molecule in solution. We show that our adaptive control algorithm is capable of taking advantage of these control pathways using simulated adaptive control experiments. Finally, we measure second-harmonic spectra of shaped laser fields discovered during an adaptive control experiment and show that these agree with simulation. These results suggest that our adaptive control experiment can be understood in the context of the elucidated spectral control pathway.

Introduction

In the past two decades, there has been significant progress toward the development and understanding of laser-control methodologies designed to affect product-selective photochemistry and photophysics in gas-phase molecular systems (see, for example, refs 1−9 and references therein). Coherent control methods in the time domain based on the theoretical work of Tannor and Rice[10−12] were first demonstrated in small gas-phase molecular systems by Baumert and Gerber.[13,14] Frequency-domain coherent control methods based on the theoretical work of Brumer and Shapiro[15,16] have also been demonstrated in small gas-phase molecular systems, notably by Gordon and co-workers.[17,18] Additionally, stimulated Raman adiabatic passage (STIRAP), first realized by Bergmann and co-workers,[19,20] demonstrates high-field coherently controlled product formation in small molecular systems. Theoretical work primarily by Rice has shown that each of these control techniques is ostensibly a manifestation of the same general methodology wherein control is achieved by exploiting light-induced interference phenomena to guide systems to desired states or photoproducts.[1]

For solution-phase systems, control is less refined. With the notable exception of chirped-pulse population control of polyatomic dye systems pioneered by the Shank[21,22] and Wilson[23−26] groups, there have been few demonstrations of coherent control in solution where the control mechanism has been experimentally determined and corroborated by theory. In general, the introduction of a solvent complicates the time-dependent distribution of energy following initial excitation and decreases the time scale over which electronic and vibrational coherences persist.[27] This can obscure information that would help experimentalists determine the external parameters that might be manipulated to exert control. Furthermore, it is still not well understood to what extent these complications limit absolute controllability in complex solution-phase systems.

For these reasons, efforts to achieve laser-induced control of molecules in condensed media have increasingly turned to adaptive many-parameter methods of the type first proposed by Judson and Rabitz.[28] These techniques afford researchers the ability to explore massive experimentally derived parameter spaces by combining femtosecond laser-pulse shapers with computer-based search algorithms. A product-specific feedback signal is used to guide adaptive optimizations within the confines of the molecule/environment Hamiltonian and experimental conditions. These methods have proven to be ideal for achieving control of structurally, electronically, and energetically complex systems and as of yet represent the only reasonable experimental method for active manipulation of such systems with light. In the gas phase, adaptive control is sufficiently powerful to affect bond-selective chemistry.[29−34] While bond-selective chemistry itself has not yet been achieved in solution, there are a growing number of successful and interesting experiments[23,35−45] which include adaptive control of energy transfer pathways in a protein/chromophore complex[36] as well as a recent report of weak-field population control in a polyatomic dye.[41]

The drawback to using adaptive control in the solution-phase lies in the fact that control mechanisms are often extremely difficult to extract from experimental results. The adaptive methodology requires no specific information from the system Hamiltonian,[46] and the optimization algorithms make no distinction between pulse features that are necessary for control and

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those that contribute negligibly to fitness.[47,48] Therefore, there is no guarantee that a control mechanism can be extracted, a priori, from an optimal pulse shape.

This difficulty is manifest in recent work of the Gerber group. They utilize a ratio technique by which a signal corresponding to one physical observable (molecular emission from a solution-phase molecular dye) is optimized relative to another physical observable (another molecular emission signal or second-harmonic generated (SHG) by the shaped laser pulse).[35,37] These experiments showed that a feedback signal consisting of a ratio of these observables can be used to remove inherent intensity dependence in multiphoton excitation pathways and that this, in principle, can reveal latent molecule-specific information in the control mechanism. However, it proved difficult to correlate the optimized pulses to specific features of the quantum systems under interrogation. In essence, it could not be determined whether the control mechanism exploited particulars of the system's dynamical evolution (which we refer to herein as dynamic control) or specifics of the system's *n*th order spectral response (which we term herein spectral control). These studies utilized the coordination complex [Ru(dpb)$_3$](PF$_6$)$_2$ (where dpb = 4,4′-diphenyl-2,2′-bipyridine) which was shown to participate in what was believed to be a dynamic control scenario[35] and what was believed to be a spectral control scenario.[37] In the first case, the emission signal of [Ru(dpb)$_3$](PF$_6$)$_2$ dissolved in methanol was in ratio to the emission of the laser dye DCM also dissolved in methanol.[35] In the second case, the emission signal of [Ru(dpb)$_3$](PF$_6$)$_2$ in methanol was in ratio to SHG in a comparable way to what is described herein.[37] Drawing on the control mechanism postulated by the Gerber group,[37] the Joffre group developed a Fourier transform method to measure the two-photon excitation spectrum of Coumarin 490. They then used this to show that the optimization of the ratio emission versus SHG could be understood as the manipulation of the laser's second-harmonic spectrum in the spectral region where the probability of two-photon absorption by the molecule is at its relative largest (i.e., spectral control). They further posited that optimization of emission relative to SHG as demonstrated by the Gerber group can be understood in this same mechanistic context,[40] although this has yet to be experimentally demonstrated. Weiner's group observed manipulation of photocurrents in two different semiconductor diodes having different two-photon absorption spectra.[49] It should also be noted that the control of molecular emission following two-photon absorption was exploited by the Dantus group for applications in microscopy using rational manipulation of broad-band laser pulse shapes.[50−52]

In our laboratory, we have recently taken steps toward reducing the complexity of adaptive control experiments. We have developed a general statistical method to extract from adaptive control results the minimum number of variables needed to exert control. This work is part of a broader effort to develop techniques that can be used to correlate the results of adaptive searches to system-specific information (i.e., control mechanisms).[53] This dimension reduction work was developed using adaptive control results obtained in our laboratory on a control problem very similar to the one reported by the Gerber group[37] (i.e., maximization of the emission signal of solution-phase [Ru(dpb)$_3$](PF$_6$)$_2$ with respect to SHG). We showed that only seven independent variables (out of an original 208 correlated variables) were needed to describe ~90% of the observed variance in laser pulse shape fitness. However, to understand the variables revealed by our statistical method, it is important that we also understand the probable control mechanism involved. Toward this end, we present a frequency-domain measurement of the emission-to-SHG ratio as a function of wavelength by rationally controlled amplitude pulse shaping. This demonstrates the existence of a spectrally controllable mechanistic pathway in this system. We then show simulations and measurements that point to this as the control mechanism exploited during adaptive control experiments on this complex system.

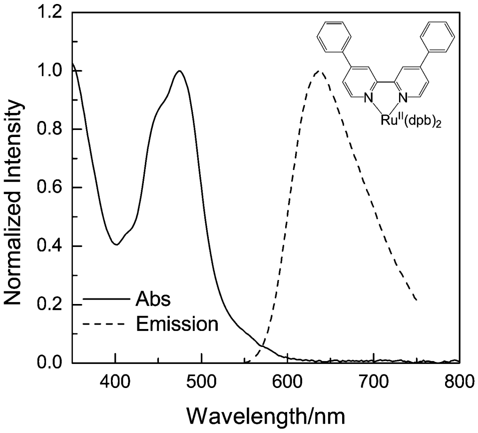

Figure 1. Normalized absorption and emission spectra of [Ru(dpb)$_3$](PF$_6$)$_2$ in 298 K acetonitrile. The complex does not absorb at the fundamental frequencies contained in the laser pulse train.

Experimental Section

General. All reagents were used as received unless otherwise noted. All solvents were purchased from Aldrich Chemical Co. Acetonitrile was of gradient grade (>99.9%). The ligand 4,4′-diphenyl-2,2′-bipyridine (dpb) was purchased from Aldrich Chemical Co. The metal complex [Ru(dpb)$_3$](PF$_6$)$_2$ was prepared according to a previously published procedure.[54] Absorption spectra were measured with a Hewlett-Packard 8452A diode array spectrophotometer. Emission spectra were measured with a Photon Technology International, Inc. 814 photomultiplier detector system.

Laser Methods. The laser and adaptive control setup used in our laboratory has been described in detail elsewhere[53] and is similar to the one described by Gerber.[37] A description of the experimental configuration and the adaptive algorithms used can also be found in the Supporting Information. This includes a description of our setup for achieving amplitude shaping which has not been previously described.

Results and Discussion

Ratio Adaptive Control Experiment. Gerber's group has reported an adaptive control experiment wherein emission from a thermalized metal-to-ligand charge transfer (^{3}MLCT) excited state of [Ru(dpb)$_3$](PF$_6$)$_2$ (where dpb = 4,4′-diphenyl-2,2′-bipyridine) in MeOH is controlled relative to the SHG from the same shaped laser field.[37] In their experiment, excited-state population responsible for emission can only occur if the molecule absorbs at least two photons from the field. They showed that the ratio of these two signals (emission/SHG) was independent of the peak intensity of the laser pulse centered at 800 nm. Thus, to manipulate the observed fitness (maximizing or minimizing the ratio), the control pathway must exploit particulars of the molecular system. As of yet, however, there has been no direct experimental verification of the control mechanism exploited in these adaptive ratio experiments.

We have undertaken similar ratio experiments for [Ru(dpb)$_3$](PF$_6$)$_2$ in 298 K acetonitrile.[55] Figure 1 confirms the well-known

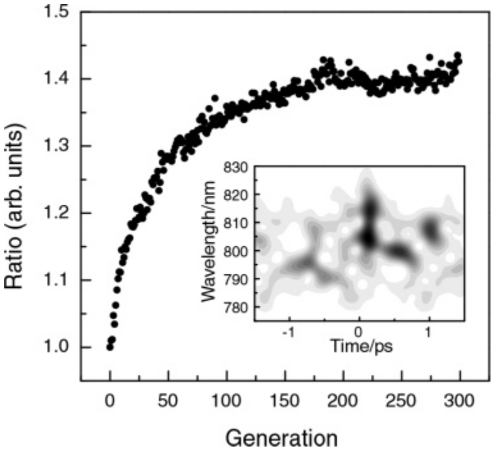

Figure 2. Evolution profile of the ratio maximization (emission/SHG). Plotted is the fitness of the best pulse measured in each generation of the adaptive optimization experiment. Inset: Husimi distribution of the best pulse from generation 299. Darker regions indicate increased probability of detecting a photon.

situation that the molecule in acetonitrile (as also observed in MeOH) absorbs negligibly at wavelengths contained in our pulse train. Figure 2 shows an evolutionary profile that plots the fitness of the best pulse in each generation for 300 generations. In the adaptive experiment, the best pulse had an improved measure of fitness (ratio) that was a factor of ~1.4 better than the best pulse of the first generation. It is clear that adaptive phase shaping is able to establish control over the system. The Husimi distribution[56−58] of the optimal pulse shape for this experiment (taken as the best pulse of the 299th generation where the initial generation is the 0th) is shown in the inset of Figure 2. It can be seen that the optimal shape involves a complex time ordering of the frequencies.[59] However, because emission requires the absorption of at least two photons from the shaped field, it is not possible, as of yet, to infer the control mechanism directly from the Husimi distribution. This is because the points of highest amplitude (i.e., largest probability of detecting a photon) do not directly correlate to increased probability of two-photon absorption.

Theory. Gerber's group has described how perturbation theory of two-photon light-matter interactions offers a *possible* explanation for control of the ratio emission/SHG in the system described above.[37] Since emission reports the extent to which excited-state population is created by the input field, the ratio of emission/SHG can be modulated if spectral properties of the shaped field take advantage of molecule-specific features in the two-photon absorption spectrum which are absent in the SHG response (assumed to be constant across the laser spectrum). The theory builds upon work by the Noordham and Silberberg groups.[60−62] Recently, Joffre's group has also confirmed such a mechanism in a related system, as described in the Introduction.[40]

A brief discussion of this theory expounded by Gerber's group[37] is given in the Supporting Information. Here, we summarize two results.

First, the fitness f (emission/SHG) of any laser pulse can be manipulated through the relationship between the two-photon excitation spectrum of the molecule $g_{\mathrm{TPA}}^{(2)}(\omega)$ and the second-harmonic (SH) spectrum of the laser $S^{(2)}(\omega)$:

$$f \propto \frac{\int p_{\mathrm{TPA}}(\omega)\,\mathrm{d}\omega}{\int I_{\mathrm{SHG}}(\omega)\,\mathrm{d}\omega} \propto \frac{\int g_{\mathrm{TPA}}^{(2)}(\omega) S^{(2)}(\omega)\,\mathrm{d}\omega}{\int S^{(2)}(\omega)\,\mathrm{d}\omega} \tag{1}$$

Because the two-photon excitation spectrum is an intrinsic (and unchangeable in the perturbation theory) property of the molecular system, the observed fitness can only be manipulated by changing the SH spectrum through variations in the spectral phase (i.e., pulse shaping). For example, the value of the ratio is increased (relative to a pulse with an approximately homogeneous SH spectrum, such as a bandwidth limited or random pulse) by manipulating the SH spectrum such that its amplitude is significant only in the frequency range(s) where the probability of two-photon excitation is also relatively large.

Second, if the width of the pulse spectrum is narrow around a central frequency ω_o, the fitness may be approximated:

$$f \propto \frac{g_{\mathrm{TPA}}^{(2)}(\omega_o) S^{(2)}(\omega_o)}{S^{(2)}(\omega_o)} \propto g_{\mathrm{TPA}}^{(2)}(\omega_o) \tag{2}$$

This equation is the basis for the measurement of a ratio spectrum described below. In essence, when a narrow band pulse is employed, the ratio (fitness) is proportional to the two-photon excitation spectrum at the central frequency of the pulse.

The perturbation theory argument for controlling the emission/SHG ratio, however, rests on two key assumptions that must be experimentally validated to confirm a spectral control mechanism.[40,61,62] The first assumption is that the magnitude of the electric field is weak relative to the intrasystem Coulombic forces. In the gas phase, a number of interesting phenomena (e.g., above threshold ionization and above threshold photodissociation) are known to result when the electric field strength is comparable to the intramolecular forces.[63] In our experiments, high-field strengths are generally not of concern because the laser intensity must be attenuated (~8×10^{10} W/cm^2 for a bandwidth-limited pulse in these experiments) so as not to be sufficient to generate white light in the sample cuvette or the solvent. During our amplitude shaping experiments, the peak pulse intensity (~1×10^9 W/cm^2) is almost an additional 2 orders of magnitude smaller.

The second assumption is that the two-photon absorption cross section is independent of the dynamical evolution of the molecule. In other words, it is imperative that we confirm that the laser pulse exerts control through the two-photon absorption process and not by coherently manipulating wave packet evolution on the excited-state potential surface to control the formation or depletion of the emissive state. As this is difficult to verify directly, we have sought methods of determining the sensitivity of the ratio to purely spectral changes.

Ratio Spectrum. A spectral control pathway is only possible in those systems that exhibit (significant) variation of the two-photon excitation cross section over the frequency range of the pulse. This can be seen in eq 1, which shows that the two-photon excitation spectrum $g_{\mathrm{TPA}}^{(2)}(\omega)$ cannot be a constant function of frequency if the fitness is to change during a control experiment. To determine the variation of the two-photon excitation spectrum of $[\mathrm{Ru(dpb)_3}](\mathrm{PF_6})_2$ in acetonitrile, we employed amplitude shaping to scan a narrow-band window across the fundamental laser-pulse spectrum creating subspectra. The laser frequencies incident on any particular pixel can be removed from the pulse by sending phase values that differ by π to each of the two layers of the SLM at that pixel. Here, we attenuated the amplitude of all frequencies to zero except for a narrow window, five pixels in width, where no attenuation was called for. Twenty-eight of these, which we term subspectra, are shown in Figure 3. We can use these subspectra to measure what we call a "ratio spectrum". In essence, we observe the ratio of emission to SHG for each subspectrum so that we

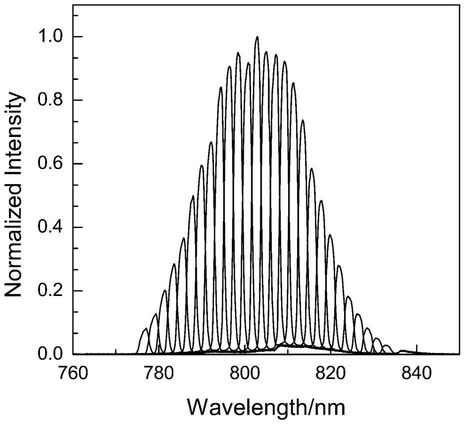

Figure 3. Spectra produced sequentially by rational amplitude shaping. Sweeping through these while measuring the emission/SHG ratio has the effect of scanning a narrow band source across the frequencies contained in the laser pulse.

characterize the variation of the ratio over the frequency range of the fundamental pulse. As can be seen from eq 2, the measured value of the ratio (emission/SHG) at each frequency point is proportional to the two-photon excitation spectrum at the central frequency of the narrow pulse. We reflect this by reporting the ratio spectrum as being centered at twice the frequency (or half the wavelength) of the fundamental pulse spectrum. We note, as can also be seen from eq 2, that the ratio (emission/SHG) is independent of the laser pulse intensity and it is inconsequential that the total amplitude is not constant for the various subspectra. Additionally, although the amplitude shaping results in significant temporal broadening with regard to the unshaped pulse (as a consequence of the uncertainty product), the spectral phase is unchanged. Therefore, the pulse associated with each subspectrum remains bandwidth-limited with regard to its new narrower frequency range. To the level of approximation of our theory (that a given molecule may exhibit at the most one second-order interaction with the field), this implies that each pulse cannot exploit any dynamic pathways for control not observed with the unshaped broad bandwidth-limited pulse. It has been pointed out in review that a molecule could interact with a longer pulse during its excited-state evolution. However, we emphasize here that our excitation pulses are weak following the amplitude shaping, and thus the probability of radiative loss occurring from additional interactions with the field on top of the original two-photon absorption is small. Furthermore, if the ratio was sensitive to radiative loss induced in the molecular system by longer pulse widths, we would expect that varying the applied quadratic phase (linear chirp), which causes substantial temporal broadening of the laser pulse, would result in variation of the observed fitness. We regularly undertake this manipulation of the field for other reasons in our lab and have never observed variation of the emission/SHG ratio.[64]

To confirm that the experiment was functioning, we first measured the ratio spectrum for the laser dye Coumarin 460. Joffre's group has reported that the two-photon absorption spectrum of this molecule (and consequently the ratio spectrum) is identical to the linear absorption spectrum over the 2ω range of frequencies contained in our broad-band laser pulses.[40] This is also what we observe.

We then applied the technique to [Ru(dpb)$_3$](PF$_6$)$_2$ in 298 K acetonitrile. The resultant ratio spectrum is shown in Figure 4. It can be seen that the value of the ratio varies significantly over the 2ω frequency range of our laser pulse. This indicates that we can vary the ratio by manipulating the second-harmonic spectrum of the laser in accordance with eq 1. The value of the ratio at ~410 nm (produced by a subspectrum at ~820 nm) is ~1.6 times greater than at its minimum in the center of the frequency range (produced by a subpulse at ~800 nm). This is consistent with the magnitude of improvement that we generally observe in the laboratory. In typical experiments (not presented in this work), we observe increases in the measure of fitness (ratio) by factors of ~1.3 to ~1.8. We believe this variability is mainly the result of (1) how successfully the algorithm is able to focus the SH spectrum in the appropriate spectral range, and (2) the bandwidth and central frequency of the laser pulse during any given experiment.

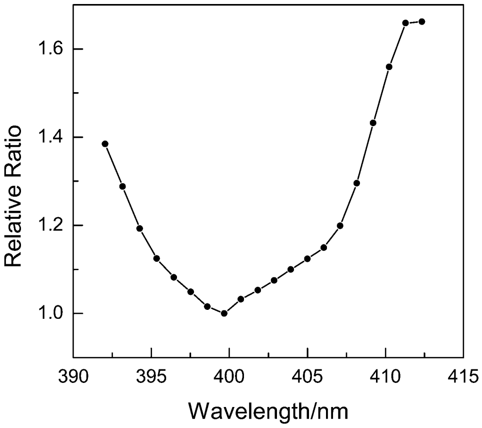

Figure 4. Ratio spectrum of emission/SHG for [Ru(dpb)$_3$](PF$_6$)$_2$ in 298 K acetonitrile. The spectrum is truncated to regions where the signal-to-noise ratio is greater than 10:1.

It is interesting to note that the ratio spectrum (effectively a ^{3}MLCT emission action spectrum following two-photon absorption) qualitatively follows the one-photon absorption spectrum of the molecule (Figure 1). While it is generally expected that a two-photon excitation spectrum (plotted over the 2ω range of frequencies) will be different than a one-photon absorption spectrum due to parity selection rules of the initial and final states,[65,66] there are many cases involving noncentrosymmetric molecules or involvement of noncentrosymmetric vibronic transitions where the selection rules are relaxed and the spectra are the same.[40,67−69] Notwithstanding, we are hesitant to claim in the case of [Ru(dpb)$_3$]$^{2+}$ that the one-photon and two-photon excitation spectra are the same. First, we cannot superimpose the two following normalization at a common wavelength as is possible in the test compound Coumarin 460 (vide supra). Second, Kawamata et al. have observed a blue-shifted peak (at 2ω) in the two-photon absorption spectrum of [Ru(dpp)$_3$]$^{2+}$ (where dpp = 4,7-diphenyl-1,10-phenanthroline) as compared to the peak of the MLCT excitation.[70] This molecule is very similar to the chromophore we have studied, and it is clear from their work[70] and the work of many others[66,67,69,71−73] that two-photon absorption draws intensity from inclusion of charge-transfer excitation. Interestingly, they observe that the two-photon absorption spectrum (at 2ω) and the one-photon absorption spectrum converge with each other at the blue edge of the MLCT band in a valley between this transition, higher lying MLCT transitions, and the ligand-based $\pi^* \leftarrow \pi$ transitions. In their case, this valley is centered at ~370 nm. This is the same valley within which our measurements have been made (in our case, this valley is centered at ~400 nm, Figure 1). To our knowledge, their measurement and our "ratio spectrum" are the only reports of the spectral response of members of this class of molecules to two-photon absorption at wavelengths longer than the onset of one-photon MLCT excitation. In related work, Castellano et al. have studied the photophysical response

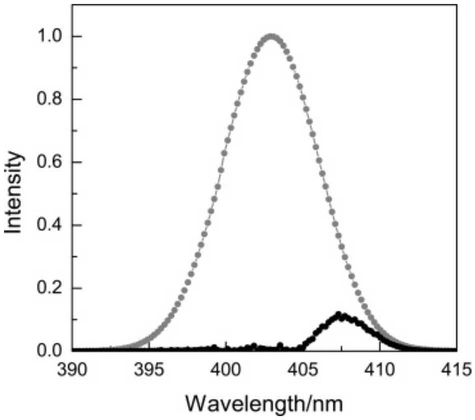

Figure 5. Calculated SH spectrum of the best pulse from generation 299 of the simulation (black). This is shown relative to the calculated normalized SH spectrum of a bandwidth-limited pulse (gray).

of polypyridyl species to two-photon excitation by near-IR laser pulses.[74] Ru^{II} polypyridyl species have also been studied for photochemical reactivity following two-photon excitation by visible and UV photons.[75−77]

Simulating Control with a Known Mechanism. The ratio spectrum confirms that a spectral control mechanism is possible for $[Ru(dpb)_3](PF_6)_2$ in acetonitrile. However, simply demonstrating that a spectral control pathway exists does not prove that this control pathway is discovered/exploited during the adaptive phase-shaping ratio experiment. Here, we explore simulated adaptive control experiments that use the experimental ratio spectrum (Figure 4) as a measure for evaluating pulse fitness. The results demonstrate that the adaptive phase shaping can exploit the spectral control pathway.

As eq 1 shows, three experimental parameters define the fitness of an arbitrary pulse: the two-photon excitation spectrum, $g_{TPA}{}^{(2)}(\omega)$, the amplitude of the electric field, and the spectral phase (the latter two determining $S^{(2)}(\omega)$ as shown in the Supporting Information). With the measured two-photon excitation spectrum (Figure 4) and the measured electric field of our laser pulses (via spectroscopic measurement of the fundamental spectrum), the ratio optimization experiment can be simulated using the applied spectral phase at each pixel of the SLM as the variable parameter[40] and the same genetic/evolutionary algorithm we employ during our experimental adaptive searches. For the data reported herein, we simulated the ratio experiment for 300 generations to determine how the spectral control pathway would manifest itself in the $[Ru(dpb)_3](PF_6)_2$ in an acetonitrile system. The results of a typical optimization are shown in Figure 5. This shows the simulated SH spectrum of the best pulse from the 299th generation relative to a normalized bandwidth-limited pulse (unshaped with a constant phase across the spectrum). It can be seen that the maximum of the SH spectrum shifts to the red where the ratio (two-photon excitation) spectrum is greatest over the frequencies contained in the laser pulse. It should be noted that the ratio spectrum (Figure 4) is truncated to values where the signal-to-noise ratio is greater than 10:1. In the simulation, the ratio fitness was fixed to the same value as the first and last point for 2ω wavelengths less than ∼393 nm and greater than ∼412 nm, respectively. This has the effect of artificially restricting the algorithm from generating SH intensity beyond ∼412 nm. The results of the simulation are intended to semiquantitatively show the behavior of the SH spectrum during optimization but not to serve as an exact reproduction of the laboratory experiment. From the simulation, we can conclude that an increase and shifting of the maximum of the SH spectrum toward the red during optimization is characteristic of spectral control in this system. In essence, the adaptive methodology is manipulating the SH spectrum such that the maximum intensity occurs in the spectral region where the probability of two-photon excitation is also large as predicted by eq 1.

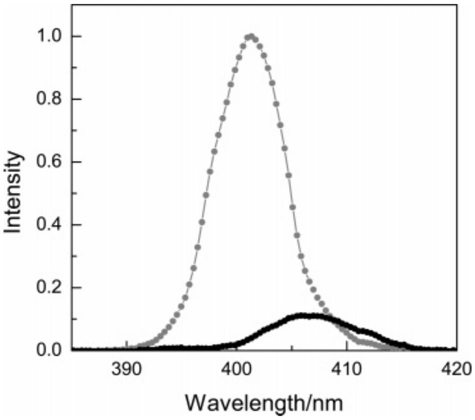

Figure 6. Measured SH spectrum of the best pulse from generation 299 (black) shown relative to a normalized measured SH spectrum of a near-bandwidth-limited pulse (gray).

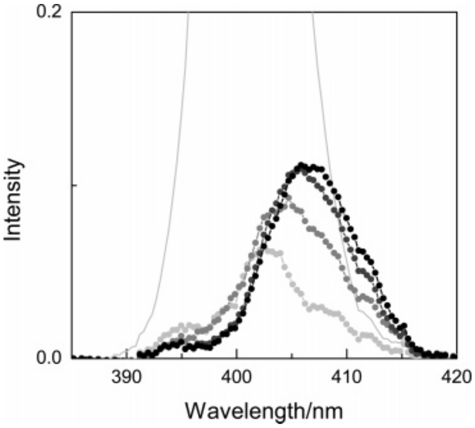

Figure 7. Evolution of measured SH spectra during the maximization of the ratio emission/SHG. Spectra from generations 0, 100, 200, and 299 are shown (light gray circles → to black circles) The light gray line is the SH spectrum of the near-bandwidth-limited pulse shown in Figure 7.

Ratio Adaptive Control Experiment Revisited. Given the results of the simulated control, we can return to the results of the experimental adaptive control represented by the evolution profile in Figure 2 where we maximized the ratio emission/SHG. To determine if the control was consistent with the simulated predictions, we measured the SH spectrum of the best pulse from the generations 0, 50, 100, 150, 200, 250, and 299. For comparison with Figure 5, the SH spectrum measured for the best pulse from generation 299 is shown in Figure 6 relative to a normalized spectrum measured for a near-bandwidth-limited pulse.[78] Clearly, the optimal pulse is red-shifted (and lower in intensity) relative to the near-bandwidth-limited pulse in agreement with the simulation. Figure 7 shows a closer view of the evolution of the SH spectrum of optimal pulses throughout the adaptive experiment. For visual clarity, only spectra from generations 0, 100, 200, and 299 are shown, although spectra from generations 50, 150, and 250 are consistent with the observed trend. It can be seen that, during the evolution of the laser pulses, the maximum of the SH spectrum increases and shifts toward the red edge of the spectrum. This is exactly what we would expect as the algorithm identifies ways to better exploit the spectral control pathway in this system.

General Discussion of Control. The measured variation of the ratio as a function of frequency presented above demonstrates the existence of spectral control in the $[Ru(dpb)_3](PF_6)_2$ system in acetonitrile consistent with the perturbation theory proposed by Gerber's group.[37] The red-shifting and intensity increasing of the SH spectrum during the adaptive optimization offer strong evidence that the algorithm is exploiting the spectral control pathway. With our experimental configuration, this result is reasonable if the quantum yield for formation of the emissive state from the Franck−Condon state is the same under two-photon excitation conditions as it is under one-photon excitation conditions where it is known to be close to unity.[79−82]

We know that SHG as an isolated phenomenon is not amenable to dynamic control. Thus, a dynamic control mechanism would have to rely on manipulation of the molecule's excited-state evolution. By virtue of our experimental setup, we only detect emission from the ^{3}MLCT state so the efficiency with which this state is formed would have to be improved by optimal pulse shapes compared to nonoptimal shapes. In our estimation, this is virtually impossible given the current configuration of our laser. We observe that the vast majority of laser pulses tested for two-photon excitation of this molecule (i.e., any pulse shape not specifically optimized for maximizing the ratio) show a high linear correlation between integrated intensity and emission yield from the ^{3}MLCT state.[37,64] For example, if either emission or SHG are optimized as isolated phenomena, the value of the *ratio* does not change during the optimization. This includes all pulses with random phase profiles and transform-limited broad-band pulses. Additionally, as stated above, linearly chirped broad-band pulses do not affect the observed ratio. We interpret this to mean that when an excited-state population is created, the emissive ^{3}MLCT state is efficiently formed consistent with what is observed following one-photon excitations. In these cases, the ^{3}MLCT state is the lowest energy excited state and is known to be formed in this and related systems with near unit quantum yield[79−82] in less that 1 ps.[83−85] The $^1A_1$ ground state is weakly coupled via nonradiative pathways to the ^{3}MLCT state ($k_{nr} \approx 5 \times 10^{-5}$ s^{-1}),[54] and it is expected via energy-gap law arguments that nonradiative coupling of the ^{1}MLCT and the $^1A_1$ ground state is even smaller. Furthermore, Lakowicz and co-workers have studied the two-photon excitation of $[Ru(bpy)_3]^{2+}$ (where bpy = 2,2′-bipyridine) over a broad wavelength range of 820−900 nm.[74] This molecule is the parent compound to $[Ru(dpb)_3]^{2+}$, the chromophore studied herein, and exhibits similar photophysics. They observe that emission yield from the ^{3}MLCT state (confirmed with emission wavelength profiles and excited-state lifetimes) has quadratic dependence on the incident power. In other words, absorption of two photons leads to emission from the lowest energy excited state (^{3}MLCT).

As has been pointed out in review, we do excite $[Ru(dpb)_3]^{2+}$ with energy in excess of the ^{1}MLCT state following absorption of two photons. With such wavelengths, the possibility exists that photochemically active metal-centered excited states could participate in the excited-state evolution of the molecule. However, we do not see evidence for photodegradation in our samples (small volumes ∼2−3 mL) even after continuous two-photon excitation with 1 kHz repetition rate for many tens of hours. Meisel et al. have seen electron loss photochemistry when the ^{3}MLCT of aqueous $[Ru(bpy)_3]^{2+}$ absorbs an additional 355-nm photon.[76] But even in this case, involving the presence of large intensity high-energy photons, the quantum yield for formation of solvated electrons is very small (0.0015) compared to formation of the lowest energy ^{3}MLCT.[76]

In short, for there to be dynamic control by laser pulses optimized to maximize the emission/SHG ratio, the Franck−Condon state produced by two-photon absorption of *non*optimal pulses would need to partition into nonemissive states along with the ^{3}MLCT state (a phenomenon not observed following one-photon absorption). We have not seen evidence for this in deviations from the linear correlation between laser pulse intensity and ^{3}MLCT emission for a very wide variety of input laser-pulse phase conditions. Nor have we seen any evidence of phodegradation. There are very few measurements of the two-photon response of Ru^{II} polypyridyl systems to near-IR radiation,[37,53,70,74] and no measurement of the quantum yield of formation of the ^{3}MLCT state from the Franck−Condon state has been made.[86] Although it is an unlikely scenario given the experimental evidence, we cannot absolutely rule out the possibility for a dynamic control in our experiment until such a measurement has been made.

Our observations suggest spectral control but there are still limits to what we can say in absolute about control mechanisms in this system. In general terms, we can imagine a molecule that admits both dynamic and spectral control pathways that allow for manipulation of some experimental observable. Because the adaptive methodology relies on heuristic algorithms that do not necessarily achieve optimization commensurate with the global maximum, it is plausible that any one experiment might converge on a solution that makes use of the spectral pathway, the dynamic pathway, or some combination of the two. Furthermore, we might imagine the inclusion of any number of possible control pathways of which any number of combinations could form the basis of a converged solution. Thus, we cannot draw definitive conclusions about all control pathways available or the controllability of the system by the results of any single experiment. Rabitz et al.[46] have argued that this is not of significant concern because there exists only one global maximum (or possibly many global maxima) and no local maxima to obfuscate the control surface. However, this derivation ultimately relies on several assumptions that are not necessarily exigent in current laboratory settings, including sufficient bandwidth to address all available pathways, sufficient resolution of the control surface, and an ideal algorithm. In adaptive experiments achievable with current ultrafast laser technologies, it is not reasonable to characterize control mechanisms in absolute terms. Researchers can only offer evidence of the existence of a particular control pathway and demonstrate that the pathway can be exploited to perform a user-specified task. In our experiment with $[Ru(dpb)_3](PF_6)_2$ in acetonitrile, this implies that showing the existence of a spectral control pathway does not disprove the existence of dynamic control pathways or prove that this is the optimal control pathway. Researchers using a different spectral range or a different bandwidth may find the system to be easily manipulated within a dynamical framework.

On a related point, we might also consider what constitutes an optimal solution given a known control mechanism. While we cannot definitively state that a particular control mechanism is the optimal control mechanism, we can establish theoretical limits as to the extent to which a system can be controlled. Of course it is impossible to separate the optimal solution from the specifics of the control apparatus (i.e., the experimental setup). For example, the ratio we have manipulated by spectral control clearly depends on both the bandwidth and the spectral range of the laser pulse because the two-photon excitation spectrum is not uniform. Therefore, the percent by which a shaped pulse can improve the ratio over a random or bandwidth-limited pulse (a figure often reported) depends on not only the intrinsic properties of the molecular system but also the specifics of the experiment and the efficacy of the algorithm driving the optimization.

Conclusion

It has been shown in our work and in previous work by the Gerber group that emission from the coordination complex [Ru(dpb)$_3$](PF$_6$)$_2$ in fluid solutions can be enhanced relative to SHG in a nonlinear crystal by phase-shaping adaptive control.[37,53] Gerber's group used a perturbation theory model to propose a possible control mechanism, but this was not experimentally verified. Here, we have established that the control mechanism they suggested is in fact active. We have shown that it can be understood in the context of controlling molecular excitation through specific two-photon absorption resonances in the molecule. First, we performed a measurement of the emission/SHG ratio as a function of wavelength using amplitude shaping of our laser pulses. Emission refers to a relative integrated intensity of the ^{3}MLCT → ^{1}A$_1$ ground state for [Ru(dpb)$_3$](PF$_6$)$_2$ in fluid (298 K) acetonitrile. The resultant "ratio spectrum" is not a constant function of wavelength and demonstrates the existence of a spectral control mechanistic pathway for [Ru(dpb)$_3$](PF$_6$)$_2$. Simulated adaptive control experiments using this information to evaluate pulse fitness confirm that the adaptive algorithm is capable of exploiting this control mechanism. Finally, we have observed that the second-harmonic spectra of laser pulses with increasing fitness toward maximization of the emission/SHG ratio red shift in accord with the spectral control mechanism.

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Supporting Information Available: Textual description of expanded laser methods and expanded theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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