Multiphoton intrapulse interference. II. Control of two- and three-photon laser induced fluorescence with shaped pulses

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Nonlinear optical processes are controlled by modulating the phase of ultrafast laser pulses taking advantage of multiphoton intrapulse interference. Experimental results show orders of magnitude control over two- and three-photon excitation of large organic molecules in solution using specific phase functions. We show simulations on the effect of phase modulation on the second- and third-order amplitude of the electric field spectrum, and demonstrate that the observed control is not caused by simple changes in peak intensity. © *2003 American Institute of Physics.*
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I. INTRODUCTION

Multiphoton processes play a fundamental role in strong-field control of laser–matter interactions and in particular control of chemical reactivity.[1–3] The four-decade long pursuit of laser control of chemical reactions,[4] has yielded the following valuable observations: (i) Laser interactions must be faster or comparable to the intramolecular dynamics, (ii) multiphoton transitions open a number of photophysical pathways simultaneously, and (iii) quantum interference can be exploited to enhance the desired and suppress the undesired pathway. In principle, the combination of these three concepts should allow general control of laser–matter interactions. Here, we explore a pulse shaping method that can control (enhance or suppress) multiphoton transitions. The method is based on intrapulse interference, which that takes place within the ultrashort laser pulse during multiphoton excitation. This work is a continuation of our work towards predictive laser control with shaped pulses determined by a reduced number of control parameters.[5]

The search for appropriate pulse shapes to control multiphoton processes can be divided into three general approaches. The first involves a smooth phase modulation, as provided by linear chirp. Results from this search include two-photon excitation,[6–9] and the yield of chemical reactions.[10–12] The second involves modulation of the laser pulses, using a pulse shaper,[13] to achieve specific time-frequency profiles. Results from this search include control of second harmonic generation (SHG) (Ref. 14) and two-photon excitation[15–18] using a sine or step phase function. The third involves closed-loop learning algorithms,[19,20] which converge towards the "optimal" pulse shape as defined by a series of phases and amplitudes in the mask. Results from this search include adaptive pulse compression,[21] one- and two-photon transitions in atoms,[22] and methods based on parameterized phase functions to compress pulses, optimize the SHG and two-photon transitions in isolated atoms and diatomics.[23] With adaptive control has come the optimization of electronic population transfer,[24,25] Raman transitions,[26,27] and control of chemical reactions.[28,29]

Here we describe the technique multiphoton intrapulse interference (MII) and its application to control multiphoton processes in large organic molecules in solution. The method is based on rationally designing an electric field required to achieve a particular target with a minimum number of parameters. The method is based on calculating the amplitude of the nth-order electric field and comparing it to the absorption spectrum of the molecules being controlled. This provides a strong physical understanding of the control process, which can be very useful in the interpretation of experiments where the field is optimized by a learning algorithm.

We begin with a brief review of the theory of multiphoton transitions and the effect of phase shaping on MII. The experimental section gives details about the laser system, the pulse shaper, and the different samples studied. The results section presents data obtained for two- and three-photon excitation for several different pulse shaping parameters. The data are also compared to simulations calculated with no adjustable parameters. The Discussion explores details of MII and explores the issue of phase interference versus pulse lengthening. The Conclusion summarizes the lessons learned here and gives a perspective for interpreting some previous experiments from other groups involving phase control in condensed phases.

II. THEORY

Multiphoton processes are maximized when the total energy $\sum_{i=1}^n \hbar \omega_i$ is resonant with a particular nth-order transition. As realized by Broers *et al.*,[15,16] two-photon transitions can focus the energy from an ultrafast pulse into a narrow frequency distribution; just like Fresnel diffraction can be used to construct a focusing lens. Conceptually, MII takes advantage of the interference term that is associated with the phase of each frequency ω_i within the pulse that contributes to the multiphoton process and can enhance or what may be as valuable, suppress a multiphoton transition. The effective electric field that drives the two-photon process through the

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induced (nonlinear) polarization is proportional to $E^2(t)$ (in the absence of intermediate resonance at the one-photon level). Its Fourier transform $E^{(2)}(\omega)$ determines the frequency response at the two-photon level. To determine the amplitude of the two-photon effective field at $2\omega_0$ we calculate[15,16]

$$E^{(2)}(2\omega_0) \propto \int_{-\infty}^{\infty} E(\omega_0 - \Omega)E(\omega_0 + \Omega)d\Omega, \qquad (1)$$

where spectral detuning is $\Omega = \omega - \omega_0$ and ω_0 is carrier frequency of the pulse. The formula integrates over all the detuning combinations that add up to $2\omega_0$.[16] Each spectral component $E(\Omega)$ can be expressed as real amplitude $|E(\Omega)|$ and phase $\varphi(\Omega)$ in complex form $E(\Omega) = |E(\Omega)| \times \exp[i\varphi(\Omega)]$. For a two-photon transition

$$E(\Omega)E(-\Omega) = |E(\Omega)||E(-\Omega)|\exp[i\{\phi(\Omega) + \phi(-\Omega)\}], \qquad (2)$$

where the exponential component carries the interference between different frequency components. A phase-modulated pulse can maximize or minimize the interference term in the exponential to suppress or enhance multiphoton excitation, respectively. We call this effect multiphoton intrapulse interference.[5]

In the early investigations on two photon excitation with shaped pulses it was clear that phase interference could be used to control atomic transitions,[17] but it was not clear if this method could be used to control two- and three-photon absorption of large molecules in solution because they have no sharp absorption band. We have recently shown that MII can be used to control nonlinear optical excitation (two- and three-photon laser induced fluorescence) in such systems including proteins.[5] Those experiments involved a phase mask defined by a cosine function with controlled amplitude, period, and phase. Here we demonstrate that the addition of linear chirp, a quadratic phase delay function of frequency, to the cosine function yields order of magnitude greater contrast and permits the selective control between two- and three-photon processes. We concentrate on the effect of chirp because it occurs naturally when optical pulses propagate through condensed phase media. Therefore, it is important to determine if chirp enhances or diminishes the desired optical control.

The phase of each frequency in the pulse $\varphi(\Omega)$ is defined for all our experiments by

$$\varphi(\Omega) = \alpha \cos(\gamma\Omega - \delta) + \tfrac{1}{2}\phi''\Omega^2 + \tfrac{1}{6}\phi'''\Omega^3, \qquad (3)$$

where α is the maximum phase retardation, $\gamma = 2\pi N/(\Omega_{\max} - \Omega_{\min})$ determines the period N of the phase function (over the entire spectrum 770–830 nm), δ determines the position of the mask with respect to the spectrum of the pulse, ϕ'' is the amount of quadratic phase modulation (linear chirp in the time domain), and ϕ''' is the amount of cubic phase modulation (quadratic chirp in the time domain). The main advantage of defining the pulse with a minimum number of control parameters is that the amplitude of the nth-order electric field can be easily calculated using an extension of Eq. (2).[5] For three-photon excitation, in the absence of intermediate resonances we obtain

$$E^{(3)}(\Delta) \propto \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\Omega_1 d\Omega_2 |E(\Omega_1)||E(\Omega_2)|$$
$$\times |E(\Delta - \Omega_1 - \Omega_2)|\exp\{i[\varphi(\Omega_1) + \varphi(\Omega_2)$$
$$+ \varphi(\Delta - \Omega_1 - \Omega_2)]\}, \qquad (4)$$

where each photon in the three-photon transition is spectrally detuned by an amount Ω_1, Ω_2 or $(-\Omega_1 - \Omega_2)$, Δ is the detuning from the third-order multiple of the carrier frequency of the pulse $(\omega - 3\omega_0)$, $|E(\Omega_i)|$ and $\varphi(\Omega_i)$ are the amplitude and phase of the intermediate frequencies i that add up to the third-order transition.[5]

In Fig. 1, we illustrate how changes in the phase mask given by Eq. (3), change the temporal profile of the pulse $|E(t)|^2$ and the spectrum of the nth-order electric field $|E^{(n)}(\Delta)|^2$. First, note that the first order spectrum of the electric field is not affected by the phase function because there is no interference term at this order. All cases are compared to transform limited (TL) pulses (thin line). For case (a), a sine function, we see that the second order field is focused to a much narrower bandwidth compared to TL pulses, the amplitude at the center wavelength matches that for TL pulses. The third order spectrum is narrower and weaker. For case (b), a cosine function, we see that the amplitude of the second order field is reduced by one order of magnitude while the third order field is reduced by two orders of magnitude. For case (c) a displaced sine function, the second order spectrum is narrow and detuned from the center frequency, the third order spectrum is also detuned and weaker than TL pulses. Case (d) corresponds to positive quadratic phase modulation. The second and third order spectra are not affected, only their amplitude is, which decreases by a factor of 4 or 10, respectively. Case (e) corresponds to negative cubic phase modulation. The second and third order spectra are narrower. This is caused by an effect similar to that observed for the sine function. A quantitative comparison between the different time profiles obtained for the shaped pulses is given in the discussion section. Clearly in all cases, the shaped pulse (darker line) is longer than the TL pulse.

In Fig. 2, we explore the combination of certain phase functions with quadratic phase modulation. This exploration is of interest because quadratic phase modulation (linear chirp) occurs naturally when ultrashort pulses propagate through optical media. For example, if a laser (centered at 800 nm) propagates through 100 mm of water it acquires 2480 fs^2 of positive chirp.[30,31] Cases (a) and (b) combine a sine function with positive or negative chirp, respectively. The temporal profile is identical in both cases. The second and third order spectra are shifted from the central frequency. Interestingly, a change in sign in the sign of ϕ'' leads to a shift from redder to bluer frequencies in the peak wavelength of the second and third order spectra. Cases (c) and (d) combine a cosine function with positive or negative ϕ'', respectively. For positive chirp, the two functions cancel their effects near the center of the pulse. This leads to a pulse that is close to TL except for some wings. The second and third order spectra are slightly narrower and attenuated compared to TL pulses. For negative chirp, the phase modulation is

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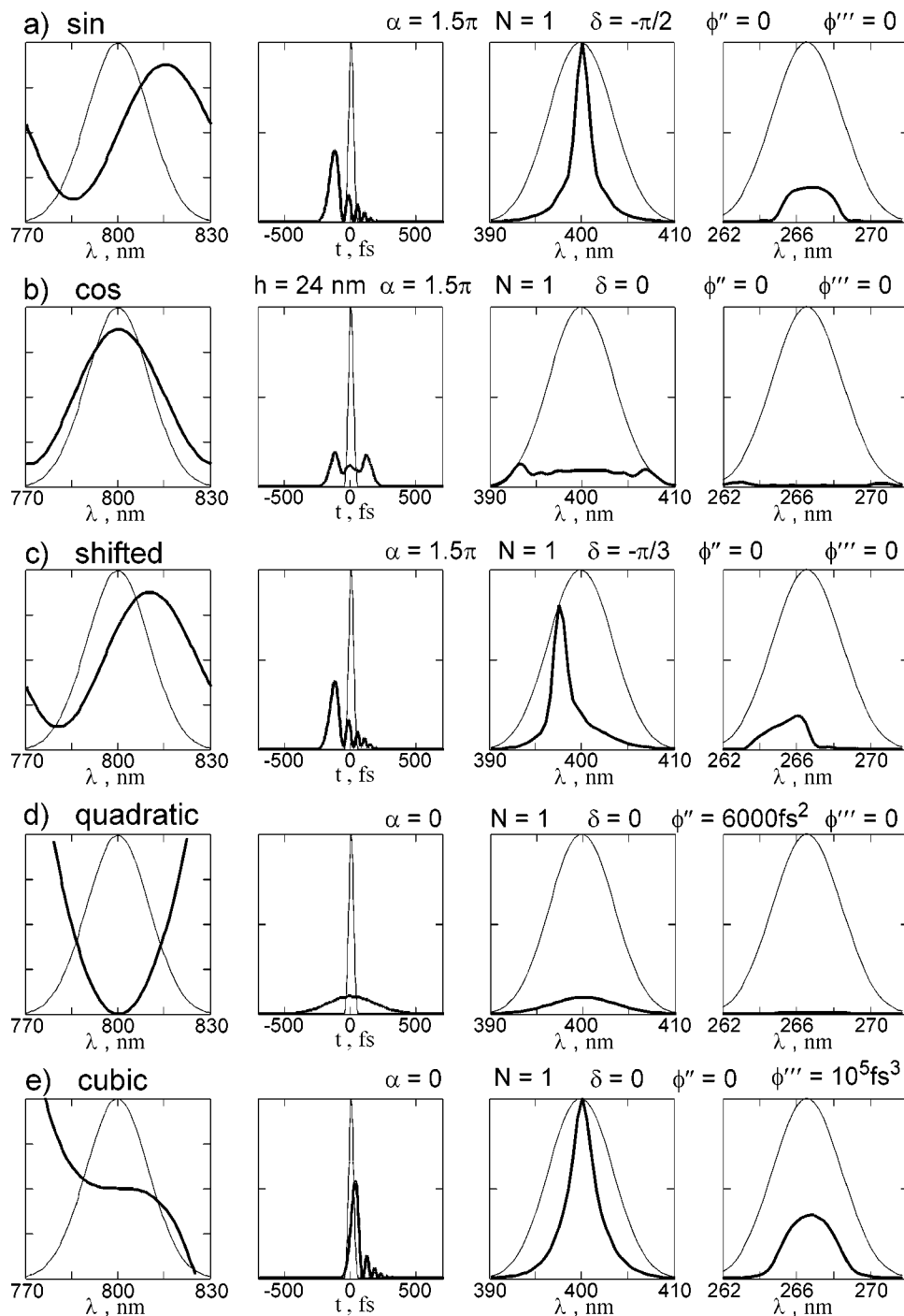Multiphoton intrapulse interference: Control   3189

FIG. 1. Multiphoton intrapulse interference effects for different phase functions: The first column shows the first order spectrum of the pulse and the phase function (dark line). The second column shows the transform limited pulse and the temporal profile of the shaped pulse (dark line). The third column shows the amplitude square of the second order spectrum for TL pulses and for the shaped pulses (dark line). The fourth column shows the amplitude square of the third order spectrum for TL pulses and for the shaped pulses (dark line). The following different phase functions are shown: (a) sine, (b) cosine, (c) shifted sine, (d) linear chirp, and (e) quadratic chirp. The relevant parameters for each phase function are given in the figure.

accentuated. This leads to very broad temporal pulses, very weak second, and third order spectra. For these cases, the change in sign of ϕ'' makes a very large difference. Case (e) combines negative cubic modulation ϕ''' with positive quadratic phase modulation. The effect is similar to case (a), where the second and third order signal is slightly detuned to longer wavelengths. In this case, the third order output is highly attenuated. Changing the sign of ϕ'', not shown, changes the sign of the detuning as observed in case (b).

From the calculations presented in Figs. 1 and 2, we learn that the phase function described by Eq. (3), achieves much more than the simple attenuation of the peak intensity of the laser pulse. The nth order spectrum can be tuned to specific resonances and the phase can be used to attenuate third order processes by two orders of magnitude. Given that higher nonlinear processes require higher peak intensities this results seems trivial, however, when third order processes cause irreparable damage of optical elements or living tissue it is useful to know how to suppress them. The simulation in Fig. 1 show that simple attenuation or attenuation using only quadratic chirp is not as efficient as the addition of a cosine function. The cosine function ($\delta = 0$) achieves maximum spreading of the pulse, well beyond what quadratic chirp alone achieves.

The spectra calculated for Fig. 1 are the spectra that the molecules experience in the presence of a phase modulated
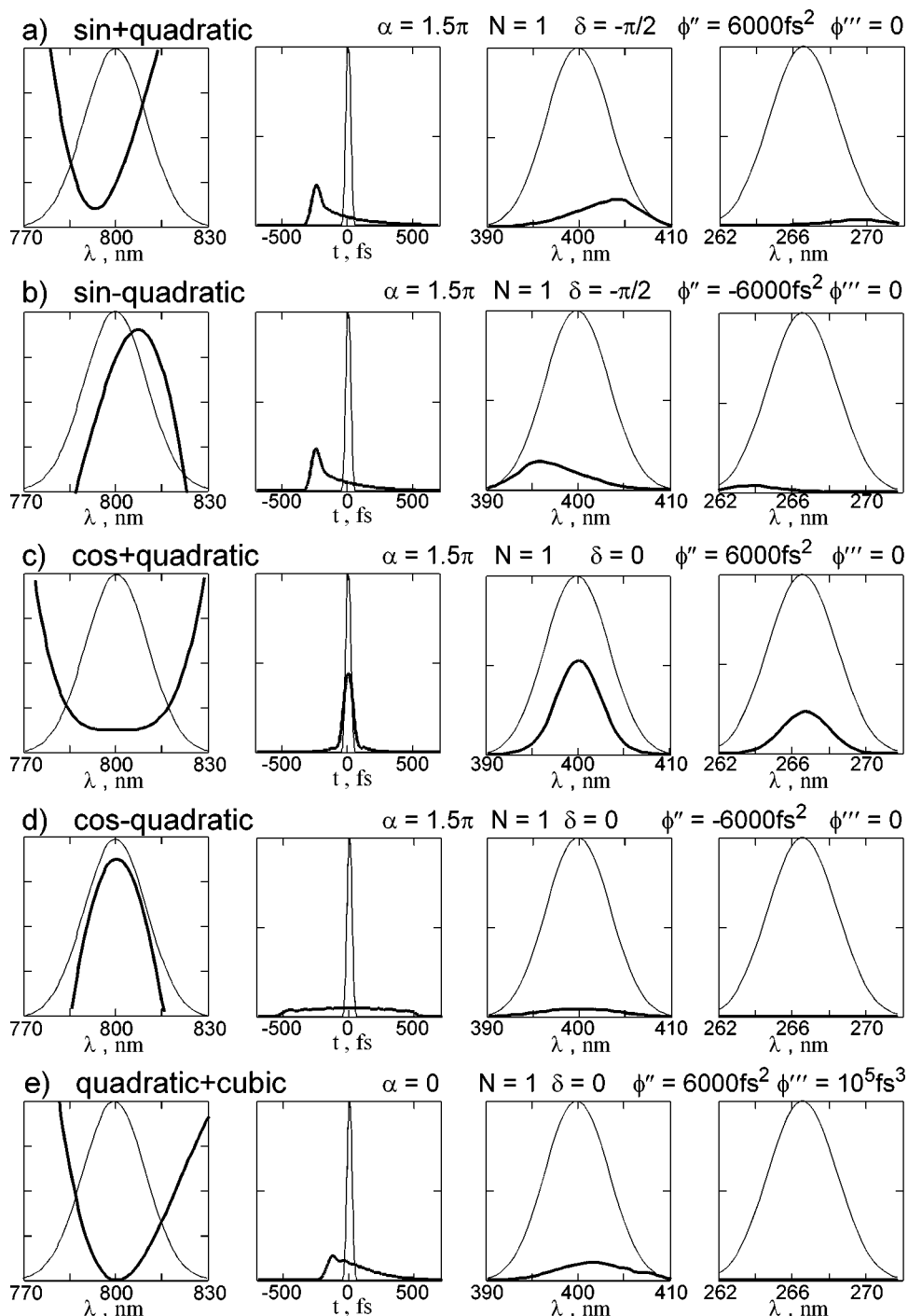
FIG. 2. Multiphoton intrapulse interference effects for different phase functions in the presence of quadratic chirp: The first column shows the first order spectrum of the pulse and the phase function (dark line). The second column shows the transform limited pulse and the temporal profile of the shaped pulse (dark line). The third column shows the amplitude square of the second order spectrum for TL pulses and for the shaped pulses (dark line). The fourth column shows the amplitude square of the third order spectrum for TL pulses and for the shaped pulses (dark line). The following different phase functions are shown: (a) sine and positive chirp, (b) sine and negative chirp, (c) cosine and positive chirp, (d) cosine and negative chirp, and (e) quadratic chirp and positive linear chirp. The relevant parameters for each phase function are given in the figure.

laser pulse. The molecular response to the electric field is determined by calculating the amplitude of the frequency dependent nonlinear susceptibility of the molecule multiplied with the nth order electric field.[32] In the case of very sharp multiphoton absorption lines (as in isolated atoms) action of the nth field depends primarily on $|E^{(n)}(\Delta)|^2$ at the resonant frequency $\Delta = \omega - n\omega_0$. In the case of large molecules in solution the action of the nth order electric field depends only from the amplitude of this field $|E^{(n)}(\Delta)|^2$ integrated over the broad nonlinear excitation spectrum $g^{(n)}(\Delta)$ because of the extremely fast intramolecular phase relaxation. Here our concern focuses control of large molecules in condensed phase. Therefore, we assume a broad absorption

spectrum ignoring intramolecular dynamics to simulate our experimental results according to

$$S^{(n)} \propto \int_{-\infty}^{\infty} g^{(n)}(\Delta) |E^{(n)}(\Delta)|^2 d\Delta. \tag{5}$$

In the two limits (isolated atom or large molecule in solution) the outcome is independent of the interaction between the individual phases $\varphi^{(n)}(\Delta)$ and the intramolecular dynamics. We have found this to be a very good approximation in our studies of large molecules in condensed phase.[5] The role of intramolecular dynamics becomes important in the study of laser control of gas phase molecular dynamics.[33–37]

III. EXPERIMENT

The experiments were performed using an ultrashort ~50 fs pulse regeneratively (1 kHz) amplified Ti:sapphire laser with ~1 mJ/pulse. The beam was sent through the zero-dispersion pulse shaper consisting of two gratings, two lenses, and two 128-pixel liquid crystal-based arrays at the Fourier plane. The programmable spatial light modulator (CRI, Inc.) was calibrated so that phase retardation at any given frequency could be accomplished without changes in the output polarization and amplitude. Phase retardation was calibrated by determination of accurate retardation versus voltage curves for each phase mask. We operated within the lower voltages with a measured accuracy of one degree (~0.0074 fs). When no phase modulation was applied, the pulses after the pulse shaper arrangement were near transform-limited with FWHM 50 fs and a maximum energy of 5 μJ. For most experiments the laser was attenuated down to 0.5 μJ. The magnitude of the quadratic phase modulation was controlled by translation of a compressor grating in the laser amplifier. Reproducibility was ensured using a mechanical indicator with 2.5 μm resolution. The quadratic phase modulation was calibrated using SHG frequency resolved optical gating.[38] The experiments presented here depend critically on the input pulses. We were very careful to use transform limited pulses to avoid these types of problems. We found that the presence of a small cubic phase modulation, for example, can distort the observed multiphoton response.

A 200 mm focal length lens focused the laser onto a quartz cell containing the dye solution. Fluorescence was detected at right angles with f/1 optics and directed to a 0.27 m spectrometer with a liquid nitrogen cooled CCD detector. In most cases we integrated the fluorescence signal for each phase function. Typical data acquisition required the signal detection for 128 different phase functions, twice. Data was collected for approximately 100 laser pulses for each phase functions and the entire scan was repeated four times.

Experiments were carried out on Coumarin 500 (Exciton), and *trans*-stilbene (Eastman), both 0.01 M solutions in methanol. The fluorescence was detected as a function of chirp (ϕ'') and phase shift of the mask (δ) across the spectrum, centered near 800 nm, with a bandwidth (FWHM) of 24 nm. For all cases the values $\alpha = 1.5\pi$ and $N = 1$, from Eq. (3), were kept constant. For the experiments on two- and three-photon excitation in the same solution we made a solution of Coumarin 500 and para-terphenyl 10^{-6} and 10^{-4} M, respectively, in cyclohexane. For these measurements $\alpha = 2.5\pi$, $N = 1$, and $\phi'' = 2000$ fs^2.

IV. RESULTS

Figure 3(a) displays the signal obtained for two-photon laser induced fluorescence (LIF) for Coumarin 500 as a function of ϕ'' and δ (darker shades indicate higher intensity). Notice that maximum and minimum values for the signal can be easily found for certain combinations of δ and ϕ'', with contrast ratios or two and more orders of magnitude. The data is normalized such that the signal induced by transform limited pulses equals unity. The maximum observed signal
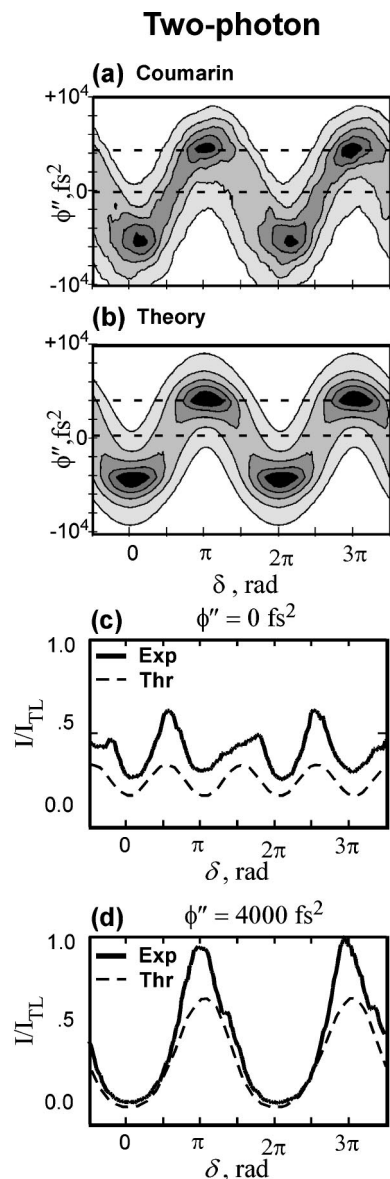

FIG. 3. Control of two-photon laser induced fluorescence in Coumarin 500 with multiphoton intrapulse interference. The contour-plots indicate increasing yield (darker color) of 500 nm fluorescence as a function of chirp ϕ'' and phase shift δ. (a) Experimental measurement of the yield of two-photon laser induced fluorescence from Coumarin 500. (b) Theoretical simulation of the data. (c) A cut through the experimental data for $\phi'' = 0$ fs^2, together with a theoretical simulation of the signal. (d) A cut through the experimental data for $\phi'' = 4000$ fs^2, together with a theoretical simulation of the signal.

matches that obtained with transform limited pulses. In general, for low intensity excitation, in the absence of saturation or an intermediate resonance, transform limited pulses optimize multiphoton transitions. The data in this article was obtained under these conditions.

In Figs. 3(b)–3(d) we present simulations of the data, calculated with Eqs. (1) and (2). Notice that the overall trends are perfectly matched by the theory. To provide a better quantitative perspective cuts for $\phi'' = 0$ and 4400 fs^2 are shown in Figs. 3(c) and 3(d), respectively. Differences between the simulations (no adjustable parameters) and the data are small and may indicate that intramolecular dynamics
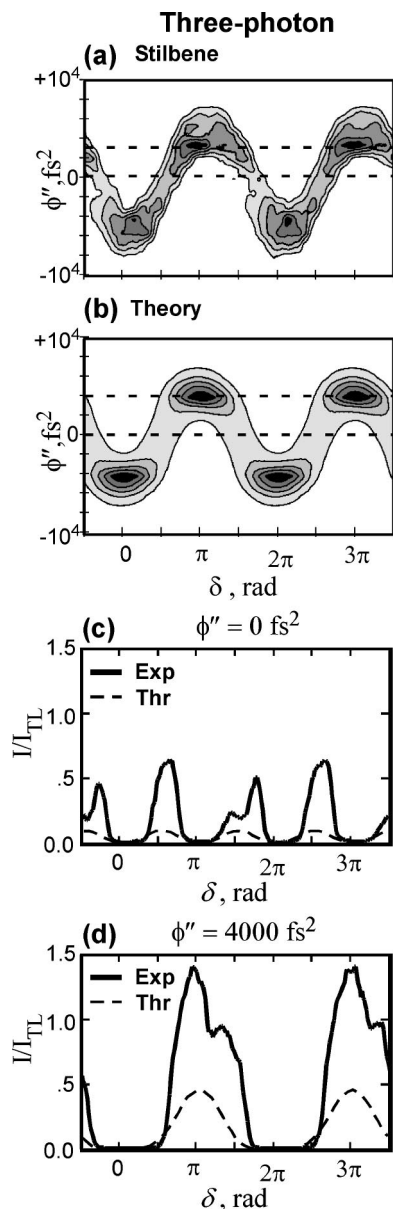
Three-photon

FIG. 5. (a) A cut along the experimental data shown in Figs. 3(a) and 4(a) showing the variation of two- (dashed line) and three-photon (solid line) induced fluorescence as a function of δ for a fixed amount of chirp $\phi'' = 2000$ fs^2. (b) A cut along the experimental data shown in Figs. 3(a) and 4(a) showing the variation of two- (dashed line) and three-photon (solid line) induced fluorescence as a function of ϕ'' for $\delta = \pi/2$. Notice that the smoother onset of two-photon processes creates regions where the lower order process dominates even under strong-field excitation. The arrows indicate the condition when two photon processes are not suppressed but three photon processes are.

and 4(d), respectively. Differences between the simulations and the data are greater for three-photon excitation. Interestingly, the signal obtained for $\delta = \pi$ and 3π in Fig. 4(d) is greater than that observed for transform limited pulses.

In general, both two- and three-photon processes have a similar response phase modulation as seen in Figs. 3(a) and 4(a). However, there are certain sets of parameters that can be chosen where the two-photon LIF signal is much more intense than the three-photon LIF signal. One such pair of values is chosen from Figs. 3 and 4. Cuts of the three-dimensional data with fixed ϕ'', are shown in Fig. 5. The arrows indicate the positions where the maximum ratio two-:three-photon excitation is observed; coinciding with a three-photon "dark" pulse. As can be seen in Fig. 5(b), for certain pulse-shaping conditions, three-photon LIF exceeds the value obtained for transform limited pulses (normalized to unity). This observation may indicate some degree of self-focusing or that additional excitation pathways are available through real electronic intermediate states.[39]

In Figure 6 we compare two- and three-photon excitation processes in a single sample containing a mixture of two different dyes. One dye has an absorption band centered at 400 nm (Coumarin 500) and another has an absorption band centered at 267 nm (p-terphenyl). The experimental results are shown as a function of δ, with $\alpha = 2.5\pi$ and $\phi'' = 2000$ fs^2 in Fig. 6(a). The two photon induced fluorescence signal, collected at 500 nm, is shown as a thin line, the three-photon induced fluorescence signal, collected at 350 nm, is shown as a heavy line, and the ratio between the two is shown as a dashed line. The contrast ratio observed between maximum and minimum signal for 3-photon induced fluorescence is almost four orders of magnitude. In fact the signal in the region of δ near zero is comparable to the systematic noise level, the reported four orders of magnitude is a lower limit. The contrast ratio observed for two-photon induced fluorescence, in this case is one order of magnitude.

FIG. 4. Control of three-photon absorption in *trans*-stilbene with multiphoton intrapulse interference. The contour-plots indicate increasing yield (darker color) of 350 nm fluorescence as a function of chirp ϕ'' and phase shift δ. (a) Experimental measurement of the yield of two-photon laser induced fluorescence from Coumarin 500. (b) Theoretical simulation of the data. (c) A cut through the experimental data for $\phi'' = 0$ fs^2, together with a theoretical simulation of the signal. (d) A cut through the experimental data for $\phi'' = 3400$ fs^2, together with a theoretical simulation of the signal.

play a minor but detectable role in multiphoton excitation.

Figure 4(a) displays the signal obtained for three-photon LIF for t-stilbene as a function of ϕ'' and δ (darker shades indicate higher intensity). Notice that maximum and minimum values for the signal can be easily found for certain combinations of δ and ϕ'', with contrast ratios or two and more orders of magnitude. The data is normalized such that the signal induced by transform limited pulses equals unity.

In Figs. 4(b)–4(d) we present simulations of the data, calculated with Eqs. (1) and (3) (no adjustable parameters). Notice that the overall trends are perfectly matched by the theory. Cuts are shown for $\phi'' = 0$ and 3400 fs^2 in Figs. 4(c)
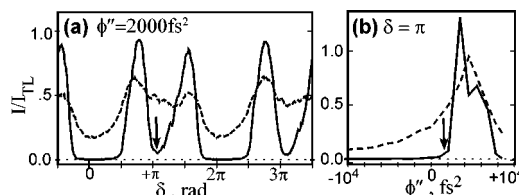
V. DISCUSSION

Our findings indicate that multiphoton processes in condensed phase molecules, where the inhomogeneous and homogeneous broadening is large, can be controlled using only
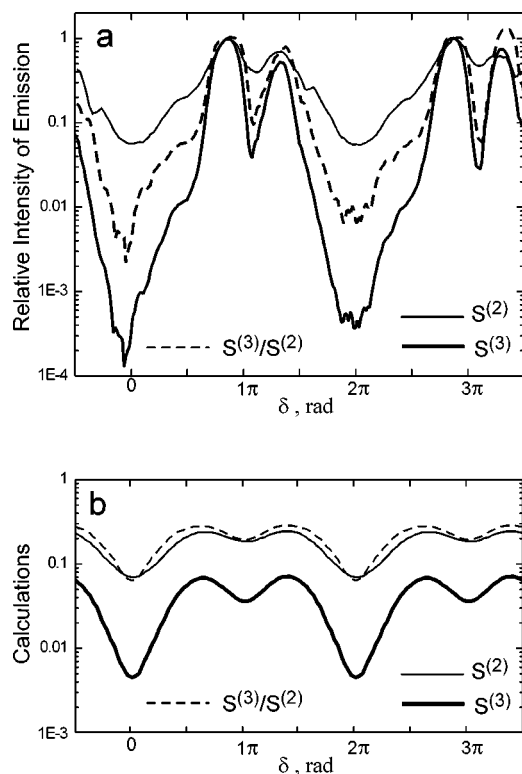
FIG. 6. Two- and three-photon excitation of large organic molecules in a single mixture as a function of phase modulation. Solid thin line is normalized on the transform limited condition two-photon induced fluorescence, solid thick line is normalized on the transform limited condition three-photon induced fluorescence, both emissions was excited in the mixture of 10^{-6} M para-terphenyl (detected at 350 nm) and 10^{-4} M Coumarin 500 (detected at 500 nm) in cyclohexane with phase modulation determined by Eq. (3) and $\alpha=2.5\pi$, $N=1$, and $\phi''=2000$ fs^2 as function of parameter δ. The dashed line is ratio of three-photon excitation to the two-photon excitation.

a few control parameters. We have explored the combination of a cosinusoidal function with linear chirp to show large contrast for two- and three-photon transitions. Our results indicate chirp has an important and nontrivial coupling with other phase modulation functions. This is particularly important if phase modulated pulses are used in applications that require propagation through dispersive media. Here we discuss to what extent control of multiphoton excitation depends on intrapulse interference and to what extent to pulse lengthening.

In comparing the two different signals presented in Fig. 6(a), we consider what role pulse lengthening plays in explaining the observed results. For this analysis we neglect interference and intramolecular dynamics leaving only peak intensity (a function of pulse duration). The signal observed following n-photon excitation $S^{(n)}$ is proportional to $I^n\tau$, where I^n is the intensity of pulse to the nth power, and τ is its duration. The energy of the pulse is given by $W\propto I\tau$, therefore the signal is $S^{(n)}\propto W^n\tau^{1-n}$. With this simple expression we can calculate the ratio between the two nonlinear signals using $S^{(n)}/S^{(n-1)}\propto W/\tau$. If the energy of the pulse is constant then

$$S^{(n)}/S^{(n-1)}\propto \tau^{-1} \qquad (6)$$

for any value of n. If we start with $n=2$, we find that the ratio is just $S^{(2)}$ because $S^{(1)}$ is independent of changes in the pulse duration (in the absence of saturation). This analysis depends only on the change in peak intensity and ignores intramolecular dynamics or quantum mechanical interference. The result, however, is very valuable to ascertain the effect of pulse duration, and indicates that the ratio $S^{(n)}/S^{(n-1)}$ is proportional to the two-photon signal $S^{(2)}$ for all n.

The simulation of $S^{(2)}$ and $S^{(3)}$ [no adjustable parameters using Eq. (5)] is shown in Fig. 6(b). Notice that $S^{(2)}$ and $S^{(3)}/S^{(2)}$ (dashed line) are very similar. Under these conditions the pure interference effect of MII is only (10%–40%) from the full contrast ratio. A much stronger MII effect is obtained for shorter laser pulses and multiphoton bands that are detuned from the center frequency of the pulse. Figure 6(a) shows the ratio of the experimental two- and three-photon signal (dashed lines). We can see that the ratio does not coincide with the 2-photon excitation. The experimental ratio of $S^{(3)}/S^{(2)}$ shows one order of magnitude greater contrasts than are predicted by theory. The main discrepancy can be attributed to the three-photon excitation signal, which differs significantly from the simulation. We cannot explain this difference based on pure two- and three-photon effects. It is possible that higher order processes and other electronic states that are detuned from the center of the excitation wavelength play an important role in the observed signal. We note that the greatest differences occur when the three-photon induced signal is minimized.

Here we make an effort to provide a quantitative analysis of pulse lengthening effects. First we determine the pulse duration Δt, using

$$\Delta t = \sqrt{\int |E(t)|^2(t-t_c)^2 dt}/\sqrt{\int |E(t)|^2 dt}, \qquad (7)$$

where the center of the pulse is defined by $t_c = \int |E(t)|^2 t dt/\int |E(t)|^2 dt$. We then calculate the effect of phase modulation on the expected two- and three-photon signal, $S^{(2)}$ and $S^{(3)}$ using Eq. (5) with $g^{(n)}(\Delta)=1$ (to eliminate spectral tuning effects). We compare these simulations to the inverse of the pulse duration Δt^{-1} and to the squared inverse pulse duration Δt^{-2} for second- and third-order effects, respectively. The results are shown in Fig. 7. When phase modulation consists of linear chirp only, we find that there is excellent agreement between the predicted effects based on pulse duration and simulated effect based on MII [Eq. (5)] [see Figs. 7(a) and 7(b)]. Interestingly, when phase modulation includes a cosine function as in Eq. (3), the agreement between the predicted effect based on pulse duration and the simulated effect based on MII [Eq. (5)] is not good, differing by 60% for two-photon effects and 300% for three photon effects at $\delta=0.5$ or 1.5π. In Figs. 1 and 2, we showed that the temporal profile of the pulse can be smooth or it can be complex (multiple pulses). When it is complex pulse duration fails to predict the observed signal. In fact, pulse duration [Eq. (7)] predicts a maximum for $\delta=\pi$ [see Figs. 7(c) and 7(d)] but this turns out to be a local minimum in the simulated signal based on Eq. (5). The experimental data agree with the predicted minimum [see Figs. 7(e) and 7(f)].
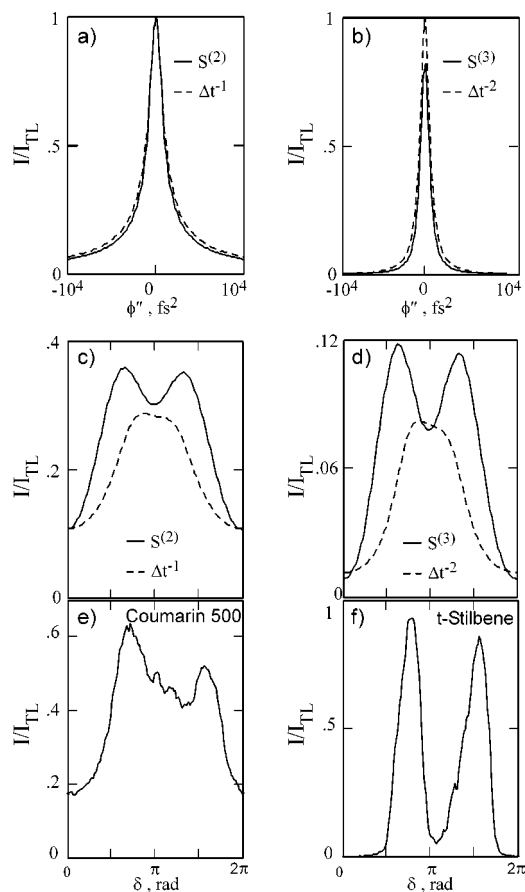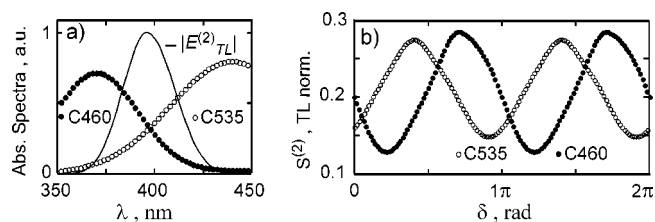
FIG. 8. Multiphoton intrapulse interference with 10 fs pulses. (a) Absorption spectrum of Coumarin 460 (dots) and Coumarin 535 (open dots). The spectrum of the laser is shown with the thin line. (b) Two-photon induced signal as a function of δ for the two different coumarin dyes. The values are normalized to transform limited pulses.

FIG. 7. Effect of pulse duration and spectral amplitude of the electric field on two- and three-photon excitation. For the (a)–(d) the solid line is the signal calculated according to $S^{(n)} \propto \int |E(\Delta)^{(n)}|^2 d\Delta$, the dashed line is calculated signal according to $S^{(n)} \propto \Delta t^{n-1}$. (a,b) Dependence of expected signal from quadratic phase modulation ϕ'', with $\alpha=0$. (c,d) Dependence of expected signal from phase δ with $\alpha=1.5\pi$, $N=1$, and $\phi''=2000$ fs^2. (e,f) Experimentally measured dependence of fluorescence yield as a function of δ with $\alpha=1.5\pi$, $N=1$, and $\phi''=2000$ fs^2 for the solutions of Coumarin 500 (two-photon excitation) and *trans*-stilbene (three-photon excitation).

This observation leads us to the conclusion that Eq. (5) based on MII is a much better predictor of *n*th order processes than simple pulse duration of the electric field.

The analysis, so far, has ignored the *n*th order spectrum of the molecule $g^{(n)}(\Delta)$. MII spectral tuning of the higher order spectrum of the field can also be used to preferentially excite one type of molecule in a mixture. Walowicz *et al.*,[5] demonstrated this experiment using 50 fs pulses and a mixture of two different coumarin laser dyes. In essence, the second order spectrum of the laser was tuned from one dye to the other. In Fig. 8 we show a simulation of the experiment obtained for 10 fs pulses.[5] Notice that with shorter pulses selective excitation becomes possible purely due to MII.

Control of multiphoton processes with phase modulated ultrashort laser pulses has been reported in the literature.[6–8] For example a 40% effect had been measured in the two-photon excitation of green fluorescent protein using linear chirp.[8] The main difference between those experiments and experiments from our group[5] is laser intensity. We have avoided saturation while those measurements were in the

saturated regime. In the case of saturation, any form of phase modulation causes pulse lengthening and this alleviates the saturation. One of the most remarkable studies on laser control of multiphoton excitation in condensed phase involves the excitation of two different dye solutions, one containing $[Ru(dpb)_3]^{2+}$ and the other DCM.[25] In that study the authors were careful to evaluate the effect of pulse energy, linear chirp, and wavelength tuning. They found that changes due to those parameters individually were minimal, however, their adaptive pulse shaper was able to find a maximum contrast DCM/$[Ru(dpb)_3]^{2+}$ of approximately 50%. They attributed this observation to long-lived molecular phase coherences that persist during the shaped pulse (100 fs–1 ps).[25]

In our studies we have concentrated on the order of magnitude differences observed in multiphoton excitation, and these can be accounted for by the MII theory, which ignores intramolecular dynamics. In all cases, there is a residual 10%–50% difference between experiment and simulation that is not accounted for. This same difference was observed when comparing results from two-photon excitation of coumarin 500 and recombinant green-fluorescent protein, or three-photon excitation of *t*-stilbene and the concanavalin A.[5] It is possible that this difference arises from the effect of electric field phase and intramolecular dynamics. The time scale for electronic dephasing in large molecule in solution has been determined to be in the range of 30 to 70 fs.[40] Perhaps shorter pulses can better harness the contribution of intramolecular dynamics in condensed phases.

A recent publication about laser control of large molecules in solution compares excitation of two different pathways of LH2.[41] That study was conducted in the saturation regime, therefore it is very difficult to determine to what extent phase modulation caused pulse lengthening and to what extent spectral tuning and phase coherence participated in the observed ~35% ratio between the two excitation pathways. The system is ideal to explore laser control because it provides two different channels. The preferential observation of ground state dynamics following excitation with negatively chirped pulses,[42] as observed in the one-photon excitation of bacteriorhodopsin, can be explained by both saturation and intramolecular dynamics that take place as the wave packet being formed in the excited state undergoes stimulated emission.

It is becoming clear that for large molecules in the condensed phase multiphoton excitation can be controlled by a number of mechanisms, and this control can be calculated in

all cases except those involving significant saturation. (i) Changing the pulse duration, for example using linear chirp, is the simplest form of control. (ii) Changes in the amplitude of the nth order electric field caused by phase modulation. These effects can be calculated using Eq. (5) ignoring the molecular absorption spectrum ($g^{(n)}(\Delta)=1$). (iii) Spectral tuning of the nth order electric field with phase modulation, Eq. (5). (iv) Phase modulation of the nth order electric field matching intramolecular dynamics of the system. This mechanism may result in 30%–50% effects, a formula for calculation has not been provided here. In some cases, particularly in the gas phase, the laser chirp (a frequency sweep) can coincide with intramolecular dynamics. In these cases slow intramolecular dynamics without fast relaxation can effect on the excitation process.[43] (v) High intensity excitation, causes competition among a number of multiphoton processes, as well as self-phase modulation and self-focusing. The quantitative simulation of these higher order effects is challenging, but it is required to explain the most intriguing results.

VI. CONCLUSIONS

The results presented here provide information about the nonlinear excitation of large molecules in solution. The results presented in Figs. 1 and 2 indicate that the phase can be used to tune the second or third order spectrum in the frequency domain as well as suppress third and higher order excitation. The data in Figs. 3 and 4 show the effect of a cosinusoidal function and linear chirp. For certain combinations of parameters three-photon processes can be significantly suppressed. The effects presented here are not caused by simple attenuation. We have made an analysis based on pulse duration alone and showed that in some cases pulse duration predicts a maximum whereas experiments and MII simulations predicts a minimum in the signal. We presented results that showed competition between two- and three-photon excitation in a single mixture of two different dyes. The ratio between the two signals followed the trend predicted by theory but the magnitude of the control found in the experiment was much greater.

The results and analysis presented here give a clearer picture about the effect of phase modulation on nonlinear optical processes. Phase modulation is introduced in this study using a pulse shaper. The analysis presented in the first two figures shows the drastic effect that phase modulation can have on second and third order processes. Our results imply that pulse characterization is critical in all studies involving nonlinear optical processes, given that unwanted phase modulation takes place in all femtosecond laser systems.

Third and higher order excitation and nonlinear optical distortions (self-focusing, for example) are usually detrimental, making strategies for their suppression technically valuable. Our findings indicate that with a simple phase mask maximum suppression can be achieved. The phase mask may be introduced with passive optics rather than a costly pulse shaper. Suppression of three-photon process will be the object of further investigation, because in medical applications,

such as photodynamic therapy, three-photon absorption causes DNA damage.[44]

In summary, we present a pulse-shaping method based on intrapulse interference that provides control of multiphoton transitions under strong field excitation using a reduced number of parameters. The results shown here were obtained with only four control "knobs" that can be adjusted independently or can be incorporated into a learning algorithm to provide control over multiphoton transitions and nonlinear optical interactions. The method is robust and the theoretical formulation simple enough to provide predictive information. We are pursuing the application of this method to situations where nonlinear optical processes must be enhanced or suppressed, or where selective excitation (three- versus four-photon absorption, for example) is desired. The phase modulation discussed here can be introduced with simple passive optics without the need for sophisticated spatial light modulators. This advantage may lead to direct applications.

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