to fit the biodiversity data. Medvedev and Melott discuss a number of ways in which a fivefold increase in the flux of extragalactic cosmic rays might kill off lots of marine genera. Cosmic-ray primaries hitting the top of the atmosphere produce showers of ionizing charged particles. What reaches the ground is mostly muons, charged pion-decay products that can penetrate through kilometers of water. The number of muons in a shower increases with the primary's energy, but the cosmic-ray flux falls off steeply with energy. That tradeoff makes 10^{12}-eV primaries the most prolific source of muons at Earth's surface. Cosmic-ray muons account for about a third of the average American's dose of natural ionizing radiation. An increase in the extragalactic cosmic-radiation flux would certainly increase radiation damage to DNA, even among deep-sea dwellers.

The authors also point out that ionization of the atmosphere by cosmic rays can affect climate, electrical storm activity, and atmospheric chemistry: There's good evidence that ionization facilitates cloud formation, which in turn increases the planet's albedo. Cosmic-ray ionization near the ground is also known to play an important role in triggering lightning discharges, which produce oxides of nitrogen. The nitrogen oxides create acid rain, and they damage the ozone layer that protects the biosphere from solar UV radiation.

For the moment, Medvedev and Melott don't advocate any particular one of those mechanisms as the culprit; nor do they argue that the cyclically increased extragalactic cosmic-ray flux is the overwhelming mechanism for biodiversity dips and major extinctions. The great extinction at the end of the Cretaceous Period 65 Myr ago was almost certainly the consequence of an enormous bolide impact. And the even greater Permian extinction 250 Myr ago is attributed primarily to an outbreak of volcanism. Furthermore, local supernovae can produce randomly episodic large increases in the cosmic-ray flux.

”What we do suggest,” says Melott, “is that the increased cosmic-ray flux induces a periodic stress—each time lasting about 10 million years—that increases the vulnerability of the biosphere to whatever else might come along.” The correlation coefficient between the two curves in figure 3 suggests that roughly half the variability of the biodiversity is attributable to the periodicity of the extragalactic cosmic-ray flux. Medvedev and Melott calculate that there's only one chance in 10^7 that the observed correlation is a statistical fluke. Of course, the authors do give the correlation a leg up by choosing an astrophysical phenomenon whose period matches that of the biological effect they seek to explain.

”Our hypothesis makes predictions that may soon be put to the test,” says Medvedev. The model predicts that the nearby bow and termination shocks to our galactic north should be prolific distributed sources of 10^{12}-eV cosmic rays, with no comparable source to our south. The most immediately promising observational opportunity, he says, is the scheduled launch early next year of NASA's *Gamma-ray Large Area Space Telescope*. Cosmic rays colliding with interstellar gas nuclei produce neutral pions that decay to pairs of gammas. If *GLAST* looks for GeV gammas coming from hydrogen clouds just outside the disk of the Milky Way, Medvedev and Melott calculate that it should be able to verify or exclude the predicted excess from clouds to the north of the disk.

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References

1. R. A. Rohde, R. A. Muller, *Nature* **434**, 208 (2005).
2. M. V. Medvedev, A. L. Melott, *Astrophys. J.* **664**, 879 (2007).
3. D. R. Gies, J. W. Helsel, *Astrophys. J.* **626**, 844 (2005).

Ultrafast laser spectroscopy measures heat flow through molecular chains

Analysis of the time-resolved disorder in hydrocarbon molecules indicates that heat propagates ballistically.

Heat travels along a temperature gradient, from hot to cold, at a rate that depends on the material's thermal conductivity. But when matter is scaled down to the level of individual atoms or molecules, the familiar concepts of heat diffusion by electrons and phonons that scatter from defects, impurities, or other excitations no longer apply. A one-dimensional molecule made up of a dozen atoms, say, carries heat through discrete vibrations over a length much shorter than the typical mean free path of electrons or phonons in a bulk molecular solid. And the vibrational modes can differ from those in the bulk material because of the reduced dimensionality and the lack of a periodic band

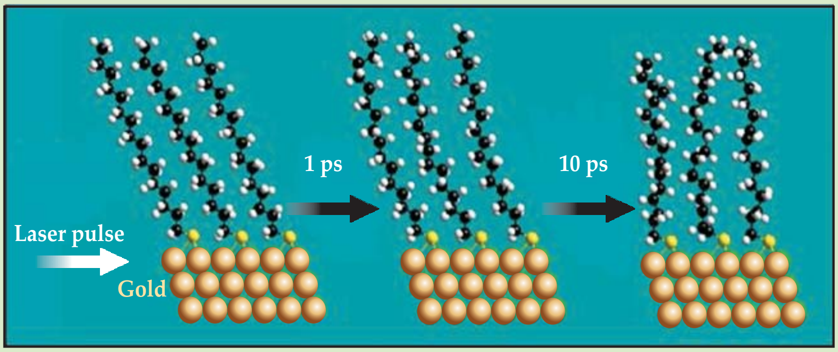

Figure 1. Molecular simulation of incipient heating in a layer of self-assembled alkanethiol molecules on gold. Within a picosecond of heating an initially well-ordered chain, the orientation of each methyl group starts fluctuating. The disorder in the methyl groups increases over time as atoms gradually equilibrate with each other along the chain. The picture corroborates the thermal evolution of optical spectra shown in figure 2. (Adapted from ref. 2.)

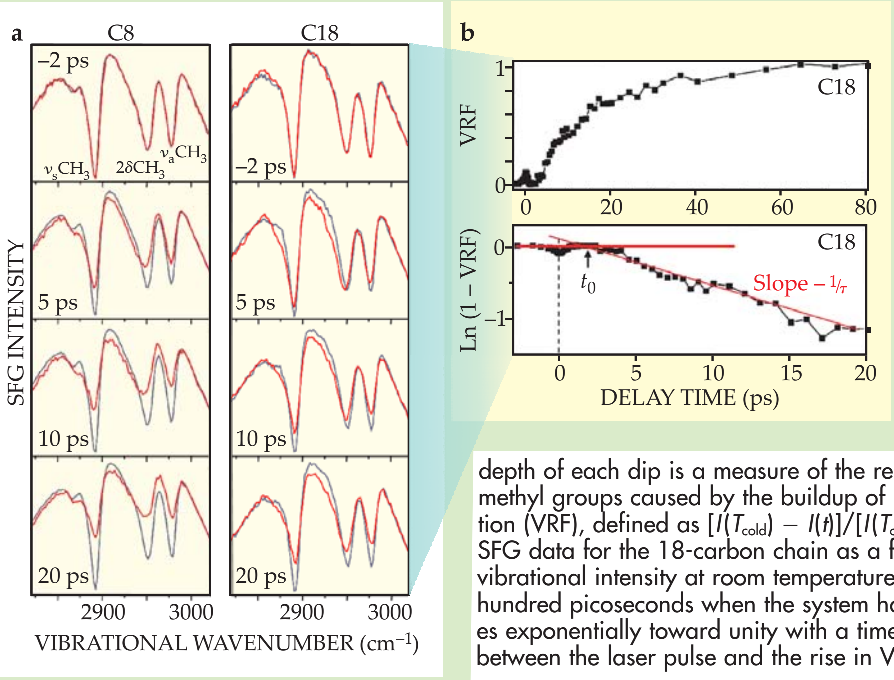

Figure 2. Sum-frequency-generation (SFG) spectra. **(a)** The time-dependent intensity $I(t)$ of dips in the spectra indicate the extent to which terminal CH_3 methyl groups are aligned in two representative hydrocarbon films, one whose chains are 8 carbons in length, the other 18 carbons. The dominant signals in both cases are the methyl groups' symmetric and antisymmetric stretching vibrations (ν_sCH_3 and ν_aCH_3) and bending overtone $2\delta CH_3$. Spectra of the chains measured at room temperature (blue) are superimposed on spectra of the hot chains (red) following a 500-fs heat pulse. The attenuation in the depth of each dip is a measure of the relative disorder in the orientation of methyl groups caused by the buildup of heat. **(b)** A vibrational response function (VRF), defined as $[I(T_{\text{cold}}) - I(t)]/[I(T_{\text{cold}}) - I(T_{\text{hot}})]$, is plotted to describe the SFG data for the 18-carbon chain as a function of time. $I(T_{\text{cold}})$ is the ν_sCH_3 vibrational intensity at room temperature and $I(T_{\text{hot}})$ the intensity after a few hundred picoseconds when the system has equilibrated. The VRF curve increases exponentially toward unity with a time constant τ. The time t_0 is the delay between the laser pulse and the rise in VRF. (Adapted from ref. 2.)

structure. Accordingly, the thermal properties of a material at macro- and microscales can be very different.

The difference matters because long-chain molecules attached to tiny electrodes can be used to control the switching and transport of electrons in molecular-electronics devices (see the article by Jim Heath and Mark Ratner in PHYSICS TODAY, May 2003, page 43). Localized heating from high currents can overwhelm the small heat capacity of delicate circuitry and threaten the reliability of devices if the heat isn't dissipated efficiently.

Last year Arun Majumdar (University of California, Berkeley) and colleagues measured the heat conductance through a thin, self-assembled monolayer of long-chain hydrocarbon molecules closely packed together by weak van der Waals forces.[1] In those insulating molecules, vibrational excitations, not electrical ones, dominate the heat transport. The monolayer was sandwiched between two thermal reservoirs—gallium arsenide and gold.

Electrical resistance in a thin film varies with temperature, so Majumdar's group could infer the thermal conductance through the organic monolayer from changes in the resistance created by an AC current applied to the gold film. The gold acted as both heater and thermometer: A value of the thermal conductance could be derived by measuring the effect of the current on the gold's temperature.

Such a steady-state measurement, however, addresses neither the transient response of the atoms to local temperature changes along the chains nor the vibrational relaxation processes that occur. Researchers from the University of Illinois at Urbana-Champaign, led by Dana Dlott and David Cahill, have now designed an approach that captures those dynamics. Using time-resolved vibrational spectroscopy, they monitored how groups of atoms in the chains react to ultrashort and intense bursts of heat.[2]

Sum-frequency generation

Dlott and company start, like Majumdar's group, by growing self-assembled monolayers of $S(CH_2)_nCH_3$ with varying molecular chain lengths n. But for each chain length they anchor their film to a single interface. One end of the alkane chain bonds to a gold surface through a sulfur atom, and the other end is free, terminated by a methyl (CH_3) group. The methyl groups thus form a 2D surface on top of the thin film. A 500-fs laser pulse heats the gold to about 800 °C, just short of its melting temperature, as hot electrons collide inelastically and give rise to phonons in the metal. Those phonons then excite stretching and bending modes in the molecules across the interface, all on the time scale of picoseconds (see figure 1).

Using a technique known as sum-frequency generation (SFG; see also the article by Gabor Somorjai and Jeong Park on page 48), the researchers measure the time it takes thermal energy from the laser pulse to reach the methyl group at the far end of each chain. Because those groups reside at the interface between the film and air, they lack inversion symmetry. Their excitations are thus sensitive to a nonlinear optical probe; the CH_2 groups and their excitations, buried in the film's centrosymmetric environment, are invisible to it.

In essence, a femtosecond IR laser pulse and a visible laser pulse intersect on the thin-film surface simultaneously, but are delayed relative to the pulse that heats the gold. When the IR pulse is tuned to the vibrational frequency of the methyl group, that part of the molecule is excited to a virtual state and emits a light signal at the sum frequency of the two pulses. In this case, the IR pulse is broad enough to cover all three vibrational transitions, from 2850 to 3000 cm^{-1}, each of which is coherently excited. In figure 2, the transitions appear as dips against a broad nonresonant SFG background from the gold.

The symmetric methyl stretch in each of the roughly 10^{11} methyl groups in the film has an IR transition dipole moment parallel to the top C–C bond, so the observed intensity of the symmetric stretch depends on the vector sum of those dipoles—the net spatial orientation of the methyl groups. When the molecules are ordered, as they are at room temperature, the symmetric stretch appears as a deep dip in the spectrum. As heat floods into the hydrocarbon chains from the heat pulse, disorder is registered as a gradual weakening of the signal over time.

Indeed, although the vibrational states excited within a picosecond can hardly be described by an equilibrium Boltzmann distribution, Dlott argues that the orientational disorder—or rather, the ensemble-averaged IR dipole moment of the methyl groups—can be likened to an effective temperature.

The time-resolved measurement of energy flow between adsorbed molecules and surfaces goes back decades. In 1990, for instance, Philippe Guyot-Sionnest (now at the University of Chicago) and colleagues determined the lifetime of coupling between the silicon–hydrogen stretching mode and vibrations of the Si surface.[3] That measurement also exploited time-resolved SFG spectroscopy, but was carried out by pumping the hydrogen adsorbate vibration with a short laser pulse and recording the loss of that energy as it decayed into the surface—in effect, the inverse of Dlott's experiment. The fundamental difference, though, lies more in the complexity of the adsorbed molecule than in the direction of energy flow. Long hydrocarbon molecules have hundreds of low- and high-frequency vibrational modes that may participate in the flow of heat.

Ballistic transport

To analyze the time evolution of the surface from the SFG data, Dlott and coworkers define a vibrational response function (VRF) and extract two characteristic times—both proportional to the chain length, it turns out. They interpret one—the time delay between the heat pulse and the first signs of disorder (t_0 in figure 2b)—as the time it takes for heat to reach the end of the molecule. For the 18-carbon chain, that delay is about 2 picoseconds. The linear dependence of t_0 on chain length indicates that the leading edge of the heat burst travels nearly ballistically—that is, without scattering—along the chain at a constant speed of about 1 km/s. That's just less than half the speed of sound in the related bulk material polyethylene.

The other time of interest—the time constant τ in the VRF curve—measures the time required for the vibrational excitations in chain molecules to relax and equilibrate with the gold. One can think of the gradual buildup in heat as a thermal impedance. Longer chains, with their larger heat capacities, require more time to heat up. Intriguingly, both t_0 and τ extrapolate to zero at a finite chain length of about 0.8 nm, the length of about 4 carbon bonds. Four years ago Dvira Segal, Abraham Nitzan, and Peter Hänggi predicted that the heat-carrying vibrations in short-chain alkanes should, in fact, be delocalized at about that length scale.[4]

The transfer of heat through the interface, controlled by the weak coupling between gold phonons and alkane vibrations, dominates the thermal conductance. The mismatch in vibrational frequencies and density of states across the interface is probably responsible. A bulk solid's spectrum is continuous and broadband, whereas a self-assembled monolayer's spectrum is discrete with narrow bands.[1] And because carbon is lighter than gold, the strong C–C bonds, which transport heat along the chain, are likely to vibrate with higher frequency than metallic bonds in the gold. But as chemists and molecular engineers find innovative ways to design chains with different types of atoms and bonding configurations, the rate-limiting conductance may change from the interface to the molecule itself. That level of control would bring researchers one step closer to the goal of designing molecular chains whose thermal properties can be chemically tuned.

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References

1. R. Y. Wang, R. A. Segalman, A. Majumdar, *Appl. Phys. Lett.* **89**, 173113 (2006).
2. Z. Wang, J. A. Carter, A. Lagutchev, Y. K. Koh, N.-H. Seong, D. G. Cahill, D. D. Dlott, *Science* **317**, 787 (2007).
3. P. Guyot-Sionnest, P. Dumas, Y. J. Chabal, G. S. Higashi, *Phys. Rev. Lett.* **64**, 2156 (1990).
4. D. Segal, A. Nitzan, P. Hänggi, *J. Chem. Phys.* **119**, 6840 (2003).