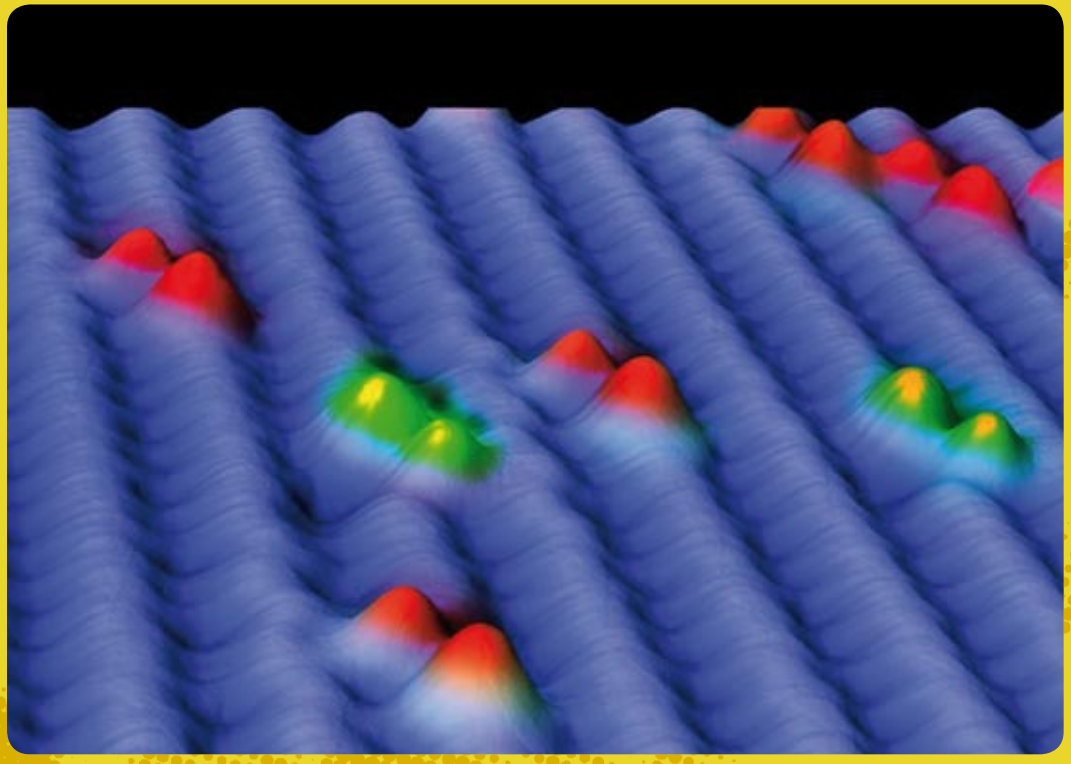
DAMIEN RIEDEL, ANDREW MAYNE, GÉRALD DUJARDIN, AMANDINE BELLEC*, FRANCO CHIARAVALOTTI*, MARION CRANNEY*, MATHIEU LASTAPIS*

Groupe Nanoscience Moléculaire, Laboratoire de Photophysique Moléculaire - Faculté des Sciences d'Orsay
* Doctorants

Probing the movements of a single molecule



In 1959, the visionary physicist Richard Feynman challenged the scientific community to get to the heart of the matter by transforming it molecule by molecule. Although an apparently crazy idea at the time, the challenge has now been taken up.

Photo : Image des molécules de biphényl (en rouge et vert) sur une surface de silicium, réalisée avec un microscope à effet tunnel.

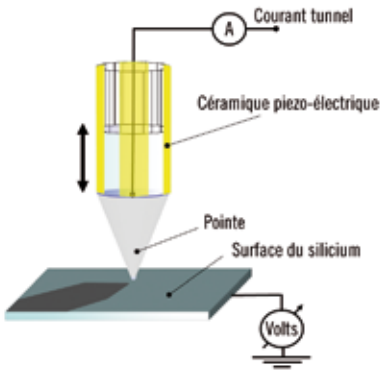
Molecular nanosciences have attracted growing interest in diverse domains of biology, materials science, astronomy and electronics. Since the 1980s, local probe microscopy has been the most suitable technique for investigating extremely small molecular structures. Our group has a particular expertise in the study of the properties and the manipulation of single molecules adsorbed onto the semi-conductor surfaces. Using a low temperature scanning tunnelling microscope, we have been able to observe certain signatures of the molecular dynamics. We have also been able to investigate new modes of excitation and control by decoupling the intrinsic molecular properties from the surface. We are interested in understanding the nano-world and, in the future, conceiving the possible electronic components of tomorrow that could be constructed "inside a molecule" to carry out calculations or boolean operations.

A microscope capable of seeing a molecule...

Among its routine projects, the "Molecular Nanoscience" group studies the behaviour and properties of single molecules* adsorbed onto semiconductor surfaces. Closely related to the field of monomolecular electronics*, an objective of our work is to understand and control the infinitely small by using the so called "bottom-up*" approach of nanotechnology. From an experimental point of view, our principle tool is the scanning tunnelling microscope. With an extremely high spatial resolution, this tool allows us to map surfaces, and also to stimulate the movement of single molecules one at a time.
We have employed a low temperature scanning tunnelling microscope over the past few years. The microscope operates in an ultra-high vacuum and uses cryogenic fluids, namely liquid nitrogen and helium, to cool it down. The big advantage of operating the microscope at such low temperatures is the gain in stability (very small thermal drift). This stability enables a high lateral resolution of the order of 50 picometers (pm*) to be achieved easily. By comparison, the distance between two silicon atoms is 235 pm. This extreme resolution raises several interesting possibilities concerning the manipulation of individual molecules, because it should be possible to use the electrons as very fine tweezers to induce excitations at very precise locations – even inside a single molecule.

FIGURE 1

Illustration of the principle behind the scanning tunnelling microscope.



1 "Visualising" matter at the molecular level

The scanning tunnelling microscope is composed of a tapered metallic probe **(tip)** positioned over a surface. The surface, in this case silicon, was prepared by heating to obtain what is known as a surface reconstruction. The heating process is crucial in reducing the surface roughness, because surface diffusion allows the atoms to be organised into large terraces with a few "steps" only one or two atoms high. The end of the probe must be very close to the surface (a few Angstroms) for the microscope to work. This is achieved using piezoelectric* ceramics: with these extremely precise piezoelectric "motors", the movement of the probe can be perfectly controlled on the atomic scale. Why so close? Because the electron tunnelling effect works only at a very small distance similar to the distance between atoms. By polarizing the surface with a continuous voltage, an electric current can circulate across the gap between the probe and the surface (see figure 1). This tunnel current is fundamental to the operation of the microscope, because we can map the surface and the molecules with it, as shown in **figure 2**. The resulting image is due to the displacement of the probe from left to right and from top to bottom; similar to the way the electron beam scans across the screen to produce an image in our old television sets. As it moves, the tip of microscope encounters the different atoms on the surface. The tip feels the variations in the local atomic conductance (or more precisely the electron density). If the tip follows a horizontal trajectory, a higher electron density will give rise to a higher tunnel current. The image obtained is thus a map of the overlapping "electron clouds" around the atoms, and does not exactly correspond to the actual positions of their nuclei.

A snapshot of molecular bistability

Different methods are available for manipulating an individual molecule adsorbed* onto a sample surface. Our group uses a particular manipulation technique that involves a tunnel electron provoking an ad-hoc electronic excitation of the molecule. Taking the specific example of a biphenyl molecule will help us to understand how the process works. Biphenyl molecules are deposited onto a silicon surface, which can then be mapped using the microscope **(figure 3)**. We observe that the molecule is attached at two positions on the silicon. When the metal probe (tip) of the microscope is placed over the molecule (indicated by the blue spot) the molecule can be excited.

FIGURE 2

Topography —height— of a surface obtained by scanning tunnelling microscopy.

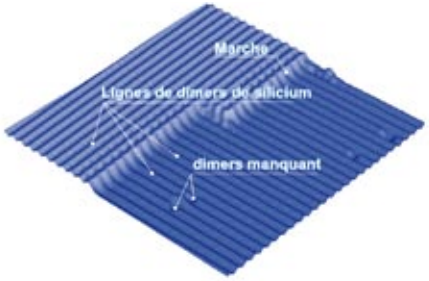
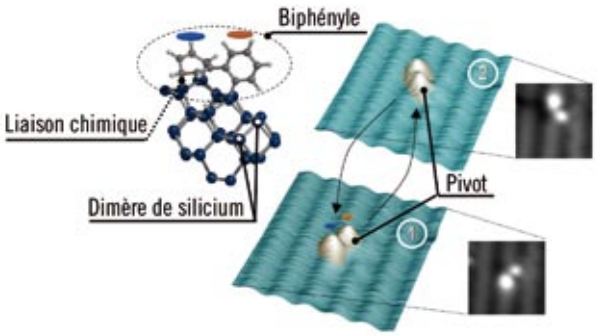


FIGURE 3

Motion of a biphenyl molecule on the silicon surface. The parallel lines correspond to dimers of silicon atoms forming ridges and grooves on the surface. The silicon atoms pair up into dimers to stabilize the surface. The two bright lobes in each image represent the electron clouds of the two benzene rings in the biphenyl molecule. Positioning the microscope tip above the different lobes of the molecule —red spot or blue spot— causes the flipping of the molecule around its pivot between configurations 1 and 2 to be more or less efficient, as the images in the centre and to the right illustrate.



Tunnelling electrons, having a much higher energy than that used for imaging, interact with the part of the molecule's electron cloud, which is located just below the tip of the microscope. Once the molecule is excited, one of its chemical bonds with the surface is broken, and it then twists around before attaching itself in a position symmetric to the former: movement from position 1 to position 2. We discovered that the molecule could be manipulated several times in this manner; the movement from position 1 to position 2 is reversible, and hence the biphenyl has a bistable* behaviour. When we look in detail at the electronic process involved in the manipulation, we see that the biphenyl molecule attached to the silicon possesses what are called spatially localized molecular resonances, a bit like "control buttons." In effect, they behave as "seeds" in the electron cloud that allow access to specific excitations. By varying the electronic excitation at different sites on the molecule, much to our surprise, we found that it was necessary to apply the excitation at the site indicated by the red spot, where the molecule pivots, for the bistable movement to be the most effective. As an analogy, imagine a balloon tied to a stake in the ground by a cord **(figure 4)**. The balloon pivots more rapidly by kicking the stake! This fascinating experiment helps elucidate the behaviour of the infinitely small and to establish certain basic rules. As a further illustration, the bistable molecule was found to possess a transitory state, as in mesoscopic electronics*. This transitory state corresponds to a metastable* conformation through which the molecule must pass as it moves from position 1 to position 2. Hence, by exciting the blue "button" of the molecule we favour the movement towards the transitory state T. The molecule then returns to its initial position after having spent a very short time in the T configuration. Surprisingly, we were able to observe the biphenyl molecule as it passes through the transition state T, that is, during the rotation around its pivot. To do this, we made the tip of the microscope rock back and forth very rapidly —100 times faster than for a standard image— along a single trajectory above the molecule such that the blue "button" is excited (indicated by the white line in the left-hand panel of **figure 5**). This trajectory crosses both the path of conformation 1 and 2 and the transitory state conformation because that is located between conformation 1 and 2. In this manner, the rapid movement of the tip excites the molecule as the tip passes over the blue point. We then probe as well the position of the molecule as it moves through the T state. The central panel in **figure 5** shows the result of this experiment. The image is constructed from a succession of profiles of the molecule as a function of time. Most of the time the biphenyl molecule is found at position 1 (upper white band). After a certain amount of time, the molecule pivots to position 2 (lower white band). However, occasionally, the molecule briefly disappears which show up within the white bands as black lines with a glimpse

of white at positions between those of conformation 1 and 2. The profiles reveal that the molecule makes one visit to the transition state T from position 1 and four visits from position 2. Thus, we are able to observe the dynamics of the single molecule during this bistable movement only because the microscope acts rather like a "molecular radar" taking a snapshot of the molecule as it moves.

The environment is important...

During the process of adsorption on the silicon surface, the biphenyl molecule loses one of its hydrogen atoms. This hydrogen atom binds to a neighbouring silicon atom. Surprisingly, we found that the hydrogen atom is bound to the surface somewhere along the path of the transitory T conformation, that is, between the stable positions 1 and 2. This hydrogen atom is particularly interesting because it affects the molecular bistable dynamics. By placing the microscope tip, the tunnelling electrons were injected into the hydrogen atom. The hydrogen-silicon bond could then be broken selectively, allowing the hydrogen atom to be removed from the vicinity of the molecule. After taking another image of the molecule, we found that the molecule itself remained unchanged following the manipulation. However, when we excited the molecule again at either its red or blue "button", we found that the molecule possessed two new configurations that could be imaged with the microscope. We thus discovered that this "modified" biphenyl molecule is multistable, because it has two new stable states along with the existing configurations 1 and 2. This multistable molecule also possesses transitory states. Most importantly, we found that the hopping rates of the multistable configuration were amplified fifty times by excitations using identical tunnel conditions to those used on the bistable state.

This experiment demonstrates how the environment can affect the functioning of a molecular "machine": in our case, removing a single atom of hydrogen near the molecule amplifies the dynamics of its movement. In certain other cases, notably during electron transport studies, modifying an atom's surroundings can cause dramatic changes in its behaviour. Other parameters can also influence the dynamic properties of the bistable molecule. The silicon surface that we use contains a large number of dopants*, atoms that give silicon its conductive properties. The concentration of these dopant atoms must be very high during low temperature experiments: under these conditions, some types of dopants influence the surface atoms by carrying millions of little positive or negative charges that become distributed over the different surface states* of the substrate. We found that these partial charges can affect the molecule's dynamics, either by repulsing or attracting the bistable molecule as it pivots.

The surface in all its states...

The bistable biphenyl molecule, being attached to the silicon surface, is an example of chemisorption. Under these conditions, the properties of a single molecule can be very different to those of "free" molecules in the gas phase. When the molecule under study possesses known intrinsic chemical functions in the gas phase, attaching it chemically to the

FIGURE 4

Illustration of the mechanism for flipping a biphenyl molecule on a silicon surface. Not only does the ball pivot when we kick it, but the ball pivots when we kick the stake! In the same way, the molecule pivots when the tip of the microscope excites one of the two lobes of the molecule (the blue or red spot, respectively).

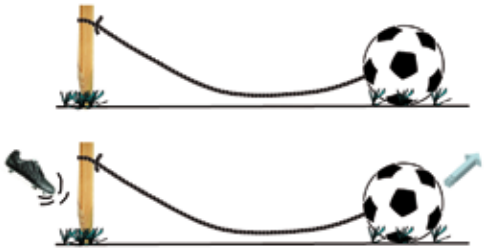
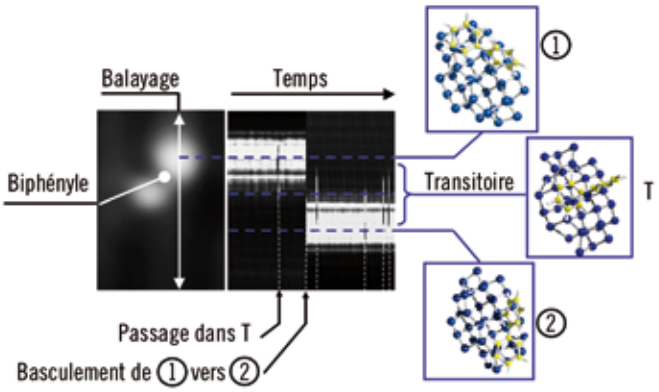


FIGURE 5

A series of line profiles of the biphenyl molecule as a function of time. The microscope tip continually passes back and forth over along the same line – passing over the lobe of the molecule corresponding to the blue spot (left-hand panel). The tunnel current is higher above the molecule which shows up as white in the profile; when the current is lower, the profile is black. At the position of the initial configuration 1 (upper white band, middle panel), very brief absences of the molecule can be seen in certain profiles reveal. After a while, the molecule flips to configuration 2 (lower white band, middle panel). Here, four visits to the transition state T can be observed – black trace in the lower white band with an offset white line at a position between those of conformation 1 and 2.



surface should be avoided. However, it is possible to reduce interaction between the surface and the molecule to a minimum by favouring what is called physisorption. Stilbene is a molecule with two isomeric forms that are well understood in the gas phase: trans-stilbene and cis-stilbene. This molecule **(figure 6)** can flip between these isomers in the gas phase by a photochemical process. When the molecule is gently deposited at low temperature on a silicon surface, we observed physisorbed molecular conformations that are very similar to the two isomers known in the gas phase. Manipulating stilbene in the same way we did with the biphenyl, we found that a cis-trans isomerization similar to that in the gas phase did not take place. Instead, new conformations appeared. We found that each isomer of stilbene (equivalent to the gas phase) —trans-stilbene and cis-stilbene— was transformed into a specific surface isomer. Thanks to the weak molecular bonding to the surface (van der Waals forces), we were able to study the effect on the molecular dynamics of the partial charged surface states induced by the doping. By measuring the efficiency of the surface isomerization of stilbene, we found that the isomerization was amplified on an n-doped* substrate. In this case, the dynamics of the electronic process induced by the tunnelling electrons during surface isomerization were modified during the excitation of the stilbene molecule. This is in contrast with biphenyl, where only the dynamics of the molecular motion were modified.

FIGURE 6

Isomerization of a molecule of stilbene. Left: in the gas phase, light induces isomerization. Upper Right: schematic showing the cis-stilbene configuration physisrobed on the surface (no chemical bonds). Lower Right: topographies of the trans- and cis-stilbene molecules on the silicon surface.

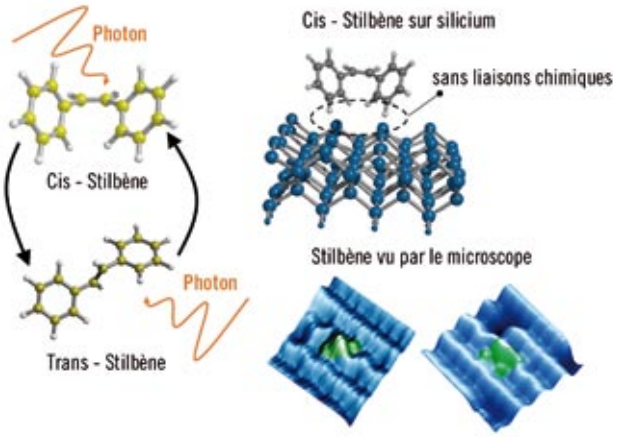
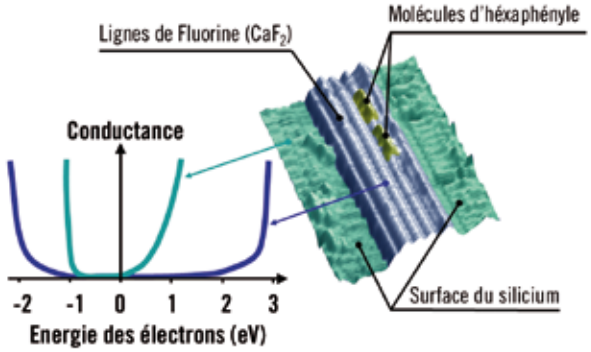


FIGURE 7

Hexaphenyl molecules on a silicon surface partially isolated by a few layers of CaF_2. The hexaphenyl molecules are adsorbed oriented along the rails formed by the CaF_2 structure. Conductance measurements reveal that the CaF_2 lines have a band gap four times larger than that of clean silicon.



An insulator and yet a conductor...

Our investigations have revealed that a molecule deposited on a semiconductor surface but not chemically bound to it can nevertheless "feel" from a distance various characteristics of the surface such as the presence of a surface charge. For this reason, we have sought a way to insulate, partially and in a controlled manner, the electronic properties of the silicon surface from those of the molecule. To do that, we covered the surface with a few layers of calcium fluoride (CaF_2). This material is found in nature as ionic crystals that are a natural insulator because it has a wide band gap of almost 12 eV — clean silicon only has a gap of 1.1 eV. By depositing only a few atomic layers of this substance, we don't quite reach the properties of a solid fluoride crystal. In fact, it is important to avoid turning the surface into a complete insulator: its conductance must be controlled following deposition of the CaF_2 because the microscope requires the presence of a measurable electric current in order to function properly. After depositing a few layers of the ionic substance onto the silicon substrate, we were able to visualize the surface with the microscope, as shown in **figure 7**. The surface presents a number of different structures formed by the molecules of CaF_2. The most interesting is composed of parallel rows that are larger than the silicon dimer rows. Measuring the conductance of the structures, we found a band gap that was four times larger than that of clean silicon **(figure 7)**. In addition to being a partial insulator, the new surface is functionalized. As an illustration, instead of depositing the previously studied molecules, we used hexaphenyl molecules composed of a chain of six benzene rings. Nearly 80% of the hexaphenyl molecules were adsorbed and oriented along the CaF_2 "rails" (or rows) demonstrating that the surface has been functionalized. Further investigation showed

that the hexaphenyl molecules could be moved laterally along the CaF_2 rails. Thus, the structure of the insulating layer guides the molecular manipulation, in contrast to stilbene, which diffuses randomly over the silicon surface. This study on the growth of thin CaF_2 layers on the silicon surface is part of the European Project PicoInside "Computing inside a single Molecule".

Are electronic components inside a molecule the stuff of dreams ?

Ultimately, the aim of this research is to use a single molecular structure, more or less complex, as an electronic component that can perform several actions or functions. For example, a biphenyl molecule can act as a commutator if it is connected to conducting atomic wires. Other examples of more complex molecular structures can be conceived for constructing a logic gate. No such device exists yet, even experimentally, because we still have not mastered the necessary junctions; nor do we have the conducting atomic wires to join two molecular structures together. We also lack a multiprobe microscope that could be used to position the molecular structures in several places at nanometer scale. Several parallel investigations can be imagined. They include exploring the possibility of confining a coherent electromagnetic field (a laser beam) or laser pulse shaping* under the probe of the scanning tunnelling microscope. This requires a better understanding of the dynamic properties of the molecular structures under study —through experiments with light— and to be able to activate the devices optically. The molecular computer has not yet been born, but investigations into the concept will undoubtedly lead to numerous exciting discoveries in fundamental physics.

Glossary

Adsorption :
Adsorption is a surface phenomenon by which molecules adhere to solid surfaces by diverse processes that vary in strength. Physisorption refers to situations involving weak interactions with the surface and chemisorption when chemical bonds are formed.

Angstrom :
A unit of distance. 1A = 10^{-10} meters.

Bottom-up approach :
The bottom-up approach is based on the construction of nano-objects from the building blocks of matter such as atoms and molecules. The top-down approach used in the semiconductor industry consists of etching a circuit or a component in solid matter, for example by lithography.

Liquid nitrogen :
Liquid nitrogen is nitrogen gas cooled down to below its boiling point of 77.36 K (-195.79°C). Helium becomes liquid at below 4.2K (-269°C).

Band gap :
In solids, the electron energy levels of atoms form bands. The allowed bands (permitted bands), which can contain electrons, are separated by energy bands where the electron levels are excluded (band gaps).

Bistable :
In electronics, a bistable signal can have one of two stable logic states: 0 or 1. Switching from one state to another can occur only when an external current is applied.

Piezoelectric ceramics :
Ionic crystals, usually barium titanate ($BaTiO_3$) or perovskite ($CaTiO_3$), that change shape when an electric field is applied.

Dopant :
An impurity (foreign atom) added with a variable concentration to a semiconductor to modify its optical and/or electrical properties;
n-type doping involves adding donor atoms (e.g. Phosphorus) that provide supplementary negative charges to the crystal lattice.

Mono-molecular electronics :
A domain of molecular electronics concerned with the study of single molecules (as opposed to the study of self-assembled molecular layers). This domain has the goal of constructing more or less complex electronic functions using a single molecule.

Surface state :
An electronic surface state forms at the abrupt transition between a solid material and a vacuum.

Laser pulse shaping :
Pulse shaping consists of controlling the phase of the different frequencies found in a laser impulse of very short duration.

Mesoscopic (scale) :
Intermediate scale between the microscopic, corresponding to the level of atoms and molecules, and the macroscopic, corresponding to visible objects.

Metastable :
Metastability refers to the ability of a state to be kinetically but not thermodynamically stable. The transition to the metastable state can be relatively slow and does not correspond to the minimum energy of the system.

Single molecules :
Molecules adsorbed in such small quantities that they are considered to be isolated from other molecules on the surface.

Picometer :
Unit of measurement. 1 pm = 10^{-12} metre

Van der Waals force :
Weak electrostatic interaction between atoms or molecules, or between a molecule and a crystal.