



Review in Advance first posted online
on November 14, 2008. (Minor changes may
still occur before final publication
online and in print.)

Quantum Coherent Control for Nonlinear Spectroscopy and Microscopy

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Annu. Rev. Phys. Chem. 2009. 60:277-92

The *Annual Review of Physical Chemistry* is online at
physchem.annualreviews.org

This article's doi:
10.1146/annurev.physchem.040808.090427

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0066-426X/09/0505-0277\$20.00

Key Words

femtosecond pulse shaping, two-photon absorption, CARS spectroscopy,
nonlinear microscopy, CARS microscopy

Abstract

The field of quantum coherent control, initially formulated with the goal of modifying and manipulating molecular systems, has had a number of applications in atomic and molecular spectroscopy in recent years. This review demonstrates how carefully designed femtosecond pulses could be used to enhance resolution and improve detection in several areas of nonlinear spectroscopy. The two effects that are most intensively studied in this context are two-photon absorption and coherent anti-Stokes Raman scattering. This article discusses the principles of the control of such processes and several possible applications in microscopy and remote sensing.

TPA: two-photon absorption

Coherent anti-Stokes Raman scattering (CARS): nondegenerate four-wave mixing technique used for the detection of vibrational levels; requires three input fields, termed pump, Stokes, and probe fields

Pulse shaping: technique for synthesizing short optical pulses with precise temporal profiles

Spatial light modulator: used in pulse shapers to tailor the phase, amplitude, or polarization of the different spectral components of a short pulse

1. INTRODUCTION

The field of quantum coherent control emerged from a number of key ideas that were formulated in the late 1980s and early 1990s, themselves born out of extensive earlier work in laser chemistry (1–8). In brief, in quantum control the goal is to drive a quantum system from an initial state to a desired final state by exploiting constructive quantum-mechanical interferences that build up that state amplitude, while avoiding undesirable final states through destructive interferences. Initial ideas exploited phase-controlled laser fields to manipulate quantum-mechanical phases, as proposed by Brumer & Shapiro (2, 4), or precisely timed sequences of ultrashort pulses, as proposed by Tannor & Rice (1, 3). Today, the most common experimental approach to quantum control uses shaped femtosecond pulses, which in a way combines these two approaches (7, 8). As decoherences need to be avoided for effective quantum control, ultrashort interactions are indeed a natural choice.

Although the initial concepts were formulated with molecular processes in mind, the ideas of quantum control were later extended to other systems, including atomic systems (9), semiconductors (10), and nanoplasmonic structures (11). Another important extension came with the realization that quantum interference effects could be applied not only to drive useful photochemical processes, but also to improve spectroscopic techniques. Therefore, whereas quantum control techniques originally attempted to modify molecules through photodissociation or photoisomerization, in spectroscopy the goal is to either detect or selectively excite a particular constituent, without necessarily modifying its final quantum state. This review concentrates on such applications of quantum control to spectroscopy.

Finally, quantum control is inherently related to nonlinear optical processes, and hence it is expected to affect mostly nonlinear spectroscopy techniques. Indeed, perturbative single-photon processes are not expected to be affected by spectral phases or quantum interferences (12). The two spectroscopic techniques that were most intensively investigated in relation to quantum control are two-photon absorption (TPA) and coherent anti-Stokes Raman spectroscopy (CARS). One of the driving forces behind these investigations is the possible application of those techniques in imaging and specifically in microscopy. This review discusses these particular applications in more detail.

2. FEMTOSECOND PULSE SHAPING

To exploit quantum interferences, one must preserve the quantum-mechanical phase and hence avoid decoherence. It is natural then to use ultrafast interactions that are faster than the lifetimes of the relevant levels or, in equivalent terms, to use laser pulses that are spectrally broader than the width of those levels. This contrasts with classical laser spectroscopy, in which one traditionally wants the laser line width to be significantly narrower than the level under study. The most common route to control utilizes the technique of femtosecond pulse shaping.

Most femtosecond lasers produce a train of pulses that are close to being Fourier (or transform) limited: They are nearly as short as their spectral content allows. This means that all the frequencies that compose the short pulse have a uniform phase, so they interfere to generate the shortest, most intense pulse at $t = 0$. For control, one can apply a sequence of such pulses to drive the system impulsively, but the most versatile approach uses an optical setup known as a pulse shaper (13) in which the short pulses are modified to generate more complex, carefully crafted synthesized pulses by modifying the individual frequencies of the short pulse.

Figure 1 shows the most common approach to pulse shaping, based on spatial dispersion in an optical system that resembles a back-to-back optical grating spectrometer. The first grating disperses the spectral components of the pulse in space, and the second grating puts them back together, while a pixilated spatial light modulator applies a transfer function $\tilde{M}(\omega)$, thereby

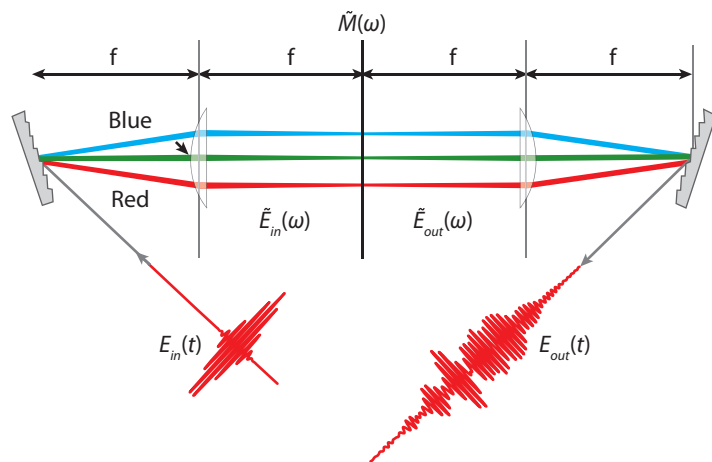


Figure 1

A schematic view of a Fourier-domain 4-*f* femtosecond pulse shaper. A transform-limited input pulse is dispersed by the input grating (*left*), and the different frequency components are modified by the mask function $\tilde{M}(\omega)$ and then recombined by the output grating to form the shaped output pulse. Figure adapted from Reference 14.

modifying the amplitudes, phases, or polarization states of the various spectral components. In essence, the shaper is an optical synthesizer that can generate complex pulses with a temporal resolution limited by the spectral content of the pulse and a maximal duration limited by the resolution of the setup and the pixel size of the spatial light modulator. As the techniques and applications of pulse shaping have been reviewed in the past by Weiner (13), and more recently in the context of control by Wollenhaupt et al. (14), this review does not discuss the details of the history or technological aspects of this technique. However, the setup shown in **Figure 1** is just one approach to pulse shaping, and a few other techniques have been employed, most notably an acousto-optical device known as the dazzler (15).

3. FEMTOSECOND EXCITATIONS OF ATOMIC LEVELS

As discussed above, quantum control normally requires pulses that are spectrally broader than the width of the quantum levels that are interrogated. As this is a somewhat unusual situation in laser spectroscopy, let us consider first the simplest case, in which an ultrashort pulse with an electric field $E(t)$ resonantly interacts with a two-level system, initially in the ground state. We assume that the interaction is weak (this is usually the situation in spectroscopy); hence perturbation analysis can be applied safely. Applying first-order, time-dependent perturbation analysis, we find that if the pulse duration is much shorter than the lifetime of the upper level, the amplitude of the upper level that is excited by the pulse is

$$a_f = \mu_{fg} \int_{-\infty}^{\infty} E(t) \exp(-i\omega_0 t) dt, \quad (1)$$

where ω_0 is the atomic frequency related to the transition, and μ_{fg} is the associated dipole moment. This Fourier-like integral has an intuitive meaning, showing that only the resonant frequency component of the field leads to excitations. This result also explains the claim (12) that single-photon perturbative interactions cannot lead to control: As only a single frequency component matters, spectral shaping and phase control do not modify the end result of the interaction.

The result of Equation 1 takes on this simple form only when one is interested in the final population of the excited level [i.e., after the pulse has ended ($t = \infty$)]. If, conversely, one is interested in the evolution of the population during the action of the pulse, a much richer response and rather surprising effects could be induced via pulse shaping. Basically, one may excite a transient population in the upper level that is significantly larger than the one that is eventually reached after the pulse has ended. Such coherent transient experiments have been performed with either chirped pulses (16) or pulses with phase inversion around the resonance (17). These transients have even been used as probes for either fields (18) or quantum state (19) measurements.

4. CONTROL OF TWO-PHOTON ABSORPTION

The full power of quantum control and pulse shaping is revealed in nonlinear optical interactions. One of the simplest and most instructive cases to analyze is that of TPA. Again, we assume a simple two-level system that is optically coupled by a two-photon transition (**Figure 2e**). Assuming that the pulse spectrum is tuned near the midpoint of the level spacing, and that no other level is excited resonantly by the light, second-order perturbation analysis predicts the amplitude of the excited level to be (20)

$$a_f \propto \int_{-\infty}^{\infty} E^2(t) \exp(-i\omega_0 t) dt. \quad (2)$$

Again, the excited amplitude is given by a Fourier-like integral, showing that a single frequency component determines the outcome of the interaction; however, now it is the spectrum of the square of the optical fields that is important. As the field $E(t)$ is real in general, its Fourier components are symmetric and centered around the carrier frequencies $\pm\omega_l$ (**Figure 2a**). The spectrum of $E^2(t)$ on the right-hand side of Equation 2 then includes three bands (**Figure 2b**). Two of these bands, centered around $\pm 2\omega_l$, are responsible for the excitations and de-excitations of two-photon transitions, whereas a low-frequency band could lead to Raman-like processes.

Let us first consider the process of TPA, that is, when the final level frequency ω_0 is within the $+2\omega_l$ band of the spectrum of $E^2(t)$. More insight can be obtained by using a frequency-domain

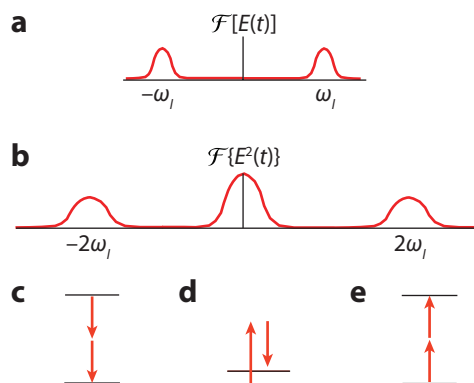


Figure 2

(a) The spectrum of the field $E(t)$ of a transform-limited pulse is characterized by two bands at $\pm\omega_l$. (b) The spectrum of $E^2(t)$ contains three bands, at $\pm 2\omega_l$ and at 0. These could lead to three different two-photon processes: (c) two-photon emission, (d) Raman excitation, and (e) two-photon absorption.

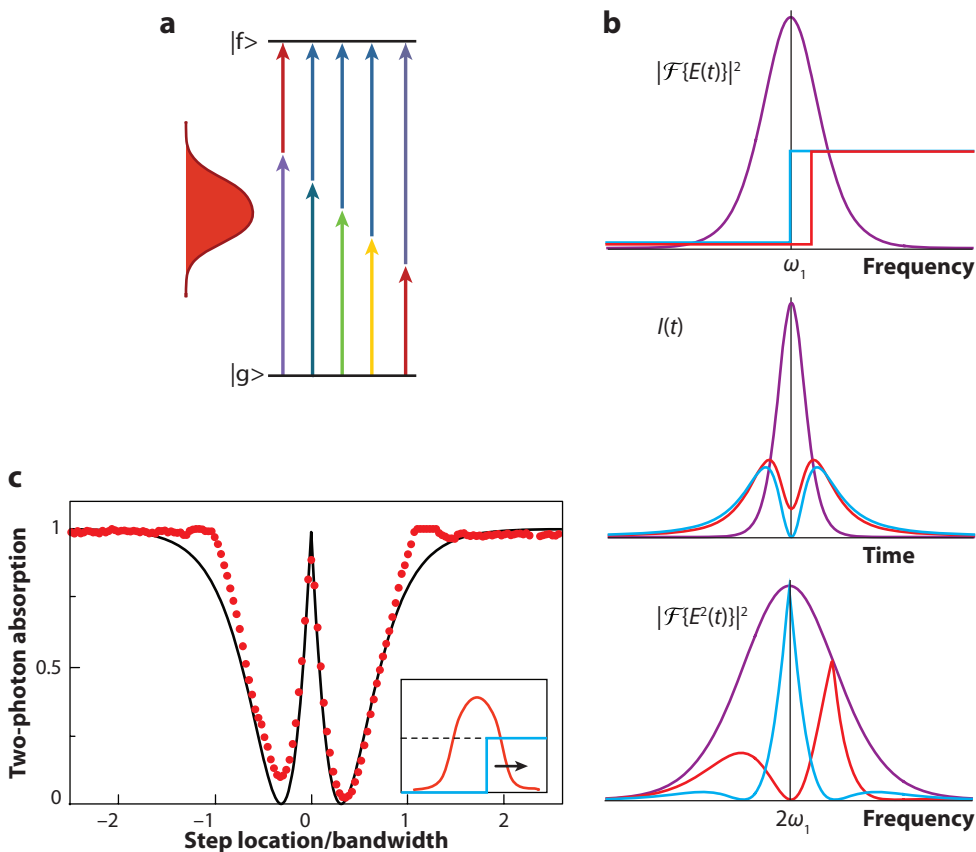


Figure 3

The principles of two-photon absorption (TPA) control by pulse shaping. (a) The pulse is tuned to the center of transition. Many combinations of frequency pairs determine the total excitation. (b) The spectrum of the pulse (top) centered at ω_1 is modified by phase-step functions with a phase jump at frequency ω_{step} (red and blue lines). A transform-limited pulse (middle, purple) is transformed into double-humped pulses. Two-photon processes are determined by the spectrum of $E^2(t)$ (bottom) near a frequency of $2\omega_1$. TPA by the shaped pulses is the same as that of the transform-limited pulse at $2\omega_{\text{step}}$. Other frequencies exist at which TPA is cancelled altogether. (c) TPA as a function of the position of a phase step for a two-photon resonance at the line's center. The black line denotes theory, whereas the red circles denote an experiment in cesium. Figure adapted from Reference 21.

representation of the field and using the convolution theorem. Equation 2 then takes the form

$$a_f \propto \int_{-\infty}^{\infty} \tilde{E}(\omega_0/2 - \delta\omega) \tilde{E}(\omega_0/2 + \delta\omega) d\delta\omega. \quad (3)$$

From Equation 3, it is obvious that the final amplitude results from contributions by all frequency pairs that sum up to the two-photon transition frequency ω_0 (Figure 3a). This is the quantum-mechanical interference that enables control via pulse shaping: By adjusting the phases of the spectral components $\tilde{E}(\omega)$, it is possible to control the total amplitude a_f .

Meshulach & Silberberg (20, 21) have demonstrated the control of TPA in cesium. They have shown that a transform-limited pulse (in which all frequency components have the same phase and hence can be taken as real in Equation 3) is optimal; i.e., it excites the transition as effectively

Dark pulses: pulses tailored to eliminate a nonlinear excitation via destructive quantum interference of all quantum paths

Closed-loop control: an iterative control scheme in which a learning algorithm is used to search for optimal pulse shapes to induce a particular process

as possible with a given power spectrum. Surprisingly, however, pulses that are modified by a phase function that is antisymmetric around $\omega_0/2$ are also optimal, even though they can be made much longer and much weaker than a transform-limited pulse. Other spectral phase functions can significantly reduce TPA, and, in particular, certain pulse shapes can eliminate TPA altogether. These so-called dark pulses can be used therefore to excite other nearby levels without perturbing this particular two-photon transition.

Figure 3 shows, as an example, how simple phase shaping can be used to manipulate the spectrum of $E^2(t)$ and thereby TPA. The phase function is a phase step that is applied to the spectral components: The phase of all frequencies larger than some frequency ω_{step} is shifted by π compared with the phase of the rest of the spectrum. Obviously, if the step location is outside the pulse spectrum, the pulse is not modified, and the two-photon transition is excited efficiently. When the step is located exactly at the degeneracy point $\omega_{\text{step}} = \omega_0$, the pulse is modified: It is transformed into a double-humped pulse, yet the TPA is not affected at all, as is expected for an antisymmetric phase function. However, on either side of this degeneracy point are step positions that yield dark pulses—no TPA is excited. At those points, all the frequency pairs that induce transitions from the ground state interfere to completely cancel the excited-state amplitude. As the step position is scanned across the spectrum, one measures a typical W-shaped profile (**Figure 3c**) (21). Spectral step functions are just one particular way to manipulate pulses; similar results were obtained, for example, with periodic sinusoidal phase functions (20).

Dark pulses could be a useful tool for the selective excitation of one quantum level in the presence of another, whether in the same quantum system or in a mixture of several systems. Indeed, it is quite likely that, in some of the complex pulses being found via closed-loop control (22, 23), such dark pulses naturally evolve because of the requirement of selectivity. However, the concept of a dark pulse is not easily extended to strong fields, in which many of these closed-loop experiments are performed.

The power of control via spectral phase shaping is most impressive in the case of resonantly enhanced TPA. This is the situation in which a resonant level is located near the midpoint of the two-photon transition, so it can be reached by the absorption of a single photon. Such a resonant level might be expected to strongly enhance the transition. However, a broadband excitation pulse excites the system both below and above the transition, thereby exciting it in opposite senses. Early experiments with chirped pulses (24) already hinted at the peculiarities of this situation. The surprising result is that transform-limited, flat-phase pulses are no longer optimal for maximizing the two-photon transition. Longer shaped pulses that contain a phase jump at the resonant frequency excite the system significantly better than a transform-limited pulse (25). Chatel and coworkers (26, 27) have shown that the interplay between the resonant, ladder-climbing process and the nonresonant two-photon paths can also be controlled via the spectral phase.

Coherent control techniques can also be applied to excite selectively states with different angular momentum. This is facilitated by a novel type of pulse shaper that can tailor the temporal evolution of the polarization state during the pulse (28, 29). Nearly degenerate states with different angular quantum numbers can be excited selectively by using polarization shaped pulses (30).

Although this review concentrates on perturbative effects that are the most useful for spectroscopy, extensive work has been performed to extend some of these ideas to the strong-field regime. Naturally, in the strong field, even when dealing with simple quantum systems, one must take into account many nonlinear effects such as level Stark shifting. There have been several approaches to this problem. For example, for certain families of optical fields, Stark shifts could be eliminated, and the simple analytic approach might still be used (31). Amitay and coworkers (32–35) have extended the analytic approach to stronger fields by adding higher-order terms to

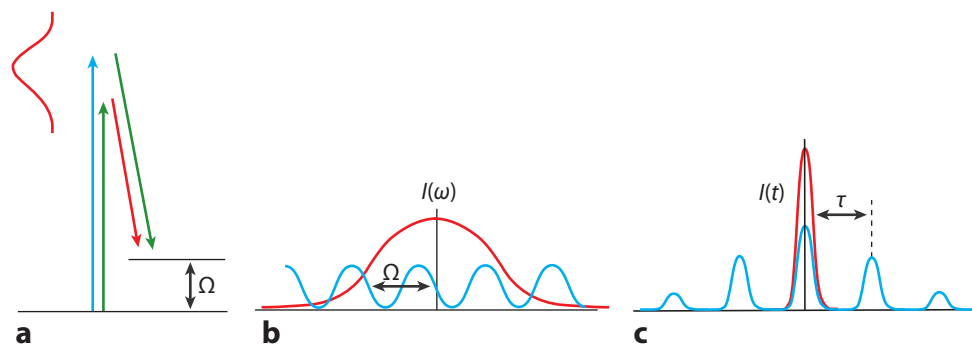


Figure 4

(a) All frequency pairs separated by the vibrational level frequency Ω contribute to its excitation. (b) When the spectrum of a transform-limited pulse is modulated by a periodic phase function with a period Ω (or a whole fraction of it, Ω/N , where N is an integer), the excitation efficiency is maintained. Such a modulation breaks the pulse into a sequence of pulses separated by $\tau = 1/\Omega$ (or a multiple of it, N/Ω), as shown in panel c.

the perturbative theory. Another approach explicitly includes the Stark shift in the time-domain model (36–39).

5. CONTROL OF RAMAN PROCESSES

We now turn our attention to the low-frequency component in the spectrum of $E^2(t)$ as expressed in Equation 2—the central band in **Figure 2b**. This low-frequency band is responsible for two-photon stimulated Raman transitions to a level with frequency Ω . This type of experiment, in which a Raman level is excited by a pulse that is spectrally broader than the Raman frequency (or, equivalently, shorter than the vibrational period), is usually referred to as impulsive Raman scattering. The excitation of the Raman level can also be expressed in the frequency domain as

$$a_f \propto \int_{-\infty}^{\infty} \tilde{E}(\omega) \tilde{E}^*(\omega - \Omega) d\omega. \quad (4)$$

This term describes the simultaneous excitation of a Raman level by all frequency pairs in the pulse that are spaced by the Raman frequency Ω (**Figure 4a**). Again, pulse shaping may affect the total efficiency of the process; as in TPA, a transform-limited pulse is optimal for impulsive excitation in the sense that all frequency pairs that contribute to the transition in Equation 4 interfere constructively. If the spectrum is modulated by a periodic phase function that matches the Raman frequency (as in **Figure 4b**), the excitation efficiency is not affected; i.e., it maintains the excitation efficiency of a transform-limited pulse. We note that periodic modulation in the spectral domain breaks the pulse into a sequence of pulses in the temporal domain. In an early pioneering experiment, the groups of Weiner and Nelson demonstrated that a periodic sequence of pulses is as effective as a single strong pulse to excite a vibrational level (40). One advantage of impulsive excitation by a periodic train of pulses rather than a single strong pulse is that undesirable nonresonant effects are much weaker (40).

6. CARS SPECTROSCOPY

The vibrational spectrum of organic molecules is rich in structure and has been used traditionally as an analytical spectroscopic tool. However, unlike in TPA, the mere nonlinear excitation of a Raman level is not usually followed by the emission of photons; hence detecting the excitation of

Impulsive Raman scattering: excitation of a vibrational level with a short optical pulse; the pulse needs to be shorter than the vibrational period

Raman levels requires additional steps. The most common technique for this purpose is CARS (41), in which two-photon excitation is followed by a two-photon de-excitation process, together forming a resonantly enhanced four-wave mixing process (**Figure 5a**). In a typical CARS process, two strong laser beams with frequencies ω_p and ω_s excite a Raman level at $\Omega = \omega_p - \omega_s$, and a third field with frequency ω_{pr} (often chosen so that $\omega_{pr} = \omega_p$) scatters off the excited vibration to form a fourth wave with $\omega_{cars} = \omega_p + \omega_{pr} - \omega_s$. CARS has several important features that make

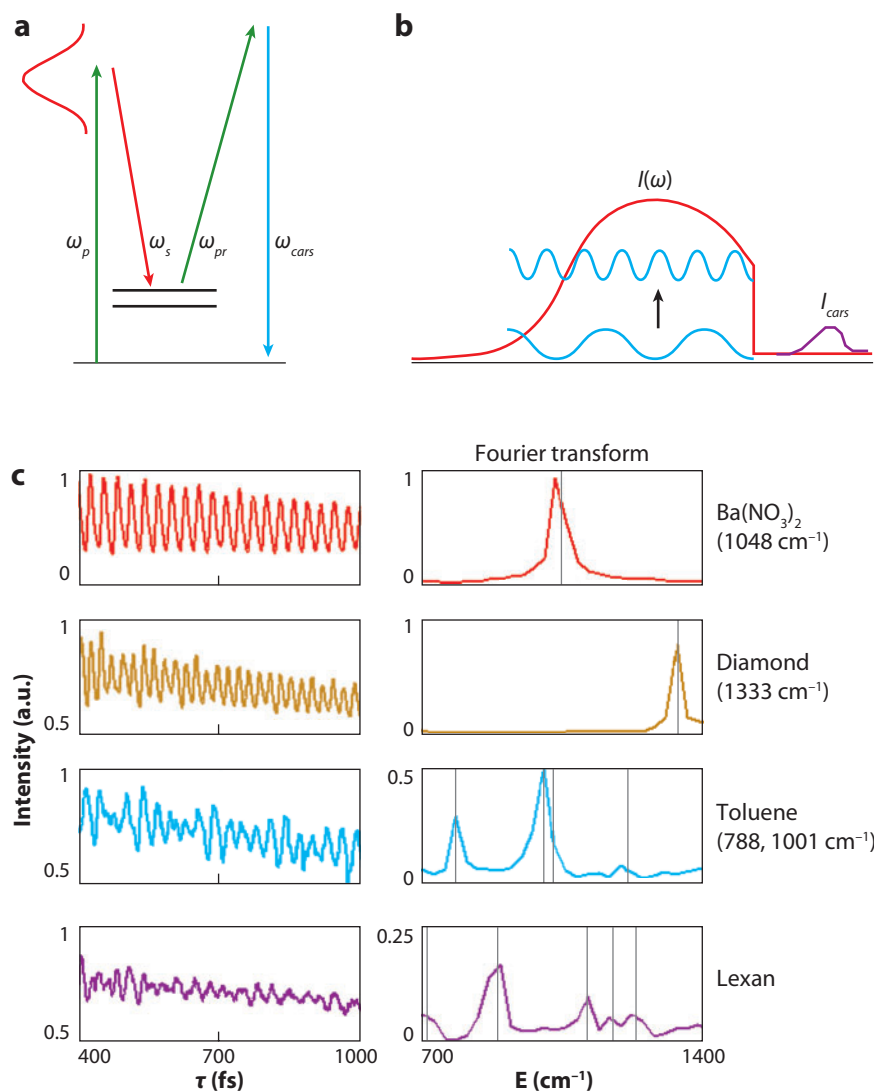


Figure 5

Single-pulse coherent anti-Stokes Raman spectroscopy (CARS) spectroscopy. (a) The excitation photons ω_p , ω_s , and ω_{pr} are derived from the same excitation pulse. (b) The high end of the pulse spectrum (red line) is trimmed on the high-frequency side, at which the resulting CARS photons at ω_{cars} are detected. The spectrum is modulated by a periodic phase function (blue). (c) By sweeping the spectral modulation period, the Raman levels are periodically excited (left column), revealing the vibrational levels (right column). Figure adapted from References 44 and 45.

it a favorable nonlinear spectroscopy tool, including the fact that the CARS signal that needs to be detected is at a frequency larger than those of all input waves; hence it is not masked by various fluorescence processes. Also, as CARS is a coherent process, the signal is directional and is proportional to N^2 , where N is the number of molecules participating in the process. However, CARS spectroscopy experiments are normally performed with narrow laser lines because the laser line width determines the spectral resolution of the technique. As the width of typical Raman transitions is a few wave numbers, femtosecond pulses normally are not employed. Not only do they lack the spectral resolution, but their high intensity also induces instantaneous nonresonant processes that mask the CARS signal.

Realizing the important applications of CARS spectroscopy, researchers naturally tried to extend the ideas of the coherent control of Raman transitions to CARS. The first experiments by Oron et al. showed how coherent control can enhance the standard CARS technique. They used either shaped pump and Stokes beams (42) or a shaped probe beam (43) to significantly enhance the resolution and, simultaneously, to reduce the nonresonant background that typically limits CARS experiments with short pulses. However, the real power of coherent control was utilized with the advent of single-pulse CARS techniques.

In single-pulse CARS, one uses a single femtosecond pulse to perform the entire CARS process. By appropriately shaping the pulse, one could regain resolution and reduce unwanted background signals. In a pioneering experiment, Dudovich et al. (44) demonstrated single-pulse CARS measurements of several molecules. The essence of their method is shown in **Figure 5**. The spectrum is modulated by a periodic phase function, whereas the higher-frequency end is blocked to enable the detection of the CARS photons. Raman levels are excited periodically by sweeping the period of the phase modulation. By analyzing the varying scattered CARS signals, one can extract the Raman spectrum with high resolution and with relatively small background (**Figure 5c**). Naturally, single-pulse CARS is limited in its spectral reach to the width of the excitation pulse, as the most energetic Raman level that can be measured is excited by the two ends of the pulse spectrum. However, the setup is attractive because of the use of a single laser source delivering a single beam into the sample. With a broader 10-fs laser (45), this method can cover almost the entire so-called fingerprint region of the spectrum, and more sophisticated shaping can help significantly reduce the nonresonant background signals. In another approach to extend the spectral reach of the single-pulse technique, Motzkus and coworkers (46) shaped the supercontinuum band that is generated in a photonic crystal fiber. They also showed that by leaking a small fraction of the pump, heterodyne detection of the CARS signal can greatly enhance the detection sensitivity (47).

In addition to periodic modulation, other schemes have been shown to lead to selective excitation. For example, von Vacano & Motzkus (48, 49) demonstrated that a pulse shaper could be used to split the two halves of the spectrum by putting a linear phase with different slopes in the two halves, causing a two-pulse excitation that leads to the preferential excitation of a single Raman level. Milner and coauthors (50) recently used a different approach, employing noisy fields, shaped by a random phase or amplitude mask for CARS spectroscopy, by utilizing the narrow autocorrelations of such fields.

In selective excitation techniques, the Raman levels are excited one at the time; hence there is no need to resolve spectrally the scattered CARS photons. An alternative approach, known as multiplexed CARS (51), excites the entire collection of levels, and probing is performed by an effective narrow-band portion of spectrum (see **Figure 6**). In multiplexed CARS, the signal is spectrally resolved, as each Raman level shifts the narrow probe by its energy; thus the spectrally resolved scattered signal yields the vibrational spectrum. Several methods of multiplexed single-pulse CARS have been demonstrated, using different ways to select the probe signal. For example, the probe can be selected by shifting the phase of a narrow band of frequencies in an otherwise

Single-pulse CARS:

a CARS technique in which all three input frequencies are supplied by a single shaped laser pulse

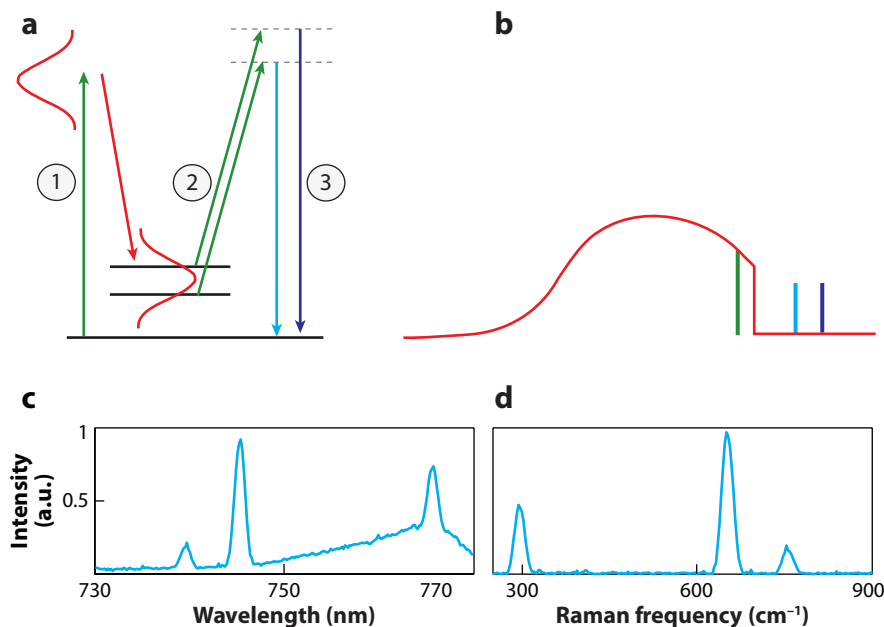


Figure 6

Single-pulse multiplexed coherent anti-Stokes Raman spectroscopy (CARS). (a) In multiplexed CARS, a broadband short pulse excites several vibrational levels (*step 1*). A narrow-band probe signal (*step 2*) scatters these levels to produce a number of CARS photons (*step 3*), with frequencies that mirror the level structure. (b) For single-pulse multiplexed CARS, a narrow band of wavelengths at the high-frequency side is modified (usually in phase or in polarization) to serve as the probe field (*green band*). The pulse spectrum is blocked at the high-frequency end to enable the detection of the CARS photons. The spectrum of these CARS photons (*blue bands*) is detected to retrieve the vibrational level structure. (c) Measured CARS spectrum of a sample of 1,2-dichloroethane via polarization shaping and (d) the resulting Raman spectrum. Figure adapted from Reference 53.

flat-phase pump (52). Alternatively, one can rotate the polarization of the probe band using a polarization pulse shaper (53). To improve detection, investigators have homodyned the scattered CARS signal with either the tail of the excitation pulse or a nonresonant, featureless background (54, 55).

Because the CARS generation process is coherent, it is possible to employ more complex probe signals that enhance particular features. Oron et al. (56) have used a variation of polarization multiplexed CARS with several narrow probe bands. By tailoring the spectral content of these probes, they were able to build one coherent feature of the scattered field that depends on the presence of several vibrational levels. Such an all-optical technique is obviously only possible with coherent scattering processes, and it is naturally combined with the coherent control methods.

Finally, there are new developments in the related spectroscopical technique of two-dimensional spectroscopy in which coherent control could greatly simplify the experimental system and data acquisition. Although the standard approach to two-dimensional spectroscopy requires a phase-stabilized setup involving three independent input beams (57), the Nelson group has shown that two-dimensional pulse-shaping techniques (58, 59) can be used to manipulate several beams with great accuracy, thereby obtaining two-dimensional time-frequency maps of a four-wave mixing process (60).

7. APPLICATIONS IN MICROSCOPY AND SPECTROSCOPY

Two potential applications have motivated many of the studies discussed above, even if indirectly: nonlinear microscopy and remote sensing. Nonlinear microscopy is presently a broad field that applies nonlinear optics for imaging. Although many connections between the two disciplines have been made in the past, the invention of the two-photon fluorescence microscope by Webb and coworkers (61) in 1990 gave the field its big push. Two-photon microscopes are usually laser scanning microscopes in which fluorescence is excited by TPA. Because the fluorescence is excited primarily at the focal spot of the laser beam, it enables optical sectioning, reduces out-of-focus photobleaching, and enables deeper penetration into thick samples because of the reduced scattering of the long-wavelength excitation beam. This was the first meeting between ultrafast optics and microscopy, a combination that keeps evolving and producing new and exciting results. Since then, many other nonlinear effects have been used to form microscopes with new modalities, each with its own advantages and potentials. It is not surprising then that the new techniques of quantum control were applied and tested in the context of microscopy as well. The conceptual setup is shown in **Figure 7**: A femtosecond source is shaped before the interaction with the specimens, optimizing the nonlinear effect in the sample. As many practitioners of the field have noted, this setup also provides a convenient way to correct for the group dispersion inevitably associated with the delivery of short optical pulses to the sample.

The ability to coherently control TPA processes as discussed above naturally led to the testing of some of these concepts in the context of microscopy. Although TPA in atomic lines could be controlled with great precision (20, 21), the organic fluorophores used as markers in biological microscopy (or endogenous fluorescence in certain specimens) exhibit much broader absorption lines, resulting in short coherence times and much less room for control. Nevertheless, studies by the Dantus (62–67) and Joffe (68, 69) groups have demonstrated that pulse-shaping techniques could be used to control the excitation efficiency and thereby to differentiate between several fluorophores in practical two-photon imaging.

Applications in microscopy were the motivating factor for much of the work in coherent control of CARS spectroscopy. The pioneering work by Xie's group (70) on CARS microscopy as a tool for molecular imaging in biology attracted significant attention. The potential for imaging particular molecular species in live specimens without the need for marking or otherwise modifying the

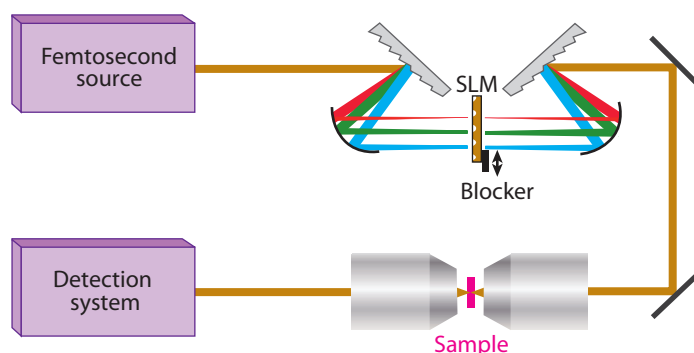


Figure 7

Conceptual setup for coherently controlled microscopy. A nonlinear interaction is excited by the shaped femtosecond pulses. The beam is raster scanned in the sample, or the sample itself is translated to collect spatial information. The scattered signal could be copropagating with the pump beam as shown or collected in an epi-geometry via the input objective. SLM, spatial light modulator.

specimens is obviously important to practically any area of biology. Most of the work in CARS microscopy uses more or less the standard approach to the technique—i.e., excitation with two lasers with relatively narrow spectral lines. Naturally, the simplicity of the single-beam approach described above makes it attractive for microscopy applications, and indeed, a simple attempt at imaging appeared already in the first publications (44). The main limiting factor in the adaptation of single-pulse CARS for microscopy is the limited bandwidth of the pulse, which translates to the inability of exciting higher-frequency vibrations. For example, the most common line used to demonstrate CARS imaging is the C-H stretch near $\sim 3000\text{ cm}^{-1}$, which would require pulses shorter than $\sim 5\text{ fs}$ to excite impulsively. To overcome this limitation, several groups have extended the single-pulse concept for broader response, for example, by employing continuum generation in nonlinear fibers (46). In particular, the groups of Motzkus (46–49), Leone (54, 55, 71, 72), and Joffre (73) have demonstrated several schemes for enhancing the sensitivity and selectivity of CARS spectroscopy, with basic demonstrations of applications in microscopy.

Another field in which coherent control techniques could find important applications is the remote detection of hazardous materials. Scully and coworkers (74–76) have considered the remote sensing of biological agents by ultrafast CARS techniques. Although standard, multisource CARS techniques could be employed for remote sensing as well, there is an obvious advantage to single-beam, single-pulse techniques that eliminate the need to combine several high-intensity beams of different wavelengths and propagate them over long distances. Indeed, a couple of recent studies have shown that single-pulse multiplexed CARS spectroscopy with shaped pulses could be applied to the stand-off detection of trace amounts of materials at distances of a few meters (77, 78).

Another intersection of control and microscopy can be identified in the concept of temporal focusing microscopy (79–81), which uses a dispersive optical system to form a dispersed pulse that compresses on its way to the focal plane of an objective, forming the shortest pulse at that plane. As a result, nonlinear processes are excited preferentially only at that plane, enabling optical sectioning without scanning (79). In a variant of this technique, video-rate imaging is made possible with just one-dimensional scanning (80). As the optical setup closely resembles an optical shaper, it is natural to combine temporal focusing with coherent control. Indeed, it has been shown that pulse shaping can help to increase axial resolution in third harmonic microscopy (81).

8. OUTLOOK

The past decade has seen an impressive advance in the development of ideas and methods that employ concepts from coherent control to spectroscopy. In parallel, there has been a steady advance in the development of short pulse sources and pulse-shaping instrumentation. The next few years, therefore, are crucial for evaluating the practicality of these ideas in the real world. Whether a particular scheme is useful for microscopy, for example, will be put to the test by end users, who will want to see performance that cannot be provided by simpler conventional techniques. Although it is likely that many schemes discussed in this review, however elegant, will not withstand such tests, it is not unreasonable to expect that some of the ideas of quantum control will find real application in certain high-end areas of practical spectroscopy.

SUMMARY POINTS

1. For effective control, one should use pulses shorter than the coherence time and hence spectrally broader than the energy levels involved.

2. In two-photon processes such as TPA and stimulated Raman transitions, there are many frequency combinations that contribute to the same process. The relative phases of these frequency components can be modified by pulse shaping, thereby controlling the total excitation of the system via quantum interference.
3. Dark pulses can be shaped to eliminate the excitation to a particular transition, enabling selective excitations of other levels.
4. Single-pulse CARS techniques perform coherent anti-Stokes Raman scattering, in which all three input photons are supplied by the same pulse. Pulse shaping enables spectral resolution and selectivity, but the spectral reach is limited by the pulse bandwidth.
5. Single-pulse CARS could simplify optical setups required for applications in microscopy and remote sensing, eliminating the need for multiple-beam combining.

DISCLOSURE STATEMENT

The author is not aware of any biases that might be perceived as affecting the objectivity of this review.

ACKNOWLEDGMENTS

I wish to thank the many collaborators who have contributed to my own group's works described here and, in particular, my former and current students D. Meshulach, D. Yelin, N. Dudovich, D. Oron, B. Dayan, E. Tal, E. Frumker, O. Katz, and A. Natan. This research was supported by grants from the Israel Science Foundation.

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