Laser control of physicochemical processes; experiments and applications†

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This review outlines experimental advances that have been made in laser control of physicochemical processes, with an emphasis on the 2004–2006 period. After a brief introduction, an overview of the technology available for delivering ultrashort shaped femtosecond pulses is presented. Special attention is given to recent progress on laser control of chemical reactions and the application of this concept to molecular identification. We also cover control of simpler systems such as atoms and diatomic molecules. Laser control of large molecules in solution is also reviewed from the point of view of selective spectroscopic excitation with applications in microscopy and control of nanoparticles. We conclude with an outlook that takes into account the physical limitations that will dictate the best strategies to achieve robust laser control of physicochemical processes.

1. Introduction

Presently, achieving the best performance from a femtosecond laser system requires a laser expert. The reason for this is that short laser pulses undergo nonlinear dispersion as they transmit through or reflect from any medium. Correction and pre-compensation of these distortions has been the subject of intense efforts for the last two decades, and a few automated methods are beginning to emerge that take care of this essential problem. In our opinion, this is the missing step that will permit the entrance of femtosecond lasers to industrial applications. The most important aspect of this development is the realization that although obtaining transform-limited pulses is useful, for many applications the introduction of certain phases and amplitudes achieves a new result that could not be achieved otherwise. It is this realization that will continue to accelerate the introduction of exciting applications using shaped femtosecond lasers. Here we give a brief introduction to the concepts and methodology being used and focus on the experimental developments leading to applications based on shaped femtosecond laser pulses.

To a great extent, advances in the field of laser control have been fueled by the dream of controlling chemical reactions with lasers. The prospect of determining the outcome of laser–matter interactions has inspired a broad range of scientists since the invention of the laser. At first, it seemed that simply delivering coherent photons with the right frequency would be enough to selectively cleave chemical bonds.[1,2] However, it was soon realized that energy deposited in one bond quickly redistributes along the various

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† The HTML version of this article has been enhanced with colour images.

degrees of freedom available to the system. In 1980, Nobel Prize laureate Ahmed Zewail[3] proposed using femtosecond laser pulses to control chemical reactions, beating the time for energy randomization within the molecular degrees of freedom. Warren and Zewail used laser pulses shaped in the time domain to demonstrate a photon echo response in molecular iodine.[4–9] The femtosecond colliding pulse mode-locked dye laser became available early in the 1980s,[10] allowing the first direct measurement of the timescales for chemical bond dissociation.[11,12] In 1990, the self-mode-locked Ti:sapphire laser was invented,[13] providing a solid state system with long-term stability, unlike the dye-based systems that preceded it. Nowadays, femtosecond lasers have reached the point of maturity; there are more than a dozen companies offering turn-key femtosecond laser systems, and pulse durations of some of these systems are less than 10 fs. In fact, femtosecond laser technology is about to reach the step of commoditization—when quality and cost become the key drivers.

Complementary to the development of femtosecond laser sources, techniques for pulse shaping were developed, at first to counteract phase distortion and achieve the shortest pulses. The most widely used method for pulse shaping, sometimes called Fourier synthetics, was developed by Weiner and Heritage in 1987.[14,15] In this shaper, the laser pulse is dispersed by a grating or prism and the different frequency components are focused on a spatial light modulator (SLM) where each spectral component gains retardance according to the voltage applied to each pixel or region (liquid crystal[16,17] or deformable mirror).[18] Warren was the first to use an acousto-optic-based SLM pulse shaper in the Fourier plane[6,19] and Nelson, Wefers and Weiner introduced the double masked SLM to allow control of phase and amplitude for each frequency component.[20–24]

Despite the availability of sources and shapers, it was difficult in the early days to figure out how to begin to control physicochemical processes. In 1992, Judson and Rabitz made a powerful suggestion that would kick-start the field. In their publication, they suggested the use of computer algorithms that would learn from feedback and guide a control experiment toward the shaped pulse that optimized the desired outcome.[25]

Kent Wilson, a great visionary, initiated the first systematic pursuit of laser control of chemical reactions with shaped pulses. In these first experiments, he showed how chirped pulses controlled optical transitions between ground and excited states,[26,27] multi-photon transitions,[28] and chirped excitation of Green Fluorescent Protein (GFP).[29] He also optimized regenerative femtosecond amplification,[30] prepared Rydberg wave packets,[31] controlled photo-dissociation,[32] used feedback to control the electronic population transfer in laser dye molecules in solution,[33] probed microscopic chemical environments,[34] and studied the effects of pulse shaping on the efficiency of multi-photon excitation for microscopy.[35]

This review focuses on the most recent (2004–2006) experimental development of applications (see Fig. 1) based on femtosecond pulse shaping for controlling physicochemical processes, leaving out hundreds of theoretical papers. For a perspective of work from 1926 to 1996, the reader is referred to the excellent review by Jörn Manz.[36] In other venues we have discussed experimental and theoretical perspectives predating 2004.[37,38] The number of publications related to laser control has increased to more than a thousand per year, making it impossible to comment on them all. We begin in Section 2 with a brief review of presently available technology for laser control. In Section 3 we focus on laser control of chemical processes, and the nascent area of laser control in photonic molecular recognition. Section 4 focuses on control of spectroscopic transitions and the

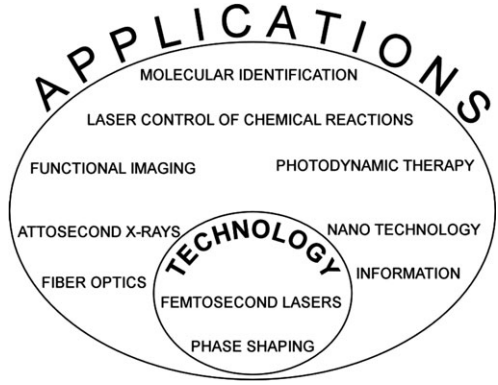

Fig. 1 Fields where applications based on laser control of physicochemical processes using shaped femtosecond laser pulses are beginning to appear.

resulting applications in the areas of microscopy and control of nanoparticles. We then conclude with some opinions about future directions and strategies based on a simple physical model.

2. Available technology for laser control

2.1. Generation of shaped femtosecond pulses

Femtosecond oscillators come in three main categories: very compact fiber based systems ($\sim$100–200 fs pulse duration), prism-compressed Ti:Sapphire systems ($\sim$10–20 fs), and chirped mirror compressed Ti:Sapphire systems ($<$10 fs). The latter can produce pulses with duration of about 5 fs[39,40] and a spectrum stretching from 600 nm up to 1100 nm, a 100 MHz repetition rate and energy per pulse up to 1 nJ. The schematic of the system used in our laboratory is presented in Fig. 2. It is based on the design of Ell,[40] and it incorporates a prism based pulse shaper.[41,42]

High energy laser systems can be divided broadly by their method of amplification into regenerative or multi-pass. Regenerative amplification provides a more efficient

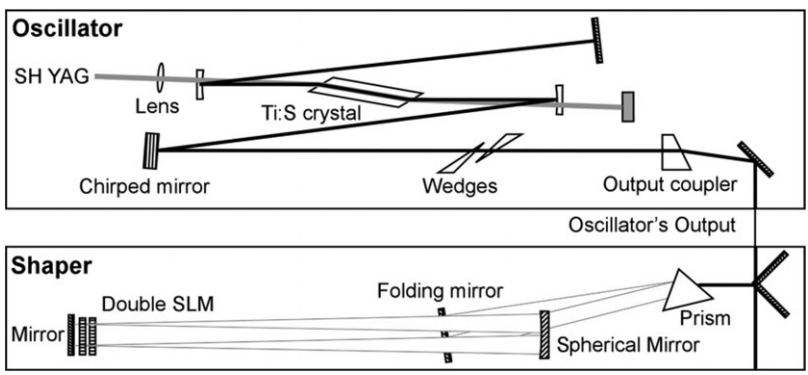

Fig. 2 Schematic of the 5 fs laser oscillator with a broadband pulse shaper. Using chirped mirrors and wedges to compensate intracavity spectral phase distortions allows generation of an octave spanning laser spectrum. The ultra-broad bandwidth shaper compensates phase distortions remaining from the oscillator and pre-compensates those farther down the beam path.

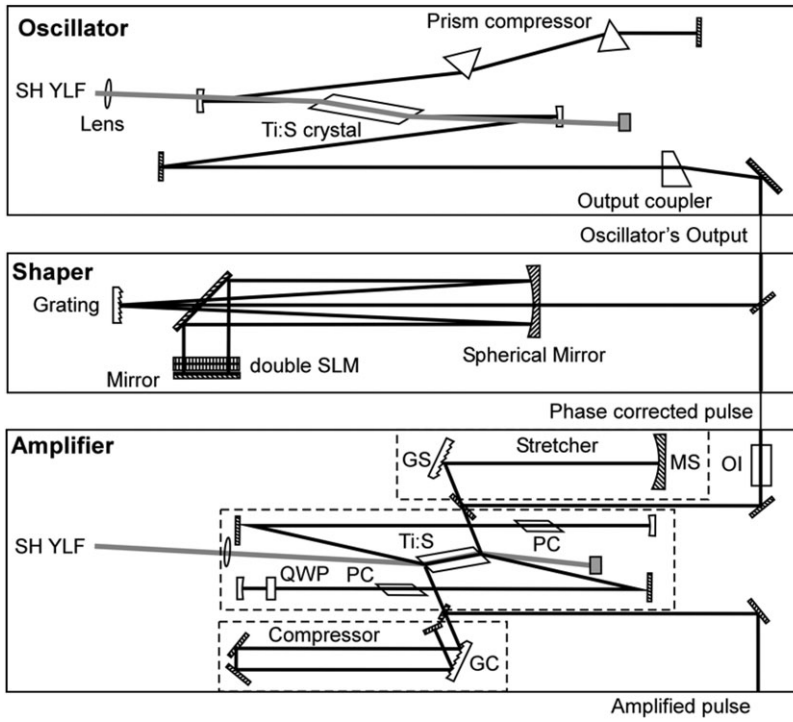

Fig. 3 Schematic of the sub-30 fs amplified laser system with internal spectral amplitude and phase correction. The pulse shaper is introduced between the oscillator and the regenerative amplifier to compensate nonlinear phase distortions introduced by the laser system itself and farther down the beam path, and to compensate for spectral narrowing in the amplifier.

use of the gain and better stability; however, the regenerative amplification cavity results in greater gain narrowing. Multi-pass amplification minimizes the number of optical elements and the number of times the laser pulse transmits through them. Shorter pulses can usually be achieved by multi-pass amplification[43] but with greater alignment difficulty and lower pulse to pulse stability than the regenerative amplification systems. The schematic of the high-energy system operating in our laboratory, capable of producing amplified phase shaped pulses with duration down to 30 fs, at a repetition rate of 1 kHz and with 0.7 mJ energy per pulse, is presented in Fig. 3. With this system we have found that most of the distortions accumulated by the laser pulse inside the regenerative amplification cavity can be compensated by the pulse shaper. At the same time, the loss introduced by the shaper is compensated at the amplifier. The result is a very stable source that in our laboratory achieves 30 fs pulse duration (33 nm bandwidth).

One of the most significant achievements in laser technology, for which the 2005 Nobel Prize was awarded, was the generation of carrier-phase stabilized trains of femtosecond pulses (time domain presentation), or octave spanning optical combs (frequency presentation). Phase stabilized optical combs will eventually replace the time clock standard, because they have two orders of magnitude greater stability than the atomic Cs clock standard.[44]

To achieve absolute phase stabilization, the full spectral width of the comb must be more than 2/3 of the carrier frequency (3.74741×10^{14} Hz); typically this comb

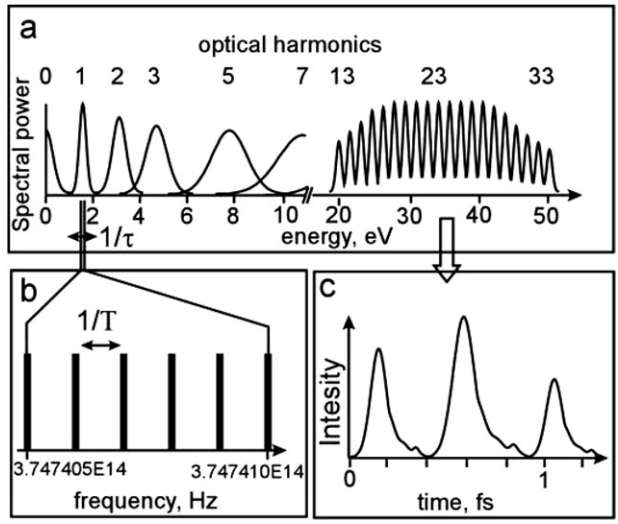

Fig. 4 Electromagnetic spectrum available using femtosecond laser systems. (a) Zero and low harmonics can be used to cover the most important spectral region for chemical manipulation. The high harmonics can reach the soft X-ray region. (b) Within the fundamental spectrum, one can discern the optical comb of longitudinal modes in the oscillator; these can be locked to provide an outstanding clocking stability. (c) When high-harmonics are phase locked it is possible to generate attosecond pulses in the X-ray region.

has 2.5×10^6 lines. It is possible to control the phase and amplitude of individual lines in an optical comb.[45,46] However, control over each of the lines in the entire bandwidth of a frequency comb is technologically impossible; if the size of each pixel were 100 microns, then the size of the required pulse shaper would be 250 m—clearly a dimension that needs to be reduced by at least two orders of magnitude. Phase stabilization technology has already made it possible to phase lock two different laser systems together to increase the spectral width of the waveform generator.[47]

We believe shaped femtosecond pulses provide the most advanced means ever available for delivering energy. With shaped femtosecond pulses one can effectively deliver optical excitation anywhere in the electromagnetic spectrum (see Fig. 4). To reach the lowest end of the energy scale, from zero to half an electron volt, shaped pulses can selectively induce stimulated Raman scattering, and for excitation above 3 electron volts and up to several tens of electron volts, two- three- and high-order nonlinear excitation can be easily achieved.[38] By controlling high harmonics, shaped pulses have been used to generate coherent X-ray beams[48–52] and attosecond laser pulses.[53–57] Projects in our laboratory are aimed at the realization of a computer-controlled universal laser source.

2.2. Using phase modulation for pulse characterization and correction

Reproducible laser control with shaped femtosecond pulses requires accurate pulse characterization. The most widely used method presently used for femtosecond pulse characterization is frequency resolved optical gating (FROG).[58] This method is good for pulses with moderate phase distortions, but is not reliable for pulses with small (<0.1 rad) or large high-order (>10 rad) phase distortions. Spectral phase interferometry for direct electric-field reconstruction (SPIDER) is another popular method

that is more reliable and provides better results for small distortions,[59] but is complicated to set up, and expensive to purchase. Because it depends on interferometry, this method is also sensitive to vibrations and changes in temperature.

Since the first demonstration by Weiner, almost all groups have used their pulse shaper to compensate phase distortions, thus achieving pulse compression.[60,61] Feedback adaptive pulse compression was successfully demonstrated by several groups.[62–68] As a proof of principle, this method works remarkably well because the feedback signal, integrated second harmonic generated (SHG) intensity, is maximized for transform limited pulses. However, this method has not been used to provide accurate measurement of spectral phase because the integrated intensity of a nonlinear process, namely the integrated SHG signal is not very sensitive to small phase distortions and the presence of noise in the signal results in large errors, especially outside the full width at half maximum of the pulse.

Recently, Dantus and Lozovoy introduced a new method, multiphoton intrapulse interference phase scan (MIIPS), that provides both characterization and correction of phase distortions down to the <0.01 rad level.[69,70] The main idea behind this method is that a calibrated phase function can be used to measure the unknown spectral phase distortions.[71] Instead of relying on the autocorrelation of two pulses, a nonlinear optical element such as an SHG crystal is used to measure the relative phase between all the different frequency components in the pulse. Not having to interfere two or more pulses in space makes this method easy to implement and makes it less sensitive to vibration and temperature changes. MIIPS provides accurate phase measurements analytically derived from the spectrum of the frequency doubled output of the laser beam. MIIPS uses the same pulse shaper to measure and compensate phase distortions, delivering transform limited pulses, as explained below.

In MIIPS, a calibrated function $f(\omega)$ is added to the unknown phase distortions $\phi(\omega)$ in the pulse . The second harmonic spectrum of the resulting pulse has a maximum amplitude at the frequency where the second derivative of the pulse has been compensated, namely when $f''(\omega) + \phi''(\omega) = 0$. Typically the calibration function is $f(\omega) = \alpha\sin(\gamma\omega - \delta)$. By measuring the SHG spectrum for each value of the scanning parameter δ, a 2D plot is recorded (see Fig. 5, left column), which is used to determine the position $\delta_{\max}(\omega)$ where the spectrum is maximized. From $\delta_{\max}(\omega)$ we extract the measured phase distortions analytically using the formula $\phi''(\omega) = \alpha\gamma^2\sin[\gamma\omega - \delta_{\max}(\omega)]$. A more detailed description of this method has been published elsewhere.[70] MIIPS has been rigorously tested and shown to provide better performance and simplicity than FROG and SPIDER.[70] MIIPS is routinely used in our laboratory for characterization and compensation of femtosecond pulses for all our experiments including those involving transmission through high numerical aperture objectives in microscopy,[70] transmission through scattering biological media,[72] reproducible femtosecond laser-induced breakdown spectroscopy,[73] remote characterization (>30 m) through air,[74] transmission and amplification in a regenerative amplifier,[75] and other applications presently in development.

Recently BioPhotonic Solutions Inc. (USA) compensated for the gain narrowing that occurs in the regenerative amplifier by amplitude modulation, and compensated the phase distortions using MIIPS to produce pulses as short as 26 fs. This technology has been licensed by Coherent Inc. (USA) and is now commercially available. Coherent's standard regenerative amplified systems can now produce 26 fs pulses with 2.5 mJ of energy per pulse. With some minor modifications, regenerative amplification should reach sub-20 fs pulse durations in the near future.

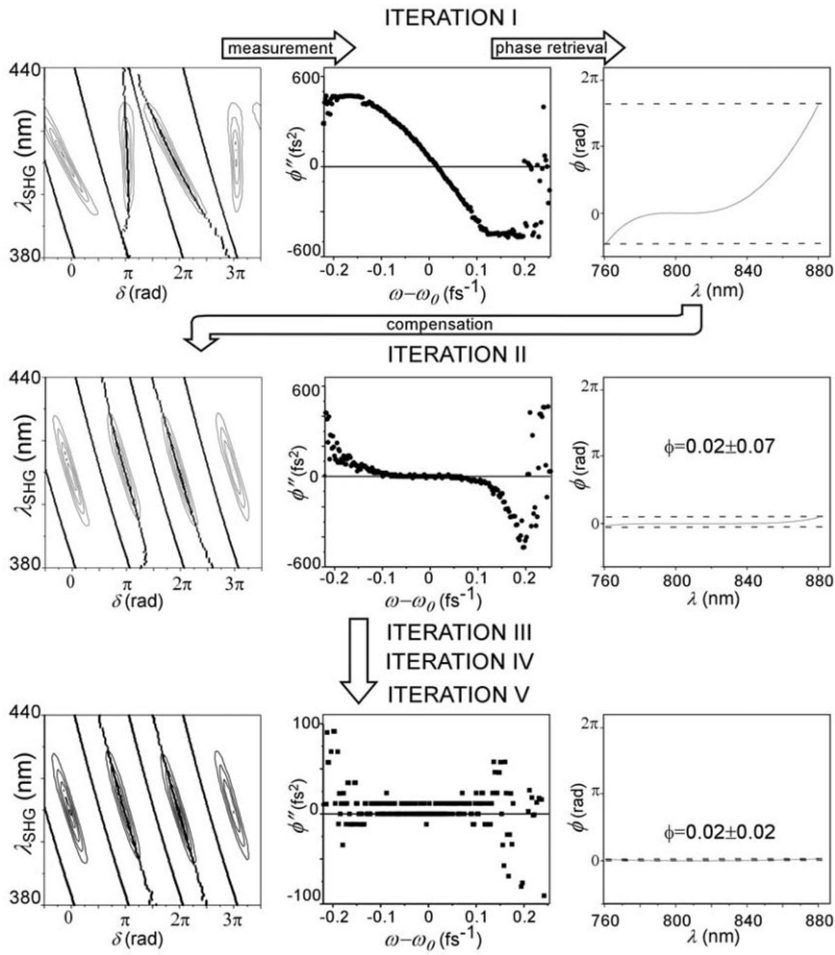

Fig. 5 Illustration of phase characterization and compensation using MIIPS. In the first iteration as a sinusoidal phase modulation with phase shift δ is scanned, SHG spectra are measured to obtain the two dimensional data shown (left). From this plot the second derivative of the spectral phase is obtained (middle), and integration results in the spectral phase (right). The system corrects for the measured phase distortions and proceeds to the next iteration. Notice that by the second iteration over 90% of the distortions have been corrected. After a small number of iterations (2–5 minutes), phase distortions are reduced to the 0.01 radian scale.

2.3. Universal binary phase, amplitude and polarization shaping

Another dimension of laser control, beyond phase and amplitude, is control of the polarization state of the field. Full control of polarization requires four independent degrees of freedom for each spectral component.[20,21,76,77] Silberberg used three shapers to control the polarization state while keeping spectral intensity constant.[78]

When using two orthogonally oriented liquid crystal spatial light modulators (see Fig. 6), the incident x-polarized light (E_x) exits with field components (E_x', E_y') that depend on the phase retardance (ϕ_A and ϕ_B) introduced by the liquid crystal elements whose slow axis is oriented at 45° and −45°. This arrangement together with an output polarizer can be used to achieve phase and amplitude shaping at each pixel.[20,21]

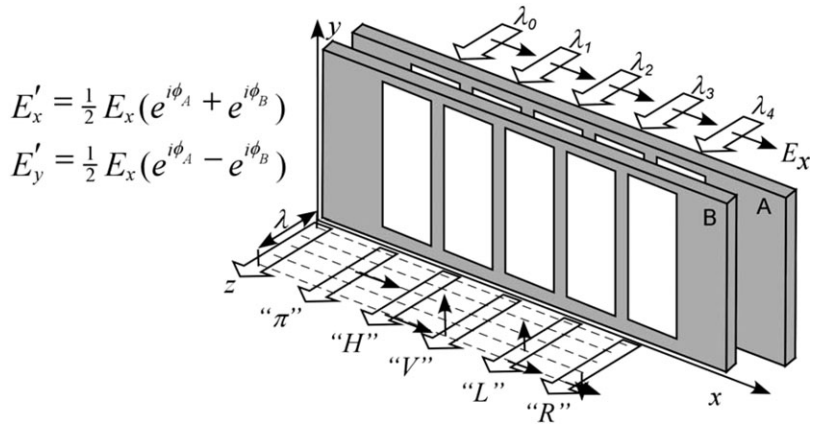

Fig. 6 Schematic of a dual mask pulse shaper used for universal binary phase shaping. For each pixel it is possible to introduce a π phase delay, rotate polarization horizontally or vertically, or to create right or left circular polarization.

It is also possible with this arrangement to generate a linearly polarized output along the x ("H") or y ("V") axes or circular left ("L") or right ("R") polarized light $E'_L = (E_x - iE_y)/2^{0.5}$; $E'_R = (E_x + iE_y)/2^{0.5}$. Using a 5-bit basis set π, H, V, L, R (see Fig. 6 and Table 1) we can produce phase amplitude and polarization shaping very efficiently. This set does not cover all possible arbitrary fields, but provides a digital binary approach for electric field manipulation that, in most cases, is sufficient to explore the sensitivity of the system to the different properties of the field.

There are other pulse shapers that have been introduced for laser control. One that has gained in popularity is commercially known as Dazzler. This system is compact because it shapes the laser pulse in the time domain.[79–81] The laser pulse is first chirped so that different frequency components enter the acousto-optic modulator at different times. While the pulse is frequency dispersed, a strong electromagnetic wave enters the crystal and shapes the pulse. The main disadvantage we see to pulse shaping in the time domain is that accurate delivery of phase or amplitude requires extremely good synchronization between the laser and the electronics driving the acousto-optic element. It is virtually impossible to know precisely the location in space and time for each frequency component because of electronic jitter limitations and because the pulse entering the crystal is not perfect. It remains to be demonstrated to what extent these uncertainties can be stabilized and corrected.

The growing availability of ultra-broad bandwidth femtosecond pulses has produced an interest in generating shaped femtosecond pulses centered at different

Table 1 Phase retardance for A and B elements to achieve binary states "0", $\phi_A^{(0)}$, $\phi_B^{(0)}$, and "1" $\phi_A^{(1)}$, $\phi_B^{(1)}$, in amplitude, phase, linear or circular polarization

	Amplitude(0, 1)		Phase (0, π)		Linear (H, V)		Circular (L, R)	
"0"	$\lvert E_x\rvert^2 = 1$		$\phi = 0$		$E_x = 1$	$E_y = 0$	$E_L = 1$	$E_R = 0$
"1"	$\lvert E_x\rvert^2 = 0$		$\phi = \pi$		$E_x = 0$	$E_y = 1$	$E_L = 0$	$E_R = 1$
$\phi_A^{(0)}$, $\phi_B^{(0)}$	0	0	0	0	0	0	$\pi/4$	$-\pi/4$
$\phi_A^{(1)}$, $\phi_B^{(1)}$	$\pi/2$	$-\pi/2$	$\pi/2$	$\pi/2$	0	π	$-\pi/4$	$\pi/4$

[a] An additional polarizer (x-oriented) is required at the output.

wavelengths. Efforts along these lines involve the use of type II parametric up-conversion[82] and the use of optical parametric amplifiers which up-convert and amplify the shaped wave form.[83–87] One more direction where significant advances in pulse shaping are being made comes from the Nelson group, which has been using two-dimensional pulse shapers to launch plasmon polariton waves whose phases and location in space are controlled.[88–91]

2.4. Control of phase distortions caused by the medium

The first motivation for introducing the pulse shaper was to use it for correcting phase distortions that broaden femtosecond pulses as they propagate or reflect from optics, or as they transmit through media such as optical fibers, water and even air. Dispersion, one of the primary sources of broadening, lowers the information density that can be transmitted by an optical fiber. By correcting phase distortions, one can achieve maximum information density. The pulse shapers also proved to be a practical means for the production of pulse sequences.[14,15,92] Here we give a brief review on recent work aimed at controlling and correcting phase distortions as femtosecond laser pulses propagate through optical media, sometimes in highly nonlinear regimes.

A number of groups have used pulse shapers for pulse compression. The groups of Silberberg, Gerber, and Reitze separately demonstrated adaptive control of distortions in femtosecond pulses occurring during amplification.[62–66,93,94] They showed that the integrated SHG intensity of the output could be used as feedback to a learning algorithm that changes the phase values at the pulse shaper to reduce the total spectral phase distortions in the output of the laser. The three groups showed that adaptive pulse compression provided a practical means to reduce unwanted phase distortions in the output pulses. Subsequent projects were aimed at compensating for the dispersion introduced by transmission of femtosecond pulses through optical fibers.[95–101]

More challenging projects involved phase compensation of nonlinear optical distortions occurring in fibers. Among these, we highlight work from Reitze's[95–97] and Motzkus'[102] groups on controlling the output from microstructured fibers and from Taylor and coworkers on controlling the soliton self-shift in fibers.[98] Adaptive learning algorithms were also used to control high harmonic generation in hollow-core fibers.[48]

Laser control of nonlinear optical processes such as supercontinuum generation in sapphire[103] have shown that one can control the output spectrum. This work was done by Wöste's group using an adaptive learning algorithm. More recently Levis and coworkers, realized that the position of the filament responsible for supercontinuum generation in water could be controlled using a learning algorithm.[104] Adaptive control has also been used to control and characterize femtosecond pulses reflected from semiconductor saturable mirrors.[105]

The Dantus group has applied the MIIPS method to measure the phase of pulses after they transmit through scattering biological tissue and to deliver phase shaped pulses to achieve functional imaging through scattering biological tissue.[72,106] More recently, they have showed that MIIPS is an ideal platform for measuring phase distortions as femtosecond laser pulses propagate through air. In their experiments, they have measured the group velocity dispersion of air and remotely corrected phase deformations as laser pulses propagated 30 meters in air.[74]

3. Control of chemical reactions and molecular identification

3.1. Coherent control of chemical reactions

The experiment that sets the stage for credible laser control of chemical reactions using shaped femtosecond laser pulses was published by Assion *et al.* on the controlled fragmentation of $CpFe(CO)_2X$ (X = Cl, Br, I).[107] The main message delivered by that work is that pulse shaping (phase and amplitude) can be used to control the relative yield of different fragment ions. At the time of that publication, there was no concrete information as to what specific aspects of the field caused the changes in the relative yields of the different fragments. However, it sparked a number of studies to try to determine how general this observation was, if it would translate to condensed phases, and if there was a system that one could use to predict controllability of other reactions.[108,109] Subsequent experiments from the Gerber group on gas phase control of relative yields include $Fe(CO)_5$,[107,110] and CH_2BrCl.[111] Experiments on $Fe(CO)_5$ indicated that this system is very sensitive to laser pulse energy. Increasing the pulse energy decreases the $Fe(CO)_5^+/Fe^+$ yield from 1.4 to 0.3. Transform limited pulses produced more molecular ions, while pulses that were modulated in the time domain produced much more Fe^+. Experiments on CH_2BrCl showed that by pulse shaping one is able to increase the ratio CH_2Br^+/CH_2Cl^+ from a value of 1.0 to 1.7, demonstrating that one can cleave the strong bond (C–Cl) rather then the weaker bond (C–Br). Results of this experiment contrast with the early multiphoton excitation experiments of the 1970s when no such control was possible. These measurements were extended to organic molecules that would be of biological interest, such as the controlled bond breaking in lactic acid.[112]

Following the observations by Gerber, Levis studied the effects of phase and amplitude shaping on the photofragmentation of acetone, trifluoroacetone, and acetophenone in the gas phase.[113,114] The most interesting observation was the apparent formation of a product with a mass-to-charge ratio equal to that of toluene (92 m/z), from the fragmentation of acetophenone. Levis pointed out that such formation required a complex reaction pathway that was 'directed' by the shaped laser field. In the subsequent publication from this research group, the same experiment was repeated. In this case TL pulses showed substantial signal at 92 m/z.[115] This product is usually much less abundant in electron impact mass spectra but its intensity increases if the background pressure increases due to ion–molecule collisions. Their most recent article focused on controlling cleavage of the C–C bond on either end of the acetophenone carbonyl group (masses 105 and 77). Results from this study showed that the relative yield between the two masses could be varied from 1 to 3 using a feedback based learning algorithm.[115]

The controlled dissociation of mixed metal clusters, Na_mK_n, offered the Wöste research group an opportunity to study systems with varying degrees of complexity.[116–126] It is important to point out that, contrary to the experiments from Gerber and Levis discussed above, in these experiments the incident beam is one photon resonant with multiple transitions in the cluster. When the beam is resonant with vibronic transitions the phase can be used to control the timing of the wave packet motion. This control was shown by Wilson in some of the earliest studies on phase control.[26] Beyond the mixed alkali clusters, Wöste and coworkers have also studied a molecule that is very similar to the transition metal complex studied by the Gerber group. In their research on the controlled photodissociation of $CpMn(CO)_3$, they found evidence for a pathway in which the optimally shaped pulse followed a molecular wave packet in two different potential energy surfaces.[127–129] The

theoretical interpretation of the results showed that pulse shaping had produced two sub-pulses: one promoting excitation of a bound rather than a repulsive state, and the second promoting ionization after a specific delay time that was related to the wave packet dynamics.[128] While this explanation is consistent with time-resolved pump–probe measurements and computer simulations carried out on *ab initio* potentials, it has remained a mystery how the initial 10 nm bandwidth 87 fs pulses are converted into two sub-pulses with pulse duration $\sim$40 fs by the pulse shaper.

More recently, the Weinacht research group has begun a systematic search to determine what parameters in the laser pulse determine fragmentation selectivity in laser initiated chemical reactions. The group has concentrated on the fragmentation of substituted acetones, CH_3COCF_3,[130–132] CH_3COD_3,[133] CH_3COCCl_3,[133] and the di-halogen CH_2BrI.[130,132] In this research, a number of different approaches to pulse shaping have been evaluated, from unconstrained phase amplitude to differential, polynomial and periodical spaces.[130,132] At the present moment, the main conclusion from the halogen-substituted acetones is that ionization takes place and is followed by enhanced autodissociation.[131]

The observation of changes in the fragmentation patterns of molecules when exposed to shaped laser fields prompted the Dantus group to explore the potential of laser control as a platform for multidimensional molecular recognition. This new direction required a level of reproducibility that had never been shown in the laser control field. It required that on any given day, when the same shaped pulse is used on the same compound, the exact same result is obtained. Experiments, such as those by Gerber and Levis had shown that learning algorithms usually reached a consistent fitness value, but each optimization run reached different phase and amplitude functions. The extreme demand on reproducibility required the ability to measure the spectral phase of the pulses at the sample. This was accomplished using the MIIPS method described in Section 2.2.[69,70] More importantly, from an applications point of view, it was important to find the minimum set of parameters that would cause the desired level of control. To fulfil this requirement, binary phase functions were introduced (discussed in Section 2.3). The use of binary phase functions offered advantages that are similar to those observed in digital electronics, namely, small variations in the absolute phase were negligible compared to the jumps from 0 to π.

A second important parameter in the design of this application was the reduction in the parameter space that needs to be evaluated in the search for optimized shaped pulses. In this regard, the Dantus group determined that control of amplitude was not necessary as long the excitation pulse was not resonant with the molecular system. For most molecules of interest, the near infrared pulse is not one photon resonant with electronic absorptions. Therefore it is sufficient to use only binary phase function and no amplitude modulation. While higher bit-phase functions provides a greater degree of control, an exhaustive search of 10-bit functions provide very quickly (under 5 minutes) results with more than 90% of the observed control level when using 16-bit phase functions. The Dantus group changed the approach from one dominated by learning algorithms to one in which a complete subset of functions was exhaustively evaluated. In addition, the measurements were repeated hundreds of times and this yielded the statistical significance of the observed control. This ensured that the observed change was not noise but a statistically significant observable.

Testing the statistical significance of laser control experiments that depend on highly nonlinear laser-molecule interactions is critical. A good amplified laser source has $<$2% pulse-to-pulse standard deviation in intensity. Given that the fragmentation processes usually involve the equivalent of 8 or more photons, the standard

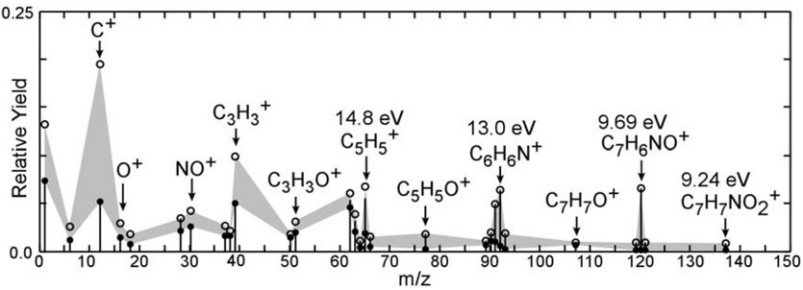

Fig. 7 Experimental mass spectra obtained for *o*-nitrotoluene. The spectrum shown with sticks corresponds to that obtained using TL, 35 fs pulses. The open and filled circles correspond to the maximum and minimum observed intensities when using 8-bit binary phase shaped pulses. The numbers above some of the main ion fragments correspond to the formation energy under electron impact excitation. In general, the larger ions are maximized by TL pulses, which also minimize the smaller fragment ions.

deviation reaches 15%. A poorly designed learning algorithm, with insufficient averaging, can pick the outlying measurements and 'evolve' in the noise without optimizing the real molecular system.

Binary phase shaping has been used to control the fragmentation of a number of compounds.[134] This article showed, for the first time, statistical evaluations obtained for different laser pulses where the degree of control was given with an associated standard deviation. More recently, we have revisited the question of bond selective chemistry using binary phase shaped pulses. In Fig. 7 we present results obtained on *o*-nitrotoluene. The mass spectrum obtained using TL pulses is shown with sticks. The open circles show the maximum relative yield for each mass, while the filled circles show the minimum relative yield obtained. These results summarize the extent of control achieved after evaluating all the shaped pulses. Note that TL pulses favor the production of heavy ions, while shaped pulses favor the production of the lighter ions.[135]

In Fig. 8, we show results obtained for *o*-nitrotoluene where the relative intensity of all ions was normalized to the values obtained using TL pulses. Based on that normalization scheme, the dashed circle with unit intensity provides the resulting mass spectrum that is obtained with TL pluses. We show that the binary pulse given by phase $\pi\pi0\pi0\pi00$ changes the relative yield of certain fragments by two orders of magnitude (notice the logarithmic scale). Using the ratio between two different masses as a measurement of control, as used in the fragmentation experiments from the Gerber and Levis groups, binary shaping results have shown changes in relative yield by factors of 100, in contrast to factors of 2–3 from studies using learning algorithms. Contrary to the observations on $Fe(CO)_5$, and other transition metal complexes, the relative yields obtained by binary phase shaping on organic compounds do not change with laser intensity. However, we do find a general propensity for seeing heavier ions with near TL pulses and smaller fragments increasing in yield with highly modulated pulses. This observed trend is not absolute, and in most cases there are fragments, typically of intermediate size, that do not show this property.[136]

3.2. Molecular identification

Having a reproducible platform for delivering shaped pulses at the sample has allowed the Dantus group to move to an area where laser control could fulfil a technological need. In mass spectrometry, it is very difficult to differentiate between isomeric

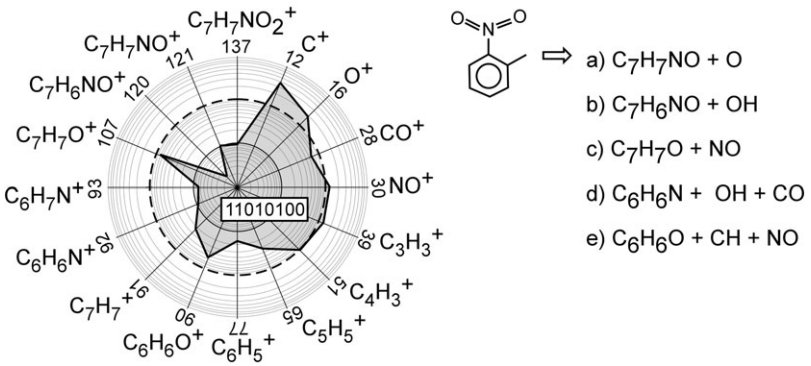

Fig. 8 "Spider" plot of the mass spectrum of *o*-nitrotoluene. The ion yields, normalized to their TL intensity, are plotted for each fragment in a logarithmic polar plot. The dashed line corresponds to TL excitation. The shaded region corresponds to a binary shaped pulse which causes complete suppression over the loss of OH (reaction b). In this diagram it is easy to see that binary phase shaping can achieve order-of-magnitude control over certain reaction pathways.

compounds. The electron impact mass spectrum of isomeric compounds is virtually identical, requiring time consuming (minutes) chromatography columns. We have demonstrated that binary pulse shaping is capable of distinguishing between isomeric pairs.[137] More significantly, by using two different pulse shapes, quantitative determination of the concentration in a mixture of two isomers becomes possible. In Fig. 9a we show a plot obtained from six mixtures containing *o*- and *p*-xylene. In the plot, we see that binary phase shaping mass spectrometry was capable of accurately determining the concentration of the mixtures. More importantly, the results shown were obtained on two different days, showing the high degree of reproducibility of the method.

Fig. 9b and c shows all the different isomers that have been successfully identified and quantified by the Dantus group.[137] We are presently evaluating the use of phase and polarization shaped pulses to distinguish enantiomeric pairs. This application would be of great interest to pharmaceutical companies given that the great majority of drugs are chiral and there is currently no efficient way to distinguish between left- and right-handed molecules.

3.3. Controlling large molecules in solution

A quantum mechanical or spectroscopic view of laser control evokes a field with frequency components whose phase and amplitude directly address distinct degrees of freedom in the molecular system. From such a point of view, the prospects of controlling a large molecular system in solution seem impossible given the enormous numbers of degrees of freedom and the inhomogeneities inherent with solvation at room temperature. Wilson pioneered the use of simple phase shapes, such as linear chirp, to control the excitation of dyes in solution, and used a pulse shaper guided by a learning algorithm to explore the parameters that improved two-photon excitation of a laser dye.[33] Gerber showed that for two large molecules whose absorption spectrum showed a great degree of overlap it was possible to use a learning algorithm to shape the pulses so that selective excitation could be accomplished.[138,139] In this experiment, independent tests of intensity, linear chirp and wavelength tuning were shown to provide little or no selectivity, whereas the shaped pulse provided a factor

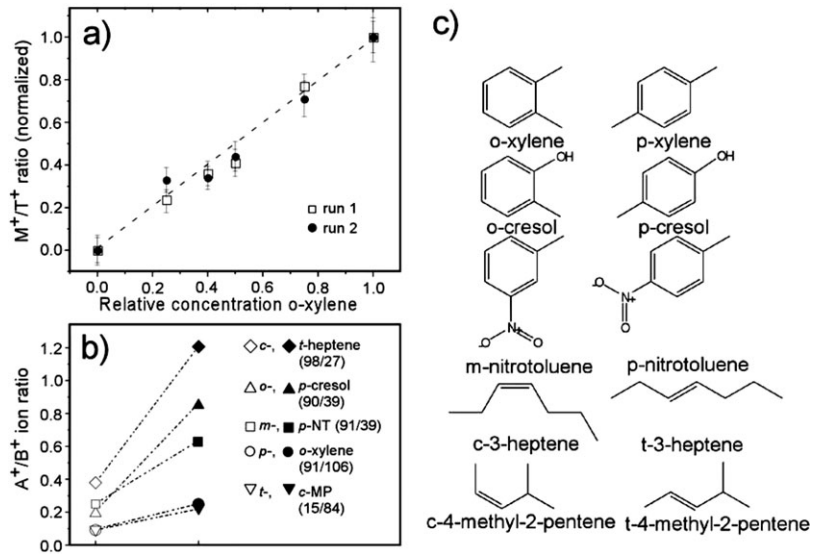

Fig. 9 Isomer identification using binary shaped femtosecond pulses coupled to a mass spectrometer. (a) Quantitative determination of the relative concentration of *o*-xylene in six different mixtures with *p*-xylene. The plot shows the experimentally obtained ($\sim$0.1 s) normalized ratio of intensity between the molecular ion ($M = 106$) and the tropylium ion ($M = 91$) for each mixture. The results were repeated on two different days. (b) Relative ion yields for pure samples of isomeric pairs of molecules; in all cases quantitative analysis is possible. (c) Structural representation of the different isomeric pairs that were studied.

of 1.4 greater excitation of one over the other. More recently, the Gerber group has studied the *trans–cis* photoisomerization of the dye NK88 in liquids.[140]

To date, one of the largest and most complex systems to be controlled is the LH2 antenna complex which plays an important role in photosynthesis. The goal of the experiment, an international collaboration between Herek, Motzkus and coworkers, was to control the ratio of internal conversion to energy transfer in liquid phase using phase and amplitude modulated pulses[141] and sinusoidal parameterized pulses.[142] In these experiments, a learning algorithm guided the modulation of the incident shaped pulse, which was resonant with the optical transition. A modest degree of control was found, demonstrating greater internal conversion (the pathway that does not provide energy to the biological system).

Prokhorenko and Miller designed a control experiment in which a laser that is resonant with the first excited state of rhodamine 101 in a methanol solution is guided by an adaptive learning algorithm.[143] The goal of this experiment was to determine if coherence can play a role in the maximum population transfer that can be achieved. The conclusion of this study was that a 30% increase in population transfer (10% above transform limited pulse) could be achieved by the optimized shaped pulse. The temporal shape of the optimal pulse corresponds to a series of sub pulses separated by $\sim$150 fs, which match the molecular dynamics of the system. The pulses were phase and amplitude modulated; the optimal pulse was centered at the absorption maximum of rhodamine 101, and the anti-optimized pulse had about 40% of its spectrum tuned to shorter and about 60% tuned to longer wavelengths, with no amplitude at the absorption maximum. These amplitude changes in the excitation spectrum obviously affect the excitation efficiency. It would be interesting

to know if phase shaping alone would be sufficient to observe a difference in the excitation efficiency. This would be a surprising result because it would contradict present understanding of laser–matter interaction in the linear regime.

Interest in optimizing the two-photon excitation of laser dyes and other fluorescent chromorphores has been fueled by two-photon excitation microscopy. Feedback phase control of two-photon fluorescence of dye solutions, pioneered by Wilson,[33] continues to be a good starting project.[144,145] Midorikawa studied feedback control and selective excitation between two-photon and three-photon fluorescence of dyes in solution.[146] In this study, a learning algorithm found shaped pulses that reduced two-photon excitation by a factor of two while reducing three-photon excitation by a factor of nine. Even higher suppression of three-photon excitation has been demonstrated based on multiphoton intrapulse interference (MII).[147,148] Midorikawa and coworkers have also shown that phase modulation can reduce photo-bleaching of green fluorescent protein (GFP).[149] Lee *et al.* used adaptive control of the two-photon excited fluorescence intensity from a DCM solution in methanol, and showed that it is possible to increase the ratio of fluorescence to SHG intensity.[150] Adaptive phase control of two-photon excitation of α-perylene crystals,[151,152] and perylene in chloroform solution has also been explored by Wada and coworkers.[153]

The Dantus group approached control of large molecules in solution with a very different perspective. Instead of testing a number of phases and amplitudes to see what is observed, we realized that nonlinear optical excitation using ultrashort laser pulses was achieved by combinations between the large number of frequency components within the bandwidth of the pulse. The relative phase between these frequency components would dictate the phase of the resulting nonlinear optical excitation. By careful delivery of specific phase functions, it was possible to manipulate constructive and destructive interference, leading to the robust control of two- and three-photon optical excitation of large molecules, including proteins in solution, based on MII.[154,147] Using MII, one can design phase functions for selective excitation of two- or three-photon transitions, to enhance excitation of GFP, and to suppress excitation of tryptophan residues in concanavalin A.[147] This approach to control has been used to demonstrate selective two-photon microscopy,[155,156] probing microchemical environments,[155] and functional imaging through scattering biological tissue.[106]

3.4. Control of simpler systems: atoms, diatomics, and bond activation

Very important progress in the field of laser control has been accomplished by the study of simpler systems such as atoms, diatomics and the activation of individual chemical bonds. In many cases these projects have had as their main goal the ability to write and read information to and from quantum mechanical systems. We start with a highly significant contribution by the Silberberg group where they controlled the two photon excitation of Cs atoms using periodical phase modulation[157] and a step function.[158] These were the first unequivocal demonstrations on how the relative phase between frequencies in a pulse that combined to give a specific frequency (the two-photon transition frequency) can interfere. These studies also showed that such control could be achieved with very simple phase functions. Silberberg and coworkers showed interference between resonant and nonresonant two-photon excitation pathways in Rb atoms using a phase step[159] and a window function.[160] More recently they demonstrated quantum control of angular momentum in Rb atom excitation using polarization shaping.[161] Interesting new research from Silberberg

and coworkers involves the use of broadband down-converted light. The resulting entangled photons have been shown to display properties that are similar to shaped laser pulses. By shaping these non-classical photons they have shown control of two-photon excitation in Rb atoms[162,163] and other two-photon interferences.[164]

Motzkus and coworkers reproduced Silberberg's control of two-photon excitation, this time in Na atoms.[165] They then used evolutionary optimization of parameterized pulses for controlling the wave packet dynamics in the excited and ground states of K_2.[166] Four-wave mixing in K_2 was tested with sinusoidal and quadratic phase modulated pulses.[167] Motzkus and coworkers carried out experiments similar to those of Silberberg, exploring the effect of chirp and π-step phase modulation on the one- and two-photon excitation pathways of Rb.[168,169]

The controlled preparation and manipulation of rotational and vibrational states and their subsequent dynamics has been a major goal of the Leone research group. To avoid the congestion brought about by thermally populated rotational and vibrational states, Leone and coworkers use a narrow bandwidth laser to excite a single rovibrational state in diatomic lithium, Li_2, which they use as their launching state. From there, they have shown the preparation of wave packets using amplitude and phase control.[170–180] Their research group has more recently focused on building quantum gates on Li_2 transitions which can be used as a model of quantum information storage and processing.[181–184] Leone and coworkers have also tested the use of evolutionary algorithms to optimize Li_2 excitation.[185]

Bucksbaum's research group, known for their ability to write and read information in Rydberg states of Cs atoms,[186–193] have controlled the stimulated Raman scattering between two different vibrational modes in methanol[194,195] and between C_6H_6 and C_6D_6.[196] They have also used learning algorithm based control of Raman scattering *via* impulsive Raman scattering of SF_6 and CO_2 in the gas phase,[197] and CCl_4 in the liquid phase.[194,198] Bucksbaum and coworkers have also studied control between ionization and dissociation of Na_2.[199] Impulsive stimulated Raman scattering of molecular vibrations using nonlinear pulse shaping and learning algorithms has also been studied by the group of Kapteyn and Murnane.[200]

Girard and coworkers have used pairs of pulses to control Rb atom excitation,[168,169,201,202] and the interference between direct and sequential paths in the Na atoms.[203,204] Tsuchiya and coworkers have used adaptive algorithms to gain phase control of two-photon resonant and nonresonant excitation of Rb atoms.[205] Yokoyama *et al*. demonstrated selective excitation of spin states in Cs atoms using a pair of phase locked pulses.[206,207] Wöste's group has more recently shown coherent control of ultracold Rb_2.[208]

The idea that isotopic substitution in small molecules results in different intramolecular dynamics has prompted pump–probe schemes for isotopic separation,[209] and the development of isotope selective fragmentation of K_2 using adaptive amplitude modulation.[121,125,126,210–213] The conclusion reached by this series of experiments from Wöste and coworkers is that the adaptive algorithm evolves towards an excitation spectrum that matches the desired isotopic molecule. More recently, Wöste's group in collaboration with Gerber's group studied the controlled double ionization of Ca.[214]

Phase modulation to control the excitation of Na_2, studied by Baumert and coworkers, provided further evidence of the role that phase modulation can play in controlling wave packet dynamics and excitation.[215,216] Baumert has also studied two-photon excitation of sodium atoms[217] and control of the Autler–Townes component in the photoelectron spectrum of sodium.[218–222]

The Corkum group has provided some of the most creative uses of lasers to control molecular dynamics and reactions. The early experiments were concerned with wave packet dynamics in I_2.[223] The synthesis of laser pulses in which a polarized field rotated with increasing frequency allowed Corkum and coworkers to demonstrate a molecular centrifuge in which molecules are forced to spin until they break apart.[224] The dissociation of H_2 and D_2 molecules has been controlled using periodically modulated pulses,[225] and their rotations have been controlled using intense few-cycle pulses.[226,227] More recent experiments involve control of vibrational wave packets using three intense few-cycle pulses.[228] In these experiments, the first pulse launches the wavepacket and the second pulse changes the potential energy, effectively splitting the wave packet. One portion proceeds to dissociation while the other portion remains bound. The third pulse probes the dynamics by Coulomb explosion.

Control of molecular alignment has been shown by Faucher and coworkers using chirped femtosecond pulses[229] and binary phase modulated pulses.[230,231] Control of molecular orientation has been demonstrated combining one- and two-photon excitation in a pair of phase locked pulses.[232] Being able to control molecular alignment and orientation may be an important step toward enhancing the selectivity that can be achieved in laser control of gas phase chemical reactions. Clearly from the experiments above, substantial progress has been achieved.

Optimal control of multi-photon ionization of I_2 with polarized pulses has been studied by Sakai and coworkers.[233] In this study, they use polarization-shaped pulses to control the probability that the first electron being pulled away will recollide with the molecule to generate I_2^{2+} (a process that is favored by linear polarization) or will miss the recollision and generate I_2^{+} or I_2^{3+}. For these experiments the molecules were aligned with a Nd:YAG nanosecond laser pulse. Gerber's group explored the use of polarization shaped pulses to optimize the yield of K_2^{+} ions.[234] Their conclusion was that being able to introduce additional polarization allowed to take advantage of excitation of different dipole-allowed transitions, and hence to increase the yield of K_2^{+} ions. It would be instructive to consider an alternative interpretation of these findings based on the similar experiment by Sakai and coworkers.[233]

The Dantus group has also been involved in research projects where the goal is controlling the formation of rovibrational wave packets in ground and excited states of diatomics. Early research involved the creation of three-pulse sequences to control population and coherence transfer, where a small change in the delay time between two pulses caused the observation of ground or excited state vibrational motion,[235] as well as studying the influence of chirp on population transfer.[236,237] Motivated by the goal of storing and processing of information in quantum states, the Dantus group explored homogeneous and inhomogeneous decoherence mechanisms using photon echo pulse sequences.[238,239] As part of that research, the Dantus group made an important distinction between microscopic (within the molecule) and macroscopic (within the ensemble of molecules) coherence.[239] These studies conclude with the use of photon echo pulse sequences using femtosecond shaped laser pulses as a vehicle for molecule-based quantum information storage and manipulation.[240]

4. Nonlinear optics with phase shaped pulses

4.1. Spectroscopy

Some of the research projects in the field of coherent control can be classified as efforts to selectively excite a particular spectroscopic transition, without necessarily

attempting bond-selective chemistry. Along these lines we highlight the first use of shaped pulses to excite coherent oscillations in a crystal of α-perylene with a train of equally spaced pulses in the time domain.[22,23] With the goal of using the shaped pulses for communications, Weiner has explored the output from two-photon excited photodetectors and their sensitivity to shaped pulses.[241,242] He has also continued his interest in creating trains of equally spaced pulses.[243,244] Weiner studied the effect of pulse shaping on thick SHG crystals and realized that phase shaping could be used to control the output of such crystals in a manner that allowed for secure communications.[245–249]

Silberberg's group has made important contributions to the use of shaped pulses for selective coherent anti-Stokes Raman spectroscopy (CARS). Their first work, using sinusoidal phase modulation, involved liquid methanol, CH_2Br_2, $(CH_2Cl)_2$, CH_3I.[250] They used interference between resonant and nonresonant transitions with a step phase gate for single pulse Raman spectroscopy of liquid methanol, CH_3I, CCl_4, mesitylene, and CS_2.[251] They demonstrated how to suppress the nonresonant signal[252] and narrow the response of CARS in liquid benzene and pyridine using phase step shaping.[253] They demonstrated single-pulse CARS using a step gate or sinusoidal modulation on $Ba(NO_3)_2$, diamond, toluene, and hexane,[254] and they used a polarization gate to suppress the non-resonant background.[255] They demonstrated the combined performance of periodical phase modulation and polarization suppression of the non-resonant background to measure CARS of liquid toluene.[256] They used constructive interference of the resonant-polarized contribution in single pulse CARS spectroscopy of liquid 1,2-dichloroethane, and optimized the probe spectra in the case of 1,2-dichloropropane.[257] Leone's group has made an improvement on single pulse CARS by detecting spectra at two polarizations (−45 and 45 degrees) of the signal resulting from orthogonally polarized pump (*y*-polarized) and probe Stokes (*x*-polarized). Taking the difference between these two spectra eliminates the non-resonant background.[258]

Motzkus' group has also been active in the use of adaptive control to gain selective excitation using CARS. They have studied control of the signal from crystalline polydiacetylene with feedback controlled polynomial parameterized phase functions.[259] They showed selective CARS spectroscopy of $CHBr_3$, $CHCl_3$, CBr_2Cl_2, solutions of halobenzenes, and β-carotene in THF solution using sinusoidal phase modulation.[102,260] Materny's group controlled ground vibrational signals from polymers using a four-wave mixing setup[259,261,262] and then measured CARS of liquid toluene.[263]

Another prime example of using interferences between two pulses to achieve spectroscopic resolution comes from the group of Murnane and Kapteyn, where they used a pair of chirped and delayed pulses to demonstrate high resolution Raman spectroscopy of liquids.[264] In this case, the frequencies from each pulse that overlap in time are the ones that contribute to create the pump–Stokes-probe combination. In a separate project, they used learning algorithm-driven control to enhance the impulsive Raman scattering from liquid CCl_4.[198] This research project followed work by the Bucksbaum group.[194,197,198]

The Dantus group showed how MII can be used for selective two-photon excitation.[147,154,155] More recently they introduced the use of binary phase shaping for achieving high selectivity in two-photon excitation and at the same time reducing the search space for learning algorithms by hundreds of orders of magnitude.[38,265] In Fig. 10, the use of binary phase functions to cause selective two-photon excitation (left) and selective stimulated Raman scattering (right) is shown. The experimental

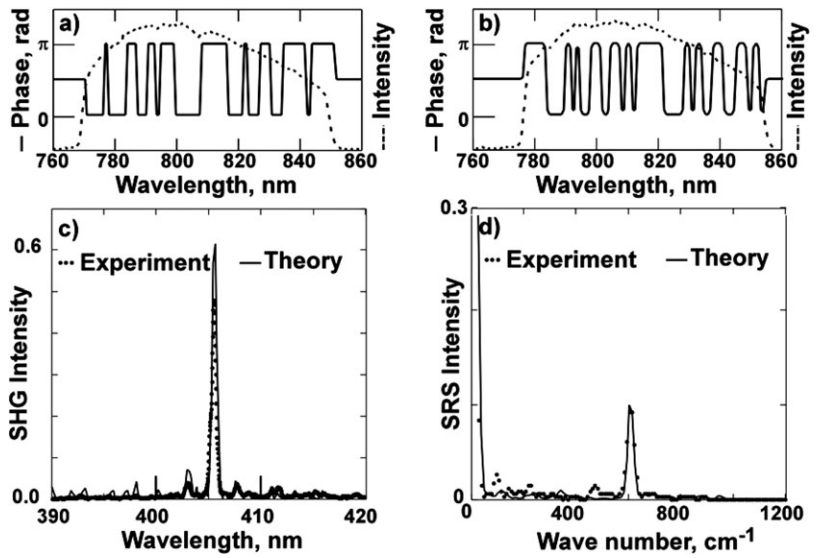

Fig. 10 Generation of narrow bandwidth selective nonlinear excitation using binary shaped laser pulses. (a) and (b) show the spectral intensity and phase of the coherent light used to control second order excitation and stimulated Raman (zero order) processes. (c) Experimentally measured and predicted spectral intensity from a thin SHG crystal. (d) Experimentally measured and predicted Fourier spectrum of the autocorrelation trace of the pulse showing highly selective excitation.

data (dots) and the simulations (lines) are in near perfect agreement and show excellent suppression of the background. Note that the wings of the pulses have been trimmed using amplitude modulation to achieve additional background suppression.

The search for phase functions that optimize excitation at one frequency and suppress excitation elsewhere can be time consuming. We have demonstrated how to search the reduced binary search space for narrow-band, low-background nonlinear spectroscopy,[266] and have used this method for highly selective two-photon excitation spectroscopy and stimulated Raman scattering.[267] Use of binary phase modulation dramatically reduced the search space size. The symmetry inherent in low order nonlinear optics is reflected in the fractal structure of the search space (see Fig. 11), where the fitness values of each binary phase sequence in the reduced search space are plotted in two dimensions—each axis indexes half of the binary phase sequence.

4.2. Microscopy

Coherent control, as well as some of the ideas that were developed for selective spectroscopic excitation, have been used to gain selectivity and contrast in microscopy. Once again, Silberberg has been one of the pioneers. His group was the first to demonstrate single pulse CARS microscopy.[250] They used two-photon interference to improve the resolution of microscopy,[268] for spatiotemporal coherent control in three-photon z-scan of glass interface,[269,270] and for two-photon microscopy of biological samples.[271,272]

Leone's group has demonstrated imaging of photoresist samples with CARS microscopy.[273] The group of Joffre has used the selective two-photon excitation

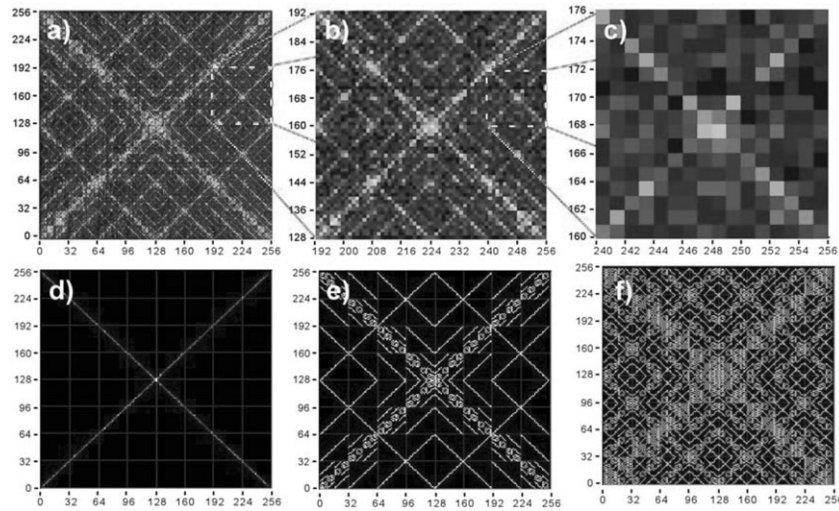

Fig. 11 Two-dimensional maps of the search space for a 16-bit binary phase shaping experiment (a–c), where the fitness corresponds to the signal to noise ratio in selective nonlinear excitation. The bright diagonals correspond to the symmetric and antisymmetric phase functions. Note that the search space has a fractal structure, as evidenced by the similarity of the structures as one zooms in on a region of the data. Panels (d–f) show the calculated positions for the maximum fitness values, (d) shows the symmetric sequences, (e and f) show the sequences that have one or two bits flipped from the symmetric functions in (a), respectively. The fractal symmetry makes it possible to perform a highly efficient search, even for phase functions with a large number of bits (pixels).

method based on sinusoidal phase modulation introduced by Dantus and coworkers for selective two-photon imaging.[274] In that study, they were able to separate endogenous fluorescence from label florescence in biological samples. Chirped delayed pulses have been used for CARS microscopy by Taylor,[275] Cicerone,[276,277] Zumbusch,[278] and Zheltikov.[279,280]

The Dantus group took advantage of MII to achieve selective two-photon microscopy with shaped femtosecond pulses (see Fig. 12).[155,156] To determine if pulse shaping would play an important role in deep tissue imaging and photodynamic therapy, the Dantus group performed experiments in which selective two-photon excitation was used to selectively excite a pH sensitive chromophore. The sample was then imaged directly, showing significant selectivity. Subsequently, a 1 mm slice of scattering biological tissue was placed in front of the sample to determine if the selectivity gained by binary phase modulation would persist even after the pulse transmitted through the scattering tissue. The selectivity was preserved in these experiments.[72,106] Having demonstrated coherent control through scattering biological tissue to achieve functional imaging opens the door to research projects on coherent control for imaging and therapeutic purposes.[106,148]

4.3. Nanoscale systems

Laser control has recently been used to address nanoparticles. Among the systems that are most amenable to control are quantum dots. These systems have a spectroscopy that has some similarity to that of atoms and molecules; therefore, they provide a natural extension of laser control of molecular systems. Unold *et al.*

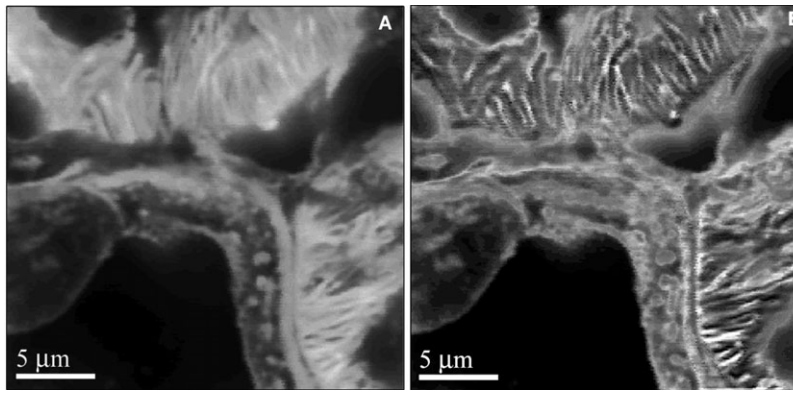

Fig. 12 Microscope images of mouse kidney sections (25 × 25 μm) labeled with fluorescent probes. The left image was obtained with phase compensated TL pulses. The right image is a composite obtained using two differently phase shaped pulses. In both cases total fluorescence with no spectral dispersion was recorded. Notice that the composite image in the right shows much higher contrast between different cellular components.

controlled a pair of quantum dots that were coupled by dipole–dipole interactions.[281]

One of the most common types of particles studied have been metallic nanoparticles which exhibit surface plasmon resonance (SPR). Given that the SPR emission results from the incident excitation by the field, it has been important to determine what the coherence lifetime of this emission is. This measurement has been carried out by Scherer on single metal nanoparticles.[282] In some experiments, it is difficult to determine the degree to which these nanoparticles are interconnected. With this in mind, Petek and coworkers used a pair of delayed femtosecond pulses to control the two-photon emission from surface plasmons on silver nanoparticles.[283] They observed coupled SPR emission from a number of emitters that kept the same oscillation frequency, and they could also see uncoupled emission that exhibited a different oscillation frequency and within a few oscillations, was out of phase.

Stockman has proposed the use of phase shaping to control the localization of electromagnetic fields in metallic nanoparticles.[284–290] The Dantus group has recently taken this as a motivation for a set of experiments in which phase and polarization shaping is used to localize ''hot spot'' emission. In particular, the Dantus group is interested in remote emission that is observed up to 40 microns away from the focal spot of the laser. The dendritic silver nanoparticle system forms accidental nanowires capable of functioning as plasmonic waveguides. In Fig. 13, we irradiated the sample at the center of the crosshairs and changed the polarization of the pump laser and the detection system. Notice that this alone is enough to control remote emission (approximately 20 beam diameters away from the focus). We have observed that phase modulation of the input pulse is also capable of controlling remote emission; these findings will be published elsewhere.

5. Conclusion

The quest for laser control of chemical reactions and, in general, a variety of physicochemical processes, has made a number of contributions to our understanding of fundamental processes involving the flow of energy in molecules. As the

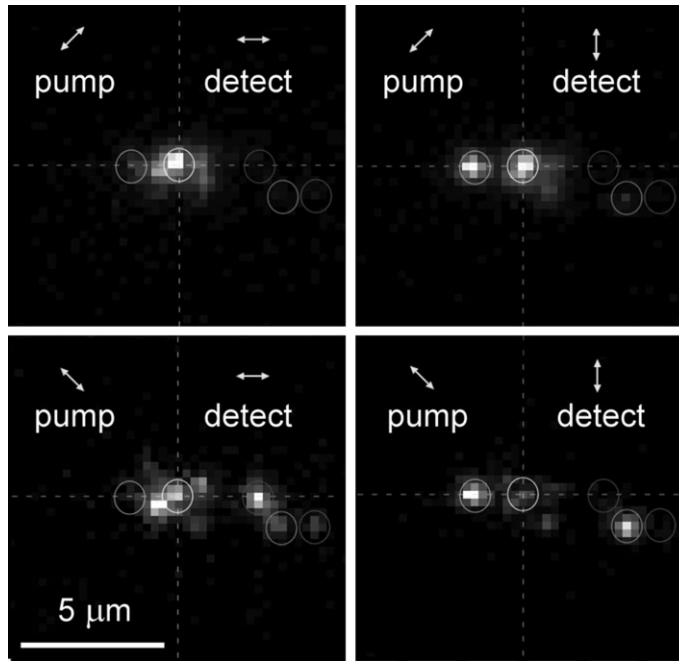

Fig. 13 Microscopic images of dendritic silver nanoparticles obtained under different excitation and detection polarization. The laser (12 fs, 100 fJ pulse^{-1}) was focused (focal diameter $\sim$400 nm) at the center of the cross hairs. Note that for some pump and detection conditions (bottom) remote two-photon plasmon emission is observed. The remote emission, occurring as far as 5 μm away, can be controlled by the polarization of the incident light.

field matures, it is to be expected that shaped laser pulses will provide information that can not be obtained by other techniques. Similarly, pulse shaping will enable a series of applications where other laser sources cannot provide the desired result. We have discussed hundreds of experimental results in this review, most of which were from the last few years. The volume of peer reviewed publications related to laser control is growing at a very fast rate, and has surpassed 1000 per year (see Fig. 14).

As we reflect on the field, we realize that while the majority of scientists are still skeptical about laser control, there is a number of pioneers that are demonstrating applications as discussed in this review and who see the limitations to be primarily technological hurdles rather than physical impossibilities. There is hope that in the near future, laser controlled chemistry in combination with mass spectrometry, will be able to 'sniff' explosives better than dogs presently do.

Unfortunately, there is no mathematical theorem which gives us absolute conditions for the successful implementation of coherent control. For example, it is well known in the field of quantum computing that there is such a theorem, which tells us that the probability of a mistake (bit flip) in a quantum state caused by decoherence must be less than 10^{-4} to build a functional quantum computer with error correction. We think that this theorem is relevant to coherent control, because quantum computing and coherent control are essentially the same. A quantum computer requires unitary transformations of qubits and laser control requires unitary transformations in Hilbert space. From this point of view, it is then possible to deduce a parameter that can tell us about the possible success for coherent control.

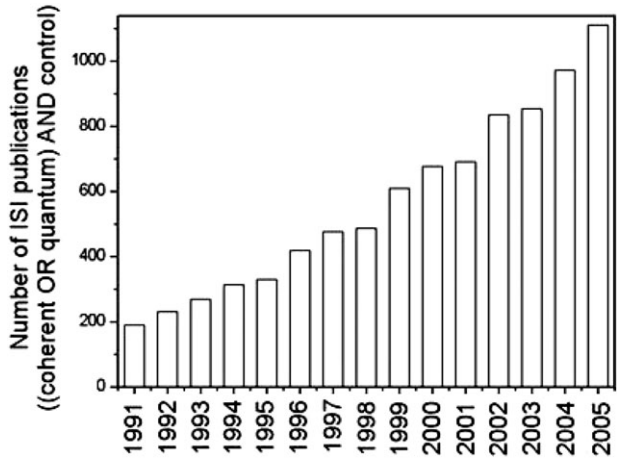

Fig. 14 Number of peer reviewed journal articles published per year in the database of the Institute of Scientific Information related to coherent (or quantum) control.

The condition for successful coherent control is keeping decoherence small while the laser interacts with the system. In other words, $\tau\gamma \ll 1$, where τ is time of evolution and γ is the decoherence rate. The time of evolution required to accomplish control over the system depends on the rates of nonlinear transfer from ground to selected states. First, population inversion between the controlled states may appear at time $2\pi/\Omega$, where Ω is difference between rates of coherent transfer in controlled states (see Fig. 15a). This difference is usually high; for the STIRAP type of transitions this difference is close to the Rabi frequency. As the states get closer in the system, the time required may equal several Rabi periods (see Fig. 15b). In the liquid phase, relaxation rates are approximately 10^{12}–10^{14} s^{-1}; therefore, the Rabi period must be very short. These Rabi oscillations result from nonresonant nonlinear oscillations, and the field must be very strong. Under these conditions, self focusing and breakdown dominates. As long as there are well separated electronic states that separately yield the desired control, this control can be accomplished even in liquids. In the case of coherent control of chemical reactions, the role of the laser is to break the symmetry between the multiple pathways, and for that brief moment influence the subsequent outcome.

Decoherence arises from interactions between a molecule and the surrounding environment (as in the case of solutions), or it may be intramolecular vibrational redistribution (IVR) from optically bright states to the dark states as in the case of isolated molecules in gas phase). For each experimental system, one can estimate the value of $\gamma\tau$. If $\gamma\tau \ll 1$ then coherent control is possible. Interesting results from computer simulations of coherent control of model systems in the presence of decoherence have been discussed in the latest article by Li *et al.*[291] The authors found that when relaxation is 10^2–10^4 times weaker than the interaction driven by the laser field, optical dynamic discrimination is possible using feedback learning algorithms.[25,292]

Selective nonlinear excitation using shaped laser pulses differs from the above discussion. By selective nonlinear excitation, different initial states can be excited because, in this case, phase modulation of the fundamental pulse modulates the spectral components of the nonlinear field (see Fig. 15a). In this case, the condition for coherent control is simple. The spectral splitting of the controlled states (Δ) must

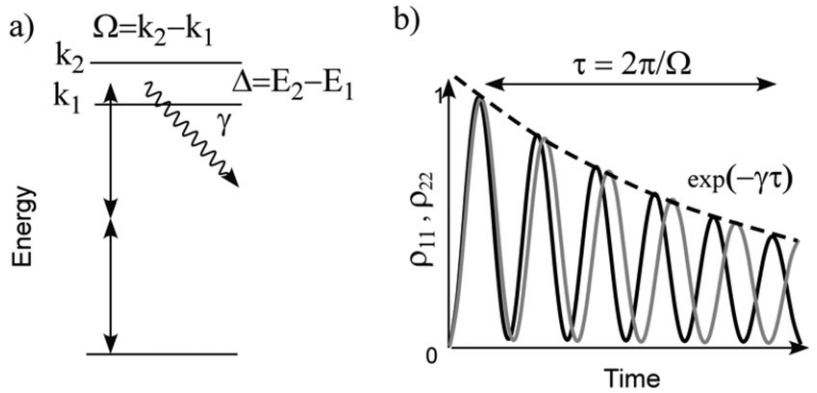

Fig. 15 Theoretical conceptualization of coherent nonlinear control and its dependence on molecular parameters (level spacing, Δ), the rate of relaxation γ, and differences in the transfer rate to the two levels, Ω. The left diagram shows an energy diagram and the right diagram shows a time dependent picture. Small differences between the excitation rates allow selectivity after a characteristic time τ. For controllability, the coherence must survive this time. This concept gives a practical guideline for separating controllable and non-controllable physico-chemical systems by direct coherent manipulation of their quantum states.

be smaller than the spectral width of the femtosecond pulse and larger than the homogeneous broadening (γ, see Fig. 15a). These requirements are realistic now that ultra broad bandwidth lasers, with more than 400 nm spectral width, are available. Implementations of MII to achieve selective nonlinear excitation are amenable to physical modeling and provide a robust platform for the design of a number of applications discussed here.

We conclude this brief review with the thought that, even after all this progress, bond selective chemistry based on coherent manipulation of the molecular degrees of freedom, (particularly in condensed phase, which would be of industrial interest), is still far from realization. However, short of that "Holy Grail," there has been significant progress in the field of laser control with shaped femtosecond pulses. Progress is expected to accelerate dramatically as the field expands to include laboratories in many different parts of the world. Soon we will be able to point to a number of applications, measurements and discoveries that would not have been accomplished if the dream of laser control of physiochemical processes had been abandoned in the late 1970s.

Glossary of acronyms

CARS coherent anti-Stokes Raman spectroscopy.
FROG frequency resolved optical gating.
GFP green fluorescent protein.
MII multiphoton intrapulse interference.
MIIPS multiphoton intrapulse interference phase scan.
MS mass spectrometry.
SHG second harmonic generation.
SLM spatial light modulator.
SPR surface plasmon resonance.
SPIDER spectral phase interferometry for direct electric-field reconstruction.

STIRAP stimulated Raman adiabatic passage.
TL transform limited.

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