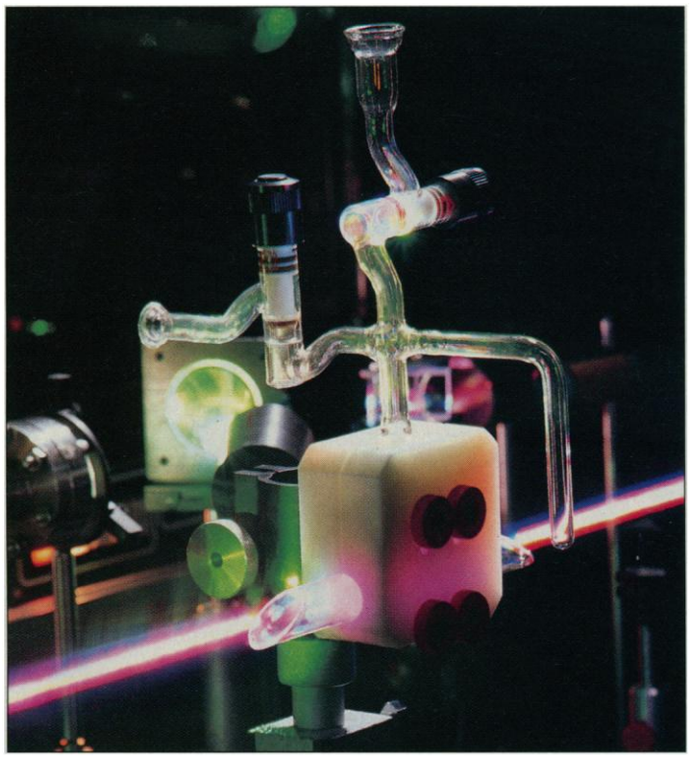
Chemistry with Photons

W. S. Warren

This summer's Telluride Workshop on Pulse Shaping and Quantum Control in External Fields (*1*) brought together many of the leading research groups working on quantum molecular control and on applications of quantum control to electronic devices and mechanical systems. Important technological developments in laser pulse shaping and a variety of calculations on realistic molecules were discussed that created a mood of encouragement about continued progress. The sense of the participants was that a number of important issues had been clarified in the 2 years since the first workshop, that pulse shape effects can become a major theoretical and experimental tool for investigating molecular dynamics, and that the decades-old dream of controlling chemical reactions with laser fields may be possible even in quite complex molecules.

With the advent of high-power lasers 30 years ago came the idea of breaking strong bonds or steering chemical reactions with intense pulses—in effect, using photons as reagents in chemical reactions (*2*). These early attempts failed because the technology needed to produce carefully controlled pulses was not yet available and because the theoretical complexity associated with the prediction of useful waveforms was not understood. Today, essentially any pulse envelope with 50-fs rise times and durations of a few picoseconds can be produced reliably. Waveforms with precisely controlled amplitude and phase (including multiple laser beams with well-defined phase shifts) have produced selective population inversions, enhanced Raman excitation, and modulated multiphoton dissociation (*3*). On the theoretical side, intramolecular energy transport is much better understood, and sophisticated calculations have predicted interesting excitation schemes for many different molecular systems (*4*).

Laser-controlled chemistry remains an important objective, but the potential applications are actually much more general. In the near term, the most common application of shaped pulses may well be to improve our understanding of molecular dynamics and reactivity. For example, shaped pulse experiments can be extremely sensitive probes of molecular potentials, enhancing the capabilities of the classic "pump and dump" experiments with femtosecond laser pulses, which still account for much of modern chemical physics work (*5*). They can also provide extremely sensitive discrimination between two nominally similar absorbers. In addition, applications of shaped pulses to design and probe novel electronic devices (such as multiple quantum wells, which can be designed to have virtually any desired potential) look promising.



Colorful chemistry. The use of lasers to control chemical reactions, given up as impossible 10 years ago, now seems reasonable because of technological and theoretical advances in quantum molecular control. Programmable, femtosecond resolution laser pulse shaping technology and a variety of theoretical insights let scientists look at steering molecular dynamics in an entirely new way—perhaps with feedback from the molecule itself. [Photo: Nat Clymer © 1993]

The recent evolution of pulse shaping technology—the critical tool for advanced applications—became particularly clear during the workshop. A variety of "hero experiments" several years ago showed that programmable pulse shaping was possible with approximately 100-fs time resolution (*6*). In the last 2 years, several groups have extended these techniques to do sophisticated femtosecond pulse shaping with only commercially available components. M. Wefers and K. Nelson (Massachusetts Institute of Technology) reported on their development of computer models that accurately deal with the imperfections in real equipment and produce predistorted waveforms to correct many of these deviations; this represents a major step forward for theoreticians as well, who will now be able to constrain computerized optimizations to realistically achievable waveforms. Techniques for rapid characterization of the phase and amplitude modulation of different laser pulses improved dramatically. In addition, a variety of new approaches, still in the demonstration stage, promise to improve pulse shaping capabilities while reducing the cost and complexity of programmable pulse shaping still further. One of these approaches, reported by C. Hillegas and myself (Princeton), uses microsecond-long radio-frequency pulses to control the shapes of femtosecond laser pulses and thus is easily implemented. We also noted that it may even be possible to have molecules design their own near optimum laser pulse shapes for some applications; for example, a Michelson interferometer with a sample cell in one arm will turn a femtosecond laser pulse into a pulse optimized for excitation of that molecule.

Calculations have come a long way in the last 2 years toward addressing practical issues such as reduction of pulse complexity and robustness to laser inhomogeneity. There has also been a great deal of clarification of the potential effects of quantum control in the weak response limit (where the laser field does not appreciably alter the internal molecular Hamiltonian, and at any one time, most of the molecules are essentially unperturbed) and the strong response limit. Both of these approaches have significant advantages for different applications. H. Rabitz (Princeton), K. Wilson (University of California, San Diego), and their coworkers presented a broad range of detailed calculations on climbing of anharmonic vibrational ladders, bond breaking, or creation of interesting wavepackets (for example, stretching the internuclear separation in diatomic molecules to double the equilibrium length at one specific instant).

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Experiments aimed at verifying many of these calculations are now under way. A. Hubler (University of Illinois) noted that some recent theoretical results suggest that much more complex systems (perhaps even as complex as enzymes) might be amenable to quantum control, particularly in the strong response limit; relaxation mechanisms actually serve to stabilize specific excitations, or intense fields may dramatically simplify the internal dynamics. The role of theory is likely to be quite different in complex systems than it is in diatomics; Rabitz noted that it is unlikely that calculations alone will be able to produce useful waveforms, and feedback between experiment and calculation (perhaps through computer programs that use molecular response to a waveform to determine optimal corrections) will be important. J. Schiano (University of Illinois) has experimentally demonstrated such feedback in the simpler case of control in nuclear magnetic resonance.

Participants of the workshop also identified a number of important directions for future work. One of the most important goals of theory is to help develop intuition as to what is possible; much work remains to be done here, and in many cases it is presently very difficult to rationalize the waveforms predicted by computerized optimization, or even to understand which features are crucial and which might be secondary. Detection of quantum control is also an important and developing field; it is central to all of the proposed schemes for the use of feedback between theory and experiment to improve waveforms. Promising methods for taking "snapshots" of molecules with ultrafast electron or x-ray diffraction (*7*) are being explored by a variety of groups as noted by Wilson.

Although the participants felt it was important to avoid perceptions of "oversell" to the broader scientific community, the consensus was that both the short-term and long-term prospects for important experiments in quantum control were excellent. The near term applications will be limited to simple systems (photons remain expensive reagents), but they will lead to a better understanding of molecules and devices and may ultimately change the way chemists approach molecular design.

References and Notes

1. The Telluride workshop (9 to 23 August 1993) was chaired by W. S. Warren with H. Rabitz, S. Rice, and D. Tannor as co-organizers. The participants agreed to meet again at Telluride in 2 years. More information can be obtained from the Telluride Academy, P.O Box 2255, Telluride, CO 81435.
2. See, for example, A. H. Zewail, *Phys. Today*, November 1980, p. 27 and references therein.
3. W. S. Warren, H. Rabitz, M. Dahleh, *Science* **259**, 1581 (1993); S. Rice, *ibid.* **258**, 412 (1992).
4. P. Brumer and M Shapiro, *Annu. Rev. Phys. Chem.* **43**, 257 (1992), J. L. Krause, R. M. Whitnell, K. R. Wilson, Y. J. Yan, S. Mukamel, *J. Chem. Phys.*, in press.
5. See, for example, G. R. Fleming, *Chemical Applications of Ultrafast Spectroscopy* (Oxford Univ. Press, New York, 1986).
6 A M. Weiner, J. P. Heritage, R. N. Thurston, *Opt. Lett* **11**, 153 (1986); A. M. Weiner, D. E. Leaird, J. S. Patel, J R. Wullert, *ibid.* **15**, 326 (1990); M. Haner and W. S. Warren, *Appl. Phys. Lett.* **52**, 1485 (1988).
7. R. Trebino and D. J. Kane, *J. Opt. Soc Am.* **A10**, 1101 (1993).

An Expanding Universe of Introns

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Eleven years after bursting onto the scene, autocatalytic introns (*1*) continue to amaze. Although representing two structurally distinct groups (I and II) that splice by different pathways, these introns share two remarkable features. Not only do they have the potential to self-splice, but they may also act as mobile genetic elements [reviewed in (*2*)]. The dynamic properties of the group I and group II introns may reflect their parallel evolution, yet their biological niches overlap only partially. Whereas both intron families cohabit fungal and plant mitochondria and plant chloroplasts, the group II introns seemed conspicuously absent from prokaryotes, which host their group I counterparts. Absent, that is, until the recent report of group II introns in both proteobacteria and cyanobacteria, the putative progenitors of mitochondria and chloroplasts, respectively (*3*). These introns reside in unidentified reading frames, one in the γ-purple proteobacterium *Azotobacter vinelandii* and two others in the cyanobacterium *Calothrix*. Not only do these findings extend the taxonomic range of group II introns, but they also raise provocative questions about intron ancestry and more recent dispersal.

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To address these questions, one must consider the potential invasiveness of these genetic elements. The mobility of both group I and group II introns appears to be imparted by the products of open reading frames (ORFs) contained within them. However, different proteins drive distinct mobility pathways in the two intron families. The mobile group I introns encode endonucleases that promote their movement within niches as diverse as bacteriophage and slime mold genomes (*2*). The well-defined group I mobility pathway is DNA based and is initiated by endonuclease cleavage in an intronless allele. Ensuing repair of the double-stranded DNA breaks results in a homing event in which the intron is duplicated between homologous exons of the recipient (Fig. 1A). This event is accompanied by coconversion of flanking exon sequences.

In contrast, mobile group II introns encode reverse transcriptase (RT)–like proteins, some of which have recently been shown to be active intron-specific enzymes (*4*). Interestingly, the presence of RT in the bacterial group II introns was used as the basis of their detection, with polymerase chain reaction (PCR) primers directed at conserved RT and splicing domains (*3*). The group II RTs have striking similarity to RTs of LINE-1 retroelements, consistent with the emerging concept of the group II introns as site-specific retroelements (*4*, *5*). Although the mobility mechanism is presently unresolved, some insights are being gained from work with two group II introns, aI1 and aI2, next-door neighbors in the *cox1* gene of *Saccharomyces cerevisiae* mitochondria (*4*, *5*). Like that of group I introns, aI1 and aI2 mobility is a highly efficient homing process in which the introns, accompanied by flanking exon sequences, move to cognate intronless alleles at efficiencies approaching 100%. However, unlike group I mobility, which is strictly DNA-based, group II homing appears to depend on the splicing proficiency of the intron (*5*).

Any plausible scenario for group II intron mobility should accommodate the coinheritance of flanking exons, the nature of the RT complementary DNA products, and the apparent requirement for splicing (Fig. 1B). Given exon coconversion (*5*) and the observation that a significant fraction of complete intron cDNA contains flanking sequences (*4*), the cDNA for integration is likely to be derived from the pre-mRNA. Splicing might then generate a mediator of, rather than a template for, mobility: A primer for cDNA synthesis? A template for RT synthesis? An RNA endonuclease to promote site-specific integration of the cDNA into the intronless allele? The last possibility is most exciting, given that endonuclease activity, which is predicted on the basis of the efficiency of homing, is well