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Combined experimental and theoretical study of charge transport across azobenzene-based single-molecule junctions unravels the long-standing debate concerning the conductance of the cis and trans forms of these photo-switchable molecules.

Photochromic molecules are promising building blocks for the realization of functional molecular circuits. In particular, and due to their simple structure, the azobenzene class of molecules has become an archetypal of molecular photoswitch research. Azobenzene-derivative molecules change their conformation as a result of a cis-trans transition when exposed to ultraviolet or visible light irradiation. Upon this isomerization their electronic properties change markedly, which is expected to induce a significant variation in the conductance of azobenzene-based molecular devices.

Despite the extensive investigations carried out on this type of molecule, a detailed understanding of the charge transport for the two isomers, when embedded in a junction with electrodes, is still lacking. Devices with the cis isomer exhibiting either higher or lower conductance than the trans isomer have been reported. In order to clarify this issue, we have performed a combined experimental and theoretical analysis of electron transport through azobenzene-derivative single-molecule break junctions with Au electrodes. Current-voltage and inelastic electron tunneling spectroscopy (IETS) measurements performed at 4.2 K are interpreted based on first-principles calculations of electron transmission and IETS spectra.

Using current-voltage characteristics, we find that the difference in conductance between both isomers is fully caused by a shift of the resonant states. This is confirmed by density functional theory (DFT) based transport simulations, which indicate that the conductance for the cis isomer is higher than the trans isomer because the current-carrying molecular state is closer to the Fermi energy. It is thus the first study in which it is shown that the cis conformation has higher conductance not only because it is shorter, but because the electronic structure of the junction is more suitable to conduct.

In addition, we report for the first time the experimental and theoretical inelastic electron tunneling spectroscopy (IETS) of the photo-switchable molecule in the two different states (cis/trans). We show how these IETS fingerprints allow to unambiguously discriminate between the molecular conformations, which thus enables an alternative readout path for identifying the state of azobenzene-based molecular switches.

Unraveling charge transport properties of azobenzene-derivative molecular junctions.
Spin-flip transitions induced by time-dependent electric fields in surfaces with strong spin-orbit interaction

J. Ibañez-Azpizroz, A. Eiguren, E.Ya. Sherman, and A. Bergara

Enhanced light induced spin-flip transitions at non-magnetic surfaces with strong spin-orbit coupling, offers an attractive possibility of an experimental approach to the spin-orbit phenomena by optical means.

Understanding electron spin transport and spin relaxation in quasi-two-dimensional (2D) systems is of capital importance due to both fundamental reasons and the potential technological applications. The spin-orbit (SO) interaction is the most prominent relativistic effect leading to the fascinating phenomena recently observed in 2D systems, such as the quantum spin Hall effect. An experimentally accessible spin degree of freedom offers a new route for the emergent field of spintronics, where the main features of charge dynamics are strongly influenced by the spin-related effects. The technical possibility of spin manipulation and control by means of an applied bias voltage is strongly supported by recent investigations on a variety of semiconducting alloy samples.

However, a strong SO coupling cannot be achieved in conventional semiconductors, where the spin splitting of conduction electrons is limited to a few meV at most. In contrast, the relativistic effects completely dominate the electronic structure of many heavy-element surface materials and overlayers. The reason lies in the breaking up of the inversion symmetry and the associated gradient of the effective one-electron potential introduced at the interface.

In this article we have presented a comprehensive theoretical investigation of the light absorption rate at a Pb/Ge(111)-\(3\sqrt{3}\times3\sqrt{3}\)R30° surface with strong spin-orbit coupling. Our calculations show that electron spin-flip transitions cause as much as 6% of the total light absorption, representing one order of magnitude enhancement over Rashba-like systems. Thus, we have demonstrated that a substantial part of the light irradiating this nominally nonmagnetic surface is attenuated in spin-flip processes. Remarkably, the spin-flip transition probability is structured in well-defined hot spots within the Brillouin zone, where the electron spin experiences a sudden 90° rotation. This mechanism offers the possibility of an experimental approach to the spin-orbit phenomena by optical means.
An STM tip can be used as a nanoscopic electron gun to promote vibrations in molecules deposited on surfaces or to induce the diffusion of adsorbed atoms. Recently, in an elegant experiment, Sykes et al. made a considerable advance in the field by facilitating atom transport below the surface with a STM tip [Proc. Natl. Acad. Sci. U.S.A. 102, 17907 (2005)]. In particular, they used the tunneling current to extract hydrogen atoms deeply buried below a Pd(111) surface. The nature of the system adds interest because of the applications in hydrogen storage and hydrocarbon synthesis, where subsurface hydrogen can boost the catalytic properties of palladium.

In this paper, scientists from the DIPC put together a theoretical model that accounts for this phenomenon and provides quantitative predictions on the rates at which hydrogen can be transported under different experimental conditions. The footing of the model is a perturbative description of the coupling between the palladium electronic structure and the hydrogen atom motion. In addition, the model uses imported ideas from the BEEM technique, formerly used mainly to image semiconductor-metal interfaces.

An intriguing experimental finding is that the extraction effect happens with different efficiencies depending on the bias voltage sign, i.e., whether the charge carriers are electrons or holes. This is a central fact that cannot be easily fitted in the well-known palladium electronic structure. The crucial ingredient of the model that reconciles both facts is the distinction between focused and unfocused carriers in the STM current propagating below the surface, as suggested by BEEM theory. Since the former carriers are less likely to interact with the hydrogen atoms, we conclude that the unfocused carriers mainly trigger transport. Focused (unfocused) carriers originate in the d(s)-band of the metal. In particular, we want to draw attention to the fact that the same carrier propagates at the same time according to both s and d-bands of the right energy depending on its momentum, and this is a case where the process of measuring the final state decides whether the carrier stays in a focused or unfocused beam.

This work not only explains a pioneering experiment of manipulation by STM. It also provides a better understanding of the link between BEEM and STM techniques, and how they complement each other. Interestingly, this work has revealed that the current that goes unnoticed during a BEEM experiment is the one that promotes mass transport.

Diffusion of hydrogen in Pd assisted by inelastic ballistic hot electrons

M. Blanco-Rey, M. Alducin, J. I. Juaristi and P. L. de Andrés

Scanning Tunneling Microscope (STM) has been used recently to manipulate hydrogen atoms deeply buried in a palladium surface. In this paper a model is proposed that explains quantitatively those observations. The usual “on-surface” physics cannot be used in this scenario. Instead, Ballistic Electron Emission Microscopy (BEEM) theory is invoked to describe how carriers propagate layer-wise in the crystal, and to prove that only carriers that propagate freely contribute to the transport of embedded interstitial hydrogen atoms.

An artist’s view of the diffusion mechanism of hydrogen atoms buried in a metal. The tunneling current can be associated to two types of carriers inside the metal: focused and non-focused. The former propagate through narrow channels (magenta), while the latter (green) span larger regions of the metal and are more likely to interact with the embedded interstitial hydrogen atoms.

Contribution from carriers on d-bands is negligible, since they progressively focus along narrow volumes during their layer-to-layer propagation in the crystal.
Ultrafast X-ray pulse characterization at free-electron lasers

Nature Photonics 6, 851-856 (2012)

A measurement technique that provides complete temporal characterization of individual FEL (free-electron laser) pulses at DESYs soft-X-ray free-electron laser FLASH.

X-ray pulses delivered by free-electron lasers provide unique research opportunities, because the pulses are ultra-intense and ultra-short. A single FEL pulse lasts for only several tens of femtoseconds, or even less. The FEL X-ray pulses are short enough to study atoms in motion, chemical reactions, and phase transitions in materials with atomic resolution on the femtosecond timescale. However, the precise arrival time and even the temporal profile of the FEL pulse can change dramatically from one pulse to the next. Therefore, to use the FEL to "film" ultrafast dynamical processes, the arrival time of each pulse must be measured to reorder the individual frames or snapshots captured with each individual FEL pulse.

For this measurements a technique used in attosecond science, the "photoelectron streaking", is adapted, so that the temporal profiles of varying light signals can be recorded. For this, the X-ray flashes were shot through neon gas on their way to their target. Each pulse ejects a burst of photoelectrons from the noble gas. The temporal profile of the photoelectrons is a replica of the FEL pulse that ejected them. With an electromagnetic terahertz (THz) field, the photoelectrons are accelerated or decelerated, depending on the exact instant of their ejection. The strength of this effect is measured using time-of-flight spectroscopy. If the exact shape of the terahertz pulse is known, the temporal profile and arrival time of the individual X-ray pulse can be revealed with a precision of about 5 femtoseconds.

The FEL pulse characterization measurements are made without affecting the FEL beam. The technique can be applied in any experiment at almost any wavelength. Until now, no other measurement has provided the complete timing information which is crucial for future application of these unique X-ray light sources. In the immediate future, laser-driven THz streaking will be used to monitor and maintain the FEL pulse duration at FLASH to study a wide variety of atomic, molecular and solid-state systems.

FEL X-ray pulses are short enough to study atoms in motion, chemical reactions, and phase transitions in materials with atomic resolution.
H-atom relay reactions in real space


Hydrogen bonds are the path through which protons and hydrogen atoms can be transferred between molecules. The relay mechanism, in which H-atom transfer occurs in a sequential fashion along hydrogen bonds, plays an essential role in many chemical, biological, and materials science processes. In this work the scanning tunnelling microscope was used to construct and operate a test-bed for real-space observation of H-atom relay reactions at a single-molecule level. In combination with ab initio simulations a detailed microscopic picture of the elementary reaction steps was established.

To circumvent this difficulty the researchers engineered a platform of hydrogen-bonded water-hydroxyl chains assembled on a Cu(110) surface in which the H-atom dynamics could be observed at the single-molecule level. By injection of a current pulse through a water molecule at one end of the chain, hydrogen atoms were found to propagate one by one along the chain like dominos in motion. The reaction turned out to be triggered by excitation of molecular vibrations and to be completely reversible. The experimental findings were rationalized by ab initio calculations for adsorption geometry, active vibrational modes and reaction pathway, to reach a detailed microscopic picture of the elementary processes.

The demonstrated control of H-atom transfer in these hydrogen-bonded molecular chains not only sheds new insight on a fundamental problem. It also opens a new class of single-molecule chemistry with the STM involving hydrogen bonds. Engineering even longer and more sophisticated H-bond systems supported on solid surfaces could provide an opportunity not only to achieve mechanical logic circuits using H-atoms but also to systematically study the fundamental steps of H-atom dynamics in heterogeneous systems. Such systems are conceivable by combining the self-assembling nature of water/hydroxyl complexes with STM manipulation techniques.

The discovery that H-atoms transfer along H-bonds is possible directly on metal surfaces further suggests that relay reactions may occur more generally at metal–molecule interfaces and, therefore, in liquids all the way down to the confining surfaces. This is of importance in diverse fields, such as nanofluidics and the design of hybrid materials for proton conduction.

Assembled water-hydroxyl chains on Cu(110) showing H-atom transfer reactions. (a) Side and top view of an H2O–OH–OH chain optimized by DFT calculations and its counterpart. (c) Simulated STM image. (d) Experimental STM images of an H2O–OH–OH chain and its counterpart superimposed on the lattice of Cu(110) (white lines). The appearance was inverted by a voltage pulse of the STM over the protrusion. The inversion was also observed for (e) H2O–(OH)3 and (f) H2O–(OH)4 chains. The dots in (d–f) indicate the nearest short-bridge sites binding oxygen atoms in the chains. The inversion of the appearance corresponds to an H-atom relay reaction in which a sequential H-atom transfer is included, as shown by the curved arrows in (a).

Calculated potential energy surface for the H-atom relay reaction in an H2O–OH–OH chain on Cu(110) along the [001] direction. The set of images from initial to final states, shown as insets, is computed with the nudged elastic band method. The H-transfer to the center OH is easy (∼0.24 eV). The transition state (∼0.25 eV) corresponds to OH–H2O–OH with a broken H-bond.

A microscopic picture of the elementary processes was achieved by ab initio calculations.
Researchers at the Donostia International Physics Center (DIPC), Materials Physics Center (CSIC-UPV/EHU), Tecnalia and University of the Basque Country (UPV/EHU) in Spain and at the Technische Universität Dresden in Germany have predicted the stability of cementitious nanotubes. Their new approach may help scientists to synthesize nanotubes made of calcium silicate hydrates, proposed as ideal mechanical reinforcements for cement pastes.

When researchers think of nanoreinforcements, carbon nanotubes come as first option. The problem with carbon nanotubes is that they are water insoluble. In order to make them compatible with water chemistry, they must be functionalized in advance. As a consequence, we thought of directly focusing on inorganic nanotubes, in general, and on cementitious nanotubes, in particular, having a chemistry that is fully compatible with the aqueous solutions of cements.

Previous experiments on nanotube reinforcements of cements haven’t fully addressed inorganic nanotubes, which is actually one of our ideas for future development of the field. We are indeed interested in doping cement pastes with already existing inorganic nanotubes, for instance, imogolite ones. By looking at cement microstructure, however, Manzano and co-workers have modelled cementitious nanotubes with the layered structures of portlandite precipitates within the calcium-silicate-hydrate gel. We have predicted that nanotubes made of portlandite Ca(OH)₂ are stable and promising candidates to be synthesised as already existing brucite nanotubes Mg(OH)₂. Nanotubes built from calcium silicate hydrates themselves are also stable, but their stability is intriguing as it depends on chirality.

The team of researchers showed that especially portlandite nanotubes support strain energies similar to those for already synthesized carbon and inorganic nanotubes. When cementitious nanotubes are synthesized, we proved that they have good elastic properties, with spring constants three times larger than the values of cement gel under compression.

Tensile stresses for cementitious nanotubes also are good for reinforcement. For instance, portlandite nanotubes fail under after a maximum strain of 27% when they reach a maximum stress of about 8 GPa, which is an order of magnitude larger than the stress supported by ordinary steel fibres. Our results strongly suggest that reinforcement at the nanoscale by cementitious nanotubes could even prevent from shrinkage to cement pastes.

Being able to calculate the stability of cementitious nanotubes is very important, as a previous step to their synthesis. Researchers have to see how these nanotubes will be fabricated, but this topic is in the hands of others. The authors in their work just showed the stability and good mechanical properties of these cementitious inorganic nanotubes. They are interested in next describing their survival in different water solutions, where myriad of reactions take place to form the cement paste.

H. Manzano, A.N. Enyashin, J.S. Dolado, A. Ayuela, J. Frenzel, G. Seifert
Advanced Materials DOI: 10.1002/adma.201103704 (2012)

Using atomistic simulations, this work indicates that cement nanotubes can exist. The chemically compatible nanotubes are constructed from the two main minerals in ordinary Portland cement pastes, namely calcium hydroxide (CH) and a calcium silicate hydrate (C-S-H) called tobermorite. These results show that such nanotubes are stable and have outstanding mechanical properties, unique characteristics that make them ideally suitable for nanoscale reinforcements of cements.
The gap generated between two opposing nanospheres of gold can change its colour when the distance between them is less than half a nanometre, according to the investigation by researchers from the DIPC and the CFM (a joint center between the CSIC-UPV/EHU), in collaboration with researchers from the Universities of Cambridge and Paris-Sud. This work enables literally “seeing” a quantum kiss between nanoparticles before touching.

To identify the tunneling regime by optical means, tour de force experiments have been combined with very advanced theories. This work, published in Nature, confirms that electrons accumulated on the gold surfaces around the illuminated gap between the two spheres can “jump” from one to the other at optical frequencies, thanks to the tunnel effect, thus reducing the accumulated charge on the surface of each of these spheres and changing the colour of the gap from red to blue, seen as a blueshifting.

When two metallic spheres with a sufficiently small separation between them are illuminated with white light, the gap between them acquires colour thanks to the interaction of the electrons on the surface of the spheres with light. The beam of light “pushes” the electrons and makes them oscillate. This charge oscillation, a plasmon, gives a red plasmonic colour to the gap. As the spheres get closer, the charge increases which strongly intensifies this red colour. When the distance between both is reduced to under 0.35 nanometres, this accumulation of charge can be seen to drop because electrons can jump across the gap by quantum tunneling, without the spheres coming into contact with each other. Just as predicted in the quantum theory developed by the research teams in Donostia and Paris, it is possible to identify this quantum electronic jump, because as the accumulated charge drains away, the red colour of the gap changes to blue; that is, a blueshifting of the colour is seen. As the spheres get closer, the colour of the gap changes to blue, seen as a blueshifting.

In order to predict the colour changes now confirmed with this experiment, the fusion of the quantum view with the classical view of the world was necessary. Modelling of so many electrons oscillating within the gold particles in response to a beam of light could not be described with existing classical theories therefore new theoretical models needed to be implemented to explain the effect.

This new result establishes a fundamental quantum limit for the minimum dimensions within which light can be trapped. Moreover, this reinterpretation of the interaction between light and matter at the sub-nanometric scale could provide new ways of describing and measuring the atomic-scale world and open doors to novel strategies for engineering even smaller optoelectric technological devices and access new limits of resolution in photochemistry.
In processes of radiation damage, as encountered in structural materials in nuclear fission or fusion plants, or in materials hosting nuclear waste, or in living tissue under radiation stress, the common culprit is an atomic (or nuclear) projectile traversing matter at high speeds, and producing damage on its passage. Depending on the velocity, many tens of thousands of host atoms can be displaced from their initial configuration in the host material. Part of the damage is by direct transfer of energy from the projectile to the host nuclei, while another part of the projectile’s energy transfers to the host electrons. The latter process is the one dominating at high projectile velocities. It is thus crucial to understand it and to be able to simulate it, if we are interested in simulating the radiation damage processes at all. And we are interested: we need to be able to propose materials for hosting nuclear waste that can withstand damage for a good fraction of a million years. Hardly amenable to direct experimentation. We need accurate predictive simulation techniques to inform that kind of engineering. While there are quite well-established first-principles techniques to describe materials for equilibrated electrons, that is not the case for “non-adiabatic processes”, that is, for processes in which the projectile moves with a velocity which is comparable or higher than that of the electrons of the host. Although there is qualitative understanding of such processes (the DIPC is a worldwide leading institution in electron stopping of projectiles in metals), the first generic method for the first-principles simulation of such processes was first proposed here in 2007, and has been now proven to be accurate and predictive.

In these two papers (appearing one week apart in Physical Review Letters) electronic excitations in a radiation damage process are accurately described from first principles. In Figure 1 the shape of electronic excitation can be seen when a swift proton moves through bulk aluminium. The rate of energy transfer from the projectile to the electrons (the electronic stopping power) as obtained in the calculations accurately reproduces what obtained experimentally for H and He projectiles in bulk gold (see Figure 2) and aluminium. The calculations use a time-dependent extension of the most standard method for electronic structure prediction, density-functional theory. Once established the predictive power of the method, it is now being applied to situations of interest for the nuclear and space industries.

Calculating the electronic stopping power from first principles

M.A. Zeb, J. Kohanoff, D. Sanchez-Portal, A. Arnau, J.I. Juaristi, and E. Artacho

A. Correa, J. Kohanoff, E. Artacho, D. Sanchez-Portal and A. Caro

The electronic response to a projectile shooting through a solid can now be quantitatively predicted.

The electronic stopping power measures the rate of energy transfer to electrons from an atom moving at high velocity through matter.
Competition between electron and phonon excitations in the scattering of nitrogen atoms and molecules off tungsten and silver metal surfaces

L. Martin-Gondre, M. Alducin, G. A. Bocani, R. Diez Muñío, J.I. Juaristi

Energy exchange in the interaction of thermal and hyperthermal molecules and atoms with metal surfaces. A model has been developed to describe phonon and electron-hole pair excitations in simulations of gas/surface dynamics.

The knowledge of the dynamics of thermal and hyperthermal molecules interacting with metal surfaces has implications in several fields of high technological interest. On the one hand, the industrial production of most of the chemical products implies the use of metallic surface as catalyst. These kinds of chemical reactions need also to be characterized and controlled to limit the erosion of the wall of fusion reactors, or the heating of the surfaces of spacecrafts in their reentry in the Earth atmosphere. For all these reasons, it is very important to be able to simulate the dynamics of gas/surface interactions and reactive processes with the greatest possible accuracy.

The state of the art of the modeling of these processes implies the simulation of the adiabatic dynamics on accurate multidimensional potential energy surfaces. However, recent experiments have shown the need to incorporate into these kinds of simulations the description of energy exchange channels such as the excitation of the movement of the atom constituents of the crystal lattice of the metal (phonons) and the electronic excitations.

This is precisely what has been achieved in this work. The model presented here has allowed, for the first time, to incorporate the above mentioned inelastic effects keeping the accuracy of the multidimensional potential energy surfaces used in the adiabatic calculations. The model has been applied to the study of two representative systems such as the interaction of nitrogen molecules with tungsten surfaces and nitrogen atoms with silver surfaces. The model has shown its validity by comparison with available experimental results and has been able to explain non-trivial effects in the relation between the rotational state and the energy loss of the reflected molecules, and the relation between the energy loss and the exit angle. This work opens new frontiers in the modeling of the elementary reactive processes in the gas/surface interactions and will allow to determine in quantitative terms the relative relevance of different nonadiabatic effects in this kind of problems.

Schematic representation of the dynamics of the interaction of a diatomic molecule with a metal surface.
The spin-orbit interaction (SOI) that causes spin splitting of electron states in inversion-asymmetric systems is expected to be efficiently exploited in spintronics. The key operating characteristic here is the magnitude of the SOI-induced spin splitting characterized by energy of split states $E_R$ and the coupling parameter $\alpha_R = 2E_R/k_R$, which measures the strength of the spin splitting. For the conventional narrow-gap semiconductor structures, the parameter $\alpha_R$ is of order of $10^{-1}$ eVxÅ. Such a small $\alpha_R$ hampers the development of spintronics devices for room-temperature applications since the latter require a significantly greater spin splitting.

Here, using ab initio calculations, we demonstrate that the 2D electron systems formed at the Te-terminated surface of bismuth tellurohalides in electron surface states (SSs), which split off from the bulk conduction band inherit the giant spin splitting and spin structure from the bulk states. These spin-split SSs provide unique quasiparticle properties of the respective 2D systems, which should be an ideal candidate for a very promising material for spintronics applications. In the figure we show the calculated surface electronic structure of the Te-terminated surface at the Brillouin zone center that demonstrates giant spin-orbit splitting.

Spintronics is aimed at controlling and manipulating the spin degrees of freedom in semiconductor devices. A promising way to achieve this goal is to make use of the tunable Bychkov-Rashba effect that relies on the spin-orbit interaction in a two-dimensional electron system immersed in an inversion-asymmetric environment. We report on a giant Rashba-type spin splitting in two-dimensional electron systems that reside at tellurium terminated surfaces of bismuth tellurohalides, in particular of BiTeCl. The giant spin splitting of the surface state band ensures a substantial spin asymmetry of the inelastic mean free path of quasiparticles with different spin orientations.
The advances of scanning probe microscopy (SPM) have significantly extended the boundaries of molecular imaging. However, even though imaging and manipulation of single atoms in inorganic materials has been routinely performed for many years, comparably high resolution on organic molecules has long remained elusive. Only recently a new benchmark for SPM has been set demonstrating its capability to directly image the chemical structures of organic molecules by tuning fork-based non-contact atomic force microscopy (nc-AFM). Functionalization of the scanning probe e.g. by individual CO molecules has facilitated superior resolution, rendering images reminiscent of wireframe chemical structures in which even differences in bond-order can be identified. In this present work we use that approach to resolve, for the first time, the structural changes and bond rearrangements associated with complex surface-supported chemical cyclization cascades, an accomplishment currently beyond any other experimental technique. We herein studied the thermally induced enediyne cyclization cascades of 1,2-bis((2-ethynylphenyl)ethynyl)benzene (1). Related precursors have previously been explored for the formation of high molecular weight poly-acenes. However, a variety of competing chemical processes has been shown to play along the traditional Bergman enediyne cyclization. As a consequence, the lack of accurate predictions of the resultant cyclized structures and the complexity of the obtained product distribution exceed the capability of traditional analytical tools to thoroughly characterize the products. We tackle this problem running the reaction under a highly controlled environment on atomically clean Ag(100) surfaces in ultra-high vacuum and by single molecule characterization. This approach has traditionally remained in the realm of scanning tunneling microscopy (STM). However, STM images represent the spatial distribution of molecular orbitals close to EF, additionally broadened and modulated by their hybridization with the electronic states of the substrate (Fig. 1). This leads to a non-trivial contrast in the images that makes the determination of unknown structures a challenging task. Instead, nc-AFM allows direct visualization of the structures of reactant and products (Fig. 1), shedding light onto the transformation reactions. Complementary ab-initio density functional theory calculations further corroborate our experimental results and increase the understanding of the particular reaction pathways.

Hence, in addition to the impact of a direct visualization of chemical reactions, by imaging the complex bond-rearrangements of 1, and complemented with DFT calculations, we provide a detailed mechanistic picture of the cyclization processes previously inaccessible by other experimental tools. In turn, this new insight will guide the design of alternative precursors for the rational synthesis of functional surface-supported molecular architectures.
Towards tunable charge carrier injection barriers at donor-acceptor/metal interfaces


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Experiments on systematically varied donor-acceptor/metal interfaces reveal shifts in the molecular levels that allow tuning charge injection barriers by adjusting the stoichiometry of the blends.

Organic semiconductor-electrode interfaces are among the key elements in charge injection devices and can be generally defined by a monolayer-thick blend of donor and acceptor molecules in contact with a metal surface. Charge injection barriers are determined by the offset from the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) of this contact layer with respect to the Fermi level of the metal electrode. However, the HOMO and LUMO alignment is not easy to elucidate in complex multi-component systems. In addition, it is not well understood how the interface energetics depend on the different supramolecular environments comparing single component layers with molecular blends. Here we demonstrate that core-level photoemission from donor-acceptor/metal interfaces can straightforwardly and transparently assess molecular level alignment. Systematic experiments in a variety of systems show a characteristic binding energy shift in core-levels as a function of molecular donor/acceptor ratio, irrespectively of the molecule or the metal.

In particular, donor levels shift to lower binding energies, whereas acceptor levels shift to higher binding energies. This is exemplified in Figure 1 for the case of pentacene (PEN, donor) and fluorinated copper-phthalocyanines (F16 CuPc, acceptor) on Au(111) surfaces. The C 1s core level spectra associated with each of the crystalline structures as a function of molecular stoichiometry are displayed in Fig. 1a, evidencing a rigid shift of all the different components. The same shift is observed in the molecular orbitals, as displayed in Fig. 1b for the respective HOMO levels, and inferred from X-ray absorption spectroscopy (NEXAFS) measurements for the LUMO levels. Interestingly, all these shifts could be reproduced with density functional theory calculations and follow a stoichiometry-dependent change in the system’s work function (Fig. 1c) in a local vacuum-level pinning scenario. The blend’s work function can be further estimated by averaging the partial-coverage of each of the molecules (Fig. 1c).

Our findings therefore demonstrate the possibility to assess interface energetics by core level photoemission, greatly facilitating the characterization of donor-acceptor blends on electrode surfaces. Furthermore, they open a route to tune critical parameters for the efficiency of devices, as are the charge injection barriers at metal-organic interfaces. The interface dipoles associated with donor and acceptor molecules can differ significantly, allowing a substantial range over which to tune the system’s work function by the blend stoichiometry in a predictable manner. With this work we therefore don’t only advance in the understanding, but also provide a handle for the control of charge injection barriers in technologically relevant donor-acceptor/metal interfaces.

The stoichiometry dependent change in the system’s work function underlies the observed molecular level shifts.
Direct evidence of two equilibration mechanisms in glassy polymers

D. Cangialosi, V.M. Boucher, A. Alegría, and J. Colmenero


Enthalpy recovery over prolonged aging times showed a complex behavior of thermodynamics and dynamics in glassy polymers. The former exhibits two free energy minima in the glassy state. The achievement of each of such minima implies the presence of two equilibration times.

Glassy materials are employed in a wide range of applications and, for this reason, have been deeply investigated along the years. Among them, glass forming polymers represent an important class and the study of their molecular dynamics and thermodynamics has been the subject of intense debate. Within this context, most studies have devoted their attention to a temperature range at which the rate of spontaneous fluctuations is shorter than several seconds. This is due to the fact that, in these conditions, equilibrated glasses can be studied over experimental time scales easily accessible in the laboratory practice.

In recent years, experiments in the so-called aging regime as a way to explore the ultraslow molecular dynamics range have been performed. In particular, either the kinetics of recovery of thermodynamic properties or the evolution of the relaxation time during physical aging were monitored on time scales considerably larger than several seconds. Several studies suggest that deviations from the behavior normally observed at relatively high temperatures exist in both the dynamics and the thermodynamics.

In our study, we follow the recovery of equilibrium of the enthalpy of several polymeric glasses previously brought out of equilibrium by cooling them from the equilibrium melt to the glassy state. This is done over prolonged time-scales extending to more than one year. We show that the evolution toward equilibrium of the enthalpy exhibits a two steps recovery. This is shown in Fig. 1 for high molecular weight polystyrene as a showcase. The first step allows partial recovery of the enthalpy, whereas full recovery occurs after the decay corresponding to the second step. This result demonstrates that the thermodynamics of glasses exhibit two free energy minima. With regard to the dynamics, Fig. 2 shows the temperature dependence of the equilibration times, that is, the time needed to reach each plateau after each step decay. The following scenario emerges analyzing their temperature dependence: i) The equilibration time corresponding to the first step recovery exhibits relatively low activation energy; ii) The equilibration time of the second decay exhibits activation energy similar to that of the polymer segmental relaxation. These results indicate a complex scenario of dynamics and thermodynamics with multiple equilibration steps.

We show that the evolution toward equilibrium of the enthalpy exhibits a two steps recovery.
Large enhancement of nonlinear optical response in a hybrid nanobiomaterial consisting of bacteriorhodopsin and cadmium telluride quantum dots

A. Rakovich, I. Nabiev, A. Sukhanova, V. Lesnyak, N. Gaponik, Y.P. Rakovich, J.F. Donegan
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The development of novel nano-bio hybrid materials that can be integrated into current technologies is one of the most important challenges facing material scientists today. The purpose of this work was to expand research studies in one largely unexplored area of nanobiotechnology: the development of nano-bio hybrid materials that exploit Förster Resonance Energy Transfer (FRET) to enhance the functionalities of technologically-promising photosynthetic biomaterials. One of very promising approaches is to employ semiconductor quantum dots having a broad absorption spectrum as nanoantennae coupled with the natural photosynthetic systems.

Recently it was shown that the nanoscale interactions between semiconductor quantum dots and protein bacteriorhodopsin in the form of Förster resonant energy transfer lead to an improvement of the biological response of bacteriorhodopsin. The reported highly efficient FRET between quantum dots and bacteriorhodopsin indicates that significant improvement of the photoelectric and photochemical properties of bacteriorhodopsin can be achieved.

Furthermore, even more attractive is the possibility to modify the photosynthetic properties of bacteriorhodopsin, which are inherently connected to the strong nonlinear properties of this protein. The unorthodox idea that FRET-based improvement of the biological response of bacteriorhodopsin in the presence of quantum dots should influence the nonlinear properties of the BR has not been looked at so far. The feasibility of this approach to develop highly nonlinear nano-bio hybrid structures operating in the FRET regime was in the focus of present work.

Results presented in this paper demonstrated that CdTe quantum dots assembled on the purple membranes containing protein bacteriorhodopsin are able to strongly (up to 4000% at 700 nm) enhance the nonlinear refractive index of bacteriorhodopsin. Using wavelength tunable z-scan technique we find that the enhancement of nonlinear refractive index was significantly smaller at higher wavelengths and only 10–25% in the region of linear absorption (500–650 nm). It is also demonstrated that the bacteriorhodopsin, being a part of an engineered hybrid material, is able to utilize the harvested energy to improve its nonlinear optical properties. Results of this study indicate that both in the linear and the nonlinear regime the quantum dots and the bacteriorhodopsin represent a highly interacting system, and as such, their hybrid material is a good candidate for utilization in device applications.
Singlet-triplet conversion and the long-range proximity effect in superconductor-ferromagnet structures with generic spin dependent fields

F.S. Bergeret and I.V. Tokatly

The long-range proximity effect in superconductor-ferromagnet (S/F) hybrid nanostructures is observed if singlet Cooper pairs from the superconductor are converted into triplet pairs which can diffuse into the ferromagnet over large distances. In this work we have shown that there are other sources of the long-range triplet component (LRTC) of the condensate and established general conditions for their occurrence.

It is now commonly known that the interaction between conventional superconductivity and ferromagnetism in S/F hybrids leads to a new type of superconducting correlations in a triplet state. Since the prediction of this intriguing phenomenon in 2001, there has been an increasing experimental activity in the field. That research focuses mainly on the creation and control of superconducting triplet correlations in hybrid structures with the ultimate goal of using polarized spin supercurrents in spintronic devices. To achieve this, it is essential to identify the optimal material combination and hence it is of fundamental interest to understand the physics that underpin triplet generation.

In the present work we have readdressed the problem of singlet-triplet conversion in diffusive S/F structures taking into account the presence of arbitrary (linear in momentum) spin-orbit coupling and go a step further. The main contribution of our work is twofold: First, we have presented a complete analogy between the diffusion of a spin density in a normal metal and the rotation of the triplet condensate in superconducting hybrids. This analogy opens a new view of the singlet-triplet conversion that helps in the understanding of the proximity effect in more complex hybrid structures and suggest the possibility of using the superconducting condensate for encoding spin information.

Second, we have presented for the first time the derivation of the quasiclassical equations for superconductivity in the presence of arbitrary type of SO-coupling. These equations are very useful not only to describe the singlet-triplet conversion but also for the study of the dynamics of S/F hybrids. With the help of these equations we have analyzed different hybrid structures (see Fig. 1) and established the condition for the singlet-triplet LRTC conversion. For example, according to our work all triplet components can be generated in a S/F/N structure (Fig. 1A), provided the conductor N exhibits a SO coupling. We also have shown that while for a transverse multilayer structure of S/F/S type, the “old” picture of magnetic inhomogeneities can explain the long-range Josephson conversion (Fig. 1C and D), in lateral S/F structures (Fig. 1B), the SO mechanism may be consider as the main mechanism for singlet-triplet conversion. For further reading we also refer to our most recent work: “Spin-orbit coupling as a source of long-range triplet proximity effect in superconductor-ferromagnet hybrid structures”, Physical Review B 89, 134517 (2014).

Our work gives a global description of the singlet-triplet conversion in hybrids structures in terms of generic spin-fields and the results are particularly important for the understanding of the physics underlying spintronic devices with superconductors.

Fig. 1: Different S/F setups for creation of triplet superconducting components: (A) A S/F/N SO structure, with a normal wire with intrinsic Rashba SO coupling (N SO); (B) a lateral S/F structure consisting of a thin ferromagnetic layer F1, a superconductor electrode and a second ferromagnetic layer, F2 between the S and the F1. (C) and (D) sketched of a transversal multilayer structure commonly used in experiments.

Fig. 2: Schematic view of the spin rotation in a system with 1D inhomogeneity. At $x = 0$, a spin parallel to the $z$-axis is injected. Due to the spin-orbit coupling also the $S_y$ component becomes finite upon diffusion. Panel (A) illustrates the spin rotation due to anisotropy of the Dyakonov-Perel tensor. (B) shows the spin rotation due to a fully isotropic spin-orbit coupling. By using our analogy the vectors can also represent the components of the triplet superconducting correlations upon diffusion into a normal region.
Chemical mapping of a single molecule by plasmon-enhanced Raman scattering


Nature 598, 82-86 (2013)

An international team led by Chinese researchers in Hefei (China) with the participation of the Donostia International Physics Center (DIPC) and the Center of Materials Physics (CSIC-University of the Basque Country [UPV/EHU]), has resolved and chemically identified, with a hitherto unprecedented resolution, a single organic molecule using light. This research opens doors to possible technological applications in microscopy, biosensing or quantum information technologies.

Research work led by researchers at the University of Science and Technology of China, in Hefei, in collaboration with the “Theory of Nanophotonics group” at DIPC, have managed to resolve and identify for the first time a single organic molecule with subnanometric-range resolution, using light.

Visible light is an electromagnetic wave whose wavelength is between 400 nanometres (nm), (blue) and 750 nm (red). Due to what is known as the resolution diffraction limit, using light, it is impossible to directly resolve or photograph objects with a size less than half of the wavelength of the light, i.e. less than 200 nm. In order to overcome this limitation, over recent years specialists in Nanophotonics have used metal particles that act as minute optical antennae, concentrating and enhancing the visible light spectrum on a nanometric scale. However, even this technique has its limitations and difficulties when trying to resolve nanometric objects. The optical resolution achieved in this research, hitherto never obtained, has been possible thanks to the combined use of the scanning tunneling microscope (STM) technique in ultra-high vacuum and low temperature conditions, with the Tip-enhanced Raman spectroscopy (TERS) technique, which dramatically enhances the field that acts on the molecule located in the cavity of the tip of the microscope. The combination of these two techniques has enabled ‘photographing’ organic molecules for the first time at a subnanometric scale. The tuning of the collective oscillation of conduction electrons at the tip of the microscope, the so-called plasmons, with the vibrational excitation of the molecule, enables generating a non linear optical signal with sub-nanometric resolution.

When the microscope tip is scanned over the molecule, the Raman signal emitted at each point enables identifying the vibrational signature of the molecule in such a way that, apart from looking “inside” the molecule, it is simultaneously possible to identify which molecule is involved. Researchers at DIPC explain that “it is like peering ‘inside’ the molecule and taking its fingerprints”. This level of resolution has only been possible to date using electrons as the probes, but in this research it is the photons of visible light that manage to achieve the miracle of identifying a molecule, going beyond all limits of optical diffraction until now known.

The results of this work open the doors to the direct identification of molecules when their concentration is very small, managing to identify even a single isolated molecule. This ability gives rise to a wide range of possible technological applications, such as in biosensor ones for the analysis of molecular chains, in health and safety for detecting dangerous substances, and in public health for the control of food quality, amongst others. Additionally, accessing to single molecule fingerprints enables the possibility to manipulate and control quantum states of use in quantum information technologies.
The potential for light to exert a force along its direction of propagation - a phenomenon known as radiation pressure - is well understood and widely documented. The first indication of this phenomenon came when scientists observed that the tail of a comet always points away from the Sun, regardless of its direction of motion. In the early 1600s, Kepler guessed that the shift of a comet’s tail was driven by the pressure of sunlight, and this conjecture still holds true for comet tails that consist primarily of dust. Kepler’s belief that the pressure of light is responsible for the solar repulsion of finely divided matter contained in the tail of a comet was accepted and used as an argument for the corpuscular theory by Newton, following which scientists pursued a range of experiments to test the concept of light pressure. On the basis of the newly developed theory of electromagnetism, Maxwell showed that momentum transfer from the electromagnetic field to an object, due to absorption or reflection, should result in a radiation pressure in the propagation direction of the electromagnetic waves.

The idea of attracting objects using only the mechanical forces of light is much less trivial. Over the years, scientists have proposed a number of schemes based on employing properties of the electromagnetic field, the surrounding environment, or the particles themselves. These efforts are all fascinating because of their mind-boggling outcome: a seemingly abnormal force that points against the flow of light. In this work we review the main approaches to solving this counterintuitive task and highlight the subtle differences between these endeavours.

The mechanical action of light depends on the structure of the incident electromagnetic fields, the properties of the objects and their surrounding environment.

Optically induced ‘negative forces’

A. Dogariu, S. Sukhov and J.J. Sáenz
Nature Photonics 7, 24-27 (2013)

The idea of using optical beams to attract objects has long been a dream of scientists and the public alike. Over the years, a number of proposals have attempted to bring this concept to life. In this work we review the most recent progress in this emerging field, including new concepts for manipulating small objects using optically induced ‘negative forces’, achieved by tailoring the properties of the electromagnetic field, the environment or the particles themselves.

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The mechanical action of light depends on the structure of the incident electromagnetic fields, the properties of the objects and their surrounding environment.
Quantum chemical study of the reactions between Pd$^+/\text{Pt}^+$ and H$_2$O/H$_2$S

O. Lakuntza, J.M. Matxain, F. Ruipérez, J.M. Ugalde and P.B. Armentrout
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Although a great deal has been elucidated regarding the mechanism of the reactions between first-row transition-metal cations with water and hydrogen sulfide, much less is known about the reactions of second- and third-row transition-metal cations and of heavier elements as well. Recall that for reactions involving these elements, relativistic effects may play a significant role. Indeed, relativistic effects dominate the chemistry of metal cations with atomic numbers greater than about 50, and the differences in the chemistry of the second- and third-row cations can be largely explained considering the lanthanide contraction. Consequently, it is expected that in the group of nickel, not only for platinum, but also for palladium, the relativistic effects should play an important role in the reactions of these metals or their cations with small molecules. This makes the mechanistic studies of the above mentioned important reactions very challenging, and only affordable at a realistic level by the highest level of theory methods. We have carried out the elucidation of the mechanisms of the reactions between Pd$^+/\text{Pt}^+$ with H$_2$O and H$_2$S at such high level of theory.

We propose that the reactions of palladium and platinum cations with water and hydrogen sulfide proceed by the successive migrations of the two hydrogen atoms over the metal center, at which a H-H bond develops to form a complex between the hydrogen molecule and the metal sulfide or metal oxide cation. From these intermediates the loss of H$_2$ proceeds without a transition state to the corresponding products. Although the energetic parameters depend on the reaction studied, we have found that, whereas both reactions of the palladium occur with two transition states, in the reactions of platinum a third transition state is needed to obtain the final products. In these cases, the second transition state leads to the formation of a dithydrodikubas-like complex, namely XPt(H)H$^+$ (X = O, S) and, through TS3, both hydrogen atoms approach each other, forming the H-H bond.

For all the reactions studied, we have found that one crossing between the doublet and quartet states potential energy surfaces occurs. This spin-crossing takes place around the last transition state, yielding a H$_2$MX$^+$ intermediate with a quartet ground state.

We have found that the ground state of the HMXH$^+$ intermediate of the four reactions is the doublet spin state, and that the quartet state lies between 1.30 and 1.90 eV above. The study of the molecular orbitals of their corresponding main valence electronic configurations reveals that, in contrast with the HNOH$^+$ but along with HNISH$^+$, they have their doublet and quartet spin states connected by a single electron flip. Furthermore, we have found that, except for the HIPSH$^+$, the energy barrier associated with the HMXH$^+/\text{MXH}^2+$ isomerization is large enough that the HMXH$^+$ should have a long enough lifetime to react with other small molecules like methane.

Our calculations predict that only the formation of platinum sulfide is exothermic in both spin states.