Global method for electron correlation

M. Pirc

This work presents a new single-reference method for capturing static and dynamic electron correlation. The reference is a determinant wavefunction formed with natural orbitals capable of recovering the static correlation. The dynamic correlation is calculated using a modified MP2 theory. Double counting is avoided by introducing the amount of correlation in each orbital as a function of its occupation. The values obtained are in very good agreement with experimental data.

In electronic structure theory, accurate solutions require a balanced treatment of both static and dynamic correlation. Nowadays, it is necessary to resort to multi-reference methods for correctly handling both types of correlation; however, these techniques are often expensive and demand prior knowledge of the system. On the other hand, single-reference correlation methods are well-established for dynamic correlation, but are unsatisfactory for systems with static correlation. In this article, a single-reference method is proposed capable of achieving both dynamic and static correlation even for those difficult cases in which both types of correlation are equally present.

The starting point is a determinant wavefunction formed with natural orbitals (NOs) obtained from a new interacting-pair model. The latter leads to a natural orbital functional (NOF) named PNOF capable of recovering the complete intra-pair, but only the static inter-pair correlation. Using the solution of the NOF, two new energy functionals are defined for both dynamic (\(E_{\text{dyn}}\)) and static (\(E_{\text{stat}}\)) correlation. \(E_{\text{dyn}}\) is derived from a modified second-order Møller-Plesset perturbation theory (MP2), while \(E_{\text{stat}}\) is obtained from the static component of the PNOF. Double counting is avoided by introducing the amount of static and dynamic correlation in each orbital as a function of its occupation. The total energy is represented by the sum \(E_{\text{tot}} = E_{\text{stat}} + E_{\text{dyn}}\), where \(E_{\text{stat}}\) is the Hartree-Fock energy obtained with natural orbitals. The resulting working formulas allow for static and dynamic correlation to be achieved in one shot, as is the case in the standard single-reference perturbation theory.

The new procedure called NOF-MP2 is extraordinarily simple and size-consistent, which is essential for applying it to extended systems. It is applied successfully to homolytic dissociation of a selected set of diatomic molecules that encompass very dissimilar interactions ranging from weak to strong bonds, thus sweeping a wide range of correlation regimes. The NOF-MP2 method is not limited to PNOF7 NOs; it can also be used with NOs obtained from other approximation able of recovering static correlation. With efficient approaches, based on recent developments of NOF and MP2 theories, NOF-MP2 could become a valuable tool for treating large systems with hundreds of atoms.

Single-reference correlation methods are well-established for dynamic correlation, but are unsatisfactory for systems with static correlation.
Riboflavin as a bioorthogonal photocatalyst for the activation of a Pt-IV prodrug

Chemical Science 8, 4619 (2017)

The combination of catalysis and bioorthogonality promises to have an impact on drug discovery and bioimaging. Bioorthogonality, a term coined by Carolyn R. Bertozzi in 2003, refers to any chemical reaction that can occur inside of living systems without interfering with native biochemical processes. Catalytic turnover can boost the efficiency of bioorthogonal chemical reactions, unveiling new strategies for prodrug activation and uncaging of molecular probes.

This work describes an original photocatalysis approach to control the reactivity of transition metal complexes in a bioorthogonal fashion. In a new type of light-driven reaction, the exogenous biological molecule riboflavin (R) functions as a bioorthogonal photocatalyst and a metal complex as unconventional substrate (Figure 1).

Metal complexes are typically regarded as catalysts that convert organic substrates into more valuable compounds; however, to date, catalytic transformations of metal complexes are practically unknown and represent a complete new way of thinking in catalysis. Their development can expand the scope of bioorthogonal chemical reactions to inorganic substances and metal-based prodrugs, fostering the creation of new inorganic chemistry tools for biology and medicine.

The photoredox features of riboflavin are crucial in this new type of catalytic process. In fact, riboflavin selectively catalyzes the photoreduction of the PtIV cisplatin prodrug cis,cis-[Pt(NH3)2Cl2]2+CCl2CH2CH2CO2H in biological environments such as in cell culture media, where numerous chemical and biological species are present and could potentially interfere adversely. Photocatalysis takes place using 460-nm light, a wavelength that is ineffective when directly applied to the PtIV prodrug.

The unusual catalyst/substrate pair enables the selective activation of the PtIV prodrug with exceptionally low doses of blue light, and induce apoptotic death in PC-3 human prostate cancer cells (Figure 2).

In principle, photocatalysis can help expand the therapeutic potential of platinum prodrugs. Efficient light activation of PtIV complexes through catalysis may help localize the cytotoxic effects of Pt drugs, increase their dosing at the tumour target, and reduce their systemic toxicity. Riboflavin (vitamin B2) is a highly bio-compatible molecule, and its capacity to function in a bioorthogonal fashion may serve to enhance the selectivity of metal-based drugs by minimizing side reactions.

Catalytic transformations of metal complexes are practically unknown and represent a complete new way of thinking in catalysis.
Width-dependent band gap in armchair graphene nanoribbons reveals Fermi level pinning on Au(111)


ACS Nano 22, 11661 (2017)

Combining local tunneling spectroscopy and ab initio electronic structure calculations, we have investigated the energy level alignment evolution of valence and conduction bands of armchair-oriented graphene nanoribbons (aGNRs) on Au(111) as their band gap shrinks with increasing width. Interestingly, valence bands are found to show Fermi level pinning as the band gap decreases below a threshold value, which is of critical importance to understand the properties of potential contacts in GNR-based devices.

Graphene nanoribbons (GNRs) have long been proposed as extremely interesting materials for a variety of applications, e.g., field effect transistors. Interestingly, it has been found that the device performance is strongly dominated by contact effects, in particular, by the Schottky barrier at the GNR-contact interface. However, despite its key role in the ultimate response of such GNR-based devices, a systematic study of the energy level alignment between GNRs and common contact materials is still missing.

In this work, we amend our understanding of such interface energetics between GNRs and gold, in particular, Au(111) surfaces. Armchair-oriented nanoribbons (aGNRs), which are known to display a width-dependent band gap, can be classified into three different subfamilies depending on the number of dimer lines \( p \) across their width (3p, 3p+1, or 3p+2), their band gaps being inversely proportional to the width within each of those families. We report a systematic study of the band gap and energy level alignment of GNRs focused on the 3p family, addressing from the smallest possible GNR (3–aGNR) to its four immediately following sister structures (6–, 9–, 12–, and 15–aGNRs). Starting from the synthesis of poly-para-phenylene wires (PPP or 3–aGNR) on Au(111), subsequent annealing drives their lateral fusion and results in the required atomically precise GNRs of varying width. The characterization by scanning tunneling spectroscopy (STS) and density functional theory (DFT) calculations reveals, in addition to the width-dependent band gap, the onset of Fermi level pinning for widths \( \geq 6 \) dimer lines.

In conclusion, we provide spectroscopic evidence of the width dependent band gap predicted for armchair graphene nanoribbons a decade ago and the associated energy level alignment. Most importantly, Fermi level pinning of the valence band is found on wide aGNRs, in qualitative agreement with DFT calculations. Our findings have important implications on the energy level alignment across GNR-metal interfaces, which may in turn be crucial for future GNR-based devices displaying similar interfaces at charge collection electrodes.

Valence bands of armchair-oriented graphene nanoribbons on Au(111) are found to show Fermi level pinning as the band gap decreases below a threshold value.
Catalysis of a 1,3-dipolar reaction by distorted DNA incorporating a heterobimetallic platinum(II) and copper(II) complex

Chemical Science & 7038 (2017)

We all know that the main role of DNA is the storage of genomic information leading to the biosynthesis of proteins via diverse forms of RNA. In turn, proteins play multiple roles in living systems, catalysis being among the most important ones. But recent discoveries add more to the complexity of these molecules: they are also catalysts. Catalytic RNAs are called ribozymes and DNAs, deoxyribozymes.

This work focuses on the latter.

Because DNA is structurally less versatile than RNA and proteins, additional molecules and functional groups are required to expand the catalytic space of DNA. The feasibility of this concept by intercalation of azo-chalcones in the double helix and subsequent coordination to copper salts was brilliantly demonstrated by Roelofs and Feringa in 2005.

Despite the relevance of (3 + 2) cycloaditions in the chemical synthesis of five-membered rings, the enzymatic version of this reaction has not been identified in living systems. Only a very recent example of a possible enzymatic 1,3-dipolar reaction has been reported to date. In addition, nonenzymatic 1,3-dipolar reactions have been postulated in the biosynthesis of several alkaloids and natural products.

Now, a team of researchers from UPV/EHU and DIPC, has described the first example of a DNA-assisted 1,3-dipolar reaction in water. It is a biomolecule-assisted (3 + 2) cycloaddition between azomethine ylides and alkenes to produce unnatural proline derivatives. The design of the covalent modification of DNA was based on the ability of Pt(II) chemotherapeutic drugs to bind mainly 1,2-intrastrand GpG units, i.e., regions of DNA where a guanine nucleotide is followed by another guanine nucleotide (GpG is short hand for guanine-phosphate-guanine), thus providing a concave-convex distortion of the double helix that could mimic the active sites of metalloenzymes. In a previous work the researchers had reported that new chiral ligands can bind Cu(II) salts and efficiently catalyze (3 + 2) cycloadditions involving azomethine ylides. They reasoned that a DNA–Pt(II)–Cu(II) heterobimetallic complex similar to that depicted in Figure 1 could catalyze this reaction. Something that was feasible according to computational modeling calculations.

The results indicate that a suitable bimetallic complex based on Pt(II) can distort the double helix of DNA to generate an active site similar to those found in well-known metalloenzymes. The proposed reaction mechanism, based on quantum mechanical calculations, is compatible with thermally allowed mechanisms leading to the exclusive formation of racemic enediyne cycloadducts.

This work demonstrates that modified biomolecules can catalyse chemical reactions in water, for which there is no equivalent in living systems.

A suitable bimetallic complex based on Pt(II) can distort the double helix of DNA to generate an active site similar to those found in well-known metalloenzymes.

Figure 1. Basic design of DNA-based catalysts for 1,3-dipolar reactions: The distortion of DNA by coordination of G bases with Pt(II) is shown.

Figure 2. (a) Fully optimized structure of a DNA double strand containing the 5′(CTGGTGGC)3′ and 3′(GGAGACCGAGC)3′ sequence. (b) The same optimized structure but showing the solvent Pt(II) and Cu(II) atoms are represented in light blue and green, respectively. Accessible surface of the DNA fragment.
Theoretical insights into unexpected molecular core level shifts: chemical and surface effects

A. Sarasola, M. Abadía, C. Rogero, and A. García-Lekue

A set of ab initio tools are employed to elucidate the influence of chemical and surface-induced changes on the core level shifts of X-ray photoelectron spectroscopy experiments. We address surface induced effects, such as splitting of the lowest unoccupied molecular orbital or local electrostatic effects, demonstrating that these cannot account for the unexpected huge core level shifts often measured experimentally. Our calculations also demonstrate that molecular hydrogenation is an alternative explanation for the appearance of such extra peaks in the XPS spectra. More importantly, it is anticipated that this hydrogenation reaction will occur in many UHV experiments where the molecular evaporation is performed at low temperatures.

Advances in scientific knowledge and technological tools achieved over the last decades, have been aimed at the development of biospired nanodevices. Covering an inorganic substrate with organic matter is an appropriate and viable architecture for such devices. The X-ray Photoelectron Spectroscopy (XPS) technique and, in particular, the measurement of the shifts in the binding energy of different core levels, make it possible to verify the chemical integrity of a molecule, to identify changes in its composition and to sense the changes in the local electrostatic environment. However, disentangling the collective electrostatic effects from the chemical shifts is not straightforward and it results crucial for a correct interpretation of experimental XPS spectra.

A team of researchers from DIPC and CFM has carried out the first exhaustive theoretical study of the origin of unexpected signals in the XPS spectra of molecule-substrate complexes. Using a set of density-functional theory (DFT) based tools, they have determined the distinct influence that chemical changes or surface-induced effects might have on the molecular core level shifts of phthalocyanine molecules deposited on Cu(111). As shown in Figure, the N1s spectra recorded with the substrate at 25K reveal an unexpected double peak structure, which is not observed when the molecules are deposited on the substrate at RT. Besides, it has been demonstrated that such extra peaks in XPS spectra are likely to be originated by the hydrogenation of the molecules due to the capture of residual hydrogen (Figure 2). Calculations, therefore, exclude LUMO splitting, surface effects and molecular demetallation as possible origins of the double peak detected in the low coverage and low temperature N1s core level spectra.

To conclude, the findings reported here might clarify a few of the uncertainties in the measured electronic properties of organic molecules on surfaces, which represents an important advancement towards the ability to tune the functionalities of molecular complexes and delivers important input for the development of nanoelectronic devices based on organic molecules.

Figure 1. Experimental N 1s XPS spectra for 1 ML of ZnPc (left) and FePc (right) deposited on Cu(111) at the substrate at RT and at 25K (L7).

A team of researchers from DIPC and CFM has carried out the first exhaustive theoretical study of the origin of unexpected signals in the XPS spectra of molecule-substrate complexes.

Figure 2. Calculated N 1s core level spectra for the optimized configurations of ZnPc and H2ZnPc deposited on Cu(111).
The role of the topological constraints in the chain dynamics in all-polymer nanocomposites

Macromolecules 50, 1719-1731 (2017)

The specific architecture of the soft nanoparticles in all-polymer nanocomposites plays a key role on the entanglements experienced by the linear matrix, which are at the origin of the viscoelastic properties of the system.

In a long-lasting effort to get a good compatibility between the nanoparticles and the linear polymer matrix, all-polymer nanocomposites are gaining increasing attention. The presence of soft penetrable polymer nanoparticles in such systems is expected to affect the fundamental topological constraints (entanglements) that originate from chain uncrossability and that control the viscoelastic properties of the system. In this pioneering computational study of all-polymer nanocomposites, we shed light on this question by discussing simulations in the framework of the tube model.

We investigate all-polymer nanocomposites, formed by strongly entangled linear chains and single-chain polymer nanoparticles (SCNPs), by means of large-scale simulations. SCNPs are soft nano-objects obtained through intramolecular cross-linking of linear chains, with potential applications as nanocarriers, catalytic or rheological agents, among others. To distinguish the role of the soft penetrable character of the SCNPs in the topological constraints from other specific contributions present in experiments, the simulations are performed at constant density and with identical segmental mobility and monomer excluded volume for the SCNPs and the linear chains. Every composition leads to a well-dispersed nanocomposite with fully penetrated nanofillers. Hence, unlike in the case of composites with hard nanofillers, the SCNPs do not exert confinement effects on the linear chains and only contribute to the topological constraints.

We determine the entanglement length of the linear chains by analyzing their tube paths as a function of the concentration and topology of the single-chain polymer nanoparticles. We determine the entanglement length of the linear chains by analyzing their tube paths as a function of the concentration and topology of the single-chain polymer nanoparticles.
Topological quantum chemistry

Nature 547, 298 (2017)

In this work we propose a complete electronic band theory, which builds on the conventional band theory of electrons, highlighting the link between the topology and local chemical bonding. This theory of topological quantum chemistry provides a way to classify the possible band structures that arise from local atomic orbitals, and to show which are topologically non-trivial. Our electronic band theory sheds new light on known topological insulators, and can be used to predict many more.

Topological materials, which hold promise for a wide range of technological applications due to their exotic electronic properties, have attracted a great deal of theoretical and experimental interest over the past decade, culminating in the 2016 Nobel Prize in Physics. The materials’ electronic properties include the ability of current to flow without resistance and to respond in unconventional ways to electric and magnetic fields.

Until now, however, the discovery of new topological materials occurred mainly by trial and error. This new approach allows researchers to identify a large series of potential new topological insulators, based on band theory. In this work the researchers first compiled all the possible ways energy bands in a solid can be connected throughout the Brillouin zone to obtain all realizable band structures in all non-magnetic space groups. Group theory itself places constraints – “compatibility relations” – on how this can be done. Each solution to these compatibility relations gives groups of bands with different connectivities, corresponding to different physically-realizable phases of matter (trivial or topological). The scientists solve all compatibility relations for all 230 space groups by mapping connectivity in band theory to the graph-theoretic problem of constructing multipartite graphs. Then the researchers developed the tools to compute how the real-space orbitals in a material determine the symmetry character of the electronic bands. Given only the Wyckoff positions and the orbital symmetry of all the elements/orbitals in a material, they derive the notion of band representation (all bands linked to localized orbitals respecting the crystal symmetry), to the physically relevant case of materials with spin-orbit coupling and/or time-reversal symmetry, and identify a set of elementary band representations (EBR). These elementary band representations allow to easily identify semimetals and topological materials. If the number of electrons is a factor of the number of connected bands forming an elementary band representation, then the system is a symmetry-enforced semimetal. If, however, the number of connected bands is smaller than the total number of bands in the elementary band representation, then the disconnected bands are topological. Thus, the researchers have provided a full classification of all topological crystalline insulators. And they show how powerful the method is by predicting hundreds of new topological insulators and semimetals.
Angular momentum induced delays in solid state photoemission enhanced by intra-atomic interactions

Science 357, 1274 (2017)

Even more than 100 years after Einstein’s explanation of photoemission the process of electron emission from a solid material upon illumination with light still poses challenging surprises. Here, ultrashort pulses of light were employed to start a race between electrons photoemitted from different initial states in a solid. Timing this race reveals an unexpected result: The fastest electrons arrive in last place.

The explanation of the photoelectric effect was the major work cited in the award to Albert Einstein of the Nobel Prize in Physics in 1921. After more than a century of theoretical, experimental, and commercial development, we could assume that we knew everything there was to be known about the photoelectric effect. Not so. In a combined experimental and theoretical effort, researchers from different German institutions, LUP/PHU, CFM, and DIPC showed in this work that the process is not correctly captured in common models of solid-state photoemission. Based on attosecond time-resolved photoemission spectroscopy, the authors show that the motion of a photoemitted electron is strongly affected by interactions inside the atom from which the electron is emitted. Electrons photoemitted from a surface remain trapped for a while, dynamically confined by the centrifugal barrier around the atoms. The motion of these electrons around the nucleus, before being eventually emitted, is kind of a dance leading to an intuitive picture that the electrons that remain longer dancing around the atom lose the race and are emitted last. In contrast, electrons going straight win the race.

Experimentally resolving the tiny delays in the photoemission process required timing the emission event, i.e. the moment when the electron leaves the material, with an unprecedented resolution of 10−12 seconds. The choice of tungsten diiodide (WSe2) as material turned out to be essential. WSe2 yields a photoemission spectrum dominated by four emission channels with different electronic initial-state characteristics. According to standard models, all these electrons should be emitted at once, but that is not what is observed there are relative emission delays.

Quantitative theoretical modelling of the intra-atomic processes and the electron propagation in the semiconductor crystal demonstrated that the initial orbiting motion shall not be neglected if the dynamics of the photoemission process from a solid is considered. The researchers reached the conclusion that the delays between the four photoemission channels can only be explained by accounting for both propagation and intra-atomic delays. The intra-atomic delays depend on the angular momentum of the initial localized state and are determined by intra-atomic interactions. Once intra-atomic electron-electron interaction and angular momentum of the initial localized state are incorporated into the model for WSe2, there is a remarkable agreement between theory and experiment.

The reported advances in understanding photoemission from solids became feasible based on recently developed attosecond laser techniques. Control of light with attosecond (10−15 second) resolution opens fascinating views on electron dynamics on the atomic scale.

Attosecond-scale processes are strong tests for theoretical models of solid-state photoemission.

Left: An artist’s rendition of the intra-atomic mechanism for which the photoemission of some electrons is relatively delayed. They remain trapped for a while, dynamically confined by the centrifugal barrier around the atom. The motion of these electrons around the nucleus, before being eventually emitted, is kind of a dance.

Right: 2D material tungsten diiodide (WSe2) was used for the timing experiment. The figure shows the kinetic energy distribution of photoelectrons emitted from WSe2 for four different delay times.
Controlled spin switching in a metalloocene molecular junction

M. Ormaza, P. Abufager, B. Verhac, N. Bachelier, M.-L. Bocquet, N. Lorente, and L. Limot
Nature Communications 8, 1974 (2017)

In this work we change the effective spin of a single molecule by modifying the molecule/metal interface in a controlled way using a low-temperature scanning tunneling microscope: A nickelocene molecule reversibly switches from a spin 1 to 1/2 when varying the electrode–electrode distance from tunnel to contact regime. This switching is experimentally evidenced by inelastic and elastic spin-flip mechanisms observed in reproducible conductance measurements and understood using first principle calculations. Our work demonstrates the active control over the spin state of single molecule devices through interface manipulation.

Nickelocene molecules consist of two carbon pentagon rings (cyclopentadienyl) sandwiching a nickel atom. Nickel contains 8 electrons placed in d-electrons. The molecule has a spin of 1 corresponding to two unpaired electrons in the d-shell of the Nickel atom. This is clearly seen in scanning tunneling microscope (STM) measurements where the differential conductance is recorded. The differential conductance is proportional to the number of possible "paths" a transmitting electron undertakes between substrate and tip. If the electron can yield part of its energy to other degrees of freedom of the system, new paths open and the conductance increases. This is the case for the present molecule, when the applied voltage is larger than ~5 mV. This bias corresponds to the energy of turning the molecule spin (S=1) by 90 degrees, and it is due to the intrinsic magnetic anisotropy of the molecule. The measured differential conductance reflects a large change in conductance at this threshold. Everything is consistent with what we know from the molecule and STM studies.

However, when the free electrode of the STM (the tip) is pressed against the molecule, the steps abruptly disappear and a peak at zero bias appears. Figure 1 shows the conductance in this contact regime (a), compared to the previous tunneling regime (b). Two shocking experimental facts: a zero bias peak appears of nowhere and the change is extremely abrupt, it is sufficient to move the tip by 0.1 Ångstrom to see this change. Calculations using DFT with two electrodes pressing a Nickelocene molecule (Figure 2) show that there is a change in the spin of the molecule. When the electrodes are pressing, the spin is 1/2. Then the peak at zero bias would be consistent with a Kondo peak caused by the random flipping of the molecular spin under interaction with electrons from the electrode. And the calculations show that the change in spin is very fast.

Moreover, our calculation tells us the mechanism. As the electrodes close on the molecule, the environmental electronic density is very much enhanced. As a consequence, the direct Coulomb repulsion between the two electrons in the molecules gets screened by the electrodes. Less repulsion leads to a larger population of the d-shell. Basically, the nickle atom gets one more electron reducing its spin by Hund’s rule.

We can reversibly switch the spin of a nickelocene molecule from 1 to 1/2 by varying the electrode–electrode distance from tunnel to contact regime.

Figure 1. Differential conductance obtained for a Nickelocene molecule when the two electrodes are pressing the molecule (a) and when they are in the tunneling regime (b). There is a clear change of conductance features signaling a change in the spin of the molecule from 1/2 at contact to 1 in the tunneling regime.

Figure 2. Atomic schemes for the systems computed using density functional theory. (a) is the setup depicting the molecule (Nickelocene, green is the Ni atom; grey the C atoms and white the H atoms, the two cyclopentadienyls are pentagonal rings) and the copper substrate and the tip. The experiments clearly show a poorly coordinated molecule with the tip; then we use a Cu adorbate to induce a lower coordination with the molecule. The substrate is just a flat Cu (100) surface. (c), (d) and (e) show the changes in molecular arrangement as the electrodes are pressed together.
Extracting chemical information from surface-enhanced Raman spectroscopy

Nature Communications 8, 14891 (2017)

Plasmonic resonances can strongly enhance the strength of the Raman signal emitted by molecules, a considerable advantage for applications that aim at detecting ultra-small quantities. At the same time, however, the plasmon can also distort the signal and thus hide some of the chemical information. This work studies how the photoluminescence signal can be exploited to recover this information.

A main objective in molecular sensing is to extract as much chemical information from as few molecules as possible, not only to identify them but also to learn about their local temperature, orientation, changes on chemical properties, etcetera. In Raman spectroscopy, the information is extracted from the exchange of energy between incoming photons and molecular vibrations. In this way, the vibrational modes can be identified as molecular fingerprints, with all the very rich chemical information that they reveal.

The main drawback of this Raman process is its weak efficiency, which requires significant amounts of molecules to provide a measurable signal. Fortunately, this obstacle can be overcome by using metallic nanoantennas, which interact very efficiently with nearby molecules due the presence of optical plasmonic resonances that strongly confine the optical energy in their proximity. The resulting technique is called Surface Enhanced Raman Spectroscopy (SERS) and allows for identifying single molecules.

While SERS has been extraordinarily successful, it does introduce some significant challenges. Notably, each molecular vibration is manifested as a narrow peak in the Raman spectra, and the relative height of these peaks contain significant information. SERS, however, enhances the vibrational peaks with different scalings, which usually does not hinder the identification of the molecules but can lead to extracting misleading information, such as a completely wrong temperature of the molecules.

The main result of the work is to propose a method to recover the real vibrational information compromised in the spectra by focusing on the analysis of the background of the signal emitted by the plasmonic particle. This background is typically ignored; however, by analyzing its physical origin as a photoluminescence process from the metal, and by comparing the theoretical expectation with the careful measurements by collaborators in Xiamen, it is shown that the emission spectral shape contains the necessary information to rescale and largely retrieve the original Raman spectra. This technique should thus represent a significant step towards recovering chemical information in a reliable manner with down to single-molecule sensitivity.

We propose a method to recover the real vibrational information compromised in the spectra by focusing on the analysis of the background of the signal emitted by the plasmonic particle.
Electronic stopping of slow protons in transition and rare earth metals: breakdown of the free electron gas concept


The electronic stopping cross sections (SCS) of Ta and Gd for slow protons have been investigated experimentally. The data are compared to the results for Pt and Au to learn how electronic stopping in transition and rare earth metals correlates with features of the electronic band structures. The extraordinarily high SCS observed for protons in Ta and Gd cannot be understood in terms of a free electron gas model. By calculating the electronic density of states, it was shown that the measured high SCS for Gd and Ta are linked to the high density of unoccupied electronic states above the Fermi level in these metals.

When ions propagate in matter, they are decelerated due to interaction with both nuclei and electrons or in other words, by nuclear and electronic stopping power, respectively. For ion velocities lower than the Fermi velocity of the metal electrons, the electronic energy loss is predominantly due to interaction with valence electrons. For many different kind of metallic targets, it has been shown that the free electron gas (FEG) model represents an adequate approximation to obtain the electronic stopping power in this velocity regime, provided the potential induced by the projectile is calculated within density functional theory.

In the present work, experimental measurements of the energy loss of protons traveling at low velocities through Gd, Ta, Pt, and Au targets were presented. It was observed that the electronic SCS of both Gd and Ta are considerably higher than that of Pt and Au. Actually, whereas the FEG model explains successfully the stopping powers of Pt and Au in terms of their valence electron densities, it fails badly for Gd and Ta. In fact, it will require to assume absurdly high valence electronic densities to fit the experimental results to those provided by the FEG for these two metals.

By calculating the electronic density of states (DOS) it was shown that the main difference is that, in contrast to Au and Pt, both Gd and Ta present a very high DOS for unoccupied states close to the Fermi energy (EF). As a consequence, the large measured SCS for protons in these metals was linked to the high DOS below and above EF, that allows for low energy excitations with high probabilities. For this reason, it was concluded that the FEG model for the electronic stopping power of slow ions is expected to fail for transition and rare earth metals featuring a high DOS below and above EF. An adequate description of the problem in these cases will require elaborated many-body theoretical models like, for instance, time dependent density functional theory.

The extraordinarily high stopping cross sections observed for protons in Ta and Gd cannot be understood in terms of a free electron gas model.
Tautomerization of an organic adsorbate driven by non-adiabatic and anharmonic effects

D. Novko, M. Blanco-Rey, and J.C. Tremblay

This letter proposes a model for chemical reactions driven by electrons injected by a STM tip. The variables are mapped onto a one-dimensional problem, accounting effectively for the inelastically scattered electron current (non-adiabaticity) and for the couplings between molecule vibrations (anharmonicity).

Indirect adsorbate transformation by hot electrons has gained prominence as a tool to control the reactivity of species in the condensed phase. In this context, tautomerization of organic molecules, i.e. intramolecular relocation of a light atom, is attractive. Since large changes in reactivity and photochemical properties are associated to tautomerization, much effort is devoted to harnessing its potential in molecular switches. Modern surface science techniques are useful for this purpose, as they allow reaction control at the single-molecule level by means of femtosecond lasers and scanning tunneling microscopy (STM).

Recently, the Kumagai group (Berlin) reported tautomerization of porphyrine (the most stable and highest symmetrical isomer of porphin) on Cu(III) by injection of electrons with a STM tip. The process breaks a NH bond in the molecule cavity and forms a new one in a neighboring N site, while the outer large aromatic ring apparently remains as a spectator. Interestingly, the reaction happens above a STM threshold voltage lower than the NH-stretching mode frequency, it can occur tens of nanometers away from the tip position, and it is irreversible at low temperatures.

D. Novko (DIPC), M. Blanco-Rey (UPV/EHU, DIPC), and J.C. Tremblay (FU-Berlin) undertook the challenge of simultaneously explaining all those observations. They have developed a general microscopic quantum-dynamical model based on density functional theory (DFT) that circumvents the need for high-dimensional dynamics. The reaction results from non-adiabatic coupling (NAC) of inelastically scattered electrons/holes and molecule vibrations. However, it cannot be described by existing non-adiabatic models, due to the large number of non-negligibly coupled vibrational modes; here the so-called skeletal modes (wide vibrational spectrum of the aromatic ring) are key. These are common limitations of organic molecular adsorbate manipulation.

![Diagram showing tautomerization](image)

**Schematic view of porphyrene/Cu(III) irreversible tautomerization. Abscissas represent the reaction coordinate (N-H stretch), where the skeletal modes are mapped, deforming the potential as they are excited. At a given threshold voltage, the deformation prompts the reaction.**

We have developed a general microscopic quantum-dynamical model based on density functional theory (DFT) that circumvents the need for high-dimensional dynamics.

First the NAC-induced anharmonic [δ]excitation rates of individual modes are calculated. Then, intermode coupling is treated as a deformation of the adiabatic potential energy curve associated to the N-H bond stretch, i.e. the procedure maps the high-dimensional problem effectively onto a one-dimensional one. All the model quantities are calculated from DFT, ensuring an accurate description of the molecule-substrate van der Waals interaction.
Strong magneto-optical response of nonmagnetic organic materials coupled to plasmonic nanostructures

Nano Letters 17, 1802-1813 (2017)

Plasmonic nanoparticles can significantly modify the optical properties of nearby organic molecules and thus present an attractive opportunity for sensing applications. In this paper, authors show that nonmagnetic organic molecules may exhibit magneto-optical response due to binding to a plasmonic nanoparticle.

Methods based on magneto-optical (MO) activity measurements, such as magnetic circular dichroism (MCD) spectroscopy and magneto-optic Kerr effect (MOKE), take an important place in the battery of tools for materials. However, direct MCD or MOKE measurements are rarely utilized in biosciences due to the usually very low magneto-optical response of biomolecules. Instead, magnetic methods for chemos- and biosensing typically rely on magneto-plasmonic effects, such as the high MO activity exhibited by plasmonic nanoparticles near their localized surface plasmon resonance. From other hand the utilization of plasmonic nanocrystals in sensing based on conventional absorption, fluorescence, or Raman spectroscopy techniques is often ineffective due to strong absorption background and light scattering, particularly in the case of turbid solutions, cell suspensions, and biological tissues.

Recently we demonstrated that the MO activity of an organic compound itself can be greatly enhanced by coupling to a resonant plasmonic nanoparticle. Specifically, we show that supramolecular J-aggregates (a good model system for assemblies in biological complexes) linked to core–shell AuAg nanorods produce strong MCD signal when the resonance of the plasmonic nanoparticles is tuned to the excitonic band of the aggregates, while exhibiting no MCD upon detuning.

We explained such an enhancement of the MO activity by strong coupling of the J-band exciton and the nanoparticle plasmon and fully support our experimental findings by theoretical modeling. Strong-field confinement around the nanoparticle selectively enhances the MO activity only in those molecules that are bound to the particle surface.

Our findings are fully corroborated by theoretical modeling. Moreover the near-complete absence of MO background from other molecular components could allow for the molecule detection even in the case of strong absorption background or light scattering. Thus, our work creates a new paradigm in sensing, which can make a large impact in materials science, medicine, biology, and pharmacology.

The magneto-optical activity of an organic compound itself can be greatly enhanced by coupling to a resonant plasmonic nanoparticle

Experimental (a) and theoretical (b) extinction spectra of the hybrid system of J-aggregates and core–shell AuAg nanorods for different aspect ratios. Experimental (c) and theoretical (d) MCD spectra measured under the applied magnetic fields of $B = \pm 1 T$. Extinction spectra of the cyanine dye in a aggregate state (a) and bare core–shell AuAg nanorods of varying aspect ratios (solid lines), overlaid with theoretical predictions (dashed lines) (b). Panels c) and d) show sketch of hybrid organic-inorganic system and corresponding extinction and MCD spectra.
Nonlocal signatures in electronic spin and charge transport in two-dimensional materials

C.L. Huang, Y.D. Chong, and M.A. Cazalilla

In this work we uncover two anomalous features in the nonlocal transport behavior of two-dimensional metallic materials with spin-orbit coupling. The observed effects can be used to identify the relative contributions of different spin-charge conversion mechanisms. They should be observable in adatom-functionalized graphene, and may provide the reason for discrepancies in recent nonlocal transport experiments on graphene.

As more transistors are packed per square mm into integrated circuits, the semiconductor industry is wrestling with a transistor overheating problem. It is believed that the solution to this problem lies in spin-electronics (spintronics, for short), which, in order to store and process classical and quantum information, exploits not only the charge of the electron but also its quantized magnetic momentum, the spin. The problem of conversion between electronic charge and spin has therefore become of paramount importance and researchers have designed many experiments to study the possible mechanisms.

Spin-charge conversion has been detected in various types of materials via non-local transport measurements, a versatile and well-established experimental technique also used to probe other important phenomena such as the quantum Hall effect. However, some of the existing experimental measures in two-dimensional materials like graphene functionalized with adsorbates cannot be explained by the existing transport theories. The latter typically account for only one type of spin-charge conversion, i.e. the spin Hall effect. However, in graphene decorated with adsorbates and possibly other types of two-dimensional materials, a different type of spin-charge conversion mechanism, namely the current-induced spin polarization, occurs and coexists with spin-Hall effect.

In this highlighted work, we formulated a transport theory that accounts for both types of spin-charge conversion mechanisms and uncovers two anomalous features that can help to identify which one dominates in a particular device. We observed that: (i) the nonlocal resistance of a Hall bar device (see Figure 1) can take negative values (in the absence of a magnetic field) when direct magnetoelastic coupling (DMC, a form of extrinsic current-induce spin polarization) dominates the spin-Hall effect (see Figure 2). (ii) The nonlocal resistance under an in-plane magnetic field (the so-called “Harle effect”) can take an asymmetric shape with the reversal of the field direction (see Figure 3). Both anomalous features are caused by a direct magnetoelastic coupling which exists in disordered materials with broken inversion symmetry but was not accounted for in previous treatments. The direct magneto-electric coupling was uncovered by the present authors in an earlier work [Phys. Rev. B 94, 085414 (2016)] and it is caused by scattering with impurities that violate local inversion symmetry, i.e. Rashba spin-orbit coupling.

In certain types of two-dimensional materials, the spin Hall effect can coexist with current-induced spin polarization. We have formulated a drift-diffusion theory that accounts for both of these spin-charge conversion mechanisms and solved it on a nonlocal geometry.

Figure 1. Nonlocal transport on a Hall bar device. A current I is injected at x = 0 between the electrodes V1 and V2. This gives rise to both a local resistance Rxx and a nonlocal resistance Ryy. The latter is enhanced by a process involving (i) a spin-charge conversion (current-induced spin polarization and/or spin Hall effect) at x = 0, (ii) diffusion from x = 0 to x = L, and (iii) the inverse spin-charge conversion at x = L. The green-dotted line indicates the direction of electron flow.

Figure 2. Nonlocal resistance Ryy versus the chemical potential µ of adatoms decorated graphene in the absence of a magnetic field, showing that Ryy > 0 when the spin Hall effect (SHE) dominates over direct magnetoelastic coupling (DMC) effects, whereas Ryy < 0 when DMC dominates.

Figure 3. The Harle precession effect Ryy versus magnetic field in the presence of direct magnetoelastic coupling, a form of current-induced spin polarization, and the spin Hall effect. The Harle precession curve becomes asymmetrical when both contributions are of the same order.
Transition-metal π-ligation of a tetrahalodiborane

H. Braunschweig, R.D. Dewhurst, J.O.C. Jiménez-Halí, E. Maitio, and J.H. Muessig

In this work we’ve succeeded in the synthesis of the first transition-metal complex of a diboranyl dianion, which has been computationally characterized as an olefin analogue.

Tetrahalodiboranes are enigmatic compounds formed by two boron and four halogen atoms. Despite the lability and immense reactivity potential of these structures, the relative absence of tetrahalodiboranes is due to their difficult preparation, involving gas-phase synthetic steps. As a consequence, the synthetic interest in tetrahalodiboranes ebbed after an initial spike in their use in the last century. Conversely, the filing of patents involving tetrahalodiboranes has outpaced their appearance in journal articles at a rate of two to one over the past five years. The latter is due to the versatility of these intriguing compounds that, among other applications, are used for the doping of silicon with B⁺ ions for semiconductor device fabrication.

Recently, the first transition-metal complex of a diboranyl dianion has been prepared and characterized by the group of Prof. Braunschweig at the University of Würzburg. The reaction of tetraiododiborane with trans-Pr[B₂I₆][PC₃₄][Cl] gives rise to the diplatinum(III) complex [{(η₅-C₅H₅)₂Pr}(η₂-B₂I₄)]₂, which is supported by a bridging diboranyl dianion ligand [B₂I₄]²⁻.

The groups of Prof. Óscar Jiménez-Halí and Dr. Eduard Maitio, an Ikerbasque Research Fellow working at the DIPC, have performed a joint computational study of these compounds using chemical bonding tools based on the topology of the electron density, electron fluctuation analysis and the intrinsic bond orbitals. The presence of ring critical points in the center of each B-Pr-B structure and the large fluctuation of the electron population among these atoms suggests the presence of two multicenter Pr-B₂ 3c-2e bonds, similar to the two B₂ 3c-2e bonds seen in Himmet’s rhomboidal B₂ unit. In other words, the B₂X₄ unit can be seen as an olefin analogue.

The compound represents the first example of intact coordination of B₂X₄ (X = halide) unit of any type to a metal center. These results provide a glimpse of the potentially exciting coordination chemistry of tetrahalodiboranes, about which very little is currently known. The experimental and computational results have been published this year in Angewandte Chemie International Edition.

Isocontour plot of the Laplacian of the electron density around the B₂X₄ unit within the tetrahalodiborane structure.

The results provide a glimpse of the potentially exciting coordination chemistry of tetrahalodiboranes, about which very little is currently known.
Imaging chemical reactions in front of a curved Pd surface: steps as active sites

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It is known that atomic steps on the surface play an important role in catalytic reactions. In this work we overcome previous methodological constraints, and perform spatially resolved measurements of the CO₂ production over a cylindrical-shaped Pd catalyst to show that the light-off temperature at different parts of the crystal depends on the step orientation of the two types of steps.

Catalysts are vital for a wide range of applications in exhausts, in the chemical industry, and in energy production, because they reduce the energy barrier of chemical reactions. To further improve industrial catalysts it is essential to understand catalytic processes at the lowest atomic level. This represents a formidable challenge, implying the development of novel analytical techniques, such as the Planar Laser-Induced Fluorescence (PLIF), combined with smart experimental approaches, such as the curved crystal approach.

The PLIF technique is designed to image the gas phase in the proximity of a surface during a chemical reaction. As explained in Figure 1, a laser beam excites the molecule of interest, which relaxes by emitting a photon, and the fluorescence light is then detected. The process is highly selective, such that a specific molecule can be targeted. But it is also very intense and can be implemented in a 2D fashion, such as to spatially resolve (50 μm) the gas phase of chemical reaction, for example, in front of a catalyst.

In our experiments the target molecule was CO₂, the product molecule in the CO oxidation, and the surface was a curved Pd crystal, which acted as the catalyst. The latter is described in Figure 2 (top). The curved shape is intended to facilitate and rationalize the role of low-coordinated Pd step atoms during the CO oxidation reaction. In fact, low-symmetry vicinal surfaces with smoothly increasing density of steps sequentially appear as we move from the high symmetry (111) plane in the center and toward the edges of the sample. Using PLIF we have been able to spatially resolve the CO₂ production over the curved Pd crystal surface at different temperatures during the activation of the CO oxidation reaction. The set of PLIF images in Figure 2 (bottom) neatly demonstrate that the ignition temperature depends on step density and type, being lower at the steps named B type, and higher at the crystal center, which contains no steps.

By using a curved Pd crystal we were able to neatly demonstrate that the ignition temperature depends on step density and type.
Submolecular imaging resolution using inelastic electron tunnelling spectroscopy at 5 K


Scanning tunneling microscopy (STM), atomic force microscopy (AFM), and inelastic electron tunneling spectroscopy (IETS) are three established techniques to image organic molecules on surfaces. Here, the three techniques are studied simultaneously by measurements using a CO-terminated tip at 5 K. The high-resolution contrast observed simultaneously in all channels unambiguously demonstrates the common imaging mechanism in STM/AFM/IETS, related to lateral bending of the CO-functionalized tip. Theoretical modeling reveals that the origin of submolecular contrast in the IETS channel consists of both a renormalization of the vibrational frequency and of a variation in the amplitude of the IETS signal.

The development of high-resolution STM, AFM, and IETS imaging with functionalized tips has allowed us to reach unprecedented spatial resolution of organic molecules on surfaces. Using these techniques, the chemical structure of molecules can now be routinely determined directly from experimental images, as well as information about, e.g., bond order, intermediates, and products of on-surface chemical reactions. The main problem of IETS is that the high-resolution contrast was so far only demonstrated at sub-Kelvin temperatures. This temperature requirement poses severe limitations for its wider application.

In this work, an international team of researchers from DIPC and Czech institutions demonstrates for the first time that high-resolution IETS is feasible at 5 K in standard laboratory conditions and experimentally confirms the common imaging mechanism for all three imaging techniques (Figure 1).

The researchers made simultaneous AFM/STM/IETS measurements of an iron(II) phthalocyanine (FePc) molecule adsorbed on Au(111) acquired with a CO-terminated tip at 5 K. Their results demonstrate that the high-resolution IETS imaging is feasible at that temperature with a spatial resolution superior to STM and comparable to AFM. Moreover, the high-resolution contrast observed in all channels simultaneously demonstrates unambiguously the common imaging mechanism related to the lateral bending of the CO-functionalized tip. Further, the IETS spectroscopy reveals that the submolecular contrast at 5 K consists of both the renormalization of the vibrational frequency and the variation in the amplitude of the IETS signal.

The team confirmed this discovery using first principles simulations, extending the probe-particle model to include these two main ingredients necessary to reproduce the high-resolution IETS contrast.

Our results demonstrate that the high-resolution IETS imaging is feasible at 5 K with a spatial resolution superior to STM and comparable to AFM.
Band gap formation and Anderson localization in disordered photonic materials with structural correlations

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Disordered dielectric materials with structural correlations show unconventional optical behavior: They can be transparent to long-wavelength radiation, while at the same time have isotropic band gaps in another frequency range. This phenomenon raises fundamental questions concerning photon transport through disordered media. Here, we investigate band gaps, and we report Anderson localization in 2D disordered dielectric structures using numerical simulations of the density of states and optical transport statistics.

Non-metallic solids and liquids can differ considerably one from the other from an optical point of view. An important role in this is played by the material’s structure. One can find clear and transparent materials, but also opaque white or iridescent reflective ones as in the case of opals. Moreover, because of a change in structure, the same material can first be transparent and then white, as can easily be observed when frying an egg. In extreme cases, it is possible, within a particular color spectrum, to produce a perfectly reflective material.

Hyperuniform disordered, all-dielectric, structures are a new class of photonic materials which, depending on the light wavelength (color), can be perfectly transparent (like glass), they can become white (like a cloud, milk or a fried egg) and, for certain colors, behave as perfectly reflective materials (having a perfect full band gap like crystals). Uniformly disordered (amorphous) materials were first postulated in 2009 by a group of researchers at Princeton University (USA) and their unusual properties raised fundamental questions concerning the multiple scattering of light and the actual nature of Anderson localization of photons in these materials.

Now, researchers at the Universities of Fribourg (Switzerland) and Erlangen (Germany), in collaboration with J.J. Sáenz, Ikerbasque Professor at DIPC, have been successful in deciphering and systematically classifying the complete optical characteristics of so-called hyperuniform materials, as recently reported in the prestigious American Journal PNAS. Using computer simulations they discover that, depending on the strength of the local ordering and wavelength of the light, entirely different optical characteristics can manifest themselves: from transparent to white or completely reflective. These findings form a basis for the design and development of modern amorphous photonic materials based on the concept of hyperuniformity.

Hyperuniform disordered, all-dielectric, structures are a new class of photonic materials which, depending on the light wavelength, can be perfectly transparent, become white, and, for certain colors, behave as perfectly reflective materials.
Magnetically-driven colossal supercurrent enhancement in InAs nanowire Josephson junctions

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In the present work we report a colossal enhancement of the critical supercurrent induced by an external magnetic field applied perpendicular to the substrate in mesoscopic Josephson junctions formed by InAs nanowires and Al superconducting leads. This striking and anomalous supercurrent enhancement cannot be described by any known conventional phenomenon of Josephson junctions. We consider these results in the context of topological superconductivity, and show that the observed critical supercurrent enhancement is compatible with a magnetic field-induced topological transition.

The coupling between a BCS superconductor (S), like Al or Nb, and a semiconducting nanowire (NW) with a strong spin-orbit coupling (SOC), like InAs or InSb may lead to unconventional p-wave superconducting correlations. Such a system may undergo a topological transition and become an artificial topological superconductor (TS) that hosts Majorana-like edge states (MS).

Majorana states have been intensively studied in the past decades, mainly because their applicability in the development of topological quantum computation. Most of the experimental efforts to demonstrate the existence of these states have been focused on normal metal-superconductor junctions realized with strong SOC NWs with the aim to detect signatures of Majorana bound states (MBs) in the dependence of the zero-bias conductance on an external applied magnetic field.

In the present work, which is a collaboration between the groups of Francesco Giazotto (CNR, Pisa), Ramón Aguado (CSIC, Madrid) and Sebastián Bergeret (DIPC/ICM, Donostia), we investigated the Josephson effect in a Al/InAs-NW/Al hybrid junction (see Figure 1). The Josephson effect is a fundamental quantum phenomenon where a dissipationless current (supercurrent) can flow through the junction between the two superconducting electrodes. The amplitude of this current depends on the macroscopic phase difference between the electrodes, and in clean systems it is associated to the bound states formed within the NW. The maximum supercurrent that can flow through the junction is denoted as the Josephson critical current ($I_c$). The latter depends on the applied magnetic field.

Measurement of $I_c$ may provide important information about the ground state of the junction, in particular it is expected to increase strongly when the topology of the junction enables the emergence of Majorana bound states.

The colloidal supercurrent enhancement observed in a semiconducting Josephson junction can be explained by assuming a topological transition.

Our experiment shows a striking and novel change of the amplitude of $I_c$ when an external magnetic field is applied perpendicular to the substrate plane. As shown in Figure 2, the critical current $I_c$ remains almost constant up to a field of 15 mT, then quickly doubles its amplitude at a switching field $B_s \approx 23$ mT, and $I_c$ finally decays at larger magnetic fields. The colossal enhancement of $I_c$ (which exceeds 100%) occurs at the same magnetic field for all the measured junctions (Figure 2c). This suggests that the origin of the effect is intrinsic to the materials combination. And is qualitatively explained by a topological transition.
Breaking bonds, forming nanographene diradicals with pressure


The present study demonstrates and rationalizes how a newly synthesized anthanthrene-based polycyclic scaffold possessing peripheral crowded quinodimethanes adopt a closed-shell butterfly-shaped structure in the ground state that can easily planarize through a low energy barrier biradicaloid transition state to a low-lying diradical state. Conversion is primarily driven by the release of strain associated with steric hindrance.

Quinodimethane nanographenes with closed-shell structure experience a concave to a convex inversion through a diradical intermediate that is kinetically trapped and has a low energy lying triplet. The study reports the preparation and characterization of a new “nanographene” based on the low-cost commercially available 4,10-dibromoanthanthrene building block. While the anthanthrene core can be viewed as a fusion of two anthracene moieties with lateral functionalization, its chemical and physical properties stand in sharp contrast with the parent anthracene subunit, exhibiting remarkable stability because of its extended delocalization. We hypothesized that the general target structure shown in Figure 1 would possess an accessible diradical state upon core planarization, as this would result in the release of steric strain along with the formation of two perpendicular π-systems and overall gaining of aromatic stability. Interestingly, this system would provide a rare example of a closed-shell to diradical transition fueled by strain release.

A relatively small energy barrier for the quinoidal to diradical conversion is found that can be overcome at room temperature through fluxional inversion giving rise to a local metastable full planar structure with a net singlet diridical character and a triplet state (Figure 2). This diradical state displays most of the spin densities at the exo-acene carbon atoms. As no new Clar sextet was formed during this transformation (2 sextets in both the closed-shell and open-shell forms), the driving force for this transformation is likely attributed to the release of strain induced by the steric hindrance at the peri-position of the anthanthrene.

In summary, under application of mild mechanical stress, the molecule undergoes planarization, forming a kinetically trapped diradical, which has been characterized by Raman and EPR spectroscopies in combination with quantum chemical calculations. While this rare example of π bond breaking by mechanochemistry opens the way to the generation of diradicaloid species with accessible high spin states from robust quinoidal structure, current work is focused on stabilizing the diradical state through the design of novel functionalized anthanthrene-based polycyclic aromatics.

Under application of mild mechanical stress, the molecule undergoes planarization, forming a kinetically trapped diradical