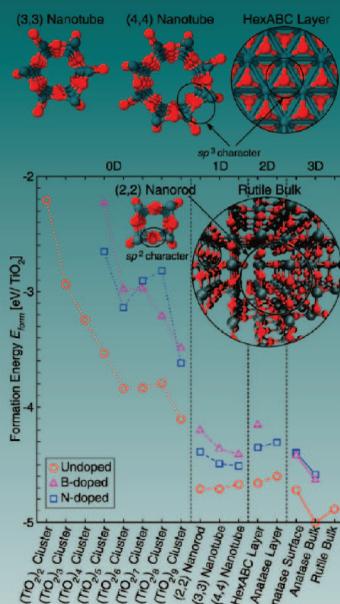
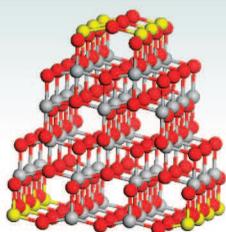
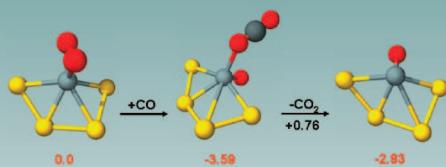
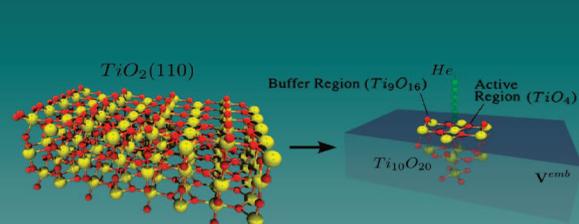


The first edition of the international workshop "Molecular Photoreactivity on Metal oxides from First Principles" (FPMPMO) has intended to bring together scientists from around the world, either to present the latest advances of their research in the field or, research from related areas to highlight problems that might stimulate the development of new (first-principles) methodological strategies to "attack" the problem of calculating excited states of molecule/metal-oxide surfaces and interfaces (i.e., local correlation cluster approaches, Time Dependent Density Functional Theory, and non-adiabatic Molecular Dynamics) and combined experimental/theoretical studies of benchmark systems. First-principle studies of molecular photoreactivity on metal-oxide (semiconductor) surfaces are of fundamental interest in order to deeply understand the photo-catalytic properties of these systems, which hold a very promising future in the development of novel material to obtain for example, solar energy (photo-voltaic energy).



2009

Molecular Photoreactivity on Metal-Oxide Surfaces from First-Principles

Workshop, December 4-5 (2009)
Madrid, Spain

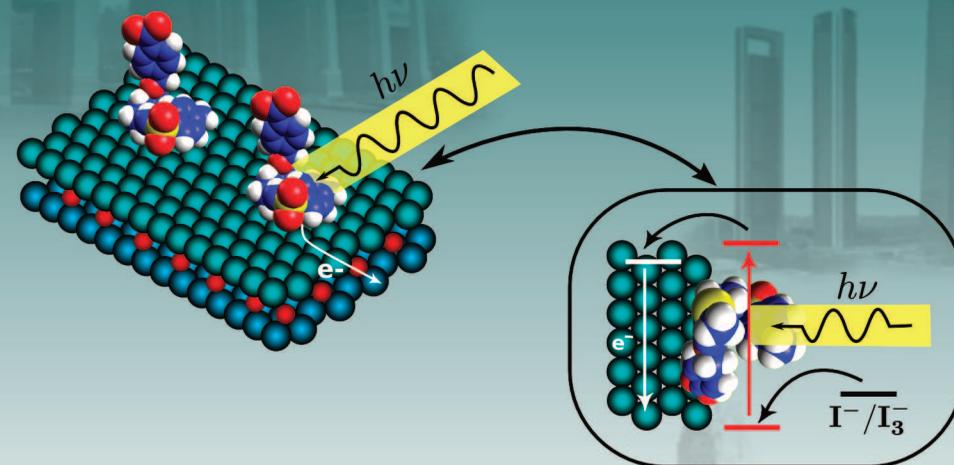
Molecular Photoreactivity on Metal-Oxide Surfaces from First-Principles

Photocatalysis and Photovoltaics

<http://www.iff.csic.es/fama/con/FPMPMO-2009/>

Book of abstracts

$$\hat{H} |\Psi(t)\rangle = i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle$$



Edited by

María Pilar de Lara Castells, Néstor F. Aguirre, David López Durán,
Alexander O. Mitrushchenkov and José Ortega Mateo



**Molecular Photoreactivity
on Metal-Oxide Surfaces
from First-Principles**

**Molecular Photoreactivity
on Metal-Oxide Surfaces
from First-Principles**

Book of Abstracts

Madrid, Spain
December 4-5 (2009)



Editors:

María Pilar de Lara Castells

Consejo Superior de Investigaciones Científicas, CSIC (Spain)

Néstor Fabián Aguirre Castiblanco

Consejo Superior de Investigaciones Científicas, CSIC (Spain)

David López Durán

Consejo Superior de Investigaciones Científicas, CSIC (Spain)

José Ortega Mateo

Universidad Autónoma de Madrid, UAM (Spain)

Alexander O. Mitrushchenkov

Université Paris-Est Marne-la-Vallée, UPEMLV (France)

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The purpose of the FPMPMO-2009 workshop was to bring together researchers working in the field of molecular photo-reactivity on metal-oxide surfaces or in related areas. The workshop was conceived from an interdisciplinary perspective, with not only an emphasis placed on the theoretical/computational understanding of this subject, but “with an eye” on the experimental studies and technological applications, as well; for example, sunlight-driven photo-voltaic cells and photo-catalysis.

The invited speakers and participants came from diverse areas of expertise, such as molecular physics, quantum-chemistry and condensed-matter physics, to promote the exchange of ideas between different fields and the exploration of new directions for addressing the complex subject of the workshop. First-principle studies of molecular photo-reactivity on metal-oxide (semiconductor) surfaces are of fundamental interest in order to deeply understand the photo-catalytic properties of these systems, which hold a very promising future in the development of novel material to obtain for example, solar energy (photo-voltaic energy). However, to study photo-chemistry at a fundamental level, sophisticated descriptions are required; including several coupled electronic states and a quantum treatment of at least a few degrees of freedom. Thus, for example, the photo-induced desorption of molecules from surfaces, the most elementary photo-reaction, poses a formidable theoretical challenge. A complete treatment must consider the dynamics of the adsorbed species on the surface, the detailed forms of the ground and relevant excited potential energy surfaces and their non-adiabatic and electronic couplings, the migration of holes and electrons through the bulk and their subsequent quenching, and the effects and influence of surface defects. Due mainly to the complexity of the quantum treatment of excited states in extended systems and the relevant degrees of freedom, these studies are scarce. On the other hand, the study of these well-controlled model systems, in close interaction with experiments, has the potential to provide basic, mechanistic information and key simplifications that can be transferred to the much more complicated reactions of industrial importance. Direct studies of industrial processes, which often involve powders, the presence of impurities, complex molecules, and multiple intermediates, are nearly unimaginable without such simplifications and preliminary results.

This challenging task implicitly involves methodological enhancements which must combine different theoretical approaches. Therefore, the scientific program is very broad, including Density Functional Theory (DFT)

and its time-dependent extension (TDDFT), wave-function-based correlated methods, ab-initio Molecular Dynamics, Quantum-Mechanics consistent embedding techniques, Quantum Dynamics and Quantum Control methodologies, and large-scale classical dynamics and metadynamics. Although this meeting had a fundamental character, there were experimental contributions that highlighted problems that might stimulate combined experimental/theoretical studies on benchmark systems. We have also done an effort to bring together the applied and the basic research in the special topic of Photo-voltaics.

The scientific program consisted of 18 invited presentations, a poster session preceded by short verbal presentations and an informal discussion table at the end of the meeting. The program was divided in six sessions.

The first session's goal was to provide a general vision of the workshop's subject from the point of view of applied, theoretical and experimental basic research. Thus, Ana Rosa Lagunas, representing the Spanish National Center for Renewable Energies, kicked off the session by focusing on applied research on Photo-voltaic cells. Thorsten Klüner's presentation on Ab-initio surface photo-chemistry followed. Thorsten Bernhardt ended the session with a talk about experimental studies on photo-reactivity on metal-oxides.

Session II, with James Lewis and Javier Fernandez Sanz as speakers, focused on the application and/or development of DFT-based methodologies to investigate the properties of TiO_2 -based materials with photo-catalysis or catalytic applications. In Session III, the combination of DFT-based methodology with classical dynamics was addressed to simulate photo-induced processes, including non-adiabatic effects, by Nikos Doltsinis, to simulate dehydroxylation reactions in solids, including metadynamics, by Alfonso Hernández Laguna, and to simulate molecular reactivity on surfaces, including new DFT approaches, by Cristina Díaz.

Session IV targeted specific subjects of the workshop such as first-principle studies of dye-sensitized semiconductors by Oleg Prezhdo, by combining nonadiabatic molecular dynamics and time-domain DFT. A presentation on water photo-oxidation on a TiO_2 surface by Alvaro Valdés was followed. Experimental pump-probe studies of the photo-reactivity on TiO_2 were shown by Michael White, whereas Philippe Sautet's lecture was centered on the theoretical modelling of hydroxylated metal oxide surfaces.

In the four presentations comprising Session V, with Gilberte Chambaud, Migen Halo, Jose Luis Pascual and Carsten Müller as speakers, post-Hartree-Fock wave-function-based methods (as embedded cluster approaches), rather than DFT, are used to describe either the interaction of molecules with metal and metal-oxide surfaces or ionic solids, including excited states and dynamical correlation effects in weakly bound systems.

Finally, Session VI focussed on the quantum control of molecular processes by Ignacio Solá, whereas José Ignacio Martínez ended the session with a talk about controlling TiO₂ photo-catalysis and photo-reactivity by combining nanostructural changes with doping.

We are grateful to the sponsors, co-organizers, colleagues and friends for making the organization of this meeting possible. In particular, we are thankful to our three funding institutions: the Consejo Superior de Investigaciones Científicas (CSIC) and the local government of the Community of Madrid (CM) through joint project centered on the workshop's subject; the Université Paris-Est Marné-la-Vallée and the Universidad Autónoma de Madrid. We are grateful also for the financial support from the GEFAM group of the Real Sociedad Española de Física and the private consortium, HP-TAISA SYVALUE SL, as well as the computational facilities provided by the supercomputing center CESVIMA. Néstor Fabián Aguirre, David López Durán, Adela Fernández and Roberto Linguetti are thanked for their valuable help in the organization. Finally, we would like to express our gratitude to all our guest speakers and participants for coming to this meeting.

On behalf of the Organizing, and Scientific Committees,

María Pilar de Lara Castells (Chair, CSIC)
Alexander O. Mitrushchenkov (Co-Chair, UPEMLV)
and José Ortega-Mateo (Co-Chair, UAM)

Conference Sponsors

Three public institutions have equally contributed to provide financial support for the organization of this meeting: the Consejo Superior de Investigaciones Científicas (CSIC, through the joint CSIC-Comunidad de Madrid –CAM- project of Ref. CCG08-CSIC/ESP-3680 within the “Programa de Ayudas a la I+D de interés Regional”), the Université Paris-Est Marne-la-Vallée (UPEMLV), and the Universidad Autónoma de Madrid (UAM). The financial support from the Real Sociedad Española de Física (RSEF) and the consortium HP-TAISA SYVALUE SL, as well as the computational facilities provided by the supercomputing center CESVIMA are also gratefully acknowledged.



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Invited talks

**Workshop Molecular Photoreactivity on Metal-Oxide Surfaces from
First-Principles
Madrid 4th – 5th December 2009**

**From first principles on light/materials interaction, until final
photovoltaic products**

Ana R. Lagunas

*CENER (Centro Nacional de E. Renovables), C/Ciudad de la Innovación 7,
31621 Sarriguren –Navarra (Spain)*

email: alagunas@cener.com

General interests

Photovoltaic Solar Energy is becoming a subject of interest from many points of view, the main reason being its capacity of direct conversion of light into electricity. Principal advantages of that kind of energy are the total modularity of the PV sources (from a few cells for a calculator up to multimegawatt plants), the almost absence of mobile parts and the zero emissions during operation.

Developing materials for photovoltaic applications, testing the devices obtained and making them live as much as possible, are the main tasks of the Photovoltaic Department of CENER.

Abstract

During the last years, and mainly as a result of the increase in prices of oil, the frightened news on the climate change due to excess CO₂ production, and the general economical situation worldwide, the so called renewable energies are attracting the interest of everybody. On one side are situated the potential users of them, on the other the scientific and engineering community developing materials and devices, and, in the middle, the manufacturers who should make possible that the products developed arrive to the end users.

Photovoltaic Solar Energy transforms the sun radiation into electricity in a direct way. The origin of that is the interaction of photons from the light with certain materials, giving rise to a separation of charges. The voltage difference achieved in this way while the light is impacting on the device, is able to provide a current through an outside circuit. The bases for the PV effect are the light, certain type of materials where the electronic structure has a forbidden zone to allow charge separation, and the capacity to contact and extract the charges to produce an electrical current through the external circuit.

The development of photovoltaic technologies¹ passes by the initial use of a bulk indirect band gap semiconductor, through various thin film materials (CdTe, CIGS,

amorphous and microcrystalline Silicon), and recently the multijunction devices based on III-V compounds, that achieve the highest conversion efficiency by means of the enhanced spectral response^{2,3}. The latest to appear are the dye-sensitised and organic based compounds that, as their main advantage with respect to the others, offer the lowest cost and the possibility of being obtained over different kind of substrates flexible, transparent....

The interest addressing most of the developments in photovoltaic cells has been the reduction of the cost of energy produced, achieved mainly by two means: increasing conversion efficiency or reducing cost of the devices. Both facts must go together with the ability of making the device to live in good working conditions for a time long enough.

In this talk we will review the development and evolution of various types of PV cells and the latest improvements achieved on the main parameters, making a special remark on the areas that need basic research.

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**Workshop Molecular Photoreactivity on Metal-Oxide Surfaces from
First-Principles
Madrid 4th – 5th December 2009**

Ab initio Surface Photochemistry

Thorsten Klüner

*Carl von Ossietzky University Oldenburg, Institute of Pure and Applied
Chemistry, Theoretical Chemistry, Carl-von-Ossietzky Str. 9-11, 26129
Oldenburg, Germany*
email: Thorsten.Kluener@uni-oldenburg.de

Abstract

Photodesorption of small molecules from surfaces is one of the most fundamental processes in surface photochemistry. Despite its apparent simplicity, a microscopic understanding beyond a qualitative picture still poses a true challenge for theory. While the dynamics of nuclear motion can be treated on various levels of sophistication, all approaches suffer from the lack of sufficiently accurate potential energy surfaces, in particular for electronically excited states involved in the desorption scenario.

In the last decade, we have developed a systematic and accurate methodology to reliably calculate accurate ground and excited state potential energy surfaces (PES) for different adsorbate-substrate systems. These potential energy surfaces serve as a prerequisite for subsequent quantum dynamical wave packet calculations, which allow for a direct simulation of experimentally observable quantities such as velocity distributions.

In this contribution, I will focus on recent results obtained for photodesorption of NO and CO from a NiO(100) surface. In contrast to previous studies, we were able to construct highly accurate potential energy surfaces based on correlated quantum chemical calculations (CASPT-2/CCSD(T)). Despite the enormous computational cost, this level of theory turns out to be crucial, since less sophisticated approaches such as density functional theory (DFT) cannot even provide a reliable description of ground state properties, not to mention electronically excited states [1].

These potential energy surfaces were used in subsequent wave packet studies which reveal new desorption mechanisms. In the NO/NiO(100) case, we observed an *anti-Antoniewicz* scenario in which the wave packet is initially repelled from the surface but eventually reaches a turning point before it is back-scattered from the surface. State resolved desorption velocity distribution have been calculated, and the results are in good agreement with experimental findings [2].

In the CO/NiO(100) system, we observe the formation of a genuine covalent bond upon photoexcitation for the first time. As demonstrated in the current study, this chemical bond formation is the crucial step in the desorption mechanism for this system [3, 4]. Again, our results are in good agreement with recent experiments.

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**Workshop Molecular Photoreactivity on Metal-Oxide Surfaces from
First-Principles
Madrid 4th – 5th December 2009**

**Ultrafast molecular reaction dynamics on metal oxide
ultrathin films**

Thorsten M. Bernhardt

*Institute of Surface Chemistry and Catalysis, Albert-Einstein-Allee 47,
University of Ulm, 89069 Ulm, Germany*
email: thorsten.bernhardt@uni-ulm.de

General interests

Femtochemistry, molecular reaction dynamics in the gas phase and on surfaces, ultrathin oxide films, metal clusters on surfaces, gas phase metal cluster reactions and catalysis, laser interaction with nano-structured surfaces

Abstract

The ultrafast bimolecular reaction dynamics of iodine atoms generated by photodissociation of CD_3I adsorbed on an insulating $\text{MgO}(100)$ ultrathin film on $\text{Mo}(100)$ was investigated in real-time employing a new experimental approach that combines time-of-flight mass spectrometry and femtosecond laser pump-probe spectroscopy [1]. Photoexcitation to the dissociative A-band initiated the decomposition of the CD_3I adsorbate molecules within about 300 femtoseconds. Subsequent to the CD_3I dissociation and simultaneously with the desorption of the methyl fragments, the bimolecular reaction of the emerging ground state and spin-orbit excited iodine atoms on the surface was probed by detecting molecular iodine in the electronically excited B-state. These iodine molecules, however, were found to be metastable exhibiting surface-induced predissociation on the picosecond timescale. By time-, mass-, and velocity-resolved monitoring of intermediate and product species it was thus possible to decipher the complex dynamics of a photoinduced surface reaction [2].

Whereas the direct photodissociation mechanism prevailed on the insulating magnesia surface, dissociative electron attachment could be identified as primary photoinduced reaction mechanism of methyl halides on a gold thin film. For small gold clusters supported on magnesia, the time-resolved methyl desorption dynamics indicate a transition from photo- to electron-induced dissociation as a function of the gold particle size [3].

Methodologies

Ultrafast laser spectroscopy on solid surfaces, fs-laser photoemission, scanning tunneling microscopy, ion trap mass spectrometry, fs pump-probe mass spectrometry

Projects

Molecular photodissociation dynamics on oxide surfaces, bimolecular reaction dynamics on oxide surfaces.

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**Workshop Molecular Photoreactivity on Metal-Oxide Surfaces from
First-Principles
Madrid 4th – 5th December 2009**

**Reactivity and Chemical Reactions of Faceted TiO₂
Nanoparticles**

James P. Lewis

*West Virginia University, Department of Physics, Morgantown, WV
26506-6315, USA*

email: james.lewis@mail.wvu.edu

Abstract

Although anatase is a less stable crystallographic phase than rutile in bulk titanium dioxide materials, it has received considerable attention in photoactive materials related applications due to increased high reactivity in the anatase polymorph (1, 2). More interestingly, it is reported that anatase, instead of rutile, becomes the preferable stable phase for TiO₂ for particle sizes less than 14nm (3, 4). Therefore, an important step in achieving a full understanding of anatase nanoparticles' photoactive functions with regards to their surface' characteristics is to examine and determine specific active sites that are available for probing molecules surface adsorption and dissociation.

In previous reported work, the (101) surface is found to be the majority surface dominating the exposed shape on nanosized anatase crystallites (3, 4, 7-9). However, the minority surfaces (001) are the most reactive for photocatalytic reactions on anatase surfaces (10-16). In this work, we attempt to understand the relationship between the unique electronic properties and surfaces of anatase nanoparticles by investigating faceted nanoparticles which have both the (001) and (101) surfaces in different percentages. A critical question is where active sites are located in relation to this intersection. In this work, we aim to address this question by theoretically investigating specially constructed anatase nanoparticles with co-existing (101) and (001) surfaces and predict where the active sites and potential adsorption and dissociation will most likely occur.

There are obviously structural changes appearing in the surface areas in the nanoparticles; the most noted structural changes occur at the edged Ti atoms which are connected between (001) facets and (101) facets. One nanoparticle (182 atoms) is shown in Fig. 1 (a) as an example which demonstrates the exact locations of edged Ti atoms in the initial structures before optimization. As a result of optimization, the

edged Ti atoms move outward which results in extended Ti-O bonds; these edged Ti atoms are lower coordinated in the optimized structures. The primary result is that the edged Ti atoms connected between the (001) and the (101) surfaces exhibit the most significant structural changes; the original four-coordinated Ti atoms become three-coordinated which make them very reactive sites exposed at these surfaces.

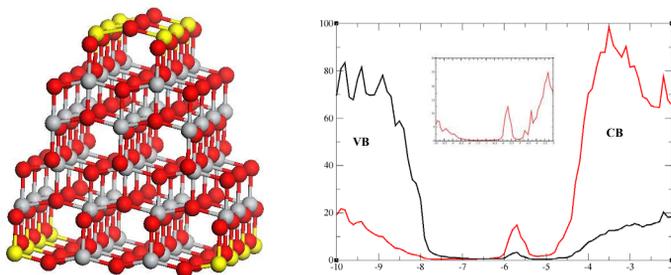


Figure 1. An example of a faceted anatase nanoparticle; the edged Ti atoms are labeled yellow which are 3- or 4-coordinated Ti atoms connected between (001) and (101) surfaces. The PDOS (projected density of states) is also displayed. The red plots represent states from Ti atoms and black plots from O atoms in nanoparticles. The peak mid-gap corresponds to the lower-coordinated Ti corner atoms.

A further analysis of the electronic structures provide a complete understanding of the relationship between these low-coordinated edged Ti atoms and the reactive properties. The density of states for the 182 atom nanoparticle system is shown in Fig. 1(b). The energy gap of our model nanoparticles are approximately 3.5 eV which are larger than bulk's band gap. A feature in the PDOS plots indicates the existence of mid-gap frontier orbitals. These small peak states occur near the Fermi energy, which is approximately 1 eV beneath the conduction band edge, and are solely due to Ti atoms. More importantly, these frontier orbitals are due to edge Ti atoms specifically located at the interface between the (001) and the (101) facets; the edged Ti atoms are low-coordinated junctures between (001) and (101) surfaces.

We also find that these frontier orbital states are very localized; the number of accessible atoms, as defined by W in Ref. (19), is no more than 10 atoms. These highly localized edged Ti atoms thus are strong adsorption sites for water or other molecules. And although it is accepted that (001) facets are more active for both adsorption and dissociation and (101) facets are less so, we find that the most reactive sites for nanoparticles are actually at the interface between these two facets on these unsaturated Ti sites. These sites therefore provide unique surface structural properties in nanoparticles where a variable of facets exist.

Methodologies

The Lewis Research Group is the primary developer and distributor of the FIREBALL electronic-structure code. This *ab initio* tight-binding code is based on density-functional theory (gradient densities included) using pseudopotentials to describe core states; a linear combination of pseudoatomic orbitals are used for the basis wave functions of the method. Judicious approximations and algorithmic choices are used, including massively-parallel algorithms, which yield computationally feasible calculations of very large systems (1000s of atoms).

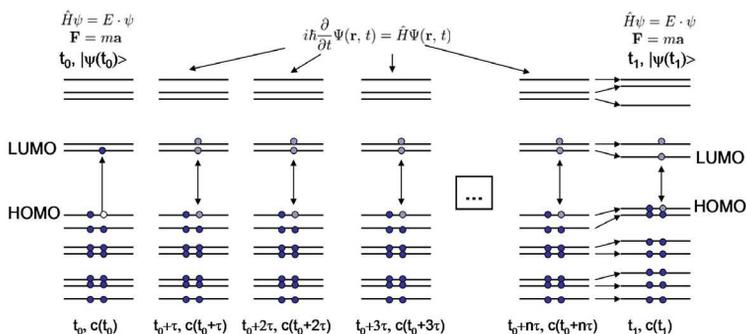


Figure 2. The algorithm for molecular dynamics with quantum (electronic) transitions.

Recently, we have devised a molecular dynamics with quantum transitions (MDQT) method (schematically drawn in Fig. 2), similar to techniques proposed by Tully (20, 21) and by Prezhdo and others (22-24), within our FIREBALL DFT tight-binding code. In the MDQT approach, the hops between potential energy surfaces are determined using the Fewest Switches Surface Hopping (FSSH) method (20) that minimizes the number of non-adiabatic transitions per trajectory, while imposing the correct state populations. This approach enables simulations of practical applications with several hundred or potentially thousands of atoms involved as FIREBALL can handle much larger systems with little loss of accuracy, it is ideal for the implementation of quantum-classical methods on these time scales.

Projects

Our research interests primarily involve investigating the electronic and structural properties of a variety of materials for photocatalysis or other applications. Several materials and their corresponding properties are currently being investigated in our research group – for instance, 1) porous organic-inorganic hybrid systems which are photoactive; 2) the optoelectronic properties of semi-conducting materials – (II-VI) nanostructure materials, transition metal oxides, and delafossites); and 3) conduction properties in biomolecules.

Acknowledgments

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**Workshop Molecular Photoreactivity on Metal-Oxide Surfaces from
First-Principles
Madrid 4th – 5th December 2009**

**Water Gas Shift Reaction Mechanism at Surfaces: Au, Cu
and CeO_x Nanoparticles supported on TiO₂(110)**

Javier Fernández Sanz^{a,*}, Jesús Graciani^a and José A. Rodríguez^b

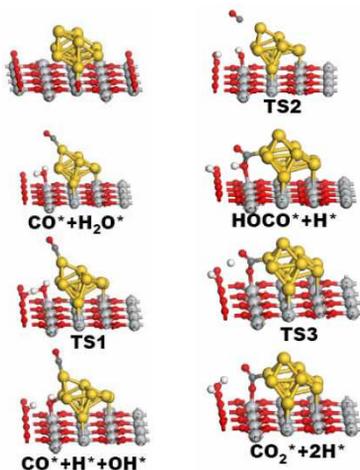
^a *Dpto de Química Física, Universidad de Sevilla, E-41012, Sevilla, Spain.*

^b *Chemistry Department, Brookhaven National Laboratory, Upton, NY
11973, USA.*

*sanz@us.es

Abstract

Although bulk metallic gold is not active as a WGS catalyst, Au nanoparticles (NPs) supported on TiO₂(110) have an activity comparable to that of Cu/ZnO(000 $\bar{1}$). Cu/TiO₂(110) is clearly a better catalyst than Cu/ZnO(000 $\bar{1}$) or Au/TiO₂(110). The catalysts that have the highest activity for the WGS have also the lowest apparent activation energy. The Cu \leftrightarrow titania interactions are substantially stronger than those of Au \leftrightarrow titania and STM images show that the average particle size in Cu/TiO₂(110) is smaller than in Au/TiO₂(110). Also, while Cu NPs are dispersed on the terraces and steps, Au NPs concentrate on the steps. The morphology of Cu/TiO₂(110) favors high catalytic activity. The results of DFT calculations indicate that the metal-oxide interface plays an essential role in the catalysis, helping in the dissociation of water and in the formation of an OCOH intermediate which decomposes to yield CO₂ and hydrogen.



Calculated structures for reactants and intermediates of the WGS reaction on a Au/TiO₂ model catalyst.

Ce deposition on TiO₂(110), shows that, at small coverage, CeO_x NPs have an unusual coordination mode. STM and DFT calculations point to the presence of Ce₂O₃ dimers, which form diagonal arrays that have specific orientations of 0, 24 and 42 degree with respect to the [1 -1 0] direction of the titania substrate. At high coverages of ceria on TiO₂(110), the surface exhibits two types of terraces. In one type, the morphology is not very different from that observed at low Ce coverage. However, in the second type of terrace, there is a compact array of ceria particles with structures that do not match the structures of CeO₂(111) or CeO₂(110). The titania substrate imposes on the ceria nanoparticles nontypical coordination modes enhancing their chemical reactivity. This phenomenon leads to a larger dispersion of supported metal NPs (M= Au, Cu, Pt) and makes possible the direct participation of the oxide in catalytic reactions. The M/CeO_x/TiO₂(110) surfaces display an extremely high catalytic activity for the water-gas shift reaction that follows the sequence: Au/CeO_x/TiO₂(110) < Cu/CeO_x/TiO₂(110) < Pt/CeO_x/TiO₂(110). At low coverage of Cu and CeO_x, Cu/CeO_x/TiO₂(110) is 8 – 12 times more active than Cu(111) or Cu/ZnO industrial catalysts. In the M/CeO_x/TiO₂(110) systems, there is a strong coupling of the chemical properties of the admetal and the mixed-metal oxide: the adsorption and dissociation of water probably take place on the oxide, CO adsorbs on the admetal nanoparticles, and all subsequent reaction steps occur at the oxide-admetal interface. The high catalytic activity of the M/CeO_x/TiO₂(110) surfaces reflects the unique properties of the mixed-metal oxide at the nanometer level.

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**Workshop Molecular Photoreactivity on Metal-Oxide Surfaces from
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Multiscale Modelling of Photoactive Materials

Nikos L. Doltsinis

Department of Physics, King's College London, London WC2R 2LS, United Kingdom
email: nikos.doltsinis@kcl.ac.uk

Abstract

A DFT-based nonadiabatic ab initio molecular dynamics (na-AIMD) surface hopping scheme [1,2] has been applied to study light-induced processes in a variety of complex condensed phase systems whose relevance range from biology [3] to materials science [4]. As part of a long-term strategy to model macroscopic phototriggered phenomena, a multiscale simulation approach is being developed linking different hierarchical simulation levels - from na-AIMD [1,2] to atomistic classical MD to coarse grained MD. In this scheme, the development of a nonadiabatic QM/MM extension [4] of na-AIMD has played a key role. Applications to a photoswitchable liquid crystal [4], based on the azobenzene chromophore, and the light-triggered unfolding of a polypeptide [5] are presented.

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Metadynamics applied to the dehydroxylation reaction

E. Molina Montes,¹ C. I. Sainz Díaz,² D. Donadio,³ M. Parinello,³ V. Timón,¹ D. Muñoz Santiburcio,¹ and A. Hernández Laguna^{1,*}

¹*Estación Experimental del Zaidín (CSIC), C/ Prof. Albareda 1, 18008 Granada (Spain)* ²*Instituto Andaluz de Ciencias de la Tierra (CSIC, Universidad de Granada), Avda. Fuentenueva, 18002 Granada (Spain)*

³*Laboratory of Physical Chemistry, EHT Zurich, USI Campus, Via Giuseppe Buffi 13, CH-6904 Lugano, Switzerland*

*alfonso.hernandez@eez.csic.es

General Interests

Our groups is mainly interested in the understanding of the influence of the isomorphic cation substitution and pressure on the crystal structure, physical and chemical properties of phyllosilicates, particularly the dioctahedral 2:1 phyllosilicate series. We have also studied adsorption of different compounds on phyllosilicates, and metal oxide surfaces.

Abstract

Ab initio Molecular Dynamics (MD) is a very general method to study chemical reactions. However, when transition states in the Potential Energy Surfaces (PES) are high, reactants have low probability to go out of their wells in a reasonable CPU time with normal computational facilities. Besides, there are systems where the entropic effects are important and the Free Energy Surface (FES) is the meaningful surface. To overcome these shortcomings a metadynamics¹⁻³ is applied in a restricted space of a few collective variables (CV). The metadynamics is based on a biased historical-dependent potential, which fills the wells with Gaussian functions as the system walks on the FES of the CV space, and overcoming the transitions states in consequence. The metadynamics of the collective variables provided a coarse-grained description of the system. The FES is reconstructed from the historical-dependent potential applied for long time.

Dehydroxylation reaction produces a water molecule from the condensation of two structural hydroxyl groups. This reaction is produced in phyllosilicates in a wide range of temperatures (350 – 800 °C), rehydroxylation reaction is also produced. This reaction is studied in pyrophyllite (Al₄Si₈O₂₀(OH)₄). This mineral is a dioctahedral 2:1 phyllosilicate in which a sheet of octahedrally coordinate Al³⁺ is sandwiched between two sheets of linked SiO₄ tetrahedra. The reaction can go through two possible

mechanisms: “on site” and “cross” mechanisms, depending whether the condensation is produced with two bridging hydroxyl groups of an octahedral Al^{3+} pair or with the hydroxyl groups in an octahedral vacancy. Car-Parrinello MD simulation at the DFT level together with the metadynamics algorithm¹⁻³ is used to explore the FES of the initial step of the dehydroxylation reaction. The CPMD package (CPMD v.3.9) is used.⁴ Both mechanisms yield similar activation energies at 0 K. Apical oxygens can assist both mechanisms, and different intermediates are also found. All of them and transition states are detailed described. At higher temperatures, the “cross” mechanism has lower free energy than the “on-site” mechanism. Rehydroxylation mechanism is also considered. A novel competitive mechanism, which is assisted by the structural apical oxygens in the high-temperature regime, is proposed.^{5,6} All results agree with the known experimental results.

The isomorphic cation substitutions (Al^{3+} is substituted by Mg^{2+} , Fe^{3+} , ...) in the octahedral sheet of the end member of the series (phyrophyllite) and different cations (K^+ , Na^+ , Ca^{2+} , ..) in the interlayer space produce different members of the series [$\text{Y}_x(\text{Al}_{4-x-z}\text{Mg}_x\text{Fe}_z)\text{Si}_8\text{O}_{20}(\text{OH})_4$]. The same methodology of dynamics and metadynamics is now applying to the dehydroxylation reaction in different members of the series.

Critical points of the PES of the reaction have also been studied by means of cluster models and introducing Fe^{3+} as substitution cation. Gaussian 98 program package is used. “Cross” mechanism is less energetically favourable and is endothermic.⁷

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Novel Approaches to study molecule/surface reactions

C. Díaz^{#,*}, P. Rivière[#], F. Martín[#], G. Laurent[#], H. F. Busnengo[§], D. J. Auerbach[¶], E. Pijper[&], R. A. Olsen[&], G. J. Kroes[&].

[#] *Departamento de Química C-13, Universidad Autónoma de Madrid, 28049 Madrid, Spain*

[§] *Instituto de Física de Rosario (CONICET-Universidad Nacional de Rosario), Av. Pellegrini 250, (2000), Rosario, Argentina*

[¶] *GRT, Inc., 861 Ward Drive, Santa Barbara, CA 93111 and Department of Chemistry and Biochemistry, University of California at Santa Barbara, CA 93106*

[&] *Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P. O. Box 9502, 2300 RA Leiden, The Netherlands*

* cristina.diaz@uam.es

General interests

It is sometimes surprising how little we know about processes that occur right under our very noses. Almost all we see are the surfaces of the objects surrounding us – surfaces pervade our lives, from the walls in our houses, to the piston chambers in the engines of our automobiles. At each of these surfaces there occur chemical processes, many of which are poorly understood.

Determining the mechanisms behind such surface reactions is more than a frivolous academic exercise; reactions of gas phase molecules with metal surfaces are of tremendous practical importance, as the production of most synthetic compounds involves heterogeneous catalysis in such conditions.

Abstract

To present day, molecule/surface interaction studies have been mainly focus on molecules on its rovibrational ground state ($v=0, J=0$), impinging the surfaces at thermal energies^{1,2}. State-of-the-art theory allow us to perform these studies using quantum mechanics for the motion of the molecule in all its six degrees of freedom, while making the so-called Born-Oppenheimer and static surface approximation. The precision achieved depends critically on the accuracy of the potential energy surface (PES). The lack of accuracy inherent in present-day density functional theory (DFT)³, the method of choice for computing PESs for molecule-surface interactions, stands in the way of a quantitative description of heterogeneous catalyzed reactions.

Aiming to overcome shortcomings associated to standard DFT we have developed and implementation of the so-called specific reaction parameter (SRP) approach to DFT⁴ that allows a quantitative description of the molecule-surface interactions (see below). We show that our SRP-PES allows a chemically accurate description of the reaction of H₂ and D₂ on Cu(111) in molecule beam experiments, of the influence of the initial rotational and vibrational state of H₂ on reaction on that surface, and of rotational excitation of H₂ scattering from Cu(111). In the case of reaction probabilities, we have obtained excellent agreement with two rather different sets of experimental data for pure H₂ beams. The calculations present the solution to a previously unsolved puzzle: at similar incidence energy, two sets of reaction probabilities differed by an order of magnitude. Analysis of the beams used in both experiments shows that the two sets of reaction probabilities are consistent: The reaction probabilities on one of the set were larger because used beams with wider velocity distributions.

We also present a new approach to study reaction saturation values⁵. Motivated by diffraction of fast atoms at grazing incidence recently proposed as a promising new tool to determine surface parameters with unprecedented accuracy, we have shown that fast light molecular projectiles can be used to determine sticking probabilities at thermal energies and beyond, from the threshold up to the saturation limit.

Eventually the development of new experimental techniques based on pulsed narrow bandwidth laser Raman, which allow the production of vibrationally excited molecular beams to study reactive scattering on metal surfaces, have spurred us to study the interactions of vibrationally excited molecules with surfaces⁶. From this study we predict a general nonmonotonic behavior of dissociative adsorption of vibrationally excited H₂(v,J=0) molecules as a function of incidence energy whenever this process becomes non activated.

Methodologies

In the new implementation of the SRP the exchange-correlation functional is a weighted average of two standard DFT functionals calculated within the so-called generalized gradient approximation, in which the energy depends only on the electron density and its gradients. The philosophy behind the methods is that by fitting a single parameter to one suitable experiment, we can obtain a functional that yields a PES that enable an accurate description of other, more detailed, experiments.

Classical calculations are used to study both reaction and diffraction probabilities. A classical trajectory is computed by solving the Hamilton equations of motion, and the probabilities are calculated as an average over the molecular initial conditions, which are obtained by using a classical Monte Carlo sampling method. Classically the intensity of a given diffraction peak with Miller indices (n,m) is evaluated as the fraction of trajectories in which the molecule scatters with a parallel momentum change contained in the 2D Wigner-Seitz cell built around the (n,m) lattice point in reciprocal space⁷.

To carry out quantum dynamics calculations we use a time dependent wave packet (TDWP) method⁸. The method uses a discrete variable/finite representation for all DOFs, the initial wave packet is propagated in time using the split-operator method and the reflected wave packet is analyzed using a scattering amplitude formalism.

Projects

The natural next step in our quest to understand how molecules interact with surfaces is to extend the SRP-DFT method to reactions where heavier molecules than hydrogen are involved. It then becomes important to include also the motion of the surface atoms in the modeling. In such applications, the dynamics calculations should incorporate the motion of the surface atoms at the stage when the SRP functional is fitted to experimental data. Approximate ways of including the effect of atomic surface motion can now be incorporated in quantum dynamical and ab initio molecular dynamics simulations. It may even be possible to extend SRP-DFT to improve the description of molecules interactions with surfaces involving electronically excited state, thus taking us beyond the almost always used Born-Oppenheimer approximation.

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**Time-Domain Ab Initio Studies of Photoinduced Electron
Dynamics in Molecule/TiO₂ Interfaces and Quantum Dots**

Oleg V. Prezhdo

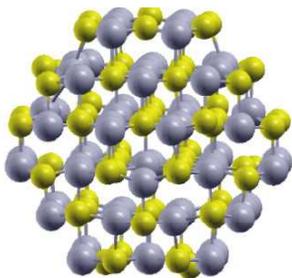
*University of Washington, Department of Chemistry, Seattle, WA 98195-
1700, USA*

email: prezhdo@u.washington.edu

General interests

Development of quantum-classical and semiclassical methods for nonadiabatic molecular dynamics in condense phase systems. Time-domain density functional theory for electron-nuclear dynamics. Modeling of nanoscale materials, including molecule-semiconductor interfaces, quantum dots, carbon nanotubes, graphene nanoribbons, carbon supercapacitors, plasmonic metal particles, etc. Further applications include bio-nano assemblies, such as DNA detection on metal surfaces and graphene nanopores, the biological catch-bond, order-disorder transitions in electro-optic polymers, retinal isomerization, ozone photochemistry, etc.

Abstract



Design of novel materials for energy harvesting and storage requires an understanding of the dynamical response on the nanometer scale. A great deal of experimental and theoretical work has been devoted to characterizing the excitation, charge, spin, and vibrational dynamics in quantum dots, conducting polymers, carbon nanotubes, inorganic semiconductors and molecular chromophores. We have developed state-of-the-art non-adiabatic molecular dynamics techniques and implemented them within time-dependent density functional theory in order to model

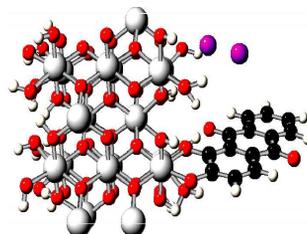
the ultrafast processes in these materials at the atomistic level and in real time.

The talk will focus on quantum dots and chromophore-semiconductor interfaces that form the basis of new generations of solar cells. Quantum dots (QD) are quasi-zero dimensional structures with a unique combination of molecular and bulk properties. As a result, QDs exhibit new physical phenomena such as the electron-phonon

relaxation bottleneck and efficient carrier multiplication, which have the potential to greatly increase the efficiency of solar cells.

Photoinduced charge separation across molecular/bulk interfaces drives the dye-sensitized semiconductor solar cell. A subject of active research, it creates many challenges due to the stark differences between the quantum states of molecular and periodic systems, as well as the different sets of theories and experimental tools used by physicists and chemists.

Our time-domain atomistic simulations create a detailed picture of these materials. By comparing and contrasting their properties, we provide a unifying description of quantum dynamics on the nanometer scale, resolve several highly debated issues, and generate theoretical guidelines for development of novel systems for energy harvesting and storage.



Methodologies

We are developing a combination of nonadiabatic molecular dynamics and time-domain density functional theory, with emphasis on proper coupling of quantum and classical subsystems, semiclassical treatments of zero-point-energy, tunneling, decoherence and other quantum effects. We implemented a number of nonadiabatic molecular dynamics approaches within time-domain density functional theory, including Ehrenfest dynamics, fewest-switches surface hopping, and stochastic mean-field approach.

Projects

See general interests.

Acknowledgments

I am greatly thankful to my current and former students, postdocs and visitors, including Dr. Yuriy Pereverzev, Dr. William Stier, Dr. Elke Pahl, Dr. Craig Brooksby, Dr. Colleen Craig, Dr. Walter Duncan, Dr. Dmitri Kilin, Dr. Svetlana Kilina, Dr. Brad Habenicht, Dr. Hideyuki Kamisaka, Dr. Kim Hyeon-Deuk, Sean Fischer, Tammie Nelson, Angie Madrid, Zhenyu Guo, Vitaly Chaban and many others.

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**Workshop Molecular Photoreactivity on Metal-Oxide Surfaces from
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Photo-oxidation of water on the rutile TiO₂ (110) surface

Á. Valdés^{1,*}, Z.-W. Qu¹, G. J. Kroes¹, J. Rossmeisl², J.K. Nørskov²

¹ *Leiden Institute of Chemistry, Gorlaeus Laboratory, Leiden University, 2300RA Leiden, The Netherlands*

² *Center for Atomic-scale materials Design, Department of Physics, nano-DTU, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark*

* avdeluxan@chem.leidenuniv.nl

General interests

During the last two years my work in the Leiden Institut of Chemistry (LIC) was devoted to the study the of the catalyst effect of oxide metal surfaces in the oxidation of water process at the photo-anode of a solar cell.

Abstract

A density functional theory (DFT) based method for computing the free energies of electrode / adsorbate/ electrolyte systems [1] is generalised from electrolysis to photo-electrolysis. The oxidation and photo-oxidation of water on the rutile TiO₂ (110) surface is investigated using periodical DFT calculations.

We studied different oxygen coverages of the surface in contact with H₂O and their relative stability as a function of the applied bias and the pH of the electrolyte, and then analyzed the reaction mechanisms of the oxidation of water on the surfaces that are stable over a particular range of bias and pH values, according to the thermochemistry of the four elementary electron transfer reactions, and analyzed the overpotential needed for the electrolysis and photo-electrolysis of water.

We found that the most difficult step in the splitting of water process is the reaction of an H₂O molecule with a vacancy in the surface to form an adsorbed hydroxyl group (OH). Comparison to experiment [2] shows that the computed overpotential for O₂ evolution (0.78 V) is available under the experimental conditions required for both oxygen and hydrogen evolution.

Methodologies

To model the material periodic boundary DFT calculations are performed. To determine whether the intermediate one electron transfer reaction steps of the oxygen evolution reaction in the surface of a semiconductor are allowed we used the method developed by Nørskov and coworkers for electrolysis [1] and extend it for the photo-electrolysis by assuming that the driving force for the reaction at the anode is provided by holes at the upper edge of the valence band..

This model, based on DFT calculations, determines whether the intermediate one electron transfer reaction steps are thermodynamically allowed, restricting the discussion of energy barriers for the different elementary steps to the barriers that come from differences in free energies of the intermediates [3,4].

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**Pump-Probe Studies of Photodesorption and Photooxidation
on TiO₂(110)**

D. P. Wilson,¹ D. P. Sporleder¹ and M. G. White^{1,2,*}

¹ *Department of Chemistry, Stony Brook University, Stony Brook NY USA*

² *Chemistry Department, Brookhaven National Laboratory, Upton NY USA*

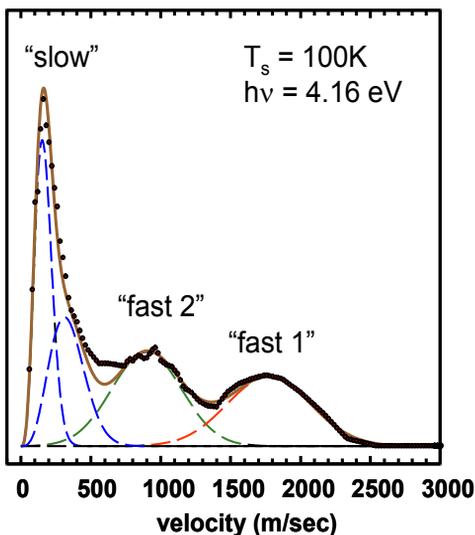
*mgwhite@bnl.gov

General Interests

Our group studies the mechanism and dynamics of photoinduced reactions on metal and metal oxide surfaces using lasers to both initiate (pump) and detect (probe) desorbed products. On metal oxide surfaces, we are particularly interested in understanding the dynamics of hole-induced reaction and the role of defects in adsorbate binding and charge transfer at the interface.

Abstract

Measurements of the final state properties of gas-phase products are being used as a probe of the mechanism and dynamics of photodesorption and photooxidation on well-characterized TiO₂(110) surfaces. This work is motivated by the widespread use of titania in technological applications where UV photooxidation is used for the degradation of organic materials.¹ Our initial studies on the photodesorption of O₂ on reduced surfaces of TiO₂(110) attempted to address long standing questions about the desorption mechanism and the identity of the photoactive O₂ binding sites.²⁻⁴ The experiments make use of a one-photon ionization scheme for O₂



Measured velocity distribution for O₂ photodesorbed from TiO₂(110) at 100 K. The excitation laser energy was 4.16 eV and the O₂

detection and a time-of-flight spectrometer for mass identification and measurements of velocity distributions. The measured velocity distributions for desorbed O_2 exhibit three distinct features, two of which are attributed to prompt desorption resulting in “fast” velocity distributions and one “slow” channel whose average kinetic energy tracks the surface temperature (see accompanying figure).⁵ The “slow” channel is assigned to trapping-desorption of photoexcited O_2^* which are trapped in the physisorption well prior to thermal desorption. The two “fast” desorption channels have mean translational energies of ~ 0.14 eV and ~ 0.50 eV and are attributed to the photodesorption of two distinct initial states of chemisorbed oxygen. Based on an analysis of previous studies of oxygen on reduced $TiO_2(110)$ surfaces, one of the “fast” photodesorption channels is tentatively assigned to O_2^- species bound at $Ti^{IV}(5f)$ sites adjacent to an oxygen molecule adsorbed in a bridging oxygen vacancy. The origin of the second “fast” channel is unknown but is likely to arise from O_2^- bound to $Ti^{IV}(5f)$ sites situated near interstitial cations ($Ti^{III}(i)$)⁶ or from molecular oxygen species bound at bridging oxygen vacancies which do not thermally dissociate below RT, *e.g.*, the recently proposed tetraoxygen complex.⁷ The velocity distributions were also found to be unaffected by annealing the as-prepared $O_2/TiO_2(110)$ surface to 260 K before taking the measurements. The latter suggests that chemisorbed species that transform irreversibly (*e.g.*, dissociate) at higher temperatures do not contribute to the photodesorption yield. We also find that the velocity distributions show no dependence on photon energy over the range studied (3.45 eV - 4.16 eV). This observation is consistent with an indirect hole-capture desorption mechanism in which an adsorbed O_2^-/O_2^{2-} species is neutralized by capturing a hole (h^+) that was photogenerated in the titania substrate.

More recently, we have used pump-probe techniques to examine the final state distributions of the gas-phase products resulting from the photooxidation of small organic molecules on $TiO_2(110)$. Recent experiments by Henderson using a UV lamp source showed that the photooxidation of small ketones on the $TiO_2(110)$ surface results in the direct ejection of radical species into the gas phase.^{8,9} Initial studies of acetone (CH_3COCH_3) and butanone ($CH_3CH_2COCH_3$) co-adsorbed with O_2 on $TiO_2(110)$ show that the primary gas-phase products of photooxidation ($h\nu = 3.70$ eV) are methyl radical (CH_3^\bullet) and ethyl radical ($C_2H_5^\bullet$) with average translational energies of 0.15 eV and 0.05 eV, respectively. In the case of butanone, we used a variety of VUV ionization wavelengths to show that other C_2 hydrocarbon products (ethane or ethylene) proposed in previous studies are not formed to any significant extent. The methyl radical translational energy distribution is markedly different than that observed in gas-phase photolysis of acetone, and can be empirically fit to a “fast” and a “slow” component. The “fast” component is attributed to a prompt intramolecular fragmentation process of the molecular precursor (surface diolate species) and the “slow” component may be associated with methyl internal energy or a second fragmentation channel.

Methodologies

Pump-probe techniques are used to measure final state distributions of the products, e.g., translational, ro-vibronic and spatial, which reflect the dynamics of the reaction and desorption steps as well as the molecule-surface binding configuration. Unique aspects of our instrumentation include the use of tunable VUV laser radiation for the sensitive detection of gas-phase products (including O₂) and the development of a velocity focusing time-of-flight spectrometer for imaging neutral angular distributions.

Projects

In the future, we hope to obtain vibrational distributions of photodesorbed O₂ as the change in bond length is expected to be substantial in going from adsorbed superoxo species O₂⁻ to the neutral gas-phase molecule. We also need help from theorists to help understand the measured O₂ velocity distributions (dynamics of desorption) and to develop a theoretical framework for understanding final state energies of fragments resulting from the hole-induced fragmentation of polyatomic molecules (photooxidation).

Acknowledgments

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**Workshop Molecular Photoreactivity on Metal-Oxide Surfaces from
First-Principles
Madrid 4th – 5th December 2009**

**Metal oxide surfaces from first principles: hydroxyls,
stability and reactivity**

Philippe Sautet

*University of Lyon, Laboratory of Chemistry, Ecole Normale Supérieure de
Lyon and CNRS, 46 Allée d'Italie, F-69364 Lyon Cedex 07, France.*
email: Philippe.Sautet@ens-lyon.fr

General interests

- Theory of the electronic structure at the solid-gas interface
- Modeling of elementary steps of heterogeneous catalysis
- Calculation of the Scanning Tunnelling Microscopy images of surfaces
- First principle calculations for chemisorption and molecular vibrations at surfaces
- Catalytic reaction pathways for molecules from DFT calculations
- Modeling grafted complexes or clusters on oxide surfaces
- Simulation of catalytic surfaces in realistic temperature and pressure conditions

Abstract

Metal oxide surfaces have a central importance in heterogeneous catalysis, either as active phase or as support. A large number of studies are hence devoted to the modeling of the surfaces of oxides, in order to understand their structure and their chemical properties. Most of the studies however deal with “clean” oxide surfaces, as they would be obtained in ultra-high vacuum experiments. The termination of the oxide will be modified however in catalytic conditions. In most cases, hydroxyl groups will be present on the oxide surface, from dissociation of water molecules.

This lecture will be centered on the theoretical modeling of hydroxylated metal oxide surfaces. Total energies and structures are obtained from Density Functional Theory applied on a periodic model of the surface. An ab initio thermodynamics approach is followed to evaluate the hydroxyl concentration as a function of temperature and water pressure. Gamma Al₂O₃ [1], TiO₂ [2] and MgO [3] surfaces will be considered. The hydroxylated surfaces are validated by simulating spectroscopic data (vibrational, NMR[4] or photoluminescence[5]) using slab or embedded cluster models.

The second part of the lecture will be centered on an overview of the chemical reactivity of the hydroxylated surfaces. When used as a support for metal catalysts, we

will explain why hydroxylated alumina gives smaller particles, compared to clean oxide surfaces. We will also show that small Pd₄ particles supported on hydroxylated alumina have different chemisorption properties for ethene [6]. OH groups are efficient grafting sites for organometallic complexes and the grafting reaction pathway will be presented for a tetra-alkyl zirconium complex [6,7]. Hence hydroxylation appears as a major chemical process to control the structure and reactivity of oxide surfaces in catalysis related phenomena.

Methodologies

Periodic DFT, plane waves, as implemented in VASP. Exploration of reaction pathways from the Nudged Elastic Band method.

Projects

Modeling catalytic systems related with energy production. Catalytic transformation of biomass. Photocatalysis, band gap engineering, excited states. Influence of dispersive forces in molecular chemisorption. Interaction of metallic particles with oxide supports, Catalytic surfaces under a pressure of gases. Modelling the liquid/solid interface.

Acknowledgments

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**Theoretical approach of the physisorption interactions of
layers of H₂ molecules on metallic surfaces**

Gilberte Chambaud

*Université Paris-Est, Marne la Vallée, Laboratoire de Modélisation et
Simulation Multi-Echelle, FRE 3160-CNRS, Cité Descartes, Champs-sur-
Marne, 77454, Marne-la-Vallée, France*
email: gilberte.chambaud@univ-mlv.fr

Abstract

The H₂/Cu(100) system has been widely used in surface science as a benchmark for the understanding of molecule-surface interactions, particularly in the domain of catalysis and many theoretical and experimental studies are dealing with the H₂/Cu dissociative adsorption. No such extensive work has been achieved on the H₂/Ag system, however several experiments have been reported on physisorbed H₂ on silver surfaces and a theoretical study of H₂/Ag(100) has been reported by Eichler *et al.*[1] providing Potential Energy Surfaces (PES) for the interaction of H₂ molecules with a surface of silver atoms for different orientations and relative positions of the H₂ molecules.

The main objective of this study is to analyse the process of approaching several H₂ molecules on a surface already covered by H₂ molecules and the goal is : **i)** to evaluate the interaction energy of this second layer of H₂ molecules , **ii)** to examine the role of the orientation of the molecule in this second layer, **iii)** to analyse the role of the metal Cu or Ag, and **iiii)** to evaluate the interaction energy in further layers (H₂)_nX(100), n>2.

In our approach we consider a model system consisting of a cluster of 13 metallic atoms (Ag, Cu) and n (n=1,2,3) H₂ molecules. The calculations of the chemi- and physisorption processes of H₂ on a (100) surface of silver and copper have been achieved by *ab-initio* methods, taking into account large part of the correlation energy, namely Multi-reference Interaction Configuration treatments, including the Davidson correction. (details of the calculation are given in [2-3]).

The dissociative chemisorption of a first H₂ molecule on the surface proceeds via a potential activation barrier and is an endothermic process in the case of Ag and exothermic in the case of Cu surface. The process is analyzed in terms of hydrides formation and it is shown that several electronic states are interacting in the vicinity of the activation barrier leading to complex electronic processes [2-3].

We have calculated the energy of the physisorption interaction of the first H_2 molecule with the metallic surface for different orientations and that of further H_2 molecules coming directly on top of the first chemisorbed one. It is found that the bond length of the H_2 molecule in the second layer remains at its standard equilibrium value. Moreover the strong polarization induced by the chemisorbed H atoms on the surface is responsible for the enhancement of the second layer's physisorption energy. The investigation of third layer interactions has shown a significant decrease of the interaction energy compared to that of the second layer, attributed to a screening effect of the non dissociated H_2 molecules in the second layer.

It has been shown that one H_2 molecule approaching a covered surface to form a second layer of molecules lies approximately at 7 bohr from the surface and interacts more strongly with the surface than the first incoming molecule: the interaction is almost twice as large but does not lead to a dissociative adsorption because of the presence of the first layer of hydrogen atoms. The perpendicular orientation of this second molecule with respect to the surface is more favoured than the parallel one. This interaction is much larger than the van der Waals interaction between two isolated H_2 molecules due to the existence of hydrides on the surface and it stabilizes the molecule in this second layer. The interaction of a third layer, located approximately at 13 bohr from the surface, is much smaller than that of the second one and only slightly larger than the van der Waals H_2/H_2 interaction. By extrapolation, we can say that further layers do not feel anymore the presence of the metallic surface.

For the $(H_2)_nCu_{13}$ and $(H_2)_nAg_{13}$ systems it is found that the physisorption energy of the second layer is enhanced by a factor close to two compared to that of the first layer due to dipolar interactions with the polarized surface. The physisorption energy of the third and further layers tends to the van der Waals H_2/H_2 interaction energy. The main results are given in the Table below.

Usual functionals of DFT have been checked but none can give reliable results for both chemi- and physi-sorption.

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System	$E_{P,1}$ (cm^{-1})	$Z_{P,1}$ (bohr)	$E_{P,2}$ (cm^{-1})	$Z_{P,2}$ (bohr)	$E_{P,3}$ (cm^{-1})	$Z_{P,3}$ (bohr)	$E_{H_2-H_2}$ (cm^{-1})
$H_2 \perp Cu_{13}$	693	6.1					
$H_2 // Cu_{13}$	228	7.0					
$H_2 \perp H_2Cu_{13}$			1064	6.24			
$H_2 // H_2Cu_{13}$			625	6.42			
$H_2 \perp (H_2 \perp H_2Cu_{13})$					75.0	13.2	
$H_2 // (H_2 \perp H_2Cu_{13})$					99.1	13.2	
$H_2 \perp (H_2 // H_2Cu_{13})$					84.5	12.8	
$H_2 // (H_2 // H_2Cu_{13})$					62.5	13.2	
$H_2 \perp Ag_{13}$	298	7.47					
$H_2 // Ag_{13}$	217	7.37					
$H_2 \perp H_2Ag_{13}$			539	7.31			
$H_2 // H_2Ag_{13}$			289	7.37			
$H_2 \perp (H_2 \perp H_2Ag_{13})$					61.1	13.9	
$H_2 // (H_2 \perp H_2Ag_{13})$					59.4	13.5	
$H_2 \perp (H_2 // H_2Ag_{13})$					95.7	13.4	
$H_2 // (H_2 // H_2Ag_{13})$					34.6	13.7	
$H_2 \perp H_2$							41.3
$H_2 // H_2$							16.9
$H_2 - - H_2$							13.0

Table: Physisorption energies of H_2 molecules on Cu and Ag surfaces. $E_{P,1}$ is for the first layer and $E_{P,2}$ and $E_{P,3}$ for the second and third, respectively. The equilibrium position $Z_{P,i}$ of the physic-sorbed molecules in the layer i is given. For comparison the interaction energy, $E_{H_2-H_2}$ is given between two H_2 molecules in different orientations.

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**L-MP2 periodic CRYSCOR code applied to the study of
small molecules physisorbed on crystalline surfaces**

Migen Halo

*Dipartimento di Chimica IFM, Universita' degli Studi di Torino, Torino,
Italy.*

email: migen.halo@unito.it

General interests

Correlation in crystalline solids.

Abstract

We present a study of adsorption of small molecules on insulating crystal surfaces performed by means of the CRYSCOR program [1], an ab-initio periodic tool that applies a second-order Møller-Plesset correlation correction in a local approach (L-MP2) on top of the accurate Hartree-Fock solution provided by the CRYSTAL program [2]. The general features of the code will be illustrated and the adsorption of N₂ on hexagonal BN [3], methane on MgO [4] and Ar on MgO [5] will be discussed as example cases.

Methodologies

CRYSCOR [1] is an ab-initio periodic tool for the estimation of the valence correlation energy in non-conducting crystals. The Møller-Plesset at the second order perturbative theory (MP2) is currently implemented in a local approach (L-MP2); the Hartree-Fock solution is provided by the CRYSTAL code [2].

Projects

My PhD project involves developing, testing and application of the CRYSCOR program to crystalline solids and to adsorbate/substrate systems.

Acknowledgments

We are grateful to Prof. M. Rérat and to Dr. D. Usvyat.

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**Workshop Molecular Photoreactivity on Metal-Oxide Surfaces from
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**Embedding Ab Initio Model Potentials for embedded cluster
calculations in ionic solids**

José Luis Pascual

*Dept. de Química Física Aplicada, C/ Fco. Tomás y Valiente, 7, Mód. 14
400_a, U. Autónoma de Madrid, 28049 Madrid, Spain.*

email: joseluis.pascual@uam.es

Abstract

The *Ab Initio* Model Potential (AIMP) [1,2] embedded cluster method provides a reliable way to perform high standard, wavefunction-based quantum mechanical calculations of the electronic structure of ions acting as dopants in ionic lattices. The calculations are performed in a cluster, typically comprising the impurity and its first neighbours, embedded in an accurate representation of the surrounding lattice. All major cluster-lattice interactions are taken into account, either classical (Madelung potential, deviation from point charge) or quantum mechanical (exchange, Pauli repulsion). Recently, an improvement in the method of production of the model potentials, related to the calculation of the Pauli repulsion operator, has been proposed and applied to some oxide lattices [3].

By using high-quality quantum mechanical techniques, static and dynamical correlation as well as relativistic effects can be included in the cluster calculations, both for the ground and excited states, providing accurate local structures, potentials curves and spectroscopic properties. Some examples of application of the method will be presented, including properties of lanthanides as dopants (Ce^{3+} in BaF_2 [4]). Applications to surface properties will be mentioned.

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**Application of the Method of increments for the
investigation of electron correlation effects in physisorbed
systems**

Carsten Müller^{#,*}, Kersti Hermansson[%] and Beate Paulus[#]

[#] *Institute for Chemistry and Biochemistry, Freie Universität Berlin,
Germany*

[%] *Department for Materials Chemistry, Uppsala Universitet, Sweden*

^{*} carsten@chemie.fu-berlin.de

General interests

In the last years I have been studying adsorption problems in the context of heterogeneous catalysis. Mainly I focused on the physisorption of CO, CO₂, NO and N₂O on different surfaces of CeO₂. For these systems I applied standard methodologies (e.g. DFT for periodic slab models) but also developed new sorts of embedded cluster models which I combined with highly accurate post-HF methods within the method of increments scheme.

Abstract

Physisorption plays an important role in many different contexts of surface chemistry. In these weakly bound systems the interaction consists of two parts: electron dispersion and classical electrostatics. Dispersion is non-local electron correlation. It is neglected in Hartree-Fock (HF) theory, not included in common DFT functionals, but recovered by Møller-Plesset Perturbation (MP2) or Coupled Cluster (CC) theory. Classical electrostatic interactions are in principle well described already at the HF or DFT level, however for some molecules e.g. CO and N₂O these methods fail to reproduce the small dipole moments and consequently fail to reproduce the electrostatic interactions, too. It is therefore important to apply very accurate computational methods in order to obtain reliable data for the adsorption energy that could be compared to experiment.

Due to the high computational costs of the ordinary MP2 and CC methods we here apply these theories in the framework of a local correlation scheme called “The Method of Increments” [1,2]. In this scheme, which can be applied for all size-consistent methods, the correlation energy is calculated as a many-body expansion in terms of localized orbital groups. Due to the local character of the electron correlation

this expansion converges quite fast with much lower requirements on computational time and resources than standard implementations of post-HF methods.

We have extended the method of increments to adsorption problems and investigated the systems CO/CeO₂(110) [3], CO/CeO₂(111) [4], N₂O/CeO₂(111) [5], and H₂S/Graphene [6]. We found that in all four systems electron correlation effects contribute to a large amount to the adsorption energy. On top of the large speed-up the method of increments yields some interesting insights into the nature of the molecule-surface bond in weakly bound systems.

Methodologies

Embedded cluster models combined with Density Functional Theory (DFT) and post-Hartree-Fock methods such as Møller-Plesset Perturbation Theory (MP2) and Coupled-Cluster Theory (CC) within the scheme of the Method of Increments

Projects

I am currently extending the method of increments to the investigation of open shell systems.

Acknowledgments

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**What have we learned from the quantum control of
molecules?**

Ignacio R. Solá

*Departamento de Química Física I, Universidad Complutense, 28040
Madrid (Spain)
isola@quim.ucm.es*

General interests

I work in the control of molecular properties and molecular reaction under the guidance of laser pulses, typically what is called Quantum Control. I am interested both in the theoretical foundations of the theory of quantum control and in its applications, among them the use of so-called adiabatic schemes with strong non resonant fields.

Abstract

In its simpler form, Quantum Control is about finding an external field that drives the wave function from the initial state to a pre-determined end state at a given time. From a theoretical point of view, the three main questions related to this program are

- i) whether there exist control fields that fill the task,
- ii) how to find them and
- iii) what are their overall properties, such as stability, required resources, etc. and the mechanism under which they operate

I shall concentrate mainly in the last two questions. Typically there are two main avenues to find the external fields. One is to fine-tune the parameters of well-known solutions obtained from simple Hamiltonian models to the problem at hand. (And sometimes new strategies are found even in these simple test systems.) In this case many of the general properties of the dynamics can be easily inferred from the behaviour of the test system. I will briefly review the most important theoretical (or guessed) control strategies designed from simple Hamiltonians, namely the control under so-called δ or impulsive pulses where the desired quantum interferences are followed in time or in frequency domain, and the so-called adiabatic control of the dynamics using resonant or non-resonant fields. In the control literature all these strategies are often regarded as one-parameter control schemes.

The second avenue is to set up a variational problem with the time-dependent Schrödinger equation and numerically find the fields that maximize the desired task.

That is, given the initial Ψ_i and final Ψ_f states, we find the control field $E(t)$ such that the required yield at time T , $P_{fi}(T) = |\langle \Psi_f | U(T,0;E(t)) | \Psi_i \rangle|^2$ is a maximum (a critical point) under changes in $E(t)$, where $U(T,0;E(t))$ is the propagator. As often is the case, the variational problem leads to non-linear equations that must be solved iteratively, and different optimal control algorithms have been designed to improve the computational burdens associated to this task. An empirical version of this scheme is to perform actual experiments with programmable pulse shapers in close-loop with computers performing learning algorithms. Then $P_{fi}(T)$ is actually measured and $E(t)$ is modified from the search space using e.g. genetic algorithms. A softer version of the optimal control problem is to find $E(t)$ such that the yield is increasing at each time, $d P_{fi}(t) / dt > 0$. The field is chosen based on the local-in-time properties of $P_{fi}(t)$ and the scheme is thus called local-control. For both local and optimal control strategies it is difficult to unravel the mechanisms under which the control operates, and it is harder to understand the general properties of the solution even resorting to heavy computations in order to sketch the landscape of $P_{fi}(T)$ under changes in $E(t)$. However, the analysis of the theoretically-motivated schemes and the numerical and experimental findings from optimal control theory has lead to the determination of the most determining control parameters: the laser bandwidth and the field intensity.

Finally, time allowing I will present some recent results of our research where we use the non-resonant adiabatic strategy to control molecular properties such as the bond length¹ and the dynamics at excited states leading to spin-orbit transitions², inter-system conversion³ or photodissociation⁴ and I will speculate on how the previous findings could be used in controlling processes in solid state or surfaces.

Methodologies

I solve the time-dependent Schrödinger equation using grid-based methods. I also develop optimal control algorithms to maximize the yields of quantum processes under external fields. All programs and codes are written and developed in our group.

Projects

- i) Quantum control of bond lengths and coherent vibrations of small molecules with strong fields under both the adiabatic and the impulsive regime.
- ii) Control of molecular photodissociation in the presence of non-adiabatic couplings, such as spin-orbit and conical intersections.
- iii) Control of coupled electronic and nuclear motion beyond the Born-Oppenheimer approximation
- iv) Control of quantum information processes in molecules in the gas phase

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**Workshop Molecular Photoreactivity on Metal-Oxide Surfaces from
First-Principles
Madrid 4th – 5th December 2009**

**Control and decoherence: control of an excited state
objective: optimization
principles for hot electron injection in solar acceptors**

Ronnie Kosloff*, Mark Ratner and Gil Katz #

*# Fritz Haber Research Center for Molecular Dynamics, Hebrew University
of Jerusalem, Jerusalem, 91904, Israel*

*Department of Chemistry, Northwestern University, Evanston, Illinois
60208-3113*

**ronnie@fh.huji.ac.il*

General interests

Quantum molecular dynamics constitutes the thrust of my research. The goal is to gain insight into realistic elementary chemical encounters. This requires the development and application of a quantum description to molecular processes. In particular the emphasis is on time-dependent approaches which can follow naturally the stream of events.

The main topics of study are: Coherent chemistry: light induced processes. and laser cooling. Coherent control Dynamical processes on surfaces. Quantum thermodynamics. Computational and teaching methods.

Abstract

Coherent control employing a broad band excitation is applied to a branching reaction in the excited state. In weak field for an isolated molecule a control objective is only frequency dependent. This means that phase control of the pulse cannot improve the objective beyond the best frequency selection. Once the molecule is put in a dissipative environment a new time scale emerges. In this study we demonstrate that the dissipation allows to achieve coherent control of branching ratios in the excited state. The model studied contains a nuclear coordinate and three electronic states: the ground and two coupled diabatic excited states. The influence of the environment is modeled by the stochastic surrogate Hamiltonian. The excitation is generated by a Gaussian pulse where the phase control introduced a chirp to the pulse. For sufficient relaxation we find significant control in weak field depending on the chirp rate. The observed control is rationalized by a timing argument caused by a focused wavepacket. The initial non adiabatic crossing is enhanced by the chirp. This is followed by energy relaxation which stabilizes the state by having an energy lower

than the crossing point. We use these principles to design an acceptor for solar energy composed from three electronic states. The acceptor dark excited state should have a soft vibrational mode with fast relaxation. The bright state should be rigid with the non-adiabatic crossing point slightly below in resonance with the excitation.

Methodologies

Propagation methods: The basic idea is to apply recursively the Hamiltonian operator to an initial state. Both time dependent and time independent information can be obtained simultaneously. The method is a much more efficient algorithm than traditional diagonalization methods or methods based on linear equation solvers[5].

Optimal control theory: Developing optimization methods to solve the inversion problem of obtaining the control field that leads to a target [2].

Dissipative dynamics: Development of the stochastic surrogate Hamiltonian method [3].

Projects:

Ultracold-Ultrafast: combining ultrafast control ideas with cold matter [7].

Surface Photochemistry: study of nonadiabatic processes and light induced processes on surfaces [6].

Quantum Thermodynamics: Quantum heat engines and refrigerators [4].

Acknowledgments

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**Workshop Molecular Photoreactivity on Metal-Oxide Surfaces from
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**Stability and Electronics of TiO₂ Nanostructures With and
Without B and N Doping. Tailoring TiO₂ Photocatalysis and
Photoreactivity Properties Across Dimensionality**

J. I. Martínez,^{1, 2, *} D. J. Mowbray,² J. M. García-Lastra,² K. S. Thygesen,²
and K. W. Jacobsen²

¹ *Departamento de Física Teórica de la Materia Condensada, Universidad
Autónoma de Madrid, ES-28049 Madrid, Spain*

² *Center for Atomic-scale Materials Design, Department of Physics,
Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark*
*joseignacio.martinez@uam.es

General interests

Theoretical framework: Density functional theory and many-body calculations.

Systems under study: Metal and metal oxide clusters, wires, surfaces and bulks, ORR and OER catalysis and photocatalysis. Hydrogen fuel cells. Metal/organic interfaces for nanoelectronics. Band-gap effects.

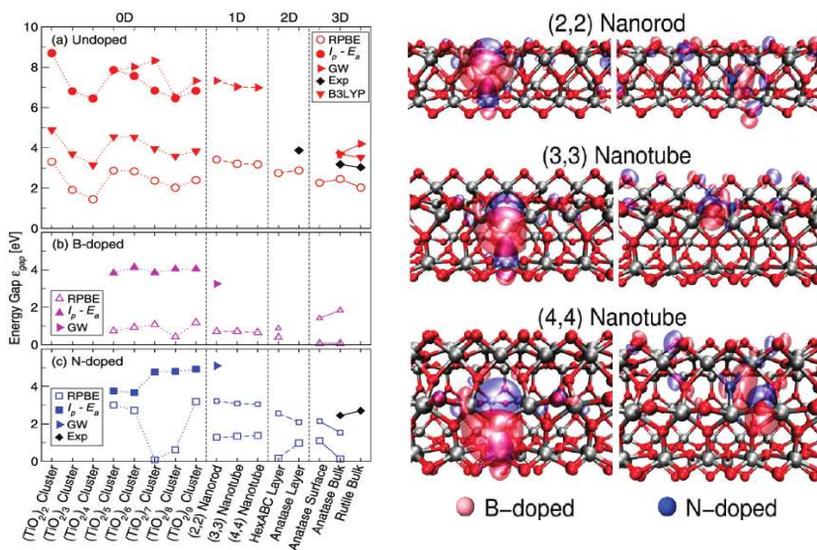
Abstract

Motivated by the world's ever increasing need for cleaner burning fuels and more viable forms of renewable energy, hydrogen production via photocatalysis has been intensely researched as a possible candidate for addressing these issues.

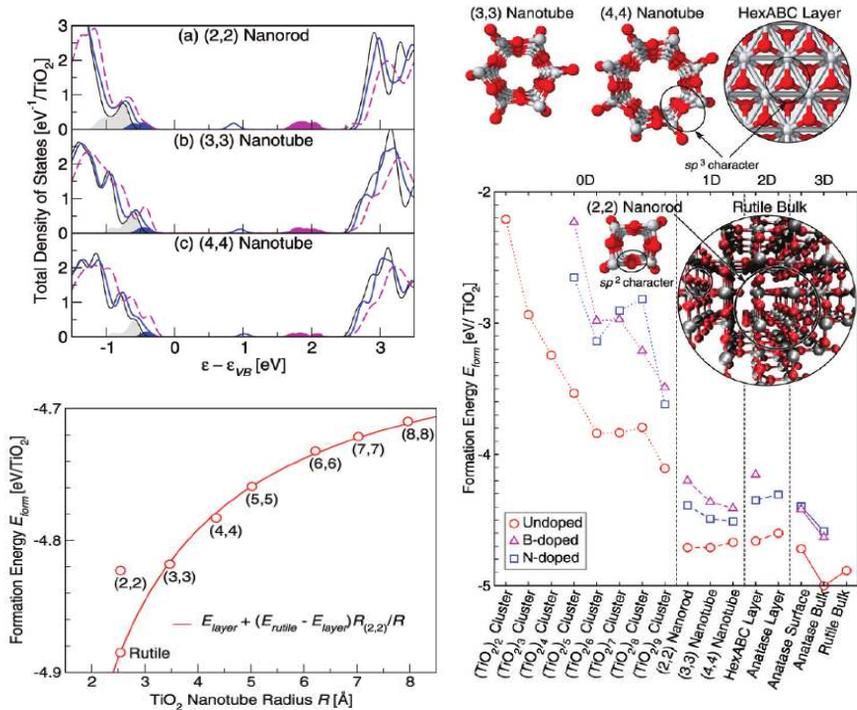
Since the first experimental formation of hydrogen by photocatalysis in the early 1980s [1], TiO₂ has been the catalyst of choice. Reasons for this include the position of TiO₂'s conduction band above the energy of hydrogen formation, the relatively long lifetime of excited electrons which allows them to reach the surface from the bulk, TiO₂'s high corrosion resistance compared to other metal oxides, and its relatively low cost [2-4]. However, the large band gap of bulk TiO₂ (≈ 3 eV) means that only high energy UV light may excite its electrons. This effectively blocks most of the photons which pierce the atmosphere, typically in the visible range, from participating in any bulk TiO₂ based photocatalytic reaction. On the other hand, the difference in energy between excited electrons and holes, i.e. the band gap, must be large enough (≥ 1.23 eV) to dissociate water into hydrogen and oxygen. For these reasons it is of great interest to adjust the band gap ϵ_{gap} of TiO₂ into the range $1.23 \leq \epsilon_{\text{gap}} \leq 2.5$ eV, while maintaining the useful properties mentioned above [5].

With this aim, much research has been done on the influence of TiO₂ nanostructure [6-10] and dopants [5,11-17] on photocatalytic activity. For low dimensional nanostructured materials, electrons and holes have to travel shorter distances to reach the surface, allowing for a shorter quasi-particle lifetime. However, due to quantum confinement effects, lower dimensional TiO₂ nanostructures tend to have larger band gaps[18]. On the other hand, although doping may introduce midgap states, recent experimental studies have shown that boron and nitrogen doping of bulk TiO₂ yields band gaps smaller than the threshold for water splitting [11,12]. This suggests that low dimensional structures with band gaps larger than about 3.0 eV may be a better starting point for doping.

We address one of the main challenges to TiO₂ photocatalysis, namely band gap narrowing, by combining nanostructural changes with doping. With this aim we compare TiO₂'s electronic properties for small 0D clusters, 1D nanorods and nanotubes, 2D layers, and 3D surface and bulk phases using different approximations within density functional theory and GW calculations.



In particular, we propose very small ($R \sim 5 \text{ \AA}$) but surprisingly stable nanotubes with promising photocatalysis and photoreactivity properties. The nanotubes are initially formed from TiO₂ layers with the PtO₂ structure, with the smallest (2,2) nanotube relaxing to a rutile nanorod structure.



We find that quantum confinement effects, as expected, generally lead to a widening of the energy gap. However, substitutional doping with boron or nitrogen is found to give rise to (meta-)stable structures and the introduction of dopant and midgap states which effectively reduce the band gap. Boron is seen to always give rise to n-type doping while depending on the local bonding geometry, nitrogen may give rise to n-type or p-type doping. For undercoordinated TiO₂ surface structures found in clusters, nanorods, nanotubes, layers and surfaces nitrogen gives rise to acceptor states while for larger clusters and bulk structures donor states are introduced.

Methodologies

All DFT calculations have employed the RPBE exchange correlation (xc)-functional [19]. The plane-wave code DACAPO [20,21] was used for structural minimization, the real-space code OCTOPUS [22] for charged calculations, and YAMBO [23] with ABINIT [24] and Pwscf [25] for GW calculations, correcting via the quasi-particle approximation the standard local density eigenvalues. A plane-wave cutoff of 340 eV was used, with a Monkhorst-Pack k-point sampling of $1 \times 1 \times 12$ for TiO₂ nanotubes, where the nanotube axis is parallel to the z-axis, $12 \times 12 \times 1$ for TiO₂ layers and

surfaces, where the normal direction is parallel to the z-axis, and $12 \times 12 \times 12$ for TiO_2 bulk phases. All structures have been relaxed until a maximum force below 0.04 eV/Å was obtained. The occupation of the one electron states was calculated at a temperature of $k_B T \approx 0.1$ eV for the periodic systems and $k_B T \approx 0.01$ eV for the clusters, with all energies extrapolated to $T = 0$ K. Spin unpolarized calculations have been performed for the undoped TiO_2 systems, while spin polarized calculations have been performed for all doped TiO_2 systems, since the unit cells for the doped systems contain an odd number of electrons.

Doping of $(\text{TiO}_2)_n$ clusters has been modeled by substituting a single boron or nitrogen atom in each geometrically inequivalent oxygen site of the most stable isomer to determine the most stable doping site. Only clusters of sufficient size to obtain experimentally realizable doping fractions $\approx 10\%$ ($5 \leq n \leq 9$) have been considered. To model TiO_2 nanotube doping, we have repeated the minimal unit cell four times along the tube axis, and substituted a single boron or nitrogen atom in each geometrically inequivalent oxygen site to obtain the most stable doped structure. In this way, dopant-dopant interactions are minimized by maintaining a dopant separation of approximately 12 Å. This corresponds to experimentally realizable doping fractions of 3.1%, 2.1%, and 1.6% for TiO_2 (2,2) nanorods, (3,3) nanotubes, and (4,4) nanotubes, respectively. Doping of TiO_2 layers, surfaces, and bulks has been similarly modeled by repeating the minimal unit cell twice in each periodic direction, and substituting a single boron or nitrogen atom in each geometrically inequivalent oxygen site to obtain the most stable structure. Experimentally realizable doping fractions of 5.6%, 3.1%, and 3.1% were thus obtained for the layers, surfaces, and bulks respectively.

Projects

- 1) Band-gap correction in metal/organic interfaces.
- 2) Reactivity on transition metal and transition metal oxide nanowires and other nanostructures.
- 3) ORR and OER activities on perovskite cathodes for fuel cells.
- 4) Stability and electronics of MO_2 nanorods and nanotubes.

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Posters

**Workshop Molecular Photoreactivity on Metal-Oxide Surfaces from
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**First principles calculation of CO adsorption on MAu_n⁺-O₂
doped cationic gold-oxygen complexes for M = Ti, Fe (n=3-7)**

E. M. Fernández^{1,*}, M. B. Torres², L. C. Balbás³

¹*Instituto de Ciencia de Materiales, CSIC, Madrid, Spain.*

²*Departamento de Matemáticas y Computación, Universidad de Burgos, Spain.*

³*Departamento de Física Teórica Atómica y Nuclear, Universidad de Valladolid, Spain*

*efernand@icmm.csic.es

Abstract

Bimetallic clusters may exhibit superior catalytic properties compared to pure elements. Here we compare the reactivity of MAu_n⁺-O₂ aggregates towards adsorption of CO for M = Ti, Fe impurities of gold cationic clusters with several sizes.

A first principles study of the CO₂ formation on oxidized doped gold complex MAu_n⁺-O₂ is presented for n = 1, 4-7 and M = Ti, Fe. Starting from the ground state geometry of MAu_n⁺ - O₂ calculated in a previous work [1] we studied the consecutive adsorption of two CO molecules [2].

After the adsorption of the first CO, two type of complexes are preferably formed, depending on the size and impurity M of the initial MAu_n⁺-O₂: a) MAu_n⁺ - O - CO₂ with a preformed CO₂ and an O atom, both bonded to M, and b) MAu_n⁺ - CO₃ with the carbonate CO₃ bonded to M. In case a) two CO₂ can be sequentially desorbed after adsorption of CO, leaving the initial doped gold cluster. In the case b) the adsorption of a second CO induces two competitive processes: one of them involves the formation of an oxalate C₂O₄ bonded to M, and the other one contains two preformed CO₂ molecules bonded to M. In both intermediate equilibrium configurations, desorption of adducts yields the initial MAu_n⁺ cluster.

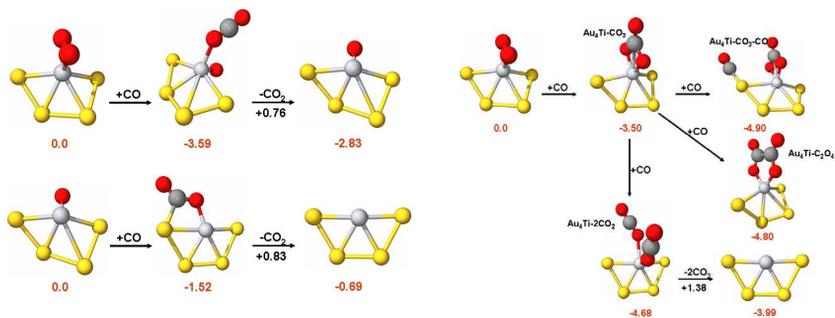


Figure 1. CO adsorption and CO₂ desorption energies over TiAu₄O₂⁺, illustrating two different mechanisms: a) sequential CO adsorption - CO₂ desorption, and b) simultaneous 2CO adsorption - 2CO₂ desorption.

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**Study about some isomers of the SiC₃ and Prediction of
Reactive Sites for
SiC₃H Using Electron Localization Function (ELF)**

Natalia Inostroza^{1,2,*}, M. L. Senent¹, P. Fuentealba³, J. R. Letelier⁴

¹ *Instituto de Estructura de la Materia, C.S.I.C, Departamento de Astrofísica Molecular e Infrarroja, Serrano 121 Madrid 28006, España,*

² *Universidad Andrés Bello, Facultad de Ecología y Recursos Naturales, Departamento de Química, Santiago, Chile,*

³ *Universidad de Chile, Departamento de Física Facultad de Ciencias, Las Palmeras 3425, Nuñoa, Santiago, Chile,* ⁴*Universidad de Chile, Departamento de Ciencia de los Materiales, Facultad de Ciencias Físicas y Matemáticas, Beauchef 850, Santiago, Chile.*

*n.inostroza@iem.cfmac.csic.es

General interests

Theoretical and computational methods for molecular astrophysics and nanotechnologies

Abstract

The rhomboidal SiC₃ isomer has been detected in the expanding envelope of the evolved carbon star IRC+10216 after being identified in laboratory [1]. Previous theoretical studies established various cyclic and linear [2] isomers for C₃Si. The study of these series of molecules is important to understand the interstellar silicon–carbon clusters SiC_nX (X=N, P, H) and for exploring the new silicon–carbon species in laboratory or interstellar space as well for the study of the mechanism of silicon–carbon material formation.

In the present work using the Electron Localization Function, ELF, we studied the nature of the chemical bonds present in these structural isomers and the possible reactivity of them toward the formation of SiC₃H.

The calculation methodologies used to obtain the wave functions have been B3LYP/6-311G (*d,p*). To obtain representative functions of our systems has been necessary to consider the symmetry of each species. For the analysis and understanding of the electron localization function (ELF) [3] we used the codes TOPMOD.

A separation of the ELF functions into its α -spin and β -spin contributions has been performed. The results show that the ELF separation yields complementary information about the localization of the unpaired electron. From the ELF α and ELF β isosurfaces we can see that in the singlet state the more important contributions in the bond are the same in all isomers, however, they are different in the triplet state.

Methodologies

We are using DFT implemented in the codes TODMOD and MOLPRO. We use original codes for obtained spectroscopic properties.

Projects

We are interested in the interface process study to understand grain surfaces problems.

Acknowledgments

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The authors acknowledge to Professor Pavel Rosmus for helping and contribution.

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**A slip model for micro/nano Poiseuille gas flows induced by
body forces**

Q.D. To, C. Bercegeay, G. Lauriat, C. Léonard^{*}, and G. Bonnet

*Université Paris-Est, Laboratoire Modelisation et Simulation Multi
Echelle, FRE 3160 CNRS, 5 Boulevard Descartes, 77454 Marne-la-Vallée
Cedex 2, France*

^{*}celine.leonard@univ-mlv.fr

Abstract

A slip model for gas flows in micro/nano channels induced by external body forces is derived based on Maxwell's collision theory between gas molecules and the wall. The model modifies the relationship between slip velocity and velocity gradient at the walls by introducing a new parameter in addition to the classic Tangential Momentum Accommodation Coefficient. Three dimensional Molecular Dynamics simulations of Poiseuille helium gas flows between copper flat walls with different channel widths are used to validate the model and to determine this new parameter. The helium-copper interaction forces are derived from Lennard-Jones potential.

Methodologies

Molecular Dynamics simulations using LAMMPS [1].

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**Molecular dynamics simulations of liquid water models:
viscosity calculation**

J.S. Medina,^{1,2,*} R. Prosimi,¹ P. Villarreal,¹ G. Delgado-Barrio,¹ Gabriel Winter,² B. González,² J.V. Alemán,³ C. Collado,³ J.L. Gómez,³ P. Sangrá,³ and J.J. Santana.³

¹ *Instituto de Física Fundamental (CSIC), Serrano 123, 28006 Madrid, Spain*

² *SIANI, ULPGC, Edif. Polivalente, Campus Universitario de Tafira, 35017 Las Palmas de G. Canaria, Spain*

³ *Facultad de Ciencias del Mar, ULPGC, Campus Universitario de Tafira, 35017 Las Palmas de G. Canaria, Spain*

*email: tlazcala@yahoo.es or jsma@imaff.cfmac.csic.es

General interests

Theoretical framework: Equilibrium Classical Molecular Dynamics. Green-Kubo equations. Transport coefficients.

System under study: liquid water.

Abstract

Molecular dynamics simulations were carried out for liquid water in the NVE ensemble for calculating shear and bulk viscosities. We used different intermolecular potential functions for the water dimer: the empirical SPC/E and SPCFw models and the *ab initio* NCC one. It was found that including the intramolecular stretching terms the obtained viscosity values are in overall much better agreement than that of the rigid SPC/E model, compared to earlier and recent experimental data available. The effect of the intramolecular degrees of freedom on transport properties of liquid water was analysed and incorporation of polarizability was discussed for further improvements. Such models, based on *ab initio* data, have been recently developed, and their incorporation for the viscosity calculations is proposed.

Methodologies

Equilibrium Classical Dynamics simulations in periodic boundary conditions of 256 water molecules with empirical (SPC/E) and/or *ab initio* (NCC) models using standard opensource packages: MOLLY, GROMACS.

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**Workshop Molecular Photoreactivity on Metal-Oxide Surfaces from
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**Adsorption and interaction of hydrogen and oxygen at
Au/TiO₂ nanocatalysts**

L. M. Molina^{1,*}, M. J. López¹, J. A. Alonso¹ and B. Hammer²

¹ *Departamento de Física Teórica, Universidad de Valladolid (Spain)*

² *Department of Physics and Astronomy, University of Aarhus (Denmark)*

*lmolina@fta.uva.es

General interests

DFT simulations of activity of nanostructured gold catalysts.

Abstract

Gold nanocatalysts have been recently found interesting for a broad number of reactions, including CO oxidation, propene epoxidation, etc... This fact, together with the well-known photocatalytic properties of TiO₂, make interesting the first-principles study of the interaction of various reactant species with TiO₂-supported gold nanoparticles. By performing *ab-initio* DFT simulations, we have studied the interaction of H₂ and O₂ on anatase-TiO₂ supported gold nanoparticles. Starting with an analysis of the interaction between the diatomic molecules and the catalyst, we have further investigated their possible dissociation pathways. Hydrogen is found to easily dissociate at the Au/TiO₂ perimeter interface, and to spillover to the TiO₂ support forming surface hydroxyl -OH groups. Then, molecular oxygen strongly interacts with those surface hydroxyls, forming reactive peroxy -OOH species as well as water. Such O₂ dissociation pathway is preferred with respect to direct dissociation at the Au nanoparticle.

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**Theoretical study of the adsorption of Ni on Anatase (001)
surface**

E. Escamilla-Roa, V. Timón and A. Hernández Laguna

*Estación Experimental del Zaidín (CSIC), C/ Prof. Albareda n° 1, 18008
Granada (Spain)*

Abstract.

In nature, TiO₂ shows three polymorphs, namely: Rutile, Anatase, and Brookite. TiO₂ nano-crystals appear to prefer the meta-stable Anatase phase rather than Rutile. Rutile and especially Anatase have been extensively investigated as supports for gold nanoparticles in catalytic CO oxidation. Besides, Ni is adsorbed on different surfaces of Rutile and Anatase, and is also used in CO oxidation and methanation. Their electronic properties, structure and composition on different surfaces were studied. Ni deposited on (110) surface of Rutile has been studied by different spectroscopic techniques,¹ a charge transfer from the surface to the Ni, at low coverage, was found, depending on the previous preparation of the surface. This charge transfer plays an important role in the chemisorption of Ni, and its catalytic properties. Furthermore, using similar techniques referred by [1], CO adsorbed on Ni-TiO₂ (110) and clean surfaces were also studied, finding there is a low charge transfer from the Ni to the surface.² Recently, using X-ray Photoelectron Spectroscopy on Ni nano-clusters adsorbed on TiO₂ (001) surface,³ at low coverage, triplet atomic states of Ni were found, with a low charge transfer, without transport of mass between Ni and the surface. These works motivate us to undertake a DFT theoretical study of periodic systems about the adsorption of Ni on Anatase (001) surface.

DMOL3, included in the Material Study package, was used. Numerical double- ζ polarization basis set and semicore-pseudopotentials were used. GGA with Revised PBE correlation exchange functional were also used. To create the surface, a vacuum was determined by enlarging the *c* axis of Anatase up to find a constant 2 \times 2 \times 1 (001) surface energy. Four and eight Ti and O layers, respectively, were included in the slab, being four internal layers of O and two of Ti fixed in the optimization procedures.

Ni adatom geometry was optimised at different positions on the surface. At the minimal energy position, in the middle of a TiO₂ hole, potential energy curves of the singlet and triplet Ni atoms approaching to the surface (S) were calculated. At a distance of 3.7 Å of the average plane of the top oxygens, the most stable system turns

out to be the $^3(\text{S}\cdots\text{Ni})$, finding a spin density of approximately 2.0 for the Ni. A maximum of the potential is found at 3.0 Å, with a barrier of 0.02 eV. From that maximum, the potential decreases up to find a minimum at 0.5 Å, with a difference of energy between the large distance energy of 2.25 eV, indicating a chemisorption process. Some 0.4 and 1 charge and spin density, respectively, were transferred from the Ni to the surface. The $^1(\text{S}\cdots\text{Ni})$ system presents an energy of 1 eV more unstable than the triplet system at a distance of 3.7 Å. No barrier at large distance was found. The energy decreases up to find a minimum at the same position and total energy than the triplet system. A charge transfer of 0.2 was also found. Following these results, an oxidation of the chemisorbed Ni is produced, with distinct charge transfer in both states.

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**Workshop Molecular Photoreactivity on Metal-Oxide Surfaces from
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**H₂ reactivity on gold nanostructures: Cluster and
embedding approach**

A. Zanchet^{1,*}, A. Dorta¹, A. Aguado², M. Paniagua², Fernando Flores³, O. Roncero¹

¹ *Inst. Física Fundamental, C.S.I.C., 28006 Madrid (Spain)*

² *Dpt. de Química Física Aplicada, Universidad Autónoma de Madrid, 28049 Canto Blanco (Spain)*

³ *Dpt. de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, 28049 Canto Blanco (Spain)*

*zanchet@imaff.cfmac.csic.es

Abstract

Gold is the noblest of the transition metals and presents a very low reactivity and catalytic activity in bulk. However, in small gold nano-structures, the reaction barriers get lower for many reactions and the chemisorption wells deeper. There is a recent increasing interest in determining their catalytic properties because their possible industrial impact [1]. The dissociation of H₂ on nanowires [2] and clusters [3] have been studied recently, showing no barrier for the reaction. In order to understand in detail the factors determining such high reactivity and the transition from clusters to bulk, here we present a study for different coordinations of gold atoms on model systems, linear and planar, paying special attention to their fluxionality [4]. It is found that apart from the coordination of gold atoms, being a fundamental factor, the reactivity is modulated by the hybridization of the gold atoms involved, explaining the reactivity change from planar to linear configurations or edges.

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**Wave Function-Based Correlation Methods for Extended
Systems:
Application to the interaction of He with a rutile TiO₂(110)
surface**

Néstor F. Aguirre¹, Alexander O. Mitrushchenkov² and M. Pilar de
Lara-Castells^{1*}

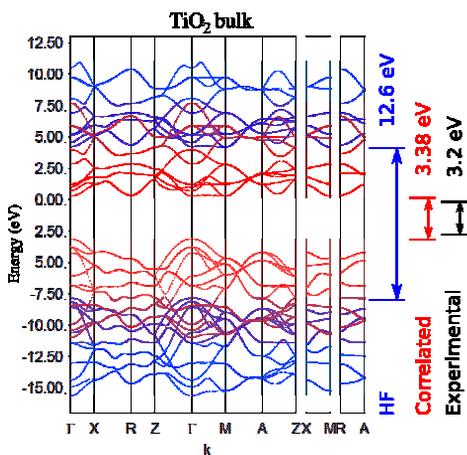
¹ *Departamento de Física Atómica, Molecular y de Agregados, C.S.I.C.,
Madrid (Spain)*

² *Laboratoire de Modélisation et Simulation Multi Echelle (MSME), FRE
3160 CNRS, Université Paris-Est Marne-la-Vallée, Paris (France)*

*delara@imaff.cfmac.csic.es

General Interests

My Ph.D. Thesis project involves quantum-mechanical studies on: (1) O₂ photo-desorption from metal-oxide surfaces; (2) He nanodroplet mediated "cold-attachment" of molecular/atomic species on metal-oxide surfaces. As a paradigmatic system to study surface photo-chemistry at a fundamental level and in photo-catalysts, we continue previous first-principle studies on molecular oxygen photo-desorption from a reduced TiO₂ surface [1, 11] in which efficient high-level ab-initio approaches were applied to calculate the quasi-adiabatic states and electronic couplings that emerge from localized ionic substrate/absorbate interactions [9]. In the last year, methodological enhancements of the previous local cluster approach were realized by using special localization techniques [2] and applied to the calculation of TiO₂ bulk correlated bands and charge population in



oxygen-deficient TiO_2 [3]. At present, my work is focused on extending and applying these local-correlation-cluster (LCC) techniques to calculate the molecule/surface interaction potentials.

Abstract

The purpose of this work is the calculation of the interaction energy between a Helium atom and the rutile $\text{TiO}_2(110)$ surface. Since the interaction of He with a metal-oxide surface is mainly dispersive, well depth being typically of about 10 mEv [4], a high accuracy is required to obtain reliable potential energy surfaces. The inclusion of dynamic correlation (e.g., using the Møller-Plesset (MP2) or Coupled-Cluster(CCSD) levels of theory) is very important. Moreover, optimized basis sets need to be used to minimize the basis set superposition error (BSSE) [5], which is quite large otherwise. This study is motivated by an attempt at theoretical modelling of "soft-landing" processes [6] on oxide surfaces through the embedding of targeted molecules and metal atoms (or bimetallic clusters) into He nanodroplets, as proposed by Vilesov, et al. in a previous experimental study [7].

In my poster presentation, I will show results for the He/ TiO_2 interaction obtained by using three approaches:

1. Standard periodic calculations of the two-dimensional extended systems using standard slab models (see for example Refs. 8,9) as implemented in the CRYSTAL06 code, employing Hartree-Fock (HF), Density-Functional-Theory (DFT) and hybrid HF/DFT electronic structure methods, including relaxation of the substrate and varying both the super-cell size and the number of atomic layers within the slab model.
2. "Classical" embedding methods by using a finite cluster to simulate the extended system and employing hydrogen atoms to saturate the dangling bonds, using both MP2 and CCSD treatments to introduce the correlation, as implemented in the MOLPRO code.
3. "Cluster-in-solid" embedded approaches (see e.g., Ref. 2): A basic feature of this approach is that the correlation is introduced with post-HF wave-functions methodologies on a selected finite cluster cut from the extended periodic system. In short, the localized Wannier functions of the periodic system are projected out on the cluster basis functions. The HF periodic solution is then used to define a HF-type embedding potential to model the effect of the infinite environment in the adsorbate/substrate region. After which correlated methods, including MP2 and CCSD treatments and their local versions (MOLPRO), can be used.

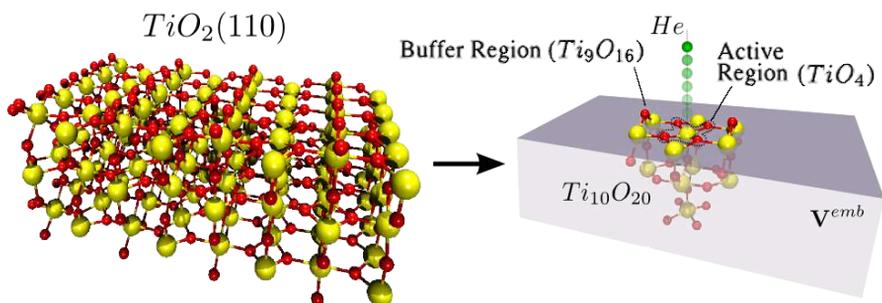
It should be stressed that cluster-in-solid embedded results strongly depend on how the electrostatic part of the embedding potential is extended to the adsorbate (He) basis functions. In fact, this point is the main novelty of our approach and turns out to be the most important one. Work is in progress to design larger clusters which, by using DF-LMP2 and DF-LCCSD methods, with hydrogen-saturated model or embedding schemes, should provide even more accurate interactions.

Methodologies

Molecule (atom)/surface interaction potentials are calculated by wave-function-based correlation methods by using either standard cluster models (i.e., saturated with hydrogen atoms) or "cluster-in-solid" embedding techniques (using both HF and DFT approaches to model the extended system). The local implemented version of the "cluster-in-solid" technique includes, among other enhancements, the possibility of considering the symmetry of the system and then employing very large aggregates. Both time-dependent and energy-domain treatments are used for the nuclear motion. Quasi-diabatic-states and electronic couplings are calculated mainly by means of the non-orthogonal configuration-interaction method (see for example, Ref. 9). Doped He clusters are simulated by quantum-chemistry-like techniques (see for example, Ref.10).

Projects

Besides the above-mentioned projects (see general interests), we seek to combine ab-initio Molecular Dynamics and DFT approaches with wave-function-based correlation methods (i.e., accounting for excited states and electronic couplings). As a natural extension to previous calculations of excited states for O_2 adsorbed on a reduced TiO_2 surface by using a classical embedding method [1,11], we will apply the local version of the "cluster-in-solid" embedding technique to the calculation of the O_2 - TiO_{2-x} potential energy surfaces in the ground and excited states. This will be followed by a time-dependent treatment for the nuclear motion, trying to account for the migration of holes and electrons through the bulk and their subsequent quenching. Our main goal within this project is to include the description of the substrate-mediated excitation mechanism within the first-principle study of O_2 photo-desorption from TiO_2 , providing a way to interpret the most recent experiments at Brookhaven Nat. Lab. [13].



Acknowledgments

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**Workshop Molecular Photoreactivity on Metal-Oxide Surfaces from
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**Metal/organic interfaces and molecular electronics: IDIS
model, molecule charging energy and transport energy gap.**

Enrique Abad^{1,*}, César González², José Ortega¹, Fernando Flores¹

¹*Dpto de Física Teórica de la Materia Condensada, Universidad Autónoma
de Madrid, 28049, Madrid, Spain*

²*Dpto de Superficies y Recubrimientos, Instituto de Ciencia de Materiales
de Madrid, 28049, Madrid, Spain*

*enrique.abad@uam.es

Abstract

In this work we combine a DFT-LDA calculation of the structural and electronic properties of metal/organic interfaces with an analysis of the interface barrier formation based on the charge transfer and the organic Charge Neutrality Level, as described by the Induced Density of Interface States model [1]. This allows us to determine the charging energy (U^{eff}) of the molecule at the interface, correct the DFT transport energy gap and obtain a realistic metal/organic barrier height. This method has been applied to a C_{60} molecule sandwiched between two Au tips, a C_{60} molecule over an Au(111) surface [2], and has been extended to deal with a full $C_{60}/\text{Au}(111)$ monolayer [3].

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3. E. Abad, J. Ortega, F. Flores, Submitted to Appl. Surf. Sci..

List of registered participants

Abad, Enrique

Dep. de Fis. T. de la Materia Condensada
Universidad Autónoma de Madrid
28049 Madrid, Spain
enrique.abad@uam.es

Bernhardt, T. M.

Institute of Surface Chemistry and Catalysis
Albert-Einstein-Allee 47, University of Ulm
89069 Ulm, Germany
thorsten.bernhardt@uni-ulm.de

Chambaud, Gilberte

Université Paris-Est, Marne la Vallée
FRE 3160-CNRS, Cité Descartes
77454, Marne-la-Vallée, France
gilberte.chambaud@univ-mlv.fr

Díaz Blanco, Cristina

Departamento de Química C-13
Universidad Autónoma de Madrid
28049 Madrid, Spain
cristina.diaz@uam.es

Fernández Sánchez, Eva María

Instituto de Ciencia de Materiales
Consejo Superior de Inv. Científicas, CSIC
Madrid, Spain
efernand@icmm.csic.es

Flores Sintas, Fernando

Dep. de Fis. T. de la Materia Condensada
Universidad Autónoma de Madrid
28049 Madrid, Spain
fernando.flores@uam.es

Aguirre Castiblanco, Néstor Fabián

Instituto de Física Fundamental, CSIC
C/ Serrano 123
28006 Madrid, Spain
nfaguirec@imaff.cfmac.csic.es

Campos Martínez, José

Instituto de Física Fundamental, CSIC
C/ Serrano 123
28006 Madrid, Spain
jcm@imaff.cfmac.csic.es

Delgado Barrio, Gerardo

Instituto de Física Fundamental, CSIC
C/ Serrano 123
28006 Madrid, Spain
gerardo@imaff.cfmac.csic.es

Doltsinis, Nikos L.

Department of Physics
King's College London
London WC2R 2LS, United Kingdom
nikos.doltsinis@kcl.ac.uk

Fernández Sanz, Javier

Dpto de Química Física
Universidad de Sevilla
E-41012, Sevilla, Spain
sanz@us.es

González Lezana, Tomás

Instituto de Física Fundamental, CSIC
C/ Serrano 123
28006 Madrid, Spain
tglezana@imaff.cfmac.csic.es

Guitou, Marie

Université Paris-Est, Marne la Vallée
FRE 3160-CNRS, Cité Descartes
77454, Marne-la-Vallée, France
marie.guitou@univ-paris-est.fr

Hernández Hernández, Marta Isabel

Instituto de Física Fundamental, CSIC
C/ Serrano 123
28006 Madrid, Spain
marta@imaff.cfmac.csic.es

Inostroza Pino, Natalia

Instituto de Estructura de la Materia, C.S.I.C.
Dep. de Astrof. Molecular e Infrarroja
Serrano 121, Madrid 28006, Spain
n.inostroza@iem.cfmac.csic.es

Klüner, Thorsten

Carl von Ossietzky University Oldenburg
Carl-von-Ossietzky Str. 9-11
26129 Oldenburg, Germany
Thorsten.Kluener@uni-oldenburg.de

Lagunas Alonso, Ana Rosa

CENER (Centro Nacional de E. Renovables)
C/Ciudad de la Innovación 7
31621 Sarriguren –Navarra, Spain
alagunas@cener.com

Léonard, Celine

Université Paris-Est, Marne la Vallée
FRE 3160 CNRS
77454 Marne-la-Vallée Cedex 2, France
celine.leonard@univ-mlv.fr

Linguerrri, Roberto

Université Paris-Est, Marne la Vallée
FRE 3160 CNRS
77454 Marne-la-Vallée Cedex 2, France
linguerr@univ-mlv.fr

Halo, Migen

Dipartimento di Chimica IFM
Universita' degli Studi di Torino
Torino, Italy
migen.halo@unito.it

Hernández Laguna, Alfonso

Estación Experimental del Zaidín, CSIC
C/ Prof. Albareda 1
18008 Granada, Spain
alfonso.hernandez@eez.csic.es

Jedidi, Abdesslem

Laboratoire de Chimie Théorique
Université Pierre et Marie Curie
3 rue Galilée 94200 Ivry sur Siene, France
jedidi@lct.jussieu.fr

Kosloff, Ronnie

Fritz Haber Res. Center for Mol. Dynamics
Hebrew University of Jerusalem
91904 Jerusalem, Israel
ronnie@fh.huji.ac.il

Lara Castells, María Pilar de

Instituto de Física Fundamental, CSIC
C/ Serrano 123
28006 Madrid, Spain
delara@imaff.cfmac.csic.es

Lewis, James P.

West Virginia University
Department of Physics
Morgantown, WV 26506-6315, USA
james.lewis@mail.wvu.edu

López Durán, David

Instituto de Física Fundamental, CSIC
C/ Serrano 123
28006 Madrid, Spain
davidl@imaff.cfmac.csic.es

Martínez, José Ignacio

Dep. de Fís. T. de la Materia Condensada
Universidad Autónoma de Madrid
28049 Madrid, Spain
joseignacio.martinez@uam.es

Mitrushchenkov, Alexander O.

Université Paris-Est, Marne la Vallée
FRE 3160 CNRS
77454 Marne-la-Vallée Cedex 2, France
alexander.mitrushchenkov@univ-mlv.fr

Müller, Carsten

Institute for Chemistry and Biochemistry
Freie Universität Berlin
Berlin, Germany
carsten@chemie.fu-berlin.de

Pascual, José Luis

Dep. de Quím. Fis. Aplicada
Universidad Autónoma de Madrid
28049 Madrid, Spain
joseluis.pascual@uam.es

Prosmi, Rita

Instituto de Física Fundamental, CSIC
C/ Serrano 123
28006 Madrid, Spain
rita@imaff.cfmac.csic.es

Sautet, Philippe

Ec. N. Sup. de Lyon and CNRS, U. of Lyon
46 Allée d'Italie
F-69364 Lyon Cedex 07, France
philippe.sautet@ens-lyon.fr

Timón Salinero, Vicente

Estación Experimental del Zaidín, CSIC
C/ Prof. Albareda nº 1
28008 Granada, Spain
vicente.timon@eez.csic.es

Medina Álvarez, Juan

Instituto de Física Fundamental, CSIC
C/ Serrano 123
28006 Madrid, Spain
jma@imaff.cfmac.csic.es

Molina Montes, Luis M.

Departamento de Física Teórica
Universidad de Valladolid
Valladolid, Spain
lmolina@fta.uva.es

Ortega, José

Dep. de Fís. T. de la Materia Condensada
Universidad Autónoma de Madrid
28049 Madrid, Spain
jose.ortega@uam.es

Prezhdo, Oleg

University of Washington
Department of Chemistry
Seattle, WA 98195-1700, USA
prezhdo@u.washington.edu

Roncero Villa, Octavio

Instituto de Física Fundamental, CSIC
C/ Serrano 123
28006 Madrid, Spain
roncero@imaff.cfmac.csic.es

Solá, Ignacio R.

Departamento de Química Física I
Universidad Complutense de Madrid
28040 Madrid, Spain
isola@quim.ucm.es

Valdés de Luxán, Álvaro

Leiden Institute of Chemistry
Leiden University
2300RA Leiden, The Netherlands
avdeluxan@chem.leidenuniv.nl

Villarreal Herrán, Pablo

Instituto de Física Fundamental, CSIC
C/ Serrano 123
28006 Madrid, Spain
p.villarreal@imaff.cfmac.csic.es

White, Michael G.

Department of Chemistry
Stony Brook University
Stony Brook, NY, USA
mgwhite@bnl.gov

Zanchet, A.

Instituto de Física Fundamental, CSIC
C/ Serrano 123
28006 Madrid, Spain
zanchet@imaff.cfmac.csic.es

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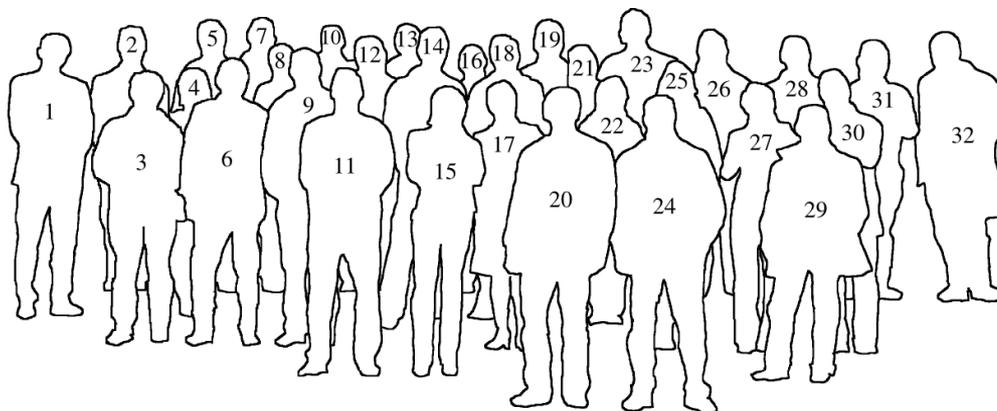
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Molecular Photoreactivity on Metal-Oxide Surfaces from First-Principles

Photocatalysis and Photovoltaics

FPMPMO-2009





**1. Thorsten Bernhardt 2. Michael G. White 3. José Luis Pascual 4. Rita Prosmiti 5. James P. Lewis 6. Philippe Sautet
7. Jedidi Abdesslem 8. Vicente Timón 9. Gerardo Delgado Barrios 10. Álvaro Valdéz de Luxán 11. José Ortega Mateo
12. Alfonso Hernández Laguna 13. José Campos Martínez 14. Oleg Prezhdo 15. María Pilar de Lara Castells
16. Ignacio Solá 17. Gilberte Chambaud 18. Enrique Abad 19. Thorsten Klüner 20. Alexander O. Mitrushchenkov
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31. Luis M. Molina 32. Octavio Roncero**

