and prey can favor escalating “arms races” among groups of interacting species, producing multispecific clusters that share some reciprocal specialization in defenses and counterdefenses. Amid these arms races, selection continually acts on prey to escape the interaction, preventing predators from incorporating an ever-increasing number of prey species into their diets. In contrast, mutualistic interactions between free-living species often favor incorporation of new species into an interaction, through convergence and complementarity of traits among interacting species. The result is a coevolutionary vortex that grows in the number of interacting species over evolutionary time. Bascompte et al. notably extend this general expectation from coevolutionary theory to suggest that species join networks in ways that ultimately create a persistent asymmetric pattern of specialization among interacting species.

The next step in such studies will be to identify the sequence of ecological, evolutionary, and coevolutionary processes that create this pattern as mutualistic webs accumulate species over space and time. Some mutualistic life histories, for example, are not even possible until mutualistic webs include many species. Honeybees, which rely upon a seasonal progression of flowering among species to maintain their hives, could not have evolved until local communities included multiple plant species that flowered at different times. Identifying the evolutionary and coevolutionary processes that shape asymmetries during the assembly of complex mutualistic webs will require studies of how particular pairs and groups of species differ in their patterns of asymmetry in different biological communities.

Studies of complex mutualistic webs are part of an overall scaling up of the fields of coevolutionary biology (8) and community ecology (9) to encompass the processes shaping the diversity of life across large geographic and temporal scales. These studies are also part of a growing realization that much of the diversification of life is about the diversification of interactions through ongoing coevolution.

References

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CHEMISTRY

The First Femtosecond in the Life of a Chemical Reaction

Philip H. Bucksbaum

When light initiates chemical change—such as photosynthesis in plants, or vision in an eye, or the formation of vitamin D in your skin—the first stages happen with breathtaking rapidity. Electrons in molecules can absorb a photon and rearrange in only femtoseconds (a femtosecond is 10^-15 s). A bedrock of chemical theory known as the Franck-Condon principle assumes that such short times are so infinitesimal that for all practical chemical purposes they are instantaneous: All the atoms in a molecule remain frozen during the critical instant of electron transition. Yet quantum mechanics requires that the atoms in molecules are never truly at rest, and the removal or repositioning of electron charge initiates motion that eventually leads to chemical transformation. These earliest atomic movements have never been observed directly, because they are far too fast and too slight to detect. But this is just what the report by Baker et al. describes and then demonstrates a new method to convert the spectrum of high harmonics into an image of the motion of molecules (such as hydrogen or methane) in the first stages of chemistry. The HHG process, in which visible or infrared laser light is converted to vacuum ultraviolet radiation, leads to chemical transformation. These early events that initiate photochemistry, but the name has been taken over to include physical observations on time scales shorter than a single cycle of visible light, or shorter than about two femtoseconds. The specific technique used here is high-harmonic generation (HHG) in molecules illuminated by intense femtosecond pulses of focused laser light.

The report by Baker et al. describes and then demonstrates a new method to convert the spectrum of high harmonics into an image of the motion of molecules (such as hydrogen or methane) in the first stages of chemistry. The HHG process, in which visible or infrared laser light is converted to vacuum ultraviolet radiation.

Tracking molecular motion. (Top) A laser field (black arrow) pulls an electron quantum wave (blue) away from the molecule, causing the two atoms (black dots) to separate. (Center) When the laser field reverses, the quantum wave smashes back into the molecule. Color represents the wave energy, with blue for fast high-energy waves and red for slow low-energy waves. (Bottom) The electron wave is absorbed, creating photons with energy corresponding to the wave energy. In this way, each color of light shows the molecule at a different time as the atoms move apart. Total time elapsed is about ½ of an optical cycle, or one femtosecond.

Illustration: C. Bickel/Science

Bombardment of reactants with high-order harmonics of a laser reveals the earliest stages of chemical reactions, which occur faster than a single cycle of visible light.

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tion, has been known for nearly two decades (2). The light takes the form of odd harmonics—that is, odd multiples of the driving laser frequency. Harmonic frequencies greater than 100 times the laser frequency have been observed in a single spectrum. This extreme phenomenon was not predicted before its initial observation, and it seems to lie outside the reach of conventional nonlinear optics, the theory that predicts parametric processes such as second- or third-harmonic generation in light interacting with atoms and molecules. Yet HHG has an elegant and simple physical explanation, based in part on classical physics (3). HHG occurs when an intense laser field pulls an electron away from the molecule in a fraction of one optical cycle, and then sends the electron crashing back into the molecule when the field reverses on the next half-cycle (see the figure). The energy dissipated in the crash of each electron is converted into a single photon of radiation. The HHG spectrum is the forward-directed portion of this light collected from all of the molecules illuminated by the laser.

The research reported by Baker et al. takes these ideas one step further. The authors note that according to this classical model, the energy of the photon must be tied to the kinetic energy of the electron that made it, which depends in turn on the precise time that the electron was pulled away from the molecule and the time that it returned. For example, electrons that leave the molecule at the very peak of the oscillating laser electric field take the longest time to return, and the field has slowed them nearly to a stop when they do. Electrons that leave the atoms a bit later will not go as far before turning back, and they return with some excess energy that can be put into a high-harmonic photon. The later an electron leaves in a field cycle, the shorter the duration of its journey, and the higher its energy upon return.

An electron that leaves the molecule about 1/20th of a cycle after the peak (18 degrees of phase) has the highest energy possible when it returns—about three times the average wiggle energy of an electron in the laser field. Electrons that leave still later in the cycle have even shorter total trajectories but return with less than the maximum energy. These “short-trajectory” harmonics were the ones used by the authors to view the just-ionized molecule. The lowest energy part of the spectrum shows the condition of the molecule at the earliest times after the ionization event, and the highest energy part shows longer times. But the total time interval covered by the entire spectral record is extremely short—about a femtosecond.

How should one interpret this spectrum to get any meaningful information, let alone a snapshot image of the molecule? Here the research team deftly switches back to quantum theory for a clue. The returning electron doesn’t have to convert its energy to a photon when it crashes back into its home port. It could just as easily scatter from the molecule and careen into another direction from which it never returns. The odds of producing an HHG photon depend on whether the shape of the quantum wave function of the target molecular ion matches the space the neutral molecule needs to occupy when the electron comes back to rest. If the shapes don’t match, the electron is likely to just bounce off. This quantum correlation between the ion and the neutral molecule is therefore reflected in the amplitude of the HHG spectrum. More HHG signal at a particular photon energy means a better match at that time. This is not much information, to be sure, but it is just enough to provide important clues used to reconstruct the motion of the molecule in the first femtosecond after ionization. Baker et al. report measurements of this motion in hydrogen molecules and in methane ionized by a laser pulse consisting of only a few optical cycles. Competing effects influence HHG, such as the spatial arrangement of the atoms in the molecule, or the tendency of the molecule to distort under the influence of the laser field even before the moment of electron release. These phenomena also alter the HHG spectrum and could confuse the analysis (4). The most important limitation of the new technique is the very short time interval involved. Only the lightest atoms in a molecule move far enough to detect motion over one femtosecond. But hydrogen, the lightest atom, is the critical actor in much photochemistry, and its motion is considerable even over these short times. Furthermore, the continued improvement of ultrafast lasers is leading to infrared sources with longer wavelength and longer cycle periods, and this technique could be extended to longer times in this way.

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APPLIED PHYSICS

Laser-Driven Particle Accelerators

Mike Dunne

A new generation of particle accelerators that use laser acceleration can sit on the benchtop. These instruments are being actively developed for widespread applications.

For many years, the high-power–laser community has been pursuing the goal of producing miniaturized particle accelerators. Limitations of conventional technology mean that kilometer-sized accelerators are required for high-energy physics research (see the bottom figure). Similarly, major installations are required for medical applications such as particle beam treatment of tumors, which excludes all but the largest research hospitals. By contrast, laser-plasma–based techniques can support accelerating electric fields at least four orders of magnitude larger than those of conventional techniques, leading to the hope that particle accelerators could one day become a commonplace tool.

Although the goal is attractive, these plasma schemes have, until recently, suffered from many shortcomings, such as poorly controlled particle energy, high divergence, and low luminosity. A host of results in the past year has provided renewed impetus, with demonstrations of quasi monochromatic, high-brightness beams in the multi-MeV energy range. Now, Toncian et al. (1) at the University of Düsseldorf have demonstrated an imaginative technique for tunable energy selection and focusing of proton beams in the multi-MeV energy range. As reported on page 410 of this issue, they show that the use of a simple capillary lens can lead to dramatic results.

Lens arrangements for proton beams are not new; but until now, there has not been a way to focus picosecond–time-scale beams with currents that are orders of magnitude higher than those of conventional beams and that require focusing over micrometer spatial scales. In the system developed by Toncian et al., a proton beam is created by irradiating a metal foil with laser pulses, and the protons are focused by the electric fields created inside a small cylinder that is irradiated on the side by a second laser (see the top figure). This new idea provides a simple tool to exploit the dramatic advances in laser-driven hadron acceleration seen over recent years.

It is easy to imagine the breadth of science disciplines that would benefit from a new generation of miniature accelerators. Potential applications include the imaging and treatment of cancerous cells, offering scale reductions and far simpler beam orientation compared with conventional cyclotrons. Nearer term applica-
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