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Catalytic Mechanism of Phosphate Cleavage Reactions

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The formation and cleavage of phosphate bonds is essential in most biological processes including nucleic acid processing. Many enzymes that catalyze phosphate hydrolysis require bound divalent metal ions. To elucidate the poorly understood mechanism of the ubiquitous metal ion catalyzed reactions, we carry out hybrid quantum-classical QM/MM free energy simulations, focusing on several systems, including Ribonuclease H (RNase H, Fig. 1.) [1], dUTPase [2], and RAF kinases [3]. RNase H is a prototypical member of a large family of enzymes that use two-metal ion catalysis to process nucleic acids. HIV-RT is essential to viral replication, which makes it an important target in HIV drug research. In our simulations, we combine [4] Hamiltonian replica exchange with a finite-temperature string method to calculate the QM/MM free energy surface underlying the catalytic reaction. I will also present a histogram-free reweighting method to obtain this surface from combined multidimensional string simulations. This method allows us to search for the optimal pathway in multiple dimensions and, therefore, to identify the detailed sequence of steps in the phosphate cleavage reactions. From our calculations, coupled proton transfer reactions emerge as central factors in the catalytic phosphate cleavage reactions.
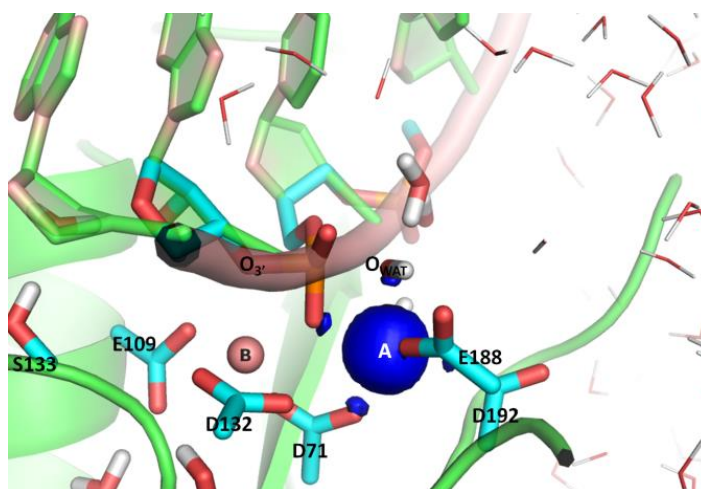

Figure 1. Active site of RNase H. The total electron density difference at metal ion A position with calcium versus magnesium is displayed at the 0.01 contour level (blue; a.u.).

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Phosphoryl and Related Group Transfer Reactions: Challenges in Interpreting Experimental and Theoretical Data.

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Understanding phosphoryl and sulfuryl transfer reactions is central to many biochemical processes. However, despite decades of experimental and computational studies, a consensus concerning the precise mechanistic details of these reactions has yet to be reached. In this contribution we present our theoretical study of the hydrolysis of key model systems for understanding phosphoryl, sulfuryl and sulfonyl transfer reactions. We demonstrate that despite seemingly simple single atom or functional group substitutions, the chemistry of these different classes of reaction is distinct, with very different solvation and protonation requirements. This raises a question of how catalytically promiscuous phosphatases and sulfatases are even able to accommodate such distinct reactions in the same active site. To partially address this question, we present our work on a highly promiscuous sulfatase from the alkaline phosphatase superfamily and illustrate the importance of chemistry-driven protein evolution.

Computational Study of the phosphorylation of RAF dimers.

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Although protein phosphorylation is one of the most common post-translational modifications in cell regulatory mechanism, little is known about the structural and mechanistic details of how phosphorylation affects the activity of kinases. In order to fill this gap we have carried out MD simulations of phosphorylated and non-phosphorylated BRAF homodimers. In particular, we are interested in finding a structural explanation for the paradoxical activation mechanism observed in RAF kinases, whereby an activator kinase forms a dimer with a receiver kinase, and thus significantly enhances its catalytic activity[1]. Our study also focus on the role played by the N-terminal acidic motif (NtA), specific of RAF, that has been suggested to be involved in the dimerization of RAF. To the best of our knowledge this motif has not been experimentally resolved, and the phosphorylation of at least one of its residues is required for RAF activation.
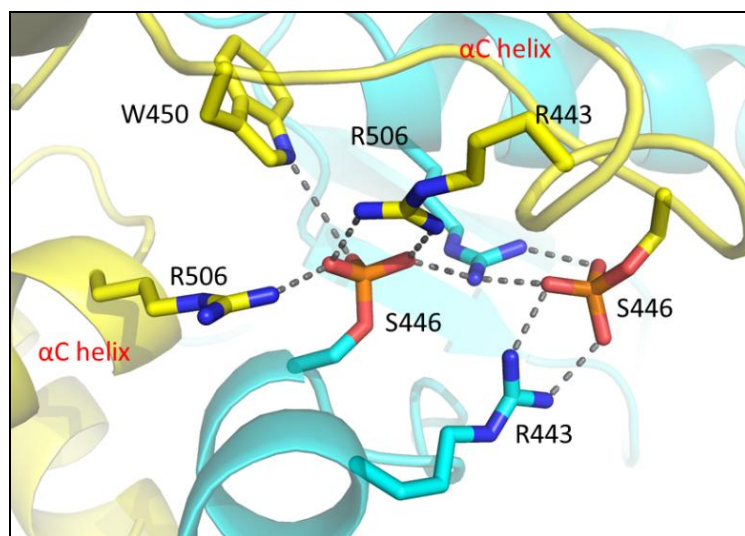
Coulombic interactions in which the phosphorylated S446 residue is involved for BRAF dimers.

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ENERGETIC AND THERMODYNAMIC PROPERTIES OF PROTONATED WATER CLUSTERS AND WATER CLUSTERS ADSORBED ON POLYCYCLIC AROMATIC HYDROCARBONS

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Polycyclic aromatic hydrocarbons (PAHs) are an important class of molecules in the field of astrochemistry due to the fact that they have been proposed as the carriers of the interstellar aromatic infrared bands (AIBs) [1]. Moreover, in the atmosphere, PAHs are formed during the combustion of fossil fuels or biomass burning and their interaction with water molecules is of key interest in atmospheric chemistry [2]. Therefore, it is of paramount importance to theoretically investigate energetic and thermodynamic properties of water clusters, PAHs and water-PAH clusters to obtain new insight about these systems and to be able to complement experimental results.

In this view, we have used the self-consistent-charge density-functional based tight-binding (SCC-DFTB) [3] method to describe the electronic structure of these systems. SCC-DFTB has already been extensively tested for these particular systems [4]. In order to extract either structural or thermodynamic properties in the framework of SCC-DFTB, it is required to accurately explore the potential energy surface (PES). This has been achieved using various methods such as molecular dynamics parallel tempering, Monte Carlo parallel tempering and smart Monte Carlo.

In this presentation, a brief introduction of the aforementioned methods will be given. Then the calculation of heat capacities, obtained from the multiple histogram method [5], of water clusters of different sizes will be presented and discussed. In particular, we will show that our calculated heat capacities for protonated water clusters, $(H_2O)_nH^+$ (n=21-23), are in qualitative agreement with recent experimental results [6].

Finally, results concerning the adsorption of water hexamer, $(H_2O)_6$, and octamer, $(H_2O)_8$, on two types of PAH molecules, coronene $(C_{24}H_{12})$ and circumcoronene $(C_{54}H_{18})$, will be discussed.

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CALCULATIONS OF CIRCULAR DICHROISM AND CIRCULARLY POLARIZED LUMINESCENCE OF BIOLOGICALLY RELEVANT CHROMOPHORES.

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Electronic circular dichroism (CD) is the differential absorption of left and right circularly polarized light by a chiral sample, while circularly polarized luminescence (CPL) is its equivalent in emission spectra. When the equilibrium structure of the electronically excited state differs significantly from the ground state geometry and the excited state has a lifetime long enough to allow the molecule to structurally relax, the CD and CPL bands are dissimilar, even to the extent of having opposite signs. That is why a comparison of CPL and CD spectra allows to investigate the molecular dynamics following the electronic excitation. Performing a quantum chemical calculations of the CPL spectra is rather a new possibility. [1,2,3]

We have carried out calculations of CD and CPL spectra for several biologically relevant chromophores, including green fluorescent protein chromophore (GFP) and it's mutants: blue fluorescent protein (BFP), enhanced cyan fluorescent protein, (CFP), enhanced green fluorescent protein (eGFP) and yellow fluorescent protein (YFP). Our main aim was to check how the protonation and deprotonation processes, and the presence of protein environment, influence the CD and CPL spectra and therefore to investigate the potential of CPL as a structural probe of electronic excited states. The presence of environment has been modeled employing PCM, polarizable embedding density functional theory (PE-DFT) method [3] in fully polarizable QM/MM/PCM model [4] and also by describing the closest environment quantum mechanically.

The CD and CPL spectra has also been calculated for thioflavin-T (ThT). This molecule is a well-known marker in the investigation of protein misfolding. Thioflavin-T itself is achiral, but it exhibits an induced CD effect in a chiral environment (for example when intercalated in a protein). [5] We have therefore decided to carry out quantum chemical CD calculations of thioflavin-T in different environments and of the associated CPL spectra, in order to investigate what are the capabilities of induced CPL of thioflavin-T in protein structural studies.

The last chromophores under study were luciferin and oxyluciferin (OxyL). This part of project was to check hypotheses which explain the presence of circularly polarized light emitted by firefly larvae in process of bioluminescence and to find the sources of this phenomenon. The molecule which exhibits emission of light is oxyluciferin, which is achiral. Therefore the circularly polarized emission has to be induced or by a macroscopic structure of the protein, or by forming a complex with protein or by twisting the dihedral angle between two rings in the OxyL molecule. To investigate this problem we decided to employ CD and CPL calculations.

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FORMATION OF NOVEL NANOPARTICLES IN HELIUM DROPLETS

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Helium droplets are large helium clusters typically composed of $10^3 - 10^8$ He atoms with an internal steady state temperature of 0.37 K. Helium droplets possess a range of unique properties, such as vanishing viscosity, transparent to a wide range of wavelengths and the ability to pick up dopants with near unity probability. In the context of nanoscience, helium droplets are able to act as a unique vessel for the formation of nanoparticles and nanowires *via* the addition of dopants to the droplets. Although still in its infancy, helium droplets have now emerged as a uniquely powerful tool for the fabrication of nanoparticles, and a number of metallic nanoparticles have been synthesized in this way, such as Ag,[1-3] Au,[1] and Ni[1] nanoparticles. The sequential addition of dopants to helium droplets means that it is possible to form core-shell nanoparticles, for example, Ni/Au nanoparticles.[1]
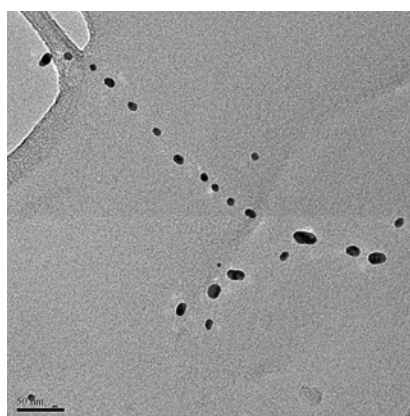

Figure 1. Transmission Electron Microscope (TEM) image of a chain of Ag nanoparticles formed in the helium droplets.

Here we report our recent progress in the fabrication of novel nanoparticles using superfluid helium droplets. When silver is added to large helium droplets, the TEM images clearly shows chains of spherical nanoparticles formed across the diameter of helium droplets (see Figure 1),[4] in addition to chains of nanorods that have been previously reported by Loginov *et al*.[3] Given that the spherical nanoparticles do not have intrinsic anisotropy the particles must experience an aligning force that will guide the nanoparticles into chains, which can only be interpreted by the presence of quantized vortices. The presence of the vortices within the helium has profound indication for nanoscience, allowing 1D nanostructures to be fabricated. To exploit this potential, we have synthesized nanowires using Au, Ni, Cr and Si, which can have lengths of several hundreds of nanometres and a typical diameter < 10 nm.[5] Finally, we report templated nanoparticles formed by the sequential addition of porphyrin and silver to superfluid helium droplets, which leads to the formation of nanoparticle dimers with a porphyrin molecule sandwiched between two silver

nanoparticles. Surface enhanced Raman scattering (SERS) of porphyrin by silver nanoparticle dimers has been observed.

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DYNAMICS OF EXCITED DOUBLY CHARGED β-ALANINE AND NEUTRAL CLUSTERS OF β-ALANINE IN THE GAS PHASE

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Already at the femtosecond timescale radiation damage of the biological tissues starts. Ionization of the biomolecules, induced with highly charged ions, produces a bunch of secondary particles: electrons, ions and radicals. Nowadays, an important research activity focuses on the understanding of these processes at the molecular level [1]. We present a combined experimental and theoretical study of excited doubly ionized β-alanine molecules in the gas phase [2]. Multicoincidence mass spectroscopic techniques together with ab initio molecular dynamics simulations and density functional calculations allow us to observe several processes in competition: isomerization, H migration, expected Coulomb repulsion and OH migration. Therefore, the hydrogen and hydroxyl group displacements have to be considered to get a complete picture of the complex fragmentation dynamics in the gas phase as previously observed in solution [3,4]. We thus show that the combination of theory and experiment is crucial to understand the early stages of radiation damage [5,6]. We also present theoretical study of neutral clusters of this amino acids. The knowledge of the stability and structure of excited clusters of neutral β-alanine molecules is essential to understand the fragmentations driven by different mechanisms.

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COLLISIONAL EXCITATION OF CN AND O_2 BY H_2 : COMPARISON OF THEORY AND EXPERIMENTS AND ASTROPHYSICAL APPLICATIONS

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The Herschel telescope and the ALMA interferometer open new windows of observation for wavelengths ranging from far infrared to sub-millimeter with spatial and spectral resolutions previously unmatched. Modeling of molecular emission from interstellar clouds requires the calculation of rates for excitation by collisions with the most abundant species. The O_2 and CN molecules are crucial molecules for the interstellar chemistry. Indeed, O_2 and CN are involved in many key reactions in the interstellar medium (ISM). CN molecule is even one of the most widely distributed in the ISM. In diffuse molecular gas, CN plays a role as a tracer of high density gas. It is then crucial to model collisions of these two species with H_2 (the most abundant collisional partner in the ISM).

We report here the first calculations of O_2–H_2 and CN–H_2 collisional data. New potential energy surface have been computed for the two collisional systems [1,2]. Potentials were obtained from the electronic structure calculations using a RCCSD(T) approach and large atomic basis set augmented by mid bond functions. Close coupling calculations of the fine structure resolved inelastic integral cross sections of O_2 and CN in collisions with H_2 were calculated at low energies which lead, after Boltzmann thermal average, to inelastic rate coefficients for temperatures ranging from 5 to 150 K.

For O_2–H_2 collisions, no significant differences exist between para- and ortho-H_2 results whereas strong differences exist between collisions with the two nuclear spin isomer in the case of CN–H_2 collision. Theoretical calculations were then compared with available experiments [2,3]. Theoretical and experimental results are in very good agreement. For O_2–H_2 collisions, both the theoretical and experimental cross sections show many low-energy resonances. Examination of the one-dimensional adiabatic-bender O_2–H_2 potential provides insight into the origin of these resonances.

These new rate coefficients were incorporated in radiative transfer code in order to see the impact of these new data on the astrophysical modeling. For O_2, the critical densities of the O_2 lines are found to be at $\sim$ 2-3 10^4 cm^3 for temperature larger than 50 K. Such findings invalidate the local thermodynamic equilibrium (LTE) approach to interpret O_2 emission from low density molecular clouds [4]. For CN, the new data have allowed an accurate estimation of the CN abundance in the Barnard 1 molecular cloud and then a quantitative estimate of the ^{15}N-fractionation in this cloud [5].

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Laboratory Astrophysics

Low temperature kinetics and astrophysical applications

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ABSTRACT

Laboratory astrophysics aims to advance our understanding of the Universe through the promotion of experimental and theoretical research on the processes driving the Cosmos. Molecules are an important component of the universe which dominate the cooling of interstellar gas clouds and regulate star and planet formation. The exploration of paths towards chemical complexity in space has direct bearing on the origin and evolution of life. Moreover, molecular transitions provide a sensitive probe of the dynamics and the physical and chemical conditions in a wide range of astrophysical objects.

Many of the molecules observed in the interstellar medium (ISM), have been observed in the cold and dense core of the molecular clouds. The large range of species detected implies that a rich chemistry does take place despite the very low temperature (~10 K) of these environments. These extreme conditions of temperature set a challenge to experimentalists who wish to measure the rates and results of the chemical reactions that occur in these objects.

The CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme or Reaction Kinetics in Uniform Supersonic Flow) technique coupled with pulsed laser photochemical kinetics methods has shown that reactions involving radicals can be very rapid at temperatures down to 10 K or below. The results have had a major impact in astrochemistry and planetology and excited interest from theoreticians. The CRESU technique is also suited to determine rate coefficients for collisional energy transfer that are necessary to interpret the emission spectra of interstellar atoms and molecules as deviations from local thermodynamic equilibrium are expected owing to the competition between the radiative and the collisional processes.

I will present recent results and current developments on low temperature kinetic experiments involving various collisional processes performed in the group of Rennes in relation to cold astrophysical environments, including molecular clouds and planetary atmospheres.

STUDIES OF THE F+DCl→Cl+DF REACTION BY USING WAVE PACKET AND TIME INDEPENDENT METHODS: ISOTOPE EFFECTS[*]

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We present accurate state-to-state quantum wave packet calculations of integral cross sections and rate constants for the title reaction. Calculations are carried out on the best available ground $1\,^2A'$ global adiabatic potential energy surface of Deskevich et al. [J. Chem. Phys., 124, 224303, (2006)]. Converged state-to-state wave packet reaction cross sections with the DCl($v = 0$, $j = 0$ - 1; $v = 1$, $j = 0$) reagent have been calculated for the collision energy range from threshold up to 0.5 eV. We find in the present calculations that the initial rotational excitation of the DCl molecule does not induce the enhancement of reactivity which is opposite to the clearly visible enhancement in the HCl isotopologue reaction. The present work also shows that the initial state vibrational excitation of the DCl molecule has an important effect on the reactivity. Accurate product vibrational and rotational distributions of cross sections have been calculated at selected collision energies. State-to-state and total initial-state resolved rate constants of the title reaction have been calculated in a temperature range of 100-300 K. The present accurate calculations at $v = 0$, $j = 0$, $J = 0$ show noticeable differences with previous calculations for the F+HCl reaction [1,2].

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IS HCL REALLY THE MAIN CHLORINE CARRIER IN MOLECULAR CLOUDS?

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Chlorine has mostly been observed in molecular hydrides like in HCl [1], and more recently in H_2Cl^+ [2] and HCl^+ [3] thanks to the *Herschel Space Observatory* . Among these chlorine-bearing species, the HCl molecule has a special interest since it is a tracer of dense molecular clouds [4] and it is supposed to be the main chlorine carrier in the interstellar medium (ISM). Indeed, chemical models predict that HCl is dominant source of chlorine in protostellar shocks and stars forming regions. Since collisions compete with radiation to the excitation of interstellar molecules, it is crucial to compute collisional rate coefficients for the HCl molecule.

For this purpose, we have studied collisions involving chlorine hydride and H_2 in order to provide collisional data for interpreting HCl observations. We have obtained collisional rates coefficients for the HCl–H_2 system using a new potential energy surface calculated from highly correlated *ab initio* calculations [5].

The rate coefficients currently used for astrophysical modelling of HCl emission are those of Neufeld & Green [6], that are actually HCl–He rates scaled by a factor 1.38, in order to approximate the HCl–H_2 rate coefficients. We have compared these rates with our new rate coefficients directly computed for the HCl–H_2 system. Differences up to an order of magnitude are found. As a first application, we have performed a set of radiative transfer calculations for typical physical conditions where HCl is observed. Using our new rates, the simulated line intensities are significantly increased in comparison to the previous ones. As a consequence, HCl abundance derived from the observations will be significantly reduced by the use of the new rate coefficients questioning the fact that HCl is the main chlorine carrier in the ISM.

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ROTATIONAL EXCITATION OF HCN BY PARA- AND ORTHO-H$_2$

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Hydrogen cyanide (HCN) can be used as a tracer of the deep dense interior of molecular clouds in the Interstellar Medium (ISM). It is also among the few molecules detected in high-redshifted galaxies. Modeling of molecular emission spectra from ISM requires the use of inelastic rate coefficients for (de-)excitation by collisions with H$_2$, the most abundant interstellar collisional partner.

In this presentation, we report a new study of the rotational excitation of the HCN molecule by collisions with para-H$_2(j = 0, 2)$ and ortho-H$_2(j = 1)$ studied at low temperatures using a new 4-dimensional (4D) potential energy surface[1]. *Ab initio* calculations of the HCN-H$_2$ van der Waals complex, considering both molecules as rigid rotors, were carried out at the explicitly correlated coupled cluster with single, double, and perturbative triple excitations [CCSD(T)-F12a] level of theory using an augmented correlation consistent triple zeta (aVTZ) basis set. The equilibrium structure is linear HCN–H$_2$ with the nitrogen pointing towards H$_2$ at an intermolecular separation of 7.20 a_0. The calculated dissociation energies for the para and ortho complexes are 37.79 cm^1 and 60.26 cm^1, respectively. The calculated ro-vibrational transitions in the HCN–H$_2$ complex are found to agree by more than 0.5 % with the available experimental data[2], confirming the accuracy of the potential energy surface.

The rotationally inelastic cross sections among the 13 first rotational levels of HCN were obtained using a pure quantum close coupling approach for energies up to 1200 cm^{-1}. Corresponding thermal rate coefficients were computed for temperatures ranging from 5 to 100 K. The HCN rate coefficients are strongly dependent on the rotational level of the H$_2$ molecule. In particular, the rate coefficients for collisions with para-H$_2(j = 0)$ are significantly lower than those for collisions with ortho-H$_2(j = 1)$ and para-H$_2(j = 2)$. Propensity rules in favor of even Δj transitions were found for HCN in collisions with para-H$_2(j = 0)$ whereas propensity rules in favor of even Δj transitions were found for HCN in collisions with H$_2(j \geq 1)$. The new rate coefficients were compared with previously published HCN-para-H$_2(j = 0)$ rate coefficients[3]. Significant divergences were found due the inclusion of the H$_2$ rotational structure in the scattering calculations. Comparison with similar calculations on the rotational excitation of HNC by H$_2$ show that both isomers present present very different rate coefficients. The consequences in astrophysical modelling will be briefly discussed.

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Quantum study and quasi-classical collisions of $H_2 + H_2^+$ reaction

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H_4^+ is an important molecule in astrophysics because together with it isotopologues are involved in reactions of formation of H_3^+, the most abundant ion in space.

The high number of degrees of freedom and some characteristics presented in the potential energy surfaces (PES) make to this molecule complicated for theoretical studies.

The H_4^+ system presents a crossing between the ground and the first excited state in the entrance channel due to the equally probable position of the charge in either diatomic molecule. The crossing is produced when both molecules have the same interatomic distance. The lowest crossing in energy is obtained just above the first excited vibrational state of H_2 and the second excited vibrational state of H_2^+. The study of dynamics considering reactants in higher vibrational excited states but the ground state needs to treat this crossing to properly describe the position of the charge. In the literature the most common method describing the entrance channel is surface hoping.

In this talk I present the recent results obtained for H_4^+ system, including the PES[1] of the ground electronic state and some preliminary calculations on the collisions of $H_2 + H_2^+$ using quasi-classical trajectories.

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Ultra-Low-Temperature Reactions of C(^{3}P$_J$) Atoms with PAH Molecules in Helium Droplets and in the Interstellar Medium

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Carbon atoms and ions are extremely abundant in the interstellar medium (ISM) [1]. In addition, no energy barrier for the reaction between atomic carbon and broad variety of hydrocarbon molecules has been demonstrated [2]. Therefore, the chemical inertness of molecules towards the reactions with atomic carbon could help them to reach a predominant abundance in the ISM.

We study the reaction of carbon atoms with benzene, naphthalene, anthracene, and coronene molecules in liquid helium droplets at T = 0.37 K. The mass spectrometry has been applied to characterize the products of the chemical reactions. The calorimetric technique was used to evaluate the amount of energy released in the reaction. The geometries and vibrational frequencies of stationary points of the reactants, intermediates, and possible product isomers were determined using the B3LYP hybrid functional and the 6-311+G(d,p) basis set.

The barrierless reactions between reactants have been found. In contrast to the previous gas-phase study of the $C + C_6D_6$ reaction [3], no loss of hydrogen has been detected. Therefore, the similar stabilization of an intermediate gas-phase reaction product could be expected when the reaction proceed on the surface of the cold dust grain. For the reaction of carbon atoms with benzene, naphthalene, and anthracene, the insertion of the carbon atom into CC bond of an aromatic ring with considerable energy release has been found. In the case of coronene, the calorimetry was unable to detect the small amount of energy released in the reaction. The quantum chemical calculations show that the carbon atom cannot be inserted into CC bond of the coronene molecule as it leads to considerable distortion of several aromatic rings.

Therefore, it is proposed that PAH molecules with aromatic rings, which have at least four common carbon atoms, could be resistant towards the reaction with carbon atoms. This may grant a predominant abundance to such PAH molecules in the ISM.

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Multi-mode multi-state quantum dynamics for photo-excited polyatomic molecules: The Hamiltonian problem.

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The numerical solution of the TDSE has become an essential tool for the study of fundamental molecular processes, and the Multi-configuration time-dependent Hartree (MCTDH) method [1] is a powerful quantum dynamics algorithm, able to include more degrees of freedom than other methods. This is particularly useful in the study of photo-excited molecules, where it is often difficult to isolate a few important degrees of freedom leading to the need to simulate a multi-dimensional problem. In addition, it is becoming increasingly clear that for accurate simulations it is necessary to include a number of excited states, which are often close in energy and coupled through vibronic and / or spin-orbit coupling.

The problem at present is how to obtain the Hamiltonian for multi-mode multi-state problems. The Vibronic Coupling model Hamiltonian is a well-used and simple Hamiltonian that can be parameterised from quantum chemistry calculations and easily combined with the MCTDH method [2]. It is, however, difficult to model long-range motions and regions of the (coupled) potential surfaces away from the Franck-Condon region. Examples showing both the power and limitations are given by calculations on the channel 3 problem in benzene and the photo-dissociation of hetero-aromatic molecules [3, 4].

Direct dynamics, in which the potential surfaces are calculated on-the-fly using quantum chemistry calculations only when required, promise to provide general flexible potential surfaces. The DD-vMCG method, which is derived from the MCTDH method, will be presented as an alternative to model Hamiltonians [5]. It is fully quantum mechanical, and promises to have good convergence properties, essential for these expensive calculations.

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Coarse master equations for peptide folding and peptide-peptide interactions

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The formation of secondary and tertiary structure in proteins is a complex process, prohibitively difficult to study in a systematic manner with current computational resources. We use coarse master equations for helix formation and helix-helix interactions based on data from atomistic molecular dynamics simulations. By balancing the effects of fast, non-Markovian transitions, on one hand, and the typically limited sampling of slow relaxation processes on the other hand, we probe the underlying network of folding-unfolding transitions between the various configuration states of a protein. Our systematic analysis method reveals the transition states and the associated folding pathways at multiple levels, from atomistic to coarse-grained representations. We validate our approach in folding studies of short helix-forming polyalanine peptides, as well as of a larger, helix-turn-helix subdomain of a viral scaffolding protein. Our analysis of local, site-specific formation of intra- and inter-chain interactions is a first step towards understanding the elementary stages of secondary and tertiary structure formation in the folding of larger, more complex proteins.

Towards High Dimensional Quantum Dynamics with MCTDH

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It is well-established that nuclear quantum effects play a major role in many relevant areas of physics, chemistry, and biology. In particular, the impact of phenomena such as proton tunnelling or zero-point energy, is recognized to extend far beyond the mere academic perspective [1].

Among the different methodological specialties [2], the Multiconfiguration Time-Dependent Hartree method (MCTDH) [3] provides a balanced solution for the full-quantum description of medium-large systems in terms of accuracy and computational expenses. Unfortunately, its grid-base nature entails an exponential scaling of data and number of operations with system size. This issue manifests severely in the grid representation of the Potential Energy Surface (PES). Solutions, in the form of tensor-decomposition schemes, exist though. In particular, in MCTDH, the PES is transformed into the so-called product form by means of algorithms, such as POTFIT or the expansion in clusters [4]. The former possesses a major advantage over the latter: its variational nature. However, it is limited in the size of the systems that can be treated (up to $\sim$6D).

To circumvent this issue, we have recently introduced Multigrid POTFIT (MGPF) [5], a variational algorithm which transforms a PES on a grid into product form (up to $\sim$12D). MGPF requires the definition of a series of partial grids, as subsets of the primitive one. A MGPF PES results from an algebraic transformation of the POTFIT expansions obtained on these partial grids. It is precisely the use of subsets of the primitive grid that makes MGPF orders of magnitude more efficient than POTFIT. To illustrate the capabilities and usage of MGPF, we have tackled the full-dimensional (9D) study of the vibrational levels of the highly fluxional hydrated hydroxide anion ($H_3O_2^-$). Using low order MGPF expansions ($<$5MB), we have been able to reproduce, for the first time, reference values: (i) ground state energy; and (ii) the experimental value of the proton transfer along the z-axis [6].

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CONFINING MOLECULES INSIDE A NANOSCALE CAVITY: THE CASE OF CLATHRATE HYDRATES

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In order to provide insights into the water-trapped gas interactions, quantum Multi-Configuration Time-Dependent Hartree (MCTDH) calculations are carried out for the two cages of the sI CO_2 clathrate hydrate [1]. The interest in CO_2 hydrate is driven in part by industrial applications, as well as due to its interest in astrophysics and its formation conditions at Mars, satellites, comets and dense interstellar clouds [2,3]. Considering that by confining a molecule into a cage leads to the quantization of its translational (T), rotational (R) and vibrational (V) states, the investigation of the dynamics of the guest molecule is made by taking the small and large cages of the sI clathrate to be rigid, and the CO_2 molecule is kept linear. Thus we carried out 5D and 7D calculations, considering the T-R-V degrees of freedom of the trapped CO_2 fully coupled. By comparisons with the data from infrared spectroscopic studies of carbon dioxide clathrate hydrate at low temperatures [4], we found that in the small cavity (5^{12}) the rotational ability of the CO_2 is hindered where an almost rigid CO_2 molecule is enclathrated, while in the large cavity ($5^{12}6^2$) a higher coupling of T-R is found. By analysing the vibrational states of the $^{12}CO_2$, $^{13}CO_2$ and ^{16}OCO isotopes in both cavities, we predict [1] the double peak profile observed in FTIR spectra [4] of such clathrate hydrates.

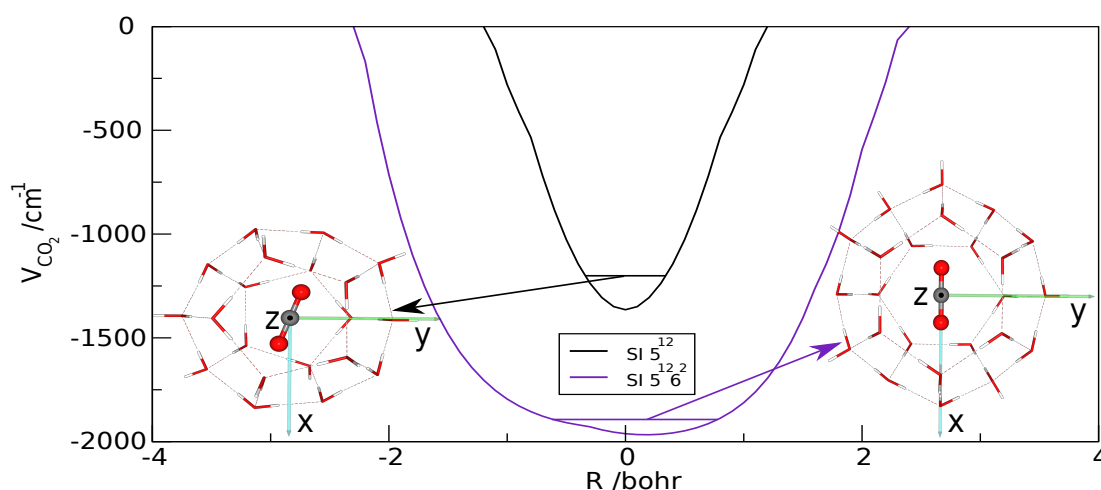**Figure 1:** *The $V_{CO_2-cavity}$ interaction potential as a function of distance R between the center of mass of the cavity and the center of mass of the CO_2 molecule. Zero point energies with their corresponding geometries are shown for the small (5^{12}) and large ($5^{12}6^2$) cavities of SI clathrate structure.*

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Probing Salt Solvation in Helium Droplets via Infrared Depletion Spectroscopy

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Helium droplets are ideal matrices for spectroscopic studies of small molecular clusters. They are chemically inert, extremely cold (0.38 K), transparent from the far-IR to vacuum UV and superfluid, allowing rapid cooling of the dopant clusters that aggregate inside them [1,2]. When the dopant clusters absorb photons, the photon energy can be rapidly converted to thermal energy, leading to evaporative loss of helium atoms and thus the shrinkage of helium droplet sizes. This frequency-dependent absorption is then registered as a depletion signal in a specific ion channel in the mass spectrum.

Here we report the solvation of NaCl inside helium droplets using infrared depletion spectroscopy. A resistively heated oven is first used to evaporate NaCl molecules to be picked-up by the helium droplets. A second pick-up cell is then utilised to add the water molecules inside the droplets and form water-salt clusters. A quadrupole mass spectrometer is used to ionise the clusters (by electron impact) and detect the corresponding $Na(H_2O)_n^+$ ions. The O-H stretching vibrations of the water-salt clusters are excited using a pulsed OPO, leading to a depletion signal in the $Na(H_2O)_n^+$ channels. Preliminary results show the presence of several $NaCl(H_2O)_n$ clusters whose spectral bands match closely to previous theoretical work [3]. The depletion spectra also indicate multiple fragmentation pathways of the clusters upon electron impact ionisation.
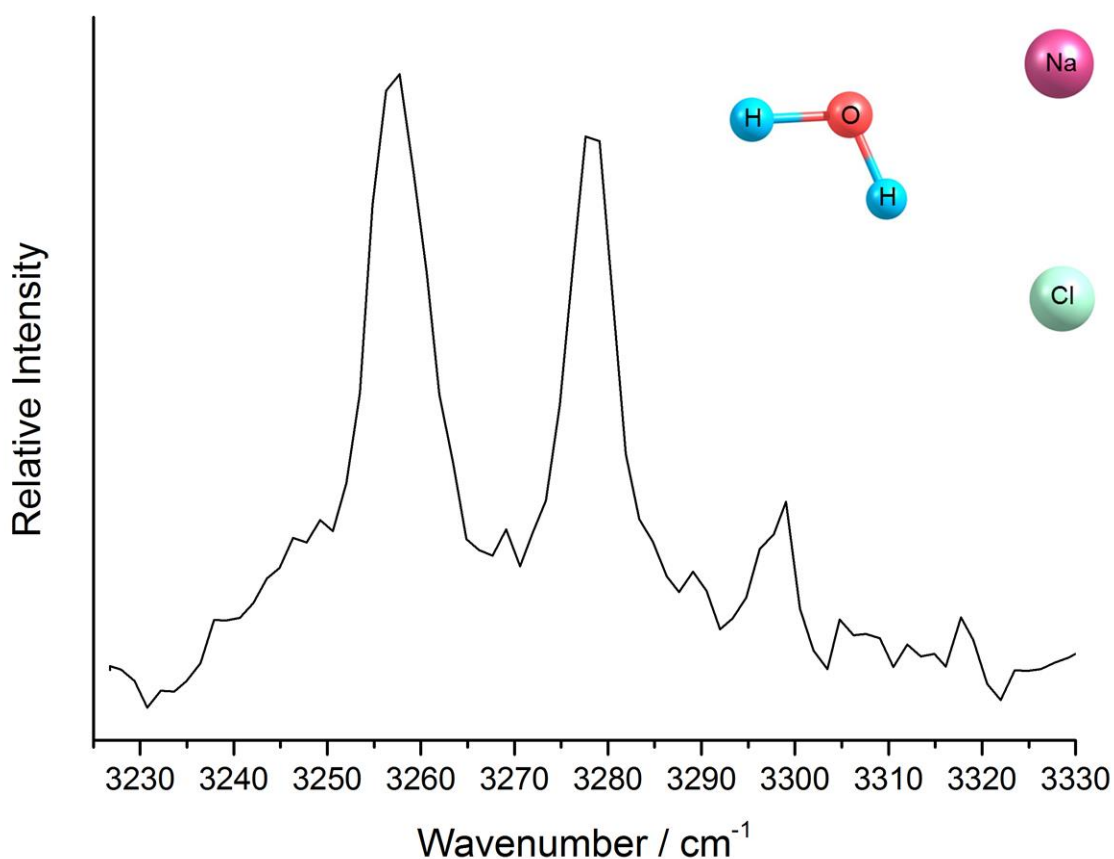
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DYNAMIC AND NON-ADIABATIC EFFECTS IN THE STEREOCONTROL OF PHOTOINDUCED ELECTROCYCLIC REACTIONS

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The stereochemistry of electrocyclic photochemical reaction products is determined by the Woodward-Hoffman rules [1] and dynamic effects that dependent on the coupled electron-nuclear dynamics [2]. We use ab initio non-adiabatic molecular dynamics based on time-dependent density functional theory [3, 4, 5] to simulate the photoinduced electrocyclic ring-opening and ring-closure reactions in bicyclic butadiene derivatives [2], cyclohexadiene, and spiropyran [6] compounds. The purpose of this study is to explain the influence of dynamic and non-adiabatic effects on the formation of Woodward-Hoffman forbidden products. Results from our simulations are compared to reaction rates, quantum yields, and product distributions from time-resolved femtosecond spectroscopic experiments.

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NON-ADIABATIC DYNAMICAL DESCRIPTION OF $H_2O^+(\tilde{B}\ ^2B_2)$ FRAGMENTATION

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The single ionization of water molecules in collisional processes leads to the formation of H_2O^+ in several possible electronic states: $\tilde{X}\ ^2B_1$, $\tilde{A}\ ^2A_1$ and $\tilde{B}\ ^2B_2$. The first two states are obtained after removal of essentially non-bonding electrons from H_2O, and the corresponding cations do not fragment [1]; however, the energy of the third state lies above the dissociation limits of the first two states and it has been measured [1] that about 92% of the ions formed in that state do fragment.

This work illustrates the fragmentation process of the $\tilde{B}\ ^2B_2$ state and estimates the corresponding fragmentation probabilities by reproducing the non-adiabatic Dynamics of the water cation. We assume that H_2O^+ ($\tilde{B}\ ^2B_2$) ions are initially produced by a vertical transition from the ground vibrational state of the water molecule, and propagate the wave packet in a diabatic representation using the Grid-TDSE method [2]. The three lowest doublet states $\tilde{X}\ ^2B_1$, $\tilde{A}\ ^2A_1$ and $\tilde{B}\ ^2B_2$ are included in the model, as well as the non-adiabatic couplings among them: a conical intersection between $\tilde{A}\ ^2A_1$ and $\tilde{B}\ ^2B_2$ states and the Renner-Teller coupling between $\tilde{X}\ ^2B_1$ and $\tilde{A}\ ^2A_1$ at linear geometries [3]. We also calculate the contribution of the lowest quadruplet $\tilde{a}\ ^4B_1$ to the dissociation by including the spin-orbit interactions with $\tilde{A}\ ^2A_1$ and $\tilde{B}\ ^2B_2$ states.
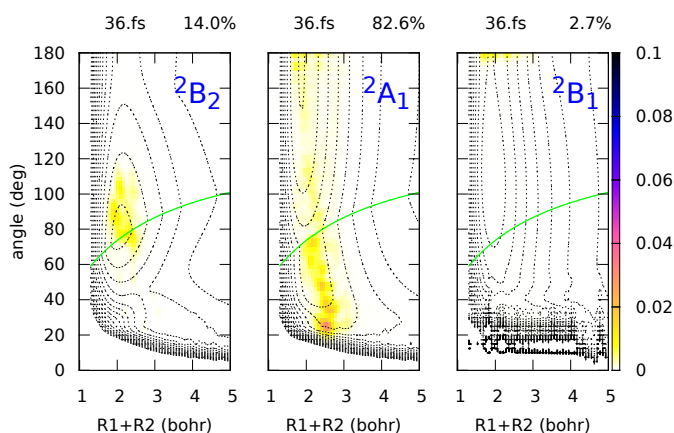

Figure 1: Probability density of the wave function after 36 fs over the adiabatic states $\tilde{B}\ ^2B_2$, $\tilde{A}\ ^2A_1$ and $\tilde{X}\ ^2B_1$ (left to right)

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MOLECULAR QED THEORY OF TWO- AND THREE-BODY DISPERSION FORCES

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An extension of the Craig-Power Hamiltonian [1], in which a body responds through its electric dipole polarizability to the square of the electric displacement field, is employed within the formalism of Molecular Quantum Electrodynamics [2,3] to obtain an expression for the retarded non-additive dispersion energy shift between three atoms or molecules, *A*, *B* and *C*, each of which is arbitrarily electrically polarizable with electric multipole moment of order *l*, *m* and *n*, respectively [4]. An index value of 1 corresponds to electric dipole (D), 2 to quadrupole (Q) and 3 to octupole (O), etc, coupling terms. As in the diagrammatic perturbation theory calculation of the Casimir-Polder potential [2,3,5], and its generalization to higher electric multipoles [6], the interaction between three bodies is viewed as arising from the exchange of two virtual photons between any two coupled species. An advantage of adopting this Hamiltonian is that only third-order perturbation theory is required, together with summation over six time-ordered diagrams, to yield the interaction energy. This is in contrast to using the usual multipolar coupling Hamiltonian that is linear in the electric field in which 360 graphs are evaluated at sixth-order. Specific higher multipole non-additive terms are then extracted from the general formula. These include DDQ, DQQ and DDO dispersion potentials. Explicit forms are given for equilateral triangle and collinear geometries [7]. Agreement is obtained for the leading non-additive DDD term first evaluated by Aub and Zienau [8], in which they extended the Axilrod-Teller-Muto result [9,10] to the retarded regime. Asymptotically limiting forms are computed for all of the potentials considered, with near-zone shifts coinciding with Bell's semi-classical results [11], recently used in the study of interactions involving rare gases and alkali and alkaline Earth metal atoms [12,13]. Interesting features occur when the octupole is decomposed into weight-1 and weight-3 contributions, with the former term only appearing when the interactions are retarded.

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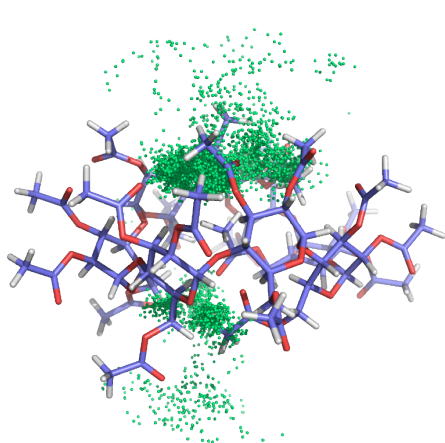[13]   L-Y. Tang *et al*, *J. Chem. Phys.* **136**, 104104 (2012).

New Routes for Improved Solubility in Supercritical CO$_2$: When Theory Comes in Handy
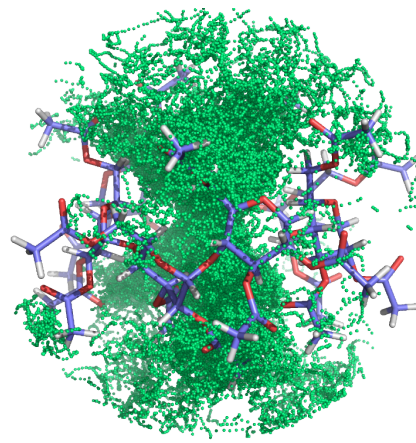
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Closed Cyclodextrin Cavity   **Open Cyclodextrin Cavity**

The use of Supramolecular Chemistry in pharmaceutical and industrial technologies based on aqueous and/or organic solutions is well established, with applications ranging from biological systems to materials. In this work, we shall explore a different solvation medium, considered as one of the most promising solvents for Green Chemistry methods: supercritical carbon dioxide (scCO$_2$). Our goal is to illustrate how the development of molecular modeling and theoretical approaches can assist in the design of new processes of industrial interest, with particular emphasis on improving the solvation strength of this solvent. Starting from studies that focus on the intermolecular interactions in the scCO$_2$, we shall concentrate on the use of β-cyclodextrins as supports for host-guest binding. In aqueous solutions, these macromolecules present a cavity that is available to host hydrophobic guests, extensively used to build molecular vectors for drug delivery. On the other hand, several attempts to form inclusion complexes in solution of supercritical CO$_2$ using these systems have failed, as reported in the literature. After studying the driving forces that could lead to host-guest binding in such a solvent (where the usual hydrophilicity/hydrophobicity balance is not applicable) we were able to propose some guidelines that were followed in collaboration with experimentalists. Thanks to these efforts, the first stable inclusion complex formed in an acetylated β-cyclodextrin in scCO$_2$ has been isolated and characterized. To conclude, ongoing work and our research perspectives will be shortly summarized.

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REACTIVE INTERMEDIATES OF ATMOSPHERIC IMPORTANCE STUDIED WITH PHOTOIONIZATION AND QUANTUM CHEMISTRY CALCULATIONS

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This talk will illustrate how quantum chemistry calculations can be used to support results from photoelectron spectroscopy and electronic spectroscopy of reactive intermediates of atmospheric importance. In this way, the spectra obtained can be fully interpreted and the electronic structure of the reactive intermediates studied probed. Also, thermochemical, spectroscopic and kinetic information on the reactive intermediates studied will be derived.

Possible examples to be discussed will be reactions DMS with several atmospheric oxidants, reactions of ozone and alkenes, and chlorine and OH reactions with several VOCs. The atmospheric implications of the results will be highlighted.

TIME-RESOLVED PHOTOELECTRON SPECTROSCOPY AND *AB INITIO* CALCULATION ON NO/NO₂ RELEASE OF NITROAROMATICS

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Volatile organic compounds (VOC) are molecules that are emitted into the troposphere by human activities. Among them, aromatic hydrocarbons form an important class and could account for more than 25 % of the total VOC-amount produced in urban areas [1]. One of these molecules which received special attention is 2-nitrophenol (2-NP) together with its methylated derivatives. 2-nitrophenol absorbs strongly in the atmospherically important UV-regime between 300 and 400 nm and is known as a source of HONO (see Figure 1) which itself is a precursor for OH-radicals. The OH radical is the key oxidant in the degradation of air pollutants and one of the defining molecules in atmospheric chemistry. In addition to HONO production, nitroaromatics in general are known to produce both NO and NO₂ upon photoexcitation. In order to investigate mechanisms and time scales of the different processes, we performed time resolved photoelectron spectroscopy studies using laser and synchrotron light as a probe pulse. For additional information on the excited state pathways, we also did first principles calculations. As target molecules, we investigated several substituted nitrophenols (NP) as well as a series of nitrobenzaldehydes (NBA).
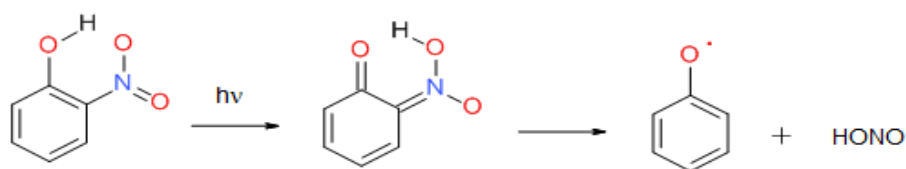

Figure 1: HONO formation process starting from 2-nitrophenol.

For both series of molecules, there exists a competition between NO and NO₂ release. The former takes place in the triplet state or the singlet ground state while the latter takes place on the excited singlet manifold. For NBA, gas phase dynamics agree well with liquid phase dynamics and NO release is the dominant process. In contrast, the dynamics in nitrophenol takes place on a shorter timescale, especially for wavelengths as low as 200 nm, which suggests a competitive reaction channel which we suspect to be NO₂ release. In the case of 200-nm excitation of NPs, a different reaction mechanism is evidenced by sub-ps dynamics in 2-NP suggesting fast intersystem crossing and subsequent HONO release while the dynamics in 3- and 4-NP take place on a 10 ps timescale, most likely due to NO release.

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MICROSOLVATION AGGREGATES OF ALKALI-METAL IONS WITH AROMATIC RINGS

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The stepwise addition of solvent molecules to an ion is usually known as microsolvation. The study of aggregates resulting from such process has shown to be a powerful methodology to understand solvation phenomena at the molecular level. From the theoretical view point, the structural and energetic characterization of microsolvation aggregates benefits of employing state-of-the-art algorithms for global geometry optimization [1-3]. In this context, our group has contributed to the development of unbiased evolutionary algorithms (EAs) that have been successfully applied for global geometry optimization of several cluster systems [4-6]. This presentation focus on our recent work concerning the microsolvation study of alkali-metal ions with either benzene [7] or hexafluorobenzene [8] by employing an empirical potential model and the EA for the global geometry optimization of molecular clusters [6]. Specifically, we have obtained putative global minima for clusters resulting from the solvation of Na^+, K^+, and Cs^+ with benzene (Bz). The potassium cation was also solvated with hexafluorobenzene (HFBz) in order to assess the solvent effect. Whereas 3 (or 4) benzenes are sufficient to complete the first solvation shell around Na^+ (or, K^+ and Cs^+), the corresponding number for the coordination of K^+ with HFBz molecules increases to 9. Nonetheless, a strong magic-number becomes associated to the completeness of the first solvation in all cases. It is worth noting that, as more solvent molecules are added to the aggregate, some global minimum structures arise with less than 9 HFBz molecules directly coordinated to the ion, which implies a reorganization of the first solvation shell during the cluster growing process. Conversely, aggregates resulting from the microsolvation with Bz keep the same number of molecules in the first solvation shell as the structure grows. Basically, all these structural features may be related to the different sign of the quadrupole moment in Bz and HFBz molecules. Moreover, we have performed *ab initio* calculations at the MP2 level of theory to further analyze the first solvation shell of the $K^+(Bz)_n$ aggregates. Essentially, the structures resulting from the optimization at the MP2 level resemble those obtained with the EA for the empirical potential.

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A DENSITY-DIFFERENCE-DRIVEN OPTIMIZED EMBEDDING POTENTIAL METHOD TO STUDY THE SPECTROSCOPY OF Br_2 IN WATER CLUSTERS AND CLATHRATE CAGES

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A density difference driven optimized embedding potential (DDD-OEP) method is proposed to obtain embedding potentials to calculate excited electronic states in large systems. This method considers the partition of the density of a system in two portions. The density on each subsystem is the solution of a Fock equation modified by the addition of an "embedding" potential. This embedding potential is obtained iteratively by minimizing the difference between the electronic densities of the total system and the sum of the subsystems[1,2].

This method is applied to study the electronic excitation of the Br_2-H_2O complex[3] where exact calculations are feasible[4]. It is found that the embedding potential for the ground and electronic states are different to properly describe the energy excitation, because the orbitals involved in the electronic excitation also participate in the forming the complex in the ground electronic state. A similar situation is found for the Br_2-$(H_2O)_n$ complex. On the relatively large $(H_2O)_{24}$ clathrate cage the water-halogen binding is considerably weaker and the excitation energy found using one unique embedding potential seems reasonable, waiting for more accurate benchmark. A diagnosis method, based on the analysis of initial density-difference is proposed to determine whether or not a single embedding potential is able to describe electronic excitation on large systems.

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Chemistry with Cold Molecules: from Universality to Quantum Resonances

Edvardas Narevicius

There has been a long-standing quest to observe chemical reactions at low temperatures where reaction rates and pathways are governed by quantum mechanical effects or long range interactions. This field of Quantum Chemistry has been dominated, to date, by theory, with almost no experiments. The difficulty so far, has been to realize low enough collisional velocities between neutral reactants, so that the de Broglie wavelength becomes long enough for the quantum wave nature to emerge as a dominating effect. We will discuss how reaction temperatures on the order of several milli Kelvin can be achieved without laser cooling by merging cold and fast molecular and atomic beams. We will show that by controlling the initial electronic state of metastable helium in the ionisation reactions with molecules we can switch reaction mechanism from the universal Langevin behavior into the quantum tunnelling dominated regime.

CONTROLLING MAGNETIC FESHBACH RESONANCES AND PHOTOASSOCIATION RATES WITH NONRESONANT LIGHT

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Magnetically tunable Feshbach resonances for polar paramagnetic ground-state diatomics are too narrow to allow for magnetoassociation starting from trapped, ultracold atoms. In the first part of this talk, we show that nonresonant light can be used to engineer the Feshbach resonances in their position and width. For nonresonant field intensities of the order of 10^9 W/cm^2, we find the width to be increased by 3 orders of magnitude, reaching a few Gauss [1]. This opens the way for producing ultracold molecules with sizable electric and magnetic dipole moments and thus for many-body quantum simulations with such particles.

Photoassociation, assembling molecules from atoms using laser light, is limited by the low density of atom pairs at sufficiently short interatomic separations. In the second part of this talk, we show that nonresonant light with intensities of the order of 10^{10} W/cm^2 modifies the thermal cloud of atoms, enhancing the Boltzmann weight of shape resonances and pushing scattering states below the dissociation limit [2]. This leads to an enhancement of photoassociation rates by several orders of magnitude and opens the way to significantly larger numbers of ground-state molecules in a thermal ensemble than achieved so far.

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Statistical product distributions for ultracold reactions in external fields

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Recent advances in producing and trapping species at temperatures below 1 mK have made ultracold chemistry a reality. For the first time, we can explore reactions in the fully quantum regime where resonances, tunnelling, quantum degeneracy and other quantum effects may dominate the dynamics. Moreover, controlling all degrees of freedom and scattering conditions becomes possible at such temperatures: reactions may be studied at the state-to-state level, typical and exotic mechanisms scrutinized with unprecedented detail--favoured or disfavoured at will--, and the effects of ``tailored" interactions and dimensionality thoroughly probed. A series of pioneering experiments at JILA, Colorado, have recently started to address many of these issues in reactions of mixed ultracold samples of K, Rb and KRb molecules [1-3]. While Quéméner and Bohn [2-5] provided the theoretical interpretation of the observed loss rates, Idziaszek and coworkers [6, 7], and Gao [8, 9] have developed simple quantum models for reaction rates and identified different universality classes. The most important open question is that of product-state distributions, or more precisely, state-to-state cross sections. These are far more sensitive than reaction rates to the details of the reaction dynamics, and hence provide an integral view and deeper understanding of the underlying physics. *A priori*, a rigorous description of these reactions can be derived from the quantum-mechanical formalism of Tscherbul and Krems [10]. Yet, as argued by Mayle *et al.* [11, 12], the huge number of ro-vibrational states involved makes such approach impractical for most cases of current experimental interest. Here, I will discuss a general and flexible framework for calculating statistical product-state distributions and state-to-state cross sections for ultracold reactions in external fields, which we have developed by connecting traditional statistical theories [13, 14] and ultracold collision theory [15]. In analogy with studies of reactions at higher temperatures, such product distributions may be used as benchmarks for the founding assumptions of the theory, providing fundamental tests for the statistical arguments of Mayle *et al.* [11, 12]. Moreover, they allow to critically evaluate possible departures from statistical behavior, being thus a powerful tool in understanding any kind of reaction.

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UNIVERSALITY IN THE COLD AND ULTRACOLD DYNAMICS OF THE BARRIERLESS REACTION $D^+ + H_2$

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Apart from being the prototype of barrierless ion-molecule reaction, the H_3^+ system is relevant due to its importance in astrochemistry [1]. We have calculated quantum reactive cross-sections for the collision $D^+ + para\text{-}H_2$ (v=0, j=0) $\rightarrow$ $H^+ + HD$ using the hyperspherical quantum reactive scattering method [2]. Considered kinetic energies range from the ultracold regime, where only one partial wave is open, up to the Langevin regime, where many of them contribute.

At very low kinetic energies, both an accurate description of the long-range (LR) region in the potential energy surface (PES), and long dynamical propagations, up to distances of hundreds or thousands of a.u., are required. Accordingly, calculations have been carried out on the PES by Velilla *et al.* which accurately reproduces the LR interactions [3]; besides, the hyperspherical methodology was recently modied in order to allow considering LR interactions while minimizing the computational expense[4]. In this work such method is proven particularly suitable for systems involving ions, where the ~ R^{-4} behaviour largely extends the range of the potential.

We have found a reaction rate coeficient which remains **largely constant in a range of more than 8 orders of magnitude of kinetic energy**. In particular, the value reached in the Wigner regime, where only one partial wave is open, is *paradoxically* the Langevin classical value (with a difference of a few percent), which is expected at high energies. Results will be discussed in terms of **universality** and related to the recently published quantum defect theory by Idziaszek and coworkers [5, 6]. Emerging experimental techniques are making possible quick advances in the analysis of cold and ultracold reaction dynamics, and the title system appears as an interesting candidate for such experimental studies.

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OBSERVATION OF PARTIAL WAVE RESONANCES IN O_2-H_2 INELASTIC COLLISIONS AT VERY LOW COLLISION ENERGY

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I will present results in the study of rotational energy transfer to O_2 by collisions with H_2 at energies approaching the cold regime, defined by temperatures below 1 K. Theoretical calculations predict that the dynamics of this system is dominated by quantum resonances, which can only be revealed at very low energies. Their experimental observation provides a stringent test for theoretical models.

Experiments were performed using a crossed molecular beam apparatus combining a variable intersection angle and cryogenically cooled fast-pulsed valves. The excitation function, *i.e.* the dependence of the integral cross sections as a function of the relative translational energy, was determined down to a few wavenumbers, below the threshold of the $\{(N = 1; j = 0) - (N = 1; j = 1)\}$ O_2 transition at 3.96 cm^{-1}. The experimental excitation function exhibits behaviours characteristic of dynamical resonances and is compared to quantum mechanical scattering calculations performed using a recent potential energy surface [1]. The results show that this collision-induced transition, which is classically forbidden, occurs exclusively in a pure quantum regime *via* shape and Feshbach resonances arising from definite partial waves. The complete assignment of the observed resonances is allowed by the very good agreement between experimental and theoretical integral cross sections [2].

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Formation of molecules with both magnetic and electric dipole moments

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At present there is a growing interest in studies of ultracold atomic mixtures where two atoms have different spin quantum number - such mixtures might potentially lead to ultracold molecules with permanent electric dipole and magnetic moments. In 2010 it was demonstrated that the Feshbach resonances can be observed in Rb+Sr mixtures [1]. However, the width of such resonances is expected to be very small and experimental realisation of magnetically tuneable mixtures will be very challenging. It is worth mentioning that broad Feshbach resonances can be produced in dimers of excited atoms [2], however, as the atoms are not in their ground states they will undergo strong decay to the ground state.

Here we present few ideas to obtain Feshbach resonances in low magnetic fields which can be detected with current. First, we demonstrate that the ultracold molecules with nonzero spin could be produced from Er+Li ultracold mixture. In this system both, L-anisotropy and spin-exchange are present, both can drive the Feshbach resonances. These terms near van der Waals minimum are on the order of tens of wavenumbers which is enough to produce broad resonances. Since vibrational spacing in this system is small we predict much smaller density of resonances compared to recently studied Er+Er mixture [3].

Another system which will be presented here is the mixture of metastable helium (He*) with Rb atom, for which the scattering length recently has been studied in details, in the group of Knoop in Amsterdam [4]. As the system undergoes the Penning ionization we consider the atoms to be in electronic spin-stretched state. In such state there can be resonances driven by electronic spin-dipole term. We analyse the width of resonance as a function of both, high-spin and low-spin scattering lengths of He*-Rb system.

Finally we present a new idea of inducing the magnetic Feshbach resonances in Sr+Rb system in presence of the microwave field slightly detuned from F=2-F=1 transition. We demonstrate that strong microwave radiation can introduce additional couplings in the system and Feshbach resonances can be induced in fields as low as tens of Gauss, with the width up to 10 mG.

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The chemistry of the early universe: a comparison among dynamical approaches

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The chemistry of the early universe plays an important role in our understanding of the formation of the first cosmological objects and on the birth and evolution of galaxies and interstellar clusters[1]. Molecular formation began in the recombination era when the temperature was low enough that the newly formed atoms could survive for further evolution. After recombination, the density was still very low and three body reactions were still very inefficient: however, it was then that the first molecular species were postulated to be formed through radiative association. In spite of the low fractional abundances which is expected to exist for species like LiH, LiH^+ and HeH^+ these molecules have nevertheless been considered to be important in that domain, due to the large permanent dipole moment and the light masses of the involved atoms. These molecules were thus considered to be very relevant because of the role they may have played as a possible coolant during the late stages of the gravitational collapse of the first cosmological objects. Because of the high density of their rovibrational states, molecules can absorb thermal energy from the surrounding atomic gas via internal excitations and then release it through emission of photons, thereby efficiently cooling the clouds. In turn, these photons can increase the density of the cosmic background radiation inducing both spectral distortions and spatial anisotropies. This cooling mechanism is considered crucial for the formation of the first cosmological objects (i.e. massive stars), that are thought to be formed by collapse of the molecular clouds. These stars have low metallicity and the only cooling mechanism could be provided by molecules like HeH^+, H_3^+, H_2^+, D_2, LiH^+. Gas phase chemistry of molecule formation and destruction is therefore fundamental to have a good understanding of how the first objects formed or how galaxies and clusters came to be.

However, to evaluate the molecular abundance in the full redshift range from the Big-Bang to the formation of the first stars and galaxies, rate coefficients in a large range of temperature (several order of magnitude) are required. Notwithstanding simplicity of the reactive atomic and ionic species, the broad range of the temperature required in the evolutionary cosmological models and the high complexity of chemical physical processes involved do not permit to obtain all the rate coefficients by

· exact· · quantum dynamical methods, so that benchmark quantum dynamical calculations are mandatory to properly assess dynamical approximations and/or models necessary to extend the numerical treatment to regimes where · exact· · quantum rates cannot be achieved.

In the conference our recent effort[2-4] in this direction will be presented taking as example some prototypical key reactions of the early universe chemical network.

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ENERGY TRANSFER AND THERMAL ACCOMMODATION IN GAS-SURFACE SCATTERING

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In this talk we will review recent work done in our group on the scattering dynamics of gases colliding with organic surfaces.[1-4] Our work is aimed at understanding the energy transfer dynamics and accommodation of a gas phase molecule when it strikes a surface.

An energy transfer model, based on simple gas-phase atom+diatom collisional models, is tested by extensive comparisons with simulation results.[1,2] The percentage of energy transferred to the surface, predicted by the model at high incident energies, decreases with the number of degrees of freedom (dof) of the projectile because they compete with the surface degrees of freedom as possible destinations of the incident energy. However, for large projectiles, the percent transfer to vibration is nearly constant, a result that can be attributed to a mass effect and also to the fact that only a reduced subset of "effective" vibrational dof is being activated in the collisions.

The distributions of the scattered projectiles over translational and rotational states show a low-energy component characterized by a Maxwell-Boltzmann (MB) distribution at the surface temperature that survives at the highest collision energies. The dependence of the fraction of the MB component on the incident energy is an exponential decay function and the rate of decay is similar for the rotational and translational distributions. A new method to categorize the trajectories, based on the residence time, shows that, at very low incident energies, thermal accommodation can be achieved in a single collision event.

Finally, for some projectiles the interaction energy with the surface is so strong that they can reside on top of the surface for hours. This phenomenon has been explained in our group with the help of accelerated dynamics techniques.[3,4]

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PHOTODISSOCIATION QUANTUM DYNAMICS OF DIATOMIC MOLECULES IN A QUANTUM SOLVENT (^{4}He NANODROPLETS)

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Superfluid helium nanodroplets (^{4}He)$_n$ are interesting systems from several perspectives. From a fundamental point of view, they are finite-size systems where the bulk quantum liquid phenomenon of superfluidity is present, allowing to obtain a deeper knowledge of this important property [1]. On the other hand, from a chemical point of view, investigations using helium nanodroplets constitute an active area of research, since they can be used as an excellent liquid environment where different important questions can be explored such as, e. g., high resolution molecular spectroscopy, chemical reactivity at very low temperature, and the synthesis of non-stable molecules and nanoclusters [2]. Up to now, there has been an important number of theoretical contributions accompanying spectroscopic experiments, but not in the field of chemical reactions. In this contribution, we investigate a prototypic and relatively simple chemical reaction, which corresponds to the photodissociation of a diatomic molecule placed inside a helium nanodroplet. To do this, we have used a Density Functional Theory (DFT) approach, using a well established phenomenological functional to describe the ^{4}He superfluid at zero temperature [3]. This treatment allows us to deal with nanodroplets containing from few hundred to few thousand ^{4}He atoms, the larger droplets corresponding to the typical ones considered in the experiments.

For the system studied here (Cl$_2$ molecule), the symmetry of the process permits the use of the wave function expressed in terms of the relative coordinate (Cl-Cl distance) to describe the Cl$_2$ molecule. The photodissociation dynamics in (^{4}He)$_n$ (Cl$_2$(X) + hv → Cl$_2$(B) → Cl + Cl*) is compared with the results obtained in gas phase, in order to determine the effect of the quantum solvent in the process, taking into account droplets of different sizes. Moreover, our results are also compared with previous results based on a partial quantum treatment of the Cl$_2$@(^{4}He)$_n$ system. Once the dissociation is completed (Cl atoms very far from the droplet), the following nanodroplet relaxation process, which is mediated by evaporation of some He atoms, is also studied.

To the best of our knowledge, this is the first quantum dynamics investigation carried out on chemical reactions in helium nanodroplets. The computational codes required have been developed in our group.

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ATMOSPHERIC PHOTODISSOCIATION OF THE NITRATE ANION

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Long-thought the end-product of the NO_x oxidation, the nitrate anion has recently emerged as an important atmospheric chromophore [1]. Upon solar light absorption the nitrate anion can dissociate and subsequently induce the formation of the hydroxyl radical; thus significantly augmenting the oxidative capacity of the atmosphere.

The n→π* transition to the excited singlet state has long been considered responsible for the nitrate dissociation. Yet this solar absorption of the gas-phase nitrate anion is symmetrically forbidden and consequently very feeble. Using the methodology of nitrate-water clusters, we show how the absorption is enabled through the hydration. We demonstrate that each successive explicit water molecule means more photoabsorption [2].

However, the experimental quantum yields of the dissociative products are only very low. We offer a new intriguing explanation of the magnitude of quantum yields based on the direct singlet-triplet absorption. Although for a molecule non-containing a heavy atom such a spin-forbidden process is highly unusual, we demonstrate that the nitrate anion is in this sense unique due to its highly symmetric structure and the forbidden nature of the singlet-singlet absorption [3].
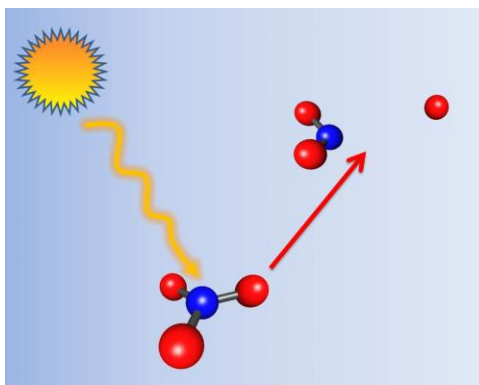
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Exact and approximate wave packet dynamics with quantum trajectories

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Abstract

Quantum fluid dynamics (QFD) is an alternative to conventional methods for the solution of the Schroedinger equation for nuclear motion on one or more electronic potential energy surfaces. Integration of the QFD equations via time propagation of quantum trajectories corresponds to a calculation of the full nuclear wave function, the only approximation being discretization. The bottleneck of this approach is clearly the numerically difficult computation of the quantum force term. The performance of different implementations of QFD is analyzed. QFD is also interesting as starting point for the development of mixed quantum-classical methods. One particular version is applied to the dynamics of coupled anharmonic oscillators and compared to the mean field ansatz.

FOLLOWING THE OH RADICAL IN HIDROGEN COMBUSTION

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Preliminary theoretical results on combustion molecular modelling suggest that the OH radical present in combustion processes are vibrationally excited and thus, not in thermal equilibrium.

Recently, we proposed a method to incorporate accurate Potential Energy Surfaces (PESs) when modelling complex reactive systems [1]. The PESs, based on *ab initio* calculations, are a powerful tool to study the rate of elementary reactions and their dynamics, being useful to compute state to state rate constants. In a more complex mechanism, we will be in the presence of different and simultaneous elementary reactions, corresponding to all the possible reactive and non-reactive collisions between the different species present and leading to the respective products. Attempting to build a traditional PES for such a system easily becomes an impossible mission. In order to circumvent this problem, a global Potential Energy Surface (gPES) can be defined integrating various PESs, each one of them representing an elementary reaction that is expected to play a role in the chemical process. READY is a program that builds such an overall PES for the process in question and performs reactive classical dynamic calculations on it.

On the other hand, kinetics models use available kinetic data, rate constants and their variation with temperature, to model complex mechanisms and have been successfully applied to model combustion processes. They rely on the assumption that the number of collisions between reactants and intermediates is large enough achieve thermal equilibrium.

We test this last hypothesis monitoring the evolution of the hydroxyl radical, OH, which is an important and very reactive intermediate in combustion, during the combustion of a mixture of oxygen and hydrogen at 3000 K and 2 atm until 3 ns, using the READY program. In this calculation we incorporate the most relevant ground and first excited state PESs involving oxygen and hydrogen up to four atoms as well as atom-atom pair potentials to mimic the short-range repulsion and long-range van der Waals forces. The overall results of this calculation have shown to be in reasonable agreement with similar kinetic model results [1].

In this work we present preliminary results of that study. They show that, in spite of the occurrence of a large number of collisions, these are more efficient in rotational and translational energy transfer than in vibrational quenching. As a consequence, the OH radical seems to be vibrational excited. To our knowledge, there are no experimental results to compare with and confirm, or infirm, this prediction.

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Water Passage through Graphynes' Pores:
First-Principles Penetration Barrier and Force Field Optimization

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Abstract: Graphynes are novel two-dimensional carbon-based materials, naturally presenting a nanoweb-like structure characterized by triangular and regularly distributed pores[1]. These intriguing features make them appealing for molecular filtering, especially for water purification technologies. First principles calculations are carried out at the MP2C level of theory to properly assess the interaction between water and graphyne, graphdiyne and graphtriyne pores. The computed penetration barriers (see Figure) suggest that water transport is unfeasible through graphyne while being unimpeded for graphtriyne. Nevertheless for graphdiyne, which presents a pore size almost matching that of water, a low barrier is found which in turn disappears if an active hydrogen bond with an additional water molecule on the opposite side of the opening is taken into account (see Figure). These results confirm the possibility of an efficient use of graphtriyne (and larger pore homologues) membranes for water filtration and purification, as very recently suggested by molecular dynamics investigations[2-5]. Still, in contrast with these studies[2-5], present findings do not exclude graphdiyne since the related first principles penetration barrier leads to water permeation probabilities[6] which are at least two orders of magnitude larger than those estimated by employing generic force fields[2-5]. The computed energy profiles for graphdiyne have also served to build a new pair potential for the water--carbon non-covalent component of the interaction which better represents the water--pore behaviour[6] and it is recommended for molecular dynamics simulations involving graphdiyne and water.

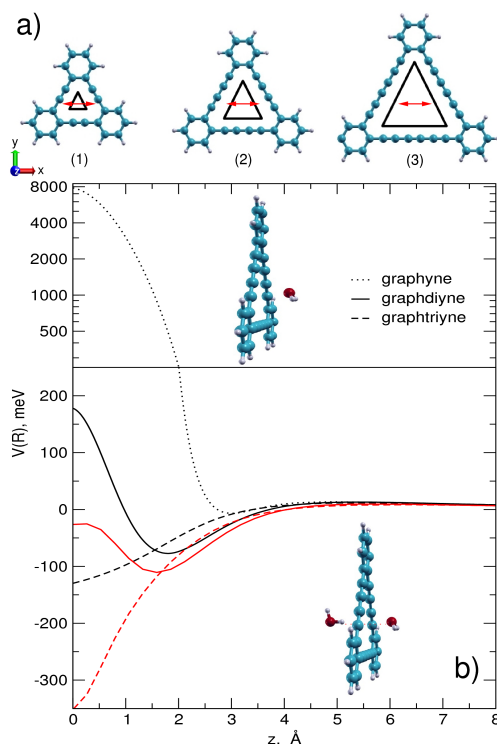Keywords: graphyne, graphdiyne, porous materials, nanofiltration, water purification, ab-initio calculations

Figure: a) Annulenic molecular structures used to study the nano-pores of graphyne(1), graphdiyne(2) and graphtriyne(3). The black triangles depicted inside the pores represent their effective available area to be compared with the van der Waals diameter of the water molecule (red double-headed arrow).
b) Energy profiles obtained at the MP2C level of theory for water perpendicularly approaching the geometric center of graphyne, graphdiyne and graphtriyne pores. Black lines correspond to the case of a single water molecule approaching the pore. Red lines refer to the case in which a second water molecule fixed on the other side of the pore is added. A catalyzing effect is noticed due to the presence of an active hydrogen bond, which for graphdiyne leads to the suppression of the penetration barrier.

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HEIGHT DEPENDENT INTEGRAL CROSS-SECTIONS AND RATE COEFFICIENTS FOR THE $O^+ + H_2$ (v=0,j=0) REACTION IN THE IONOSPHERE

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Earth's ionosphere reacts strongly to the intense X-ray and ultraviolet radiation released by the Sun. The molecular ion O_2^+ and neutral H_2 are important constituents and the concentration of each is changing hourly, daily, seasonal and yearly with height. The variation of all the components at this reaction and mean temperature of the ionosphere are taken from IRI-2012 (International Reference of Ionosphere). Then, the temperatures of the ionosphere and the reaction are compared [1]. In this work, the profile of reaction cross sections and rate coefficients of the $O^+ + H2 \rightarrow OH^+ + H$ scattering have been calculated for equinox days (21 March, 21June, 23 September and 21 December) of 2009 depending on the height of the ionosphere.

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Stability of rare gas–water clusters under pressure: the Ar and Kr case

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Classical parallel-tempering Monte Carlo simulations in the isothermal-isobaric ensemble were carried out for the $Ar/Kr(H_2O)_{20}$ clusters, over a wide ranges of temperatures (30–1000 K) and pressures (3 kPa–10 GPa) [1], in order to study their thermodynamical properties and structural changes. The TIP4P/ice water model is employed for the water-water interactions, while both semiempirical and *ab initio*-based potentials are used to model the rare gas-H_2O ones.

Temperature-pressure phase diagrams for these systems clusters were constructed by employing a two-dimensional multiple-histogram method [2]. By analyzing the heat capacity landscape and the Pearson correlation coefficient profile for interaction energy and volume, structural changes were detected (see Figure 1–right panel). Those at high pressure correspond to solid-to-solid transitions and are found to be related with clathrate-like cages around the Ar or Kr atoms (see Figure 1–left panel). It is also shown that the formation and stability of such structures are determined by the intermolecular interaction between the rare-gas and host molecules.
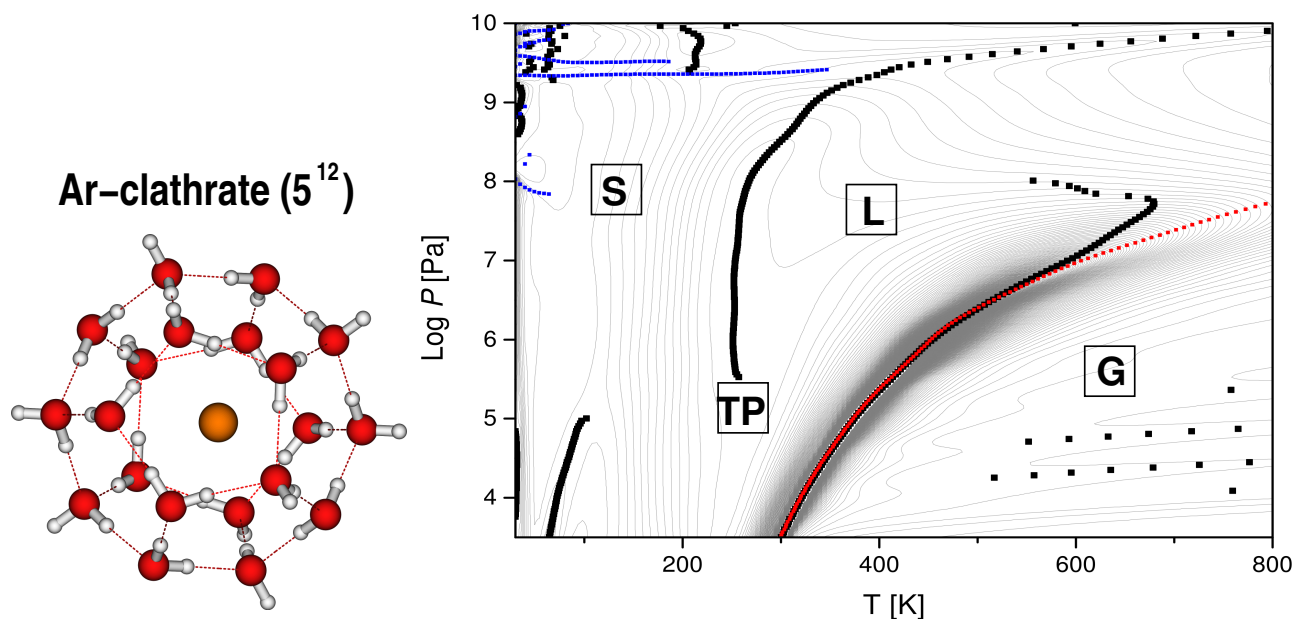

Figure 1: The Ar atom inside the 5^{12} cage (left panel) and phase diagram of the $Ar(H_2O)_{20}$ cluster (right panel). Black dots correspond to the maximum values of the heat capacity, red dots to the maximun values of Pearson correlation coefficient, while blue ones to the minimum values.

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SIMULATIONS OF X-RAY ABSORPTION SPECTRA OF FERRIOXALATE UPON UV EXCITATION

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Ferrioxalate ions, $[Fe(C_2O_4)_3]^{3-}$, form upon UV irradiation $[Fe(C_2O_4)_2]^{2-}$, oxalate anion and CO_2. Such reactions of Fe(III)-carboxylate complexes are involved in geochemical processes and in the formation of active oxygen species in natural water systems. The mechanism of the primary photochemical processes is, however, unclear [1]. Time-resolved X-ray absorption spectroscopy offers one way for its revealing [2].

Here, we present simulations of the X-ray absorption spectra of the ferrioxalate cation and its various possible decomposition intermediates. The calculated spectra are compared with available experimental data for the time-resolved K-edge XAS of the ferrioxalate ion. Analogical complexes of other transition metal complexes are studied as well.

The modeling of the transition metal XAS is in several direction challenging. First problem is connected to the electronic structure description. We have used the time-dependent density functional theory approach; comparing various functionals. The relativistic description of the system needs to be used. The other problem is connected to the simulations of excitation process into states of finite lifetime. We apply a modified reflection principle allowing quantitative estimate of the both the width and intensity of the spectra. The approach had been tested for model complexes before it was used for the ferrioxalate.

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How many adiabatic states are needed for diabatization?

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In this poster we analized a diabatization scheme based in the solution of the diferential equation that eliminates the non-adiabatic coupling for the dimension considered,

$$\frac{\partial T_{a\alpha}}{\partial R} = \sum_{\beta} T_{a\beta} \mathcal{F}_{\beta\alpha}$$

where T is the transformation matrix between the diabatic and adiabatic states and $\mathcal{F}$ is the non-adiabatic coupling matrix.

This diabatization method can be used for the case of a diatomic molecule. We study the behavior of the diabatic states when more adiabatic states are added. In particular we are interested in analyzing changes when ionic states are included. For this reason, we choose as a model the MgH diatomic molecule, where the swapping of charge is possible, giving rise to the $Mg^+ + H^-$ asymptotic limit. The nine $^2\Sigma^+$ states that correlate to the first nine atomic levels of Mg are considered.

DENSITY FUNCTIONAL THEORY STUDY OF WATER ADSORPTION ON IrO$_2$(110), RuO$_2$(110) AND Ru$_x$Ir$_{1-x}$O$_2$

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IrO$_2$ and RuO$_2$ are the most used catalyst materials for water electrolysis in the anode electrode of the so-called polymer electrolyte membrane water electrolyzers (PEMWE) [1]. This is due to the fact that such materials present the highest efficiency in comparison with other metal oxides [2]. The main difference between RuO$_2$ and IrO$_2$ is that the former presents a higher activity and the latter a higher resistance to corrosion. Therefore alloys, Ru$_x$Ir$_{1-x}$O$_2$, have also been proposed in order to enhance the stability of the anode electrode without affect its activity. However, up to date, the origins of such an improvement are not elucidated.

In this study, we propose to progress on that question by exploring the adsorption properties of water on model surfaces of RuO$_2$(110), IrO$_2$(110) and Ru$_x$Ir$_{1-x}$O$_2$(110) from density functional theory (DFT) calculations. Several initial configurations of water molecule above the metal oxide surfaces have been considered in order to find the most stable geometry. Energetics of adsorption of water on those materials is presented and compared. In particular, the role of the second metal in the alloy oxide surface on the adsorption properties is addressed by playing with the relative composition and alloying structure.

This work is a prerequisite towards a systematic investigation of the adsorption of intermediate species for the oxygen evolution reaction (OER) on model surfaces of IrO$_2$(110), RuO$_2$(110) and Ru$_x$Ir$_{1-x}$O$_2$(110). The perspective is the prediction of kinetics of the OER from DFT calculations and to integrate it in full cell multiscale simulation models such as in [3].

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Theoretical study of the reaction of S^+ with vibrationally excited H_2

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The SH^+ molecule has been recently observed in interstellar medium, althrough its mechanism of formation is still not clear. One of the possible reaction leading to this molecule is the collision of the sulfure ion with H_2, the most abundant molecule in interstellar medium. The reactions $S^+ + H_2 \rightarrow SH^+ + H$ is endothermic by 0.86 eV and, therefore, is expected to have small rate constant at low temperature. Nevertheless, recent studiess indicate that vibrationally excited H_2, which can be encountered in dense photon dominated regions, may favour this reaction and make it the main source of SH^+ in such interstellar regions [1].

In this work, we will present the reaction dynamics study of the title reaction, taking in account the vibrational excitation of the H_2 molecule. The caclulations were done using quantum and quasi-classical dynamics methods using an acurate potential energy surface we built based on *ab initio* electronic structure calculations. The cross sections and rate constants were calculated for several vibrational level of H_2 to check the effect of vibration of H_2 and how it enhance the reactivity of this system.

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On the basis size problem in ultracold molecular scattering:
Approximate hyperfine cross sections from hyperfine-free calculations

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Understanding (ultra)cold collisions is crucial to assess both the prospects of cooling techniques that rely on thermalization and trapping lifetimes. However, brute-force application of the coupled-channel method to many low-temperature scattering problems finds two main obstacles: (1) the need for large basis sets that are computationally intractable, and (2) the need to explore a multidimensional parametric space in order to tackle questions concerning real experimental conditions. The "basis size" problem arises because many interactions that are negligible at thermal temperatures become comparable to, or larger than, the collision energies involved. Taking all such terms into account significantly increases the size of the basis needed for convergence, with dramatic effects on the computing effort. Here, I will discuss an approximate method to account for the effect of hyperfine interactions in ultracold molecular scattering. The method naturally resolves the effects discussed by González-Martínez and Hutson in calculations on Mg+NH [1], and may be combined with those by Tscherbul *et al.* [2-5] and Croft *et al.* [6-8] to tackle problems which are computationally intractable to date. Depending on the system, the proposed method may lead to one to four orders-of-magnitude savings in computing times.

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QUANTUM DYNAMICS OF $O + H_2^+ \rightarrow OH^+ + H$, $OH + H^+$. INFLUENCE OF NONADIABATIC EFFECTS

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We present the Born-Oppenheimer (BO) and Renner-Teller (RT) quantum dynamics of the collisions $O(^3P) + H_2^+(X^2\Sigma_g^+) \rightarrow OH^+(X^3\Sigma^-) + H(^2S)$, (H) channel and $O(^3P) + H_2^+(X^2\Sigma_g^+) \rightarrow OH(X^2\Pi) + H^+$, (H⁺) channel. We consider both the OH_2^+ ground ($\tilde{X}^2A''$) and first excited ($\tilde{A}^2A'$) potential energy surfaces (PESs) [1], which correlate adiabatically with the (H) and (H⁺) reaction channels, respectively, and with a $^2\Pi_u$ species at linearity. The electronic angular momenta $\hat{L}$ and $\hat{L}^2$ as well as the associated RT effects are considered in benchmark nonadiabatic coupled-channel (CC) calculations, considering the H_2^+ molecular ion in the ground vibrational state and in the rotational levels $j_0=0$ and 1. Thus, CC initial state resolved reaction probabilities, integral cross sections, and rate constants are obtained using recently developed MRCI *ab initio* PESs [1] and couplings [2] and employing the real wavepacket and flux analysis methods [3,4]. The results show the different role of the diagonal and off-diagonal RT terms. The $\tilde{X}^2A''$ cross sections are about 4 times larger than the $\tilde{A}^2A'$ ones and the RT effect nearly halves the cross section values with respect to the BO ones. The rate constant values confirm that the $OH^+(X^3\Sigma^-) + H(^2S)$ products are the preferred ones, with a (H)/(H⁺) branching ratio of ~3.5 at 300 K. Because rotational effects are not particularly important here, we estimated for each channel the thermal rate constant from T=100 up to 500 K.
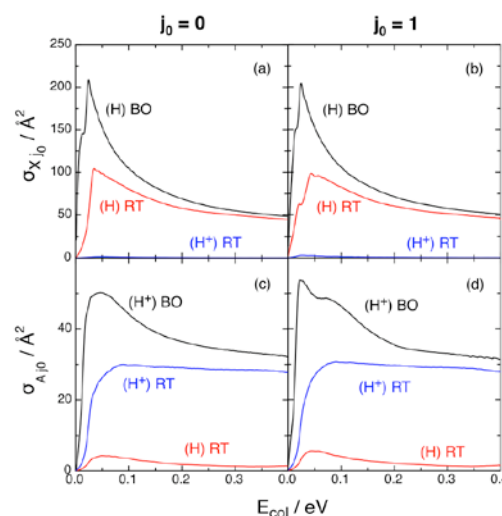
Figure 1. Cross sections for the (H) and (H⁺) product channels with $j_0=0$ (left) and 1 (right). BO (black) and RT (blue and red) cross sections for the ground (above) and excited (below) PESs.

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OXIDATION OF ATMOSPHERIC MERCURY BY THE OH RADICAL. AB INITIO AND QUASICLASSICAL TRAJECTORY STUDY

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Mercury is an atmospheric pollutant of neurotoxic character. In the emissions it is mostly produced as elemental mercury (Hg 0), which has an atmospheric lifetime of ~1 year. Atmospheric models generally consider that the gas phase reactions involving the OH and O_3 species are the main oxidation processes of mercury, although it seems that the oxidation produced by atomic bromine is also playing an important role [1]. The OH radical is the main "cleaner" agent (oxidant) acting during the day in the troposphere, and despite the interest of the Hg + OH reaction (which leads eventually to the precipitation of HgO on the ground), there are few kinetics and mechanistic data on this process [2, 3].

In the present contribution, we have investigated the Hg + OH → HgOH (adduct), HgO + H reaction from a theoretical perspective. Thus, we have considered both the icMRCI (internally contracted Multi Reference Configuration Interaction) *ab initio* calculation and analytical fitting of the ground potential energy surface (PES), while the subsequent dynamic and kinetic study has been performed using the quasiclassical trajectory (QCT) method. From the energetics of the system it is clear that formation of HgO does not take place directly from the elementary reaction involving Hg + OH, due to the high energy requirement involved in Hg + OH → HgO + H (as it also happens for Hg + O_3 → HgO + O_2 [4]). However, formation of HgO could take place in a second reaction involving the HgOH (adduct) and another OH radical (HgOH + OH → HgO + H_2O). The capture process has been analized determining the rate constant and the HgOH collision complex lifetime distribution, as a function of temperature (T: 200-400 K). Further details will be given in the IMAMPC 2014 meeting.

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