Ultrafast stop and go

Theoretical physicists have predicted that ultrashort laser pulses can be used to drive electrical currents through single molecules, and also to stop currents in molecular junctions.

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Finding ways to generate electrical currents with light is a problem of great practical importance and has occupied the minds of scientists for more than a century. Much of this research has focused on understanding photosynthesis or making solar cells more efficient, but the potential to control fast circuits optically will also require an understanding of the fundamental limits for transferring light to electrical energy. In particular, downscaling in nanoelectronics has reached the level at which a single molecule controls the operation of a device. For these systems, the quantum mechanical nature of electrons becomes important, and it may be possible to observe novel effects when they interact with light.

Writing in *Physical Review Letters*, Ignacio Franco and Paul Brumer of the University of Toronto in Canada and Moshe Shapiro of the Weizmann Institute in Israel[1] propose how to drive an ultrafast current in a single molecule with a laser pulse. Conversely, in *Europhysics Letters*, Guan-Qi Li and Ulrich Kleinekathöfer from Jacobs University and Michael Schreiber of the Technical University Chemnitz, both in Germany[2], predict what appears to be the opposite effect: they demonstrate that a laser pulse impinging on a molecular junction can interrupt a steady current, giving rise to a gap in an otherwise regular train of electrons. What is notable about both of these studies is that light assumes the role

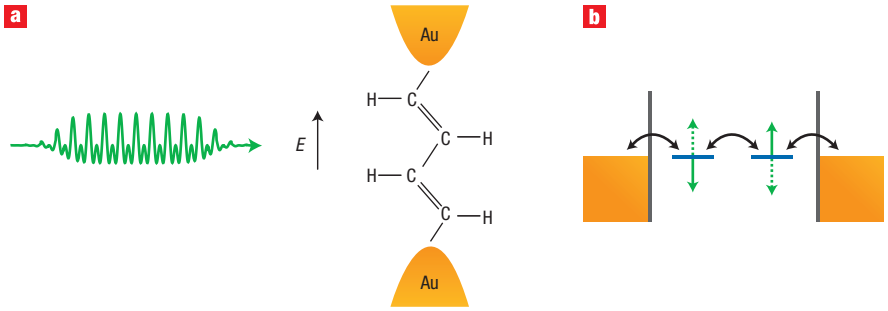

Figure 1 A laser produces an ultrafast current pulse in a molecular wire. **a**, Sketch of the trans-polyacetylene dimer between two gold electrodes considered by Franco and colleagues. The laser pulse (green) on the sample is a mixture between two pulses, one with a frequency twice that of the other. For the case shown here, the maximum amplitude of the electric field, *E*, is directed up and drives a net current in the same direction in the molecule. The phase between the two laser pulses determines if the maximum electric-field amplitude (and hence the direction of the current) is directed up or down. **b**, The energy levels associated with the π-orbitals (blue line) and the metal electrodes (orange). In the presence of the electric field produced by the lasers, the molecular energy levels oscillate in time (up or down in the figure), bringing them in and out of alignment with each other and permitting a current to flow through the molecule.

of a voltage — either starting a current without applying any voltage across the molecule, or stopping a current while leaving a voltage in place.

These two theoretical papers also both draw on recently pioneered ideas for how to excite a constant (d.c.) current in a molecular wire. Franco and colleagues explore the effects of optically exciting a current by mixing together two lasers with different frequencies[3], and Li and his co-workers explore an idea for suppressing the quantum mechanical tunnelling of electrons with an oscillating electric field[4]. The new aspect of these two works is that they explore whether current excitation is robust in the presence of ultrashort laser pulses, as opposed to continuous-wave radiation, which was assumed in the past. The authors predict that it is feasible to control the current through a molecule on the level of a few electrons, and at rates that are much faster than the switching times of previously devised single-electron transistors.

Franco and colleagues consider the molecular system that is shown in Fig. 1a. A single molecule — in this case, a trans-polyacetylene oligomer — is sandwiched between two gold electrodes. A laser is directed at the molecule so that the time-varying electric field of the light exerts a force on the electrons in the molecular π-orbitals that points along the length of the molecule.

The laser 'perturbs' the energy of the electrons, which would otherwise stay near the positive ions in the molecular backbone. This perturbation, known in quantum mechanics as the 'dynamic Stark shift', essentially makes the energy of the electrons in the π-orbitals oscillate in time with the same periodicity as the laser. As the energy levels of the electrons oscillate, they go in and out of alignment with each other (see Fig. 1b), permitting electrons to flow through the molecular circuit.

This effect depends on the shape of the laser electric field. For laser radiation, the amplitude of the electric field varies sinusoidally in time and the excitations described above would therefore produce an equal current up and down in the molecule shown in Fig. 1a. So, how is it possible to obtain a net current (in one direction) with light alone? The solution is to make the amplitude of the electric field along one direction greater than the amplitude in the opposite direction. This can be done by mixing together two laser fields — one with a frequency twice that of the other — to produce an asymmetric waveform (Fig. 1a). Moreover, by tuning the relative phases of the lasers, it is possible to make the maxima of the field point in a given direction, and therefore switch the direction of the current.

This effect was demonstrated experimentally in the late 1970s when two microwaves of frequency ω and 2ω were used to generate a finite voltage between either end of a molecular crystal[5]. In the new proposal, this idea is extended to a laser pulse that lasts only 500 femtoseconds. The pulse contains about twenty oscillations of the electric field and the induced current consists, on average, of one electron[1]. Interestingly enough, the current flow sets in after only a few periods of oscillation.

The opposite effect, which was studied by the German group — namely the suppression of a current by an oscillating field[4] — is possible as well. The simplest way to explain the phenomenon is to say that the light causes the energy levels to oscillate in such a way that the average rate at which electrons can tunnel from one level to the next is reduced. This diminishes the overall electron mobility through the molecule and, consequently, any current through the molecular junction becomes smaller. For certain ratios of laser amplitude and frequency, the current can be quenched almost perfectly. An appropriately engineered laser pulse will suppress the current accordingly during a finite time[2].

It takes a fairly large electric field — of the order of 10^5 V cm^{-1} — to produce such an effect. In this context, the design of the contact tips proves rather helpful. These tips act as antennae that can deform and enhance the electric field by several orders of magnitude — an effect that is well known from surface-enhanced Raman scattering. As a result, it would be possible to achieve a sufficiently intense local field at the molecular π-electrons without using an overly intense source.

Several groups have tried to make measurements on real molecular systems that use lasers to control a current. The main difficulty is focusing the laser on the molecule and the tip well enough that the leads do not heat up too strongly and spoil a controllable output. Setups in which coated scanning tunnelling microscope tips act as wave guides and/or robust carbon nanotubes act as leads may help to solve these problems. Alternatively, coupled quantum dots, which can trap electrons in much the same way as an ionic molecule, could be used as artificial molecules.

Not surprisingly, a number of theoretical questions remain open, and more in-depth quantitative analysis, potentially using time-dependent density functional theory, will be required. Unfortunately, this represents a formidable computational challenge. It would also be of interest to know how noise may affect these molecular currents. If the resulting fluctuations are small, the ideas presented in these theory papers could lead to a new standard for current.

References

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