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1. RESUME DE LA PROPOSITION DE PROJET / EXECUTIVE SUMMARY

Grapho (« I write » in greek) is a coordinated experimental-theory project aiming at a better understanding of the adsorption-desorption as well as the reaction of hydrogen and oxygen on graphite and graphene (named gg collectively). The project encompasses both physisorption and chemisorptions processes. Physisorption is important for the development of graphene based nanotechnologies like NEMS (Nano-ElectroMechanical-Systems) as well as for grain interstellar chemistry. Chemisorption is relevant for nanoelectronic devices which use a combination of conducting graphene with insulator graphane, the hydrogenated form of graphene. It is also involved in the plasma wall interactions in nuclear fusion facilities. The experimental part of the project involves the FORMOLISM experimental set-up at LERMA in Cergy : a cold (<10 K) sample in a UHV chamber is exposed to molecular or atomic beams of hydrogen and/or oxygen. Probing the evolution of the incident or nascent populations by mass spectroscopy or laser provides insight in the dynamical processes taking place on the surface: adsorption, desorption, reaction.

The theoretical part of the work will be undertaken by ISMO in Orsay and LCAR in Toulouse, coordinator of the project. The main objective is the development of a proper description of a dissipative process, then solving quantitatively the problem of the sticking of atoms on gg surfaces. We will evaluate the capability of different approaches (classical, mixed classical-quantum and quantum) in the treatment of dissipative processes. This will involve potential energy surface calculations (in particular for the oxygen case), force field computation, and then dynamical calculations at different levels of approximations. Sticking probabilities and desorption rates will thus be obtained as a function of incoming species energy and surface temperature.

2. CONTEXTE, POSITIONNEMENT ET OBJECTIFS DE LA PROPOSITION / CONTEXT, POSITION AND OBJECTIVES OF THE PROPOSAL

2.1. CONTEXTE ET ENJEUX ECONOMIQUES ET SOCIETAUX / CONTEXT, SOCIAL AND ECONOMIC ISSUES

Gas-surface interactions are ubiquitous in many technological processes, so that the present project is relevant from a technological point of view for several reasons.

First, it has relevance in the field on nanotechnologies because graphite and graphene are very similar with respect to the processes considered here. Indeed, the weak van der Waals interaction between graphene layers in graphite do not significantly modifies adsorption [Ferro02] as well as sticking properties of the surface [Lepetit11b]. The present project will often address simultaneously graphene and graphite, which we be referred to as “gg” in the following. Our study has implications in nanotechnologies for at least two aspects.

The first is the study of physisorption which is at the heart of the development of (possibly toxic) gas sensors. These devices rely on mass detection of adsorbates on membranes using electromechanical resonators. Indeed, such electromechanical resonators with high quality

factors are widely used to measure the masses and other properties of adsorbed layers by monitoring changes in the device resonance frequency. Reduced at the nanoscale, such devices have demonstrated high mass sensitivity, down to the level of a few adsorbed atoms [Yang11]. Recently, a new generation of graphene based mass sensors has appeared [Schedin07, Bachtold08]. Operated at low temperatures, such devices are very sensitive detectors of stuck atoms and molecules and can reach the zeptogram accuracy limit. Such low temperature conditions are also the ones encountered in cold interstellar clouds.

The second is the study of chemisorption, which leads to the formation of graphane [Elias09]. This hydrogenated material induces a change of the hybridization of the carbon atoms from sp^2 to sp^3 . This induces a local change of the electrical properties of the material from a conductive to a non-conductive state. This new material therefore opens the way for tuning the electrical properties of materials which could be building blocks of graphene based new electronic devices. Band gap opening inducing the conductive-isolating transitions has been obtained from patterned hydrogenation [Balog10]. Similar hydrogenation studies were performed for graphene on transition metals [Ng10].

Finally, in the frame of the development of nuclear fusion reactors, let us mention that numerous studies have focused on the problem of hydrogen-graphite interaction, with the objective of controlling better the erosion of graphite walls in fusion devices [roth91,roth08]

But beyond these technological issues, the present project is a fundamental one, aiming at a better understanding of hydrogen and oxygen sticking processes on carbonaceous grains.

In the interstellar medium, the role of dust grains and reactions at their surface is nowadays recognized as very important in the astrophysics and astrochemistry communities. The codes that they are developing to describe the evolution of interstellar media include surface assisted reactions (see review [Wakelam10]). As an example, it has been proposed that the large abundance of molecular hydrogen in the universe is a result of atomic hydrogen combining on interstellar dust grains [Gould63, Lepage09], which are known to have graphitic components [Li05]. It has been suggested that this reaction is of the Eley-Rideal type, where an H atom in the gas phase collides and reacts with an H atom adsorbed onto the dust grain, forming H_2 . It is also possible that two adsorbed H atoms could diffuse on the dust grain and react via a Langmuir-Hinshelwood mechanism. But both mechanisms require that one or more H atoms first stick to these dust grains, which is one of the focus of the present project. A second example is the reaction from O+H reactants leading to the formation of the hydroxyl radical and subsequently to the formation of water, as assisted by surfaces of bare dust grains present in the interstellar medium.

2.2. POSITIONNEMENT DU PROJET / POSITION OF THE PROJECT

The project objective is to undertake in a concerted manner at the LCAR, LERMA-LAMAp ISMO laboratories, theoretical (LCAR, ISMO) as well as experimental (LERMA-LAMAp) studies of the dynamical steps leading to adsorption and to desorption of atomic and molecular species on/from surfaces. These are the most elementary and fundamental

processes that takes place at a gas-surface interface. The dynamical view of the adsorption step corresponds to trapping and sticking.

The question is how atomic and molecular species present in the gas-phase above the substrate surface can adsorb/desorb onto/from this surface. Adsorption is very often the limiting initiating process of different atomic and molecular mechanisms assisted or catalyzed by surfaces, such as reactive processes leading to molecule formation. The interaction of hydrogen atom with sp^2 carbon systems as a graphene sheet or the upper carbon layer of a graphite surface is a challenging system for many applications. Among them let us mention the modification through controlled hydrogen adsorption of the electronic properties of a graphene sheet, or of its mechanical properties as a membrane, or the way sp^2 carbon surface and gaseous H atoms participate in the copious quantity of molecular hydrogen formed in the diffuse interstellar medium, opening the questions of H adsorption probability in the low temperature regime.

The adsorption takes place through trapping and sticking processes ; there are dynamical processes that imply energy dissipation. The system formed by H atoms and an sp^2 carbon layer can be thought as one of the simplest systems to address this question of dissipation. This is a challenging benchmark system. Our consortium feels able, on collaborative and concerted way, to address a few debated questions and to give answers on several questions. The project includes addressing the questions of energy dissipation in the elementary adsorption step, as well as in the elementary desorption process for the H atom on graphenic/graphitic substrate. H atom on a graphene layer forms a physical as well as a chemical bond as a function of temperature ; the two regimes will both be considered. We will also address the questions of molecular hydrogen interaction with graphenic/graphitic surface. An extension to another system of very strong interest for applications is also proposed. It concerns the study of physical adsorption of atomic oxygen and molecular oxygen on graphene/graphite surfaces. The elementary process of surface assisted molecular formation, in the present case O and H, will also be investigated, both experimentally and theoretically, focussing on the physisorption regime and the Langmuir-Hinshelwood mechanism.

2.3. ÉTAT DE L'ART / STATE OF THE ART

The present project aims at achieving improvements on our understanding and ways to model sticking with quantum methods. Concerning H sticking on gg, some basic facts are well established. Electronic structure calculations have shown [Jeloaica99, Sha02, Ivanovskaya10] that when hydrogen chemisorbs onto a graphene/graphite surface, the carbon atom closest to the hydrogen puckers out of the plane of the surface, as a result of a change in the hybridization of the C orbitals from sp^2 to sp^3 . As a result of this lattice distortion, there is a barrier to chemisorption on the order of 0.2 eV. Thus, in the low energy regime characterizing cold interstellar media, chemisorption is energetically forbidden, and any adsorbed H is likely to be physisorbed, as there is no barrier to this process. The physisorption well is about 40 meV deep, and has been characterized by the selective adsorption resonances observed in experimental studies of hydrogen atom scattering from

graphite [Ghio80], as well as from recent, accurate electronic structure calculations [Bonfanti07, Ferullo11].

Several theoretical studies have estimated that the probability for sticking into this physisorption well at low energies is on the order of a few percent [Buch89, Medina08, Lepetit11a]. However, for specific values of the incoming atom's energy, selective adsorption resonances can occur. Particles trapped near the surface in these long lived quasi-bound states can dissipate energy by exciting vibrations of the substrate, eventually sticking. For the case of hydrogen physisorption on graphite, it was predicted that the corrugation of the surface could lead to enhanced sticking via diffraction mediated selective adsorption [Medina08]. More recently, a study involving a more realistic phonon model for the case of graphene, produced large sticking probabilities, close to 1 at low collision energies and for low surface temperature [Lepetit11b].

These trapped or stuck particles can diffuse on the substrate for some time, and engage in chemistry, until they eventually desorb, with a rate determined by the substrate temperature. Quantum scattering calculations have shown that the Eley-Rideal cross-sections for H₂ formation involving a physisorbed target H atom is large [Sha02b, Martinazzo06a]. Other quantum scattering calculations have also shown that Langmuir-Hinshelwood cross-radii are large in the physisorption regime [Morisset05].

Electron-hole excitations have already been considered in the group of Peter Saalfrank, recent examples are [Monturet10, Tremblay11]. These studies were limited however to metals. Additionally, information about the non adiabatic couplings is obtained from density functional theory. The approach proposed here is different and rely on a minimum albeit ab-initio representation of the wavefunction.

Concerning H sticking in the chemisorption case, several approaches have been considered. Classical models were performed in [Kerwin06, Kerwin08]. Their estimated value for the sticking probability into this chemisorption well is of the order of a few percent which is smaller than the experimental values [Zecho02]. Quantum calculations with a simplistic phonon model performed in [Sha05] provide a sticking probability in the same order as of the experimental measurements. A fully quantum with a more realistic phonon models and one dimensional H-surface interaction was developed by a member of the ISMO team [Morisset08, Morisset09]. It provided results in good agreement with experimental data [Zecko02]. More recently, a mixed quantum-classical model was also developed [Morisset10]. Quantum scattering calculations have shown that the Eley-Rideal cross-sections for H₂ formation are large for both physisorbed H as mentioned above and chemisorbed [Sha02b, Morisset03, Martinazzo06b]. Desorption of these chemisorbed species has been studied in combined experimental/modeling works [Baouche09, Gavardi09].

Concerning O physisorbed on the gg surface: Physisorption of atomic oxygen involves the ground open shell O^{3P} electronic state. This regime is widely unknown. It is however of major interest in various domains of application among them physics and chemistry in the interstellar medium. The ISMO team has already produced a preliminary study for the O physisorption energy, based on a Density Functionnal Theory (DFT) calculation and an ab

the capability of different approaches (classical, mixed classical-quantum and quantum) in the treatment of dissipative processes. The present project mainly concerns a benchmark process, sticking, on a benchmark system atomic H on an graphitic/graphenic sp^2 carbon system. On this system, several topics will be considered closely.

One difficulty is to couple the vibrational motion of the substrate with the motion of an H atom coming from the gas phase: we plan to include explicitly the C motions at the surface into the dynamics calculations: a force field will be developed based on the modified Brenner potential [Bachellerie09].

Another topic is to assess the effect of trapping resonances on sticking. These trapping resonances are supported by the chemisorption well. A previous study has shown that they can have significant lifetimes which can be much larger than the picosecond timescale, the one usually considered for dissipative processes to be effective [Sha05]. This means that this trapping may significantly enhance sticking. Although at large surface temperature, stuck species will eventually desorb, at low temperature, 10 K or so to be representative of astrophysical conditions, stuck species can be considered as stable.

Still another topic is to consider the effect of electron-hole excitation on sticking. Electron-hole excitation is not expected to play any role for insulators. Indeed, electronic excitations from the filled valence band would require a minimum energy associated to the valence-conduction band gap, which is usually too large to be provided by the incoming atom or molecule. However, for a conductor, which has a zero band gap, even an infinitesimal excitation can be absorbed by the substrate by electronic excitation. Being a semi-metal, graphene/graphite also has a zero-band gap, such that electron-hole may be a possible dissipative mechanism leading to sticking. However, it also has a vanishing density of electronic states at the gap, and it is thus not clear how efficient this dissipative mechanism will be. The relative efficiency of this mechanism with respect to the phonon mediated sticking, already well known for gg in the case of physisorption [Lepetit11a, Lepetit11b], will be studied.

One particular difficulty is to deal with electronic excitations of the surface and to be able to express the electronic coupling induced by the incident atom. We plan to use a semi-empirical method akin to what we developed for phonon excitation [Lepetit11a, Lepetit11b]. Phonons were described by a parametric harmonic expansion, which was adjusted to reproduce the known experimental dispersion curves. gg electrons will be described by a simple tight-binding model, the parameters of which can be adjusted to reproduce the electronic band structures. Matrix elements of the electrostatic interaction between atom and surface will be obtained in a product basis of gg and hydrogen states. If necessary, the surface representation will be enriched to represent its polarization by the incoming H atom.

The methods developed for the benchmark H-gg system will be extended to the simulation of oxygen atoms $O(^3P)$, hydroxyl radical $OH(^2\Pi)$, and oxygen molecule $O_2(^3\Sigma_g^-)$ in the physisorption case, studies undertaken by the experimental LERMA-LAMAP partner. All

the experiments will be performed using the FORMOLISM set-up located in Cergy-Pontoise, as described above. . This will be the first study at very low temperature (<10 K) and low flux implying pure physisorption processes. Most of the previous studies have been performed with hot atoms, or very high flux. The effect of the kinetic temperature (20 – 300K range) of incident atoms or molecules will be also studied for the first time, and this should finally enhance the coupling with the state-of-the-art calculations. The novelty of the study is grounded on the well characterized substrates, the experimental techniques and protocols have been established for amorphous surfaces (ice and silicates) and should not require long adjustment times.

3. PROGRAMME SCIENTIFIQUE ET TECHNIQUE, ORGANISATION DU PROJET / SCIENTIFIC AND TECHNICAL PROGRAMME, PROJECT ORGANISATION

3.1. PROGRAMME SCIENTIFIQUE ET STRUCTURATION DU PROJET / SCIENTIFIC PROGRAMME, PROJECT STRUCTURE

The program is set up in such a way to cover the different aspects of sticking and reaction on surfaces, involving hydrogen and oxygen, from both theory and experimental sides, as evidenced by the description by tasks shown below.

3.2. MANAGEMENT DU PROJET / PROJECT MANAGEMENT

A key of the project is the complementarity of the partner tasks. This is obvious for the experimental partner (LERMA) with respect to the theory ones (ISMO+LCAR), but this is also true between the 2 theory partners, who will explore distinct and complementary topics : the oxygen problem is covered exclusively by ISMO, the hydrogen one being shared, but whereas the LCAR partner focuses on electron-hole excitation and quantum models, the ISMO partner focuses on electronic potential calculations as well as classical or/and mixed quantum/classical dynamics methods.

Another key is interaction. We plan semester advancement meetings, in addition to as many as necessary informal interactions. We plan, if possible, to hire the same post-doctoral fellow for the 2 theory partners. He would spend one year in each of the two sites, enhancing his training as well as its productivity.

3.3. DESCRIPTION DES TRAVAUX PAR TACHE / DESCRIPTION BY TASK

TÂCHE 1 / TASK 1 : HYDROGEN-GG INTERACTION

Task 1.1 : Developing a force field (ISMO).

The ISMO team proposes to develop a force field able to treat the H interaction with a layer of carbon atoms as in a graphene sheet. The chemisorption takes place at the top of an active carbon. The chemisorption is qualitatively associated to an hybridization change of the active carbon from sp^2 to sp^3 . The main question concerns the barrier to overcome to reach the chemisorption well. This barrier is as high as 0.2eV when considered along the minimum energy path. This barrier prevents adsorption in the conditions of the diffuse clouds of the interstellar medium. A high precision in the resulting multidimensional potential resulting from the force field is requested for application in the context of cold H atom of the interstellar medium. The “floppy” character of the graphenic sheet under H chemisorption has recently been put in evidence by the ISMO team ; the force field has to be able to account for the property that the puckering effect affects a few C atoms around the adsorbent one involved in the C-H bond. First successful steps towards this goal have been made at ISMO [Bachelier09]. However this force field needs to be slightly modified so as to improve the precise location of the barrier. This will be done by checking with DFT calculations so as to carefully test the developed force field. This will be done in the first few months of the ANR project at ISMO.

Such a force field description is able to provide the potential interaction energy at any set of atoms positions (a multidimensional potential) as well as the forces between all the atoms and then at each time step of a complex treatment of the dynamics, in particular for a classical (see task 1.4.1) or for a mixed classical-quantum calculation (see task 1.4.3) using 1 or 2 dimensional wave packet propagation.

The treatment of the particles interaction via the force field will then allow comparison with the description of the dissipative medium as phonons coupled with the incoming species, as recently presented and currently used by the theory partners [Morisset10, Lepetit11a, Lepetit11b].

Task 1.2 : Computation of the chemisorption trapping resonances (LCAR).

Such a calculation has been performed only for the collinear configuration [Sha05], where one hydrogen atom moves on top of a carbon atom of the surface. In this case, there are only two degrees of freedom, the H-surface distance, and the extension of the puckering of the C atom away from the plane of the surface.

The present task will be to compute resonances for 3 degrees of freedom : a possible lateral deviation of the incoming atom away from colinearity will be considered. The resonances will be obtained by an iterative Lanczos diagonalization scheme, already used for the 2D case. A Hamiltonian supplemented by an optical potential is used. Complex eigenvalues of this Hamiltonian provide energies (real part) and lifetimes (imaginary parts) of the resonances.

Task 1.3 : Physisorption

Task 1.3.1 Model for electron-hole excitation (LCAR)

This process can compete with the already known [Lepetit11a, Lepetit11b] phonon excitation in promoting sticking of incident atoms. We propose to follow an approach similar to the one we developed for phonons [Lepetit11a], in which we use a semi-empirical model to describe the surface excitation. Phonons were described semi-empirically by harmonic modes, which were fitted to known dispersion relations. A simple tight binding model can be used to describe the electronic structure of the surface. Electrons are interacting pz orbitals, interaction coefficients between neighbors can be adjusted semi-empirically to reproduce expected band properties. The semi-metal character of gg can be modeled within this frame [Castro09].

Couplings can be obtained by expression of the matrix elements of the electrostatic interaction in the product basis of gg states and hydrogen states. The dipolar approximation can be performed conveniently in the physisorption case. A first order Taylor expansion could also be performed to fit with the Reduced Density Matrix (RDM) formalism.

Using the RDM formalism, sticking will be computed as a function of collision energy and surface temperature. A comparative evaluation with the phonon excitation process will be performed.

Task 1.3.2 Experimental Sticking and Physisorption of Hydrogen on cold graphite surface (LERMA)

The first goal of the experimental part of this project is to measure the sticking and physisorption properties of H₂, HD and D₂, without any reactivity aspects. The physisorbed states are expected to be low in energy (<50 meV) and will require a very cold graphite surface (<8K). We will use the King and Wells technique and will vary the beam temperature parameter, and the surface temperature. The sticking law that has been established for amorphous surfaces (water and silicates) will be compared to results obtained with graphite substrate. We expect to find an isotopic effect, but we would be surprised if the theoretical prediction of the low lateral corrugation does not change the distribution law. A feed back to theory should be necessary, like it has been for amorphous water ice. The sticking of the atoms will be estimated through the total recombination efficiency, even if it is an upper value.

Task 1.3.3 Reactivity of H and D atoms physisorbed on cold surfaces (LERMA)

The physisorbed state of H atoms have been theoretically reported, and is so low (<42 meV, without zero point energy), that it should require surface temperature lower than 8 K. Molecules formed are expected to instantaneously return to gas phase where we can detect them in the vicinity of the surface thanks to 2 techniques. We will use the QMS detection under the ionisation threshold [Amiaud07, Congiu09], to explore the coverage effects, and thus, to complete the study, use the laser detection [Lemaire10] if necessary and/or benchmark with former studies at higher temperatures and flux [Price08].

Task 1.4 : Chemisorption

Task 1.4.1 : classical dynamics for chemisorption (ISMO)

The new multidimensional potential (task 1.1) will be included in a classical treatment of the dynamics. This will provide a description with a full account of the coupling between the colliding H and the substrate C atoms, including the substrate C thermal motions. Comparison with calculations treating quantum mechanically one or a few degrees of freedom will be possible, however with the classical restriction of collision energy above the top of the barrier. Some simulations of classical dynamics have already been done in ISMO group for reactive processes resulting from atoms recombination at surfaces and leading to molecule formation either through the Eley-Rideal mechanism ([Bachelier07], [Bachelier09b], [Sizun10]) or through the Langmuir-Hinshelwood [Bachelier09a] mechanism in the recombination of physisorbed H atoms. In the present project, the sticking/trapping process in the chemisorption well or desorption process from the chemisorption well will be investigated using the new multidimensional potential resulting from the new version of the force field.

Task 1.4.2 : Thermal Quantum bath and Molecular dynamics (ISMO)

The thermal bath will be modeled quantum mechanically and molecular dynamics will be classical. A recent work (Dammak et al PRL 2009, 103(2009)190601) proposes a Langevin-type quantum bath for sampling quantum fluctuations in classical molecular dynamics simulations. This has been applied to recover a few physical properties (heat capacity of a solid, mean energy of a vibrational oscillator for a molecular system). An exploratory study will be undertaken by the Orsay theory team so as to determine if this approach is meaningful in the present context of adsorption and desorption.

Task 1.4.3 : Mixed classical-quantum dynamics for chemisorption (ISMO)

The multidimensional potential coming from the force field (Task 1.1) will be used in a mixed classical-quantum dynamics. The possibility will be then opened to describe a few motions quantum mechanically using wavepacket propagation method and the others classically as previously proposed in [Morisset10]. The H motion in collinear (and non-collinear) geometry as well as the adsorbing C atom motion will be treated by quantum dynamics. The dissipation process is here described by classical forces between the other degrees of freedom and particles.

Task 1.4.4 : Quantum dynamics for chemisorption (LCAR)

Performing this calculation requires the following ingredients :

- Un H-gg interaction potential : either 2D (collinear case) or 3D
- A phonon model
- Coupling terms.

Interaction potential and phonon model are already available. Couplings will be obtained by assuming that only the C atom nearest to the H approaching one is significantly displaced from its equilibrium position. For each of this C and H positions, we compute the forces exerted on the nearby C atoms, assumed to be close to equilibrium, such that the interaction potential can be approximated by first order Taylor expansion with respect to the displacements of these nearby atoms. These forces are used to couple the phonon bath with the motion of the incoming atom. They can be extracted from DFT calculations. The calculation will be performed 2D, and then extended to 3D.

The close coupling wavepacket method (CCWP) used previously for physisorption at low temperature [Lepetit11a,Lepetit11b] is not adapted for the present chemisorptions problem. Indeed, multiphonon processes occur when couplings or surface temperature are significant. For instance, sticking may occur in several steps, involving successive phonon excitations, and maybe subsequently followed by desorption, which now involves phonon absorption. In the CCWP method, a wavefunction is expanded on a basis involving a thermally averaged bath state, and a set of bath states differing from the initial only by one phonon. This expansion could be extended to include states differing by more than one phonon from the initial one, but at the cost of an exponential growth of the size of the basis. It is therefore more efficient to use RDM formalism, where the bath states are traced out. An equation of evolution can be written for the RDM, which can include without problem multiphonon processes [Lepetit11a].

The RDM method provides stuck states population as a function of surface temperature and collision energy. First the 2D case will be considered. As trapping resonances are already present in this case, possible enhancement will be considered.

TÂCHE 2 / TASK 2 : OXYGEN-GG INTERACTION

TASK 2.1 : Model for physisorption (ISMO)

The project will address the physisorption properties of oxygen, both as atomic and molecular species, sticking at the graphite/graphene surface in the physisorption regime. Physisorption of atomic oxygen involves the ground open shell O 3P electronic state. This regime is widely unknown. It is however of major interest in various domains of application among them physics and chemistry in the interstellar medium. The ISMO team has already produced a preliminary study for the O physisorption energy, based on a DFT calculation and an ab initio approach at the MP2 level on a PAH system as model of sp^2 surface [Bergeron08]. We plan to revisit this important question developing a new strategy for the building of the basis set to obtain a tractable MP2 ab initio approach on larger PAH molecules than previously used (coronene instead of pyrene). The purpose is to produce unquestionable new data both theoretically and experimentally. This new study will provide data for the sticking and reactive theoretical and experimental studies both developed in the present consortium. The recent new strategy in the production of atomic oxygen by

molecular oxygen dissociation in the Cergy experiment produces mainly if not exclusively atomic oxygen in its ground electronic state. This is a major experimental improvement that makes now feasible physisorption studies. We are aware from discussions with the participants to the Leiden workshop on "Challenges in modelling the reaction chemistry of interstellar dust" last September that other European leading groups plan to study adsorption and reactive processes as induced by atomic oxygen. It is then timely for the French community which is at the forefront worldwide in this field to keep involved at the highest competitive level with the necessary support.

Molecular oxygen will be also considered since it is present in the irradiating oxygen beam in the experiments. Only a very few theoretical studies have addressed the description of its adsorption on carbonaceous substrate. There is a strong need to further study this system in interaction with C sp² surfaces and it will be required to interpret the experiments developed in Cergy.

Task 2.2 Experimental determination of O₂ and O sticking via its reactivity (LERMA)

Thanks to the Cergy O beam that have now an excellent dissociation rate (80%), we will compare the O₂ behaviour (with a purely molecular beam) with the O₂ and O₃ formation, when O beam is used. By varying the surface temperature, the mobility of O atoms will be changed, and the O₂/O₃ production ratio should vary. No such measurements have never been reported. On the contrary to H measurements, the O reactivity should lead to physisorbed species and gas phase release. The balance of both mechanisms will reveal insight into the dynamics.

Chemical reactivity of O with the substrate will be monitored with IR spectroscopy.

Task 2.3 : Model for Molecule formation (ISMO)

The present consortium will address the question of formation of molecules assisted by surfaces. In the interstellar medium, the role of dust grains and reactions at their surface is nowadays recognized as very important in the astrophysics and astrochemistry communities. The codes that they are developing to describe the evolution of interstellar media include surface assisted reactions [Wakelam10]. The reaction from O+H reactants leading to the formation of the hydroxyl radical and subsequently to the formation of water as assisted by surfaces of bare dust grains present in the interstellar medium is then of a strong interest. The Orsay team has already tackled this question. The dynamics of the reaction involving both physisorbed partners has been described by classical molecular dynamics however the surface was kept rigid [Bergeron08]. The Orsay team is going to develop a dynamical study that includes surface atom motions. A realistic description of the surface as a dissipative medium will be developed at the classical mechanics levels. The Cergy experimental team plans to study this reaction measuring reaction probability and extracting information on the internal energy of the formed molecules. This team has already acquired a strong experience for molecular formation on ice covered dust grains as present and representative of solid surfaces in cold clouds of the interstellar medium. Their planned experimental study is of a strong interest in this new context of crystalline and bare carbon

surfaces. This work on the formation of the hydroxyl radical will also be extended to the case of water formation. This program will require a preliminary study of the adsorption properties of the radical hydroxyl as well as the water molecule on bare surfaces of the gg type.

Task 2.4 : Experimental study of molecule formation by mixed oxygen-hydrogen experiments (LERMA)

Water is expected to be formed via several chemical pathways [Dulieu11]. The efficiency of this reaction is the first goal of these mixed experiments. These experiments should also reveal the morphology of the ice [Accola11]. They will be coupled with a STM study, carried in Aarhus University, by Andrew M. Cassidy in the frame work of the LASSIE International training network. The present project just covers the experiments that will be performed in Cergy-Pontoise.

TÂCHE 3 / TASK 3 : THE CONSORTIUM THEORY-EXPERIMENT INTERFACE

Collaborative works between theory and experiment teams have already been developed in the recent years [Matar10, Chaabouni11]. The present project will directly benefit from this already active collaboration and will extend it. The present consortium proposes to address the sticking and desorption of atoms and molecules as well as the formation of molecules by atoms recombination as assisted by bare surfaces of the graphenic/graphitic types. The experimental conditions are created to mainly investigate the physisorption regime (low surface temperature, low kinetic energy of reactants and well controlled electronic state of atomic O).

Recent Cergy experimental measurements on sticking have stimulated the development of models by the Orsay theory team. The main issue in this collaboration was the rationalization of the experimental sticking data and the quantitative interpretation of isotopic effects. This collaboration also results in theory based predictions for the sticking of some species yet not measured [Matar10, Chaabouni11]. These studies concern hydrogen and deuterium atoms and molecules at amorphous ices and bare silicates. These laboratories experiments were mimicking conditions and systems of the diffuse interstellar medium. The isotopic effect is of paramount importance for the modeling of the interstellar medium processes. This common experience is planned to be extended from amorphous systems as previously studied to the crystalline ones as for graphitic substrate. Here again the measurements of isotopic effects are carrying a highly valuable information. Velocity scaling, related to the mass changes from hydrogen and deuterium, is the key parameter of dynamical effect. The other one is the associated strong change in the quantization levels. Isotopic studies are then at the forefront of the theoretical and experimental methods to investigate the dynamics of processes such as the elementary sticking process.

3.4. CALENDRIER DES TACHES, LIVRABLES ET JALONS / TASKS SCHEDULE, DELIVERABLES AND MILESTONES

Tasks	Year 1		Year 2	
	S1	S2	S3	S4
Task 1 : Hydrogen-gg interaction				
Task 1.1 : developing a force field (ISMO).				
Task 1.2 : Computation of the chemisorption trapping resonances (LCAR).				
Task 1.3 : Physisorption				
<i>Task 1.3.1 Model for electron-hole excitation (LCAR)</i>				
<i>Task 1.3.2 Experimental Sticking and Physisorption of Hydrogen on cold graphite surface (LERMA)</i>				
<i>Task 1.3.3 Reactivity of H and D atoms physisorbed on cold surfaces (LERMA)</i>				
Task 1.4 : Chemisorption				
<i>Task 1.4.1 : classical dynamics for chemisorption (ISMO)</i>				
<i>Task 1.4.2 : Thermal quantum bath and molecular dynamics (ISMO)</i>				
<i>Task 1.4.3 : Mixed classical-quantum dynamics for chemisorption (ISMO)</i>				
<i>Task 1.4.4 : Quantum dynamics for chemisorption (LCAR)</i>				
Task 2 : Oxygen-gg interaction				
Task 2.1 : Model for physisorption (ISMO)				
Task 2.2 : Experimental determination of O ₂ and O sticking via its reactivity (LERMA)				
Task 2.3 : Model for Molecule formation (ISMO)				
Task 2.4 : Experimental study of molecule formation by mixed oxygen-hydrogen experiments (LERMA)				
Task 3 : the consortium theory-experiment interface				

4. STRATEGIE DE VALORISATION, DE PROTECTION ET D'EXPLOITATION DES RESULTATS / DISSEMINATION AND EXPLOITATION OF RESULTS. INTELLECTUAL PROPERTY

Usual scientific dissemination of results will be carried out : presentations at conferences and meetings, publications...

5. DESCRIPTION DU PARTENARIAT / CONSORTIUM DESCRIPTION

5.1. DESCRIPTION, ADEQUATION ET COMPLEMENTARITE DES PARTENAIRES / PARTNERS DESCRIPTION & RELEVANCE, COMPLEMENTARITY

Partner 1 : LCAR, Toulouse

This partner is focused on the development and use of quantum methods to describe sticking processes. It is complementary of ISMO that will be focused in the project on the development and use of classical or mixed quantum-classical methods.

LCAR has been involved in the development of quantum dissipative methods, both in the Markovian [Lepetit11a, Lepetit11b] and non-Markovian cases [Meier99, Meier10]. It also has expertise on quantum modeling of dynamical processes at surfaces such as recombination [Lemoine01]. This know-how will be a basis for the present development.

Partner 2 : ISMO, Orsay

The ISMO background is complementary to the LCAR one.

The ISMO theory group has a long time expertise of the electronic structure calculation for atoms at graphitic/graphenic surfaces (for example : [Jeloaica99], [Sidis00], [Rougeau06], [Bergeron08], [Rougeau11]) as well as other systems such as molecules at metallic surfaces (work from S. Nave). These calculations provide properties such as adsorption geometries, adsorption energies as well as potential energy surfaces [Rougeau11] and also dynamical matrices [Morisset08] as requested for the treatment of the dynamics of the processes. The ISMO group has also expertise in the development and use of classical and mixed quantum-classical methods at surfaces [Morisset10].

Partner 3 LERMA, Cergy

LERMA is a laboratory of the Paris Observatory and CNRS (INSU). The team involved is hosted by the Cergy Pontoise University. It is member of the Labex MICHEM. LERMA Cergy team has developed state-of-the-art atomic molecular beam technologies, and surface physics experimental tools. It has an international recognized expertise in gas-surface

interactions applied to astrophysical medium. It is involved in international training network LABORATORY ASTROCHEMICAL SURFACE SCIENCE IN EUROPE It has a well established collaboration with partner 2.

5.2. QUALIFICATION DU COORDINATEUR DU PROJET / QUALIFICATION OF THE PROJECT COORDINATOR

The coordinator has at the same time expertise in the scientific field of quantum dynamics through decades of publications, as well as experience in the art of management, as laboratory head in the aerospace industry in the 90's.

D. Teillet-Billy is the coordinator of the ISMO partner in this project. She is simultaneously coordinator one of the 8 ISMO teams : the ISMO theory team "Approches théoriques en dynamique quantique" -15 permanent members-. The group "Structure, Dynamics, Reactivity" involved in the present project is part of this theory team.

5.3. QUALIFICATION, ROLE ET IMPLICATION DES PARTICIPANTS / QUALIFICATION AND CONTRIBUTION OF EACH PARTNER

Partenaire / partner LCAR	Nom / Name	Prénom / First name	Emploi actuel / Position	Discipline* / Field of research	Personne. mois** / PM	Rôle/Responsabilité dans le projet / Contribution to the project 4 lignes max.
Coordinateur/responsable	Lepetit	Bruno	CR CNRS		12	Setting up the models
Autres membres	Meier	Chris	PR UPS		6	Dissipative dynamics support
	Lemoine	Didier	CR CNRS		3	Resonance study
	TBD		Post-Doc		12	Computation realization

Partenaire / partner ISMO	Nom / Name	Prénom / First name	Emploi actuel / Position	Discipline* / Field of research	Personne. mois** / PM	Rôle/Responsabilité dans le projet / Contribution to the project 4 lignes max.
Coordinateur/responsable	Teillet- Billy	Dominique	DR CNRS		7	Force field ; Classical Dynamics; Hydrogen, Oxygen, molecular formation (hydroxyl)
Autres membres	Aguillon	François	PR UPSud		5	Force field (Resp.); Classical (Resp.) and Quantum Dynamics
	Bergeron	Hervé	MCF Phys. UPSud		6	Sticking/Desorption : interfacing with experiment (Resp.); Classical Dynamics ; Methodology : thermal quantum bath and molecular dynamics(Resp.)

	Morisset	Sabine	CR CNRS (PIIM Marseille) En mission longue durée à l'ISMO		7	Mixed classical-quantum dynamics (Resp.)
	Nave	Sven	MCF Chimie UPSud		4	DFT calculation ; Dynamics
	Rougeau	Nathalie	MCF Chimie UPSud		5	Structure calc. (DFT ; ab initio methods, MP2) (Resp.) ; Reactivity; Hydrogen, Oxygen, molecular formation (hydroxyl, water)(Resp.)
	TBD		Post-Doc		12	Computation realization

Partenaire / partner LERMA	Nom / Name	Prénom / First name	Emploi actuel / Position	Discipline* / Field of research	Personne. mois** / PM	Rôle/Responsabilité dans le projet / Contribution to the project 4 lignes max.
Coordinateur/responsable	Dulieu	François	PR		6	Coordinator Responsible of the Oxygen experiment
Autres membres	Baouche.	Saoud	Research engineer		2	Experimental support
	Chaabouni	Henda	MCF		16	Responsible of the Hydrogen experiment
	Congiu	Emanuele	MCF		2	Experiment
	Diana	Stephan	Engineer (IE)		2	Computer support
	Lachevre, Francois	François	Technician		2	Experimental support
	Somsom	Eric	Assistant engineer		2	Electronic support
	Minissale	Marco	Doc		8	Experiment
	TBD		Post-doc		12	Experiment

	Nom de la personne participant au projet / name	Personne . Mois / PM	Intitulé de l'appel à projets, source de financement, montant attribué / Project name, financing institution, grant allocated	Titre du projet : Project title	Nom du coordinateur / coordinator name	Date début & Date fin / Start and end dates
	Lepetit	7.2	ANR 08-BLANC-0047 / 114 k€	ITER-NIS	Simonin	01/01/2009-31/05/2012
	Lemoine	21.6	ANR 08-BLANC-0047 / 114 k€	ITER-NIS	Simonin	01/01/2009-31/05/2012
	Meier	14	ANR BLANC/ 115 k€	Dynamix	Meier	2008-2010
	Meier	7	ANR BLANC "DYNHELIUM", 132 k€	Dynhelium	Lewerenz	2009-2012
	Lepetit	2.4	FR-FCM+EFDA / 14 k€ HT	Production of H- ions by surface mechanisms	Lemoine	01/01-31/12/2009
	Lemoine	4.8	FR-FCM+EFDA / 14 k€ HT	Production of H- ions by surface mechanisms	Lemoine	01/01-31/12/2009
	Lepetit	2.4	FR-FCM+EFDA / 4 k€ HT	H atoms-gr,Ag,Ta surfaces	Lemoine	01/01-31/12/2011
	Lemoine	4.8	FR-FCM / 4 k€ HT	H atoms-gr,Ag,Ta surfaces	Lemoine	01/01-31/12/2011

	Nom de la personne participant au projet / name	Personne . Mois / PM	Intitulé de l'appel à projets, source de financement, montant attribué / Project name, financing institution, grant allocated	Titre du projet : Project title	Nom du coordinateur / coordinator name	Date début & Date fin / Start and end dates
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	Aguillon	11	ANR 07-BLANC-0129 / 143 k€	IRHONI	Lemaire	2007-2011
	Rougeau	36	ANR 07-BLANC-0129 / 143 k€	IRHONI	Lemaire	2007-2011
	Teillet-Billy	28	ANR 07-BLANC-0129 / 143 k€	IRHONI	Lemaire	2007-2011
			RTRA Triangle Physique 2009-060T / 60 k€	IRAHOC-MIS	Teillet-Billy	2009-2010

	Nom de la personne participant au projet / name	Personne . Mois / PM	Intitulé de l'appel à projets, source de financement, montant attribué / Project name, financing institution, grant allocated	Titre du projet : Project title	Nom du coordinateur / coordinator name	Date début & Date fin / Start and end dates
	Dulieu	36	ANR 07-BLANC-0129 / 143 k€	IRHONI	Lemaire	2007-2011
	Chaabouni	36	ANR 07-BLANC-0129 / 143 k€	IRHONI	Lemaire	2007-2011
	Congiu	36	ANR 07-BLANC-0129 / 143 k€	IRHONI	Lemaire	2007-2011
	Diana	27	ANR 07-BLANC-0129 / 143 k€	IRHONI	Lemaire	2007-2011
	Somsom	18	ANR 07-BLANC-0129 / 143 k€	IRHONI	Lemaire	2007-2011

6. JUSTIFICATION SCIENTIFIQUE DES MOYENS DEMANDES / SCIENTIFIC JUSTIFICATION OF REQUESTED RESSOURCES

6.1. PARTENAIRE 1 / PARTNER 1 : LCAR

- *Équipement / Equipment*

Equipment funding will be used to upgrade our local cluster, which will be used for the present project. We have a policy of maintaining our cluster to up-to-date technology to deal with intensive computations.

- *Personnel / Staff*

A one year post-doc will be hired to perform part of the computations. The emphasis will be on running the computations rather than model development, which will be performed mainly by B. Lepetit. The candidate search will be performed in collaboration with the ISMO team. If possible, the same post-doc will be hired by both labs, and will spend a year in each of both.

- *Prestation de service externe / Subcontracting*

- *Missions / Travel*

Travels to conferences and between Paris (Orsay-Cergy) and Toulouse for the coordination of the project will be necessary.

- *Dépenses justifiées sur une procédure de facturation interne / Costs justified by internal procedures of invoicing*

- *Autres dépenses de fonctionnement / Other expenses*

6.2. PARTENAIRE 2 / PARTNER 2 : ISMO

Équipement / Equipment

Equipment (16 K€): 2 hexacore bi-processors units to be included in the ISMO theory team's rack cluster, for the requested computationally-intensive DFT and dynamics calculations.

Personnel / Staff

Manpower (54K€): A one-year postdoctoral fellowship is requested to perform electronic structure and dynamics calculation

Missions / Travel

Travel expenses (6 K€) for conference communications and intra-consortium events and exchanges.

6.3. PARTENAIRE 3 / PARTNER 3 : LERMA

- *Équipement / Equipment*

Sample holder modification: 3000 euros

Up-grade acquisition and control system: 5000 euros

- *Personnel / Staff*

1 year post-doc. (54 k€)

- *Missions / Travel*

- *Dépenses justifiées sur une procédure de facturation interne / Costs justified by internal procedures of invoicing*

Internal procedures (5 K€): Mechanical and electronic workshop, Communication service (web provider, science diffusion).

- *Autres dépenses de fonctionnement / Other expenses*

running costs (24K€) including :

HOPG sample, glue, specific materials : 2000 €

Maintenance (turbo pump, primary pump, cryogenerator, laser...): 8,000 €

Possible breakdowns and repairings: 5000 €

Gas cylinders (manometers, rental, ...) : 1,000 €

Consumable (copper gaskets, liquid nitrogen for IR detectors, He for cryogenerator, CsI windows, glassware, oil, laser maintenance...) : 8,000 €

7. REFERENCES BIBLIOGRAPHIQUES / REFERENCES

Note importante : les annexes éventuelles au document scientifique doivent être déposées sur le système de soumission sous forme de documents séparés.

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