Ultrafast laser spectrometer measures heat flow through molecules

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Global warming isn't the only heat scientists are feeling. Another area in which heat flow is becoming crucial is the field of molecular electronics, where long-chain molecules attached to tiny electrodes are used to transport and switch electrons.

"How electrons flow through molecular wires has been studied, but less attention has been given to how the heat flows," said Dana Dlott, a physical chemist at the University of Illinois. "One of the problems has been the lack of a measurement technique that could operate over short distances, short time intervals and large temperature bursts."

As reported in the Aug. 10 issue of the journal *Science*, Dlott, engineering professor David Cahill and colleagues at Illinois have now developed an ultrafast thermal measurement technique capable of exploring heat transport in extended molecules fastened at one end to a metal surface.

"The ability to selectively probe the atomic groups that terminate the chains allows us to investigate the transport of heat through the chain molecules themselves," Dlott said.

To study heat flow through long-chain hydrocarbon molecules anchored to a gold substrate, the researchers used an ultrafast laser spectrometer technique with picosecond time resolution (a picosecond is 1 million-millionth part of a second).

First, the flash from a femtosecond laser (a femtosecond is 1,000th of a picosecond) heated the substrate to about 800 degrees Celsius in one picosecond. This heat flowed quickly into the base of the hydrocarbon molecules and through the chains.

When heat reached the methyl groups at the ends of the chains, which were originally lined up in order, they began to shake and twist. An extremely sensitive form of coherent vibrational spectroscopy was used to probe this disordering.

The researchers' study showed how the familiar concepts of heat transport do not apply at the level of individual molecules.

One cool finding, for example, is that heating the molecule to 800 degrees Celsius doesn't destroy it. "Because the molecule stays hot for only a billionth of a second, it doesn't have time to evaporate, burn up or chemically react," said Cahill, a Willett Professor of Materials Science and Engineering.

Another surprising finding is that heat moves ballistically – that is, at a constant velocity – through the molecule. Each time two more carbon atoms were added to the chains, the heat took a little longer, about one-quarter of a picosecond, to reach the end.

"Heat usually travels at different velocities as it diffuses through its surroundings," said Cahill, who also is a researcher at the Frederick Seitz Materials Science Laboratory and at the Coordinated Science Laboratory, both on the Illinois campus. "We found the leading edge of the heat burst traveled ballistically along the hydrocarbon chains at a velocity of 1 kilometer per second."

The researchers also determined the overall rate of heat flow in the molecule. They calculated a thermal conductance of 50 picowatts per degree Celsius.

“This is a new way of measuring temperature within a molecule,” Dlott said. “It’s the first step toward making a more precise thermometer with very high spatial resolution and with very high time resolution.”

Source: University of Illinois at Urbana-Champaign

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