

Programme & Résumés

6^{ème} réunion annuelle du GDR ThéMS

Dynamique quantique dans les systèmes moléculaires :

Théorie, Modélisation, Simulation

Dijon, 8-9 novembre 2018



Organisateurs : Grégoire Guillon, Pascal Honvault, Maxence Lepers, Dominique Sugny
Laboratoire Interdisciplinaire Carnot de Bourgogne (UMR 6303 CNRS/UBFC)

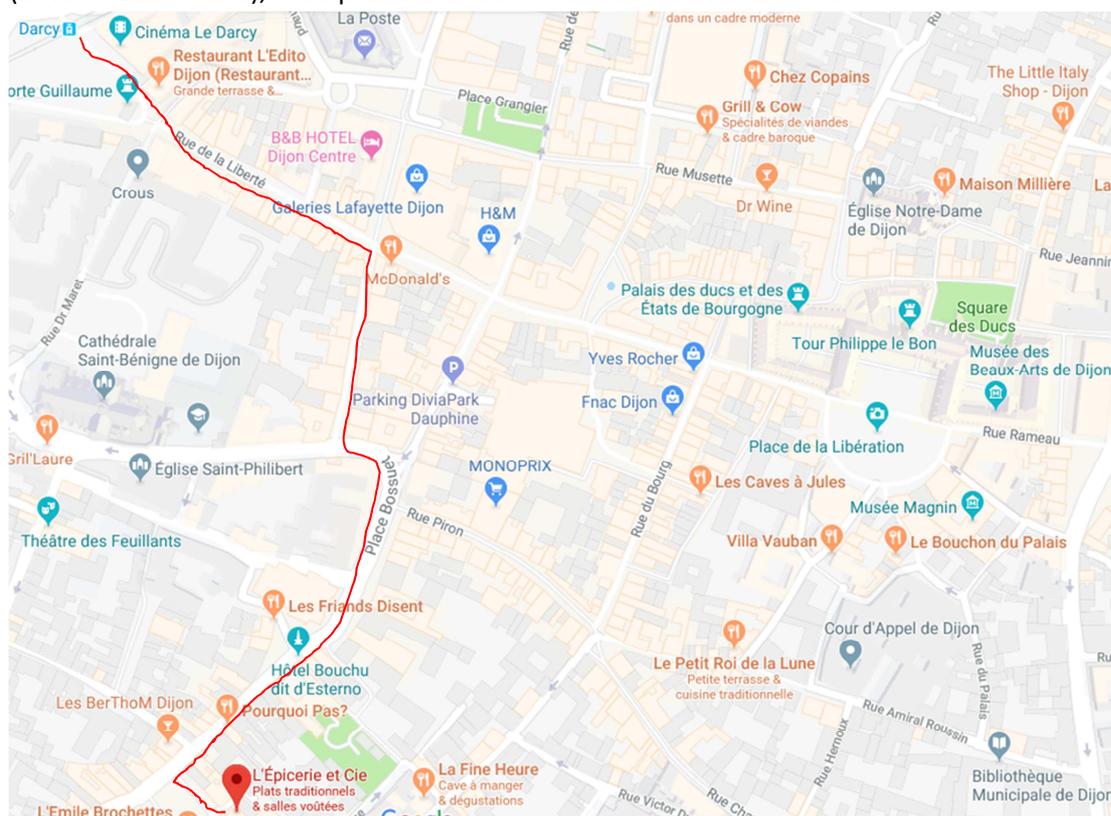
Informations pratiques



Pour rejoindre le lieu de la conférence, l'hôtel Kyriad Dijon Est Mirande (12-14, rue Pierre de Coubertin, tél : 03 80 31 69 12) depuis la gare SNCF de Dijon :

Prendre le Tram T1 à l'arrêt Dijon Gare (sur le parvis de la gare) en direction de Quétigny centre. Descendre à l'arrêt Piscine Olympique (environ 20 minutes). Puis suivre le trait rouge sur le plan ci-contre (environ 5 minutes à pied).

Pour aller de l'hôtel Kyriad Dijon Est Mirande au restaurant l'Épicerie (Place Emile Zola, dîner du jeudi à 20h) : Prendre le Tram T1 à la station Piscine Olympique en direction de Dijon Gare. Descendre à la station Darcy (environ 20 minutes). Puis suivre le trait rouge sur le plan ci-dessous (environ 10 minutes), ... ou prendre un autre itinéraire de votre choix.



PROGRAMME

Thursday, 8th November 2018

9:30-10:00	Registration	
		Chairwoman: Nadine Halberstadt
10:00-10:10	Organizers/Olivier Dulieu	<i>Welcome/Introductory remarks</i>
10:10-10:55	Astrid Bergeat	<i>Low energy scattering in crossed molecular beams</i>
10:55-11:15	Samrit Mainali	<i>Towards quantum control involving the conical intersection of Pyrazine</i>
11:15-11:30	Coffee break	
11:30-11:50	Ayad Bellili	<i>Dynamics and Reactivity in Supercritical Carbon Dioxide</i>
11:50-12:10	Lucas Lassablière	<i>Controlling the Scattering Length of Ultracold Dipolar Molecules</i>
12:10-12:30	Miguel Lara Moreno	<i>Quantum tunneling in weakly bound complexes: the case of the CO₂-N₂ dimer</i>
12:30-14:00	Lunch	
		Chairman: Arnaud Leclerc
14:00-14:45	Rosario González-Férez	<i>Rotational dynamics of complex molecules in external fields</i>
14:45-15:05	Vincenzo Laporta	<i>Elementary molecular processes driven by electrons in cold plasmas</i>
15:05-15:25	Matthieu Sala	<i>The origin of the large amplitude oscillations in the pump-probe spectra of pentafluorobenzene: a full-dimensional QM investigation</i>
15:25-16:00	Coffee break and Poster Session	
16:00-16:20	Etienne Mangaud	<i>Adaptive Quantum Thermal Bath: a tool to evaluate and reduce zero-point energy leakage</i>
16:20-16:40	Pierre Béjot	<i>Strong field description of laser filamentation</i>
16:40-17:00	Sabine Morisset	<i>Reactivity of O(3P) with coronene</i>
17:00-18:00	Mathieu Arbogast	<i>Gender equality in research: can we do better?</i>
20:00	Dinner	

Friday, 9th November 2018

		Chairman: Thierry Stoecklin
9:00-9:45	Sylvain Picaud	<i>Modeling organic aerosols and their oxidation at the molecular scale</i>
9:45-10:05	Sabine Kopec	<i>vdW-TSSCDs: An automated procedure for the computation of stationary points on intermolecular potential energy surfaces</i>
10:05-10:25	Adrien Devolder	<i>Terahertz Feshbach resonance : a new tool for controlling the formation of heteronuclear molecules</i>
10:25-11:00	Coffee break and Poster Session	
11:00-11:20	Ugo Ancarani	<i>Generalized Sturmian approach to study the single ionization of small molecules by electron impact</i>
11:20-11:40	Etienne Gindensperger	<i>Ultrafast photo-induced quantum dynamics in transition-metal complexes</i>
11:40-12:00	Emna Sahnoun	<i>Theoretical studies of molecular collisions of astrophysical interest</i>
12:00-12:20	Saikat Nandi	<i>An ultrafast look at the coupling between nuclear and electron dynamics inside a molecule</i>
12:20-14:00	Lunch	
		Chairman: Majdi Hochlaf
14:00-14:20	Basile Wurmser	<i>Photoemission delays in 2D model molecules</i>
14:20-14:40	Ting Xie	<i>Optical shielding of ultracold 39K-Cs binary collision</i>
14:40-16:00	Round table, concluding remarks	

Résumés des communications orales

(dans l'ordre du programme)

Low energy scattering in crossed molecular beams

Etudes expérimentales de collisions moléculaires à basse énergie

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This presentation aims at giving a flavour of what happens when molecular collisions (reactive or inelastic) occur at low energy / temperature, in the *near cold* regime (1-50 K). In this domain, resonances are predicted by theory for many small systems [1]. Moreover, cross-sections (or rate coefficients) at low energies (or temperatures) are needed to understand the chemistry in dense clouds of the interstellar medium. Cross sections for the rotational or spin-orbit (de)excitation of a molecule by collisions with H₂ and He are needed to estimate correctly the interstellar abundance of the molecule at low temperature (as low as 8 K in the dense clouds).

Experiments conducted with a crossed, molecular beam apparatus with variable crossing angle allowed us to determine the integral cross sections (ICSs) as a function of the relative translational energy down to a few wavenumbers. Reactants and products are probed using REMPI time-of-flight spectrometry. A dielectric barrier discharge source to create very cold plasma inside the nozzle was also used to generate a supersonic beam of carbon atoms in Ne. Our results show that the carbon atoms are mainly in the ground electronic state, ³P₀.

The S(¹D) + D₂(j=0) reaction which is barrierless and exoergic, is a prototypical insertion atom + diatom reaction. The experimental results will be compared with the theoretical ones obtained with different methods and with data for its isotopic variants [2].

The spin orbit excitation ICSs of C(³P₀) + He → C(³P₁) + He or C(³P₂) + He were observed experimentally for the first time and compared with theoretical calculations [3]. The new experimental results on the inelastic collisions of C with H₂ or D₂ will be also presented and compared with the theoretical ones.

We acknowledge the financial support of the “Agence Nationale de la Recherche” (ANR-HYDRIDES, contract ANR-12-BS05-0011-01) and the Programme National “Physique et Chimie du Milieu Interstellaire” (PCMI) of CNRS/INSU with INC/INP co-funded by CEA and CNES.

[1] Book: “Cold Chemistry: Molecular Scattering and reactivity Near Absolute Zero”, Ed. O. Dulieu and A. Osterwalder, RSC (2017).

[2] M. Lara, S. Chefdeville, P. Larregaray, L. Bonnet, JM Launay, M. Costes, C. Naulin, A. Bergeat, J. Phys. Chem. A 120, 5274 (2016).

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Towards quantum control involving the conical intersection of Pyrazine

Vers un contrôle quantique de l'intersection conique de la Pyrazine

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Thanks to the recent advances in laser science, one can visualize and even control the combined motion of electrons and nuclei in real time. Very high sensitive detectors used in pump-probe experiments lead to the detailed observation of the evolution of angular resolved distributions. Concerning control issues, we are interested by branching ratios of different product channels, by energy distributions and population transfers in large molecular systems, emphasizing the role played by vibronic couplings and conical intersections through coherent control.

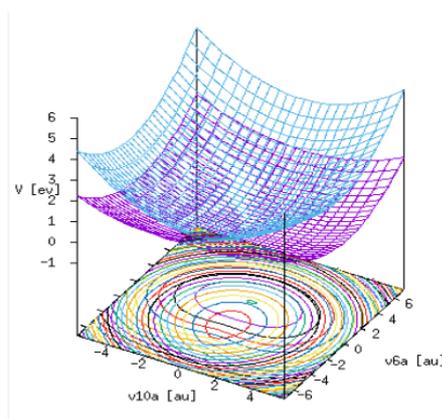


Fig: Conical intersection in Pyrazine

The method we are referring to is MCTDH, and the specific molecular system Pyrazine, addressing both spectroscopic and dynamical observables. Among the 24 degrees of freedom of Pyrazine, we have retained but two particular normal modes for spectroscopic data comparison based on the autocorrelation function and its Fourier transform, the power spectrum. Different population transfer scenarios assisted by the conical intersection are investigated, depending on the way the molecular system is excited. The two normal modes model turns out to be in good agreement with the full 24-dimensional calculation and greatly facilitates further calculations of the eigenenergies and eigenstates.

Dynamical calculations based on the two modes concern population transfers between the ground state and two excited states, using short (10 fs) and intense (10^{12} W/cm²) laser pulses. Basically two effects have quantitatively been evidenced: (i) Increasing the intensity leads to more efficient transfer, (ii) The transfer rate is also highly increased with the laser intensity. In the future, a full laser control strategy is planned to be looked for by varying all other laser pulse parameters as frequency, chirp, pulse duration and envelope.

Dynamics and Reactivity in Supercritical Carbon Dioxide

Dynamique et réactivité dans le dioxyde de carbone supercritique

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The changes in industrial processes promoted by the increasing attention toward societal challenges have motivated, in the past years, the development of novel techniques in Chemistry. In order to reduce the environmental impact of industrial solvents, new technologies have been envisaged, among which the use of supercritical solvents. In the case of supercritical CO₂ (scCO₂), a molecular understanding of the intermolecular interactions taking place with this molecule has allowed a significant improvement of its solvation power, opening the door to wider industrial applications.[1] In addition, the thermodynamic conditions of the fluid in the supercritical phase may affect the reactivity of solvated molecules, with increased yields and improved kinetics. We shall present an overview of theoretical studies performed in our group in the past years, providing a molecular explanation of the solute-solvent interactions in scCO₂ and some ideas toward the rational design of CO₂-phile molecules.[2] We shall then move to our more recent results, obtained for reactive systems[3] from quantum calculations of model systems and molecular dynamics simulations in the condensed, supercritical phase.

We acknowledge the financial support by the INC of the CNRS (project RéScMol, Emergence 2018 Call).

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Controlling the Scattering Length of Ultracold Dipolar Molecules

Contrôle de la longueur de diffusion de molécules dipolaires ultra-froides

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Recently, ultracold dipolar molecules have been at the core of many ultracold gases experiments. Their rich internal structure offers unique properties which are ideal for quantum simulation or controlled chemistry [1]. Therefore, a lot of effort is devoted nowadays to control the molecule-molecule scattering length. The scattering length is an effective parameter which describes the range of the particles interactions. Its value and its sign control both the strength and the stability of such gases [2,3].

In experiments of ultracold atoms, the control of the scattering length is usually possible in the vicinity of a Fano-Feshbach resonance [4,5] when a magnetic field or an optical electromagnetic field is tuned to an appropriate value. However, for experiments with ultracold molecules, the task is more challenging because of the very high density of tetramer bound states in the vicinity of the low-energy collisional threshold [6]. That's why, the ability to tune the scattering length seems compromised for molecules.

We present a method to control the molecule-molecule scattering length. If we use a circularly polarized and slightly blue-detuned microwave field with respect to the first rotational excited state, we can engineer, at long range, a shallow potential in the entrance channel of the two colliding partners. As the applied microwave ac-field is increased, the long-range well becomes deeper and can support more bound states, which in turn brings the value of the molecule-molecule scattering length from a large negative value to a large positive one [7]. By adopting an adimensional approach, we show that this method can be used for many molecules of experimental interest. This method opens the door for a rich, strongly correlated, many-body physics for ultracold molecules.

We acknowledge fundings from the FEW2MANY-SHIELD project (ANR-17-CE30-0015), the BLUESHIELD project (ANR-14-CE34-0006) and the COPOMOL project (ANR-13-IS04-0004) from Agence Nationale de la Recherche.

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Quantum tunneling in weakly bound complexes: the case of the CO₂-N₂ dimer

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Quantum tunneling is a common fundamental quantum mechanical phenomenon. The dynamics induced by this effect is closely connected to the shape of the potentials [1,2]. Here we illustrate this effect by computing the bound states of the CO₂-N₂ van der Waals complex using a first principle treatment where nuclear motions and nuclear spins are fully considered. The CO₂-N₂ dimer is shown to be an interesting prototype for studying systematic (as in NH₃) lifting of degeneracy due to tunneling effects and large amplitude motions while vibrational memory and quantum localization effects are also evidenced. We expect that the present findings could be useful for understanding complex quantum effects for similar systems exhibiting several potential wells separated by potential barriers as commonly found for polyatomic organic and inorganic molecules (e.g., *cis-trans* isomerization, enol-keto tautomerism).

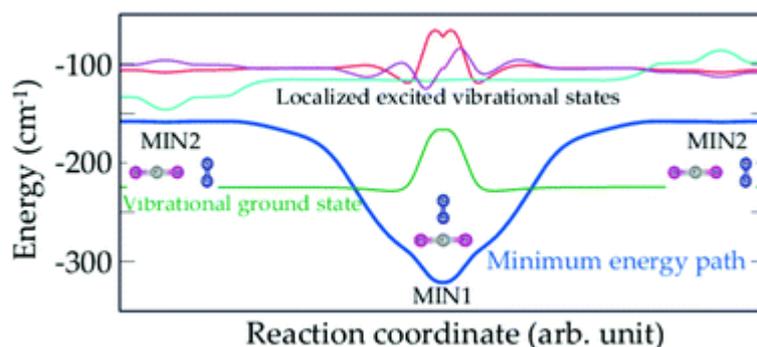


Figure 1: Minimum energy path (blue line) between minima MIN1 and MIN2 and selected vibrational wave functions computed at the points of the minimum energy path

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Rotational dynamics of complex molecules in external fields

Titre de la contribution en Français

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Fixing molecules in space is the goal of many theoretical and experimental studies because it facilitates the study of their structure and dynamics. Techniques used to fix molecules in space include adiabatic and impulsive alignment and mixed-field orientation. Strong degrees of alignment and orientation have been achieved for different symmetric and asymmetric top molecules using these methods. In the first part of this talk, we theoretically investigate the rotational dynamics of molecules without rotational symmetry in combined non-resonant laser fields and static electric fields. It was experimentally demonstrated that asymmetric top molecules with a permanent dipole moment non parallel to any principal axis of polarizability can be 3D aligned and orientated using elliptically polarized laser pulses in combination with weak dc electric fields [1]. Here, we solve the time-dependent Schrödinger equation for different field configurations for 6-chloropyridazine-3-carbonitrile (CPC) and show that nonadiabatic phenomena play an important role on its mixed field orientation dynamics [2]. In the second part, we theoretically investigate the impact of the coupling of the rotational angular momentum and internal rotation on the alignment and mixed-field orientation of different molecular systems. As an example, we analyze the adiabatic alignment and mixed-field orientation of the prototypical indole(H₂O) cluster where the water molecule undergoes and internal rotation. Our results for the rotational and torsional dynamics show that the coupling of the internal and overall rotation is small and that indole(H₂O) can be treated as a rigid molecule for typical laser field strengths used in experiments. In addition, we explore the parameter space for which this approximation holds and when the field-free and field-induced coupling of the two motions can no longer be neglected [3].

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Elementary molecular processes driven by electrons in cold plasmas

Processus élémentaires moléculaires pilotés par les électrons dans les plasmas froids

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Les sections efficaces et les vitesses de recombinaison dissociative, attachement dissociative, excitation vibrationnelle et excitation dissociative par impact d'électrons seront montrés à la fois pour molécules neutres et pour ions moléculaires impliqués dans la cinétique des plasmas froids. En particulier seront considérées les molécules N₂ [1], CO [2], O₂ [3], BeH⁺ [4], CO₂ [5], ArH⁺ [6] intervenant notamment dans les plasmas d'entrée atmosphériques planétaires, près des parois des machines à fusion magnétique contrôlée, dans la combustion assistée par plasma et dans les milieux froids d'intérêt astrophysique.

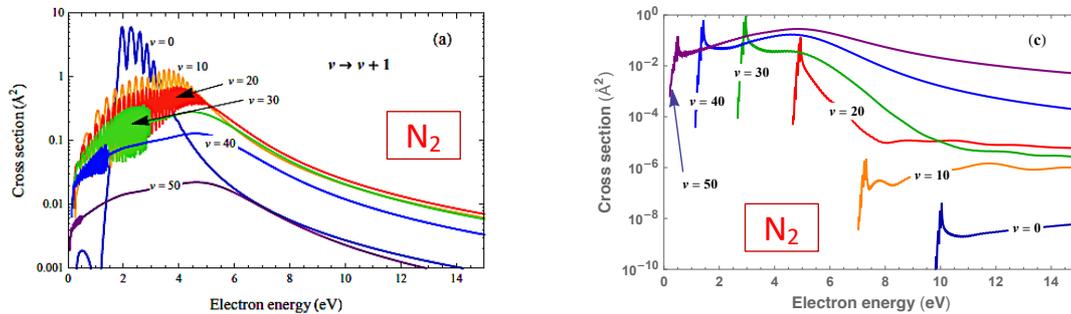


Figure 1: Sections efficaces electron-N₂ pour excitation-vibrationnelle (gauche) et dissociation (droit).

Les auteurs remercient LabEx-EMC3 et FEDER pour les projets EMOPlaF et RIN-VIRIDIS-CO₂.

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The origin of the large amplitude oscillations in the pump-probe spectra of pentafluorobenzene: a full-dimensional quantum dynamics investigation

L'origine des oscillations de grande amplitude dans les spectres pompe-sonde du pentafluorobenzène : une étude de dynamique quantique en dimensionnalité complète

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Transient absorption pump-probe spectroscopy experiments in solution performed on highly fluorinated benzenes more than ten years ago revealed the existence of unexpectedly large amplitude oscillations in the measured signals [1]. In addition, the stationary absorption and emission spectra of the same compounds showed unusually large Stokes shifts. The latter observation was attributed to an internal conversion process from the initially excited $\pi\pi^*$ state to a close-lying $\pi\sigma^*$ state while the oscillations on the pump-probe signals were attributed to electronic coherences between these two states.

Recently, gas-phase time-resolved photoelectron spectra of pentafluorobenzene were recorded in the group of Friedrich Temps [2], showing large amplitude oscillations living for more than 10 ps. Electronic structure and quantum dynamics simulations were performed to better understand the origin of these oscillations. We found the existence of highly anharmonic double-well potentials along out-of-plane vibrational modes coupling the close lowest $\pi\pi^*$ and $\pi\sigma^*$ electronic states. Preliminary quantum dynamics simulations on a reduced dimensional model revealed large amplitude wavepacket motion along these out-of-plane modes. In addition, it was found that this motion drives a periodic mixing of the $\pi\pi^*$ and $\pi\sigma^*$ electronic character.

We have extended our model to include all the vibrational degrees of freedom and the five lowest electronic states to obtain a deeper understanding of the photoinduced dynamics of the molecule. We present quantum dynamics simulations using this model [3] performed with the Multilayer Multi-Configuration Time-Dependent Hartree (ML-MCTDH) method [4,5]. The implications of our results for the interpretation of the experimental observations are discussed.

We acknowledge the financial support from the Alexander Von Humboldt Foundation

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Adaptive Quantum Thermal Bath: a tool to evaluate and reduce zero-point energy leakage.

Bain Thermique Quantique adaptatif : un outil pour évaluer et réduire la fuite d'énergie de point zéro.

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Quantum Thermal Bath^[1] (QTB) is a semi-classical method based on a colored-noise Langevin equation. It acts as a quantum thermostat in order to modify the energy distribution of the system to mimic the quantum delocalization. However, it suffers notably from zero-point energy leakage^[2] (ZPEL). In this work, we present a criterion to evaluate the amount of leakage and propose a method to reduce its influence.

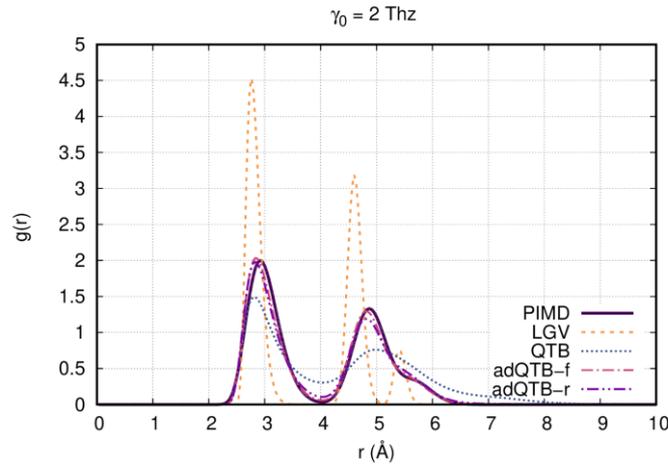


Figure 1: Pair correlation function of a Ne_{13} neon cluster at 4 K computed with Path Integral Monte Carlo (PIMD, reference), classical Langevin (LGV), quantum thermal bath (QTB) and adaptive quantum thermal bath (adQTB-f and adQTB-r, results of this work).

After having derived a criterion based on the quantum fluctuation-dissipation theorem, we propose two methods to compensate the ZPEL in a systematic way either by modifying the colored noise (adQTB-r) or by using a non-Markovian friction kernel (adQTB-f). We have tested this method on a simple model (coupled harmonic oscillators) and on more realistic systems as aluminium crystal or neon cluster (Fig. 1). In all cases, the adQTB method provides significant improvements in comparison to the standard QTB. In the future, we hope this methodology can be applied to relevant physics and chemistry systems and enables to take into account at a reasonable cost approximate statistical quantum effects.

We acknowledge the financial support of Labex Matisse for post-doctoral grant.

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Strong field description of laser filamentation

Description en régime champ fort de la filamentation laser

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Atoms and molecules exposed to very intense laser fields exhibit highly nonlinear dynamics that has motivated a wealth of experimental and theoretical studies and led to the observation of phenomena such as above-threshold ionization (ATI) [1], high harmonics and attosecond pulses generation (HHG) [2-3], or filamentation [4]. Understanding the first three processes has required to describe the atomic and molecular dynamics under strong-field excitation. In this regime, the electric field is comparable to the intra-atomic field, so that the atomic optical response can no longer be described as a perturbative series of the field. Instead, the atom dynamics and its associated optical polarization must be evaluated during the interaction by solving the time-dependent Schrödinger equation (TDSE) describing the interacting atom. As far as the filamentation process (i.e., the propagation dynamics of ultra-short and ultra-intense laser pulse) is concerned, it is generally interpreted through a perturbative approach as resulting from a dynamic balance between Kerr self-focusing and defocusing by the free electrons originating from ionization during the interaction (Drude model). Retrospectively, it is surprising that this process is still described in the perturbative framework, contrary to HHG or ATI. Indeed, since the typical intensity in filaments (≈ 50 TW/cm²) is of the same order as those used in HHG or ATI experiments, it seems natural to wonder whether filamentation can still be accurately described within the lowest order perturbation theory, i.e. using the commonly used Kerr and Drude (KD) model.

In this seminar, I will present the basic concepts of laser filamentation, and the problematic associated to its theoretical description within the perturbative framework. Next, we will focus on the strong field description of the light-matter interaction and how it can be used for describing the filamentation process [5,6]. In particular, we will see how the gas polarization can be evaluated in the strong field regime and how such an observable is related to the filamentation process. Finally, we will discuss on the limitations of such a model, in particular, in the context of simulations of ultrashort ultra-intense laser propagation over very long distances.

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Reactivity of O(³P) with coronene

Reactivité de O(³P) avec du coronene

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The Polycyclic Aromatic Hydrocarbons (PAH) represent about 10% of galactic carbon. Moreover small carbonaceous dust grains as PAHs are known to catalyse the reaction of formation as H₂. PAHs are not observed in dark regions: this may be due to either the UV excitation or to their chemical reactions with atoms or molecules. The aim of our work is to study, experimentally and theoretically, the reaction of coronene with atomic oxygen in triplet state. Experimentally, we find that the oxygenation of coronene is efficient and leads to the fragmentation. Theoretically, we performed Density Functionnal Theory (DFT) calculations on the coronene plus O atom in triplet state. Starting from oxygenated coronene, our DFT calculations show the existence of a possible route leading to the fragmentation.

Gender equality in research: can we do better?

Égalité femmes-hommes dans la recherche : peut-on faire mieux ?

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Gender equality is a cross-cutting issue in the Horizon 2020 program. So is it for CNRS, which created the first gender-equality unit (Mission pour la Place Des Femmes au CNRS, MPDF) in a French research performing organization, in 2001. Ever since, efforts are being made to improve the recruitment of female researchers, as well as to equalize the career perspectives of both sexes.

From high school to tenure positions, the proportion of women drops dramatically in all STEM fields. This presentation will provide an overview of the key mechanisms involved in this “leaky pipeline”. Unconscious biases operate in many ways, contributing to the eviction of women from STEM research even though most men and women truly believe in equality and value meritocracy. We will try to explain the reasons of this paradox.

Modeling organic aerosols and their oxidation at the molecular scale

Modélisation à l'échelle moléculaire des aérosols organiques et de leur oxidation

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Organic aerosols represent a significant fraction of the particulate matter in the atmosphere. These aerosols, which are often characterized by an intricate composition, generally have chemical groups on their surface that can form hydrogen bonds with water molecules and/or react with atmospheric oxidants. Organic aerosols are thus suspected to be effective condensation nuclei for the formation of liquid water droplets in clouds in the lower stratosphere. Similar process is also suspected to be effective for the formation of ice clouds in the upper troposphere.

The importance of organic aerosols on the physico-chemistry of the atmosphere therefore requires a better understanding of their interaction with the surrounding molecules, to which studies at the molecular level can contribute.

In the present work, we used numerical simulations based on the molecular dynamics (MD) methods to model organic aerosols and to study their behavior in the presence of water molecules. We also used multilayer first principle techniques to study the first elementary steps of the reactions of the aerosol interfacial molecules with the most common reactive oxygen species in the atmosphere, aiming thus at characterizing the aging process of the atmospheric organic aerosol.

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vdW-TSSCDS: An automated procedure for the computation of stationary points on intermolecular potential energy surfaces

vdW-TSSCDS: Une procédure automatique pour la détermination des points stationnaires sur des surfaces d'énergie potentielle intermoléculaires

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Characterisation of the topography of Potential Energy Surfaces (PESs) is a tedious task and for large dimensional systems not an evident one. Recently, an automatic methodology (TSSCDS) for the automatic determination of the stationary points on a PES was proposed by one of the authors [1].

Given a chemically bound molecular system, this methodology relies on a comprehensive sampling of the PES using direct dynamics (semiempirical) simulations and a graph-theory based algorithm to provide transition state guess structures, which are subsequently optimized at an appropriate higher level of theory. A relevant concept in this algorithm is the definition of an adjacency matrix, a square symmetric matrix of dimension of the number of atoms, whose elements indicate whether the corresponding atoms are bound or not. This character, in turn, depends on the definition of a set of covalent radii values.

We have generalized the TSSCDS methodology to study van der Waals and more generally non-covalently bound complexes (vdW-TSSCDS) [2]. Considering such a complex as composed by two well-identifiable fragments, the key idea is the redefinition of the adjacency matrix in a block structure. In this picture, diagonal blocks correspond to the isolated fragments and off-diagonal blocks provide the intermolecular connectivity. To this end, we introduce a new definition of bound or not in a van der Waals sense, by utilizing an extra set of van der Waals distances to determine the elements in the off-diagonal blocks.

Additionally, instead of the widely employed rigid approach to the study of intermolecular PES, we have relaxed this condition by adopting a semi-rigid approach in which one of the fragments remains fixed at its equilibrium geometry whereas the other is fully flexible. This gives us the opportunity to study the influence of a substrate on the spectroscopy and reactivity of an adsorbed molecule.

We here present the application to test systems, showing that vdW-TSSCDS does lead to the correct ab initio topography even in limiting cases such as extremely flat regions of the surfaces or non-trivial topologies such as in the case of bifurcation points.

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Terahertz Feshbach resonance : a new tool for controlling the formation of heteronuclear molecules and interspecies scattering length

Resonance de Feshbach resonance : nouvel outil pour contrôler la formation de molécules hétéronucléaires et la longueur de diffusion inter-espèce

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The implementation of Magnetic Feshbach Resonances (MFR) in ultracold atom gases has allowed the precise control of the scattering length between ultracold alkali atoms and of the formation of ultracold diatomic molecules. They originate from the difference of magnetic moments between a molecular state and a state of colliding atoms. This circumstance is easily achieved with magnetic species like alkali atoms or lanthanides, but not obvious or even impossible with non-magnetic species like alkaline-earth atoms. In particular, the formation of molecules composed of one alkali atom and one alkaline-earth atom, which are a promising system for future applications in quantum simulation [1], is still a current challenge [2].

To circumvent this difficulty, we propose the implementation of a new kind of Optical Feshbach resonances: the Terahertz Feshbach Resonances (TFR), applicable for all heteronuclear diatomic species. The TFR are based on the dressing of the electronic ground state – which possesses a permanent electric dipole moment in its own frame – by terahertz photons (fig 1). Furthermore, we will show how the formation of molecules by adiabatic transfer can be implemented by chirping the terahertz frequency, in the same spirit than the formation of molecules via MFR. Finally, we will illustrate how the interspecies scattering length can be modified in the vicinity, depending on the chosen values for the intensity and the frequency of the terahertz laser.

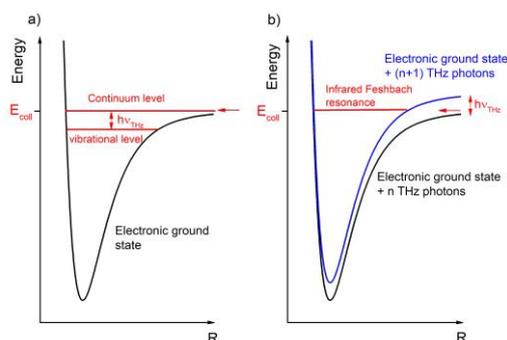


Figure 1: Schematic diagram of terahertz Feshbach resonances

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Generalized Sturmian approach to study the single ionization of small molecules by electron impact

Ionisation de petites molécules par impact électronique avec une approche Sturmiennne généralisée

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The single ionization of molecules by charged particles tests our capacity to describe collision mechanisms but also the molecular initial state. In the case of electron impact, the most severe test is provided by the so called (e,2e) processes in which triple differential cross sections (TDCSs) are measured or calculated. Under appropriate kinematical and geometrical configurations, the cross section angular structure reflects the nature of the molecular orbital that is ionized.

In this contribution we look at the ionization by electron impact of methane and water. We calculate TDCSs using, within the first-Born approximation, a Sturmian approach [1] based on Generalized Sturmian Functions (GSFs). The method has been successfully implemented and applied to study a number of single and double ionization phenomena in atoms and molecules [2-5]. In brief, in a one-active electron approach, the scattering wave function is expanded in a set of one-particle GSFs that have an appropriate asymptotic Coulomb outgoing-type behavior; this property allows one to extract the scattering amplitude directly from the asymptotic behavior of the scattering solution (essentially the expansion coefficients), without the need of calculating a transition matrix element.

We investigate coplanar asymmetric geometries, fixing the incident energy to 250 eV (as in some experiments [6-7]), and vary the momentum transfer value with the purpose of exploring how the cross section structure changes. In particular, we are interested in the presence (or not) in the binary region of a double peak which is a signature of the p-nature of the initial molecular orbital one is ionizing. Such a feature has been predicted [5] and has recently been observed by the Manchester group for the 1t₂ orbital of methane.

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Ultrafast photo-induced quantum dynamics in transition-metal complexes

Dynamique quantique photo-induite ultrarapide dans des complexes de métaux de transition

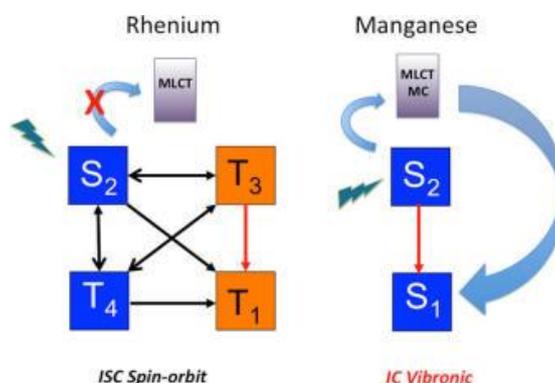
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Transition-metal complexes are fascinating molecules. Their spectra are characterized by low-lying excited states of various nature: transitions can occur within a ligand (intra-ligand), be centered on the metal, involve metal-to-ligand charge transfer... In addition, spin-orbit coupling cannot be neglected, and states of various spin multiplicity participate in the excited-state dynamics.

It is known that the intersystem-crossing time scale do not correlate to the strength of the spin-orbit coupling [1,2], and can even go against the so-called heavy-atom effect [3]. In this presentation, we shall discuss the spin-vibronic mechanism leading to ultrafast intersystem crossing and internal conversion in a series of Re(I) complexes [4-7]. Comparison with first-row analogues of Mn(I) will shed further light on the role of the metal center in the photo-induced dynamics.



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Theoretical study of molecular collisions of astrophysical interest:

The HNC0-H₂ system

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La modélisation astrophysique des nuages moléculaires requiert la détermination des taux de collisions des molécules interstellaires et des enveloppes circumstellaires avec les espèces les plus abondantes qui sont He et H₂. Ces données moléculaires sont essentielles pour la détermination des caractéristiques physiques des milieux astrophysiques, qui ne sont pas en équilibre thermodynamique. De nos jours, le télescope HERSCHEL et l'interféromètre ALMA ouvrent de nouvelles fenêtres d'observations dans le domaine sub-millimétrique avec des meilleures résolutions spatiales et spectrales. Ces instruments nécessitent l'utilisation des données moléculaires de grande précision dans les codes de transfert radiatif et dans la modélisation des milieux astrophysiques. Pour interpréter ces observations, il est nécessaire de connaître les populations des niveaux de molécules observées et par conséquent les taux d'excitation collisionnelle par les espèces les plus abondantes (H, He, H₂).

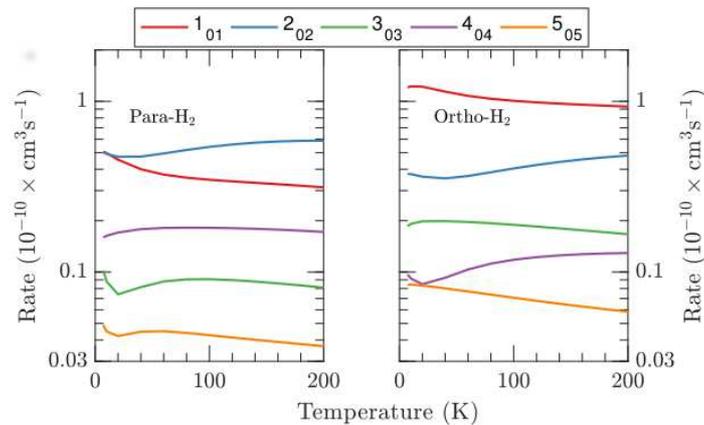


Figure 1: Taux de collision

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An ultrafast look at the coupling between nuclear and electron dynamics inside a molecule

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The development of attosecond photoelectron spectroscopy based on two-color (extreme ultraviolet or XUV, and near infrared or NIR) interferometric techniques [1] has provided a unique tool to study electron dynamics in atoms [2], molecules [3] or solids [4], in their natural timescale. Of particular interest is the simultaneous achievement of high spectral and temporal resolution, shown recently in photoionization of Neon atoms [5]. However, in atoms one can probe the combined effect of the other electrons and the ionic core on the ionized electron. Extending such methodologies to molecules requires additional understanding of the coupling between the electronic and nuclear degrees of freedom. One such example is the molecular shape resonance which results into a strong photon energy dependence of the corresponding vibrational branching ratios [6], a breakdown of the Franck-Condon rule.

Here, we study the shape resonance in photoionization of nitrogen (N_2) molecules at attosecond timescale, using an interferometric technique over the photon energy range of 25 to 40 eV. The photoelectrons for different vibrational levels for both the X - and A -states in the N_2^+ ion were detected using a magnetic bottle electron spectrometer. The variation of the amplitude of the sideband ($XUV \pm NIR$) from two adjacent harmonics as a function of the delay between the XUV and NIR pulses was measured to extract the photoionization time-delays. Unlike previous experiments close to the ionization threshold of for N_2 [7], in our case, the departure of the photoelectron can be hindered by the existence of a centrifugal barrier in the molecular potential and the photoelectron can be trapped temporarily close to the ionic core. In this situation, the motion of nuclei can no longer be considered separate from that of the electrons. This interplay between the electron and nuclear dynamics appears in the corresponding photoionization time-delays: for X -state, the differences between photoionization time-delays for the $v = 0$ and $v = 1$ vibrational levels vary dramatically as a function of the photon energy, but it remains almost constant for the A -state. Theoretical efforts are currently ongoing to better interpret the results.

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*The research was performed when the author was at Atomic Physics Division, Lund University, 22100 Lund, Sweden.

Photoemission delays in 2D model molecules

Retard de photoémission dans des molécules modèles à 2 dimensions

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In quantum physics, the dynamics of an electron is encoded in the phase of its wave function. The ionization continuum being degenerated, there are multiple ways to describe it. The Selected Continuum Wave Function (SCWF) [1] embeds all the information needed to describe the dynamics of photoemission, and provides an unambiguous and straightforward interpretation of the delays that have been recently discussed in the framework of attosecond science [2,3]. The two-dimensional approach allows to retrieve the angular dependent delays. Time-independent computations have been run to investigate ionization in an H_2^+ model molecule for a single-photon transition. The photoemission delays obtained from the time-independent approach are to be compared with a time-dependent propagation of a state at the same energy in order to validate the formalism of the SCWF. This work is the first step to the extension to more realistic molecules.

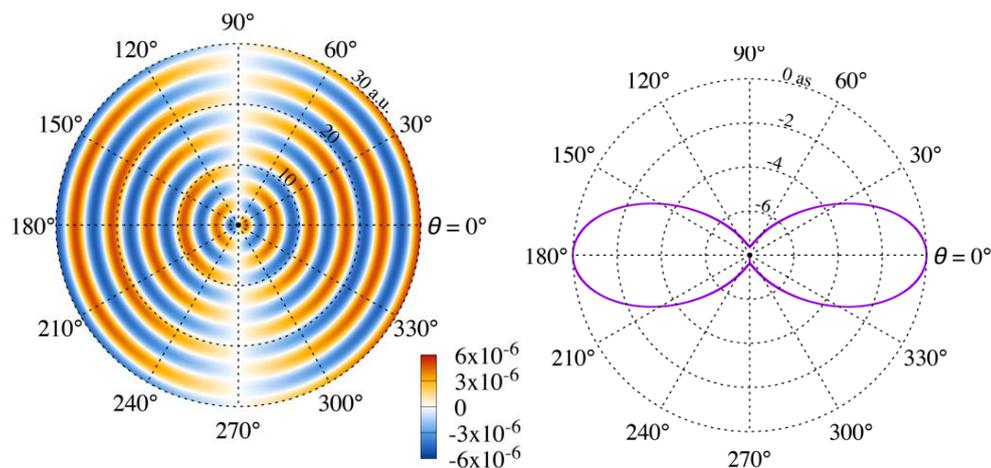


Figure 1: The beautiful logo of the GDR ThéMS

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Optical shielding of ultracold $^{39}\text{K-Cs}$ binary collision

Écrantage optique des collisions binaires ultra-froides $^{39}\text{K-Cs}$

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Research focusing on the formation of ultracold atomic and molecular quantum gases is a continuously expanding field due to its envisioned applications such as quantum-controlled chemistry or quantum simulation. The aim of our theoretical work is to find ways to suppress inelastic or reactive processes between colliding particles in ultracold quantum gases. Using a laser field detuned to the blue of a relevant transition, we propose to couple the initial colliding particle state to a repulsive excited one, thus preventing the particles to come close to each other. This “blueshielding” technique is applied for ultracold quantum gases, close to quantum degeneracy. We investigate the optical shielding in ultracold $^{39}\text{K-Cs}$ collision by using close-coupling channel method. As the $(3)^3\Sigma^+$ and $(2)^3\Pi^+$ molecular states are repulsive in long range [1], one verified effective optical shielding can be realized via driving the transition from the ground $a^3\Sigma^+$ state to these excited states in the presence of linear-polarized light. We demonstrate that a strong field with a small blue detuning to the atomic transition is to the benefit of shielding since the Condon point is farther away from the inner region of ground triplet state. The spontaneous emission effect is taken into account by considering excited optical potentials with the modified formula of shielding rate [2]. We expect the shielding efficiency could be improved by using circular-polarized light [3].

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Résumés des posters

(par ordre alphabétique)

Representation of Generalized Sturmian Functions with Gaussians

Représentation des fonctions Sturmiennes généralisées avec des Gaussiennes

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Generalized Sturmian Functions (GSFs) [1] are solutions of a Sturm-Liouville problem and are such that they have an asymptotic behavior, unique for all the basis, appropriately chosen for the system under scrutiny. This property makes Sturmian bases very efficient, considerably reducing the necessary computing resources in applications. A Sturmian approach can be proposed to investigate -within the same theoretical framework- both bound and continuum states, and so far has been applied mainly to atoms. In order to extend the approach to molecules, one needs to deal with their multi-center nature. To do so we plan to use some of the quantum chemistry tools based on Gaussian functions. The combination of the two techniques (Sturmian-Gaussian) will provide an original tool to study a series of bound and scattering problems. As a first step we wish to represent Sturmian functions in a Gaussian basis and we have explored two approaches. The first one consists in performing a fitting based on the least squares method [2]. We use an existing program [3] to minimize the square of the difference between Sturmian functions and their fitting with Gaussians. In the second method we look for the solution of the Sturm-Liouville equation using a linear combination of Gaussians. After a projection we obtain a generalized secular equation problem, with Gaussian exponents as parameters that need to be optimized. We have written a program to solve this problem taking the Gaussian exponents as an input. With a clever choice of exponents, GSFs, their eigenvalues, their orthogonality property and the expected asymptotic behavior are all well recovered.

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Rotational (de)-excitation of cyclic and linear C₃H₂ by collision with He

(Dé)-excitation rotationnelle de cyclique et linéaire C₃H₂ par collision avec He

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Among the closed-shell hydrocarbons, the carbenes c- and l-C₃H₂ are the lightest ones to display a permanent dipole moment and be detectable by rotational spectroscopy. The cyclic form, Cyclopropenylidene, is ubiquitous in the Interstellar Matter (ISM) of the Milky Way and external galaxies. As such, it serves as a marker to help in characterizing the physical conditions of the ISM. The linear form, Propadienylidene, is less abundant. In order to get access to their absolute and relative abundances, it is essential to understand their collisional excitation/quenching schemes. We compute here a precise ab initio Potential Energy Surface for the interaction of c- and l- C₃ H₂ with helium, by means of a CCSD(T)-F12a [1] formalism and a fit onto relevant hyper-spherical functionals. We conduct quantum dynamical scattering in order to get precise cross sections with Coupled-Channels and average those into rates for rotational quenching from 5 to xxxK. We show that these new rates are vastly different, up to more than an order of magnitude, from the older rates presented in the literature, computed with angular algebra only. We expect large differences in the astrophysical analyses of C₃H₂, including the chemical history of those ubiquitous carbenes.

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Optimal control of the torsion in biphenyl-like molecules

Contrôle optimal de la torsion de molécules de type biphényle

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The strong electric field of a terahertz or a non-resonant laser pulse allows us to coherently control molecules, i.e., manipulate their degrees of freedom [1,2]. For gas phase molecules, the external degrees of freedom are described by the Euler angles which can thus be modified. For instance, subjecting an SO₂ molecule [3] to non-resonant laser pulses leads to a value of the direction cosine squared $(\cos\theta_{zc})^2$ as large as 0.68. The internal degrees of freedom corresponding to the torsional angles of non-rigid molecules can be similarly controlled [4]. In the biphenyl molecule [5], the angle of internal rotation describing the relative orientation of the two phenyl groups undergoes field free oscillations after subjecting the molecule to a non-resonant laser pulse.

A more efficient control can be achieved using pulse shaping in conjunction with quantum optimal control theory [6,7]. The expectation value of a selected operator can thus be maximized or minimized at the end of a theoretically designed pulse. Although there are numerous investigations concerning external degrees of freedom [8,9], there are much less results in the case of internal degrees of freedom.

In the present talk, quantum optimal control theory [6,7] will be used to design laser pulses allowing us to manipulate the internal degree of freedom corresponding to the torsion of the non-rigid biphenyl-like molecule B₂F₄. Starting from a simplified 1-D model and a physically more satisfactory 2-D model, the laser pulse allowing us to reach the planar D_{2h} configuration at time T will be computed. For each model, and depending on the hindering potential, the time evolution of the wavefunction will be studied and we will try to understand how the molecule interacts with the laser pulse. In the case of the 2-D model, an important issue is the coupling between the torsion and the overall rotation.

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Modeling spin-orbit coupling in the photodissociation of cold $^{87}\text{Rb}^{138}\text{Ba}^+$ molecule

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Nowadays collisions between atoms and ions at ultracold temperatures have attracted considerable attention, especially for their prospects toward a novel cold chemistry dominated by quantum effects [1]. For this reason hybrid traps are required, merging a cold atom trap and an ion trap, where both species are laser-cooled. At low atomic density the spontaneous formation of cold molecular ions by radiative association is expected for many species [2], but it has been experimentally probed only for two cases [3, 4]. When the atomic density is higher, these molecular ions are preferentially created by three-body collisions, as demonstrated in the Ulm group with the $\text{Ba}^+ + \text{Rb}$ combination [5, 6]. However in all these experiments, the observation of cold molecular ions is hindered by the strong photodissociation induced by the numerous lasers. We model the photodissociation of RbBa^+ molecular ions induced by the relatively intense 1064 nm wavelength laser used for the dipole trap and find the most probable dissociation channel is $\text{Rb}(5s) + \text{Ba}^+(5d)$, which involves six excited molecular states ($^1\Sigma^+$, $^3\Sigma^+$, $^1\Pi$, $^3\Pi$, $^1\Delta$, $^3\Delta$). In this work we discuss the influence of the spin-orbit interaction on the photodissociation process. Indeed the dissociation channel actually splits into two channels, namely $\text{Rb}(5s) + \text{Ba}^+(5d_{3/2, 5/2})$, where the atomic spin-orbit splitting of $\text{Ba}^+(5d_{3/2, 5/2})$ reaches 801 cm^{-1} . Therefore, in order to obtain more precise potential energy curves, we have constructed a model where both atoms are represented as a one-electron system. The RbBa^+ electronic structure is thus reduced to an effective two-electron problem, which is treated with a semiempirical methodology which has been successfully applied to describe kinds of diatomic systems before [3,4]. Taking into account the atomic spin-orbit coupling, this allows us to predict the amount of atomic ions which are produced in the $\text{Ba}^+(5d_{3/2})$ and $\text{Ba}^+(5d_{5/2})$ states, to be compared with upcoming experimental results.

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PROGRAMME

Thursday, 8th November 2018

9:30-10:00 Registration

Chairwoman: Nadine Halberstadt

10:00-10:10 Organizers/Olivier Dulieu

Welcome/Introductory remarks

10:10-10:55 Astrid Bergeat

Low energy scattering in crossed molecular beams

10:55-11:15 Samrit Mainali

Towards quantum control involving the conical intersection of Pyrazine

11:15-11:30 Coffee break

11:30-11:50 Ayad Bellili

Dynamics and Reactivity in Supercritical Carbon Dioxide

11:50-12:10 Lucas Lassablière

Controlling the Scattering Length of Ultracold Dipolar Molecules

12:10-12:30 Miguel Lara Moreno

*Quantum tunneling in weakly bound complexes:
the case of the CO₂-N₂ dimer*

12:30-14:00 Lunch

Chairman: Arnaud Leclerc

14:00-14:45 Rosario González-Férez

Rotational dynamics of complex molecules in external fields

14:45-15:05 Vincenzo Laporta

Elementary molecular processes driven by electrons in cold plasmas

15:05-15:25 Matthieu Sala

*The origin of the large amplitude oscillations in the
pump-probe spectra of pentafluorobenzene: a full-dimensional QM investigation*

15:25-16:00 Coffee break and Poster Session

16:00-16:20 Etienne Mangaud

*Adaptive Quantum Thermal Bath: a tool to evaluate and
reduce zero-point energy leakage*

16:20-16:40 Pierre Béjot

Strong field description of laser filamentation

16:40-17:00 Sabine Morisset

Reactivity of O(3P) with coronene

17:00-18:00 Mathieu Arbogast

Gender equality in research: can we do better?

20:00 Dinner

Friday, 9th November 2018

Chairman: Thierry Stoecklin

9:00-9:45 Sylvain Picaud

Modeling organic aerosols and their oxidation at the molecular scale

9:45-10:05 Sabine Kopec

*vdW-TSSCDs: An automated procedure for the computation of stationary
points on intermolecular potential energy surfaces*

10:05-10:25 Adrien Devolder

*Terahertz Feshbach resonance : a new tool for controlling the formation
of heteronuclear molecules*

10:25-11:00 Coffee break and Poster Session

11:00-11:20 Ugo Ancarani

*Generalized Sturmian approach to study the single ionization of small molecules
by electron impact*

11:20-11:40 Etienne Gindensperger

Ultrafast photo-induced quantum dynamics in transition-metal complexes

11:40-12:00 Emna Sahnoun

Theoretical studies of molecular collisions of astrophysical interest

12:00-12:20 Saikat Nandi

*An ultrafast look at the coupling between nuclear and electron dynamics
inside a molecule*

12:20-14:00 Lunch

Chairman: Majdi Hochlaf

14:00-14:20 Basile Wurmser

Photoemission delays in 2D model molecules

14:20-14:40 Ting Xie

Optical shielding of ultracold 39K-Cs binary collision

14:40-16:00 Round table, concluding remarks