The International Meeting « Chemical Reactivity, from Accurate Theories to Simple Models », will be held at the University of Bordeaux 1 (Talence / France) from January 21th to 23th, 2014. Given in honour of Prof. Jean-Claude Rayez’ career, this conference will offer a stimulating exchange of ideas between theoretical chemists coming from various horizons, like electronic structure, spectroscopy, or chemical dynamics and kinetics in gas and condensed phases.

Chairs: L. Bonnet and P. Larregaray
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http://web.ism.u-bordeaux1.fr/chemreac/
Hybrid quantum mechanical/classical mechanical methods for modeling large molecular systems

Jean-Louis Rivail
UMR 7565 « Structure et réactivité des systèmes moléculaires complexes »
CNRS - Université de Lorraine

The aim of this lecture is to review the problems encountered in chemical modeling of large disordered molecular systems and to develop the principles of the main methods mixing a quantum chemical approach with a classical description of the part of the system of reduced chemical interest.
The systems considered are molecular solutions and bio macromolecules from a point of view of structure, reactivity and spectroscopy.
On the Role of Extended Intersection Seams in Ultrafast Photochemistry

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Conical intersections (CI) between electronic potential energy surfaces are very often invoked in explaining molecular photophysics and photochemistry. This results from the fact that (i) conical intersections are ubiquitous in large molecular systems, and (ii) computational tools for locating such surface crossings and for determining how accessible they are from an excited state are now widely distributed. However, conical intersections should not be viewed as simple crossing points between electronic states but rather as extended crossing seams. The intrinsic multidimensional nature of the conical intersection can be crucially important, as large parts of the extended crossing seam can be sampled by the system during excited-state vibrational relaxations (see figure below). Thus, being able to locate lowest energy crossing points, also called minimum energy conical intersections (MECI), between electronic states offers often only part of an explanation and the nature of the intersection away from such minimum can also play a major role, as we will illustrate in this communication. Another important point to consider is how the intersection seam can be affected by an external perturbation. As an example, we will discuss the case of a protein chromophore in solution.

Understanding the photoactivity of molecular switches within complex systems: a simple approach.

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Photochromic entities may undergo a light-induced reversible transformation between two isomers presenting distinct structural and electronic features. Obviously, if the properties of the two forms are significantly different, like in diarylethenes (DA), photochromes may act as the main building blocks in on/off nano-devices. To store more complex information than a "simple" 0/1 pattern, one can couple several photochromes in one molecule. However, such entities present experimental limitations e.g. switching on one part of the compound may interfere with the photoreactivity of other fragments. In addition, the current operative systems only demonstrate increased contrast rather than emergent properties. In that framework, Density Functional Theory and its Time-Dependent counterpart (DFT & TD-DFT) are useful tools for investigating the origin of these limitations. In this presentation, we will consider a series of diarylethene dimers, proposing a three-step approach to understand the photochromism of multi-DA systems [1]. We have also used this methodology to study the photoreactivity of photochromic molecules grafted on metallic nanoparticles [2].

Directions of chemical change

Vincenzo Aquilanti

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This talk is presented at the International Meeting « Chemical Reactivity, from Accurate Theories to Simple Models », dedicated to honour Prof. Jean-Claude Rayez' career. This presentation is given with the aim of drawing the attention to the versatility of current experimental investigations on the leading rôle that molecular orientation and alignment play on the outcomes of chemical reaction and photodissociation dynamics, vigorously assisted by quantum chemistry and molecular dynamics.

The use of advanced molecular beams techniques together with a combination of modern tools for specific preparation, selection and detection permits us to discover new trends on reactivity in the gas phase as well as at surfaces.

Experimental evidence is presented on novel paths in reaction dynamics in photodissociation and stereodynamics. We will consider specifically new aspects on stereodynamics, namely chirality effects in collisions and the non-linear Arrhenius behavior in temperature dependence.

A few topics from last year activity will be selectively illustrated, as time will permit. Relevant references follow.


Quasiclassical trajectory, Statistical and Time Dependent Wave packet studies of the Si + OH $\rightarrow$ SiO + H reaction.

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The SiO molecule is the most widespread silicon-bearing molecule in the interstellar medium. The largest abundances of SiO are found in shocked layers of molecular outflows associated with regions of star formation. For this reason, the detection of SiO emission is ideal for the comprehension of the mechanism involved in the formation of nascent star. The model currently adopted to explain the abundance of SiO invokes the erosion of interstellar dust grains made of silicates by shock waves [1]. The subsequent release of silicon atoms into the gas phase can lead to the formation of SiO via the following two reactions:

\[
\text{Si}(3\text{P}) + \text{O}_2 (X^2\Sigma^\text{g}_\text{u}) \rightarrow \text{SiO}(X^1\Sigma^\text{g}_\text{u}) + \text{O}(4\text{D}) \quad (1) \quad \text{and} \quad \text{Si}(3\text{P}) + \text{OH} (X^2\text{II}) \rightarrow \text{SiO}(X^1\Sigma^\text{g}_\text{u}) + \text{H}(2\text{S}) \quad (2)
\]

While reaction (1) has been measured [2] in the range 15 $\leq$ T $\leq$ 300K and studied theoretically [3], there is no experimental nor theoretical data existing for reaction (2). Given that recent observations [4] suggest a very low abundance for molecular oxygen in the interstellar medium, it is of importance to get accurate data for reaction (2) that could help the modeling of SiO interstellar chemistry.

We present here the first theoretical results obtained for the title reaction. Dynamics calculations have been carried out using a recently developed [5] three-dimensional potential energy surface (PES) for the ground $X^2\text{A}'$ electronic state of the HSiO/SiOH system. The reaction dynamics has been treated using three different approaches: QuasiClassical Trajectory (QCT), Mean Potential Phase Space Theory (MPPST), and Time dependent wave packet (TDWP). The quantum TDWP calculations have been performed for total angular momentum J = 0 and the “J-shifting” has been used to take into account the contributions of all J $\neq$ 0 partial waves. The theoretical calculations performed show that this reaction is a barrierless one with a reaction probability less than 60% for collision energies between 1meV and 1000 meV. The reaction proceeds through an indirect mechanism involving a long life complex. The reaction cross sections for a wide range of collision energies and for several initial ro-vibrational states of OH have been calculated. The thermal rate constants have been computed for the range of kinetic temperatures 10 K $\leq$ T $\leq$ 1000 K. When the fine-structure partition function of the reactants is accounted for, it is found a strong temperature dependence of the rate constant, which reaches a maximum of about $4 \times 10^{-10}$ cm$^3$.s$^{-1}$ at 20 K, and then decreases down to $2.4 \times 10^{-11}$ cm$^3$.s$^{-1}$ at 1000 K. This feature is different from the constant value of $10^{-10}$ cm$^3$.s$^{-1}$ which was previously assumed in the chemical reaction network [6]. The products energy distributions show a mix between statistical and not statistical behaviour.

Références

From single- to multi-sheeted potentials and femto- to subfemto-second time dynamics

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We discuss two issues. First, recent progress on representing global potential energy surfaces: analytic vs numerical, and single- vs multi-sheeted. Second, quantum dynamics studies with emphasis on: (a) new code for atom+diatom reactive scattering in hyperspherical coordinates and results for $\text{D}^+\text{H}_2$ reaction; (b) photoelectron spectra of CH$_4$ and CD$_4$, and implications on the analysis of high-harmonic spectra.
Quantum reactive scattering calculations for systems of astrophysical interest

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We are interested in the reactive collisions of astrophysical interest between open-shell atoms (C,N,O) and the hydroxyl radical OH. The ortho-para conversion of H₂ through the H⁺ + H₂(v=0,j) → H₂(v=0,j') + H⁺ reaction has also been studied, as well as the isotopic variant reaction D⁺ + H₂ → HD + H⁺. Opacity functions, product state-resolved integral cross-sections, differential cross sections, state-specific and thermal rate constants have been obtained by means of a time independent quantum mechanical (TIQM) approach [1] or a quasi-classical trajectory (QCT) method [2], combined with high accuracy ab initio potential energy surfaces. The TIQM and QCT results are compared with experimental results (as available) and also with those obtained using a time dependent wave packet approach and statistical methods [3-7].

Dynamics and Spectroscopy of Small Molecular Systems

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We use different ab initio methods to compute multi-dimensional potential energy surfaces for spectroscopic and dynamical purposes. This includes standard coupled cluster, complete active space self-consistent-field, internally contacted multi reference configuration interaction and the newly developed CCSD(T)-F12 methods. Our data show that the CCSD(T)-F12/aug-cc-pVTZ approach represents a compromise for good description of the PES and computation cost. This technique leads to results as accurate as those obtained using CCSD(T)/aug-cc-pV5Z, whereas the CPU time and the disk used are reduced by ~30 [1,2]. This is valid for monoconfigurational electronic states. For multi configurational systems and electronically excited states, we should use the costly configuration interaction methods (MCSCF, MRCI).

I will treat the following examples: N2H+ [1], C4-He [2], N2HAr+ [3], ArNO+ [4], HSiNH [5], HCl-He [6].

Is $C_2$ a nucleophilic or an electrophilic system?

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Highly correlated ab-initio wavefunctions within the MRCI and UCCSD(T)-F12 formalisms are used to study the long range interactions and the reactive path between $C_2$ and the three hydrogen halides $HX$ ($X = F, Cl, Br$).

The asymptotic regions are investigated for different relative orientations of the two moities. It is shown that the three van der Waals systems $C_2 + HX$ are bound through nucleophilic interactions between $C_2$ and $HX$ for approaches perpendicular to the C-C axis, with decreasing interaction energies from HF to HBr. For $HX$ approaching $C_2$ along its axis, the van der Waals interactions, governed by the electrophilic character of $C_2$ are weaker, with decreasing interaction energies from HBr to HF. Activation barriers towards the molecular systems HCCX or CCHX (0.64 eV and more) are calculated at short distances, making difficult the reaction towards the corresponding tetra-atomic systems.
How to compute IR spectra of complex systems from DFT methods: the case of microhydrated molecular clusters

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Vibrational spectra of small molecules are easy to determine precisely using ab initio and DFT methods. However, their reliability is not the same for the study of bigger systems mainly because of the difficulty to obtain an accurate potential energy surface (PES). Another problem is caused by the eventual presence of Fermi and Dennison resonances which make the vibrational treatment more complex. Even if computations of spectra of isolated molecules have become more and more usual last ten years, no precise strategy was developed to determine vibrational spectra of molecules in different environments. We can cite especially microhydration and aqueous solution.

A computational strategy will be proposed here for two microhydrated systems. First, the most probable structures of these microhydrated molecular clusters will be determined from the use of a global search algorithm called GSAM (for Global Search Algorithm of Minima exploration) and recently developed in our laboratory [1].

Then, the best strategy will be defined to compute infrared vibrational spectra of such systems. Time dependant and independent approaches will be used and theoretical results will be compared to experimental data available in the literature to validate our strategy. The influence of the dispersive correction in the method of determination of electronic structure will be also studied.

The presented results, recently published [2,3], concern both organic and inorganic systems, i.e. microhydrated thymine and nitrate aerosols respectively.

[2]. Sandrine Thicoipe, Philippe Carbonniere, Claude Pouchan PCCP acceptée, DOI: 10.1021/jp401130a
Calculation of IR-shifts of Water Clusters

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Shifts of monomers' intramolecular vibrations with respect to the free monomer ones constitute the signature of the hydrogen bonds in hydrogen bonded networks. While these shifts can be computed quasi-exactly for the water dimer (H$_2$O)$_2$ [1,2], approximate methods (beyond the crude harmonic approximation) have to be developed for larger clusters. We describe a new method, based on a mean field description of the intermolecular modes, which explicitly considers their large amplitude motions essential for a correct description. Application to larger clusters is presented.

Heterogeneous chemistry in the Troposphere: importance and modeling of the carbonaceous particles

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Carbonaceous surfaces have recently attracted much attention for their influence on atmospheric chemistry as products of combustion processes. Characterizing the chemical reactivity of these surfaces, especially with atmospheric oxidants, is thus of great importance because this reactivity may change the properties of these carbonaceous particles (hydrophilicity, optical properties ...) and modify, for instance, their influence on climate.

In the present work, we make use of first-principle calculations to characterize the interaction of large carbonaceous clusters with atmospheric oxidants such as atomic oxygen, O₂, O₃, H₂O and NO molecules. Both perfect and defective surfaces containing vacancies are studied. In a general way, we show that the oxidation of carbonaceous surfaces occurs more likely at defective sites and depends on the type of site considered in the calculations. For instance, carbon atom vacancies characterized by an odd number of missing carbon atoms are more reactive than those where an even number of atoms is missing and, as a consequence, they can be oxidised more easily. We also show that the interaction of water with the oxidised carbonaceous particles strongly depend on the chemical sites that have been created by the oxidation process at the surface. These results can be used to better understand oxidation processes that likely occur in carbonaceous systems of environmental interest.


† the following former PhD students were also involved in this work: B. Collignon (2006), G. Hantal (2010), M. Oubal (2011)
Density functionals that are paramaterized to include dispersion interactions: Problems with the conception, parameterization and results

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Within the past few years, several new density functionals designed to account for dispersion interactions through various parametrized functions have appeared. We show that these behave erratically due to several problems. 1) They contain as many as 39 parameters fitted to flawed databases. 2) They do not properly account for the fact that induction, when present, significantly reduces the amount dispersion present. 3) These functionals do not generally describe dispersion correctly as a function of basis set size. Most of this work has been published.[1-4]

Electronic friction in metals and molecular relaxation.

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The absence of a threshold for electron-hole excitation in metals gives rise to a friction, for the relaxation of motion in any molecular degree of freedom, linear in the associated “velocity”. The coefficient of this linear behaviour, improperly named “friction coefficient”, is a \(3N\times3N\) tensor (\(N\): number of nuclei in the molecule) which makes its evaluation apparently a formidable task, even when discarding the technicalities for its evaluation with present-days band structure codes. Starting with the simpler case of a single atom moving in a crystal, we have shown \cite{1} that the friction coefficient can be evaluated, in principle, exactly with a static ensemble Kohn-Sham procedure, using a generalization of the “Shifted Fermi Surface” procedure established initially for an atom moving within an homogeneous electron gas (jellium). As the friction coefficient corresponds to a first order calculation in the atom velocity, it is determined only by local quantities, i.e. it does not (and must not) involve any information on the variation of the system with atomic position. Generalization to a molecule is rather straightforward and leads to the important conclusion that all terms of the \(3N\times3N\) tensor can be evaluated in terms of \(3N\) quantities only, the latter requiring a single band structure calculation for a given molecular conformation and position with respect to the lattice. Still remains to be worked out the implementation of the “Shifted Fermi Surface” procedure into existing codes, a non-trivial problem.

\cite{1} Salin A., arXiv:1302.0986 [cond-mat.other], 2013
Forty five years of Theoretical Chemistry
Quarante-cinq années de Chimie Théorique

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L’auteur se propose d’évoquer quelques propos et souvenirs personnels sur l’évolution de la Chimie Théorique au cours de ces 45 dernières années.
The author will present a summary on 45 years of Theoretical Chemistry associated with personal memories.
Stereo-dynamical understanding of Arrhenius equation

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Chemists for a long time have recognized that energy is not the only factor affecting the rate of chemical reaction and the branching ratio to products. \cite{1} The stereo-dynamical factor should be such a factor as this typical example on the electron transfer in the K+CF$_3$Br $\rightarrow$ KBr+CF$_3$ reaction provides.\cite{2} We traditionally find the “steric factor $\rho$” in Arrhenius equation (1) as well.

$$k_2 = \rho Z \exp(-E_a/RT) \quad \text{(eq.1)}$$

where $k_2$ is the rate constant for a bimolecular reaction, $Z$ is the specific gas kinetic collision frequency, $E_a$ the activation energy, $R$ the gas constant, $T$ the absolute temperature.

In a more complex reaction of AB+CD, the collisional geometry becomes more important.\cite{3-5} Stereodynamics studies under controlling mutual orientations among reactants in experiment together with the aid of theory would be a powerful strategy to clarify detail reaction mechanisms at the molecular level as in the microscopic view. On the other hand, there must be a manifestation of the steric effect even in the overall reaction and its temperature dependence as in the macroscopic view.\cite{6} In this lecture, we will try to explore and find out a linkage between the microscopic and macroscopic views to understand stereo-dynamical behaviors in chemical reactions. Such challenging comparison with these two views would lead us to overlook some unexpected new aspects of chemical reactions.\cite{7}

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\end{thebibliography}
Statistical product-state distributions for cold exoergic reactions in external fields

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There is currently great interest in producing high-density samples of ultracold polar molecules, fuelled by their many potential applications in, e.g., quantum information science, the study of collective effects in condensed-matter systems and the development of quantum-controlled chemistry \cite{1}. Very recently, the first experiments on ultracold chemistry were performed at JILA, Colorado. Using an ultracold gas of ground-state \(^{40}\text{K}^{87}\text{Rb}\) molecules, the JILA group observed strong effects on the reaction rates due to quantum statistics \cite{2}, external electric fields \cite{3}, reduced dimensionality and orientation \cite{4}. While Quéméner and Bohn assisted in the theoretical interpretation of the observed loss rates, Idziaszek and co-workers \cite{5} and Gao \cite{6} have developed simple quantum models for the reaction rates, as well as identified different universality classes. At present, the most important pending question is that of product-state distributions. These are far more sensitive to the details of the reaction dynamics and could thus lead to a deeper understanding of the underlying physics. Although a full description of low-temperature reactions can be derived from rigorous quantum-mechanical calculations in electro-magnetic fields \cite{7}, the huge number of ro-vibrational states in reactions involving relatively heavy species makes such approach impractical for most cases of experimental interest \cite{8}. In this talk, I will discuss our recent efforts in deriving statistical product-state distributions for cold exoergic reactions involving polar molecules in external fields. In analogy with studies at higher temperatures, such distributions can be used as benchmarks for the funding assumptions of the theory, as well as provide tests for recent statistical arguments \cite{8}. Our work aims at extending traditional theories such as phase-space theory (PST) to cases where the strength of the interaction with external fields dominates over, or is comparable to, the incident collision energies.

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\bibitem{3} Ni, K.-K., et al., \textit{Nature}, 2010, 464, 1324
\bibitem{4} de Miranda, M. H. G., et al., \textit{Nat. Phys.}, 2011, 7, 502
\end{thebibliography}
Theoretical and experimental developments on the chemical reactivity of atmospheric interest in Bordeaux during the last decades: a subjective overview

Eric VILLENAVE\textsuperscript{1}, Françoise CARALP\textsuperscript{1}, Robert LESCLAUX\textsuperscript{1}, Marie-Thérèse RAYEZ\textsuperscript{1}, Jean-Claude RAYEZ\textsuperscript{1}

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During the last decades, a lot of work has been performed in Bordeaux on the chemical reactivity of gas-phase reactions of atmospheric interest. In the troposphere, most of the oxidation processes of organic compounds (RH) are initiated by OH radical reactions, leading to the formation of different radicals (alkyl, acyl, etc.) that will further react with oxygen to form peroxy radicals (RO\textsubscript{2}). These are important as their reactions will either form alkoxy (RO) species whose fate will for instance generate HO\textsubscript{2} radicals involved in many important atmospheric processes, or stable products like aldehydes, ketones, alcohols, etc. The secondary nature of the sources of oxygenated organic compounds in the atmosphere is often more important than their primary emissions. In Bordeaux, most experiments studying the reactions of volatile organic compounds (VOCs) were performed using either conventional- or laser-flash photolysis setups. Such systems allow to study the kinetics of the reactions of interest on typically a ms-to a second-time scale, following by time-resolved spectroscopy the UV-absorption of the different absorbing species present in the reaction mixture at a specific wavelength. Thus the fate of many compounds like aromatics, aldehydes, ketones but also alkenes, etc. has been studied, varying the temperature and pressure conditions when necessary. As experiments were logically not often possible, theoretical developments (from “simple” semi-empirical to ab-initio, RRKM and DFT calculations) appear rapidly essential and for once people were only separated by stairs in the same building... In this presentation, some examples of successful collaborations between theoreticians and experimenters from Bordeaux will be presented and commented.
Electronic properties of major atmospheric oxidants at the air-water interface from QM/MM Molecular Dynamics simulations

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The understanding of heterogeneous processes and multiphase chemical reactions in aerosols and water droplets is a challenging and important issue because such processes are believed to play a significant role on the overall troposphere chemical balance. On one hand, the uptake of a compound into an aerosol or a water droplet modifies its gas phase concentration and chemical kinetics. On the other hand, the condensed phase allows for otherwise unfeasible processes to occur in the atmosphere, ionic reactions in aqueous environments being a prototypical example. Besides, specific reactions at the air/water interface can take place. Such reactions may differ from those occurring in gas phase or bulk water and therefore they may have significant atmospheric implications. However, experimental and theoretical studies on this topic are still scarce.

In a series of recent theoretical studies [1-4] we have analyzed solvation effects at different water interfaces using our combined QM/MM Molecular Dynamics approach [5] (QM/MM stands for Quantum Mechanics/Molecular Mechanics). We have found that the electronic properties of adsorbed species at the interface may indeed be remarkably different from properties in the two bulk phases, and not necessarily intermediate, as often assumed. In this talk, the results of simulations for some oxidant species of atmospheric interest at the air/water interface will be presented.

Light absorption and structural aspects of photosynthetic pigments in solvent environment

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Light absorption by photosynthetic pigments triggers one of the most important reactions in nature that is the photosynthesis by plants, algae and bacteria. The understanding of this process is at the heart of the so-called artificial photosynthesis where new materials should be developed for possible use and storage of sun light. It is known that the environment can alter the photo absorption properties. Two aspects are then generally considered. One is the study in the presence of proteins. The other, closer to laboratory conditions, is the study of the absorption spectrum in solvent environments. We have been involved \cite{1-3} with this second line and using combined classical and quantum approaches (QM/MM) for understanding the solvent effects on the light absorption by chlorophylls.

In this presentation we will show the results of both classical (Monte Carlo) and quantum (Born-Oppenheimer molecular dynamics) approaches combined with spectral calculations to study the solvent effects on the absorption spectrum of chlorophyll \textit{c} \textsubscript{2}. We will discuss, in particular, the solvent effects on the Soret and Q bands, possible structural changes and the important question of the coordination of the central metal atom.


Work partially supported by CNPq, CAPES, FAPESP and INCT-FCx.