Ultrafast Optical Waveforms

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The ability to generate optical pulses with durations under 100 fs has revolutionized spectroscopy and opened up many exciting possibilities in optical communications. Recent advances with ultrafast laser sources and amplifiers indicate that millijoule pulses shorter than 20 fs will soon be available. The peak intensities of such fields can produce strong light-matter interactions that are well beyond the regime described by simple perturbation theory. Unprecedented flexibility will be achieved when these high-energy ultrafast pulses can be "shaped" into optical waveforms with arbitrary temporal profiles. This capability will vastly expand the applications of ultrashort pulses, just as radio frequency (RF) pulse-shaping has expanded the scope of nuclear magnetic resonance (NMR) spectroscopy and made possible magnetic resonance imaging (MRI). As in multiple-pulse NMR and MRI, the technical details of complex waveform generation must be handled by computer and will be largely hidden from the user.

There is substantial theoretical literature on the application of ultrafast optical waveforms to "mode-selective chemistry" (*1*), which expands the use of spectroscopy from simple observation of chemical events to active control over them. In preliminary demonstrations, pairs of femtosecond excitation pulses, in some cases with specified optical phases as well as overall timing, have been used to control molecular motion and reactivity (*2, 3*). Even more exciting are the possibilities for extensive optical control over collective material behavior as well as molecular behavior. In recent prototype experiments, timed sequences of up to 20 femtosecond pulses were used to selectively drive lattice vibrations in molecular and ionic crystals (*4, 5*). Each pulse delivered an "impulse" to the selected lattice vibration, increasing its amplitude coherently in the same way one repetitively pushes a child in a swing. With high-power optical waveforms, lattice distortions of very large amplitude might be reached, yielding highly controlled structural or chemical changes. Optical control over collective motion in plasmas may also be realized with high-power femtosecond waveforms.

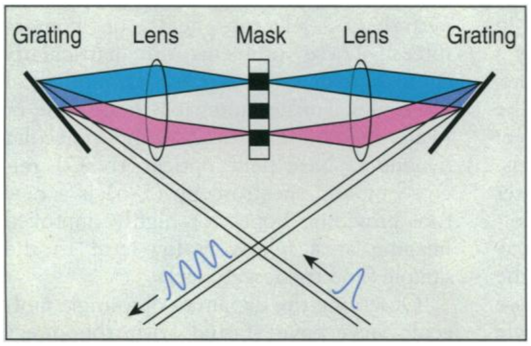

Fig. 1. A grating angularly disperses a broad-bandwidth ultrashort pulse, and a lens collimates and focuses the laterally dispersed frequency components on a spatially varying mask. The mask attenuates or retards selected frequency components. A subsequent lens and grating recombine the spectrally filtered light, producing a shaped waveform in the time domain.

Techniques for computer generation of arbitrary, ultrafast optical waveforms are being developed (*6*). With our first-generation programmable pulse shaper, constructed entirely from commercial optical components, waveforms with good fidelity containing features as short as our 70-fs input pulse and extending for several picoseconds can be generated. We can switch between different waveforms in less than 1/10 s.

Production of complex sequences of femtosecond pulses with controlled amplitude and phase profiles was pioneered by Weiner and Heritage at Bellcore, who were aiming for applications in ultrafast optical communications and information processing (*7*). The technique involves passing an incident femtosecond pulse through a simple optical network that includes two gratings, two lenses, and one or two spatially varying masks (Fig. 1). The broad spectrum of wavelengths contained within the ultrashort pulse is angularly dispersed by the first grating, and the different frequency components are collimated and focused onto different parts of the mask. The mask is used to block or retard selected frequency components, thereby altering the amplitude or phase profile of the dispersed frequency spectrum; amplitude and phase masks may be used alone or in series. The second lens and grating recombine the manipulated frequency components to create a shaped pulse whose temporal amplitude and phase profiles are related through Fourier transformation to the spectral profiles and therefore to the spatial patterns on the masks.

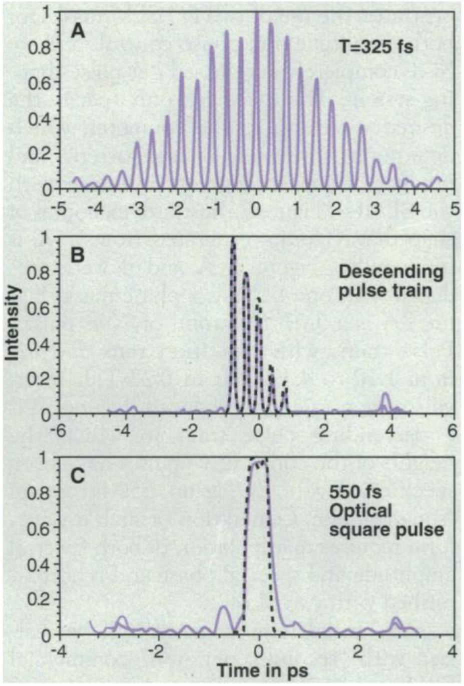

Fig. 2. Examples of shaped ultrafast waveforms generated from a 70-fs input pulse with the pulse shaping setup. (**A**) 3.07-THz train of 70-fs optical pulses. (**B**) Descending pulse train in which the heights of the consecutive pulses have been specified. (A) and (B) were produced with only a single SLM as a phase mask. (**C**) 550-fs Optical "square" pulse. Generation of such a waveform required two SLMs to manipulate both spectral amplitude and spectral phase. The dashed curves in (B) and (C) give the anticipated waveform assuming perfect calibration and alignment.

Originally, mask patterns were etched onto glass substrates. These yielded excellent results, but each pattern had to be fabricated in advance for a given desired waveform. Weiner *et al.* (*8*) later demonstrated a programmable mask based on a liquid-crystal (LC) spatial light modulator (SLM) consisting of a linear array of electronically addressable pixels. This opened the door to versatile pulse shaping suitable for general spectroscopic applications.

The commercial SLM devices initially available were of limited potential because of the small number of pixels and the rather large dead spaces between them. In general, the complexity (number of distinct features) of the shaped waveform can be no more than the number of pixels on the SLM. Additional problems include light transmitted through the gaps between pixels or diffracted by pixel edges, and practical issues such as precise alignment of the masks and lenses and accurate calibration of the masks (that is, accurate determination of the applied voltage needed to generate a desired amplitude or phase change). All of these concerns are magnified when both phase and amplitude masks are used.

Despite these difficulties, we have dem-

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onstrated the use of two LC SLM masks for both amplitude and phase control, and we have completely automated our pulse shaping system. The user need only specify the desired waveform to the computer, which determines the needed mask patterns and produces them through its interface with the SLM(s). Figure 2 illustrates examples of shaped waveforms generated from a 70-fs input pulse. Figure 2, A and B were produced with one SLM as a phase mask. Figure 2A is a 3.07-THz train of 70-fs pulses. Pulse trains with repetition rates ranging from 1.10 to 4.39 THz in 0.22-THz intervals were also easily produced. Figure 2B is a descending pulse train in which the heights of the consecutive pulses have been specified. Figure 2C is an 550-fs optical "square" pulse. Generation of such a waveform requires manipulation of both spectral amplitude and spectral phase and is accomplished with two SLMs.

Substantial improvements will be realized with "second-generation" commercial SLMs, which have many more pixels and much smaller gaps. In addition, techniques for rapid and complete characterization of amplitude and phase profiles have been demonstrated (9). Finally, preliminary results indicate that amplification of shaped waveforms in a titanium:sapphire regenerative amplifier introduces little or no loss of fidelity. This is crucial for achieving the high-power waveforms necessary in many "optical control" applications. Given current developments, we can anticipate an amplified pulse shaping system in which the amplified output is characterized and used in a feedback loop to refine the SLM masks iteratively, so that high-power, user-specified waveforms are generated.

Such waveforms will be used for control over molecular and material behavior. Spectroscopic applications that can be readily imagined include multiple-pulse vibrational spectroscopy within and beyond the harmonic oscillator (small-amplitude) regime, fluorescence-detected photon echoes, and optical analogs of multiple-pulse NMR techniques, such as dipolar decoupling, in which the electronic interactions of molecules with their neighbors are altered. For the most ambitious applications in material control, in which permanent structural changes are achieved, the entire experiment must be over in a single laser shot because the sample never returns to its initial state. Such a transformation could be monitored with recently developed real-time femtosecond probing techniques, by which the entire time-dependent response of a sample is recorded in a single shot (*10*).

In most optical-control applications, the optimal pulse sequence is not known in advance because the molecular or material properties, especially if they are far from equilibrium (on the way toward chemical or structural rearrangement), are not known precisely. Imperfect knowledge of a material Hamiltonian can, however, be the basis for a trial waveform, and the response of the material to this input can be analyzed to improve the waveform by iteration. Learning algorithms to realize this possibility have been proposed (*11*), raising the prospect that a material can actively participate in its own modification.

The development of femtosecond lasers and spectroscopic techniques has made the past decade one of remarkable advance in our ability to observe ultrafast molecular and material processes. Elementary molecular motions involved in chemical-bond breakage and elementary collective motions involved in structural phase transitions have been observed directly in the time domain. Automated generation of high-power femtosecond waveforms in the current decade will extend our capabilities from observation of, to control over, molecular and collective behavior, including chemical and structural rearrangements.

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12. We thank A. Weiner for his insights and advice. M. M. W. acknowledges a Canadian Natural Science and Engineering Research Council graduate fellowship. This research was supported in part by National Science Foundation grant CHE-8901722.

Near-Field Optics: Imaging Single Molecules

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Can we image a single molecule in vivo? Can we see it wiggle or react or break up? Can we simultaneously measure its energy dynamics? Can we monitor directly and in real time the ions or radicals released by a single ion gate or enzyme? More and more, these questions are being answered in the affirmative (*1*). Impressive evidence of progress is provided on page 1422 of this issue in the report by Betzig and Chichester on their success in imaging single molecules (*2*). Moreover, they do it in a way that reveals the orientation of each. At the same time, Betzig and Chichester have been able to turn the tables, using a single molecule to map the electric field distribution in the vicinity of a nanometer light source.

Traditionally, molecular structure and dynamics have been observed by averaging techniques, such as x-ray crystallography, electron diffraction, and various spectroscopies. On the other hand, electron microscopy and related methods do indeed image single molecules but at a heavy cost to their integrity—observing them in a vacuum or under highly perturbative conditions. Recent methods such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM) come closer to the ideal, but the molecules are still exposed to perturbative electric fields or contact forces. These problems are particularly acute for the soft organic and biological molecules. Furthermore, it is impossible or nearly unfeasible to observe the molecular dynamics. Near-field optical (NFO) microscopy and spectroscopy (*3–6*) is a new tool providing hopes for highly improved imaging at a relatively low cost to the sample (and the researcher).

Observing the dynamics of a single molecule may have started with the direct patch-clamp–assisted observation of single sodium gates, and in particular the voltage jumps accompanying their opening and closing (*7*). Recent, very elegant single-molecule observations in the energy domain have been performed and reviewed (*8, 9*). In this case, single molecules move around in the very high resolution laser spectral domain in samples of dilute, mixed molecular crystals and polymers. Optical spectroscopy observations of single molecules have recently been made (*10,11*). Here, dye molecules are in a thin flow cell (*10*) or levitated microdroplet (*11*) and are fleetingly observed by laser fluorescence.

The report by Betzig and Chichester (*2*)

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