

IBER 2015

XIII Iberian Meeting on Atomic and Molecular Physics
September 6-9th, 2015
Universidade de Aveiro, Aveiro, Portugal



BOOK OF

ABSTRACTS

The Iberian Meeting on Atomic and Molecular Physics (IBER) is a biannual conference organized by:

- Real Sociedad Española de Física and Real Sociedad Española de Química,
through the network Grupo Especializado en Física Atómica y Molecular (GEFAM)
- Sociedade Portuguesa de Física,
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PL1

**New portable XRF instrumentation for field-based studies:
validation on the bench and in the field****P. Parsons¹, D. Guimarães¹, M. Praamsma¹, M. Tehrani¹, D. Gao¹, S. Lin¹**¹ New York State Dept. of Health, New York, United states of America*E-mail: Patrick.parsons@health.ny.gov*

The primary goal of this study was to validate a new prototype X-ray Fluorescence (XRF) instrument, the HD Mobile. This portable XRF instrument is intended to be used to assess metal/metalloid contaminants in food, medicines and personal care products, in field-based studies. The HD Mobile is a monochromatic XRF spectrometer manufactured by X-Ray Optical Systems (XOS), of East Greenbush NY (USA). The instrument uses a High Definition XRF (HDXRF) technique that comprises Double Curved Crystal (DCC) optics to enhance measurement intensities.

The HD Mobile was designed for the analysis of samples with different matrices. For this project, the “plastic mode” was used, and validation was performed both on the bench and under field conditions. Laboratory-based performance including accuracy, precision and detection limits was characterized using a variety of reference materials: IAEA-413 Algae, NRC-CNRC TORT-2 Lobster Hepatopancreas, NIST SRM 1571 Orchard Leaves, IRMM BCR-627 Tuna Fish, NIST SRM-2976 Mussel Tissue, NRC DORM-2 Dogfish Muscle and IRMM ERM-CE464 Tuna Fish. Bias for As, Cd, Hg and Pb ranged from -9% to 10% for one prototype and -12% to 14% for a production model (n = 5 days). Archived samples from our public health investigations (herbal medicines, ethnic spices and cosmetic products) were analyzed in the laboratory by XRF and results compared to values obtained using inductively coupled plasma atomic emission spectrometry (ICP-OES). Agreement between the prototype and production model proved to be fit-for-purpose for the majority of the samples.

Validation under field conditions was conducted as part of a public health investigation of the Chinese-American community living in Albany, New York. A total of 75 Chinese homes were visited as part of this investigation, and the HD Mobile was used in situ to analyze up to 15 Chinese foods, medicines and personal care products. CRM IAEA-413 Algae was used as a quality control material in the field to monitor XRF instrument performance.

The rapid screening of these products provides a real-time assessment of potential environmental exposures to Pb, As, Hg and Cd, in addition to other elements. The samples collected are currently being analyzed for elemental content using ICP-Mass Spectrometry (ICP-MS).

IL1

Applications of Wavelength Dispersive XRF in trace elements research

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Determinations on some hundreds of the 500000 vegetal species and hundreds of the 1.1 million animal species have shown that 25 to 30 of the 92 natural elements are particularly important in Biology. Of these absolutely essential elements to life, 11 are major elements while 17 occur at trace levels. Although essential, some metals can induce adverse effects on the Human Health, and in that aspect they are not different from typical toxic metals. Therefore, exposure to such elements must be controlled, either in occupational sites or in the general population, where it may occur through the consumption of a wide variety of products, from foodstuff to drug products and dietary supplements.

This presentation is a brief description of WDXRF applications to trace elements in medical, environmental and forensic sciences, in which our research group has been involved since 2011. The emphasis is on the role of some toxic metals in the etiology of bone diseases, such as osteoporosis [1,2] and arthritis [3], on the serum levels of trace elements in impaired nutritional status due to cancers [4], but also on the monitoring of those elements in the general population, in cases of exposures through drug products [5], infant milk powders [6] and "legal highs" [7].

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IL2

Induced molecular dissociations as a radiation damage descriptor: nanodosimetry

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Traditional dosimetry is based on the proportionality between the energy absorbed by the medium (absorbed dose) and the induced damage. This assumption applies for relatively high irradiated volumes and requires some equilibrium conditions. However, for small volumes being relatively far from the central irradiated areas these conditions are not observed and radiation damage is mainly driven by low energy secondary species (electrons and radicals) which induce molecular dissociations via electronic and vibrational excitations, electron attachment and chemical reactions. We will present here an integrated modelling procedure to simulate particle radiation tracks including those of all generated secondary species and their further interactions with the molecular constituent of the medium. For any selected volume of interest, this model provides not only the total energy transferred to that area but also the number and type of interactions taking place in it [1].

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PL2

The GBAR project, or how does antimatter falls

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The Einstein classical Weak Equivalence Principle (WEP) specifies that the trajectory of a particle is independent of its internal structure and composition, when only submitted to gravitational forces. Some theoretical models, like supergravity or the one proposed by J. Scherk[1] may contain fields inducing repulsive gravity thus violating the WEP. The WEP has never been directly tested with antimatter. The GBAR project (Gravitational Behavior of Antihydrogen at Rest) proposes to measure the free fall acceleration of ultracold neutral antihydrogen atoms in the terrestrial gravitational field. The experiment follows the method proposed by Walz and Hänsch [2]. It consists in preparing antihydrogen ions (one antiproton and two positrons) and sympathetically cooling them to a few 10 mK with Be⁺ ions. The ultracold ions will then be photo-ionized just above threshold with a laser in the horizontal plane, and the free-fall time over a known distance will be measured. I will describe the present status of the design of the experimental setup. I will discuss the accuracy that can be reached either by standard techniques or by using quantum reflection of antihydrogen on surfaces [3] to use quantum methods of measurements, similar to what has been used on neutrons [4].

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Single differential electron impact ionization cross sections in the binary-encounter-Bethe approximation for the low binding energy regime

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An analytical expression based on the binary-encounter-Bethe (BEB) model for energy differential cross sections in the low binding energy regime is presented. Both the binary-encounter-Bethe model and its modified counterpart are extended to shells with very low binding energy by removing the constraints in the interference term of the Mott cross section, originally introduced by Kim *et al.*[1]. The influence of the ionic factor is also studied for such targets. All the binary-encounter-Bethe based models presented here are checked against experimental results of low binding energy targets, such as the total ionization cross sections of alkali metals. The energy differential cross sections for H and He, at several incident energies, are also compared to available experimental and theoretical values.

The attractiveness of the BEB models is related with their rather simple analytical expressions both for the total and differential cross sections, and its applicability to a large set of elements and/or subshells. This makes them ideal candidates for use in Monte-Carlo charge transport codes such as PENELOPE [2] and GEANT4 [3].

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Transmission of Helium through Graphynes' Pores: a Quantum Mechanical Study

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Graphynes are novel two-dimensional carbon-based materials that exhibit regular and uniformly distributed sub-nanometer pores (Fig. 1). These features make them very promising materials for gas filtration applications at the molecular level[1]. Our goal is to study the interaction and dynamics of transmission of small molecules through graphynes' pores from first principles quantum mechanics calculations.

We will focus on the properties of graphdiyne (whose molecular precursor is shown in the center of FIG. 1) as a filter of ^3He from ^4He . Accurate electronic structure calculations have served to obtain a new force field suitable for molecular dynamics simulations[2]. By means of the Transition State Theory (TST)[3] we have analyzed the role of tunneling as well as of the in-pore degrees of freedom in the selectivity for isotopic separation[4]. In addition, we will present preliminary three-dimensional time-dependent wave-packet calculations of the transmission of the ^3He and ^4He through the graphynes' pores, which will allow us to compare with the results from the TST as well as with previous one-dimensional wave-packet simulations[2].

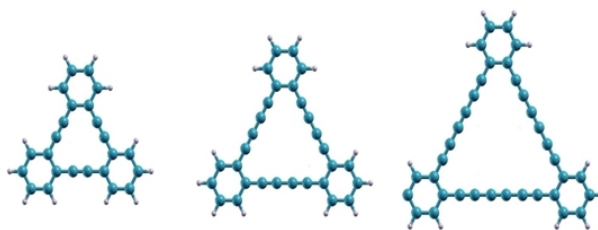


Fig. 1: Annulenic molecular precursors of graphyne, graphdiyne and graphtriyne.

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Molecular chirality in the gas phase: rotational spectroscopy and three-wave mixing of pulegone

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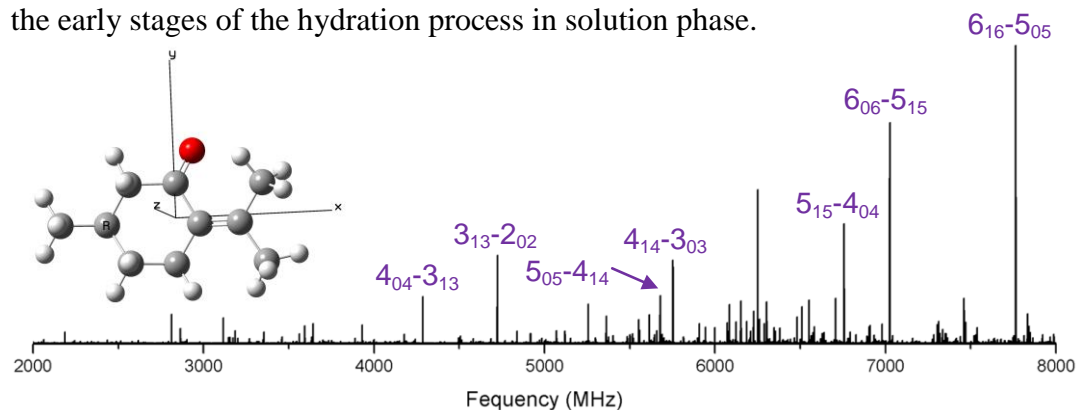
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Terpenes are the main components in essential oils and show a great diversity in structure and bioactivity. In addition, they are atmospheric pollutants. Hence, a deep knowledge of the molecular structure and possible conformers of this type of compounds would be desirable. Pulegone is a natural monoterpene obtained from the essential oils of a variety of plants. This molecule has been studied theoretically and experimentally in liquid phase by chiroptical (Vibrational Circular Dichroism) and non chiroptical (IR, Raman) vibrational techniques.

Here, our aim was to apply chirality-sensitive broadband microwave spectroscopy on the two enantiomers of this molecule and to analyze its rotational spectrum, not yet characterized. The conformational landscape in gas phase was previously studied using DFT and *ab initio* calculations. All these calculations showed only one conformer lower than 5 kJ/mol, which was identified under the cold conditions of the molecular jet in the 2-8 GHz range. It exhibited strong *b*-type transitions while *a*-type and *c*-type transitions were weaker. This information can be used to perform microwave three-wave mixing which allows the enantiomeric differentiation.

The following step is to analyze the pulegone-water clusters with special attention to monohydrates and dihydrates (work in progress). This last work will allow us to study the water-solute interactions under microsolvated conditions, being closer to the early stages of the hydration process in solution phase.



The experimental rotational spectrum of pulegone and the molecular structure of its most stable conformer.

PL3

Femtochemistry and laser control of photochemical reactions

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Laser control use the light-molecule interaction in order to drive a molecular system into a desired final state, e.g., with the goal of obtaining selective bond breakage [1]. It is sometimes possible to obtain the desired goal at sufficiently low laser intensities such that unwanted processes (e.g. ionization) are suppressed.

Genuine laser control takes, e.g., advantage of the coherence of laser light and allows for the manipulation of quantum interferences in the molecular system. Recently, the possibility of quantum interference control of photochemical reactions in the weak-field limit has been discussed [2-5]. To that end, we demonstrate quantum interference control of the final state distributions of photodissociation fragments by means of pure phase modulation of the pump laser pulse in the weak-field regime [5-7].

One example is based on realistic wave packet calculations of the transient vibrational populations of the $\text{Br}_2(\text{B}, \text{v}_f)$ fragment produced upon predissociation of the $\text{Ne-Br}_2(\text{B})$ complex, which is excited to a superposition of overlapping resonance states using pulses with different phase modulation. Transient phase effects on the fragment populations are found to persist for long times (more than 50 ps) after the pulse is over. Another example is the non-adiabatic process: $\text{I} + \text{Br}^* \leftarrow \text{IBr} \rightarrow \text{I} + \text{Br}$, where the relative yield of excited Br^* can be changed by pure phase modulation. This control can be extended beyond transient effects to “infinite time” by weak-field excitation via the bound A state of IBr.

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IL3

Computer simulations of soft landing of ions on self-assembled monolayers

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In mass spectrometry, soft landing (SL) refers to a process in which collisions of polyatomic ions (in vacuum) with target surfaces lead to intact deposition of the ion at the surface, with or without retention of the initial charge [1-3]. The ability to select the projectile ion by mass spectrometry, as well as to control its kinetic energy and charge state, makes SL a convenient technique for preparation of modified surfaces. Applications of soft landing include preparation of protein arrays and novel catalytic materials, selection of pure compounds from mixtures, and biomolecule immobilization for bioactive metal surfaces.

At hyperthermal energies (kinetic energy < 100 eV), SL may compete with other processes, specifically, non-reactive scattering of the projectile ion, surface-induced dissociation, sputtering and reactive landing. The main factors that govern the efficiencies of these processes are the physical and chemical properties of the surface, the nature of the ion, the collision energy and the incident angle.

Our aim is to understand the factors that control SL of ions on self-assembled monolayer (SAM) surfaces. To this end, we use chemical dynamics simulations, which can give a qualitative picture of the SL process from an atomistic point of view. We propagate classical trajectories on potential energy surfaces described by molecular mechanics force fields, in which the intermolecular potential between the ion and the surface plays a crucial role in the efficiency of SL.

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04

New improvements in the description of the PES and collisions of $\text{H}_2 + \text{H}_2^+$ system

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

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

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

In this talk I present the new improvements that we have made in the potential energy surfaces, where the derivatives are now fully analytical. The collisions using quasi-classical trajectories include the surface hopping approach, which allows the jump of the system to the excited state, necessary for the description in the entrance channel. The last results that I would like to show are the preliminary quantum collision calculations using the full dimensionality of the system. For the quantum collision we used MCTDH package².

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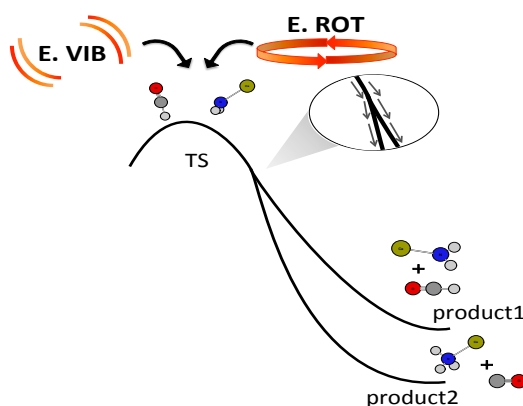
Can reactivity be governed by rotational energy? The role of rotational activation on bifurcating PES.

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Beyond the established use of thermodynamics *vs.* Kinetic control to explain chemical reaction selectivity, the concept of bifurcations on the potential energy surface (PES) is proving to be of pivotal importance with regard to selectivity [1,2]. We studied, by means of post-transition state (TS) direct dynamics simulations, the effect that vibrational and rotational activation energy may have on the selectivity on a bifurcating PES. We studied $[\text{Ca}(\text{formamide})]^{2+}$ ion PES, which exhibits several bifurcations for which Coulomb explosion and neutral loss unimolecular reactions compete [3,4,5]. We could show that kinetic selectivity does not reduce to a simple choice between paths with different barrier heights, but the dynamic behaviour after the TS can be crucial. Also importantly, rotational activation may play a pivotal role on reaction selectivity favouring non-thermodynamic products.



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PL4

Product branching ratios and extent of intersystem crossing in atomic oxygen reactions with unsaturated hydrocarbons

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Because of their relevance in combustion and other gaseous media, the rate coefficients for the reactions between ground state ^3P oxygen atoms and unsaturated hydrocarbons have been determined in kinetics experiments as a function of temperature. Much less is known, instead, on the chemical identity of the primary products and their branching ratios (BRs). This piece of information is fundamental, however, because the products of one elementary reaction are the reactants of a subsequent one in the complex scheme of elementary reactions that account for the global combustion process [1]. For multichannel reactions like these, the primary products and their BR are not easy to predict because intersystem crossing (ISC) from the triplet to the underlying singlet potential energy surface (PES) can occur, opening up other reaction channels not accessible on the triplet PES. The quantification of ISC as a function of temperature is a demanding task which requires an experimental or theoretical investigation.

For this reason, following the pioneering work of Y.T. Lee and coworkers [2], we have undertaken a systematic experimental investigation of this class of reactions by means of the crossed molecular beam technique [3] with mass spectrometric detection empowered by soft electron impact ionization. Results on the reactions of atomic oxygen with alkynes (ethyne [4] and propyne [5]) and alkenes (ethane [6], propene [7], 1-butene [8]) will be presented. Implications in combustion chemistry and astrochemistry will be noted.

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Distinct influence of vibration on the two channels of the D+MuH($v=1$) reaction

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Muonic chemistry has provided most useful information, not always free from controversy, for the investigation of tunneling, zero point energy effects, and vibrational adiabaticity in reaction dynamics [1, 2]. Recently, the possibility of inducing a fundamental change in the nature of chemical bonding (vibrational bonding) upon muonic substitution [3] has been also stressed.

The present study extends a previous work by the authors on the dynamics of the asymmetric D+MuH ($v=0$) isotopic variant [4] of H+H₂. Quantum mechanical calculations of integral (ICS) and differential reaction cross sections (DCS), as well as cumulative reaction probabilities (CRPs) and rate constants $k(T)$ have been performed for the two channels of the D+MuH($v=1$) reaction leading respectively to DMu and DH. Vibrational excitation is found to be globally more efficient than translational energy for promoting the reaction. This is particularly so for the DMu channel whose reactivity increases rapidly, showing a sharp resonance peak, as soon as the MuH ($v=1$) channel is energetically open. No peak was observed in the ICS for $v=0$. In comparison with the DH channel, the DMu exit path has a more “quantal” nature, with marked structures in its ICS and DCS. The dynamical implications of these results are analyzed in terms of the vibrationally adiabatic potentials.

Acknowledgments: This work has been funded by the MICINN of Spain under grants CTQ2012-37404 and CDS2009-00038 and by the MINECO of Spain under grant FIS2013-48087-C2-1P, and by the Junta de Castilla y Leon under grant SA244B12-1, VJH acknowledges also funding from the EU project ERC-2013-Syg 610256

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Statistical fluctuations of photoelectron emission from CsI photocathodes in Noble gases

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CsI photocathodes coupled to Gaseous Photomultipliers have long been used in experiments and applications due to their high gains, fast response and coverage of large areas of detection at reasonable costs [1, 2]. In the future, experiments based on rare event detection, namely Dark Matter [3, 4] and Double Beta Decay [5] research, are faced with the problem of the prohibitive costs of the use of PMTs [6]. High mass pressurized GPMs with noble gases and CsI photocathodes are a promising solution; a note-worthy example is the research on single and double-phase Xenon-based detectors [7].

The drop in extraction efficiency caused by the photoelectron backscattering in gases is a well-known aspect of CsI photocathodes [8], but the way this affects the uncertainty over the number of electrons extracted is still not known. In this work we present the first results of our experimental investigations on the statistical aspects of the photo-electron extraction efficiency of CsI photocathodes. For that purpose, a detection chamber was assembled consisting of a photo converting plane and a thin aluminum layer above so a drift electric field can be applied. The CsI photocathode is irradiated with pulsed UV light and the photo-electrons are collected and measured without electron multiplication in the gas, thus allowing the study of the statistical fluctuations of the photon conversion process itself. Results are presented for different noble gas media at various pressures.

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PL5

New advances in femtochemistry

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Femtosecond-resolved imaging (fs-VMI) will be illustrated on the photodissociation of chlorine azide (ClN₃). Dissociation time, energy balance and anisotropy of emission have been recorded to enlighten the formation of the cyclic isomer.[1]

In the second part, high harmonic spectroscopy is used to reveal nuclear dynamics in SF₆ with an extreme sensitivity.[2] A shape resonance encountered in the recombination process results in a VUV emission with a circular polarization.[3] This VUV source opens the path to attosecond metrology of circular dichroism.[4]

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Control of ultrafast molecular photodissociation in laser-induced potentials

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The versatility of laser light turns it into an ideal tool to intervene in the course of a chemical reaction and change its outcome. While schemes based on weak laser fields have obtained considerable success [1,2], the possibility to control a chemical reaction with light increases immensely when the intensity is sufficiently high to distort the potential energy surfaces involved in a reaction.

Here we explore the transition from the weak- to the strong-field regimes in laser control of the dissociation of a polyatomic prototype molecule, methyl iodide, whose ultrafast photodissociation dynamics is well understood [3]. Control of the branching ratio of the reaction is achieved by the preparation of a light-induced conical intersection between an electronically excited valence state and the ground state. The control of the velocity of the product fragments requires external fields with both high intensities and short durations. This is because the mechanism by which control is exerted involves modulating the potentials around the light-induced conical intersection, that is, creating light-induced potentials [4].

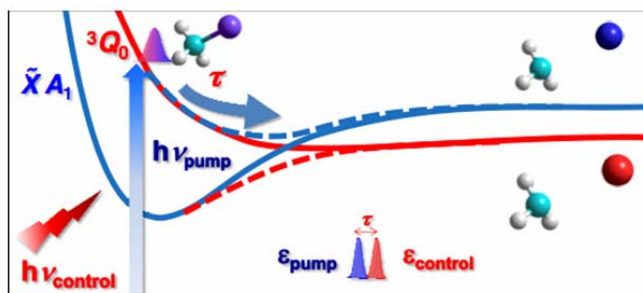


Figure: Laser control scheme used for the modification of the A-band ultrafast dissociation process in methyl iodide.

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Glucose Clusters: Unraveling the interaction of terminal Glucoses by IR Laser spectroscopy in supersonic expansion

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Carbohydrates are one of the most versatile families of biomolecules: it fulfills a lot of key functions, interacting often with peptides, lipids and sugars. The glucose is prototype of C6-atoms sugar ($C_6H_{12}O_6$) and being the most abundant monosaccharide plays many key roles in the nature. Deepening on the behaviors between different terminal glucoses appears fundamental in order to achieve more information about the forces that govern the molecular recognition processes that are involved.[1,2]

Here, we present a study on glucose clusters, using a strategy which combines mass-resolved laser spectroscopy in supersonic expansions and DFT calculations. These techniques allow the study of isolated clusters. In addition, the laser desorption has been used to investigate thermally unstable systems which opens up the possibilities of generating sugars in gas phase. These methodologies allow obtaining specific spectroscopic data for each cluster and conformer. The present study unravel the interaction of monosaccharides dimers; more precisely, using phenyl- β -D-glucopyranose as a chromophore, several clusters are investigated: those with methyl- β -D-glucopyranose and methyl- α -D-glucopyranose in order to simulate the interactions with the beta- and alpha-chain terminal glucose, respectively. Furthermore phenyl- β -D-glucopyranose is used to determine the steric hindrance of the substituent.

These results can help to characterize the contributions of the side chain during the cluster generation and understanding the processes that guide to their stabilization.

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PL6

From electronic structure to dynamics within the Born-Oppenheimer approximation and beyond

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The talk begins with a brief analysis of the Born-Oppenheimer approximation which stems from the fact that nuclei are much heavier than the electrons, and hence their motions can be approximated as separable. A simple model that allows a quantitative assessment of such an approximation is then presented. The solution of the electronic problem is next addressed by surveying recent progress on the extrapolation of the correlation energy to the complete one-electron basis set limit. A protocol employing a single raw ab initio point is highlighted. The advantages of analytically representing the calculated energies is then pointed out, and a scheme presented that allows single-sheeted forms to even mimic cusped behaviors. Developed thus far for triatomics, the method is illustrated for ground-state C₃ which shows four conical intersections due to combined Jahn-Teller plus pseudo-Jahn-Teller interactions. The remaining part of the talk addresses the solution of the nuclear equations of motion by focusing on: a) a new code in hyperspherical coordinates for atom-diatom reactive scattering, and recent results for the D⁺⁺H₂ reaction, some outside the BO approximation; b) the photoelectron spectra of methane and water, with emphasis on the fast rearrangement of CH₄⁺ from its initial T_d structure to equilibrium (C_{2v}). Besides the good agreement obtained between the calculated and measured vibronic bands of CH₄⁺, it is shown that attosecond-resolved dynamics occurring at the triply-degenerate ground electronic manifold of CH₄⁺ can be studied with regular dynamics by simulating the ratio of the emitted high-harmonic signals. Indeed, the predictions are shown to agree with recent experiments [Baker et al., Science 312, 424 (2006)] that use high-order harmonic generation to probe the attosecond proton dynamics. Prospective remarks conclude the talk.

A dynamical study of the predissociation of H_2O^+

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Water molecules can be ionized by removing an electron from the two highest molecular orbitals, leading to the formation of the water cation in the lowest electronic states $\tilde{X}^2\text{B}_1$ and $\tilde{A}^2\text{A}_1$. In these ionization processes, the Franck-Condon vibrational wave packet formed does not dissociate. However, the electron removal from the b_2 molecular orbital yields H_2O^+ in the $\tilde{B}^2\text{B}_2$ electronic state. For many nuclear configurations, the potential energy of the $\tilde{B}^2\text{B}_2$ state lies above the dissociation limits of states $\tilde{X}^2\text{B}_1$ and $\tilde{A}^2\text{A}_1$, which leads to the breakdown of the water cation. Two fragmentation channels: $\text{H}^+ + \text{OH}$ and $\text{H} + \text{OH}^+$ can be formed, and the corresponding fragmentation rates were measured in [1].

We have carried out a 3D quantum dynamics study of the evolution of the Franck-Condon vibrational wave packet in the $\tilde{B}^2\text{B}_2$ state to calculate the fragmentation probabilities (see Fig. 1). Our calculation employs ab initio potential energy surfaces and dynamical couplings and we have solved the time dependent Schrödinger equation for the nuclear motion by employing the code GridTDSE [2], modified to include non-adiabatic transitions. We have obtained fragmentation probabilities in excellent agreement with the experimental ones, and the simulations allow us to follow the time evolution of the nuclear wave packet. We have found [3] that the fragmentation takes place through a mechanism that involves a fast transition in the conical intersection between the potential energy surfaces $\tilde{B}^2\text{B}_2$ and $\tilde{A}^2\text{A}_1$. The fragmentation branching ratios are determined by the Renner-Teller coupling between the states $\tilde{X}^2\text{B}_1$ and $\tilde{A}^2\text{A}_1$ near the linear geometry.

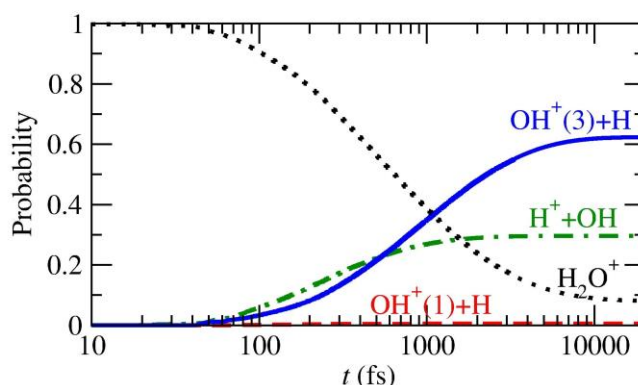


Fig.1 Time evolution of the fragmentation probabilities.

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Molecular recognition at water/air interfaces illustrated with inclusion complexes of calixarenes with metal cations

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Predicting molecular recognition from first principles is formidably challenging, as it demands an accurate description of macromolecular conformations and the underlying energetic (intramolecular, intermolecular and solvent interactions) and entropic contributions. Our group is carrying out a research program aimed at the characterization of selective host-guest binding processes with a combination of experimental (mass spectrometry, UV and IR spectroscopy) and theoretical methods (e.g., see [1-4]). We will illustrate this line of research with our most recent results on the inclusion complexes formed by a calixarene with alkali metal cations, for which the binding affinities have been obtained in qualitatively different environments, namely under full solvation (in aqueous, organic or ionic solutions), under “half-solvation” at solution/air interfaces and under isolated solvent-less conditions (see Figure 1). In the absence of any solvent, the calixarene- Li^+ complex is most stable, and the stability decreases rapidly with growing cation size. However, this trend is completely reversed in aqueous solution where the most favored binding occurs for the calixarene- Cs^+ complex. Somewhat unexpectedly, the selectivity of the calixarene for Cs^+ is even more marked when it occurs in calixarene monolayers formed at the water/air interface and competitive binding takes place with the alkali cations from the solution. This result is remarkable and may have an impact in the design of molecular sensors.

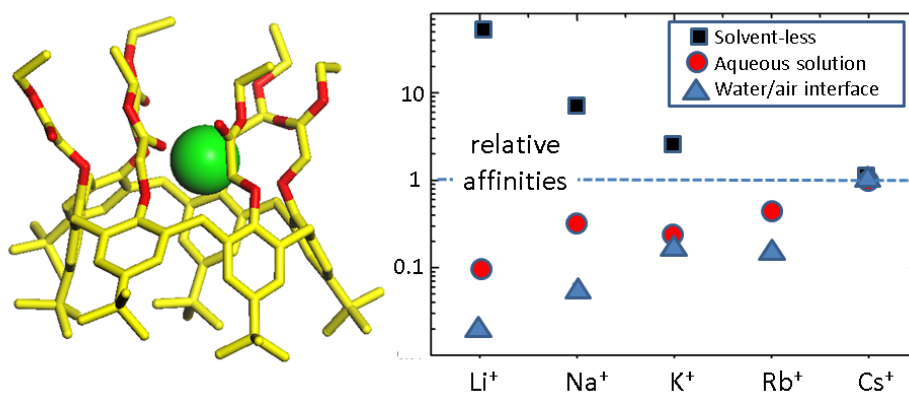


Figure 1: Relative binding affinities of 4-tert-Butylcalix[6]arene-hexaacetic acid hexaethyl ester for alkali metal cations in aqueous solution, at the water/air interface and under solvent-less conditions

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Mapping the dissociative ionization dynamics of molecular nitrogen with attosecond resolution

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N₂ is the most abundant element in the earth's atmosphere and as such is of integral importance to processes induced by solar radiation, in particular its dissociation induced by solar XUV light in the upper atmosphere.

We present the experimental and theoretical investigation of the ionization and dissociation dynamics of N₂ induced by XUV radiation. Isolated attosecond pulses [1] were used to ionize N₂ molecules, through a single photon transition. After a variable delay, NIR/VIS CEP controlled pulses were used to probe the subsequent dissociation dynamics. The angularly resolved momentum distribution of the produced N⁺ fragments was measured as a function of the pump-probe delay using a velocity map imaging (VMI) spectrometer.

To understand the origin of the dynamics a model was developed: The ionization process was simulated assuming an instantaneous transition from the electronic ground state of N₂ to a set of electronic levels of the N₂⁺ ion, obtained using *ab initio* multiconfigurational methodology. The relative initial populations of said set of ionic PECs were approximated using Dyson orbitals in first order perturbation theory [2,3] and modelling the leaving electron by a Coulomb wave. The dissociating ion subjected to the IR pulse was modelled by solving the TDSE using Split Operator and Fast Fourier [4] techniques.

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PL7

Attosecond molecular dynamics**F. Martin¹**¹ Universidad Autonoma de Madrid, Spain*E-mail: fernando.martin@uam.es*

The development of attosecond laser pulses allows one to probe the inner working of atoms, molecules and surfaces on the timescale of the electronic response. In molecules, attosecond pump-probe spectroscopy enables investigations of the prompt charge redistribution and localization that accompany photo-excitation processes, where a molecule is lifted from the ground Born-Oppenheimer potential energy surface to one or more excited surfaces, and where subsequent photochemistry evolves on femto- and attosecond timescales. In this talk I will present a few theoretical examples of realistic molecular attosecond pump-probe experiments in which simple molecules are ionized with a single attosecond pulse (or a train of attosecond pulses) and are subsequently probed by one or several infrared or xuv few-cycle pulses. The evolution of the electronic and nuclear densities in the photo-excited molecule or remaining molecular ions is calculated with attosecond time-resolution and is visualized by varying the delay between the pump and probe pulses. The results of these calculations [1-7] allow us to explain several experimental observations as well as to guide future experimental efforts to uncover ultrafast electron and nuclear dynamics in molecules.

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IL6

Electron transfer to acetic acid: OH⁻ formation via diol intermediate

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Secondary electrons with energy distribution below 20 eV, produced by primary (high) energy radiation when interacting with (bio) matter, can effectively produce reactive species such as radicals and ions along the track radiation. [1] These secondary species are found to be more capable to produce degradation than the primary radiation. It is now well-established that electron induced decomposition of key biomolecular targets may be responsible for the nascent stages of DNA/RNA loss of integrity. [2] Notwithstanding, such electron induced decomposition is also prevalent in other molecular targets in particular those related to proteins and their subunits. So, electron transfer studies in potassium collisions with simple organic molecules, such as aliphatic amino acids, have been performed allowing to identify particular intramolecular mechanisms that lead to fragmentation. [3, 4] However, some of these mechanisms were shown to involve not single cleavage but complex internal rearrangement in the transient molecular anion.

In the present communication we discuss OH anion formation in electron transfer experiments with acetic acid fully hydrogenated and with deuterated analogues in the carboxylic and methyl groups through a comprehensive combined experimental study together with state-of-the-art calculations. Mechanisms for such anion formation have been properly explored and two different but competitive pathways have been identified. These leading to OH anion formation will be thoroughly discussed. In both cases diol formation has been identified as a key intermediate species. [5]

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O11

Huge quantum symmetry effect in the O+O₂ exchange reaction

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Molecular oxygen O₂ is one of the most important molecules in Earth's atmosphere. It lies at the heart of the very complex chemical network describing its evolution. On the other side, the ozone molecule O₃ protects us from the UV radiation when present in the stratosphere, but is very corrosive in the troposphere. The natural abundance in ¹⁶O being roughly 99.8%, molecular oxygen and ozone exclusively formed from this isotope are dominant in the atmosphere. Any process happening with these entities is therefore taken as a reference.

Surprisingly, a strong enrichment of about 10% with respect to what happens for O₂, of O₃ in both ¹⁸O and ¹⁷O species, which seems independent of the isotope mass, and thus known as the so-called mass-independent fractionation (MIF) [1,3], has been observed several decades ago. It has also been reproduced in several laboratory experiments [2]. This phenomenon remains unexplained for the most part and its solution is considered a big challenge within the atmospheric chemistry community.

The three-body recombination $O + O_2 + M \rightarrow O_3 + M$ is believed to be the main process leading to the isotope enrichment, among other reactions leading to ozone formation. At sufficiently low pressures, it can be partitioned into two steps: firstly the formation of O₃ in a highly excited rovibrational state, from reaction $O + O_2 \rightarrow O_3^*$ (step 1), and its subsequent stabilization by deactivation collision with an energy absorbing partner M, $O_3^* + M \rightarrow O_3 + M$ (step 2).

Thus, the efficiency of the exchange reaction $O + O_2 \rightarrow O_3^* \rightarrow O_2 + O$, which gives back the same chemical species as reagents and involving O₃^{*} as an intermediate, is one of the key parameters to understand ozone formation. During this talk, we will show that this reaction, initiated by step 1, is very fast with three identical ¹⁶O atoms involved, because of a quantum permutation symmetry effect. Consequently, it competes ferociously with step 2 described above, the latter becoming in this way much less effective.

We will present results of a computationally intensive full-quantum investigation of the dynamics [4] of the ¹⁶O + ³²O₂ supported by a recent accurate global potential energy surface for the ground state of ozone [5]. Our study based on a time independent approach incorporates explicitly the indistinguishability of the three atoms and yields quite accurate cross sections and rate constants. Other results concerning the ¹⁸O + ³²O₂ exchange reaction will be also presented [6]. Both isotopic and quantum symmetry effects have been found. Our results will be compared with recent time dependent wave packet results [7,8,9].

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O12

Unraveling the conformational preferences of DNA-bases Aggregates by Electronic Spectroscopy in Molecular Beams

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Non covalent interactions between DNA bases are essential in the stabilization of the DNA chains. This stability is due to the presence of multiple hydrogen bonds between them and the π - π interactions connecting adjacent dimers. In this work, a combination of mass-resolved excitation spectroscopy (REMPI and IR/UV double resonance) and DFT calculations (M06-2X/6-311++G(d,p)) were used to explore the conformational preferences of DNA-bases aggregates. Gas phase makes it possible to remove the solvent effects, providing a good insight on the non-covalent interactions which take place between the building blocks of the DNA and establishing the interactions and conformations which are more favorable in the aggregation of DNA-bases.

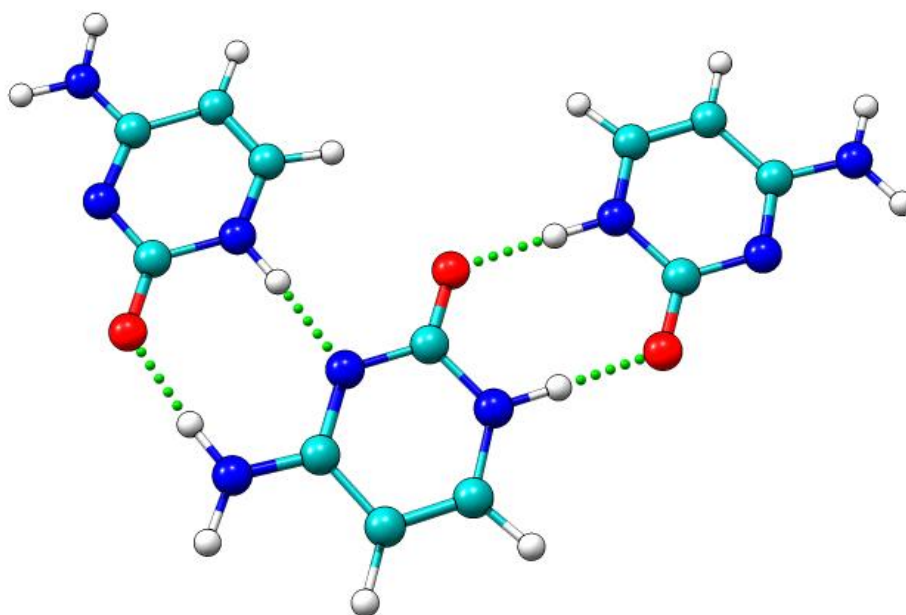


Figure: One of the possible structures for cytosine trimer

PL8

Condensed phase molecular dynamics simulations at the frontiers of high-performance computing, physics, and digital aesthetics

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Dirac famously wrote ‘...The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to the main features of complex atomic systems without too much computation’. Certainly when it comes to chemistry, Dirac’s statement is arguably as accurate now as it was then, although our operational definition of what constitutes ‘too much computation’ has changed appreciably from what one might have imagined in 1929, and has in fact undergone continual revision since the 1950s.

The last decade has seen another significant shift in perspective, due to the increasingly prominent role that massive parallelism and stream processors like GPUs have come to play across many fields of scientific computing. In this talk, I will give an overview of recent work in my lab, carried out at the interface of molecular physics, high-performance computing, scientific visualization, human-computer interaction, and digital aesthetics. Exploiting stream computing architectures, parallel software frameworks, and interactive molecular simulation platforms, I will describe developments and applications of a number of approaches which have furnished significant insight into a range of complex molecular systems with atomic-level resolution, across a range of different areas of chemistry, including: non-equilibrium effects that determine reaction outcomes in typical organic chemistry solvents [1-4], the role that excited molecular quantum states play in shuffling energy within biological light-harvesting complexes [5-6], and exciting new interactive approaches for tackling conformational path sampling on rugged potential energy surfaces in biomolecular and condensed phase systems [7-8].

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IL7

Origami rules for the construction of localized eigenstates of the Hubbard model in decorated lattices

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Geometrically frustrated itinerant electronic systems exhibit flat bands in the energy dispersion, reflecting the existence of compact localized states. In this talk, we describe the state of the art in this field and discuss some of the results of our recent research in these systems, namely:

1. A set of rules for the construction of exact localized many-body eigenstates of the Hubbard model in decorated lattices, both for $U=0$ and $U\rightarrow\infty$ [1]. Using this simple set of rules, a tight-binding localized state in a plaquette can be divided, folded and unfolded to new plaquette geometries. This set of rules is also valid for the construction of a localized state for one hole in the $U\rightarrow\infty$ limit of the same plaquette, assuming a spin configuration which is a uniform linear combination of all possible permutations of the set of spins in the plaquette.

2. The two-terminal electronic conductance through the AB₂ ring which is an simple example of the family of itinerant geometrically frustrated electronic systems [2]. For zero magnetic flux, localized states in this system act as a filter of the zero frequency conductance peak, while for finite flux, the conductance exhibits a zero frequency peak with a dip which is a distinct fingerprint of the variable extension of the localized states.

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Global optimization of coarse-grained models for virus capsids and astrophysically relevant molecules

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Coarse-grained modeling provides a general approach to address large scale structures and assemblies by reducing chemical complexity. Here we present the results of global optimization performed for a minimalist model of the self-assembly of virus capsids [1] and for coarse-grained models of polycyclic aromatic hydrocarbon (PAH) molecules [2].

Using the basin-hopping global optimization technique [3] we reproduce the geometrical structures of icosahedral virus capsids ranging from the T=1 and T=3 families (12 and 32 capsomers) to capsids as large as the bacteriophage T4 prolate head (167 capsomers). We also demonstrate that the main factors determining the form of the virus capsid structures is the directionality and the strength of the capsomer-capsomer anisotropic interaction [1]. In the case of the PAH clusters, a coarse-grained model was developed based on the Paramonov-Yaliraki potential [4] and parametrized to reproduce the results of all-atom reference calculations. With this simple model we find that the most stable structures exhibit a stacked motif, a structural transition toward three dimensional shapes being observed for larger clusters [2].

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O14

Extending the boxed molecular dynamics algorithm to undertake adaptive dynamical path sampling in multidimensional collective variable space

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The boxed molecular dynamics (BXD) rare event algorithm [1] is a simple technique for accelerating the simulation of rare events that has proven useful for calculating kinetics and free energy profiles in molecular dynamics simulations across a range of one dimensional collective variables. BXD works by locking dynamics between user-specified hypersurfaces sequentially located along a specified path defined by user-specified collective variables.

This poster will present two new algorithmic developments that considerably expand BXD's ability to map free energy and kinetics in complex molecular systems. First, we have implemented an algorithm that undertakes on-the-fly statistical analysis during a trajectory, in order to automatically determine the optimal hypersurface locations with minimal user input. This not only makes BXD considerably more 'black-box', and therefore easier to use; it is also more computationally efficient. Second, we have implemented an efficient and general extension of BXD that enables us to map free energies and kinetics in more than one collective variable. This allows us to sample rare events that cannot be captured with a single collective variable. We will illustrate our results so far by presenting some initial adaptive tests carried out in 2-dimensional condensed phase systems, namely the reaction of $F + CD_3CN \rightarrow DF + D_2CN$ in a strongly coupled explicit CD_3CN solvent.

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IL8

WHAT CAN WE EXPECT OF HIGH-RESOLUTION SPECTROSCOPIES ON SUGARS?

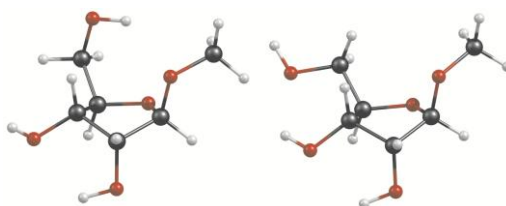
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Carbohydrates are one of the major families of building blocks in biology, playing numerous key functions in living organisms. We present several studies on sugars exploiting an experimental strategy which combines microwave and laser spectroscopies in high resolution, computation and synthesis. Microwave spectroscopy coupled with ultrafast laser vaporization provides great resolution and direct access to molecular structure of monosaccharides. On the other hand, laser spectroscopy offers high sensitivity coupled to mass and conformer selectivity, making it ideal for larger systems like polysaccharides and glycopeptides. This combined approach provides not only accurate chemical insight on conformation, structure and molecular properties, but also benchmarking standards guiding the development of theoretical calculations.

In order to illustrate the possibilities of a combined microwave-laser approach I present results on the conformational landscape and structural properties of several monosaccharides[1,2] polysaccharides[3] and glycopeptides including microsolvation and molecular recognition processes.[4]



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IL9

SERS and SEF Nanosensors based on Nanostructured Metal Surfaces: Linkage of plasmonic nanoparticles in colloidal suspensions for enhanced molecular sensing

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The optical properties of metallic Nanoparticles (NPs) strongly depend on their size and shape. The resonant excitation of the LSP originates a very important enhancement in the cross sections of SERS (*Surface Enhanced Raman Scattering*) and SEF (*Surface Enhanced Fluorescence*) techniques.

The detection of different kinds of molecules, as biomolecules and pharmaceuticals drugs by optical means is of particular interest in several areas such as biotechnology and biomedicine. SERS has been shown to be sensitive to molecular orientation and to the distance from the metal surface. Hence it is well suited for studies in which specificity, sensitivity and orientation of the molecule are very important. Also, the establishment of better conditions for the obtention of SERS spectra of macromolecules is not as trivial as it is in the case of small molecules.

The manufacture of nanoparticles (NPs) with metallic plasmonic properties, displaying advanced spectroscopic applications is one of the tasks of our research Group. In fact, shape control of metal nanostructures is a promising strategy to tailor their physical and chemical properties. In this context, star-shaped NPs or metal nanostars (NS) have shown to play an extraordinary role in the intensification of the Electromagnetic field, with promising applications in bioimaging and detection. In particular, core@shell nanoparticles display advantageous properties to be used as SERS substrates.

On the other hand, drug delivery constitutes one important research field. It is necessary to maximize the therapeutic effects jointly with a minimization of the undesired secondary ones. A molecular characterization of nanocarrier systems using SERS and SEF by using metallic NPs as drugs nanocarriers will be presented. These NPs are able to transport several therapeutic molecules adsorbed on their surface and the presence of LSP Resonances increases the sensitivity allowing to detect them.

Acknowledgements

This work has been supported by the Spanish Ministerio de Economía y Competitividad (MINECO, Grant FIS2014-52212-R)

IL10

Characterization and modification of semiconductor nanostructures by ion beams

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Ion beams have been extensively used in the past 50 years for the modification of a wide range of materials. In particular, ion implantation has been a key technology for doping and implant-isolation in silicon-based microelectronics. In parallel to the advances in ion beam modification, ion beam analysis techniques such as Rutherford Backscattering Spectrometry/Channelling (RBS/C) have found wide applications in materials research. In recent years, ion beam techniques have been increasingly used in nanotechnology. However, it is important to understand the potential as well as the limitations of these techniques with respect to spatial resolution and sensitivity when studying nano-scale materials.

In this presentation we will discuss these issues with the help of several examples where ion beam techniques were applied to wide bandgap semiconductor nanostructures. RBS/C was used to study the crystal quality and composition of III-nitride quantum well structures which compose the active region of blue and green LEDs. For the case of GaN nanowires, orientation, twist and tilt can be investigated by RBS/C complemented by Monte Carlo simulations. These structures were further processed using ion beams for doping and defect engineering. Finally, we will present first results obtained in a new experimental chamber installed at the microprobe of the Laboratory of Accelerators and Radiation Technologies of IST allowing the in-situ and temperature dependent (~ 77 K up to room temperature) study of optical and electrical properties of nanomaterials during proton irradiation.

O15

Atoms inside Casimir cavities within the realm of Stochastic Electrodynamics

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Stochastic Electrodynamics (SED) is a modern version of the relativistic classic electrodynamics theory with the implementation of a random electromagnetic zero-point field (ZPF) background. This theory has astoundingly described many atomic systems until now explained only by quantum electrodynamics, for example the atomic orbital stability, whose energy levels would be predetermined by the ZPF [1]. Since a Casimir cavity suppresses some of the ZPF modes, the atoms inside such cavity can undergo level shifts in their ground and excited states. Through this principle, the switching of ground or excited atoms between Casimir cavities and the free space could induce emission of radiation or gains in their transition energies. According to SED, this excess of energy comes from the averaged positive work done by the ZPF on the electrons in their orbits [3].

In order to evaluate this potential method to extract energy from the ZPF, we started studying by computational means the atom-ZPF interaction inside and outside a cavity. For this purpose, we simulated the electron's motion in the Hydrogen atom using the approximated model suggested in Ref. [4]. We were still able to extend the integration time, and thus we found an unexpected divergence from the quantum mechanics' prediction. Our results also showed a continuous trend towards spontaneous ionization. These stability problems were demonstrated, being related, at least partially, to some inconsistencies found in the model's conceptual foundations. Due to these difficulties, it was not possible to theoretically describe the process. Even so, we assembled an experimental system to flow low pressure Xe through Casimir cavities formed by nano-porous aluminium coated membranes. Two monochromators, one coupled to a Vacuum Ultra-Violet (VUV) lamp and another one to a Photomultiplier Tube (PMT), allowed us to excite atoms using well-defined wavelengths and, simultaneously, analyse their emitted radiation.

With the preliminary excitation of atoms we didn't observe any gain in their radiative properties induced by Casimir cavities. However, our instruments were not optimal for these energy ranges. We performed a second set of experiments where Xe atoms flowed through the membrane without being excited. At first, a spectroscopic study was performed and, afterwards, we placed the PMT few mm away from the membrane, increasing the sensitivity significantly. However, in both cases, we didn't detect any radiation emitted from the Xe atoms. Furthermore, from the results of the latter case we can conclude that most likely there is no radiation emission from the Xe ground state reduction in the energy range from 1.9 to 7.8 eV and for pores of 50 nm in diameter.

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PL9

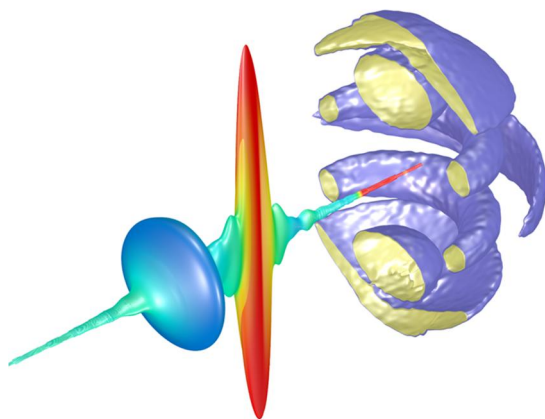
Designer photons for designed bound and free electron wave-packets

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Ultrafast coherent laser control is a fascinating facet of femtochemistry as it seeks to steer any type of photophysical systems from an initial state to a predefined target state (traditionally) on the time scales of nuclear motion with the help of suitable polarization shaped femtosecond laser pulses¹. In addition direct control of valence electron dynamics in molecules is conveniently achieved with the help of state of the art pulse shaping devices having unprecedented temporal precision².



In this talk I will concentrate on our current experiments devoted to direct control of bound and free electron dynamics: First I will discuss the creation and tomographic reconstruction of 3D designer electron wave packets in the continuum with the help of polarization shaped laser pulses and the electronic structure of atoms^{3,4}. As an application I will present the current status of our approaches to chiral recognition in the

gas phase^{5,6}. Finally I will highlight our experiments devoted to charge oscillation controlled molecular excitation⁷.

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IL11

Analysis of heterogeneous samples and simple stratigraphies using X-Ray Fluorescence – Applications to Cultural Heritage

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X Ray Fluorescence (XRF) spectrometry is one of the most powerful tools in studies of material characterization of Cultural Heritage, due to user friendly features and quick qualitative interpretation of the spectra. Moreover, its non-destructive nature is of paramount importance when dealing with Cultural Heritage objects, due to the availability of portable setups enabling analysis to occur in the controlled Museum environment and avoiding the collection of samples. However, these materials analyzed are seldom homogeneous and are mostly stratigraphies with more or less complexity. This way, the evaluation of the spectra and interpretation of the results is not straightforward, and calculations and specific software. In this talk, some case studies will be presented concerning the application of XRF to the study of simple stratigraphies and non-homogeneous samples, namely, the analysis of coins from the Portuguese's first dynasty (13th and 14th centuries) the characterization of gilding and the determination of gold leaf thicknesses in Namban folding screens (16th and 17th centuries) and Manuelin foral charters (16th century).

Acknowledgements

S. Pessanha would like to acknowledge FCT for the postdoc grant SFRH/BPD/94234/2013.

Electroluminescence yield of xenon with small quantities of CH₄ and CO₂ additives

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The NEXT collaboration aims to use a high-pressure xenon gas time projection chamber (TPC) for neutrinoless double-beta decay search [1]. Xenon is a slow gas, allowing very large electron diffusion, which is a drawback for the pattern recognition required in the TPC. The use of a molecular gas additive to xenon, in small quantities, such as CH₄, CF₄ and CO₂, will have a great impact on the reduction of diffusion and increase of the drift velocity. However, drifting electrons may undergo about 10⁴ elastic collisions before gaining enough energy from the electric field to excite the Xe atoms and produce scintillation. If the electron collides with a polyatomic molecule, the electron energy may be lost without resulting in scintillation, transferring its energy to the molecule through vibrational and rotational excitation, thus reducing drastically the electroluminescence yield. A compromise must be found between the reduction of secondary scintillation and additive amount.

A small driftless gas proportional scintillation counter (GPSC), capable of withstand few bar, will be irradiated with low-energy X-rays below 6 keV to determine the electroluminescence yield as a function of the reduced electric field in the scintillation region, for molecular additive concentrations between 0.1 and 2.2%, for pressures in the range of 1 to 2 bar. The pulse waveform will also be monitored and compared for the different molecular species, concentrations and electric field strengths in order to access the electron drift velocity for the applied range of electric field strengths.

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IL12

Laser Spectroscopy in Muonic Atoms: The Lamb-shift Measurement

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The CREMA Collaboration aims to provide precise measurements for the charge radii of low- Z nuclei through the determination of the Lamb-shift (energy difference between the 2S-2P levels) in muonic atoms, using laser spectroscopy. In muonic atoms, the heavy muon orbits a bare nucleus with a 200-times smaller Bohr radius, compared to its electronic equivalent. This results in high sensitivity of the muonic atom's S states to the finite charge and magnetic radii of the nuclei.

Low-energy negative muons are stopped in a low-pressure gas target, forming highly excited muonic atoms/ions. While most of these promptly decay to the ground state, a very small fraction ends up in the 2S metastable state with a longer lifetime. A tuneable laser pulse induces the 2S-2P transition of the latter, which immediately decays to the ground state, emitting characteristic X-rays. A resonance line is obtained by scanning the laser frequency and recording the number of X-ray photons in coincidence with the laser pulses.

First results were obtained for proton and deuterium. The proton charge radius, $R_p=0.84087(39)$ fm [1,2], ten times more accurate than before, was found to be 7σ away from the CODATA value [3]. Potential reasons for the "proton radius puzzle" include unforeseen behaviour of the proton, but also the existence of possible physics beyond the Standard Model.

This triggered efforts for improved measurements currently pursued at MPQ [4]. These measurements, together with new data for muonic deuterium and helium [5] may help to understand this puzzle.

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Quantum interferences in laser spectroscopy of muonic atoms

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In this presentation, we address a subtle quantum effect that occurs in the process of light scattering by atoms, i.e., the process of absorption and emission of a photon that happens in resonant laser spectroscopy. This effect occurs due to the coherent interference between the main resonant path and other non-resonant paths, which leads to energy shifts that depend on the relative position of each resonance. This is an important, yet frequently overlooked systematic effect in precision laser spectroscopy experiments [1, 2], which measure transition frequencies with uncertainties below 10⁻⁵ [3, 4]. High-precision spectroscopy of atomic systems is primarily devoted for the determination of fundamental physical constants; thus, a careful analysis of these quantum interference effects is mandatory. Here, we introduce the effects of such interference in laser spectroscopy of muonic atoms, which consists of an exotic muon and nucleus. Previous measurements of energy transitions by laser spectroscopy in these exotic atoms, conducted by the CREMA collaboration, lead to the determination of the proton charge radius with high accuracy [3]. We discuss here the effect of quantum interference in several resonances of muonic hydrogen, deuterium and helium-3, giving emphases to geometrical and polarization scenarios that minimize it.

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O18

High precision tests of QED – Measurement of the alpha-particle and helion rms charge radius and the transition energies in highly-charged ions

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The recent scientific and technological developments in the study of exotic states of matter like muonic atoms and highly charged ions have enabled the possibility of making measurements of several parameters with unprecedented accuracy. The absolute (reference-free) energy measurement of a heliumlike argon transition with an accuracy of 2.5 ppm in the SIMPA (Multicharged Ion Source of Paris) at the Laboratoire Kastler Brossel (École Normale Supérieure, Université Pierre and Marie Curie (UPMC) and CNRS), using a double-crystal spectrometer (DCS), is one example [1]. Another well-know example is the recent measurement of the proton root-mean-square (rms) charge radius with an uncertainty of 0.1% (20 times better than the previous values) by the Charge Radius Experiment with Muonic Atoms (CREMA) collaboration in the Paul Scherrer Institute (PSI). These has led to a disagreement with other methods of 7 error bars (the so called proton size puzzle) [2, 3].

Motivated by these successes, the CREMA collaboration measured the alpha-particle and helion rms charge radii, which is currently in the analysis phase, aiming a relative accuracy of 3×10^{-4} (equivalent to 0.0005 fm). In parallel, the SIMPA group aims to extend the accurate transition energy measurements to other ions and species (Kr, K and S) aiming now an accuracy less than 2 ppm with the update and improvement of the experiment, in particular a better control of the crystals temperature and horizontality. These measurements will aim at testing QED and finding what could lead to such a large disagreement.

The setup of both experiments and the current status of the experiments will be presented focused in the topics in which I'm more involved.

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Laboratory analogs of interstellar carbonaceous dust: plasma deposition and energetic processing

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Carbonaceous compounds, both solids and gas-phase molecules, are found in very diverse astronomical media [1]. A significant amount of the elemental carbon is found in small dust grains. This carbonaceous dust, mostly formed in the last stages of evolution of C-rich stars, is the carrier of characteristic IR absorption bands revealing the presence of aliphatic, aromatic and olefinic functional groups in variable proportions [2]. Among the various candidate materials investigated as possible carriers of these bands, hydrogenated amorphous carbon (a-C:H) has led to the best agreement with the observations. Carbonaceous grains are processed by H atoms, UV radiation, cosmic rays and interstellar shocks in their passage from asymptotic giant branch stars to planetary nebulae and to the diffuse interstellar medium. The mechanisms of a-C:H production and evolution in astronomical media are presently a subject of intensive investigation.

In this work we present a study of the stability of carbonaceous dust analogues generated in He+CH₄ radiofrequency discharges [3]. In order to simulate the processing of dust in the interstellar environments, the samples have been subjected to electron bombardment, UV irradiation, and both He and H₂ plasma processing. IR spectroscopy is employed to monitor the changes in the structure and composition of the carbonaceous films.

Acknowledgements

This work has been funded by the MCINN of Spain under grants FIS2013-48087-C2-1-P and the Consolider Astromol, CDS2009-00038. We thank also the European Research Council for additional support under ERC-2013-Syg 610256-NANOCOSMOS. MJR has received funding from the FPI program of the MCINN.

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P2

Supramolecular organization of perfluorinated 1*H*-indazoles in the solid state by using vibrational spectroscopies sensitive (VCD) and non sensitive (MIR, FIR and Raman) to chirality: The case of 3-pentafluoroethyl-4,5,6,7-tetrafluoro-1*H*-indazole

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Supramolecular chirality is present in certain crystals of some of the complex molecular systems formed by a particular number of subunits (chiral or not) linked by non covalent interactions. It is the case of some 1*H*-indazoles that crystallize as catemers with subunits connected through H-bondings, where only one enantiomer is present (or at least preferably on the other one, presenting the mixture enantiomer excess) in the unit cell for a given crystal that can be separated manually (spontaneous resolution). This is the case for 1*H*-indazole (**INDAZL**) [1] and for 3-trifluoromethyl-4,5,6,7-tetrafluoro-1*H*-indazole (**LIDGEL**) [2], which have already been characterized (including the determination of their P or M absolute configurations) by us using different techniques of vibrational spectroscopy both sensitive (VCD) and non sensitive (MIR, FIR and Raman) to chirality combined with quantum chemical calculations which take as a reference experimental data determined from X-ray diffraction.

In this work, the supramolecular characterization (including its absolute configuration) of the crystals of the perfluorinated derivative of 1*H*-indazole named 3-pentafluoroethyl-4,5,6,7-tetrafluoro-1*H*-indazole is accomplished according to the above cited vibrational methodology. This compound was originally synthesized and X-ray characterized by Etienne et al [3]

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Double pulse femtosecond laser ablation of Co/ZnS

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Ultrashort lasers offer attractive features for the controlled synthesis of materials through pulsed-laser deposition processes [1]. The ability to inject energy in a material in a time scale shorter than energy redistribution times can take the material to states far from equilibrium [2], and the dynamics can to a certain extent be tailored through the control of the properties of the laser pulses in terms of temporal profiles, spectral content, polarization or intensity.

In this work we show the ability to modify the cationic content of a laser ablation plasma of mixed targets of Co/ZnS through a double-pulse femtosecond laser ablation scheme where the role of the individual pulse intensities and the relative delay between the two pulses was explored. This result provides a promising route for the controlled synthesis of diluted magnetic semiconductors [3], where transition metal elements like Co replace a fraction of the cations in the semiconductor lattice.

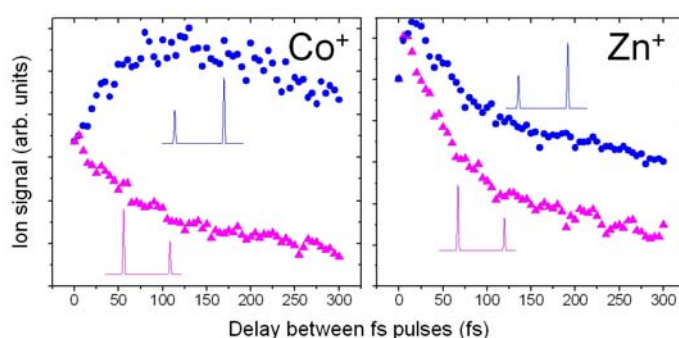


Figure: Ion intensities of Co^+ and Zn^+ obtained in ablation plasmas of Co/ZnS with double pulse femtosecond ablation as a function of delay and relative energy of the pulses.

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Third harmonic generation in fs-ablation plasmas of metals

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Species showing nonzero third order nonlinear optical susceptibility can be used as frequency tripling media, and the efficiency of the tripling process depends on the species number density, the laser intensity, the nonlinear susceptibility at the given wavelength and the phase matching conditions [1]. Thus, third order harmonic generation can be regarded as a universal detection technique, sensitive to the presence of all forms of matter, be it in solids, liquids or gases. Due to this property, third order harmonic generation has recently received considerable attention as a diagnosis technique of laser ablation plasmas [2,3], which are complex media that may contain several compositionally or energetically diverse components. The use of separate laser systems for ablation and for harmonic generation allows the free exploration of the ablation medium both in space and in time, thus directly revealing distinct populations when they are present in the plasma.

In this work we present results on third order harmonic generation of a ns NIR (1064 nm) laser pulse in 800 nm fs-laser ablation plasmas of metals under vacuum. The study covers Al, Ag, Cu and Mn. We demonstrate that the technique is sensitive to the presence of metal nanoparticles in the narrow range of ablation conditions where these constitute a large fraction of the ablated species.

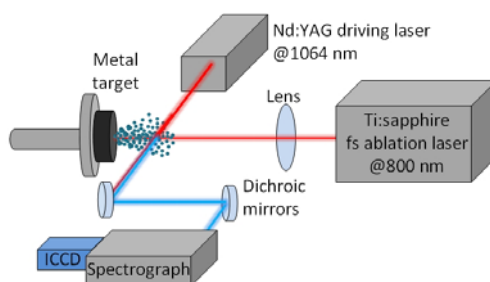


Figure: Scheme of the experimental setup employed to detect third-order harmonic generation from a fs laser ablation plasma.

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Predissociation dynamics of the methyl radical measured in real time with velocity map ion imaging

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The methyl radical, as the simplest alkyl radical, has been historically regarded as a benchmark system for the photochemistry of larger open-shell hydrocarbons. Since the early discovery of the two-photon transitions to members of the Rydberg series [1], these have been widely used for detection of the methyl radical in the gas phase [2,3]. However, the spectra are adversely affected by broad natural linewidths caused by rapid predissociation [4], and these state-dependent predissociation rates preclude obtaining quantitative data on product state distributions in reactions where CH₃ is formed. In this contribution, we will present a direct, real-time measurement of the lifetimes of selected vibrational levels of the 3p_z Rydberg state of CH₃ and its deuterated form, CD₃. In the experiment, CH₃, obtained from laser photodissociation of CH₃I, is two-photon excited to the 3p_z Rydberg state, and later ionized. This three-color ultrashort laser pulse scheme permits the distinct measurement of lifetimes for each vibrational level of CH₃ in the Rydberg state. Additionally, *ab initio* calculations have been performed that allow us to propose a mechanism for 3p_z predissociation of CH₃.

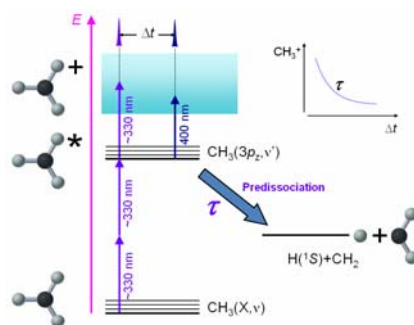


Figure: Scheme used for the measurement of predissociation lifetimes in CH₃.

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Emission characteristics and dynamics of species in a TEA-CO₂ laser-produced CaO plasma

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Laser-produced plasmas (LPPs) are currently a topic of great interest in fundamental and applied areas of Physics such as fabrication of thin films by pulsed laser deposition, spectrochemical analysis through laser-induced breakdown spectroscopy (LIBS) [1], production of nanoparticles, etc. Laser-target interaction involves complex processes and the analysis of LPPs can be a very difficult considering its transient nature as well as large variations in plasma properties with space and time. In this work, we present a spatial and temporal analysis of the LPP plume generated on calcium oxide CaO. We investigated the emission features of Ca, Ca⁺, O⁺, Ca²⁺ and O²⁺ species in a laser-ablated CaO plasma using time and space resolved optical emission spectroscopy. The plasma was generated by focusing 10.532 μm , 64 ns pulses from a transversely-excited atmospheric (TEA) CO₂ laser. The laser-induced plasma was found to be ionized in Ca⁺, O⁺, Ca²⁺ and O²⁺ species and rich in neutral calcium and oxygen atoms. In addition, different electronic molecular bands of CaOH ($A^2\Pi-X^2\Sigma^+$, $B^2\Sigma^+-X^2\Sigma^+$ and $D^2\Sigma^+-A^2\Pi$) were observed in the spectra. The temporal behavior of specific emission lines of Ca, Ca⁺ and Ca²⁺ has been characterized (see for example figure). The results show a faster decay of Ca²⁺ and Ca⁺ ionic species than in the case of neutral Ca atoms.

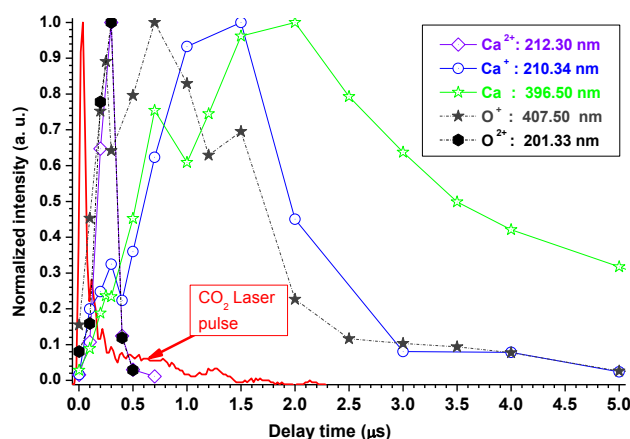


Fig. Number density time of flight distributions of different species as a function of delay time (fixed gate width time of 0.1 μs) for a laser intensity of $4.35 \text{ MW} \times \text{cm}^{-2}$.

Spectroscopic diagnostics were used to determine the time-resolved electron density, excitation temperatures and three-body electron-ion recombination rate constants.

Acknowledgments: We gratefully acknowledge the support received in part by the DGICYT (Spain) project MICINN: CTQ2013-43086 for this research.

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Time and space-resolved study of a laser-produced SiO plasma

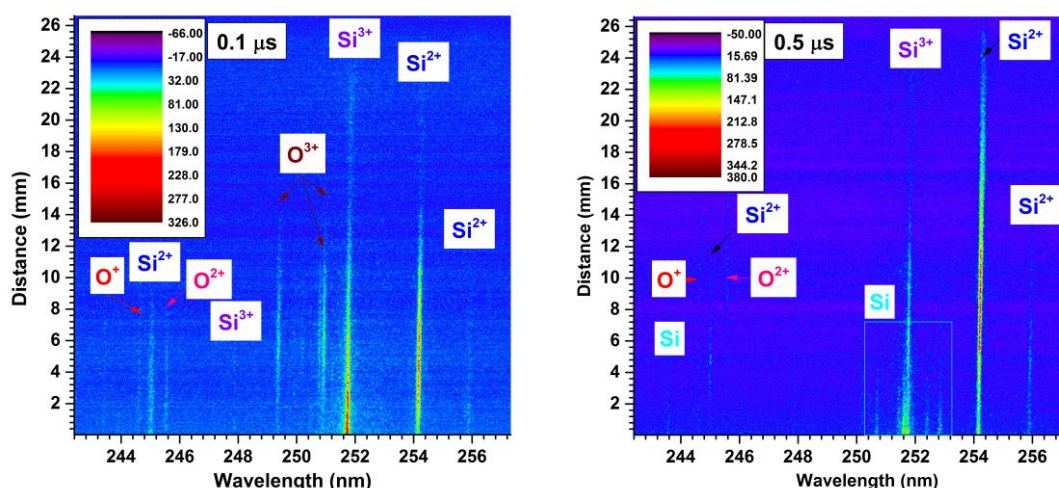
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Nanosecond laser-sample interaction involves complex processes of heating, vaporization, ejection of ions, electrons, atoms and molecules, shock waves, plasma initiation, expansion and recombination. Analysis of laser-produced plasmas (LPPs) can be a very challenging task considering its transient nature as well as large variations in plasma properties with space and time. There are numerous diagnostic techniques that can be employed to study the characteristics of laser ablation such as shadowgraphy, interferometry, self-emission imaging using fast gated cameras, optical emission spectroscopy (OES), Langmuir probe, Faraday cup, etc. Each plasma diagnostic tool has its own advantages and limitations. In this work, we present a spatial and temporal analysis of the LPP generated on silicon monoxide SiO. Time-resolved two-dimensional (2D) OES is used to study the expanded distribution of different species ejected during CO₂ laser ablation.



The formed plasma was found to be strongly ionized yielding Si⁺, O⁺, Si²⁺, O²⁺, Si³⁺, O³⁺ species, rich in neutral silicon and oxygen atoms and very weak molecular bands of SiO [1]. Typical 2D spectral images (transversely excited atmospheric CO₂ laser fluence = 72 J/cm² and $P_{\text{air}} = 0.01$ Pa) recorded at 0.1 and 0.5 μs delays for a fixed gate width time of 0.1 μs are given in the above figures. The results show a faster decay of Si³⁺, O³⁺, O²⁺, and Si²⁺ than of O⁺, Si⁺ and Si. The Stark broadening of isolated Si⁺ lines was employed for deducing the electron density during the plasma expansion. The relative intensities of some Si²⁺ lines were used to calculate the time evolution of the plasma temperature. By tracking the maximum intensity displacement for some species, its corresponding velocities were deduced.

Acknowledgments: We gratefully acknowledge the support received in part by the DGICYT (Spain) project MICINN: CTQ2013-43086 for this research.

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P8

Theoretical studies of the reactions $\text{LiH} + \text{H}$ **Wenli Wang¹, Carolina M.A. Rio¹ and João Brandão¹**¹ Universidade do Algarve, Faro, Portugal*E-mail: wwang@ualg.pt*

The lithium chemistry has received a great attention in recent years due to the importance that LiH molecules and its ionic variants can have in the primordial universe. The reaction $\text{LiH} + \text{H} \rightarrow \text{Li} + \text{H}_2$ is considered to contribute to LiH depletion, while the hydrogen-exchange reaction $\text{LiH} + \text{H} \rightarrow \text{LiH} + \text{H}$ leads to the retention of LiH in this process.

In this work we report our recent studies on the long-range interactions between the reactants of the title reactions and reaction dynamics calculations using classical trajectory methods and accurate quantum dynamic calculations.

Spectroscopic analysis of TSAG and TSLAG crystals

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Terbium aluminium garnet, $\text{Tb}_3\text{Al}_2\text{Al}_3\text{O}_{12}$ (TAG) has been exploited as a potential candidate to substitute yttrium iron garnet (YIG) as Faraday rotator in optical isolators [1]. However, the growth of TAG crystals is no easy task due to its incongruent melting. Vllora *et al.* [2] showed in 2011 that the substitution of Al_2 by $\text{Sc}_{1.95}\text{Lu}_{0.05}$ allows to stabilize the garnet structure. Despite their promising results as Faraday rotators a detailed analysis of these stabilized garnets is still scarce and might contribute to a better understanding of their fundamental properties.

In this work, terbium scandium aluminum garnet (TSAG) and terbium scandium lutetium aluminum garnet (TSLAG) single crystals grown by the Czochralski technique [2] were investigated by structural and optical techniques. As-grown and thermal annealed TSAG and TSLAG samples were studied by Rutherford Backscattering Spectrometry (RBS), Raman spectroscopy, absorption, steady state photoluminescence (PL), PL excitation (PLE) and time resolved PL (TRPL). Additionally, the scintillation properties of the materials under gamma ray irradiation were evaluated.

The TSAG and TSLAG samples crystalline quality was found to increase after annealing in air at 1200 °C. In the 200-850 nm spectral range, the absorption is mainly due to Tb^{3+} intra-configurational $4f^8$ transitions. Additionally, an intense absorption line occurs at 317 nm in the expected inter-configurational region, followed at shorter wavelengths than 298 nm, by a steeper increase in the absorption due to the materials' band edge. Independently of the used selective excitation (above band gap, inter or intra-configurational excitation) the room temperature PL spectra is dominated by the emission arising from the $^5\text{D}_4$ multiplet to the $^7\text{F}_{6,5,4,3,2}$ levels of the Tb^{3+} ion, producing bright green luminescence due to the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition. The preferential population mechanisms of the samples were identified and the recombination models of luminescence are discussed.

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Optical and Structural analysis of LYSO:Ce crystals

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Rare earth orthosilicates are among the most widely used scintillator materials in the last decades. Particularly, lutetium-yttrium oxyorthosilicate (LYSO), is known for its great potentialities in the development of detectors for medical imaging [1]. Despite the interest in such applications the investigation of this material fundamental properties is still scarce nowadays. Therefore a more detailed analysis is required in order to improve the material in-depth knowledge.

In this work the spectroscopic properties of commercial cerium doped lutetium oxyorthosilicate crystals (LYSO:Ce) were investigated by Raman spectroscopy, steady state photoluminescence (PL), PL excitation (PLE), time resolved PL (TRPL) and gamma ray excitation.

The crystals have monoclinic crystalline structure (C2/c space group) and exhibit at 14 K two main emitting optical centers with distinct spectral shapes and peak positions assigned to the $5d^1 \rightarrow 4f$ transitions from the Ce^{3+} ions in two distinct sites in the studied host. By using site selective excitation (266 nm; 325 nm) and temperature dependent PL (14 K to room temperature) the spectral evolution of the LYSO:Ce luminescence was investigated and models for the recombination processes were purposed. At RT the blue emission was found to be fast, in the order of tens of nanoseconds, and preferentially excited with 360 nm wavelength radiation.

The samples were further submitted to gamma-ray excitation in order to evaluate their energy resolution (12.5% at 662 keV) and quantum yield (26 photons/keV).

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P11

Induced molecular dissociations as a radiation damage descriptor: nanodosimetry

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Traditional dosimetry is based on the proportionality between the energy absorbed by the medium (absorbed dose) and the induced damage. This assumption applies for relatively high irradiated volumes and requires some equilibrium conditions. However, for small volumes being relatively far from the central irradiated areas these conditions are not observed and radiation damage is mainly driven by low energy secondary species (electrons and radicals) which induce molecular dissociations via electronic and vibrational excitations, electron attachment and chemical reactions. We will present here an integrated modelling procedure to simulate particle radiation tracks including those of all generated secondary species and their further interactions with the molecular constituent of the medium. For any selected volume of interest, this model provides not only the total energy transferred to that area but also the number and type of interactions taking place in it [1].

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Ultrafast Photochemistry of Solvated p-Toluidine

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Aromatic chromophores, which are characterized by having strong $\pi\pi^*$ transitions, provide molecular systems with the ability to efficiently absorb UV-Vis radiation. Additionally, often mixed with the $\pi\pi^*$ states, $\pi\sigma^*$ type transitions present dissociative character along the X-H stretching coordinate. As a consequence, the preparation of the molecule into these $\pi\sigma^*$ states gives rise to complicated photophysical and photochemical processes in the condensed phase, which are thought to be responsible for key phenomena involving proton and electron transfers such as proton concerted electron transfer (PCET), photoacidity, etc.

Femtosecond transient absorption spectroscopy has been employed to investigate the photochemistry of the p-toluidine molecule in methanol and cyclohexane. The studied range of excitation energy, 267-290 nm, covers the absorption of the lowest $\pi\pi^*$ excitation (S_1) and the dark state $\pi\sigma^*$ (S_2), which in the gas phase is found among two bright $\pi\pi^*$ transitions.^[1] The temporal evolution of the molecule, with a resolution of 75-100 fs has been tracked by collecting broadband absorption spectra from 290 to 750 nm. The observed transient bands, which are preliminarily assigned to the solvated electron, p-toluidine radical, p-toluidine cation and the p-toluidine S_1 excited state, reveal a very complex photochemistry that is being analyzed with the help of *ab initio* calculations.

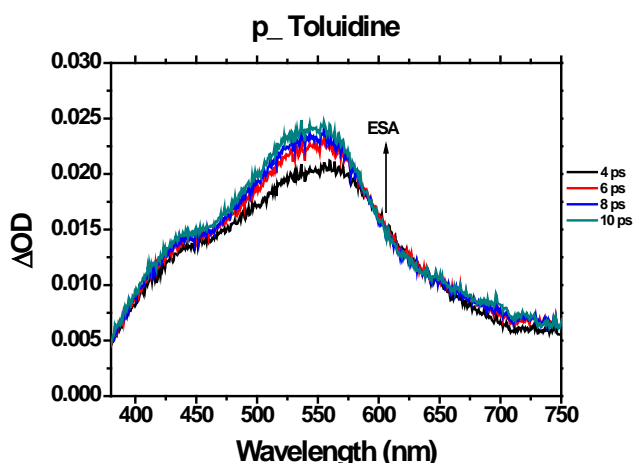


Figure. Transient absorption spectra of p-toluidine in methanol after excitation at 277 nm at different delays. Vertical arrow indicate evolution of excited state absorption (ESA).

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Ultrafast Photochemistry of N-Methylpyrrole

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The understanding of photochemical processes that biologically relevant molecules undergo in the gas phase, in particular, aromatic chromophores as Pyrrole and some of their simple derivatives as N-methylpyrrole, which are important building blocks of proteins and nucleic acids, has gained a broad interest.[1]

Our group is interested in understanding the ultrafast relaxation mechanisms involving $\pi\sigma^*$ surfaces in a set of isolated aromatic chromophores. Herein, we present a femtosecond resolved study with ion/electron detection on the ultrafast evolution of NMP after excitation in the (244-217) nm range of UV absorption spectrum, with the required sensitivity to measure mayor and minor relaxation channels simultaneously. The technique has been successfully applied, providing a general view of the photophysics of the system.

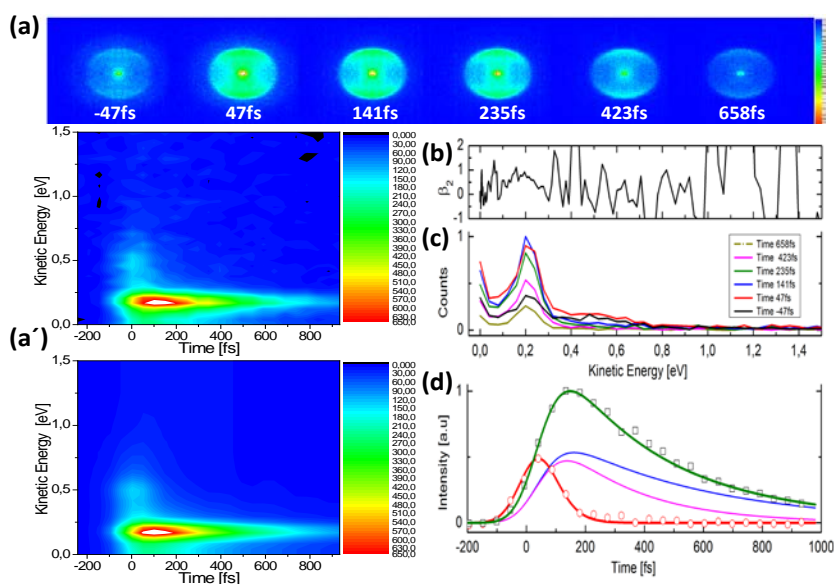


Fig. (a) Time-resolve photoelectron spectra of NMP^+ excited at 222nm and probe with 400nm photon. A sequence of the symmetrized raw images at selected pump-probe delays shown on the top. (a') The obtained fit of Time-resolve photoelectron spectra of NMP^+ . (b) β_2 Anisotropy parameter obtained at zero delay time. (c) Photoelectron spectrum at selected pump-probe delays shown. (d) Time dependence of the electron signal integrated in the regions delimited by the solid lines, the dots correspond to the experimental data, and the solid lines are the best obtained fits.

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Evaluation of the two-photon decay of the metastable $1s^2 2s 2p^3 P_0$ state in berylliumlike ions with an effective potential

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Detailed analysis of two-photon properties have revealed unique information about electron densities in astrophysical plasmas and thermal x-ray sources, as well as highly precise values of physical constants [1-2]. The study of two-photon decay in *high-Z* ions with one or two electrons also provided a sensitive tool for exploring subtle relativistic and retardation effects that occurs in such strong atomic fields. As in the case of *low-Z* ions, predictions for two-photon decay in these kind of ions are in good agreement with experimental data [3, 4].

Yet, scarce investigations have been performed so far for *ions with more than two electrons*. We address here to Berylliumlike ions with zero nuclear spin. Owing to the 0-0 selection rule, the first excited state $1s^2 2s 2p^3 P_0$ is metastable and its transition to the ground state $1s^2 2s^2^1 S_0$ is strictly forbidden for all single-photon multipole modes.

In this work, we evaluate decay rates considering a *relativistic* evaluation of the second-order summation in a *jj*-coupling active-electron model. To take into account the electron correlation, we incorporate the evaluation of the second-order summation via a finite-basis-set and an effective local potential, with a few key intermediate states calculated using the MultiConfiguration Dirac-Fock (MCDF) method.

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Micro analytical techniques to study the effects of abusive use of whitening products in dental enamel

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Aesthetic dentistry has received extensive focus in recent years, particularly because of the importance that people give to the appearance of the smile [1-3]. It is desired a smile as white as possible and preferably easy to obtain, effective, fast, economic and less invasive [2] [4]. In order to satisfy this need, a high diversity of Over The Counter (OTC) products have appeared on the market. OTC products can be easily bought by anyone and at a low cost, such as through internet sites. Many of these products have active agent concentrations well above the European Commission safety levels. Many authors have demonstrated a concern for safety and consequent effects on the tooth surface due to the possible abuse of these products [1]. The purpose of this in vitro study is to assess whether the elemental content and trace elements in tooth enamel are altered when bleaching the teeth with two different OTC bleaching gels, exceeding the recommendations of the manufacturer. In order to perform this evaluation, twelve healthy teeth that were extracted for periodontal or orthodontic reasons were used. Six samples were treated with the bleaching product (Teeth Whitening Home Kit) and the other six samples were treated with the OTC product (WHITE! -Bingo-UK) for the period of 39 days and stocked in human saliva between each application. The elemental content of each sample, before and after was obtained by micro Energy Dispersive X-ray Spectrometry (μ -EDXRF) and phosphate (PO₄³⁻) profile was evaluated with micro Raman Spectroscopy (μ -Raman). No significant differences were obtained in the elemental concentrations, however, the obtained results show that after 14 days the phosphate band decreased. This could happen due to superficial changes in the surface of the enamel that are not perceived in the XRF spectra because the analyzed volume is larger than the superficial approach that we find when using μ -Raman.

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P16

Applications of Raman spectroscopy in dental research: interface between dentin and direct composite restorations

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The restoration of a decayed tooth with a direct filling is one of the most common procedures in dentistry. Nowadays, the material most often used for this purpose is a resin composite. Since this material, a polymer, cannot adhere directly to the tooth, an intermediate adhesive system must be used to infiltrate the tooth structure and copolymerize with the restorative resin, under the application of a curing light source. The procedure involved in this kind of restorations is very sensitive, with some limitations and concerns, mainly due to the instability and durability of the interface, created by the adhesive, between the composite and the tooth substrate. Over time, degradation of the adhesive interface occurs, with subsequent nanoleakage of saliva and bacteria, leading to secondary decay and restoration failure.

In this study, we intend to study two alternative application protocols, beyond the manufacturer's recommendation, for one of the adhesives most frequently used in the clinical practice (Scotchbond 1XT, 3M ESPE). We also made a six-month ageing of the specimens after the restoration procedure, since it is more relevant for clinical practice than immediate results and since the consequences of the interface degradation become more evident over time. A gauge of the quality of the adhesive

interface is its degree of conversion (DC), since it has a direct correlation with the permeability of the interface. DC represents the amount of monomers that are chain linked and the greater the DC, the better the quality of the adhesive interface.

Six specimens (n=6) were made covering slices of dentin with the adhesive system, and a restorative resin above, both light cured independently. Three experimental groups were created according to the application protocols in study: 1) manufacturer's recommendations 2) three adhesive layers, 3) extra hydrophobic adhesive layer. The specimens were immersed in distilled water with an antibacterial and stored in a greenhouse, at 37°C, for 6 months. Raman spectra were acquired with the XploRA confocal Raman spectrometer and a 785 nm laser was used. Two line scans with steps of $\sim 1 \mu\text{m}$ were performed per specimen. DC was determined by comparing the band at $\sim 1608 \text{ cm}^{-1}$ in the C=C bond region with the band at $\sim 1638 \text{ cm}^{-1}$ not affected by polymerization.[1]

For all the application protocols, the DC varied throughout the hybrid layer, with lower values close to dentin and higher close to adhesive. Also, the two alternative protocols in study, achieved higher DC values than the manufacturer's. The DC for the two alternative protocols had always values above 80%, unlike the manufacturer's protocol that revealed DC values below 80% for the deepest measurements (near dentin).

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P17

Synchrotron radiation and Raman Spectroscopy for investigating tattoo inks.

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Tattooing practice is adopted worldwide and represents a socio-cultural phenomenon, but the injection into the skin of coloring (inorganic) agents, such as metals might pose a serious health problem. Nowadays, azo pigments are frequently used for tattooing because of their intensity color and their longevity [1]. The origin of chemical and toxicological specifications of these coloring agents are hardly known by the producers, the performers, or even by the professionals involved in these procedures and certainly not by the consumers [2].

A set of tattoo inks from the brand Kuro Sumi was analysed by means of Synchrotron-based X-ray Fluorescence spectrometry (Sy-XRF) at BAMline @ BESSY II and Raman Spectroscopy @ LIBPhys-UNL. The first qualitative results have shown potential hazardous substances. The color black has revealed to be coal by the Raman spectrum (figure 1a). However, a wide range of transition and heavy metals was revealed by Sy-XRF (figure 1b). A semi-quantitative analysis has revealed, in some cases, amounts higher than the allowed according to the resolution adopted by the Council of Europe on the safety of tattoos and permanent make-up (PMU) [3].

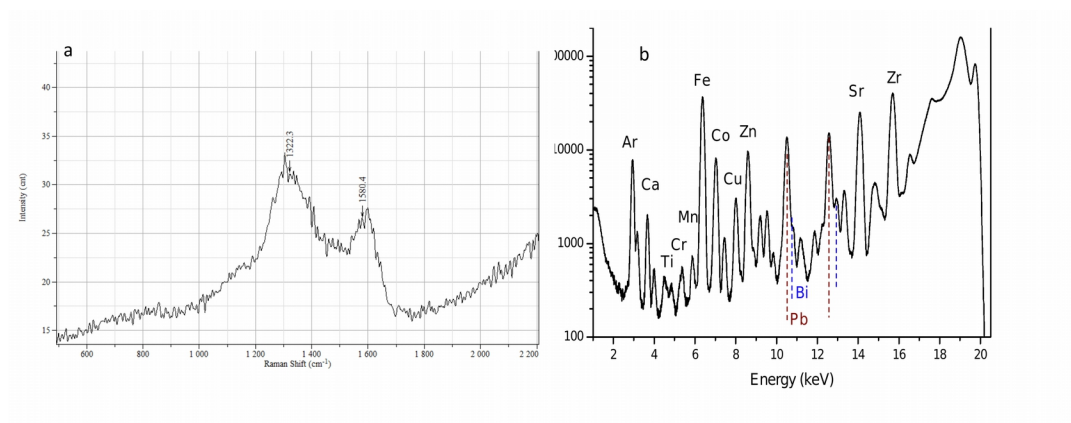


Figure 1 - Color black: a) Raman spectrum identifying coal; b) Sy-XRF spectrum identifying various

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White chalk ground layers of the 15th and 16th centuries paintings assessed by multianalytical spectroscopic techniques

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The phenomenon of reflection of light by chalk material, provided largely by calcareous (mainly cocoliths and calcispheres) is well known since 15th century. Its excellent workability comes from its fineness and softness. This is afforded by the rounded shapes of microfossil limestone, which facilitates the sliding in the application, thereby increasing the speed of handling. The fast application of the chalk as a painting ground layer allows its homogenization before drying, thus facilitates the aggregation of particles and their subsequent flattening. Concerning the grain size of the material and its coloring power, the thinner material gives the best color effect. These characteristics have been used to optimize the pictorial technique [1]. In addition to the fineness and smoothness characteristics, chalk has a special feature required and explored by the artists who used it - a particular light reflection. The mixture of chalk and animal glue has refractive index characteristics of surface light, since the chalk constituent elements remain suspended in adhesive bonds, causing the light to penetrate in depth and reflecting mainly in the surface. The oil mixed with chalk provides the phenomenon of deep light, since the slow-drying oil oxidation polymerization encapsulates the particles. This factor allows light to penetrate deeply, but being partially absorbed [1].

In this perspective, it is justified the existence of a characteristic painting ground layer stratigraphy containing a proteic binder in the lower region and in the upper region an oily binder. X ray fluorescence, SEM-EDS and μ XRD are the used analytical techniques to study these ground layers.

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FTIR Spectroscopy and X-Ray Diffraction to characterize Moroccan Cedrus wooden artifacts dating to 21th, 19th and 16th centuries

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Wooden artifacts from past civilizations are a large part of Moroccan national heritage. They are valuable and therefore require careful attention, conservation and study. The present state of conservation of wooden objects of cultural heritage is a serious problem for the restorers' community all over the world. There is a combination of degradation factors. So, in order to elucidate both the nature of the degradation process, and to develop a new consolidation and conservation technique for ancient wooden artifacts, it's primordial to study the different changes of wood components. In this study, we will provide an overview of chemical and structural changes of four rare samples dating to 21th, 19th, 16th centuries, and the last one is taken from a dead fraction of tree. The comparison of these historical wood samples during its long-term use and storage has been made using FTIR spectroscopy, and X-Ray Diffraction.

FTIR results suggest that the observed decrease of intensities of bands assigned to different vibrations of lignin and carbohydrates, with appearance of typical bands assigned to photooxidation reaction such as quinone (photooxidation of lignin) refer to the destruction phenomenon that can affect the samples' compounds during the ageing process.

X-Ray Diffraction technique was used to define the wooden degradation that was observed for old samples by decreasing crystallinity index with insignificant changes in the size of crystallites, except for some aged wood which can be justified that partially degraded cellulose was capable of forming new and larger crystals, or caused by reduction of the crystalline fractions of wood, and, consequently, to the enrichment of the relative crystalline content. So, the effect of degradation was less evident on microcrystalline structure.

Finally, scientists, art historians and conservators' sectors must establish more detailed data records to evaluate the adequate conditions of archaeological wood in order to protect it from extinction.

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Assessment of postmortem elemental characterization of 18th century human remains by EDXRF

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The human remains of 15 individuals buried between the mid-18th to early 19th century, were analyzed by energy dispersive X-ray fluorescence technique (EDXRF), to study the elemental composition. The aim of this research is to evaluate dietary behavior, environmental surroundings and exposure to toxic elements of a particular population. Furthermore, there is a possibility of post-mortem contamination from the surrounding soil of the burial site.

The samples, bone, hair, teeth and brain matter, were collected from a church in Almada (Portugal), called Ermida do Espírito Santo, located near the Tagus River.

The results were obtained using two setups: one with triaxial geometry that allows improved detection limits for lower Z matrices[1], and another setup that allows micro beam as well as performing analysis under a vacuum system which improves the detection limits for lighter elements.

The detected elements for both setups were P, K, Ca, Fe, Cu, Zn, Br, Sr and Pb. It was observed high levels of Zn and Sr for bones which are indicative of dietary habits rich in proteins and fish. The results show a particular individual that has high concentrations of Pb, especially in brain matter, pulp and root of the tooth and in spongy bones, reaching about 600 µg/g in the ribs. Moreover, there is also a woman over 50 years old, which presented an extremely high concentration of Hg in the hair,

about 60000 $\mu\text{g/g}$, and a lower, but still representative, concentration in the skull of 43 $\mu\text{g/g}$.

Good agreement was observed between the results obtained by the two setups.

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P21

Multielemental composition of vegetables grown in agricultural soils irrigated with reclaimed waste waters Application of microanalytical X-ray fluorescence

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Reclaimed wastewater coming from treatment plants (TWW) has been increasingly used as an additional water supply on the best management practices of hydric resources in water-deficient regions. TWW can be used for different applications being the irrigation in agriculture one of the most commonly used ones. Despite the fact that the organic matter and nutrients present in the TWW provide fertilizer value, giving benefits on the soils and on the crops, the presence of microcontaminants may hinder a more confident and widespread application.

The aim of the present contribution is to contribute to the assessment of the effects of TWW irrigation in elemental composition of crops. In this context, Na, Mg, Al, Si, P, S, Cl, K, Ca, Mn, Fe, Cu, Zn, Br, Rb and Sr were determined in *Raphanus sativus* (radish) and *Daucus carota* (carrot) specimens grown in experimental plots irrigated with TWW (from secondary and tertiary treatments) and with tap water (control samples). Multielemental analysis was performed using benchtop micro X-ray fluorescence spectrometry systems (μ -XRF) that allow the rapid analysis of vegetation material without complicated previous sample pre-treatments [1]. The lateral resolution of the μ -XRF (reaching down to 25 μ m) was thought to be small enough to study the distribution of the aforementioned elements within vegetable sections providing relevant information not available from standard bulk techniques such as plasma emission spectrometry and atomic absorption spectroscopy. Additionally, in order to correlate the fluorescence intensity of an element (from two-dimensional mappings) and its concentration, a set of several vegetation certified reference materials prepared in the form of pressed pellets were analysed using the same analytical conditions used in the analysis of the vegetables grown in agricultural soils irrigated with reclaimed waste waters.

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Multianalytical techniques used to characterize the work of
José de Escovar, the Alentejo most famous 16th-17th mural
painter, in the Chapel of Souls

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José de Escovar is a well-known artist in Alentejo due to the *fresco* technique that he profoundly used to decorate a significant number of churches in this region [1, 2]. Nevertheless, most of his work is not documented and the authorship is based mainly on stylist aspects. Additionally, very few works using the oil technique are attributed to Escovar. For this reason, the case of the parish church of Vila Nova da Baronia, Alvito, is a singular one, since the contract between the master and the costumer survived and it certifies that Escovar was the responsible for the decoration of the walls and the altarpiece of the Chapel of Souls. In order to better define and compare Escovar *fresco* and oil painting techniques in this chapel and crosscheck with other works in the region, characterization of the materials used in both supports was carried out using several in situ techniques and microsampling. X ray fluorescence spectrometry supplied information about the pigments used by the master, while micro Raman and micro Fourier transform infrared spectroscopy completed the

knowledge about pigments and binders and varnishes, respectively. Other characterization techniques that were also fundamental for the characterization of the technical work and pallet definition were technical photography, spectrophotometry, micro X ray diffraction and scanning electron microscopy with coupled energy-dispersive X-ray spectrometry.

Acknowledgement

The authors acknowledge Fundação para a Ciência e Tecnologia for financial support (Post-doc grant SFRH/BPD/63552/2009) through program QREN-POPH-typology 4.1., co-participated by the Social European Fund (FSE) and MCTES National Fund and Project PRIM'ART PTDC/CPC-EAT/4769/2012, financed by national funds through the FCT/MEC and co-financed by the European Regional Development Fund (ERDF) through the COMPETE - Competitiveness Factors Operational Program (CFOP)

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A review on (un)stability of HgS in alkaline environments, green and blue basic copper carbonates in 16th-17th frescoes paintings

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The selection of proper pigments for painting in *fresco* were the major concerns of almost all painting treatises authors since Classical Antiquity¹⁻⁴. Only natural pigments were recommended, specially earth pigments such as ochres, burnt and raw umbers. In what concerns mercury sulphide (HgS) or the mineral basic carbonate copper malachite $\text{Cu}_2(\text{OH})_2\text{CO}_3$ and azurite $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$, their use in walls were mainly advisable with a *secco* technique due, apparently, to lime incompatibility and/or UV instability. However, mural painters did not seem to have always followed these recommendations and the three mural paintings under study appear to be a clear example of it. A review on the pigments nature and (un)stability in alkaline environments is presented in this paper through elemental analysis by portable X-ray fluorescence, complemented by Optical and electronic scanning microscopy and Raman spectroscopy.

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A robust large area x-ray imaging system based on 100 μm thick Gas Electron Multiplier (GEM)

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Imaging applications with Gas Electron Multipliers as amplification devices traditionally make use of discrete channel readout. These solutions provide excellent spatial resolution (of the order of hundreds of μm) for areas as large as $10 \times 10 \text{ cm}^2$. However they require complex and expensive electronic systems. For applications where spatial resolutions in the order of the mm are required, a simpler and cheaper solution is to determine the position of the interaction using the resistive charge division method. This solution greatly simplifies the electronic system, since it requires a minimum of only 4 readout channels to achieve 2D imaging over large areas. It is however very much dependent on obtaining a high signal-to-noise ratio. This means that the GEM's must be operated at high gain and, in some cases, near the discharge limit. The consequence of operating at such a regime is the higher probability of discharge, hence higher probability of detector damage.

We have developed a non-standard GEM, made from a 100 micron thick kapton foil (2-fold thicker than standard GEM's). The 100 micron thick GEM is produced using the same wet etching technique as the standard GEM and has already proven [1] to be virtually immune to the damage caused by discharges, creating a robust detector that can safely operate at the high gains necessary to achieve an adequate signal-to-noise ratio for imaging applications.

In this work we present the results obtained with a detector composed by two 100 micron thick GEM and a $10 \times 10 \text{ cm}^2$ 2D readout electrode with resistive lines. We have recorded energy resolution of 21% and charge gains above 104 when the detector was irradiated with 5.9 keV X-rays emitted by a ^{55}Fe radioactive source. We also present some $10 \times 10 \text{ cm}^2$ images acquired with our detector when irradiating a target with X-rays from an X-ray tube and the results of our investigations aiming to maximize the signal-to-noise ratio.

Trace Element Characterization of Dried Baby Shrimp: Bulk Analysis by Portable High Definition XRF compared to Elemental Mapping by Synchrotron Radiation μ XRF using a MAIA detector

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A study of the trace element content of Dried Baby Shrimp was conducted as part of a broader research investigation into exposure to toxic metals/metalloids among the ethnic Chinese community in Upstate New York. During field visits, samples were analyzed by a new portable XRF Analyzer (HD Mobile), which uses doubly curved crystal optics to provide focused monochromatic X-Rays. A total of 75 Chinese and 25 non-Chinese homes were visited, and more than 1,500 samples were analyzed including various foods, personal care products and traditional Chinese medicines.

During the home visits, three Chinese families provided Dried Baby Shrimp samples for analysis. These were obtained from local Chinese markets or home made and are consumed without separating the tail from the shrimp head. Preliminary results obtained by the HD-Mobile indicated a arsenic (As) content (5-30 $\mu\text{g/g}$) that warranted further investigation from a public health perspective.

Further studies of the As content/elemental distribution in these baby shrimp samples were conducted at bend magnet station F3 at the Cornell High Energy Synchrotron Source (CHESS). Monochromatic X-rays of 17.2 keV were selected using a Si(220) monochromator and focused to a 20- μm diameter beam using a single bounce monocapillary (PeB605) fabricated at CHESS [1]. XRF data were collected by a 384-pixel Maia detector system [2]. This detector enhances trace elemental sensitivity affording high definition imaging in much shorter time than was previously possible.

XRF elemental mapping of the Dried Baby Shrimp provided high resolution images for As, Ca, Br, (among others), and show localized accumulations of As within the abdominal body. Quantification was achieved using a reference material pellet (NRC-CNRC TORT-2 Lobster hepatopancreas). Results were in reasonable agreement with those obtained in the field using the HD Mobile. Speciation analysis of the shrimp is currently underway to identify which As compound(s) are present.

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EDXRF imaging system based on a gaseous detector: characteristics and adequacy

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When large areas of detection with position and energy resolution are needed in the radiation detection field, micropatterned gaseous detectors (MPGDs) are an interesting and unique solution in some cases.

In this work, a characterization of a EDXRF system based on a THCOBRA detector is presented. The system is composed by an external radiation source (X-ray tube), a pinhole and the gaseous detector, filled with Ne/5%CH₄. The THCOBRA [1] is a MPGD with two charge multiplication stages, which makes it a simple and cost effective device.

The ‘holy grail’ of EDXRF elemental imaging is acquiring elemental images of areas larger than the probe beam spot size. The use of a large area elemental imaging MPGD is an elegant approach for a long standing problem.

The low cost detector based on the THCOBRA device has an active area of 10×10 cm², making it very promising for this kind of purposes. The 2D-THCOBRA have already shown good prospects and promising results in the field [2]. Within this project a characterization of the whole system will be presented as well as its adequacy for this applications. Position resolution and elemental map discrimination as a function of pinhole diameter, image magnification and detector parameters, such as detector energy resolution and energy linearity will be shown.

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Acknowledgements: A. L. M. Silva is supported by the QREN programme Mais Centro – Programa Operacional Regional do Centro, FEDER and COMPETE, through the project Biomaterials for Regenerative Medicine (CENTRO-07-ST24-FEDER- 002030).

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High pressure Xenon GSPC based detector for hard X-ray and gamma spectroscopy

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In this work we will present the initial characterization of a high pressure Xenon Gas Scintillation Proportional Counter (GSPC) envisaging gamma spectroscopy, covering the energy range from tens to few hundreds keV.

The detector comprises a high pressure absorption region where the gamma photons are converted into electrons followed by a scintillation region where the light is produced through the electroluminescence process. Finally, the photons are collected through a PhotoMultiplier Tube (PMT) producing a electrical signal with an amplitude proportional to the energy of the detected gamma photons.

The detector performance is characterized according to gain and energy resolution as function of the gas pressure, ranging from 1 to 10 bar, and electric fields in the drift and scintillation region and for different photons energy ranging from a few tens a few hundreds keV. High signal to noise ratio was achieved as well as energy resolutions close to the intrinsic values.

The detector system and detailed results will be presented, as well as the possibility to replace the PMT by a large area and low cost position sensitive gaseous photomultiplier[1] that will allows position sensitivity of the gamma interaction in the GSPC detector volume.

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