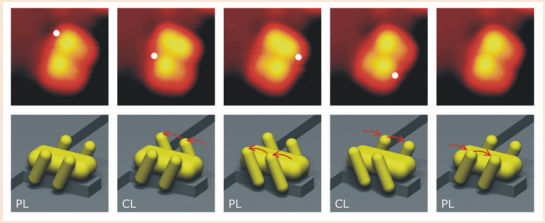
Tips for switching molecular conformation

CHARACTERIZATION

Researchers at Freie Universität in Berlin, Germany and CEMES-CNRS in France have used a scanning tunneling microscope (STM) tip to switch between two conformational states of a molecule reversibly while characterizing the required driving forces [Grill *et al.*, *Nano Lett.* (2006) doi:10.1021/nl0615017]. When adsorbed to a Cu(111) surface, the four di-tert-butyl-phenyl 'legs' extending from the flat body of a Reactive Lander (RL) molecule can take up either a parallel leg (PL) orientation where both pairs of legs face the same direction, or a crossed leg (CL) orientation where both pairs lie in opposite directions. Either conformation is energetically stable.



A series of four sequential manipulations of the RL molecule: (top) STM images, and (bottom) schematics of the molecular configuration. The white dot in the STM images (which are 4 nm x 4 nm in size) marks the lateral position of the STM tip during manipulation while the arrows indicate the induced rotation of one pair of legs. (© 2006 American Chemical Society.)

At a constant bias voltage, the STM tip approaches the molecule vertically until a point is reached at which one pair of legs is induced to rotate and the molecule changes conformation. Successful manipulation shows up as a sharp increase in tunneling current and is also confirmed by STM imaging of the molecule.

The molecular switching is driven by the electric field present between the tip and the surface, which induces a dipole in the legs of the molecule. The height of the potential barrier between the two conformations is thought to be dependent on the molecule and its environment. "We show how an exceptionally high rate of success of more than 99% can be achieved for a single molecule in molecular manipulation", says Leonhard Grill.

Quantum yields (the number of switching events per tunneling electron) can be determined from the STM current and the time taken for a manipulation to take place. Values of 10^{-10} events/electron at voltages greater than 50 mV are recorded. The maximum yield is observed when the tip approaches the front of the molecule, suggesting that a directional force induces conformational changes. The quantum yield is also found to be smaller when changing from CL to PL than for PL to CL as a result of the higher energy barrier involved.

The team hope to study the role of electrostatic forces during the manipulation of similar molecules that exhibit a permanent dipole as opposed to switching by electrostatic forces on an induced dipole as seen here.

Katerina Busuttil

Ultrafast transitions captured with single electrons

CHARACTERIZATION

Researchers at the California Institute of Technology have recorded movies of fast-changing atomic structures using single electrons to create a sequence of images only 100 fs apart. [Grinolds *et al.*, *Proc. Natl. Acad. Sci.*(2006) doi: 10.1073/pnas.0609233103].

The ultrafast electron microscope (UEM) can image complex structures nondestructively in four dimensions (space and time) with the spatial resolution of a transmission electron microscope. Images and diffraction patterns of materials' transient structures can be obtained by releasing bursts of timed single-electron packets derived from a sequence of optical pulses. Time resolution is determined by the duration of the optical pulse that generates the photoelectrons. The team induce a delay in producing subsequent optical pulses, enabling them to set a well-defined time frame for each electron burst arriving at the sample. The series of images produced can then be put together to give a movie.

As single-electron packets show little space-charge broadening, the images and diffraction data obtained are able to show atomic-scale resolution.

"All the work for 50 years in electron microscopy has recorded static images – now we can see things moving", says Ahmed H. Zewail, winner of the 1999 Nobel Prize in Chemistry.

The researchers used the microscope to obtain data for the metal-insulator phase transition in VO_2. This phase transitions occurs in just over 3 ps and as such is a suitable candidate for the study. VO_2 undergoes a first-order transition from a low-temperature monoclinic phase to a high-temperature tetragonal rutile phase at ~67°C. The UEM data for the transition is able to show this structural change over time. Zewail hopes to develop the techniques further so that the team can study the movement of defects in materials and investigate the behavior of surface catalysts and biological nanoparticles.

Katerina Busuttil

New slant on molecular junctions

CHARACTERIZATION

UK researchers at the Universities of Liverpool, Durham, and Lancaster have measured conductance changes in single-molecule junctions as the molecular tilt and conformation are changed [Haiss *et al.*, *Nat. Mater.* (2006) **5**, 995].

A single molecule can be picked up by lowering a scanning tunneling microscope (STM) tip onto a layer of adsorbed molecules on a Au substrate. The tip pulls the molecule upwards, bridging the gap between tip apex and surface. Electrons can then tunnel through the molecular wire and current is detected by the STM. Increases in the current show discrete steps, with the lowest value corresponding to a single molecule, the next value up representing conduction through two molecules, and so on. In this way, the conductance of single, flexible molecules can be studied. Molecular conductance appears to be temperature dependent at intermediate gap spacings. The molecule can adopt different conformations, each showing different conductance, with higher energy conformers obtained as the temperature increases. A theoretical study shows that, as the tilt angle is increased from 10° to 70°, the highest occupied molecular orbital and lowest unoccupied molecular orbital resonances broaden and shift toward lower energies. This indicates that the strength of the coupling between surface and molecule increases as tilt angle is increased. While such data can lead to information on the position of the Fermi level with respect to molecular orbital energies, contact fluctuations need to be reduced for the study to be applicable to room-temperature devices.

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