

sion. Perhaps harder to explain is why an active self-cleaving ribozyme sequence exists within an intron.

The similarity between the *CPEB3* and HDV ribozymes is unlikely to be coincidental. Could it be that, long after proteins had become the dominant biological catalysts, HDV chose to adopt a ribozyme from the cellular genome?

The two papers will stimulate more studies about the mechanism of self-cleaving ribozyme activity and how they control gene

expression. Origin-of-life remnants or not, self-cleaving ribozymes serve diverse and highly specific functions in today's protein-rich cellular world. Given the apparent versatility of self-cleaving ribozymes, future studies are likely to reveal further roles for such ribozymes.

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CHEMISTRY

A Pixellated Window on Chemistry in Solids

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Freezing usually arrests chemistry, stopping even the most reactive free radicals from reacting by trapping them in a “cage” in the solid lattice. Yet, some of the most violent reactions occur in solids. An example well known to students is the explosive reaction of nitrogen triiodide (1). In a display of showmanship, the teacher rubs the crystalline solid with a feather attached to the end of a long pole to generate a loud bang, caused by the breaking of N–I bonds and the formation of N–N and I–I bonds. This violent solid-state reaction requires the stress applied by the feather to be amplified locally by about 18 orders of magnitude in order to break individual chemical bonds: It is as if a zipper were undone by the action of an earthquake.

The same type of multiscale dynamics is manifest in the sparkles visible when chewing candy that glows in the dark, or in the tiny bursts of light produced when “nipping” sugar into smaller chunks, as first noted by Francis Bacon (2). The phenomenon, coined triboluminescence in 1895, is another illustration of the conversion of mechanical friction to electronic excitation—generating electrical discharge and light emission (3).

Yet despite the age-old fascination with these phenomena, our understanding of the underlying processes remains far from satisfactory. From the inexorably slow chemistry that accompanies petrification to the violence of shock-sensitive detonation, multiple time and

length scales govern solid-state chemistry, posing serious challenges to atomic-scale understanding of these processes. On page 1756 in this issue, Poulin and Nelson (4) report a method that overcomes some of these problems by probing molecular dynamics occurring at different times in a single experiment.

The primary experimental difficulty in dissecting solid-state chemistry is the irreversibility of the processes at issue. Consider the liquid-phase counterpart to triboluminescence: the process of sonoluminescence. Despite the relative novelty of this phenomenon, current understanding of sonoluminescence has progressed considerably (5). Ultrasonic waves can be converted into electronic energy, and possibly even nuclear fusion (6), through cavitation (bubble formation), cavity oscillations, and implosion to generate local temperatures as high as 1 million to 10 million K. Knowledge of the molecular structure and composition of these processes is now sufficiently detailed to find practical application in sonochemistry (7).

The rate of elucidation of these related phenomena differs so widely because sonoluminescence measurements can be repeated, whereas triboluminescence experiments are irreversible. A single bubble can repeatedly be driven into sonoluminescence at acoustic rates of $10,000\text{ s}^{-1}$, resulting in perfectly synchronized picosecond-long flashes from the same sample for millions of cycles. In contrast, little material is left behind when a solid detonates. The measurement cannot be repeated on the same sample.

One way to overcome this difficulty is to

Reaction dynamics in solid samples can be studied with a laser beam that has traveled through specially cut windows. Events happening at different times are probed in a single shot.

carry out measurements on carefully prepared homogeneous plates. To emulate repetition, the plates are translated in a laser beam to expose a fresh spot of nearly identical material for experimentation. This approach has been used successfully to characterize shock-induced chemistry and detonation with nanometer-scale space resolution and picosecond-scale time resolution (8). In addition to characterizing temperature and pressure profiles of chemically driven shock fronts that arise during detonation, the chemical transformations that sustain the front can now be studied with nonlinear ultrafast spectroscopies (9).

The alternative to investigating a complete process on the multiple time and length scales peculiar to chemistry in solids is the reductionist approach. Under the assumption that a complex process may be reconstructed from its parts, elementary steps are isolated for scrutiny. This approach guides the more extensive body of work in solid-state chemical dynamics. For example, doped rare gas solids have been used to dissect the elementary steps of energy flow within and between molecules, energy deposition in molecular bonds up to breakage, caging, and cage escape and migration of atomic fragments into the lattice (10). To allow repetition, these measurements are performed in model systems that are designed to be reversible.

However, understanding the elementary steps in isolation will never be sufficient. It is essential to also carry out measurements of real-world processes, which are invariably irreversible. To this end, techniques that do not require repetition and yield the complete

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record of the course of molecular dynamics in a single measurement would be invaluable. In this context, the article by Poulin and Nelson represents a valuable advance.

The authors show how one can obtain—in a single shot—time-sequenced transient absorption spectra of irreversible chemical reactions that are initiated with a laser in a solid sample. To do so they use echelons, which are windows cut in steps to provide stripes of different thickness through which the laser traverses. By crossing two echelons, pixels of square profile are created. Each pixel generates a different time delay, allowing events happening at different times to be probed in a single shot.

Poulin and Nelson use this method to record the caging process of the triiodide ion upon its photodissociation in organic crystals. Caging results in the reformation of the broken bond. The bond reformation proceeds

coherently in the tight cages, while there is significant dispersion in the timing of recombination in the looser solids. Although the observed caging process is reversible, discoloration of the irradiated spot indicates that nonreversible structural change also occurs, precluding the repetition of measurements on the same spot. The work also highlights that in condensed-phase systems, linear spectroscopies are not uniquely interpretable: Simulations are essential to connect the one-dimensional spectra to the underlying multidimensional dynamics (4).

Poulin and Nelson have successfully put into practice the concept of the pixellated window in time. The use of echelons, however, limits the observation window to the picosecond time range. Clever optics will be required to follow processes on femtosecond to millisecond time scales and thus unravel the multiscale dynamics peculiar to solids; for exam-

ple, to follow not only the bond breaking, but also the process of permanent discoloration seen in the crystals used in their experiments.

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GEOPHYSICS

Do Earthquakes Rupture Piece by Piece or All Together?

Chris Marone and Eliza Richardson

Violent shaking and destruction caused by earthquakes are the result of rupture and frictional slip on tectonic faults, and bigger earthquakes break bigger fault segments. But how do brittle ruptures of Earth's crust grow? Seismologic evidence shows that quakes begin in a small nucleation region and propagate at speeds up to 16,000 kilometers per hour. Two competing models of rupture growth describe this expansion (see the figure). In the crack model, the nucleation region slips throughout the quake and the slipping region expands until the rupture stops, a process akin to stretching a penny into the size of a half-dollar. In the pulse model, only a small portion of the total fault area slips at any one time, so as to cover the fault surface the way an inchworm crawls. Distinguishing between the two models is important for hazard assessment because they predict different degrees of strong shaking and ground acceleration with distance from the nucleation site. Recent seismological observations favor the pulse model, but efforts to connect these data with theoretical models of

earthquake physics have been stymied because rupture pulses have never been reliably observed in the laboratory. However, as reported on page 1765 by Lykotrafitis *et al.* (1), new laboratory experimental evidence on brittle fracture, showing the existence of pulse-like ruptures and the conditions under which they exist, may help resolve the debate.

Lykotrafitis and co-workers sheared photoelastic material in frictional contact in a dynamic impact apparatus and monitored rupture propagation with high-speed photography. They show that the rupture propagation mode varies systematically with the strength of initial forcing (as produced by impact speed). Pulse-like ruptures are favored by slower impact speeds relative to those for crack-like ruptures. Also, the frictional slip velocity during rupture is lower for pulse-like ruptures than for crack-like ruptures. Thus, pulse-mode ruptures are the slow cousins of breaks that propagate as classical cracks. The data of Lykotrafitis *et al.* show a clear relationship between stress level and rupture propagation mode, with larger shear stress levels resulting in crack-like propagation.

The experiments of Lykotrafitis *et al.* address perhaps the most important question in earthquake physics: What controls seismic slip

Laboratory measurements are being used to resolve which of two models is better at explaining how Earth's crust ruptures to create earthquakes.

at a point on a fault? Virtually every quantifiable aspect of earthquakes depends on slip, but local fault slip cannot be measured directly from seismograms. If the initial tectonic shear stress determines slip, it would imply that dynamic frictional strength is zero and that stress on the fault drops to zero during an earthquake. In this scenario, seismic slip ceases because the local energy budget is depleted, but this runs counter to laboratory data on frictional stick-slip and seismic estimates of radiated energy, which indicate that seismic stress drop is a mere 10% of the tectonic stress level. Or, if the boundary conditions of fault strength determine seismic slip, then earthquake rupture stops when it encounters a strong barrier. Alternatively, frictional behavior during rupture—possibly abetted by dynamic variations in normal stress—could determine slip. The self-healing pulse model belongs to this last class of models. In order for rupture to propagate as a slip pulse, the fault must strengthen rapidly after slip so that local slippage ceases.

The crack model of earthquake rupture emerged in the 1970s as an extension of the mechanics of dislocations in solids, and much progress has been made in connecting seismic phenomena with the mechanics of

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