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# **BOOK OF ABSTRACTS**

# XII International Meeting on Photodynamics and Related Aspects

















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# Ultrafast laser control of dynamics and stereodynamics in photodissociation

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#### Abstract

With current technology, ultrafast laser radiation can easily achieve electric fields that are intense enough to induce changes or even dramatically modify the behavior of molecules. Thus, a strong external laser field can be regarded as an additional reagent in molecular processes such as chemical reactions, and one that may be used to steer the reaction towards desired targets [1].

In recent experiments, we have studied ultrafast molecular photodissociation processes taking place under the influence of strong laser fields. We have shown that it is possible to modify observables such as quantum yields [2,3], lifetimes [2], translational energies [3], or spatial distributions of the ejected fragments (*i.e.* the reaction stereodynamics) [4], by using strong picosecond or femtosecond near-infrared pulses. The control is achieved by opening new strong-field-induced reaction channels [2], or by creating light-induced conical intersections and modulating the potentials around them by light-induced potentials [3]. These control scenarios, which can be resonant or non-resonant [5], and the outlook for future work will be the subject of this presentation.



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# Laser Based Photoelectron Circular Dichroism

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Exploiting an electric dipole effect in ionization [1], photoelectron circular dichroism (PECD) is a highly sensitive enantioselective spectroscopy for studying chiral molecules in the gas phase using either single-photon ionization [2] or multiphoton ionization [3]. In the latter case resonance enhanced multiphoton ionization (REMPI) gives access to neutral electronic excited states. The PECD sensitivity opens the door to study control of the coupled electron and nuclear motion in enantiomers. A prerequisite is a detailed understanding of PECD in REMPI schemes. In this contribution I will report on our investigations on PECD with coherent light sources whose pulse durations span from femtoseconds to nanoseconds [4]. By this we address impulsive excitation on the femtosecond time scale to highly vibrational state selective excitation in mixtures with the help of high resolution nanosecond laser techniques [5]. The reflection of the number of absorbed photons in the PECD [6] will be discussed as well as subcycle effects in bichromatic fields [7].

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# Angle-Resolved Attosecond Photoionization Time delays, from atoms to molecules

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#### Abstract

The development of new attosecond light sources has opened the possibility of accessing electron dynamics in atoms and molecules in its natural time scale [1, 2]. In particular, XUV pump-IR probe techniques have been used to access not just the ionization amplitudes but also the phases associated with the scattering states describing the ejected photoelectron. This unfolds the prospect of steering electron and nuclear dynamics, extracting photoionization time delays and even reconstructing electronic wave-packets. Currently, two methods are mainly used to retrieve the phases and amplitudes: the streaking technique, which combines a single attosecond pump pulse with an infrared probe pulse, and the RABBITT technique, which combines a train of attosecond pulses with the infrared pulse used to generate them. In particular, RABBITT is a well-established technique for retrieving photoionization phases and amplitudes in atoms and molecules.

In this work, we theoretically investigate the laser-assisted photoionization dynamics in atoms and molecules, using the RABBITT technique. We use a fully correlated ab-initio method, that treat electron correlation in both the ion and neutral states, as well as correlation of the photoelectron with those of the target. We report energy and angularly-resolved photoionization time delays in three systems of increasing complexity: the Ar atom, the NO and  $H_2O$  molecules. Special attention is given to energy regions where Rydberg autoionizing states or shape resonances dominate photoionization spectra. These resonant states strongly modify the angularly-resolved photoionization amplitudes and phases (time delays) [1, 2, 3]. In addition, the dependence of the phase variation with the probe bandwidth and pump wavelength will be also discussed.



Figure 1: Sideband signal in Ar for an IR pulse centered at 780 nm and 8 fs duration.

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# Effect of electron phonon coupling on the vibrational relaxation of dipolar molecules on transition metals.

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#### Abstract

In the last years it has been proposed to use the internal stretch mode of polar molecules adsorbed metal surfaces to monitor ultrafast processes in pump-probe experiments with femtosecond time resolution. In the majority of systems, the large transient temperatures that are induced in these experiments cause a red-shift on this mode due to the coupling to hot carriers. Conversely, it is commonly accepted that the blue-shift that has been observed in a few systems arises due to the coupling to other phonon modes, ie. adsorbate frustrated translations or frustrated rotations. Here, we study the CO/Pd(111) system with a robust theoretical framework that includes electron-hole pair excitations and electron-mediated coupling between the vibrational modes [1]. Our results reveal a new mechanism that screens the electron-phonon interaction and originates a blue-shift under current state-of-the-art pump-probe experimental conditions. We show that this has an intimate relation with the presence of an abrupt change in the density of states around the Fermi level [2-3].



Figure 1: Transient changes induced in CO/Pd(111) by a pump pulse of fluence of 40 J/m<sup>2</sup> (a) Electron  $T_e$  (t) (blue) and lattice T<sub>i</sub>(t) (orange) temperatures Inset: top view of the  $c(4\times2)$ -2CO<sub>bridge</sub> unit cell. (b) Transient frequency shift of the CO IS mode:  $\Delta\omega(t)$  (black solid), and the different contributions to it.

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XII International Meeting of Photodynamics and Related Aspects.

# Identification of isomers and unknown metabolites of biomolecules using prompt UV photofragmentation.

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Functionality of biomolecules is largely determined by their chemical and 3D structure. NMR may solve 3D structures of molecules with high accuracy, but require their mg-scale quantity. Mass-spectrometry (MS) is a time-proven massive techniques that owns exceptionally high sensitivity, but often fails to identify isomeric biomolecules. A dream method should combine MS sensitivity with NMR capabilities of solving structures.

Spectroscopy reflects structure of molecules on fundamental level, since it can precisely measure optical transitions between quantum levels of molecules. To resolve optical transitions between numerous vibrational levels of large non-volatile biomolecules, they have to be, however, brought to the gas phase to suppress interactions with solvent and deeply cooled to reduce spectral congestion.<sup>[1]</sup> A recently developed combination of high-resolution mass spectrometry and cold ion photodissociation UV/IR spectroscopy benefits from synergy of the two approaches and enables library-based identification of isomeric molecules and solving primary structure of unknown metabolites.

The presentation will report on application of this combined 2D UV-MS method (i) to quantify enantiomers of biomolecules using non-covalent interactions, and (ii) to solve primary structures of metabolites of hormone estrogen by detecting specific UV absorption and characteristic photofragments. The latter results from prompt photodissociation of ions in the electronic excited states, which leads to local photofragmentation at the chromophore prior thermal-like dissociation of ions.



# Action spectroscopy of CN containing PAH cations for astrochemical consideration

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#### Abstract

The detection of cyano-group containing aromatic structures such as benzonitrile, cyanonaphthalene and cyanoindene in dense interstellar clouds by radioastronomy [1, 2, 3] has motivated recent laboratory investigations into their stability. Experiments at the DESIREE storage ring revealed that relatively small polycyclic aromatic hydrocarbon (PAH) cations may be more stable in the interstellar medium than previously believed, attributing this to inverse internal conversion and recurrent fluorescence [4]. This has motivated us to obtain the electronic and vibrational spectra of these cations to facilitate searches for them in interstellar environments. PAH type structures have long been proposed to be responsible for the unidentified infrared emission bands, and such species have also been suggested as candidates for the enigmatic diffuse interstellar bands [5]. In this talk recent experiments results, obtained by action spectroscopy in a cryogenic trap, will be presented and discussed in the context of these astronomical observations [6, 7].

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### Normal and hyperspherical analysis of nanoparticles' shape dynamics upon irradiation with ultrashort laser pulses

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#### Abstract

The oscillation patterns associated with the shape dynamics of gold nanospheres upon irradiation with ultrashort laser pulses have been followed using a normal and hyperspherical analysis. In previous work [1-3], it was shown that the shape of the nanoparticles can be somewhat controlled by properly choosing the parameters of the laser, solvent and particle size. In this work, we look at the shape changes and its understanding in terms of activated frequencies during the process. The possibilities of spherical nanoparticles as possible ultrasound sources are also commented.

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# Singlet fission in water by dynamic dimer formation

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#### Abstract

Singlet fission is a spin-allowed process whereby one singlet excited state is converted into two triplet states. Since this process is spin-allowed, it can proceed in less than several picoseconds, outcompeting most other energy loss mechanisms and even reaching power conversion efficiencies up to 45%. Due to its high quantum efficiency, singlet fission is very promising for many photophysical application such as the development of more efficient photovoltaic cells.

We provide the first direct evidence of singlet fission occurring with water-soluble compounds. We show that perylene-3,4,9,10tetracarboxylate forms dynamic dimers in aqueous solution, with lifetimes long enough to enable intermolecular single fission in addition to other photochemical processes.

The structures of this compound have been determined by Density Functional Theory (DFT) with the exchange-correlation functional M06 and the basis set 6-31G, which we validated by comparison with the experimental absorption spectra. These structures have then been used to analyze the dynamics of the compound in water by means of AIMD. The presence of dimers has been both validated experimentally and theoretically. These dimers are greatly mobile, leading to energy fluctuations which are large enough to induce changes in the energy ordering of the excited states, selectively promoting the stabilization of either S1 or  $^{1}(TT)$ , or even inducing charge-separated configurations.

Within this dynamic behavior, we have verified the possibility of singlet fission by computing singlet and triplet transition energies for the perylene molecular dianion. During the AIMD, singlet-triplet energies show sometimes the right energetics. Coupling between the S1 and the <sup>1</sup>(TT) states has also been computed. We show that the great geometrical variability of the dimers in water solutiton enables the dectivation of the excited states of the dimer via singlet fission and charge transfer processes. Furthermore, we demonstrate that the deactivation mechanism is determined by the relative orientation of the monomers in the dimer. In other words, given the great geometrical variability during the AIMD, both pathways are expected to occur in the water solution.

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### Revealing vibrational structures and dynamics in cryogenic matrices using multidimensional IR spectroscopy

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#### Abstract

Two-dimensional Infrared (2D-IR) spectroscopy, a non-linear method based on the generation of the third order polarization, is a powerful tool for investigating and unraveling molecular vibrational dynamics and their dependence on different environments. We are particularly interested in studying molecules trapped in cryogenic solids, as it allows us to observe subtle environment effects in controlled conditions. Matrix spectra may exhibit complex structures and narrow bandwidths (<1 cm<sup>-1</sup>). We recently built a time-domain 2D-IR setup [1,2] that covers a broad range of frequencies with a good spectral resolution (<0.5 cm<sup>-1</sup>) on both excitation and detection axis, adapted to the study of matrix samples.

We trapped W(CO)<sub>6</sub> in rare gas or nitrogen solids. This rather large molecule occupies different trapping sites [3], inducing a complex structure in the FT-IR spectrum of its degenerated  $T_{1u}$  mode in the CO stretch range. For example, there are four bands in N<sub>2</sub>, as opposed to a single peak in solution (see figure a). The 2D-IR spectra of W(CO)<sub>6</sub> help us unravel the complex band structure. In N<sub>2</sub> matrices, we observe cross-peaks only between three of the four bands (see figure, bands 1,3 and 4): it means that these three bands come from the same site. The 2D-IR map demonstrates thus the existence of two sites in N<sub>2</sub>. In one site, the O<sub>h</sub> geometry is conserved – and thus the degeneracy of the T<sub>1u</sub> mode - (band 2), whereas it is not in the other (bands 1, 3, and 4). In the latter, there is a symmetry breaking in the molecule+lattice system, and therefore the degeneracy removal of the probed mode. This confirms our prior results in FTIR and photon echo experiments [4]. In addition, the spectra exhibit new interesting features, such as positive anharmonic coupling (see figure b, red bands), coherent excitation transfer between non-degenerate modes, or the proof of excitation transfer to dark states at the timescale of hundreds of ps. Matrix effects and dynamical processes at play will be discussed.



Figure: (a) FTIR spectrum of  $W(CO)_6/N_2$  at 20K with a scheme of  $W(CO)_6$ ; (b) part of a 2DIR map of  $W(CO)_6/N_2$  at 20K [waiting time = 200 fs]; (c) scheme of the levels involved in the probed vibrational transition in the two kinds of sites in nitrogen matrices.

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# Unveiling the Reaction Dynamics of Electron-Induced Chemical Reactions by Femtosecond Time-Resolved Mass-Spectrometry

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#### Abstract

Electron-initiated reactions with chemically relevant electron energies (10-200 eV) are a fundamental and intricate phenomenon with profound implications across diverse fields such as astrochemistry, atmospheric chemistry, and plasma processing [1]. When energetic electrons collide with molecules, they transfer sufficient energy to cause electron detachment and bond cleavage, forming multiple ions. Our understanding of how medium-sized molecules produce tens to hundreds of ions following ionization is limited, largely due to challenges in monitoring dissociative ionization dynamics with femtosecond precision. This presentation introduces a method utilizing the strong-field electron recollision processes, acknowledged by the 2023 Nobel Prize in Physics, to achieve time-resolved electron-induced chemical reactions [2]. Through femtosecond time-resolved electron-ionization mass spectrometry, our laboratory has explored various reactions, such as the McLafferty rearrangement [3], retro-Diels Alder reaction [4,5], and neutral species roaming [6,7]. Our experimental findings reveal the ultrafast dynamics that take place upon ionization, offering insights into high-energy chemical processes marked by multiple ionization and fragmentation pathways. Furthermore, our results contribute to validating quantum mechanical models that aim to predict product ion distributions, thus enhancing our knowledge of electron-molecule interactions and their broader implications.

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### In silico design of bio-marker detection fluorescent probes

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#### Abstract

Molecules capable of sensing biological mediums are of great importance nowadays. These molecules must fulfill different requirements to avoid interference with the biological medium (e.g. hemoglobin), tissue photodamage, scattering of the emitted light, and autofluorescence. In this sense, two important conditions are directly evaluated in this work. The emission wavelength must be between 650 and 950 nm and the Stokes shift should be greater than 150 nm. On top of these characteristics photostability and high fluorescence quantum yield are also desirable. In this work, we showcase the in-silico design of excited state intramolecular proton transfer (ESIPT)-based fluorescent 1,2,4-triazoles as potential probes for biomarkers detection. Starting from 3-hydroxypyridyl-1,2,4-triazole (initially far from biological standards), we illustrate how to tune the emission wavelength and Stokes shift through heteroatomic substitution and conjugation increase.

# Photoinduced dynamics in organic chromophores: nonadiabaticity, vibronic couplings, and and coherences.

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Photoinduced processes of multichromophoric organic conjugated materials frequently involve concerted dynamics of coupled electronic and vibrational degrees of freedom (i.e. vibronic couplings) that can give rise to multiple relaxation pathways, and persisting phase relations or coherences. Fundamental insights into the coherence creation and destruction mechanisms can potentially allow the manipulation of photoexcited non-radiative pathways to achieve desired efficient transfer of energy and charges.

Atomistic Non-Adiabatic Excited-State Molecular Dynamics (NEXMD) using quantum/classical methods, like surface hopping (SH), Ehrenfest, and Multiconfigurational Ehrenfest and Ab Initio Multiple Cloning (AIMC) approaches have proved to be suitable for the analysis of exciton redistributions and vibronic dynamics during electronic relaxation in this class of molecular systems [1,2,3]. Particularly, AIMC results a controllable approximation to non-adiabatic dynamics that naturally includes electronic decoherence. Their modeling results can be used to predict nonlinear UV-visible and X-ray signals that track excited state dynamics and its coherent behavior.

Vibrational funnels may support persistent coherences[4,5]. The ultimate confirmation of their role on the inter-chromophoric energy transfer can be achieved by performing nonadiabatic excited state molecular dynamics simulations by selectively freezing the nuclear motions in question[6,7]. This results a useful tool to identify and evaluate the impact of these vibrational funnels on the energy transfer processes and guide in silico design of materials with tunable properties and enhanced functionalities

Herein, NEXMD simulations have been applied to different organic chromophores to illustrate different aspects of their photoinduced energy relaxation and redistribution.

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### Photoionization of the CH molecule

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Photoionization plays an important role in fundamental physics and several applications, especially in plasmas with many small molecules present — such as those present in astrophysical environments, planetary atmospheres, and terrestrial plasmas. However, it is experimentally challenging to measure photoionization cross sections from molecules in specific excited states and can be theoretically challenging if the molecules have complex electronic structures. We combine molecular R-matrix theory, multichannel quantum-defect theory, and a vibrational frame transformation to obtain state-selected photoionization cross sections for the CH molecule. Unlike previous theoretical approaches this method includes the vibrational structure of both the neutral molecule and the resulting ion. We benchmark our results by comparing them to the most recent experimental results at the SOLEIL synchrotron, with which we find good agreement.



## Mapping Electronic Decoherence Pathways in Molecules

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#### Abstract

Establishing the fundamental chemical principles that govern molecular electronic quantum decoherence has remained an outstanding challenge. Fundamental questions such as how solvent and intramolecular vibrations or chemical functionalization contribute to the decoherence remain unanswered and are beyond the reach of stateof-the art theoretical and experimental approaches. Here we address this challenge by developing a strategy to isolate electronic decoherence pathways for molecular chromophores immersed in condensed phase environments that enables elucidating how electronic quantum coherence is lost. For this, we first identify resonant Raman spectroscopy as a general experimental method to reconstruct molecular spectral densities with full chemical complexity at room temperature, in solvent, and for fluorescent and non-fluorescent molecules. We then show how to quantitatively capture the decoherence dynamics from the spectral density and identify decoherence pathways by decomposing the overall coherence loss into contributions due to individual molecular vibrations and solvent modes. We illustrate the utility of the strategy by analyzing the electronic decoherence pathways of the DNA base thymine in water. Its electronic coherences decay in  $\sim 30$  fs. The early-time decoherence is determined by intramolecular vibrations while the overall decay by solvent. Chemical substitution of thymine modulates the decoherence with hydrogen-bond interactions of the thymine ring with water leading to the fastest decoherence. Increasing temperature leads to faster decoherence as it enhances the importance of solvent contributions but leaves the early-time decoherence dynamics intact. The developed strategy opens key opportunities to establish the connection between molecular structure and quantum decoherence as needed to develop chemical strategies to rationally modulate it [1].



Figure 1: Mapping electronic decoherence pathways opens exciting opportunities to unlock the chemical principles of electronic quantum decoherence.

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# Transition state theory with dynamical corrections.

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#### Abstract

Transition State Theory (TST) is widely recognized as the most successful and extensively used theoretical framework for studying reaction rates of species at or near thermal-equilibrium conditions, where direct dynamical calculations are often impractical. However, TST is known to provide an upper bound for rate coefficients because it assumes that any crossing of the transition state results in a reaction. This limitation can be addressed by calculating short-time trajectories initiated at the transition state to determine the so-called dynamical correction factors [1]. Recrossing events, which challenge the validity of TST, can arise due to the inseparability of the reaction coordinate from other degrees of freedom. Additionally, the excitation of electron-hole pairs, commonly occurring when molecules interact with metal surfaces, could also contribute to dynamical recrossing.

We study two competing gas-surface reactions for which conventional TST fails to reproduce experimental observations. Precisely, we focus on thermal CO2 recombinative desorption and CO desorption from covered Ru(0001)-(0.5 ML O + 0.25 ML CO) surface in the honeycomb structure. While the former is predicted to dominate due to much higher reaction rate constant predicted by TST, the later is the only outcome in experiments. Calculating short time trajectories within the classical dynamics approach the dynamical correction factors are evaluated and the reaction pathways scrutinized.

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# Full Dimensional Quantum Approach to the Vibrational Relaxation of $H_2O$ by collision with $H_2$ .

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#### Abstract

For several years, astrochemical models of the Interstellar Medium (ISM) only took into account the rotation of the detected molecules, mainly due to the cold temperatures ( < 100K ) prevailing in the Interstellar clouds. However, the study of warmer environments, such as star-forming regions or the envelope and atmospheres of evolved stars, has led to the detection of some of the most abundant polyatomic molecules in the ISM, such as HCN[1],  $C_3[2]$ , and  $H_2O[3]$ , in highly excited vibrational levels. The astrochemist and astrophysicist require collisional rate coefficients for these molecules with the most abundant element in the ISM,  $H_2$ . To address this need, the Close Coupling (CC) and Coupled States (CS) equations for a linear rotor  $(H_2)$  colliding with a rigid asymmetric top molecule  $(H_2O)$  presented by Phillips et al. [4] have been extended. This extension includes, for the first time, the coupling of rotation with all the vibrational modes of the water molecule. Our group has developed a new code called Divitas [5], which enables us to calculate the Rovibrational Bound States of the water molecule and solve the space-fixed CC and body-fixed CS equations using a log derivative propagator. We have conducted, within the Waterstars French national research agency project, a study on the collision of para-H<sub>2</sub>O and ortho-H<sub>2</sub>O with the two spin modifications of H<sub>2</sub> for several initial states of the water molecules. Based on our findings, it appears that the vibrational relaxation process is controlled by near-resonant energy transfer between  $H_2O$  and  $H_2$ . The calculated Rovibrational Bound States and bending relaxation rate at 295 K are in good agreement with experimental results[5]. These rate coefficients may assist astrochemists and astrophysicists in developing more precise models of various astrophysical environments.



Figure 1: Discovery of vibrationally excited  $H_2O$  in the atmosphere of a red supergiant star through the ATOMIUM ALMA Large Program[3]. (Cover picture from Ref. [5])

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# VUV photoionization of pure PAH and cyano-PAHs

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#### Abstract

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the interstellar medium (ISM), acting as reservoirs of carbon and accounting for about a quarter of the total carbon mass of the ISM. The aromatic infrared emission bands (AIBs) in the 3-20 µm range are the signatures of the existence of PAHs in the interstellar and circumstellar medium which are exposed to ultraviolet radiation. Although their presence is well acknowledged, the individual detection of PAHs by rotational spectroscopy is notoriously difficult owing to their highly symmetric structures. In this context, substituted PAHs being less symmetric are promising candidates, leading to the detection of two isomers of cyanonaphthalene and of 2-cyanoindene in the dark, cold TMC-1[1]. Upon absorbing the VUV radiation emitted by the hot stars, the PAHs relax via photoionization and photodissociation processes in competition with radiative cooling. The laboratory UV-VUV spectroscopy and photo-dynamics of PAHs in neutral and cationic forms are then essential to investigate and understand in detail their behavior in specific astrophysical conditions.

A particular question concerns the fast electrons emitted during ionization [2] which lead to the gas heating of the ISM by dissipating their kinetic energy to the surrounding gas molecules by collisions, what is known as photoelectric heating, and should play an important role [3] since PAHs have low ionization energies and high ionization cross-sections.

I will present the VUV photoionization and fragmentation of several pure PAHs of varying sizes (between 13 and 20 carbon atoms) plus 1- and 2- cyanonaphthalenes [4] using a double imaging photoelectron photoion coincidence spectrometer (i2PEPICO), coupled to the DESIRS undulator-based VUV beamline of Synchrotron SOLEIL, France [5]. I will focus on how electron kinetic energy distributions can be extracted from our data for any given incoming photon flux (see Figure), their dependence on the PAH structure, and how they can be reduced to a form that is usable for photochemical models, in addition to the thermochemical values such as adiabatic ionization energies and 0K fragment appearance energies.



**Figure**: Ionization signal of 1-CNN as a function of outgoing electron and incoming photon energies taken from Ref. [3]. Two different interstellar radiation fields are shown as green and red solid lines.

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# Tracking coupled electronic and structural dynamics in condensed phase matter with ultrashort X-ray pulses

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#### Abstract

With the advent of soft- and hard X-ray Free Electron Lasers (XFEL) sources, entirely new scientific opportunities and prospects have been become available in the field of structural studies. One of the most unprecedented features of XFELs is their ability to produce high intensity and fully coherent pulsed X-ray beams, with single pulse duration well below 100 femtoseconds (1 fs  $=10^{-15}$  s). This property allows dynamical studies of light-matter interactions virtually in any medium on the very fundamental timescales of interatomic motions, from gas-phase, solvated molecules and biomacromolecules to complex strongly correlated solids.

In this seminar I will present a state-of-the-art overview of the abovementioned research venues, which highly benefit from the continuous progress in the field of XFEL technology. It will focus on those aspects, which profit most from the very high temporal resolution achievable in time-resolved XFEL experiments in combination with atomic spatial resolution. Some recent examples of femtosecond-resolved XFEL pump-probe studies on molecular complexes and semiconductor quantum dots will be shown as examples.



Figure 1: Layout of the FXE instrument at the European XFEL facility. FXE is a versatile pump-probe beamline dedicated to studies of structural dynamics in condensed matter systems using a vast range of X-ray spectroscopic and X-ray scattering techniques.



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#### Abstract

I will present reaction probabilities for the  ${}^{15}N + {}^{14}N^{14}N$  inelastic and reactive collision processes, computed up to high energies (4.5 eV), within the framework of time-independent (TIQM) and time-dependent (TDWP) quantum mechanics. They will be restricted to the ground potential energy surface for N<sub>3</sub> (<sup>4</sup>A"). The two nuclear spin isomers o- ${}^{14}N^{14}N$  and p- ${}^{14}N^{14}N$  can be considered independently as reagents. These processes, related to "active" nitrogen chemistry at temperatures in the range [1 000, 20 000] K, are of great interest for shock wave induced plasma re-entry physics, in the context of spacecrafts' heat shields penetrating nitrogen rich atmospheres (Earth or Titan). The possibility of isotope exchange, for kinetic energies higher than 2 eV, will be specifically considered. I will also discuss the effect of the collision on products vibrational states distribution, the influence of reagents vibrational excitation and that of total angular momentum on reaction thresholds.



Figure 1: Comparison between TIQM and TDWP computations for the reaction probability associated with the  ${}^{15}N + o^{-14}N^{14}N(v = 0, j = 0) \rightarrow {}^{14}N + {}^{15}N^{14}N$  exchange process.

# **Probing Transition State Dynamics via Anion Photodetachment: Theoretical Perspective**

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Due to the flitting nature of the transition state, information on its dynamics is often difficult to obtain. In cases where the geometry of the saddle point on the reactive potential energy surface is close to the equilibrium geometry of a stable anion, it is possible to gain detailed knowledge of the transition state dynamics via photodetachment of the anion. The vertical transition from the anionic to the neutral state via the ejection of the electron prepares a wave packet near the transition state, which evolves in time to report the subsequent dynamics. Here, we discuss our recent effort to understand the quantum dynamics of photodetachment of several anions, including  $H_2CC^-$ ,[1]  $H_2O$ - $F^-$ ,[2]  $CH_3OH$ - $F^-$ ,[3]  $NH_3$ - $F^-$ ,[4][5] and  $SO_2$ - $OH^-$ ,[6] which shed light on the transition state dynamics in both unimolecular and bimolecular reactions and role of resonances.

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# Real Time Dynamics Simulation of Pure and Doped Helium Nanodroplets using ${}^{4}$ He-TDDFT

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#### Abstract

The time-dependent dynamics of doped or pure helium nanodroplets poses numerous challenges due to the highly quantum nature of this unusual "solvent" and to its eminent superfluid properties. Helium Time-dependent Density Functional Theory (<sup>4</sup>He-TDDFT), which describes the time evolution of the helium density rather than that of the many-body wave function, results from a compromise between accuracy and feasibility. It has emerged as a powerful tool to simulate and help understand many experimental results over the years.[2]

In this lecture the method will be presented, focusing on its recent and future applications in our groups. These include

- Nanodroplet collisions as a possible alternative mechanism to nucleate vortices[3]
- A direct view on time-dependent ion solvation using pump-probe techniques[1, 5]
- Coulomb explosion of dialkali molecules on the droplet surface
- Pickup and clustering inside helium droplets[4]

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# Creation of Charge Transfer States for Photocatalysis by Polar Boundaries in $\pi$ -Conjugated Doped Systems

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#### Abstract

Photocatalysis is a promising way to convert solar energy into storable fuels. Among the various processes, solar-driven water splitting stands out as a capable way to create hydrogen. In recent years, novel organic photocatalysts have drawn significant attraction because of the use of  $\pi$ -conjugated aromatic compounds allowing the construction of several types of photocatalysts. In this work we are concentrating on two classes of catalysts: (i) graphene flakes and (ii) graphitic carbon nitride. The initial stages of the photocatalysis consists of two processes, the light absorption and the separation of the resulting exciton into a positive hole and an electron creating charge transfer (CT) states, which then can be used to perform the formal reduction step  $4H^+ + 4e^- \rightarrow 2H_2$  and the oxidation step  $2H_2O + 4h^+ \rightarrow 4H^+ + O_2$ , leading to the overall water splitting  $2H_2O \rightarrow 2H_2 + O_2$ . The work presented in this talk concentrates on the generation of the CT states occurring preferentially at donor/acceptor (D/A) interfaces. Two model conjugated  $\pi$  systems have been generated from a 5-armchair,5-zigzag (5a,5z)-periacene (Figure 1a) and a graphitic carbon nitride (g-C\_3N\_4) (Figure 1b) by B,N doping to create D/A interfaces. Figure 1a shows a horizontal row of borazines inserted into the 5a,5z-periacene acting as the D/A boundary; in Figure 1b graphitic N doping has been achieved by addition of two H atoms to two N atoms in the upper heptazine and by replacing two N atoms by BH groups in the lower-right heptazine. As an example, Figure 1a shows CT character for the S<sub>2</sub> state as indicated by the natural transition orbitals (NTOs) presenting CT from the transition density) displays the hole-particle transition in a compact way based on the division of the whole sheets into three segments. Similar CT states are being observed for the tri-heptazine system. Different doping topologies have been investigated to find optimal doping constellations, which will be used to demonstrate efficient ways for solar-driven

The calculations have been performed using high-level multireference configuration interaction with singles and doubles (MR-CISD) using COLUMBUS and time-dependent density functional theory (TD-DFT) using the  $\omega$ B97XD functional.



Figure 1: a) characterization of a CT state for a B,N-doped 5a,5z-periacene in terms of NTOs, the  $\omega$  matrix and the segment definition; b) B,N-doped tri-heptazine

# Local structure of liquid oxygen up to supercritical conditions from *ab initio* pair potentials

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The local structure and orientational correlations of liquid oxygen up to supercritical conditions have been determined using highly accurate *ab initio* pair potentials[1,2] and a spin-average approximation. The predicted radial distribution functions are in excellent agreement with all the available experimental data[3,4] covering a wide range of temperatures and pressures, something which could not be accomplished in any previous studies of this type[5]. In particular the elusive shoulder characteristic of several diatomic fluids is accurately reproduced and more importantly its true origin elucidated by performing an exhaustive analysis of the orientational correlations (Figure 1) indicating the relevance of specific configurations which had not been taken into account before[6].



Figure 1: Radial distribution function contributions of eight important configurations

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### How do molecules break in cavity quantum electrodynamics?

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#### Abstract

Current efforts for implementing cavity QED in the ultrastrong coupling (USC) regime using molecular vibrations in mid-infrared nanoresonators opens exciting opportunities for exploring novel chemical reactivities that exploit quantum correlations with the electromagnetic vacuum at room temperature. While most theoretical studies have primarily focused on rationalizing previous experimental reports of modified chemical reactions in collective strong coupling [1,2], the possibilities for single-molecule chemistry in the fully-quantum regime of light and matter still remains largely unexplored. We developed a coordinate representation approach for the light-matter Hamiltonian (DVR) that together with exact quantum dynamics techniques provides key physical insights on the evolution of molecular and photonic observables over sub-picosecond timescales [3-5]. We use these methods to understand the quantum mechanical nature of molecular dissociation in infrared cavities under USC. For polar anharmonic bonds, we show that the combined influence of Bloch-Siegert shifts, wavepacket spreading, nuclear anharmonicity and vacuum field polarization via permanent dipoles, can lead to significant enhancement of the molecular dissociation rate relative to free space, for experimentally relevant non-equilibrium scenarios [6]. Our work thus provides conceptual and numerical tools for understanding the new possibilities that cavity QED physics can bring to nanoscale chemistry.

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### Proton transfers at interfaces and applications.

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Using first-principles computational methodologies, we investigate the microsolvation of proton at organic/inorganic and water clusters. For instance, we considered protonated water clusters interacting with aromatic compounds, [1] and protonated aromatics [2] or protonated polyhedral oligomeric silsesquioxane [3] complexed to water clusters. For these species, we identified the most stable forms, where the solvation of the protonated organics due to a network of water clusters, whereas the excess proton undergoes a complex dynamic at the water-organic/inorganic interface, resulting in the formation of Eigen and Zundel features. These identifications are based on diverse analyses of the bonding and of weak interactions occurring at these interfaces. Besides, we discuss the extension of our finding to 2D and 3D materials. Our work should be useful for understanding, at the microscopic level, of the effects of water interacting with organic/inorganic compounds relevant for organic chemistry, inorganic chemistry, atmospheric chemistry, combustion and materials science.

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# Ultrafast dynamics in microsolvated biomolecules

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#### Abstract

Interactions between proteins and their solvent environment can be studied in a bottom-up approach using hydrogen-bonded biomolecule-solvent clusters. The ultrafast dynamics following UV-light-induced electronic excitation of the biomolecular chromophores, potential radiation-damage, and their dependence on solvation are important open questions. Specific and precise studies of the microsolvation effect are challenging due to the inherent mix of the produced gas-phase aggregates.

We<sup>1</sup> used the electric deflector 1 to spatially separate different molecular species in combination with pumpprobe velocity-map-imaging experiments, including applications of 4D "cameras" based on Timepix3 2 3. We demonstrated that this powerful experimental approach reveals intimate details, e.g., on the radiation damage of water-water 4 and pyrrole-water 5 dimers as well as on the UV-induced dynamics in the near-UV-absorbing prototypical biomolecular indole-water system 6.

We determined the time-dependent appearance of the different reaction products and disentangled the occurring ultrafast processes. This novel approach ensures that the reactants are well-known and that detailed characteristics of the specific reaction products are accessible – paving the way for the complete chemical-reactivity experiment.

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# Semiclassical corrections into the classical description of diatom scattering on metal surfaces in the quantum regime

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#### Abstract

When elementary reactive processes occur at such low energies that only a few states of reactants and/or products are available, quantum effects strongly manifest and the standard description of the dynamics within the classical framework usually fails. We illustrate here, for H<sub>2</sub> scattering on Pd(111) and on W(100), that by pseudoquantizing in the spirit of Bohr the relevant final actions of the system, along with adequately treating the rovibrational adiabatic scattered trajectories, classical simulations achieve an unprecedented agreement with state-of-the-art quantum dynamics calculations. [1, 2, 3]



Figure 1: Sticking curve for  $H_2$  colliding on Pd(111) and W(100) at normal incidence by Time Dependent Wave Packet (TDWP) (black), Quasi-Classical Trajectories (QCT) (blue) and SemiClassically corrected trajectories (QCT-SC) (yellow)

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# Imaging photodynamics governed by conical intersections in polyatomic molecules

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#### Abstract

Radiationless transitions between electronic states of the same multiplicity, referred to as internal conversion (IC), constitute a universal first step in the photo-induced dynamics of polyatomic systems leading afterwards to a variety of outcomes including dissociation or isomerization. The topology characterizing the potential energy surfaces of the electronic states involved directly determines the efficiency and the associated timescale of this type of process. While IC can occur between bound electronic states where no curve crossing is located leading to a remarkably slow transfer of population [1], the presence of crossings between electronic states mediating the IC can allow for an efficient fast transfer of population. In such non-adiabatic crossings and in particular in conical intersections, strong couplings between electronic and nuclear motions arise allowing the molecule to switch from one surface to another.

In this work, we employ electron and ion imaging techniques in combination with ultrafast laser pulses or synchrotron radiation to investigate the photo-induced dynamics in different molecular systems with the support of high-level *ab initio* calculations. Different cases of non-adiabatic reaction dynamics in which conical intersections allowing IC are determining steps for the photoinduced dynamics will be presented. In particular, we will show how a double bond strongly modifies the non-adiabatic dissociation of vinyl iodide in the vacuum ultraviolet (VUV) and how an elusive conical intersection is revealed to mediate IC from the first excited state into the ground state of cationic methyl iodide [2].



Figure 1: Threshold photoelectron spectrum of methyl iodide along with the geometry of the conical intersection revealed [2].

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# Electronic field emission on contaminated tungsten surface

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#### Abstract

The electronic emission taking place at the electrodes of high voltage systems is known to be strongly dependent on the cathode surface state. This electronic emission can be responsible for detrimental breakdown processes in many engineering installations.

The deterioration of certain components in these systems can be very detrimental, both for the installation itself and the intended benefits it is trying to produce. To better understand the effects of contamination on cathode electronic emission, we have used density functional theory calculations to reproduce the emission properties of tungsten surfaces with and without contaminants such as carbon [1, 2, 3], oxygen[4], and various combinations[5] thereof.

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# Stereodynamics of hydrogen atom scattering off a tungsten surface covered with hydrogen

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#### Abstract

Recent studies have shown that when hydrogen atoms collide with metal surfaces at energies of a few electron volts, the loss of translational energy is mainly due to electron-hole pair excitations [2]. In the case of hydrogen atoms interacting with a tungsten surface covered with hydrogen atoms, theoretical studies have only examined the energy lost under specific conditions of incident energy, azimuthal angle and polar angle [3, 1]. Quasi-classical trajectory simulations were here carried out to investigate the energy transfer during the scattering of hydrogen atoms from hydrogen-covered tungsten surfaces. The theoretical approach investigates the effect of hydrogen coverage, collision energy and direction of incidence on the energy loss. The scattering can be explained by three different dynamical mechanisms, the contribution of which varies depending on scattering conditions. These results help to explain why the energy loss spectra significantly differs if they are analysed in the whole space or only at the scattering plane. In addition, a previously unknown reflection channel at low energy and grazing incidence is suggested at high coverage, which needs further investigation.

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# Excited States with Green's Functions: From Brute Force to Stochastic Methods

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### Abstract

Investigating excited electronic states inherently involves modeling the excitation dynamics induced by lightmatter interactions. These simulations typically rely on time-dependent (TD) electronic structure methods, such as TD density functional theory (DFT) or TD wavefunction-based techniques. However, achieving a balance between accuracy and efficiency in these methods remains challenging. On one hand, DFT methods, which are recognized for their efficiency, require using an unknown exchange-correlation functional to capture electronelectron interactions. This makes it difficult to develop systematic and universal approximations. On the other hand, wavefunction methods suffer from a steep computational cost (commonly with complexity ranging from  $O(N^5)$  to exponential with system size), limiting their use to small systems. An alternative to DFT and wavefunction-based methods is the many-body Green's function (MBGF) formalism, which is widely used in condensed matter physics and is gaining popularity in the molecular sciences. One key advantage of the MBGF formalism is that it enables the development of systematic approximations for electron correlations from first principles. However, it also faces high computational costs, similar to other ab initio approaches.

In this talk, I will present an overview of the key concepts for developing time-dependent electronic structure methods within the MBGF formalism and discuss how to enhance their efficiency using stochastic-orbital techniques. This will be demonstrated through simulations of neutral excitations in molecules and nanostructures, employing widely used approximations for capturing electron correlations, such as the GW approximation and second-order Green's functions. The developed theories allow the simulation of absorption spectra of systems containing hundreds to thousands of electrons, which are typically inaccessible to most deterministic ab initio methods[1, 2, 3].

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# Detection and Characterization of Reaction Intermediates using Synchrotron Photoionization Mass Spectrometry

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Abstract

As a part of our continuing effort to characterize noteworthy combustion and atmospheric reaction intermediates and products, recent results are presented from experiments carried out at the Advanced Light Source at the Chemical Dynamics (now called Chemical Transformations, Vacuum Ultraviolet) Beamline of Lawrence Berkeley National Laboratory using multiplexed synchrotron photoionization mass spectrometry [1,2]. Species are identified by their mass-to-charge ratios and PI (photoionization) spectra.

Comparison of experimental PI spectra with literature or calculated curves is routinely done to assure the identity of a given species. With the aid of electronic structure calculations, Franck-Condon spectral simulations are obtained. Electronic structure calculations are also employed to compute the potential energy surface of the reactions to explain the formation of products. Examples of these experiments are discussed ranging from new intermediates characterization [3] to reaction mechanisms elucidation [4], and biofuels oxidation pathways identification [5,6]. Preliminary results for the first-time observation and characterization of a tetraoxide intermediate, also known as Russell intermediate [7], will be presented.

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# Exploring Chemical Space with Linear Notations

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## Abstract

Several methods exist for exploring potential energy surfaces, each with its own strengths and weaknesses. These methods often rely heavily on complex geometric information. This presentation will explore an alternative approach that utilizes linear notations, represented by character strings, to explore the vast realm of chemical possibilities.

For instance, just 217 SMILES strings can describe the entire chemical space for small molecules like benzene ( $C_6H_6$ ), excluding unusual structures and mirror images. However, as molecules become larger and incorporate different types of atoms (heteroatoms), the number of potential isomers explodes.

To address this growing complexity, we propose a novel algorithm that combines principles from:

1) Natural selection: We employ a genetic algorithm to mimic the process of evolution.

2) Local adaptation: The algorithm incorporates a local optimizer, inspired by Lamarckian evolution, to refine solutions.3) Phenotypic expression: Similar to how traits influence an organism, the algorithm considers how potential solutions influence their corresponding linear representation.

One exciting application lies in the detection of stable molecules in space, where stability on the PES is crucial. This approach has the potential to significantly enhance our understanding of Interstellar Medium chemistry.



# Machine Learning Inter- and Intramolecular Interactions: Applications to Chemical Reactions and Spectroscopy

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## Abstract

Machine Learning has fundamentally changed how we think about chemical problems. One area which has specifically benefited from this development is atomistic molecular simulations. In this talk I will discuss recent advances and unresolved issues with machine learning applied to inter- and intramolecular interactions. Questions of particular relevance concern the amount of reference data required, the size and complexity of the underlying model and their application to concrete physico-chemical questions. Specific recent examples include photodissociation reactions of small Criegee intermediates, roaming reactions, and applications to the infrared spectroscopy of small reporters to probe protein dynamics.

# Ligand-protected gold clusters. Optical and Excited State Properties From Calculations, Leading to Photomechanical Variations.

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Polynuclear coinage metal complexes with d<sup>10</sup> electronic configuration are related to unique features arise from the interactions between closed-shell centers, which promote the formation of building blocks leading to functional molecular and supramolecular materials with tailored and fascinating properties.<sup>1,2</sup> In particular, numerous gold(I) complexes possess remarkable luminescence properties with long-lived emission and sizable Stokes shifts, which turn them into promising luminescent materials for various practical applications.<sup>2-4</sup>

In this talk, we highlight our results on photomechanical variation of well defined molecular clusters, featuring variation in linear  $Au_2$ , two-dimensional  $Au_3$  and three-dimensional  $Au_{12}$  gold kernels.<sup>5,6</sup> From such results, optically induced structural variations, which are useful towards development of photomechanical motifs at the molecular scale.

In addition, the formation of molecularly conceived aggregates from individual building blocks will be revisited.<sup>7-9</sup>



Figure 1, Schematic representation of a dual-luminiscent ligand protected Au<sub>6</sub> cluster.

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# Quantum Stereodynamics of Cold Molecular Collisions and Reactions

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## Abstract

A central goal in chemistry is the absolute control of quantum states of both reactants and products. This is not achievable at normal temperatures due to a thermal population of internal quantum states. By cooling atoms and molecules to temperatures close to absolute zero and confining them in electromagnetic traps controlled chemistry experiments can be performed between trapped atoms and molecules in the deep quantum regime. This allows unprecedented level of control over initial quantum states, molecular orientation, and even final states in certain cases. Electronically non-adiabatic effects also a play an important role in many chemical reactions at cold and ultracold temperatures. I will discuss recent progress in our group on the description of the K+KRb $\rightarrow$ K<sub>2</sub>+Rb chemical reaction that involves conical intersection with an excited electronic state that is accessible in ultracold collisions of rovibrationally ground state KRb molecules with K atoms. I will also discuss recent work on stereodynamic control of cold collisions involving vibrationally and rotationally excited HD and D<sub>2</sub> molecules.



# Comparing quasi-classical and classical dynamics: $H_2$ dissociation on tungsten surfaces covered with impurities

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#### Abstract

Tungsten (W), chosen for its advantageous properties, is used as a plasma-facing material in devices like the tokamak divertor, including the ITER (International Thermonuclear Experimental Reactor) project. The primary role of the divertor is to remove impurities and heat from the plasma, thereby assuring a complete fuel recycling. Fuel recycling is the ratio between the flux of particles reaching the divertor surface and those returning back to the plasma. It is essential for understanding plasma behavior, though it does not always reach 100%. The strong coupling between plasma and tungsten surfaces leads to reciprocal reactions that can significantly disrupt ideal plasma behavior. Controlling these interactions is a key challenge in the development of magnetic fusion reactors, requiring a profound understanding of the fundamental mechanisms of tungsten's interaction with hydrogen on a microscopic scale. The tungsten surface in ITER can be pristine or covered with intrinsic impurities such as oxygen (O) or extrinsic impurities like nitrogen (N). The interaction of hydrogen molecules shows a different behavior on a clean tungsten surface compared to those covered with impurities. The type and amount of impurities play a crucial role in influencing the processes involved.

In a previous study, our research team carried out a theoretical analysis of hydrogen  $(H_2)$  dissociation dynamics on the clean W(110) surface [3] and on O-covered one [4]. The approach revealed a substantial decrease of the sticking coefficient with increasing coverage, in agreement with experimental findings. The present investigation focuses on the impact of nitrogen covering the W(110) surface on H<sub>2</sub> dissociation dynamics. The Pfnür team investigated the chemisorption of N<sub>2</sub> on the W(110) surface in 1986, noting surface reconstruction [2]. We aim here to examine the influence of this reconstruction on the H<sub>2</sub> dissociation process by studying it on two distinct tungsten surfaces covered with nitrogen, using ab-initio molecular dynamics (AIMD) both with and without considering the zero-point energy of the H<sub>2</sub> molecule. The first one involves N adsorption on the W(110) surface, while the second involves N inside W(110) surface, as observed experimentally by the Pfnür research group. This reconstruction results in a significant increase in H<sub>2</sub> dissociation compared with other W(110) surfaces clean and covered with either oxygen or nitrogen adsorbed on the surface. Consequently, the sticking coefficient of H<sub>2</sub> is considerably increased, even at low collision energies, exerting an attractive effect towards H<sub>2</sub> dissociation, as experimentally [1] suggested in polycrystalline tungsten, where the formation of deuterated ammonia, ND<sub>3</sub>, was detected. However, when nitrogen is present on the surface, it tends to inhibit the H<sub>2</sub> dissociation.

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# Cutting-Edge Developments in Natural Orbital Functional Theory: Probing Molecular Dynamics and Beyond

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#### Abstract

Natural orbital functional theory (NOFT) is an alternative formalism to both density functional and wavefunction based methods. It is currently an active research field [4], applicable to large molecular systems of general chemical interest [1] using open-source software like DoNOF [5]. In this talk, I will first introduce the recently proposed global NOF (GNOF) [3], which has shown a balanced treatment of electron correlation effects in challenge molecular systems [2]. Secondly, I will present a GNOF-based ab initio molecular dynamics (AIMD) within the Born-Oppenheimer approximation [6]. The most notable feature of GNOF-AIMD is its ability to display the real-time evolution of natural orbitals, offering detailed insights into the time-dependent electronic structure of complex systems and processes, including reactive collisions. Two examples of reactive collisions will be discussed: the quartet ground-state reaction  $N(^4S) + H_2(^1\Sigma) \rightarrow NH(^3\Sigma) + H(^2S)$ , and the competition between bimolecular nucleophilic substitution (SN2)  $F^- + CH_3CH_2Cl \rightarrow CH_3CH_2F + Cl^-$  and base-induced elimination (E2)  $F^- + CH_3CH_2Cl \rightarrow CH_2=CH_2 + HF + Cl^-$  reactions.



Figure 1: Time evolution of the three natural orbitals involved in the bond pattern change during E2 reaction.

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# Modeling guest-host(lattice) interactions: He inclusion in hydrates

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### Abstract

He hydrates present an intriguing and relatively unexplored systems. Computational investigations on the He@hydrates were motivated by the recent experimental synthesis of He@sII [1], and in relation with the emerging research on new low-density ice polymorphs [2]. Thus, we performed quantum chemistry computations considering both aperiodic ice/clathrate-like finite-size structures [3, 5, 6] and periodic 3D crystal frameworks [4, 7]. In this way, we demonstrated the importance of conducting a systematic benchmark study of conventional and modern DFT-D approaches, including fundamental units (e.g. He-H<sub>2</sub>O) and building block clathrate cages (e.g.  $5^{12}$  or  $5^{12}6^4$ ) or ice channels present in the most common sI, sII and sH clathrate hydrates or ice II and Ih. In turn, we analysed the stability of the cages forming the He@sII clathrate, considering single and multi-occupancy [8], through thermochemical calculations at a range of T-P conditions comparable to the experiment [1] (see Figure 1). Finally, we explored the effects on the encapsulation of He atoms in the sI/sII crystal lattices by computing structural, mechanical and energetic properties in both empty and He-filled systems. For a more direct comparison with measurements on He@sII structural properties, multiple cage occupancy, similar to those established by diffraction experiments [1], is considered [8]. All these insights serve to better understand the role of the entire guest-guest, guest-host and host-host interactions in the stabilization of such clathrate hydrates, they address accuracy issues on weakly-bound systems, providing valuable reference data that can be utilized for developing future predictive data-driven models using either traditional fitting or emergent machine-learning techniques (see Figure 1).



Figure 1: Data-driven modeling and first-principles DFT-D computations on He@hydrates.

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# On the CO ice UV-induced desorption mechanism: The role of vibrational relaxation highlighted.

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## Abstract

The UV-induced desorption of molecules at the ice surface, which may explain the high abundance of gas phase molecules in the coldest environments of the ISM, has been extensively studied for CO, the second most abundant species in the ISM. Experimental and theoretical investigations have revealed that in pure CO ices, UV photodesorption may predominantly follow an indirect "Desorption Induced by Electronic Transition" (DIET) mechanism [1-3]. However, understanding the underlying molecular mechanisms, especially the nature of the energy transfers involved in indirect desorption pathways, has been a topic of ongoing scientific discussion.

In this astrochemical context, we introduce an innovative study utilizing ab initio molecular dynamics (AIMD) simulations based on Density Functional Theory (DFT) to investigate an indirect desorption mechanism in CO ice [4]. Here, a highly vibrationally excited CO molecule (v=40) within 50 CO molecules aggregates initially created, optimized, and then thermalized at 15K, triggers the indirect desorption of surface molecules. Our study meticulously analyzes the redistribution of vibrational energy into translational, rotational, and other vibrational modes within the aggregate post-excitation, as well as the desorption mechanism.

Our AIMD theoretical insights reveal that the desorption process starts with a sequence of energy transfers initiated by a collision between molecules, culminating in the desorption of vibrationally cold CO molecules. In addition, the theoretical energy distributions—vibrational, rotational and kinetic—of the desorbed molecules, are in perfect agreement with the experimental ones, which supports the pivotal role of vibrational relaxation in the desorption process.

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Dynamics of Electronically Excited Metal Atoms (Zn and Cd) in Rare Gas Matrices: Simulation of Multiple-band Emission using Molecular Dynamics with Quantum Transitions

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Molecular dynamics with quantum transitions approach is employed to simulate the spectroscopic characteristics of the  ${}^{1}P_{1}-{}^{1}S_{0}$  transitions in atomic zinc and cadmium in order to gain insight into the excited state behavior of these atoms isolated in solid rare gases neon, argon, and krypton. The absorption and emission spectra are simulated. Non-radiative processes play a fundamental role in the transfer of population among the three electronic states initially accessed in absorption. Three distinct relaxation pathways were identified. Two of these are related to the dynamical modes described in previous works [McCaffrey and Kerins, J. Chem. Phys. 106, 7885 (1997); Kerins and McCaffrey, J. Chem. Phys. 109, 3131 (1998)] in which the system evolves to form a square planar configuration around the metal atom. The third distinct pathway involves motion on a hexagonal close packed plane. The temperature dependence of complex formation was also determined for the three relaxation pathways.



# Photofragmentation dynamics study of van der Waals clusters using two theoretical methods: quasiclassical trajectories and trajectory surface hopping.

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Ideally, dynamic calculations provide the most detailed information about end-state distributions in collision or semi-collision processes. In this sense, it is often the case that practical drawbacks severely restrict the application of intrinsically accurate quantum calculations, which is particularly a problem if large clusters are to be studied. In most cases, however, quasi-classical methods exhibit a relatively high interpretive power / computational cost ratio and allow the full dimensionality of the system to be included. However, although quasi-classical calculations are important for constructing intuitive models of molecular processes, the limits of their validity and applicability remain uncertain.

During the last two decades, the van der Waals complex has been the subject of intense investigation from both experimental and theoretical points of view. In this work, we show how a very good description of the available data can be achieved by conducting a study of full-dimension quasi-classical trajectories on the process in electronic molecular states. The influence of two quantum effects such as the dissociation channel closure and the intramolecular vibrational relaxation (IVR) mechanism on the agreement with experimental rotational distributions. A discussion is presented on the feasibility of similar quasi-classical methods to model VP dynamics.

The vibrational predissociation of RG- ( $I_2$ .Br<sub>2</sub> and IBr), has been studied using a variety of theoretical and experimental methods, producing a large number of results. Therefore, it is a useful system to compare different theoretical methods. We apply the methods of quasiclassic trajectories and trajectory surfaces hopping (TSH). The dynamics of the system was propagated on a potential energy surface (PES) corresponding to quantum molecular vibrational states with the possibility of jumping towards other surfaces until the van der Waals bond dissociates. This allows adding quantum vibrational effects to a classical dynamics approach.

We have also incorporated the kinetic mechanism for a better understanding of the evolution of the complex.

The novelty of this work is that it allows us to incorporate all the surfaces into the dynamics of the system. The calculated half-lives are similar to those reported experimentally. The rotational distribution, the rotational energy are also calculated and compared with the experiments.

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# WaterFEL: Advancing Photodynamics with Cutting-Edge Electron-Based Methods

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## Abstract

Observing atomic motions during chemical reactions and phase transformations has long been a coveted goal in scientific research. The advent of ultrafast electron diffraction (UED) cameras, which utilize ultrashort electron bursts, has turned this aspiration into reality [1-6].

The primary research focus of our laboratory includes investigating quantum phenomena and phase changes in twodimensional materials, employing liquid-phase electron diffraction and microscopy, and advancing dynamic imaging techniques, particularly for weakly scattering biological specimens.

In this talk, I will discuss the technological advancements that enable this precision, review the current forefront of the field, and provide an outline of the upcoming plans to establish an integrated infrared free-electron laser (IR-FEL) [7] and UED facility at the University of Waterloo (WaterFEL). This facility will enable advanced spectroscopic and structural studies of gaseous, liquid, and solid samples.



Figure 1: Power spectrum of Water-FEL based on the Fritz Haber Institute IR-FEL.

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# Guiding complex photodissociation reactions from the get-go

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## Abstract

The manipulation of quantum interference plays a crucial role in coherent control, one that has been used in applications ranging from quantum-state preparation, photochemical reactions and quantum information [1]. A cornerstone of quantum control in Chemistry is the manipulation of chemical reactions, to maximize their yields and particularly to improve the selectivity, obtaining the desired product among the possible fragmentation channels. The control paradigm is a two-step process where first a pump pulse ignites the dynamics, creating a vibronic wave packet in the excited states, and then a so-called control pulse guides the wave packet along the reaction coordinate, adjusting the phases or inducing transitions between different electronic states, as necessary. In many practical implementations, the pump pulse and the control pulse are integrated into the same pulse, whose complex structured is refined by choosing the proper parameters through pulse shapers and learning algorithms [2].

In this work we develop a different paradigm, called the Geometrical Optimization [3,4], where the control is exerted by optimizing the initial wave function driven by the (fixed) external field. In practice, this amounts to reversing the order of the sequence: first applying a control pulse, and then the pump pulse. The information conveyed in the initial coherences is sufficient to determine the outcome of the reaction and even to select the fragmentation channel in polyatomic molecules under the effect of strong nonadiabatic couplings, as we illustrate for the A band of  $CH_3I$ .



Figure 1: Quantum yield of the I channel in the A band of  $CH_3$  as a function of the number of vibrational states participating in the initial superposition. Also shown is the photo-dissociation cross section for the I channel in arbitrary units.

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# A comparative QCT and Quantum Close Coupling study of the HeNa<sup>+</sup> and HeK<sup>+</sup> three body association

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The termolecular reaction between three atoms, whereby a diatomic molecule is formed while the third atom remains free, is the process under investigation, which is designated as threebody association (TBA). It has recently been the subject of renewed theoretical and experimental interest as it is engaged in research activities pertaining to a number of scientific disciplines, including cold and ultracold chemistry, astrophysics, plasma physics, atmospheric physics, and physical chemistry. From a technical standpoint, the enhanced capabilities of cryogenic ion traps were instrumental in driving recent advancements, enabling the measurement of three-body association in hydrogen and helium to cold ions [1]. The fundamental theory of TBA was established long ago while its application to real systems became possible only very recently because of the challenging complexity of the calculations. TBA can be described in two ways: either a simultaneous three-body collision or a two-step process by which two of the atoms collide first, yielding an excited diatomic molecule, that is further stabilized by collisions with the third body. The latter is known as the Lindemann-Hinshelwood energy mechanism [2, 3] and represents the primary source of quantum studies on the subject of three-body association. A significant benefit of this approach is that only two two-body collision steps need to be described. The Quasi Classical trajectory method is an interesting alternative approach which has recently been successfully applied to several systems. [4] In the present work we will compare the results of these two approaches for  $Na^++$  $He + He \rightarrow HeNa^{+} + He$  and  $K^{+} + He + He \rightarrow HeK^{+} + He$ . In order to achieve this objective, two PES will be constructed, and the bound and quasi-bound states of the resulting diatomic cations calculated. Subsequently, the collisional relaxation rates will be calculated, and the TBA rate obtained within the framework of the local thermodynamic equilibrium hypothesis. The comparison between the QCT and quantum approaches will ultimately allow us to gain complementary insight into the temperature dependence of TBA.



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# Combining QM-cluster and Hybrid QM/MM Models to Study Enzyme Catalysis

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## Abstract

Simulating enzyme reactions is a challenging task because it involves modeling the formation and breaking of bonds as part of the catalyzed reaction, necessitating the use of quantum mechanics (QM). However, the large size of proteins, along with the critical role of the protein environment, precludes the application of QM to the entire system. Over the past few years, two primary approaches have been used to address this issue. The simpler approach involves isolating a small model of the active site from the protein and studying it using QM methods. The effect of the surrounding environment is typically modeled by fixing a few atoms at the periphery to their crystal positions and performing calculations in a continuum solvent. Another more realistic approach explicitly studies the entire protein, including the surrounding explicit water molecules, using a hybrid QM/MM method. In this method, the active site is studied by QM methods, while the rest of the system is modeled at the molecular mechanics (MM) level.

An effective strategy is to integrate both approaches, optimizing the benefits and minimizing the drawbacks. Here, we present two examples where we have successfully combined QM-cluster models and hybrid QM/MM methods to study important details of the reaction mechanisms of enzymes: Ascorbate Peroxidases, which help to detoxify  $H_2O_2$  using vitamin c [1] and MCR-1, responsible for antibiotic resistance to colistin [2].



Figure: Left, Ascorbate Peroxidase featuring a channel to the solvent bulk, presumably the source of protons for catalysis. Right: MCR-1 active site in contact with bacterial membrane.

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# Chemical compound space of light-driven molecular nanomotors

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### Abstract

Light-driven molecular nanomotors (MNMs) convert light into mechanical energy. Due to their temporal and spatial controllability, MNMs have several potential applications in biomedical sciences, including drug delivery and permeabilization of membranes[1]. Improving their efficiency requires optimization of various molecular properties. Above all, a high product quantum yield (PQY) [6] for the photochemical isomerization that drive the conversion of photon energy into mechanical work is needed. This typically goes in hand with a high absorption cross section. Due to improved tissue penetration, near-IR light is the desired source of energy. However, due to the excitation energy required to drive the isomerization, this often requires usage of two-photon excitation. Based on quantum chemistry and ab initio non-adiabatic molecular dynamics, I will report efforts to design new MNMs with improved PQY, one- and two-photon absorption cross sections. To allow screening of a large number of molecular candidates, machine learning methods for the prediction of excited state properties [3, 5] take a crucial role in this development.



Figure 1: Left: Photoinduced isomerization of a unidirectional MNM, simulated by ab initio non-adiabatic molecular dynamics. Right: A sample of substituted NMN derivatives for virtual compound screening.

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# Infrared photodissociation assisted by vibrational strong light-matter coupling

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#### Abstract

Vibrational strong light-matter coupling is one of the most studied research topics currently due to the unexpected modifications of chemical reactions rates and branching ratios. However, despite great theoretical efforts, there is not a theory that explains completely the influence of a confined electromagnetic environment [2]. We study the photodissociation mechanism of a single anharmonic non-polar molecular mode coupled to a infrared vacuum in the vibrational strong light-matter coupling regime. We implement the MCTDH ansatz to solve the time-dependent Schrödinger equation for two continuous wave driven scenarios, i molecule-driving and ii nanocavity-driving. The results show an enhancement of intracavity dissociation probabilities in comparison with out-of-cavity scenarios for the same laser intensities. Further, the cavity-driving scenario reveals similar dissociation probabilities with laser intensities of up to two orders of magnitude smaller than the employed in the molecule-driving case [4]. Our findings are based in the modified ladder climbing process in the polariton quasi-continuum below dissociation threshold respect to single anharmonic energy levels scheme [1, 3]. Our work extends the understanding of cavity-modified chemistry on resonance with fundamental transition of a molecular mode and will be useful to control dissociation yields of small molecules in confined infrared electromagnetic environments.

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# XII International Meeting on Photodynamics and Related Aspects

# Title

"Effective phase space representation of ultrafast quantum dynamics"

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# Abstract

Trajectory-based methods constitute a promising alternative to perform quantum dynamical simulations of multidimensional systems, owing to their favourable scaling properties compared to wavepacket propagation techniques. We illustrate the performance, in terms of numerical accuracy and efficiency, of the recently developed Interacting Trajectory Representation (ITR) to study ultrafast quantum dynamics. The ITR is a trajectory-based description without reference to any wave function, where the effect of the quantum potential is mimicked by effective pseudo-particle interactions. The method maps the originally quantum problem into the motion of an equivalent, higher-dimensional classical-like system. The comparison with standard quantum calculations on several model quantum systems, both for bound and scattering problems, shows that the interacting trajectory approach reproduces paradigmatic quantum effects such as zero-point energies, ground state densities, tunneling, correlation functions and energy spectra [1,2]. The method is applied subsequently to two different test cases, namely the ultrashort laser ionization of a model hydrogen atom [3], and the vibrational predissociation of a triatomic van der Waals complex [4,5]. We show that the trajectory-only approach is capable of correctly describing the large amplitude motion and energetics of the laser driven electron and of reproducing carrier-envelope effects onto the photoelectron spectra. In addition, the predictions of the present methodology are in very good agreement with the available experimental data for the vibrational predissociation rates, while it provides an intuitive picture of the dynamical quantum processes involved.

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# Computational spectroscopy investigations of low-mass molecular endofullerenes

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#### Abstract

We explore the origin of the anomalous splitting of the  $1_{01}$  levels reported experimentally in different systems composed by a small molecule encapsulated in a C<sub>60</sub> fullerene such as the H<sub>2</sub>@C<sub>60</sub>, HD@C<sub>60</sub>, HF@C<sub>60</sub> and H<sub>2</sub>O@C<sub>60</sub> systems.[1, 2] An efficient quantum fully coupled computational scheme within the multiconfiguration time-dependent Hartree (MCTDH) approach is used to handle the otherwise extremely costly computations of translational-rotational-vibrational states and energies of light-molecule endofullenes.

We introduce two competing physical models, and discuss the observed unconventional quantum patterns in terms of anisotropy in the interfullerene interactions. The first one consists of a change in the off-center position of the encapsulated molecule and the second of an uniaxial  $C_{60}$ -cage distortion, arising from noncovalent bonding upon water's encapsulation, or exohedral fullerene perturbations.[3, 4]

Our results on the HF@C<sub>60</sub> and H<sub>2</sub>O@C<sub>60</sub> systems show that both scenarios could reproduce the experimentally observed rotational patterns although quantitative agreement with the available experimental rotational levels splitting value has been achieved by the model that considers an uniaxial deformation of the C<sub>60</sub>-cage (Figure 1a). Following these findings a series of DFT calculations to study the effect of an uniaxial contraction or elongation of the cage is performed for the HF@C<sub>60</sub> system and a potential form that reproduces the effect of the distortion is then used to calculate the bound states and spectra of the endohedral system (Figure 1b).[5]



Figure 1: (a) Minimum energy potential curves obtained (upper panels) for the indicated values of the  $C_{60}$ -cage distortion for the  $H_2O@C_{60}$  system and evolution of the indicated rotational state energies (lower panel). (b) Infrared spectra for the HF@C\_{60} molecule using the contraction and elongation potential models.

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# Path Integral Molecular Dynamics Simulations on Cationic Dimers Solvated in <sup>4</sup>He Clusters

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## Abstract

The structures and energetics of  $X_{2}^{+}$ -doped He clusters (X=alkaline) are firstly determined by means of evolutionary programming optimizations and classical molecular dynamics simulations [1]. The underlying interactions in the He<sub>N</sub>  $X_{2}^{+}$  complexes are described by sum-of-potentials *ab initio*-based models [2]. The classical pictures of the He atoms surrounding the cationic dimers show a selective growth of the clusters. Figure below depicts a contour plot of the classical probability distribution in the (*z*, *r*)-plane (left panel) and the quantum one (right panel) obtained later by applying the Feynman-Hibbs second order approach [3] for the X=Li, N=30 cluster at T=2 K. The *z* axis is along the cationic dimer.





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# Reaction dynamics of excited sulfur cation with molecular hydrogen.

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## Abstract

 $SH^+$  is a widespread molecular ion in diffuse interstellar clouds, and has also been detected in emission toward the Orion Bar photodissociation region (PDR). In warm and dense PDRs,  $SH^+$  is predicted to be formed by exothermic reactions of  $S^+(^4S)$  with vibrationally excited  $H_2$  (v;1). The viability of this hypothesis have been confirmed by theoretical simulations which demonstrate that for vibrational level v=2 or higher of  $H_2$ , the reaction exhibit high rate constants. To validate these precedictions, it is however necessary to contrast theoretical results with those obtained by a guided ion beam experiment.

The photoexcitation of  $CS_2$  with UV photons of 15 eV provides enough energy to inonize and fragment the molecule to produce sulfur cation in its ground state:  $S^+({}^4S)$ . With a photon energy of 17 eV, it is also possible to produce it in its electronically excited:  $S^+({}^2D)$ . Once produced, these atomic ions can be captured and guided in order to collide with molecular hydrogen to study the production of the hydride cation SH<sup>+</sup>. Since theoretically, it is possible to simulate the reaction in the experimental conditions from the first principles of quantum mechanics, in this presentation, we will see up to which degree of accuracy theory is able to reproduce experimental measurements. The theory/experiment comparison will allow to get insights on the mechanism of the title reaction and also on fundemental processes such as intersystem crossing (ISC).



Figure 1: Correlation diagram and schematic reaction mechanism of  $S^{+}(^{4}S)+H_{2}$ 



## Dynamics and Mechanism of DNA Repair by a Bifunctional Cryptochrome

2

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### Abstract

Photolyase and cryptochrome belong to a group of structurally similar flavoproteins but with two distinct functions of DNA repair as a photoenzyme and signal transduction as a photoreceptor, respectively, under blue-light illumination. Here, we studied a recently discovered bifunctional cryptochrome (CraCRY) with focus on its repair of a type of DNA lesion, (6-4) photoproduct (6-4PP). We used femtosecond spectroscopy and site-directed mutation to map out the critical elementary steps by following the dynamics of initial reactants, various intermediates and final products. We observed initial direct ultrafast electron tunneling from the hydroquinone flavin cofactor to 6-4PP in 300 ps through an intervening adenine as a mediator, minimizing the electron bifurcation of a two-step hopping pathway bridged also by the adenine as an intermediate. The subsequent proton transfer from the neighboring histidine to anionic 6-4PP in 2 ns is critical and competes with the futile back electron transfer in 151 ps. The mutations of either of two histidine residues at the active site nearly abolish the repair, indicating their essential role on repair reactivity and structural integrity. These results elucidate the electron-coupled proton transfer (ECPT) mechanism and the repair photocycle of this bifunctional cryptochrome at the molecular level, further implying the hydroquinone flavin probably being the active state *in vivo* for dual functions or one of the two functions is excessive.

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# Potential Energy Surface studies using PIP-NN: the $C_2O$ molecule case.

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#### Abstract

The development of potential energy surfaces (PESs) is fundamental in studying molecular reactions and spectroscopy. The development of PESs varies considerably in computational cost depending on the ab initio methods used and the number of energy points required to fit them to an analytical function. An alternative to achieving high accuracy at a relatively low computational cost is using neural networks trained with permutation invariant polynomials (PIP-NN) [1]. In this work, we focus on developing a PES for the <sup>3</sup>A'' electronic state of the C<sub>2</sub>O molecule using PIP-NN. We used a set of energies computed at the MRC+Q/aug-cc-pVTZ level of theory, divided into three sets: training, validation, and test. We used the mean square error (MSE) of the energy fit as an optimization parameter for the training and validation sets, varying the hyperparameters of the network to achieve better optimization of the fit. We find RMSD close to those of traditional methods but using lower ab initio energies.

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# Relativistic Quantum Chemistry Studies of Rhenium(I) Tricarbonyl (bipyridine or 1,10-phenanthroline derivatives) Compounds With Amino-Pyridine Schiff Base Phenol (APSB-Phenol) as Ancillary Ligands

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## Abstract

Rhenium(I) tricarbonyl complexes have emerged as promising fluorophores, particularly for biological applications. The *fac*-Re(CO)<sub>3</sub>(N,N)L complexes, where N,N represents a substituted dinitrogenated ligand (bipyridine or derivatives with relatively small substituents) and L is an ancillary ligand [a amino pyridine Schiff base phenol (APSB-Phenol), with an intramolecular hydrogen bond (IHB)], have shown significant potential as fluorophores, especially for walled cells (*e.g.*, bacteria and fungi).<sup>1,2</sup>

This work presents a relativistic theoretical analysis of a series of *fac*-[Re(CO)<sub>3</sub>(N,N) (APSB-Phenol)]<sup>1+</sup> complexes (N,N corresponds to 2,2'-bipyridine (bpy) (series A) or 4,4'-bis(ethoxycarbonyl)-2,2'-bipyridine (deeb) (series B) to elucidate the role of the IHB in the ancillary ligand concerning their photophysical behavior. Our findings indicate that all complexes absorb in the visible light range. Complexes with a APSB-Phenol containing an IHB exhibit luminescent emission suitable for biological purposes, characterized by a large Stokes shift, emission in the 600-700 nm range, and lifetimes ( $\tau$ ) in the order of 10<sup>-2</sup> to 10<sup>-3</sup> seconds. Conversely, complexes with APSB-Phenol lacking the IHB show predicted emission with the lowest triplet excited-state energy entering the near-infrared (NIR) region.<sup>3</sup>

These results suggest that the IHB plays a crucial role as a switch between visible and NIR emissions in these kind of complexes. Given that the APSB-Phenol can be substituted to modulate the properties of the entire Re(I) tricarbonyl complexes, further exploration of other substitutions and their effects on photophysical properties, particularly the emission range, is warranted.

## ACKNOWLEDGMENTS

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# Carbon defects as independent photon emitters in hexagonal boron nitride: controlling spin and emission energy

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#### Abstract

Carbon defects in hexagonal boron nitride (h-BN) layers have garnered significant interest due to their optical and quantum properties [3]. These color centers, see Fig. 1, particularly those with a spin greater than or equal to 1 ( $S \ge 1$ ), hold promise for applications in quantum technologies [2]. Furthermore, identifying such defects with this property is intriguing due to the limited information available in the literature regarding carbon defects with these characteristics.

Additionally, it has been observed that the emission energy of carbon defects can be influenced by the number of h-BN layers in which they are embedded [1].

In this poster, we will demonstrate how to identify and characterize these spin-active carbon defects embedded in an h-BN multilayer through their luminescence.



Figure 1: Color center in an h-BN monolayer. The green light is the color of the laser incident on the defect, and the red light is the color of the photons emitted from the color center.

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# Quantum Chemical Elucidation of activation/deactivation of Luminescence Mechanism in

# Europium (III) doped UiO-66-(COOH)<sub>2</sub> Chemosensor Selective to Cadmium (II)

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Cadmium(II) is one of the most dangerous heavy metals due to its high toxicity and carcinogenicity [1], which is why considerable attention has been devoted to its detection and quantification. This has led toward the application of sensitive and selective methods for the detection of these elements in different matrices. In this regard, luminescent chemosensors based on Metal Organic Frameworks (MOFs) have emerged as a promising solution for the detection and monitoring of metal ions [2]. Recently, lanthanide doped MOFs (Ln@MOFs) have been synthesized as luminescent sensors for metal ions in aqueous media[3]. Among these, Eu<sup>3+</sup> doped MOFs are expected to be part of effective sensor devices. In this study, we investigated the luminescence properties and Cd<sup>2+</sup> sensing mechanism of a novel UiO-66-(COOH)<sub>2</sub> type MOF, doped with Eu<sup>3+</sup> ions [1]. From a computational point of view, the study of MOFs represents a challenge due to the large size of this system[4]. Here, we have developed a theoretical procedure to elucidate the response of the sensor to Cd<sup>2+</sup> ions. Our methodology employs a finite model to accurately depict the Eu@UiO-66-(COOH)<sub>2</sub> structure, using well-known and rigorous multiconfigurational *ab initio* methods combined with time-dependent Density Functional Theory (TD-DFT).

The most probable sensitization pathway involves the intersystem crossing (ISC) from the S<sub>1</sub> to the T<sub>1</sub> state of the 1,2,4,5-benzenetetracarboxylic acid (H<sub>4</sub>btec) linker ( $S_1 \rightarrow T_1$ ), followed by an energy transfer from the T<sub>1</sub> electronic state of the own linker to the <sup>5</sup>D<sub>0</sub> electronic state, of Eu<sup>3+</sup> ions, T<sub>1</sub> (H<sub>4</sub>btec) $\rightarrow$ <sup>5</sup>D<sub>0</sub> (Eu<sup>3+</sup>). Finally, finally the emission from the  ${}^{5}D_{0}$  state to the  ${}^{7}F_{J}$  state of the Eu<sup>3+</sup> is observed. We found that in presence of Cd<sup>2+</sup> ions, due to the heavy atom effect, the most probable sensitization pathway involves a feasible intersystem crossing process  $(S_1 \rightarrow T_1)$ . This leads to a more effective intramolecular energy transfer from the T<sub>1</sub> electronic state of the (H<sub>4</sub>btec) linker to the <sup>5</sup>D<sub>0</sub> electronic state of Eu<sup>3+</sup> ions (T<sub>1</sub>(H<sub>4</sub>btec) $\rightarrow$ <sup>5</sup>D<sub>0</sub>  $(Eu^{3+})$ ), resulting in the "*Turn-on*" of the sensor luminescence in the presence of the Cd<sup>2+</sup> ion.

Based on the results, we consider that the proposed methodology addresses the theoretical elucidation of the sensing mechanism proposed for doped MOFs chemosensors.

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# Elucidation of the electronic properties of UiO-66 type MOF doped with Europium(III) ions, a sensor reported to be selective to Hg(II) ions: A quantum chemistry approach.

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Accurate detection of mercury is crucial due to its high toxicity and the serious risks to human health and the environment.[1] The bioaccumulation of mercury in the food chain and its ability to cause neurological damage and other health problems highlight the importance of investigating on effective detection methods.[2] In this regard, chemosensors based on Metal Organic Frameworks (MOFs), especially UIO-66-type MOF from mixed linkers containing isophthalic acid (TPA) and 2,6-pyridinedicarboxylic acid (DPA) doped with lanthanide ions such as Europium (III), emerge as promising tools to monitor the presence of mercury in different environmental matrices and food products.[3] These advanced systems not only allow sensitive and selective detection, but also contribute significantly to the protection of public health and the preservation of environmental quality by facilitating the identification and control of mercury contamination.

The computational study of the electronic structure and optical properties of  $Eu^{3+}@UiO-66(DPA)$ , reported as a selective chemical sensor to  $Hg^{2+}$  ions, was performed. The elucidation of the selective turn-off luminescent sensing mechanism toward  $Hg^{2+}$  ions were addressed, using combining molecular and periodic density functional theory (DFT) approach.

The band gap, the Projected Density of States (PDOS) and the change in the electronic structure of the system upon interaction with  $Hg^{2+}$  were studied using the periodic DFT approximation.[4]

According to the results, we found that in the UiO-66(DPA) doped with  $Eu^{3+}$ , sensitization pathway is activated from the DPA linker to  $Eu^{3+}$ , with the subsequently emission europium centered. On the other hand, in the Hg<sup>2+</sup>@UiO-66(DPA), nonradiative deactivation processes of excited states are predominated, resulting in the quenching of luminescence and sensing event. This approach provides a deep understanding of how the incorporation of  $Eu^{3+}$  and Hg<sup>2+</sup> ions affect the electronic structure of the UiO-66(DPA) framework.

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# Intercalation of luminescent lanthanide complexes with DNA mismatch.

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#### Abstract

The integration of multidentate organic ligands into lanthanide complexes has enhanced their selectivity and capacity for recognizing DNA mismatch via intercalation, positioning them as promising molecular probes and potential therapeutic agents.[3] This study presents a comprehensive in silico analysis of 8 multidentate organic ligands interacting with DNA sequences containing various mismatches (GA, AC, GG, GT) and Watson-Crick base pairs (AT, GC). Molecular dynamics (MD) simulations were conducted using the AMBERTools suite, employing the OL15 force field for DNA and GAFF2 for ligands, with trajectories extending to 20 ns. The MD simulations demonstrated stable ligand intercalation at the DNA binding sites. Binding free energy calculations were performed using the MM/GBSA approach, implemented through the MMPBSA.py module in Amber22,[1] to quantify ligand-mismatch interaction strengths. Further, an energy decomposition analysis (EDA) was executed using the Amsterdam Density Functional (ADF) package, applying the Morokuma-Ziegler partitioning scheme at the BP3LYP/TZ2P level of theory.[2] Non-covalent interactions were characterized using the Non-Covalent Interaction (NCI) index. MM-GBSA analyses revealed that specific multidentate phenanthroline-derived ligands exhibit optimal affinities (up to  $-38\pm2$  kcal/mol) towards G-A and G-G mismatched sequences, while others demonstrate higher affinity (up to -39±2 kcal/mol) for G-C and A-T canonical base pairs, indicative of liganddependent selective recognition. EDA results elucidated the nature of these interactions, with dispersion forces contributing 50-60%, covalent interactions 19-25%, and ionic interactions 23-30% eV. NCI analysis corroborated the predominance of weak interactions in the ligand-DNA complexes. These findings provide critical insights for the rational design of complexes with selectivity towards specific DNA base-pairing errors, offering significant potential for biomedical applications.



Figure 1: Ligand intercalated in DNA mismatch

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# Quantum reaction dynamics of S + NH reaction in the $1^{3}A'$ electronic state

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#### Abstract

The chemistry of interstellar sulfur-bearing species remains incompletely understood. [1, 2, 3] The NS molecule is particularly intriguing because it serves as a potential tracer of photodissociation regions and may act as a sulfur reservoir in the interstellar medium. [3] This study aims to investigate the N + SH reaction and propose a plausible reaction mechanism for the  $1^{3}A'$  state. To achieve this, we developed an analytical potential energy surface (PES) based on *ab initio* calculations, which we then employed in quantum and quasiclassical simulations. Our work presents a PES for the  $1^{3}A'$  state, identifying the global minimum of the S + NH system at NH =  $1.9a_{0}$ , NS =  $3.6a_{0}$ , and SH =  $4.4a_{0}$ , with an energy of -0.64 eV. Our findings highlight that the cumulative reaction probabilities on the  $1^{3}A'$  surface are significantly higher than those on the  $1^{1}A'$ ,  $1^{1}A''$ , and  $1^{3}A''$  surfaces previously reported, [4, 5] suggesting the importance of the  $1^{3}A'$  state in the S + NH reaction dynamics.



Figure 1: Contour plot of the Potential Energy Surface (PES) for the S + NH channel with  $r_{NH} = 1.97a_0$  (panel a). The zero-energy reference point corresponds to the energy minimum of the asymptotic H + NS channel. Cumulative reaction probability (J = 0) for the S + NH  $\rightarrow$  NS + H reaction on the 1<sup>1</sup>A', 1<sup>1</sup>A'', 1<sup>3</sup>A', and 1<sup>3</sup>A'' states as a function of total energy (panel b).

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# Tunning the Electronic and Photophysical Properties of Metalloporphyrin-based MOFs: A quantum chemistry study

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#### Abstract

Lorem Hydrogen production (H<sub>2</sub>) is gaining interest as a clean energy source. [1] Thus, photocatalytic water splitting is a key method thanks to its eco-friendly nature. Metal-organic Frameworks (MOFs), due to their tunable optical properties, are excellent materials for hydrogen evolution via water splitting using sunlight. [2] Specifically, metalloporphyrins-based MOFs (TCPP(M) MOFs) have shown potential for this application. [3] In this report, TCPP (M) MOFs containing nodes based on metal ion d<sup>10</sup> Zn<sup>2+</sup> and TCPP(M) as linkers, where M, is a non-noble metal ion, such as, Fe<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup> and Cu<sup>2+</sup> introduced into the TCPP core, has been studied using theoretical tools. The electronic structure and optical properties of all Zn-TCPP(M) MOFs were investigated using the density functional theory (DFT) methods along with periodic-DFT calculations. The study revealed a band gap reduction related to the open-shell metals in the TCPP linker, with an optimal value for the photocatalytic process under sunlight. TD-DFT calculations show that the inclusion of open shell ions enhances the linker-centered ligand-tometal charge transfer process. These results support the strength of the bond between the central metallic atom in the TCPP linker. Finally, it some directions for the design and synthesis of new melloporphyrine-based MOFs was suggested, potentially leading to new materials for photocatalytic H<sub>2</sub> production via water splitting, see Figure 1.



Figure 1. Energy level diagram of the ZnTCPP(M) including the redox potential a gains vacuum for the HER (green dashed line) and OER (cyan dashed line).

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# Rhenium(I) Tricarbonyl (5,6-Epoxy-1,10-phenanthroline) Compounds Employing APSB-Phenol, Harboring an Intramolecular Hydrogen Bond: A Computational Study

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## Abstract

Rhenium(I) tricarbonyl complexes, known for their photophysical properties, stability, and low cytotoxicity, have been tested as fluorescent markers for mammalian cells (non-walled cell).<sup>1</sup>Recently, our group demonstrated their efficiency as stains for bacteria, yeasts, and molds. <sup>2,3</sup> These complexes use ((E)-2-((3-amino-pyridin-4-ylimino)-methyl)-4,6-di-

*tert*-butylphenol) amino-pyridine, a Schiff base phenol (APSB-phenol) as ancillary ligands with an intramolecular hydrogen bond. Notable examples include *fac*-[Re(I)(CO)<sub>3</sub>(4,4'-diethanoate-2,2'-bpy) APSB-phenol]<sup>1+</sup> and *fac*-[Re(I)(CO)<sub>3</sub>(2,2'-bpy) APSB-phenol]<sup>1+</sup> for staining fungi and, neutral complex *fac*-Re (CO)<sub>3</sub>(5,6-epoxy-5,6-dihydro-1,10-phenanthroline) Br for Gram-negative bacteria.<sup>2,4</sup>



In this work, we analyzed Re(I) tricarbonyl with 5,6-epoxy-5,6-dihydro-1,10-phenanthroline as the equatorial ligand, modifying (E)-2-((3-amino-pyridin-4-ylimino)methyl)-4,6-di-tert-butylphenol) as ancillary ligands by

Figure 1. Molecular architecture of Re(I) complexes proposed.

substituting groups on the phenol ring (Figure 1) to predict the photophysical changes induced by the presence of these substitutions. Therefore, a detailed analysis of the electronic configuration of the ground and excited states (singlet  $S_1$  and/or triplet  $T_1$ ) is essential to compare Re(I) complexes in terms of their predicted absorption and emission, Stokes shift, and luminescent lifetimes ( $\tau$ ), as well as to understand the role of the IHB in emission modulation.

The study employed density functional theory (DFT), incorporating scalar relativistic effects and spin-orbit coupling with the two-component Hamiltonian and ZORA. Natural bond orbital (NBO) analysis was also performed for the formation of IHB, time-dependent relativistic density functional theory (TDDFT) for absorption and emission, and zero-field splitting (ZFS) to clarify the emissive states. Thus, the best candidates for synthesis and future experimental tests with cells were selected.

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# Lanthanides (II) coordination complexes: Electronic Structure and Magnetic Properties

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Divalent lanthanides (Ln) offer the opportunity to consider how it would be possible to improve the magnetic properties in Ln complexes by increasing the magnetic moment of it taking advantage of the additional opportunity offered by the 4f<sup>n</sup>5d<sup>1</sup> configuration from the point of view of the covalent bonding. This idea has been considered by Long et al. who analyzed the [LnCp'<sub>3</sub>]<sup>-</sup> series.<sup>1</sup> In addition, Evans et al. reported the synthesis of new divalent lanthanide complexes of the type [Ln(OAr')<sub>3</sub>]<sup>-</sup>, (Ln = Gd, Dy, Ho, Er; OAr' =  $OC_6H_2^tBu_2$  - 2,6 - Me - 4 aryloxide) where the metal-ligand interaction in a stronger crystal-field environment should produce more interesting properties with respect to the organometallic analogues.<sup>2</sup> Moreover, the  $[Ln(NR_2)_3]$  complexes (R = SiMe<sub>3</sub>), also synthesized by Evans et al., were studied by means of electronic structure and magnetic properties.<sup>3</sup> In both systems the SOMOs (single - occupied molecular orbitals) have  $d_z^2$  character, as found previously for [LnCp'<sub>3</sub>]<sup>-</sup> complexes, with an increased possible to achieve stabilization of the 4f<sup>n</sup>5d<sup>1</sup> configuration in a trigonal symmetry.<sup>2</sup> However, the level of theory used in these studies is based on DFT. In contrast, since these systems are highly correlated, ab initio calculations would provide a more accurate theoretical representation of the wavefunctions, enabling the description of the properties studied below. CASSCF wavefunctions were conducted, considering various active spaces. Spin-orbit coupling was introduced by state interactions between the CASSCF wave functions, using the Restricted Active Space State Interaction (RASSI) program. Magnetic properties (effective magnetic

moment, g-factor and magnetic susceptibility) were calculated using the SINGLE\_ANISO module of MOLCAS. Results indicated a significant increase in magnetic moment for certain complexes, with  $[Dy(OAr')_3]^-$  (11.67 µB) and  $[Ho(NR_2)_3]^-$  (11.64 µB) showing the highest reported values.



Figure 1. Structures of  $[Ln(OAr')_3]^-$  and  $[Ln(NR_2)_3]^-$  alongside a  $\chi T$  vs T diagram of  $[Dy(OAr')_3]^-$ .

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# $Magnetostructural\ analysis\ of\ bimetallic\ U(V)\ complex\ bridging\ by\ oxygen\ ligands:$

## A computational study of diamond-shape structure.

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Elucidation of a diamond-shaped configuration within oxygen-bridged U<sup>V</sup> dimeric complexes has attracted considerable attention due to their unique magnetic and structural properties. The comprehension of solid-state and solution-phase chemistry of these species is predicated on the linear coordination exhibited by actinyl moieties, which engenders cation-cation interactions (CCIs) in bimetallic systems.[1] These CCIs provide a versatile approach for the fabrication of discrete pentavalent uranium clusters and facilitate intermetallic magnetic exchange pathways. In comparison to their hexavalent counterparts, these uranyl(V) systems demonstrate a near-degenerate ground state, attributable to the presence of an additional electron. The variability of this electronic configuration is contingent upon the uranium-oxygen bond length and the surrounding chemical environment.[2] This characteristic renders these complexes particularly intriguing for computational investigations in the realm of materials design and actinide chemistry.[3] In this work, a magnetostructural analysis of pentavalent uranyl complex  $(\mu - O_2)[UO(\beta - \Omega_2)]$ diketone)<sub>2</sub>]<sub>2</sub> is theoretically studied using Density Functional Theory (UKS B3LYP DKH-def2-TZVP). This type of analysis allows correlating crystal structure and coordination geometry with magnetic properties, providing a deeper understanding of these systems. Computational calculations were carried out with ORCA to calculate the magnetic coupling constant (J) employing the Broken-Symmetry approach (BS) which makes use of an unrestricted or spin-polarized formalism. Into magnetostructural exploration we focused this study over two specific structural parameters: variation of U-U bond distance and changing of dihedral angle of internal coordination sphere of diamond structure. Both parameters were compared with changes in J. Findings obtained from the magnetostructural analysis reveal a very pronounced change in the J parameter when there are small variations in the dihedral angle. This is due to spatial changes impacting the electronic delocalization between centers, affecting the orientation of the involved orbitals of both the ligand and the metal. This orientation is crucial for overlap, and as a result, the superexchange weakens, leading to these low values of J. Additionally, a proportional decay of J is observed relative to the U-U bond distance; that is, the greater the distance between the metals, the lower the value of J. These results are crucial in order to develop innovative strategies that can be utilized to investigate magnetic interactions and intermetallic communication in actinides, as well as to develop innovative functional materials involving actinides.



Figure 1: Molecular structure of  $(\mu - O_2)[UO(\beta - diketone)_2]_2$  with parameters studied in this work.

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# Covalency in Uranyl(VI) complexes with O K-edge X-ray Absorption Spectroscopy

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#### Abstract

The f shell is primarily responsible for the optical and magnetic properties that characterise the f elements [1]. These properties are modulated by the interaction metal-ligand, which is particularly important for the actinides due to the involvement of 5f orbitals. In this study, we understand that favoured the conditions of symmetry-restricted and central field, we can consider a molecular orbital ( $\Psi_{ML}$ ) as a combination of metal ( $\Phi_n f$ ) and ligand ( $\Phi_L$ ) orbitals:  $|\Psi_{ML}\rangle = \sqrt{1-\lambda^2} |\Phi_{nf}\rangle + \lambda |\Phi_L\rangle$ .  $\lambda$  represents the ratio between  $H_{nfL}$ , off-diagonal Hamiltonian matrix element for orbital interaction (overlap-driven covalency) and  $\Delta \epsilon_{nfL}$ , denotes the energy difference between the metal and ligand orbitals (energy-driven covalency) [2].

Experimental and theoretical studies suggest that the importance of overlap and near-degeneracy varies depending on the ligand's nature and the metal's oxidation state [4]. Traditional theoretical approaches like AIM theory or various population analysis methods may not comprehensively capture the covalent nature of these interactions and are rather complementary qualitative methodologies. In this context, ligand K-edge X-ray absorption spectroscopy (XAS) emerges as a potent technique for quantifying covalency, correlating the intensity of the 1s - > np transition with the value of  $\lambda$  [3].

Simulations of X-ray absorption spectroscopy (XAS) spectra for the uranyl ion  $(U-O_{yl})$  and its derivatives (having various equatorial ligands) carried out by RASCI approximation in ORCA software, with three active spaces: RAS1 encompassed core (1s) orbitals, RAS2 included non-bonding orbitals ( $\delta_u$  and  $\phi_u$ ), and RAS3 covered both bonding and anti-bonding orbitals ( $\sigma_u, \pi_u, \sigma_u^*$ , and  $\pi_u^*$ ). Significant alterations in transition wavelength and intensity were observed relative to the uranyl ion. The most prominent signal corresponds to the anticipated transition. The shift of this signal towards lower energy reflects the reduction in energy of the uranium anti-bonding orbitals due to equatorial coordination, while the variation in intensity corresponds to the p-contribution of the ligand, which is influenced by charge-donating or charge-withdrawing ligands nature.



Figure 1: (Left) Representation of the contributions to the ligand K-edge transition energies. (Right) Simulated O K-edge XAS spectra for  $[UO_2]^{2+}$  (orange line) and uranyl derivates with axial ligands. Spectra obtained from RASCI calculation with a 0.3 eV Lorentzian broadening of individual transitions.

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# Theoretical Study of Crotonaldehyde (2-Butenal) adsorption on PtSn(110), Pt<sub>3</sub>Sn(111)/Pt(111), Pt<sub>3</sub>Sn(111) and PtSn4(010) surface

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Abstract

In this study, adsorption of crotonaldehyde ( $C_4H_6O$ ) on catalysts composed of Pt and Sn was examined using periodic density functional theory (periodic-DFT). Different compositions of the materials were evaluated such as, PtSn(110), Pt<sub>3</sub>Sn(111), PtSn<sub>4</sub>(010) surfaces. Besides, the model Pt<sub>3</sub>Sn(111)/Pt(111) which consists of a slab of Pt(111) where Pt atoms of the exposed layer were replaced by Sn, was incorporated in this study [1,2].

In all systems, when Sn atoms are on the surface layer, O(cro)-Sn interactions occur and the C(cro)-Pt distances get shorter. Otherwise, the presence of Sn in  $PtSn_4(010)$  decreased considerably the number of interacting configurations toward Pt atoms, being the O(cro)-Pt the most observed interactions. The results could lead into deep conclusions such as, the interactions might induce the conversion of crotonaldehyde toward hydrogenation products, i.e. those interactions through the carbonyl oxygen with the catalysts could result in crotyl alcohol, while those with the olefin double bond on the surface could produce butyraldehyde or 1-butanol. Importantly, trans-crotonaldehyde had a higher adsorption energy on the Sn-enriched surface,  $PtSn_4$ , with an energy of -1.69 eV, highlighting the role of Sn in stabilizing crotonaldehyde through carbonylic oxygen.

These results provide initial insights into understanding crotonaldehyde adsorption on  $Pt_xSn_y$  at the atomic level, particularly the role of Sn adsorption sites and surface reactivity, and inform future experimental studies with Sn in  $Pt_xSn_y$  phases



Figure 1: Adsorption configurations of crotonaldehyde on (a) PtSn(110), (b) Pt3Sn(111), (c) Pt3Sn(111)/Pt(111) and (d) PtSn4(010).

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## Global potential energy surfaces for the $CO + C \leftrightarrow C_2 + O$ reaction

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#### Abstract

The C<sub>2</sub>O molecule is a significant intermediate in hydrocarbon combustion and has been detected in the interstellar medium (ISM)[1]. This molecule is also relevant in the hypersonic flight regime, particularly during atmospheric reentry when gas temperatures reach tens of thousands of Kelvin[2, 3]. Current chemical models for aerothermodynamic studies require accurate reactive rate coefficients for numerous reactions, including the CO+C reaction[4, 5]. This study addresses the limited experimental and theoretical investigations of CO+C and its reverse reaction  $C_2 + O$  by developing a new full-dimensional potential energy surface (PES) for the  $1^3A''$ ,  $2^3A''$ , and  $1^3A'$  electronic states of C<sub>2</sub>O. We employ extensive ab initio calculations using the multireference configuration interaction (MRCI+Q) method to generate a large grid of energies over a wide range of geometric configurations, which are then used in quasiclassical simulations.

The results indicate that in the three electronic states studied, the  $C_2 + O$  reaction does not possess an entry barrier, as seen in panel (a) for state  $1^3A''$ . On other hand the exchange reaction is not an spontaneous process as shown is (b) panel. The developed PESs are utilized to calculate rate coefficients for the  $C_2 + O$  and CO + Creactions at various temperatures. The findings rate coefficients for  $C_2 + O$  have shown good agreement with the available experiment data, see panel (c), providing a valuable understanding of the reactive dynamics of  $C_2O$  and its significance in both combustion and atmospheric reentry scenarios.



Figure 1: The contour plots illustrate the formation of CO+C from  $C_2+O$  in panel (a) and from CO+C in panel (b) for a specific angular configuration at  $1^3A''$  electronic states. Additionally, calculated rate coefficients for the  $C_2+O \rightarrow CO+C$  reaction is presented in panel (c), along with available experimental data for comparison.

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### Quantum chemistry studies of new Ru (II) complexes as potential fluorophores

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#### Abstract

Complexes featuring d6 transition metals, such as Re(I) and Ru(II), are distinguished by their optical properties, including high luminosity, narrow emission spectra, diverse emission wavelengths, significant Stokes shifts, photobleaching resistance, and stability. These characteristics, coupled with the use of suitably chosen dinitrogenated ligands, render these complexes viable as fluorophores in fluorescence microscopy. In the present work, we examined Ru(II) complexes paired with dinitrogenated ligands that exhibit an intramolecular hydrogen bond (Figure 1). These complexes had been studied with relativistic effects. Spin-orbit coupling (SOC) promotes swift intersystem crossing (ISC) and subsequent luminescent emission. At the scalar relativistic level, transitions between the singlet ground state ( $S_0$ ) and the first triplet excited state ( $T_1$ ) are inherently forbidden; however, SOC facilitates the mixing of these states, allowing such transitions to occur. Therefore, the design of novel and enhanced luminescent compounds requires precise theoretical methods that account for excited states influenced by SOC. Addressing the emission characteristics of these compounds necessitates consideration of SOC, particularly when triplet states are implicated, due to the zero-field splitting (ZFS) these states undergo. This magnetic attribute, along with the emission lifetimes, can only be modeled accurately within a relativistic framework that includes spin-orbit interactions, as achieved at the TDDFT level. All structures were optimized using Density Functional Theory (DFT) within the ADF code framework, incorporating both scalar and spin-orbit relativistic effects via the two-component Hamiltonian with the zero-order regular approximation (ZORA). The emission behavior

of the complexes was analyzed using the forbidden spin phosphorescence model, which considers a vertical transition from the optimized triplet state to the singlet ground state  $(T_1 \rightarrow S_0)$ , as illustrated in Figure 1. Our research primarily concentrates on the electronic transitions spanning the visible to ultraviolet spectral regions.



Figure 1. Diagram of the electronic states involved in the theoretical protocol used to predict optical properties

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# Revisiting the role of octahedral symmetry in the interpretation of spectroscopic properties of [OsF<sub>6</sub>]<sup>2-</sup> and PtF<sub>6</sub> complexes

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#### Abstract

The electronic structure of  $[OsF_6]^{2-}$  and PtF<sub>6</sub> [1] complexes was studied by means of CASSCF/NEVPT2 multiconfigurational calculations [1], including spin–orbital coupling, which is very relevant in the case of these metals. From these calculations, it is possible to establish that in the octahedral symmetry (Oh), the ground state is non-magnetic (Jeff = 0) because of the strong ligand field, and the interaction with paramagnetic excited states is almost negligible, resulting in a non-magnetic behavior, which is in agreement with the experimental evidence.



**Figure 1:** Electronic state diagram obtained at spin–orbit free NEVPT2 level of theory and considering the spin–orbit coupling (SOC) effect for [OsF6]2– and PtF6 complexes.

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