Control of Chemical Reactions by Feedback-Optimized Phase-Shaped Femtosecond Laser Pulses

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Tailored femtosecond laser pulses from a computer-controlled pulse shaper were used to optimize the branching ratios of different organometallic photodissociation reaction channels. The optimization procedure is based on the feedback from reaction product quantities in a learning evolutionary algorithm that iteratively improves the phase of the applied femtosecond laser pulse. In the case of CpFe(CO)2Cl, it is shown that two different bond-cleaving reactions can be selected, resulting in chemically different products. At least in this case, the method works automatically and finds optimal solutions without previous knowledge of the molecular system and the experimental environment.

When lasers were invented they were considered the ideal tool for microscopic control of chemical reactions, that is, selective cleavage or formation of chemical bonds (1, 2). By exactly tuning the monochromatic laser light according to the local mode frequency of a specific chemical bond, it was thought that enough energy could be deposited in this specific mode to cause selective bond breakage (3). In most experiments, however, selectivity is lost because of rapid intramolecular energy redistribution (4). Several control schemes have been proposed that make use of the coherent nature of laser radiation. Known as “coherent control,” these schemes access

References and Notes
8. We discuss only films with a thickness within the range of the dispersion forces, that is, not thicker than ~100 nm.
20. Ripening of these structures was too slow to be observed on experimental time scales.
21. The possibility of imaging polar liquids has recently been demonstrated [A. Fery and S. Herminghaus, Ultramicroscopy 69, 211 (1997)].
22. The system thus relaxes toward a film of finite thickness, that is, incomplete wetting. This justifies the well-established term “dewetting,” even though the process does not leave a perfectly dry surface.
27. An intermediate layer of a few monolayers of chromium (thickness <2 nm) was deposited to improve the adhesion of the films.
29. For simple monatomic liquids such as gold, the liquid is not expected to slip along the substrate. In the absence of slippage, the holes grow linear with time [J. Brochard, P. C. DeGennes, H. Hervet, C. Redon, Langmuir 10, 1566 (1994)].
32. Stimulating discussions with G. Reiter, A. Sharma, and P. Leiderer are gratefully acknowledged.
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the broad range of quantum interference effects. Brumer and Shapiro (4), for example, showed theoretically that in a quantum mechanical system simultaneous one- and three-photon excitation can lead to constructive or destructive interference of different reaction pathways, depending on the relative phase of the light waves. Experimental realizations have been carried out on atomic and small molecular systems (5). A somewhat different control scheme makes use of the rapid progress in ultrashort laser pulse technology. For example, Tannor, Kosloff, and Rice (6) suggested a “pump-dump” technique, which has been realized experimentally by several groups (7).

Both types of control schemes are based on a limited number of optimization parameters: the phase difference between the two lasers and the time delay between the pump and dump laser pulses, respectively. In more complex systems these parameters may not be sufficient. Shi, Woody, and Rabitz (8) proposed that in order to reach a specific reaction channel, the electric field of the laser pulse should be specifically designed and fitted to the molecule, such that the amplitudes of the different interfering vibrational modes add up in a given bond some time after the photoabsorption, causing its breakage. To calculate the electric fields of these control schemes, “optimal control theory” has been used (9). In this approach, an “objective function,” consisting of the specific product yield in a chemical reaction, is maximized with respect to the electric field by solving Schrödinger’s equation. This iterative optimum-seeking process has been theoretically applied to small model systems. For chemically relevant large molecules, however, this approach fails because molecular potential energy surfaces are not known accurately enough. Moreover, it has proved to be extremely difficult to generate the complex laser fields exactly as demanded by the theory.

Judson and Rabitz (10) introduced an idea for directly including the experimental output in the optimization procedure. A suitable algorithm forms an ultrashort laser pulse, uses the desired output as feedback in a learning algorithm, and iteratively improves the applied laser field, thus letting the system itself solve its Schrödinger equation in real-time without any approximations, under the constraints set by the laboratory conditions. Evolutionary algorithms (10, 11) and simulated annealing algorithms (12) were suggested to serve this purpose. Some implementations have been demonstrated for automated femtosecond pulse compression (13, 14) and optimized electronic population transfer in a dye molecule (15). In a recent article the field of laser control of chemical reactions has been reviewed (16).

Here we report an experimental realization of the automated optimization of coherent control of independent chemical reaction channels. We use a computer-controlled femtosecond laser pulse shaper together with an evolutionary algorithm and feedback from the femtosecond laser-driven photodissociation reaction output. Observing directly the product yields, it is possible to achieve an optimization without having to deal with the electronic population transfer within the parent molecule. Reaction pathway branching ratios of different organometallic molecules are either maximized or minimized automatically, without any knowledge of the specific molecular Hamiltonian.

The femtosecond laser system used in our experiments is capable of producing pulses with a duration of 80 fs and an energy of 1 mJ, at a center wavelength of 800 nm and a repetition rate of 1 kHz. The pulses are modified in a pulse shaper based on the design of Weiner et al. (17), which is set up as a zero dispersion compressor (18) with a liquid crystal spatial light modulator (SLM) in its Fourier plane. The SLM contains 128 rectangular pixels whose refractive indices can be changed separately by applying specific voltages. In this way different optical path lengths can be introduced to the spatially separated spectral components of the laser pulse, resulting in a shift of the relative phases. The emerging pulses are then focused into a high-vacuum chamber where they interact with a molecular beam of the educt molecules, leading to different multiphoton ionization and fragmentation processes. The ionic products are detected with a reflector time-of-flight (TOF) mass spectrometer (19) from which the product yields can be fed directly into the controlling computer algorithm through boxcar averagers (Fig. 1).

We use an evolutionary algorithm (20) to optimize the spectral phase of the femtosecond laser pulses. The “genetic configuration” of a single individual corresponds to the SLM pixel voltage encodings. An “individual’s fitness” is set equal to the measured branching ratio of the two competing reaction channels, that is, to the ratio of the respective ion signals. The “environmental adaptation” is found in the shaped laser pulse’s capability of producing the desired experimental output. In the course of the evolutionary process, the reaction product in the numerator is favored at the cost of the reaction product in the denominator, because in each generation only the fittest individuals are selected for reproduction. A detailed description of our implementation of an evolutionary algorithm is given elsewhere (13). The algorithm automatically finds the best configuration for the SLM under the given laboratory conditions, no matter how complicated the molecular response may be. Laser and molecular beam density fluctuations, as well as different input pulse shapes, are automatically accounted for because experimental changes simply favor different pulse-shaper configurations. The algorithm works directly with the voltage encodings and not with any kind of expansion of the phase function. Therefore, there is no need to calibrate the SLM.

Organometallic molecules are widely used as photocatalysts in many organic reactions (21). Another application is found in microelectronics, where complete photodissociation of these compounds is essential for thin ultrapure metal film growth on surfaces (22). Microscopic control of their different fragmentation reactions could open up new applications. We have chosen to perform experiments on two sample substances: Fe(CO) 5 (iron pentacarbonyl, CAS [13463-40-6]) and CpFe(CO) 2Cl (dicarbonylchloro(η 5 -cyclopentadienyl)iron, CAS [12107-04-9]).

The experiments on the well-studied Fe(CO) 5 molecule are carried out primarily to test our method for self-learning coherent control. We have shown previously (23) that absorption of 800-nm femtosecond laser radiation...
induces different multiphoton ionization and fragmentation processes of this molecule, depending on the pulse duration. Direct ionization of the parent molecule occurs efficiently with ultrashort laser pulses of less than 100-fs duration. A more complex process consists of combined ionization and fragmentation in which the parent molecule loses not only an electron but also from one up to all five of its carbonyl ligands. Complete dissociation is predominantly initiated by long laser pulses of several picoseconds duration.

The branching ratio of two different exit channels [Fe(CO)\(_5\)-, and Fe\(^+\)] was used as feedback signal in the automatic coherent control optimization scheme. Maximization is achieved within 30 generations of the evolutionary algorithm, yielding the product distribution of Fig. 2 (solid blocks). The result of this optimization is a very short (bandwidth-limited) laser pulse. If, on the other hand, we choose to minimize the Fe(CO)\(_5\)-/Fe\(^+\) ratio, that is, to maximize the inverse, an optimum is found almost immediately, after only very few generations (Fig. 2, open blocks). This optimization leads to a long laser pulse of picosecond duration. Several possible optimum pulse shapes (of picosecond pulse duration) are found by the algorithm that all yield the relative product distribution of Fig. 2 (open blocks). The individual mass peak heights depend on the experimental conditions, that is, the molecular beam intensity is lowered by attenuation at several mass peaks. The result of this optimization procedure, a significantly different product distribution is obtained (Fig. 3, open blocks). The branching ratio has dropped from 4.9 in the maximization experiment to 1.2 in the minimization experiment, and the resulting laser pulse shape has evidently changed (Fig. 4B). In an additional experiment we used an ultrashort (bandwidth-limited) laser pulse (Fig. 4C) and compared the Fe(CO)\(_5\)-/Fe\(^+\) ratio with those from the optimized laser pulses. The ratio in this case is only 2.4, proving that in the complex CpFe(CO)\(_5\)Cl molecule (with different types of chemical bonds), simple bandwidth-limited laser pulses are not the best possible solution to the given problem. Arbitrarily shaped long laser pulses of picosecond duration do not yield an optimum ratio either.

Because our pulse shaper modulates only spectral phases and not amplitudes, the evolutionary algorithm produces optimized laser pulse shapes for a given pulse energy and for a given spectral intensity distribution. The fact that indeed the spectral optical phase and not
the pulse intensity is responsible for the optimization results can also be seen from the following argument. In the maximization as well as in the minimization experiment, the increased pulse duration leads to a reduced laser pulse intensity in the time domain as compared with the bandwidth-limited laser pulse. But in one case this reduction leads to a maximization, and in the other case it leads to a minimization, of the desired product branching ratio. It is therefore not possible to obtain the same or similar results by a trivial intensity reduction. Although it is not certain that the algorithm has found the global optimum, significant control between the two reaction channels was achieved, which cannot be obtained by a trivial adjustment of the laser pulse length or the laser pulse intensity.

The results demonstrate automated coherent control of photodissociation reactions with tailored femtosecond laser pulses from a computer-controlled pulse shaper. No information about the sample substance is needed in the optimization procedure, which always starts with completely random genetic configurations. By directly optimizing different final products yields of bond-breaking reactions, we achieve a qualitative change from electronic population manipulation toward direct control of different reaction channels. The experiments reported here represent a step toward synthesizing chemical substances with higher efficiencies while at the same time reducing unwanted by-products.

References and Notes

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The Effect of Alumina on the Electrical Conductivity of Silicate Perovskite

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Measurements of the electrical conductivity of silicate perovskite at 25 gigapascals and 1400°C to 1600°C show that the conductivity of (Mg,Fe)SiO3 perovskite containing 2.89 weight percent Al2O3 is about 3 times greater than that of aluminum-free (Mg0.915Fe0.085)SiO3 perovskite. The conduction mechanism in perovskite between 1400°C and 1600°C is most likely by polarons, because Mossbauer studies show that the aluminum-bearing perovskite has about 3 times the amount of Fe3+ as the aluminum-free sample. A conductivity-depth profile from 660 to 2900 kilometers based on aluminum-bearing perovskite is consistent with geophysical models.

The lower mantle consists predominantly of (Mg,Fe)SiO3 perovskite coexisting with about 20% (Mg,Fe)O by volume. Aluminum is a minor element in the lower mantle, and it mainly goes into the perovskite phase (1). The partitioning of Fe and Mg between perovskite and magnesiowüstite is strongly coupled to Al2O3 concentration (2), and the proportion of Fe3+ in perovskite may increase greatly if perovskite contains a small amount of Al2O3 (3). If the conduction mechanism for perovskite is electron hopping from Fe2+ to Fe3+ (4), the electrical conductivity of perovskite should depend on the concentration of Fe3+ and is thus sensitive to substitution of Al2O3 into perovskite. Here, we evaluate this notion using in situ electrical conductivity measurements of perovskite at lower mantle conditions.

The starting materials for coexperiments were two polycrystalline pyroxene samples with similar Fe/(Fe + Mg) ratios: San Carlos (Mg0.915Fe0.085)SiO3 orthopyroxene containing 2.89% Al2O3 by weight and an Al-free synthetic orthopyroxene, (Mg0.915Fe0.085)SiO3. The samples were first transformed to perovskite at 25 GPa and 1600°C in a multianvil apparatus and then prepared as disks for in situ complex impedance spectroscopy in subsequent experiments at 25 GPa and 1400°C to 1600°C (5).

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Fig. 1. Electrical conductivity of perovskite as a function of reciprocal temperature at 25 GPa. Squares and inverted triangles are for Al-bearing perovskite H826 and H858, respectively, and diamonds and circles are for Al-free perovskite H852 and H862, respectively. Closed symbols refer to the first heating and cooling cycle and open symbols refer to the second heating and cooling cycle.

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