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Generation of Shaped Femtosecond Laser Pulses: New Approaches to Laser Selective Chemistry

Abstract

We discuss two new approaches to pulse shaping which have major potential advantages over existing techniques for making complex waveforms. These approaches are needed to create nonlinear frequency sweeps and other modulations which are useful for coherent control of chemical dynamics.

Introduction

The idea of using controlled radiation fields to alter molecular states or drive chemical reactions – laser selective chemistry – has a very long and checkered history (for recent reviews see Rice 1992 and Warren 1993). The development of high-power lasers in the 1960s led almost immediately to efforts to dump energy into specific chemical bonds (for example, through overtone absorption) in the hope that this would change reaction dynamics. By the late 1970s (many person-years and guilders later) these studies had produced valuable insights on intramolecular energy redistribution, but the original goal seemed farther away then ever, and the concept of 'photons as chemical reagents' had fallen into disrepute.

Today the coherent control community includes dozens of theoretical and experimental groups, and the prospects for optical control of chemical dynamics seem quite bright. Two major and complementary sets of developments over the last decade have changed the outlook dramatically. First and foremost, the technology for controlling optical fields improved dramatically. Coherent laser spectroscopy has fluorished since the late 1970s and early 1980s (in large part due to contributions from the chairman of this meeting, for example Morsink 1980), but mainly by the clever use of pulse sequences which were extremely insensitive to pulse shape and phase shift effects. Indeed, the first experiments which used even nonoverlapping nanosecond pulses with a completely controlled phase shift came in 1981. Phase shifting technology rapidly evolved in the 1980s into the femtosecond time domain (Mukherjee 1986, Spano 1987, Warren 1988, Scherer 1990). In addition, optical pulse shaping capabilities evolved from nanosecond resolution with pieces chopped out of a continuous laser to < 100 fs time resolution with amplified laser pulses and programmability (Weiner 1986,

1989, Haner 1988). Suddenly the kinds of multiple-pulse experiments which led to such dramatic breakthroughs in magnetic resonance twenty years earlier became technically conceivable in the optical regime, on a timescale which was short enough to compete with molecular relaxation, with high enough powers to significantly perturb populations. Experimental work has demonstrated modulation or enhancement of overall signals (in stimulated Raman scattering, multiphoton ionization, or fluroescence) in a variety of applications. Just as importantly, by the mid-1980s these technological developments had begun to fire the imagination of the theoretical community. Starting with simple model molecules, and gradually evolving into more complex systems, calculations have shown that appropriately shaped and phased optical pulses can prepare selected rotational states, pump up anharmonic vibrational ladders or modify internal relaxation dynamics (for recent reviews see Rice 1992 and Warren 1993).

Despite the tremendous progress over the last decade, there is still a gap between what the experimentalists have achieved and what the theoreticians expect will be possible. This gap is narrowing visibly as calculations get more sophisticated, but it is still clear that technological capabilities provide an ultimate limitation to what will be achieved in the foreseeable future. While 100 femtosecond, programmable pulse shaping has been achieved by several approaches, this does not imply that *any* waveform with such a risetime is possible. For example, nonlinear frequency modulation remains extremely difficult (and, unfortunately, central to many proposed schemes). In addition, schemes to make molecules act as 'quantum mechanical computers' to design their own optimal waveforms (Rabitz, 1992) require the ability to change waveforms quickly, and the most common approach to programmable pulse shaping (multielement LCD modulation of a spatially dispersed waveform) can only be updated at approximately 100 Hz – far lower than the repetition rate of even many amplified laser systems.

We discuss here two new pulse shaping methods developed in our laboratory over the last few months. First we discuss a method for letting molecules design their own optimal pulse shape by absorption within a Michaelson interferometer. This makes it possible to fabricate pulses with dozens or hundreds of different Fourier components, individually matched to specific molecular absorptions. In addition, we show that acousto-optic modulators can be used in place of LCDs to produce programmable pulse shaping. The ultimate potential advantages of this technique include very high resolution, pulse shape updating at MHz repetition rates, and absence of distortions due to gaps between LCD pixels.

Interferometric Pulse Shaping

One of the most important issues in coherent laser spectroscopy is *robustness*. It is one thing to calculate waveforms which in principle would force molecules into a specific state, given the exact Hamiltonian and no inhomogeneities; real-

istic implementation is quite another matter. For this reason, one of our major thrusts over the last few years has been applications of frequency swept laser pulses (Melinger 1991, 1992, Goswami 1993), which in the adiabatic limit produce population inversion or state-to-state transfer even if the sweep is not perfectly linear or if the intensity is not uniform. For example, we have shown that frequency swept pulses can simultaneously invert a large number of transitions in molecular iodine (Melinger 1991). However, the simplest version of this technique (a linear frequency sweep) only works far from the rotational bandheads. Explicitly, the population in state $J'' = N$ will only be transferred into the excited state if the frequency separation between the two transitions including this state ($R(N)$-$P(N)$) is larger than the pulse bandwidth.

It is possible to do much better with more sophististicated laser pulses. In the weak-response limit, the optimum laser pulse for exciting any molecule with discrete spectral lines would be a pulse which contains only those frequency components. Such a pulse would also do the best possible job of selectively exciting a specific molecule in a background of competing absorbers. In the strong-response (adiabatic) limit, pulses with such a frequency structure are a natural and logical starting point for generating efficient inversion, particularly if phase modulation or frequency sweeps can be imposed on this overall structure as well.

Such waveforms could look quite complex. In iodine, for example, the spectrum of a room-temperature bulb has 5-10 intense transitions per wavenumber. Thus even a 1 ps pulse (bandwidth $\approx 13\ \mathrm{cm}^{-1}$) excites approximately 100 different transitions, which are separated only slightly in frequency. No existing pulse shaping techniques have such frequency resolution or could generate waveforms with such complexity. However, the *molecule itself* knows how to generate such a waveform easily; the optical free induction decay after a single short pulse has exactly the right frequency characteristics.

We save the free induction decay while deleting the intense original pulse with a Michaelson interferometer (Fig. 1). When the two arms of the interferometer are exactly equal, it produces constructive interference in one direction and

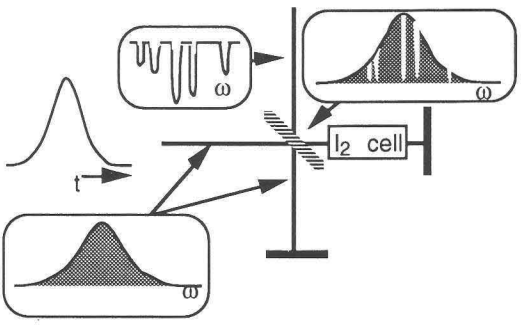

Fig .1. A Michaelson interferometer plus an iodine cell shapes a picosecond pulse to create a waveform which, when amplified, is extremely efficient for iodine inversion.

destructive interference in the other, independent of wavelength. Inserting a sample cell into one of the arms attenuates the resonant frequency components, and also introduces some phase shifts (depending on the optical density of the cell). This destroys the perfect cancellation in the destructive interference direction (counterpropagating with the entering laser pulse), leaving only the molecular free induction decay. The beams can be separated by polarization rotation (using a polarizing beamsplitter and a quarter-wave plate); we find it more convenient to misadjust the Michaelson by $\lambda/2$, thus separating the destructive interference direction from the input beam. Since the iodine cell is relatively large (10 cm) the delay line is stabilized with a collinear HeNe laser and a PZT on one arm.

Analysis with a 10 ps resolution streak camera (Hamamatsu) verifies that an elongated pulse is produced. We are currently producing amplified shaped pulses with a conventional excimer-pumped dye amplifier.

Generation of Tailored Ultrafast Laser Pulses with Tailored Microsecond Radiofrequency Pulses

Subpicosecond resolution pulse shaping is always achieved by indirect modulation schemes, since no electronic devices are capable of responding that quickly. In one approach, pioneered in our laboratory a few years ago (Haner 1988), fast electro-optic modulators are inserted into a pulse stretcher-compressor combination. After the stretcher, an initial ultrafast pulse can be lengthened to ≈ 100 ps; a programmable microwave pulse generator can act with a risetime of approximately 10 ps, so the stretched pulse can be significantly altered. One major advantage of this idea is that the waveform can be updated quite rapidly (in one application, new pulse shapes were generated within approximately 10 ns). Also, the pulse shape is controlled by a single temporal voltage waveform, which is relatively easy to characterize with modern electronics. However, the effective number of 'bits' of modulation which can be imposed on a pulse is relatively small (6-10). In addition, the technology is cutting-edge and difficult to use.

Heritage and Weiner developed a pulse shaping approach in the mid-1980's using spatial dispersion of an ultrafast pulse within a grating pair (Weiner 1986). Programmability was ultimately achieved with multielement LCD spatial modulators for phase or amplitude modulation (Weiner 1989). The advantage of this approach is that these modulators are commercially available, and thus shaped waveform generation is dramatically simpler than with fast electro-optic modulators. However, the gap between pixels leads to an additional modulation on the desired waveform. In addition, alignment and calibration of each individual pixel can be complex, and the fundamental response time of the devices is relatively slow (a few hundred Hertz). The LCD devices are fundamentally phase modulators, and while they can be used with polarizers to produce amplitude modulation, the isolation is also not particularly good.

We present here a new pulse shaping approach which promises to combine

many of the advantages of the two earlier techniques. It uses a shaped radiofrequency pulse of long duration (up to a few microseconds) to control the ultrafast laser pulse shape. The apparatus is essentially the same as the Heritage-Weiner pulse shaping setup, with the LCD spatial modulators replaced with acousto-optic modulators. In the simplest approach (Fig. 2) the AOM is operated at the Bragg angle. We have previously shown that amplitude and phase modulation applied to the radiofrequency AOM driver is imposed on the laser output; however, this is limited to generating shaped pulses with nanosecond risetimes. In our new approach, the laser pulse entering the AOM is spatially dispersed to a width of approximately 5 mm. The speed of sound in our TeO_2 modulator is 4.2 mm/μs. Thus, the sound wave takes approximately 1.2 μs to traverse the entire laser beam, and a 1.2 μs modulated r.f. pulse produces different diffracted intensities at different positions in the crystal.

Preliminary experimental data is shown in Fig. 3. The output of a LeCroy model 9109 arbitrary waveform generator (resolution 5 ns) was mixed with a 200 MHz frequency source to generate the r.f. driver pulses for a Crystal Tech-

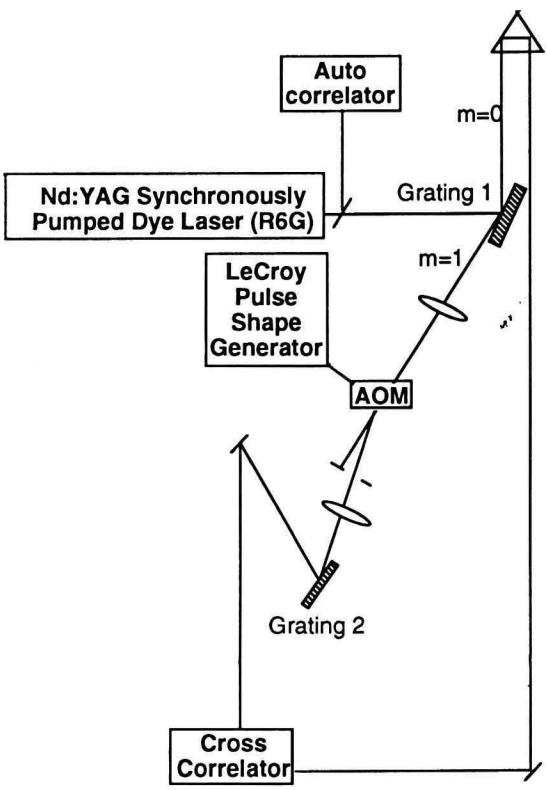

Fig. 2. Pulse shaping apparatus. The gratings were used at near-grazing incidence, and the spatially dispersed pulse was modulated with an acousto-optic modulator and an arbitrary waveform generator.

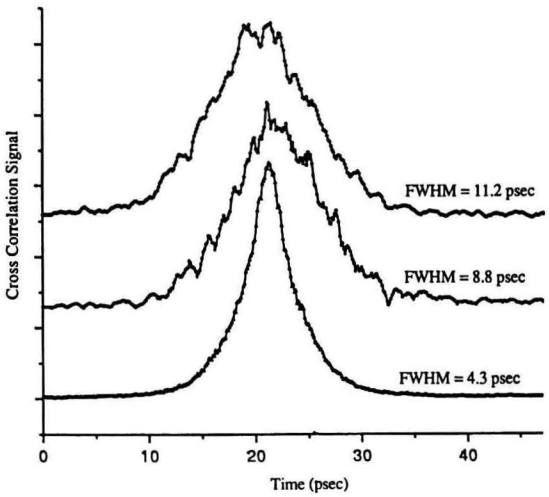

Fig. 3. Cross-correlations of the recompressed AOM output with the initial pulse. Bottom: continuous rf irradiation. Middle and top: irradiation with sinc-envelope rf pulses (30 and 60 ns FWHM). The observed cross-correlations are in good agreement with our predictions.

nology model 3200 AOM (risetime 10 ns). In this experiment, we started with a relatively long laser pulse (autocorrelation width 3.8 ps) from our YAG-pumped dye laser, and applied sinc-function r.f. pulses to lengthen the laser pulse. If the sinc function pulse is sufficiently short (in the crystal) to make the dispersed pulse nearly uniform in intensity, this will create a rectangular laser pulse. In fact, starting from our picosecond pulse, we only dispersed the frequency components over approximately 2.5 mm, and thus the edges are expected to be strongly broadened. Fig. 3 compares cross-correlations generated with continuous r.f. irradiation (4.3 ps, compared to the 3.8 ps autocorrelation); a sinc function with FWHM 60 ns, which is 250 μm in the crystal (8.8 ps); and a sinc function with FWHM 30 ns, which is 125 μm in the crystal (11.2 ps). In the latter case, the crosscorrelation shows the structure expected from the imposed r.f. pulse (with these parameters, a fully rectangular crosscorrelation was not expected). Note that the cross-correlation risetime and falltimes are very similar for the two sinc-modulated laser pulses, and far longer than the risetime of the unmodulated pulse, as expected.

The major advantage of using Bragg diffraction is the very low background; the typical isolation of such a modulator is 40 dB. However, spatial dispersion because of the Bragg condition $\mathbf{k}_{in} = \mathbf{k}_{out} + \mathbf{k}_{rf}$ must be taken into account. The variation of Bragg angle with optical wavelength is not a serious issue, even for femtosecond pulses; the extra spatial dispersion could be corrected by prisms. However, the Bragg angle also varies as the r.f. frequency is changed, which could send different frequency components in different directions. In TeO_2, the Bragg angle varies by 0.1 mrad/MHz of r.f. frequency at $\lambda = 600$ nm, so a waveform with 10 MHz modulation bandwidth would spread the output beam by

only 1 mrad. Larger r.f. bandwidths might create an intolerable spreading (unless the modulator is double-passed). However, even restriction to a 10 MHz bandwidth (risetime 40 ns) would imply an effective 'pixel size' in the AOM of 0.17 mm. Our modulator has a clear aperture of 0.5 cm, but this is not a fundamental limitation (far longer modulators are available; the acoustic attenuation across the crystal was less than 10%). An inexpensive AOM and a much lower resolution waveform generator could still be equivalent to a 100-pixel LCD array, with additional advantages of no pixel gap, rapid waveform updating, high isolation, and simple calibration.

It is also possible to consider using the acousto-optic modulator in other modes, and in this case far higher resolution can be achieved. For example, the undiffracted beam can be used if pure amplitude modulation is desired, and then the full bandwidth of the modulator can be employed. Here the major disadvantage would be decreased isolation (20 dB, comparable to an LCD modulator, implies 90% diffraction efficiency), but again a double-pass configuration would work. Raman-Nath mode (perpendicular to the transducer) would convert the device into a phase modulator.

Summary

We have briefly discussed here two new approaches to pulse shaping which have major potential advantages over existing techniques for making complex waveforms. The interferometric approach can make laser pulses with high complexity, but tailored in a robust manner to the real absorption spectrum of individual molecules. The acousto-optic approach promises to substantially simplify the process of complex pulse shape generation. Both of these approaches can be expected to contribute significantly to the next generation of experiments for coherent control of chemical reactions.

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