IBER2019

IBERIAN JOINT MEETING ON ATOMIC AND MOLECULAR PHYSICS

Book of Abstracts

ÉVORA | 10-12 July 2019

UNIVERSITY OF ÉVORA

Welcome

The Joint Iberian Meeting on Atomic and Molecular Physics (IBER) is the biannual conference organized jointly by the Atomic and Molecular Physics Specialed Group (GEFAM) of the Spanish Royal Society of Physics and the Portuguese Society of Physics.

The main purpose of this series of IBER conferences is to bring together scientists of Iberian community dedicated to Atomic and Molecular Physics and related areas of to facilitate the interaction and exchange of knowledge between their research groups. Researchers and scientists from all over Europe and the world are invited to attend this conference and share knowledge with the Iberian community.

About Évora

Évora is a Portuguese city in the municipality of Évora. This small but beautiful city is located in the Alentejo, a large region of wide plains on the south of Portugal, bordered on the North by the Tagus River and on the South by the region of Algarve.

The city is relatively close (140 km) from the capital of Portugal, Lisbon, and 80 km far from the Spanish border (Badajoz). The city has a very well preserved historical centre, partially enclosed by Medieval walls, where many valuable monuments can be visited: a Roman temple, a Museum, churches and chapels, university, etc.

Évora is a UNESCO World Heritage Site (UNESCO - Historic Centre of Évora) and also a member of the Most Ancient European Towns Network.

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SCIENTIFIC PROGRAM

Wednesday, 10 July

Colégio Luís António Verney, Anfiteatro 2

Session 1 - Luísa Carvalho	
08:00 - 08:45	Registration
08:50 - 09:00	Welcome
09:00 - 09:30	IL 1 - Catarina Miguel - “*And there will be light – unveiling molecular specificities of ancient manuscripts by spectroscopic techniques*”
09:30 - 10:10	PL 1 - J. Pisonero - “*Glow Discharge spectroscopy and laser-induced plasma spectroscopy for direct chemical characterization of solid samples*”
10:10 - 10:25	OC 1 - Pedro Barrulas - “*LA-ICP-MS in Cultural Heritage Studies and Archeological Materials*”
10:25 - 11:00	Coffee Break + Poster Session
Session 2 - Miguel Reis	
11:00 - 11:40	PL 2 - A. Brunetti - “*X-ray fluorescence and Monte Carlo simulation as a tool for quantitative chemical composition determination: limits of applicability*”
11:40 - 11:55	OC 2 - Sofia Pessanha - “*Non-invasive determination of gold leaf thickness in Indo-Portuguese panel paintings using X Ray Fluorescence spectrometry and Monte Carlo simulation*”
11:55 - 12:10	OC 3 - Sara Valadas - “*Spectroscopy and materials study of easel paintings: discoveries & challenges*”
12:10 - 12:55	OC 4 - V.Antunes - “*Analytical approach on materials and techniques of Jorge Afonso workshop compared to Flemish painting*”
12:25 - 13:05	PL 3 - Ignasi Queralt - “*Usefulness of X-ray spectroscopy data in forensic scienses*”
13:05 - 14:30	Lunch + Poster session
Session 3 - Jose Miguel Vadillo	
14:30 - 14:45	OC 5 - Alberto Lesarri - "*Intermolecular clusters in jet expansions: Molecular rotation spectra of sulfur hydrogen bonded clusters*"
14:45 - 15:15	IL 2 - Pierre Çarçabal - "*Gas phase spectroscopy of biomolecules and their mimics*"
15:15 - 15:30	OC 6 - P.Ortega - "*Spin-forbidden addition of O2 catalyzed by DpgC*"
15:30 - 15:45	OC 7 - I. Léon - "*The dipeptide Ala-Ala isolated in the gas phase*"
15:45 - 16:30	Coffee Break + Poster Session
Session 4 - Thomas Stöhlker	
16:30 - 17:00	IL 3 - J.M. Sampaio - "*Atomic Physics Inputs for Enhanced Targeted Therapy*"
17:00 - 17:15	OC 8 - I.Otel - "*Development of Raman instrumentation for in vivo dental research*"
17:15 - 17:30	OC 9 - P.Carvalho - "*Preliminary studies with an EDXRF imaging system based on a 2D-THCOBRA detector for applications in biological tissues*"
17:30 - 17:45	OC 10 - Micaela Fonseca - "*Complementary use of PIGE and Raman spectroscopy for the eval-uation of Fluorine uptake and enamel demineralization caused by Gustatory Stimulants of Salivary Secretion*"
17:45 - 19:00	Poster session

🟨 PL - Plenary Lecture 🟥 IL - Invited Lecture 🟩 OC - Oral Communication

Thursday, 11 July

Colégio Luís António Verney, Anfiteatro 2

Session 5 - José Marques	
09:00 - 09:40	PL 4 - Thomas Stöhlker - "*Relativistic Quantum Dynamics Explored For High-Z Ions*"
09:40 - 10:10	IL 4 - Manuel Melle-Franco - "*Novels materials and virtual science, are we there yet?*"
10:10 - 10:25	OC 11 - M. L. Murillo-Sánchez - "*Structural dynamics effects on the UV electronic predissociation of alkyl iodides at 201 nm*"
10:25 - 11:00	Coffee Break + Poster Session
Session 6 - Asier Longarte	
11:00 - 11:40	PL 5 - Martin Quack - "*Parity Violation in Chiral Molecules: From Theory towards Spectroscopic Experiment and the Evolution of Biomolecular Homochirality*"
11:40 - 12:10	IL 5 - José Miguel Vadillo - "*Phase-change microscopy in combination with spectroscopy to understand early processes during femtosecond laser ablation*"
12:10 - 12:25	OC 12 - S.Sério - "*Graphene Oxide thin fils for hybrid solar cells: characterization by VUV, UV-visible, infrared and impedance spectroscopy*"
12:25 - 12:40	OC 13 - P.Amaro - "*Strong contribution of resonant excitation in the 3s-2p line formation of Fe XVII*"
12:40- 12:55	OC 14 - Iker Lamas - "*Ultrafast Nonradiative Relaxation Channels of Azaindoles*"
13:00 - 14:30	Lunch + Poster session
A Tribute to Delgado Barrio	
14:30 - 15:00	P.Villareal - "In Memoriam of Gerardo Delgado-Barrio"
15:00 - 15:30	R. Prosmiti - "Benchmarking interactions in guest-free/host clathrate hydrate"
15:30 - 16:00	A. García-Vela - "Weak-field coherent control of photodissociation in polyatomic molecules"
16:00 - 16:30	Coffee Break
16:30 - 19:00	Free Time + Conference Dinner

🟨 PL - Plenary Lecture 🟥 IL - Invited Lecture 🟩 OC - Oral Communication

Friday, 12 July

Colégio Luís António Verney, Anfiteatro 2

Session 7 - Jorge Miguel Sampaio	
09:00 - 09:40	PL 6 - Andreas Karydas - "*Experimental and theoretical study of the Ge-L emission spectrum excited by tunable synchrotron radiation near and above the Ge K-shell threshold.*"
09:40 - 10:10	IL 6 - Miguel Reis - "*X-ray Microcalorimeter Spectrometers a new window to previous unsuspected problems in atomic and molecular physics.*"
10:10 - 10:25	OC 15 - M.Guerra - "*High-accuracy X-ray spectrometry for S.I. traceable calibration standards*"
10:25 - 11:00	Coffee Break + Poster Session
Session 8 - Raul Montero	
11:00 - 11:40	PL 7 - Laurent Nahon - "*Isolated species in interaction with high resolution variable polarization VUV synchrotron radiation from the DESIRS beamline @ SOLEIL.*"
11:40 - 12:10	IL 7 - Rosário Correia - "*In-situ probing laser-induced chemical reactions at the semiconductor's surfaces by Raman spectroscopy*"
12:10 - 12:25	OC 16 - P.G.Jambrina - "*Quantum Stereodynamics at cold energies*"
12:25 - 13:10	PL 8 - Luis Roso - "CPA lasers: the ultrafast ultraintense scientific revolution"
13:10 - 14:30	Lunch + Poster session
Session 9 - Ana Luísa Silva	
14:30 - 15:00	IL 8 - Maria Raposo - "*Detection of Triclosan in Complex Molecular Matrices by Impedance Spectroscopy: difficulties and achievements*"
15:00 - 15:30	IL 9 - Tomás González-Lezana - *A theoretical investigation of fhe dynamics of atom-diatom reactions*
15:30 - 16:00	OC 17 - A.Camiruaga - *DNA base...Xanthine aggregates: a spectroscopic study of non-covalent interactions in purine derivatives*
16:00 - 16:30	Closing

🟨 PL - Plenary Lecture 🟥 IL - Invited Lecture 🟩 OC - Oral Communication

Plenary Lectures

Jorge Pisonero **-** Glow Discharge spectroscopy and laser-induced plasma spectroscopy for direct chemical characterization of solid samples.

Antonio Brunetti - X-ray fluorescence and Monte Carlo simulation as a tool for quantitative chemical composition determination: limits of applicability.

Ignasi Queralt - Usefulness of X-ray spectroscopy data in forensic sciences.

Thomas Stöhlker - Relativistic Quantum Dynamics Explored For High-Z Ions.

Martin Quack - Parity Violation in Chiral Molecules: From Theory towards Spectros- copic Experiment and the Evolution of Biomolecular Homochirality.

Andreas Karydas - Experimental and theoretical study of the Ge-L emission spectrum excited by tunable synchrotron radiation near and above the Ge K-shell threshold.

Laurent Nahon - Isolated species in interaction with high resolution variable polarization VUV synchrotron radiation from the DESIRS beamline @ SOLEIL.

Luis Roso - CPA lasers: the ultrafast ultraintense scientific revolution

Glow Discharge spectroscopy and laser-induced plasma spectroscopy for direct chemical characterization of solid samples.

Jorge Pisonero, Cristina González-Gago, Luis Fernández, Jonatan Fandiño, Cristina Méndez, Ana Méndez, and Nerea Bordel.

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Atomic spectroscopy techniques, such as Glow Discharge (GD) spectroscopy or Laser Induced Breakdown Spectroscopy (LIBS), provide excellent analytical capabilities for the direct characterization of innovative materials, geological samples or biological tissues. These techniques provide high sensitivity and high spatial resolution (depth resolution and/or lateral resolution). Moreover, they complement other well-established analytical techniques, including Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS), providing higher sample throughput analysis or capabilities for fast stand-off or in-situ analysis. [1-3] In particular, pulsed GD plasma sources are known to provide a dynamic plasma due to the temporal evolution of applied power (with time domains along the GD pulse profile, denominated pre-peak, plateau, and after-glow). This pulsed mode allows high instantaneous power, increasing the atomization and ionization processes while minimizing thermal conversion of the sample.

In this work, we revise the fundamentals and evaluate the recent developments of Glow Discharge (GD) spectroscopy and Laser Induced Breakdown Spectroscopy (LIBS) for different applications related to direct solid analysis of samples, including depth profiling and imaging applications.

Acknowledgements

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X-ray fluorescence and Monte Carlo simulation as a tool for quantitative chemical composition determination: limits of applicability

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X-ray fluorescence (XRF) is widely used as an experimental technique for the determination of the chemical composition of a sample under examination. It requires relatively cheap instrumentation which can also be easily made to be portable. This is particularly important for unmovable samples such as Cultural Heritage ones. However, XRF-based quantitative determination of the chemical contents, in some cases, can be a hard task, such as for ancient, corroded metallic artifacts. In fact, the presence of an irregular surface, the way the corrosion/ patina layers are, superimposed to others layers, makes the estimate of composition and structure complicated. Some help can be obtained by combining the XRF measurements with Monte Carlo simulation of the same measurement. The simulated spectrum obtained is then compared to the measured one: when the simulated spectrum matches almost perfectly the experimental one, the model of sample used for the simulation can be regarded as a good reproduction of the real sample. In this case both the composition and the structure of the multilayered structure could be estimated. However, a few years ago reasonable doubts were raised by [1] about the capability of XRF, with or without Monte Carlo simulation, to determine the real thickness of the layers. The error is this determination stems from the presence of void in the superficial layer, due to the corrosion or to the manufacturing technique such as in the so-called Tumbaga gold artifacts [2,3]. In the latter case the determination is also complicated by the presence of gradient-like variation from the surface to the bulk of gold concentration. In this work, we will try to answer to these quests and so to determine the limitation of application of this technique.

Acknowledgements

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Usefulness of X-ray spectroscopy data in forensic sciences

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X-ray spectroscopy (XRS) has been widely used in forensic science and related fields to check evidences for authentication or counterfeit identification. Main strengths of XRS are its non-destructive nature, thus preserving crime evidences and materials integrity, its ability to identify chemical compounds from its physical properties, to determine elemental chemistry and, in some cases, the possibilities to ascertain elemental speciation. Moreover the versatility of the X-ray techniques permits the analysis of very diverse materials, -inorganic, organic, metals-, in powder, solid or liquid forms.

Different X-ray spectroscopy based tools, just as many other analytical techniques, have been used in forensic science for several decades. Classical X-ray based techniques used in forensic work are X-ray powder diffraction (XRD), X-ray fluorescence (XRF), X-ray imaging and energy dispersion X-ray emission linked to an electron microscope (SEM-EDX). These complementary techniques are mainly used in both micro- and macrotrace analysis. Conventional macro-XRF, whilst attractive for the forensic analyst, sometimes cannot be applied because in the majority of cases crime scene specimens are microscopic in nature.

During the last two decades noticeable development was made in the instrumental aspects of X-ray spectrometry, especially in the improvement of X-ray optics and detection systems. All this resulted in a wide variety of instrumentation becoming available today. Significant advances in focusing optics (design of micro-focus beam sources, development of collimators and polycapillary lenses) have promoted the analysis of small regions by X-ray instrumentation. The use of automatized XYZ stages allows the possibility to choosing point, line profile or mapping analyses. A microscopic particle from a crime scene can be directly analysed without any sample preparation, simply located using optical cameras, and subsequently characterized for elemental content.

A selection of both real forensic evidence of different nature (glasses, cosmetics, gunshot residues, counterfeit currency) and Cultural heritage objects (ceramics, coinage, pigments) inspected by XRS methods (XRD, XRF, micro-EDXRF) are described.

Relativistic Quantum Dynamics Explored For High-Z Ions

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Relativistic interactions with matter involving heavy high-Z ions provide a unique testing ground for our understanding of quantum electrodynamics in the non-perturbative re- gime as well as of elementary atomic processes mediated by ultrafast electromagnetic interactions. For this realm of physics, the future international accelerator Facility for Antiproton and Ion Research (FAIR) has key features that offer a range of new and challenging research opportunities [1]. The proposed facility will provide the highest intensities for relativistic beams of both stable and unstable heavy nuclei at high nuclear charge, in combination with the strongest possible electromagnetic fields, thus allowing to extend atomic spectroscopy virtually up to the limits of atomic matter. In this talk, I will review recent experimental progress of atomic physics research in the realm of extreme electromagnetic field with particular emphasis on the novel research opportu- nities provided by the ion storage rings of FAIR. Examples include e.g. laser spectros- copy exploiting the large Doppler boost associated with relativistic ions, resonant co- herent excitation of ions passing through crystals at relativistic speed, as well as preci- sion x-ray spectroscopy. Experiments at the border between atomic and nuclear phys- ics will addressed in addition with emphasis on rare nuclear decay modes only possible for nuclei at high atomic charge states.

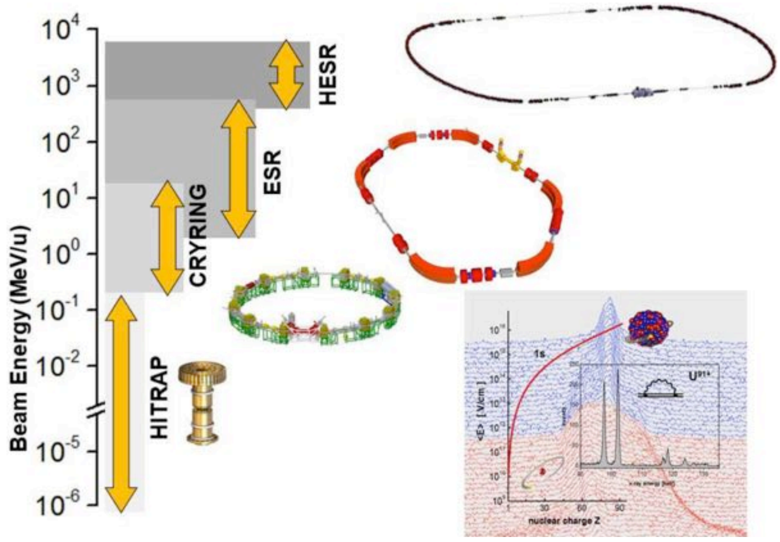

Figure 1. Portfolio of trapping and storage facilities for ions at the international FAIR facility [1]. In the lower right side of the figure, the Lyman x-ray spectrum of hydrogen-like uranium (U91+) is depicted along with a presentation of the electric field strength for K-shell electrons in H-like ions as function of the nuclear charge.

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Parity Violation in Chiral Molecules: From Theory towards Spectroscopic Experiment and the Evolution of Biomolecular Homochirality

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Symmetry with respect to space inversion was assumed to be fundamental in the theory of chemical bonding and stereochemistry. Symmetry and asymmetry are concepts, which are, indeed, used in a wide range of contexts, from the fundamental sciences, mathematics, physics, chemistry and biology to the arts, music and architecture [1]. We shall start with an introductory discussion of **three fundamental questions on symmetry, relating physics to molecular quantum dynamics and stereochemistry:**

1. To what extent are the fundamental symmetries and conservation laws of physics and their violations reflected in molecular quantum dynamics and spectroscopy, in general?

2. How important is parity violation –the violation of space inversion symmetry- for the quantum dynamics and spectroscopy of chiral molecules, in particular?

3. How important is parity violation for biomolecular homochirality, i.e. the quasi exclusive preference of L-amino acids and D-sugars in the biopolymers of life (proteins and DNA)?

The observation of biomolecular homochirality can be considered to be a quasi-fossil of the evolution of life [1], the interpretation of which has been an open question for more than a century, with numerous related hypotheses, but no definitive answers. We shall briefly discuss the current status and the relation to the other two questions. The discovery of parity violation led to important developments of physics in the 20th century and is understood within the standard model of particle physics, SMPP. For molecular stereochemistry it leads to the surprising prediction of a small energy difference D of the ground state energies of the enantiomers of chiral molecules, corresponding to a small reaction enthalpy for the stereomutation between the R and S enantiomers [2].This reaction enthalpy would be exactly zero by symmetry with exact parity conservation. Theory predicts D to be in the sub-femto eV range, typically, depending on the molecule (about D= 100 aeV for ClSSCl or CHFClBr, corresponding to a reaction enthalpy of about 10 pJ/mol). We have outlined three decades ago, how this small energy difference D might by measured by spectroscopic experiments [3], and recent progress indicates that experiment might be successful in the near future [4-7]. We shall discuss the current status of our experiments including alternatives pursued in other groups and the possible consequences for our understanding of molecular and biomolecular chirality as well as the design of molecular quantum switches for a possible future quantum technology and possible tests of CPT symmetry. For background reading see [1-7].

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Experimental and theoretical study of the Ge-L emission spectrum excited by tunable synchrotron radiation near and above the Ge K-shell threshold

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The cascade X-ray emission dominates the intensity of characteristic X-rays emitted after the relaxation of less-inner shell vacancies in the presence of deeper lying ones [1, 2]. Characteristic examples with relevance to X-ray Fluorescence (XRF) analysis are the cases when the exciting X-ray beam is adequately energetic to ionize the K or L atomic shells of an element, and thus the cascade emission of L or M lines takes place manifesting the contribution from the direct photoionization process [1, 2].

In the present work we have studied and compared experimental and theoretical Ge-L emission spectra. The measurements were carried out using with tunable monochromatic synchrotron radiation (3.7-14 keV) at the XRF beamline of Elettra Sincrotrone Trieste, operated using a Si(111) double crystal monochromator at 2.4 GeV electron beam energy [4]. As a target, a ~9.6 nm thin Ge deposited onto 200 nm silicon nitride membrane was used and the Ge-L x-ray emission spectrum was recorded by a silicon drift detector equipped with a polymer thin window [4]. A full ab initio theoretical investigation of the Ge-L x-ray emission processes was also performed based on a detailed straightforward construction of the cascade decay trees within the Pauli-Fock approximation.

Theoretical and experimental Ge-L spectra and production cross sections are compared and discussed with respect to the accuracy of advanced atomic models, but also concerning the characterization capabilities of x-ray fluorescence (XRF) analysis. Further on, the enhancement in the cascade Ge-L x-ray emission resulted due to the near K-edge phenomenon of Resonant Raman Scattering (RRS), is experimentally demonstrated and discussed.

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Isolated species in interaction with high resolution variable polarization VUV synchrotron radiation from the DESIRS beamline @ SOLEIL

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DESIRS is an undulator-based VUV beamline at SOLEIL featuring high flux, high resolution and fully variable and calibrated polarization.[1] Its scientific case is mainly focused into the study of neutral and ion spectroscopy, fragmentation, reactivity, photoionization dynamics and various types of circular dichroisms, on isolated species - from atoms, to cold molecules, chiral molecules, radicals, clusters, large biopolymers and nanoparticles - relevant to physics, chemistry, biology, astrophysics and planetary science.

After an introduction to its scientific case, the beamline and its two permanent endstations will be presented:

- a unique wavefront-division based Fourier-Transform spectrometer [2,3] for absorption spectroscopy, on closed- and open-shell systems, reaching an unprecedented resolving power of 106.
- a molecular beam chamber [4] coupled to a double imaging electron/ion coincidence spectrometer (i2PEPICO) [5], allowing the study of photoionization and dissociation dynamics on a wide range of gas phase targets.

Their capabilities will be illustrated by a few recent selected scientific results including diatomics high resolution absorption spectroscopy[6], DNA basis tautomers [7], water clusters [8], chiral amino-acids [9] and planetary-related nanoparticles [10] photoionization.

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CPA lasers: the ultrafast ultraintense scientific revolution

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Half of the Nobel Prize of 2018 has been awarded jointly to Gérard Mourou and Donna Strickland “for their method of generating high-intensity, ultra-short optical pulses” This is based on a work done at the University of Rochester around 1985. That pioneering work allowed the T3 lasers (for Table Top Terawatt) since the existing Terawatt lasers before 1985 were monster lasers. Today a Terawatt laser is reasonably compact, a Petawatt is possible (we have a Petawatt laser at Salamanca) and the road for the Exawatt is in progress. The talk will review the origins of this technology and the present status.

But there is another more relevant question, what is such a laser good for? Such extreme lasers can be tightly focused and the intensity -peak intensity- available for experiments can exceed 1022 W/cm2. What happens to an atom inside this extreme laser field? Answering this question you will understand why our Petawatt laser needs a license form the Consejo de Seguridad Nuclear (Nuclear Safety Council) in spite of being an optical (infrared) laser.

The focus of such intense lasers in a huge concentration of photons, infrared photons, impossible to be achieved by any other means, and represents an electric field that accelerates particles much more violently that any other accelerator in the world. Electron acceleration from rest to GeV energies is now achieved in many labs only in a few mm!!! Can we dream with future mini accelerators?

Also the fundamental limits will be discussed. Photons are bosons, so we could pack as many as we want of the same state? But many means infinite, or there is a limit? And then it will justified that the evolution of extreme intensity lasers will be relevant also in particle physics. However they have nothing to do with a laser beam, they are hard light bullets.

Figure 1. General view of the Salamanca Petawatt laser.

Acknowledgements

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Invited Lectures

Catarina Miguel - *And there will be light* – unveiling molecular specificities of ancient manuscripts by spectroscopic techniques.

Pierre Çarçabal - Gas phase spectroscopy of biomolecules and their mimics.

Jorge Sampaio - Atomic Physics Inputs for Enhanced Targeted Therapy.

Manuel Melle-Franco - Novel materials and virtual science, are we there yet?

José Vadillo - Phase-change microscopy in combination with spectroscopy to understand early processes during femtosecond laser ablation.

Miguel Reis - X-ray Microcalorimeter Spectrometers a new window to previous unsuspected problems in atomic and molecular physics.

Maria Correia - In-situ probing laser-induced chemical reactions at the semicon- ductor’s surfaces by Raman spectroscopy.

Maria Raposo - Detection of Triclosan in Complex Molecular Matrices by Impedance Spectroscopy: difficulties and achievements.

Tomás Gonzáles-Lezana - A theoretical investigation of fhe dynamics of atom-diatom reactions.

And there will be light – unveiling molecular specificities of ancient manuscripts by spectroscopic techniques

Catarina Miguel

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Illuminated manuscripts are among the most important testimonies of medieval and early Renascence Society. In this sense, the study of the materials used to produce illuminations allows us to infer more on the political, social and economic aspects behind the production of the manuscripts, contributing to its contextualization and its valorization [1, 2]. In this lecture, the use of spectroscopic techniques for material characterization of ancient manuscripts will be explored. For this, a set of eight national and international case studies making use of the FixLab and MoLab facilities of HERCULES Lab will be presented, and the results discussed.

Figure 1. In-situ h-XRF analysis of the Codex Manizola 116C, f.13v. ©BPE and HERCULES Lab.

Acknowledgements

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Gas phase spectroscopy of biomolecules and their mimics

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Carbohydrates are found everywhere in living systems and play a wealth of fundamental roles in immune response, infection and inflammation or cell growth.[1] They are also key players in cell-to-cell recognition at the molecular level. In glycotherapy mimic molecules are synthesized to exploit the natural potential of carbohydrates, while giving them an enhanced therapeutic activity. A good understanding of their conformational preference is then a prerequisite for the design of new mimetic drugs.

In the gas phase, we combine data provided by vibrational laser spectroscopy experiments and computational chemistry to establish the preferred conformation of complex molecules, either free of any perturbation in the case of the fully isolated system or influenced by few solvent molecules in hydrated clusters.

In this study, we have focused on the trisaccharide Lewis X antigen (LeX) which is recognized by several selectins involved in fundamental pathogenic biological processes. In solution, it has been shown that the bio-active conformation of LeX adopts a stacked arrangement of two of its components, stabilized by an H → CO "unconventional hydrogen bonding".[2] In contrast, a previous gas phase study showed that the intrinsic preferred conformation of Lewis X, free of any perturbation from the environment, was stabilized by cooperative OH → O interactions where the same two carbohydrate units are hydrogen bonded instead of stacked.[3] This suggests that the role of solvent molecules is central for the activity of LeX.

By studying the conformational preferences of the hydrated complexes of LeX studied by means of experimental double resonance IR/UV laser spectroscopy and computational quantum chemistry, we have shown that the bio-active conformation of LeX is solvent driven. We will also present results on different mimics of LeX and discuss their similarities and robustness with respect to the natural carbohydrate.

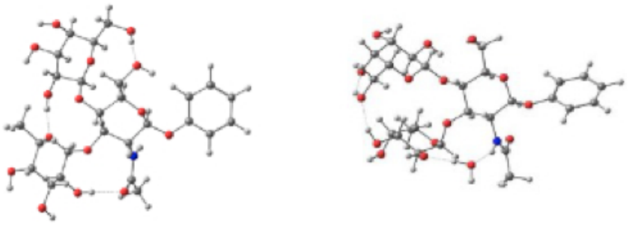

Figure 1. The observed conformation of isolated LeX (left) and its singly hydrated complex (right)

Acknowledgements

This work has been financially supported by the ANR/SNF Lead Agency Program.

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Atomic Physics Inputs for Enhanced Targeted Therapy

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Most of the radionuclides used in Nuclear Medicine for diagnostic and therapy purposes take advantage of the ionization properties of the gamma and X-rays emitted in the decay process of these isotopes. The X-ray emission competes with the Auger process by which an electron from an outer level fills a vacancy in an internal level and an external electron is emitted. As this process propagates from the inner level vacancy to the outer level, a cascade of X-ray and Auger emissions is formed. These Auger electrons have a very low energy but a very high linear energy transfer (LET). Due to their ability to cluster a large number of ionizations in a very short range, it has been studied the use of biomolecules bound with Auger emitters radionuclides to induced radiation damage in the vicinity of the DNA structures [1-3].

Another very recent research topic is the possible addition of nanoparticles (NPs) to the tumor cells as strategy to combine external ion beam (photons and ions) and internal targeted radiotherapy. The effectiveness of NPs to improve the performance of ion therapy has been shown in several experiments [4]. However, current dosimetric studies using Monte Carlo simulations do not explain this enhancement [5], but they attribute an important role to the Auger electrons produce in the sequence of the inner-shell ionization of the NP.

Current Auger spectra data [6] from radionuclides relevant for target therapy is based on the EADL [7] values of atomic transition amplitudes. These amplitudes were calculated in the past framework of the independent particle model. This approach is known to give incorrect values for the outer shell transitions from where the very low energy Auger electrons are produced. In this work we used the multi-configuration Dirac-Fock method [8] to compute the Auger transition amplitudes for selected radionuclides. This approach accounts for electronic correlation. The dose at the DNA scale was simulated using the Monte Carlo code PENELOPE [9]. The simulations performed with this new data seem to indicate that these differences might have some impact inside the cell nucleus in the DNA range.

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Novel materials and virtual science, are we there yet?

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Computer modelling has become a fundamental tool to understand and rationalize new molecules and materials, and there is an increasing volume of research that is purely computational or virtual. Through the years, we have applied and developed computational models to complement several experimental problems on carbon-based materials.

We will discuss, from the experimental point of view and in a fully non-technically manner, when state of the art computer modelling can be predictive and how difficult and complex is to perform these simulations. This will be illustrated by our computational studies complementing experimental observations of different materials such as carbon nanotubes [1], graphene [2], and molecular crystals [3]. More philosophically, we will try to answer how far we are today from trustable virtual science.

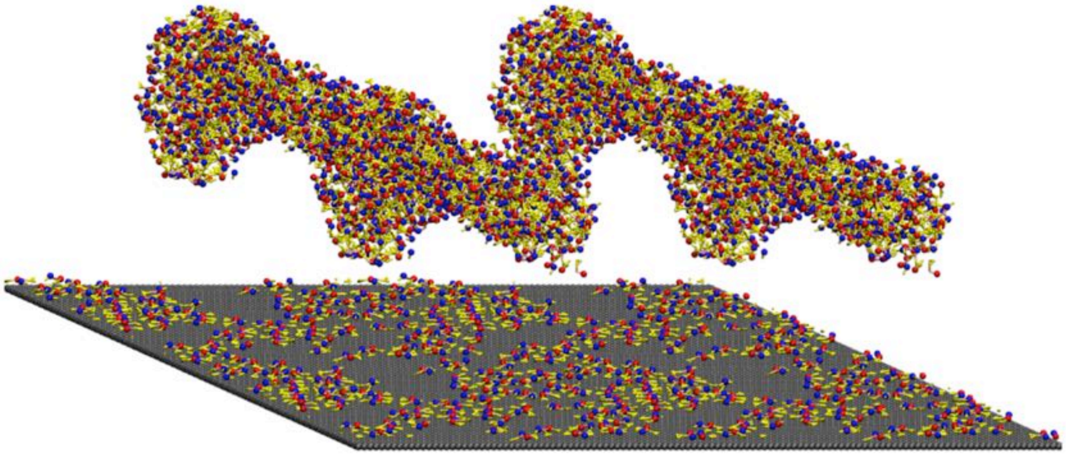

Figure 1. Model of a peptide gel in water on a graphene surface [1].

Acknowledgements

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Phase-change microscopy in combination with spectroscopy to understand early processes during femtosecond laser ablation

José M. Vadillo, Irene M. Carrasco, S. Manzoor and J. Javier Laserna

Femtosecond ablation is unique in comparison to nanosecond one. From the perspective of the events sequence, the time gap since the arrival of the first photon to the sample surface and the starting of a plasma during femtosecond laser ablation offers a unique chance to visualize surface transformations while performing spectroscopic measurements. It is easier said than done, as the frame width must be in the sub-ns regime to provide a proper time-chopping of the process. Sub-ns time-resolved microscopy is clearly not an easy task, that requires the use of non-conventional approaches based on stroboscopic pump-probe schemes to succeed in the recording of time-gated images. Concerning spectroscopy, although the sub-ns resolution is achievable with state-of-the-art detectors, the differences in rise-time and jitter associated to the electronics limit to some extent the possibility of recording single-shot events with the accuracy required. The talk will describe the experiments performed with emphasis in the results obtained in diferent samples.

X-ray Microcalorimeter Spectrometers a new window to previous unsuspected problems in atomic and molecular physics

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The C2TN X-ray Microcalorimeter Spectrometer (C^{2}TN-XMS) was installed at what was still ITN (Instituto Tecnológico e Nuclear) in 2008. Until today it provided experimental data for two PhD works, eight papers, and several oral presentations at conferences, workshops and seminars. Although few, breakthrough results where reached and shown. XMSs open a wide window to important secondary effects like Radiative Auger Emission or multiple ioniza- tions. They clearly point problems on atomic fundamental parameter databases at levels so fundamental as transition energies or fluorescence coefficients. Beyond these, C^{2}TN-XMS data has also raised an important question upon the physical models traditionally used to de- scribe heavy charged particle ionization processes, and de-excitation processes that follow. More than 10 years have passed over the installation of this first generation XMS system, and a factor between 2 and 10 of improved resolution has been reached and is now avail- able for new systems. This brings us at or even below the natural width of many atomic and molecular transitions, and a whole new set of problems emerges, including significant differ- ences between different inner-shell ionization processes, which were assumed negligible un- til now. New models, new algorithms and new software codes will be necessary in the near future to properly explain all details in XMS systems data. In this talk, an overview of results and some of the present or near future challenges emerging from the exploitation of these spectrometers will be presented.

In-situ probing laser-induced chemical reactions at the semiconductor's surfaces by Raman spectroscopy

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Laser-matter interactions have long been of interest in materials science targeting different applications in integrated optics, electronic devices, optoelectronic and sensors, among others. It was established that laser chemical processing induces surface doping, oxidation, alloying, etching and deposition, just to name a few [1].

Raman spectroscopy is an extremely sensitive, potentially non-destructive and contact- less technique, successfully used to characterize different types of materials and nanostruc- tures, whose influence has recently expanded across a wide range of new areas and applica- tions [2]. Nevertheless, the local modifications that might be induced by laser in-situ probing during the measurement should be better understood and controlled. This effect is particularly relevant and cannot be neglected when the surface to volume ratio is high, as in nanowires, nanoparticles, and 2D materials. A thorough analysis of materials surface instabilities yields fundamental information allowing to understand and improve their performance for different applications.

In this work, surface's sensitivity of different materials systems such as GaAs nanowires, Sb2Se3 thin films [3], Fe3Se4 nanoparticles, and InP nanoparticles is evidenced by in-situ Raman scattering analysis. The time evolution of the chemical reactions occurring at the surface of functionalized GaAs nanowires with Au nanoparticles is object of detailed analysis.

Acknowledgements

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Detection of Triclosan in Complex Molecular Matrices by Impedance Spectroscopy: difficulties and achievements

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Access to safe fresh water is of paramount importance worldwide since water pollution is one of the biggest contemporary problems of mankind. Conventional pollutants are pesticides and industrial intermediates but pharmaceuticals and personal care products (PPCPs), including not just prescription drugs and biologics, but also diagnostic agents, soaps, fragrances, sun-screen agents, and numerous others, are used in large scale and are continually released on the environment and contributing for water pollution. Triclosan (TCS) is an antibacterial agent used in soaps, toothpastes, first-aid products, fabrics and plastic goods with pernicious effects in human and biota. Actually, TCS concentrations of about 1480 ng/L and 107 ng/L are detected in influent and effluent waste water, meaning that it is necessary to find cheap sensors to detect traces of this molecule in complex solutions [1,2]. Our approach to solve that problem is develop an electronic tongue based in impedance measurements and in an array of sensors prepared by deposition of Layer-by-Layer (LbL) films onto interdigitated electrodes. Results revealed that this methodology allows the detection of TCS in water [1] and in aqueous complex solutions with concentrations in the range of 10^{-15} to 10^{-6} M. In this presentation will be presented the obtained results and will be discussed the major difficulties found in a detection of traces of a determined molecule on a complex solution.

Acknowledgements

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A theoretical investigation of fhe dynamics of atom-diatom reactions

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The dynamics of atom-diatom reactions which proceed via the formation of an intermediate complex between reactants and products can be analyzed by means of statistical techniques. Over these past years, we have been applying a statistical quantum method [1, 2] in order to analyze the possible role played by this kind of insertion mechanisms in reactive collisions of an atom with molecular hydrogen. In this talk we will review recent results for the case of O(^1D) + H_2 [3] and C(^1D) + H_2 [4] and isotopic variants in which at least one of the hydrogen atoms is substituted by deuterium.

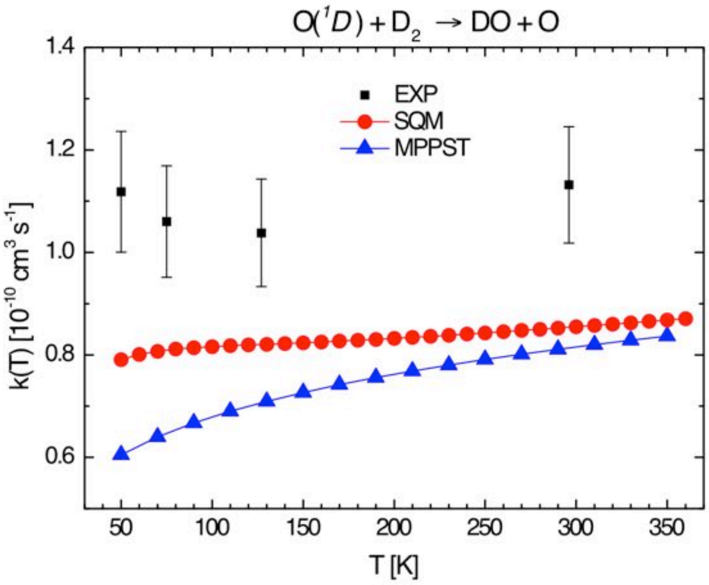

Figure 1. Comparison of theoretical and experimental rate constants for the O(1D) + D2 reaction as a function of the temperature. Red solid circles are results of a statistical quantum mechanical calculation, blue triangles are from a mean potential phase space theory calculation and solid squares with error bars are experimental measurements [3].

Acknowledgements

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Tribute to Delgado Barrio

Pablo Villarreal - In Memoriam of Gerardo Delgado-Barrio.

Rita Prosmiti - Benchmarking interactions in guest-free/host clathrate hydrates.

Alberto Gárcia-Vela - Weak-field coherent control of photodissociation in polyatomic molecules.

In Memoriam of Gerardo Delgado-Barrio

Pablo Villarreal

Instituto de Física Fundamental (IFF-CSIC), Serrano 123, 28006-Madrid, Spain.

Without intending to be exhaustive, we review in this talk the scientific and professional career of the founder and first president of GEFAM, Professor Gerardo Delgado-Barrio, who died in July 2018. We will show from his first publication on nucleic acid bases using a semi-empirical ω-technique of electronic structure calculation [1], to his last paper concerning quantum molecular dynamics simulations on the formation of rubidium dimers along the surface of helium clusters [2], going through pioneering quantum calculations on vibrational predissociation of triatomic van der Waals molecules [3, 4], in particular HeI_2(B) species, see Figure 1.

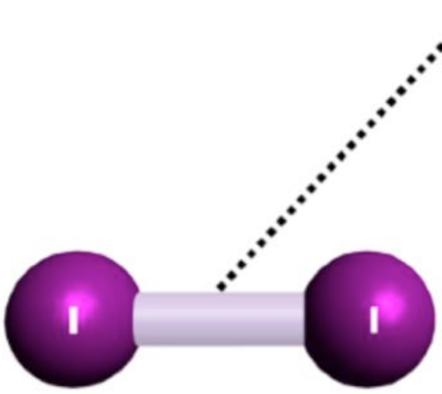

Figure 1. The HeI_2*(B)* van der Waals molecule. Photonic excitation of the iodine from the ground *(X)* to an upper electronic state *(B)* in a given vibrational level leads, by energy transfer to lower vibrational states, to the weak bond breaking up, i.e., vibrational predissociation of the complex.

Acknowledgements

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Benchmarking interactions in guest-free/host clathrate hydrates

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Despite the increasing interest in inclusion compounds, mainly due to their technologi- cal applications, a molecular-level understanding of their formation and properties is still far from complete. We focus our study on non-covalent interactions in clathrate hydrates. Such guest-host systems offer the opportunity to validate the ability or inability of current first-prin- ciples methods to simultaneously describe both the hydrogen bonding within the water net- work and the predominantly dispersion bound gas-water interactions. Energy reference data from accurate quantum-mechanical calculations are essential for testing both force fields and DFT methods [1]. Therefore, we first propose a systematic protocol for benchmarking the in- termolecular interactions in finite-size systems of individual aperiodic cages, such as those of guest-free and CO_2@sI, CO_2@sII, and CO_2@sH clathrates, and then for their entire periodic unit cells [2, 3] (see Fig. 1). Results from such bottom-up and top-down approaches will be presented and discussed in comparison with semiempirical force fields (widely used in simu- lations), as well as analytical pairwise model potentials available in the literature.

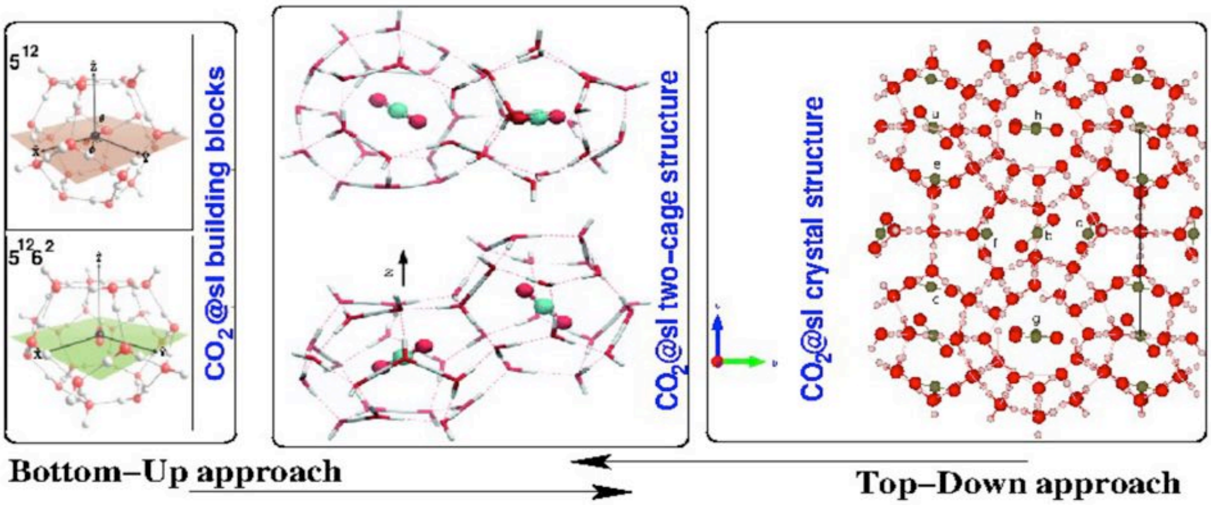

Figure 1. CO_2@sI: building blocks and crystal structures.

Acknowledgements

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Weak-field coherent control of photodissociation in polyatomic molecules

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It has been shown experimentally [1-3] and theoretically [4] for atomic and diatomic systems that when a weak electric field combining two pulses delayed in time is applied, by varying the time delay between the pulses it is possible to modify the shape of the spectral profile associated with the field, which implies to change the relative populations of the different states excited within a superposition. The shape of the profile changes as the delay between pulses is varied due to interference between the pulses. While such a combination of pulses changes the shape of the spectral profile, its bandwidth, which is independent of the delay between the pulses, remains fixed. Thus, the spectral bandwidth of the laser field applied is not modified when the time delay between the pulses is varied.

Based on the above interference effect, a weak-field coherent control scheme was proposed for the first time to modify the asymptotic photofragment state distribution of a polyatomic system, Ne-Br_2(B,v'), produced upon resonance decay [5,6]. The control scheme applied an electric field consisting of two pulses that overlap spectrally and with a time delay between them. When that time delay is varied, the shape of the corresponding fixed bandwidth spectral profile changes, causing modulation of the initial population of the different resonances populated in a superposition, leading to variation of the asymptotic Br_2(B,v_f<v') fragment vibrational distribution, and making possible its control. More recently, the scheme has been applied to control the output of photodissociation of the CH_3I molecule in the A band [7]. Specifically, control is achieved on different observable quantities associated with the two dissociation channels CH_3 + I ($^2P_{3/2}$) and CH_3 + I*($^2P_{1/2}$), such as the final populations in those channels, the branching ratio between them, and the anisotropy parameters associated with the angular distributions produced through both channels.

Acknowledgements

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Oral Communications

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LA-ICP-MS in Cultural Heritage Studies and Archaeological Materials

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Currently, LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry) is one of the most powerful and popular techniques in archaeological research due to its remarkable characteristics like high sensitivity, low detection limits, fast multi-elemental analysis, minimal sample preparation, micro-invasive approach and high spatial resolution analysis. Acting as an irreplaceable tool for elemental composition determination of heritage goods or archaeological materials and elemental distribution through compositional maps on major, minor and trace elements, the use of this cutting-edge technique can reveal valuable and important information about provenance of raw materials used and about the technology applied on the production of these materials.

In this communication, besides the potentialities of the LA-ICP-MS technique itself, we will present two cases studies performed in HERCULES laboratory.

In the first case study, a multi-analytical minimally invasive methodology was used to determine the chemical and mineralogical composition of the large glass bead assemblage found in Vinha das Caliças 4 [an Iron Age necropolis located in the outskirts of the town of Trigaches (southwestern Portugal)]. LA-ICP-MS was used to determine the trace element composition, which is essential to answer questions related to glass sourcing and production technology. Together with all the multi-analytical approach, this study contributes to a deeper knowledge regarding pre-Roman glass production technology in the Iberian Peninsula in the 6th century B.C..

The second case is based on the material and technical study of the paintings works attributed to Frei Carlos workshop, where the author attribution was a key question: Are all the works correctly attributed to Frei Carlos or are some of the paintings from his followers? Did the followers use the same raw materials? To address these main questions, a multi-analytical approach was performed, where LA-ICP-MS was applied in order to investigate calcium carbonate raw materials to discriminate between different sources of raw materials and its relationship to hypothetical groups/unresolved issues. Data obtained by LA-ICP-MS allowed our multidisciplinary team to conclude that different raw materials were used for the preparation of the studied paintings works.

This communication intends to summarize the basics and potentialities of the LA-ICP-MS in some of the current needs in the Heritage Science field.

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Non-invasive determination of gold leaf thickness in Indo-Portuguese panel paintings using X Ray Fluorescence spectrome-try and Monte Carlo simulation

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In this work, we present the combined use of in situ X ray Fluorescence spectroscopy and Monte Carlo simulation using PENELOPE code for the completely non-invasive determination of gold leaf thickness in artworks using lead white as mordant. The gold leaf thickness is determined by comparing the attenuation of the characteristic Pb line intensities in the X ray fluorescence spectra.. Firstly, this methodology was calibrated using model samples of simple stratigraphy, namely pure Au leafs of 1, 2 and 2.5 μm thickness covering a Pb infinitely thick sheet. The modelled X ray setup was then used to study the gold thickness of three panel paintings belonging to the Museum of Christian Art in Old Goa (India): two paintings, from the 18th century, concerning to the same series but different themes: Our Lady of Sorrows (MoCA1) and Our Lady of Seven Sorrows (MoCA2), and a third painting entitled Monstrance (MoCA3), from the 17th century. These panel paintings were analyzed to understand the differences and similarities between techniques, according to the time/epoch and technique of its manufacture. The obtained values for MoCA2 tend to be slightly lower than for MoCA1, however, the t student test revealed that the differences were not statistically different ($p = 0.37$). Regarding the MoCA3 painting, the average thickness was determined to be statistically different ($p<0.001$) and higher than for the other two paintings. These results emphasize the use of different techniques concerning gold leaf beating. In the 17th century painting it was verified the use of a thicker gold leaf while in the group of the 18th century, the gold leaf was thinner and manufactured with a similar thickness in both paintings. These results are in consonance with the accuracy of leaf beating technology, increasing with the experience acquired during the ages.

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Spectroscopy and the material study of easel paintings: discoveries & challenges

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A high range of sensitive micro-analytical techniques is being extensively applied in the field of cultural Heritage, providing new data about materials and techniques of artistic production and for instance a new range of possible comparisons. However, envisagingan analytical methodologys implies the practical need to adjust it in order to answer main questions related to the works of art, to deal with work field conditions and decisions/protocols related to the application of non-invasive / micro-invasive techniques.

This presentation will present three case studies revealing scientific contributions and new challenges achieved in the study of easel paintings by using complementary imaging and micro-analytical instrumentation.

Portable Energy Dispersive X-ray Fluorescence (EDXRF) spectrometry, as a non-destructive technique has been widely used for in-situ analysis of easel paintings allowing the identification of pigments through the detection of specificelements. Additionally, it can also give information about techniques of artistic production by comparing strategic points of analysis based on interpretation of physical imaging exams. On the other hand, MA-XRF mapping has been introduced and explored in order to deal with painting multi-layers/underpaintings, and again thinking about how to overcome instrumental limitations related to X-rays penetration into the paint layers. It must be underlined, though, that EDXRF cannot be considered alone when investigating paintings and artworks, for it suffer from some limitations; therefore, a multi-analytical approach is necessary.

The possibility to collect micro-samples allows to access complementary and relevant data. Microfragments of representative areas were collected and mounted in epoxy resins in order to expose the paint layers for further analysis by optical microscopy, giving information about layers build-up, pigments admixtures and granulometry and colour. Relevant information about the binders and pigments used was obtained by combining scanning electron microscopy coupled with energy dispersive x-ray spectrometry, μ-FTIR, μ-Raman spectrometry micro-X-ray diffraction analysis.

LA-ICP-MS complemented the results allowing the discrimination of ground layers due to its detection limits that goes up to ppb levels.

Finally, we will discuss the compromise between sample size and accurate data in analysis of paintings and the challenges and limitations of the instrumental setups [1].

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Analytical approach on materials and techniques of Jorge Afonso workshop compared to Flemish painting

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This study compares the materials and the techniques employed by two artists in two paintings with a different origin, Flemish and Portuguese, but under the same theme- the “Apparition of the angel to Santa Clara, Santa Inês and Santa Coleta”. This aspect leads to believe that one of the paintings might have been the reference for the other. The Flemish painting, assigned to Quentin Metsys (1466-1530) and made circa 1491-1507, is probably a gift from the emperor Maximilian to his cousin Queen D. Leonor who offered it to the Convento de Jesus, in Setúbal, Portugal. The nuns from this convent would have commissioned a panting with the same theme to Jorge Afonso (c. 1470-1540), the most important painter of Lisbon workshop (1517-19/1530), being this altarpiece his last and most significant work [1, 2]. The aim of this study is to compare the materials and the techniques of Flemish and Portuguese workshops to determine their differences and similarities. Was the Portuguese painter Jorge Afonso influenced by the Flemish techniques, or has he followed the Portuguese workshops concerning techniques and materials? To perform this study, the support materials were studied and dendrochronology was made, and pigments were analysed by portable X-ray fluorescence spectroscopy, μ-X-ray diffraction, Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy, μ-Confocal Raman and High-Performance Liquid Chromatography coupled to Diode-Array and Mass Spectrometry detectors. Pigments found in both paintings were similar but ground layers differ in their constitution, as well as the overlapping of the pigment layers. Differences and similarities between both paintings showed that the Portuguese painter followed the Flemish tradition in using certain materials such as the Baltic oak for the support and similar pigments, but the use of ground layer materials and the overlapping of pigment layers technique was different. This study brings new insight into the tendencies of Flemish and Portuguese paintings, highlighting Flemish influences in the Portuguese painting concerning materials and painting techniques.

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Intermolecular clusters in jet expansions: Molecular rotation spectra of sulfur hydrogen bonded clusters

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Molecular rotation spectroscopy investigates non-covalent interactions using weakly-bound neutral intermolecular clusters, generated and isolated in supersonic jet expansions. In this communication, we will report on the aggregation and microsolvation of several homo/hetero-dimers and trimers containing sulfur atoms, analyzed in the cm-wave (2-8 GHz) microwave region by chirped-pulse or single-tone impulse excitation. The spectral results will inform of the structural and conformational properties of the clusters, highlighting the differences with their oxygen counterparts and the balance of intermolecular forces. The experimental results will be complemented with computational calculations using density-functional theory, simultaneously evaluating the accuracy of the theoretical models. The examples included will extend previous reported investigations [1,2], including aromatic thiols (thiophenol, phenylmethanethiol, 2-phenylethanethiol, etc) and thenyl derivatives (thiophenemethanol, thiopheneethanol, etc).

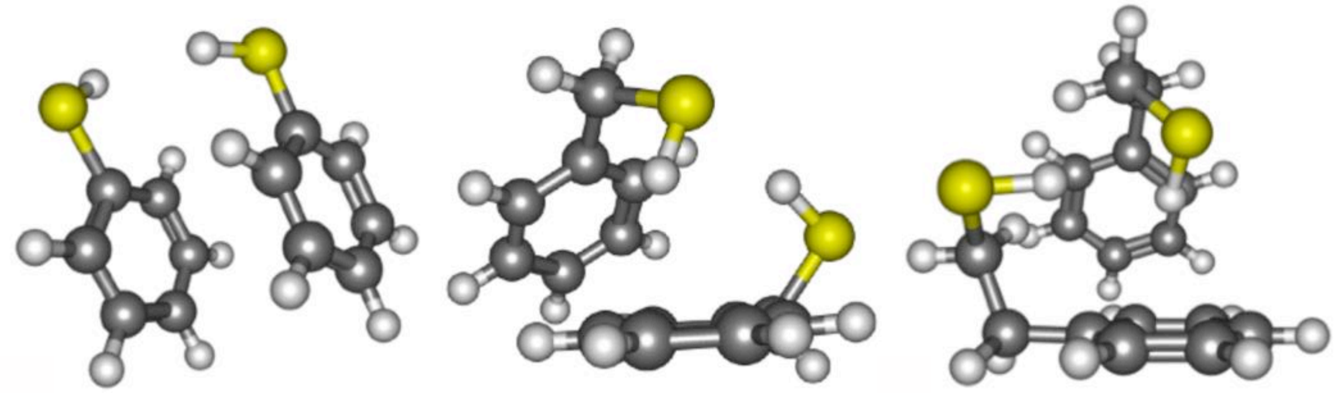

Figure 1. Dimers of aromatic thiols observed in a jet expansion with rotational spectroscopy.

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The dipeptide Ala-Ala isolated in the gas phase

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Herein solid samples of Ala-Ala dipeptide have been vaporized by laser ablation and two different structures have been unveiled for the first time using chirped pulse Fourier-transform microwave (LA-CP-FTMW)[1,2] and molecular-beam Fourier-transform microwave (LA-MB-FTMW) [3,4] spectroscopies. Accurate rotational constants and the nuclear quadrupole coupling constants extracted from the analysis of the spectra allowed a complete structural characterization of both species, which are stabilized by different type of intramolecular interactions forming C_5 and C_7 arrangements. Additionally, conformer interconversion distorts the equilibrium conformational distribution, giving rise to missing conformers in the conformational landscape.

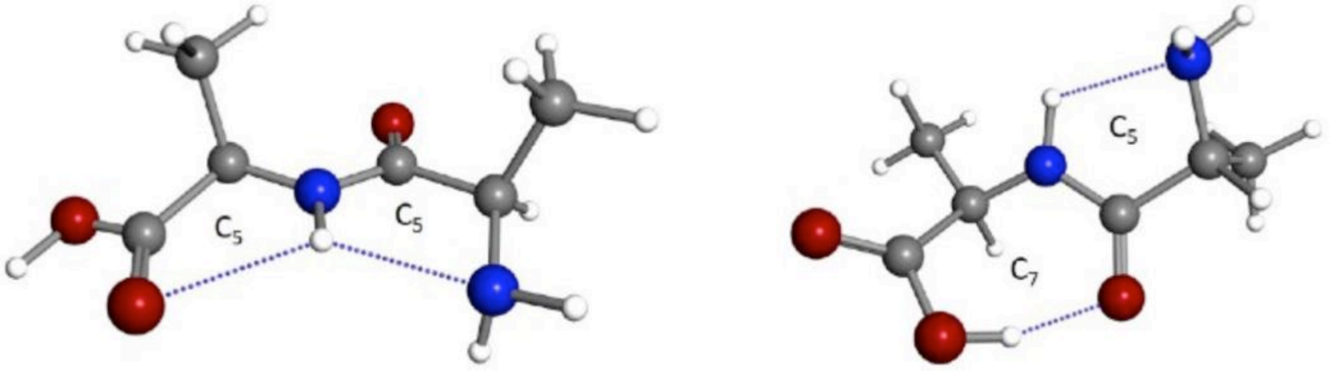

Figure 1. The two detected conformers of Ala-Ala dipeptide showing C_5 and C_7 intramolecular interactions.

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Spin-forbidden addition of O2 catalyzed by DpgC

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Most of the stable chemical molecules involved in biological processes only populate their ground electronic states and are stable closed-shell molecules. The oxygen molecule is an exception to this rule and in its ground state is a diradical (triplet). Therefore, enzymatic reactions in which oxygen reacts with a singlet organic molecule leading to products with paired electrons, should be spin-forbidden reactions, involving transitions between PESs with different spin-multiplicity.

Typically, proteins rely on metal cofactors that can activate O2 before the reaction. Interestingly, other proteins1, such as DpgC2, which catalyse the addition of O2 to DPA-CoA (Fig. 1) do not use any cofactor but are still capable of carrying out its catalytic function. In this communication, we will combine MD, QM/MM and multireferential electronic structure calculations to unravel the mechanism used by DpgC to catalyse O2 addition to CoA and why metal cations are not required.

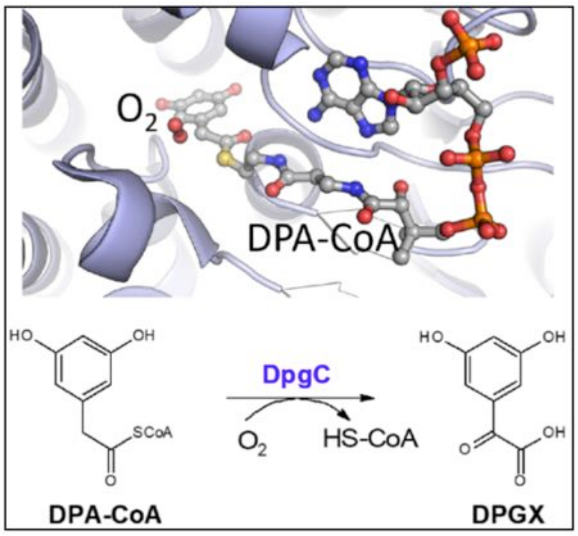

Figure 1. Top panel: Active site of DpgC. Bottom panel: reaction catalysed by DpgC .

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Development of Raman instrumentation for *in vivo* dental research

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One of the main goals of modern medicine is the early detection and treatment of diseases. Recently, despite all research studies dedicated for the development of improved methods for the early detection of dental carious lesions, in clinical practice the caries detection is still utmost limited to conventional visual and visual-tactile techniques such as sharp explorers and dental radiographs [1]. Raman spectroscopy, a form of vibrational spectroscopy, is presently considered a viable optical method for biomedical applications mainly due to its non-destructive modality to analyze molecular composition. This method is becoming progressively important in biomedical research especially for its high biochemical specificity, low water sen- sitivity and capability to work in the near-infrared (NIR) region with fiber-optics [1,2]. Raman spectroscopy has shown to be a very suitable modality to analyze inorganic superficial tis-sue (such as phosphate and carbonate molecule concentration, as shown in Figure 1), since it is possible to acquire accurately spectroscopic information on present minerals through the observation of the characteristic energies of their vibrational modes [2, 3]. Therefore, Raman spectroscopy is suitable for the characterization of dental tissues, from caries detection to the evaluation of demineralization caused by acidic external agents. The sensitivity of this spectroscopic technique for alterations in the symmetric stretching band of phosphate ions in the hydroxyapatite matrix could be used as a powerful tool for early diagnostics, even before signs of demineralization are detected with conventional methods [1-3].

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Preliminary studies with an EDXRF imaging system based on a 2DTHCOBRA detector for applications in biological tissues

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The Energy Dispersive XRay Fluorescence technique is employed to simultaneously identify and determine the concentration of several major and minor elements in an analyte, in a nondestructive way. One promising application of EDXRF is the analysis of trace element concentrations and of their distribution in biological samples as a complementary method in the diagnosis of pathologies.

An EDXRF system based on a MicroPatterned Gaseous Detector (MPGD), the 2DTHCOBRA, is being developed for imaging of biological tissues. The 2DTHCOBRA detector allows the determination of the position of interaction and of the energy of each photon that reaches the detector's active area, making it possible to map the distribution of elements in samples. EDXRF imaging systems based on MPGDs have already been successfully implemented in cultural heritage and biomedical studies [1,2]. Currently, these systems are being studied for applications in biological tissue imaging, specifically for mapping the distribution of trace elements in cancerous and healthy tissues. Combined with the determination of the concentrations of the elements using other EDXRF systems (e.g. M4 TORNADO), it should be possible to understand the relation between trace elements and carcinogenesis.

The principle of operation of the 2DTHCOBRA and its characteristics will be presented, focusing on the preliminary studies conducted, that yielded an energy resolution of approximately 16% at 5.9 keV (FWHM), and position resolution values of 300 μm. Applications of the system, namely the analysis of biological tissues will also be addressed.

Keywords

EDXRF, MPGD, biological tissue imaging

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Complementary use of PIGE and Raman spectroscopy for the evaluation of Fluorine uptake and enamel demineralization caused by Gustatory Stimulants of Salivary Secretion

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The purpose of this in vitro study is to gauge the fluorine uptake in human enamel after use of Gustatory Stimulants of Salivary Secretion (GSSS) using PIGE – Particle Induced Gamma-Ray Emission. Moreover, we aim at evaluating the enamel demineralization potential caused by the same products using Raman Spectroscopy. GSSS are non-pharmacological products that have the ability to stimulate salivary glands but are composed of malic acid that can accelerate human's teeth erosion due to salivary pH values decreasing below the critical level of 5.5. This effect can be minimized by fluoride present in new generation of GSSS, as fluorapatite is less susceptible to demineralization than hydroxyapatite. In this work, 8 specimens of human enamel, exposed to Xeros^{TM}, were analyzed before and after treatment with PIGE and Raman spectroscopy. The experimental work for PIGE was carried out at the CTN/IST Tandem accelerator and the gamma-rays were detected by a 45% Ge(HP) detector located at 130° in relation to the incident beam direction. In order to quantify F, we used a standard free method for PIGE in thick samples, based on the ERYA code [1]. Demineralization effect was evaluated based on the depolarization ratio determined in Raman spectra before and after treatment [2]. No significant differences were found in the depolarization ratio before and after treatment with Xeros^{TM}.

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Structural dynamics effects on the UV electronic predissociation of alkyl iodides at 201 nm

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In order to investigate the correlation between chemical structure and predissociation dynamics, femtosecond time-resolved velocity map ion imaging experiments have been carried out in the second absorption band (B-band) of a series of linear (CH_3I, C_2H_5I, n- C_3H_7I, n-C_4H_9I) and branched alkyl iodides (i-C_3H_7I, t-C_4H_9I), at an excitation wavelength of 201.2 nm, *i.e.* around the wavelength where the origin of the *B*-band of CH_3I originates and where several absorption maxima of the remaining alkyl iodides are found [1, 2].

The energy distribution resulting from the angular integration of the measured asymptotic I*($^2P_{1/2}$) fragment images obtained through (2+1) REMPI has allowed us to distribute the available energy content into translational and ro-vibrational content of the fragments.

On the other hand, predissociation lifetimes have been determined for all alkyl iodides from measurements of time-resolved I*($^2P_{1/2}$) fragment images as a function of the time delay. These time-resolved measurements also provide the angular character of the transition directly through the observation of fragments appearing early with respect to both predissociation lifetime and molecular rotation.

The obtained results indicate that the energy content, predissociation lifetimes and angular character of the images and its evolution over time (which give us a hint of the molecular rotation prior to dissociation) strongly depends on the alkyl iodides increasing complexity and degrees of freedoms and the atomic distribution around the carbon-iodine bond involved in the molecular photodissociation.

Acknowledgements

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Graphene Oxide thin films for hybrid solar cells: characterization by VUV, UV-visible, infrared and impedance spectroscopies

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The development of organic thin film devices to capture and conversion of solar energy into electrical energy, based on photoactive polymer materials represent a promising technology capable of providing energy at low cost and easily available [1]. In this study, devices have been produced using different substrates, on which were deposited thin films of graphene oxide (GO) as cast and films with alternating layers of poly (allylamine hydrochloride) (PAH) and GO produced by the layer by layer (LbL) technique. To finalize the devices, aluminum electrodes were deposited by sputtering or by thermal evaporation. The characterization of the optical properties of PAH/GO LbL films and GO cast films, was performed using UV-Vis spectroscopy, vacuum ultraviolet spectroscopy (VUV) and infrared Fourier transform spectroscopy (FTIR). The UV-Vis and VUV spectroscopy measurements of PAH/GO films showed a linear increase in absorbance with the increase of the number of deposited bilayers, allowing the determination of the amount of GO adsorbed per units of area of each bilayer (10,7 ± 0,1 mg.m^{-2}). Studies of GO and PAH/GO films using VUV spectroscopy, allowed the determination of the positions of bands as well as the assignment of the electronic transitions. The morphological characterization of the films was performed through optical microscopy (OM), scanning electron microscopy (SEM) and atomic force microscopy (AFM). Based on the OM and SEM images it was possible to conclude that the films of (PAH/GO)$_{20}$ are not completely uniform. From the SEM images was possible to estimate the thickness of PAH/GO films (210 ± 20 nm) and therefore, estimate the bilayer thickness (10,5 ± 0,7 nm). By AFM measurements it was also confirmed that PAH/GO films show the formation of GO and/or PAH/GO fibers and that GO is completely adsorbed on the top of PAH. The electric properties of the produced films were characterized by impedance spectroscopy, which allowed to conclude that the produced devices evidence a typical semiconductor behaviour.

Acknowledgements

This work has been financially supported by FEDER, through Programa Operacional Factores de Competitividade – COMPETE and Fundação para a Ciência e a Tecnologia – FCT, project UID/FIS/00068/2013.

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Strong contribution of resonant excitation in the *3s-2p* line formation of Fe XVII

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Soft x-ray emission in Fe XVII after electron recombination has been measured in an electron beam ion trap with an electron energy spread six times more resolved. This enables a clear distinction between the atomic processes of resonant excitation (RE) and direct collision excitation (CE) leading to the *2p53s* manifold. A pronounced contribution of RE is observed, as well as the stepwise cascade mechanism of forbidden states into this manifold. Measured cross-sections are of interest for opacity diagnostic of astrophysical plasmas [1].

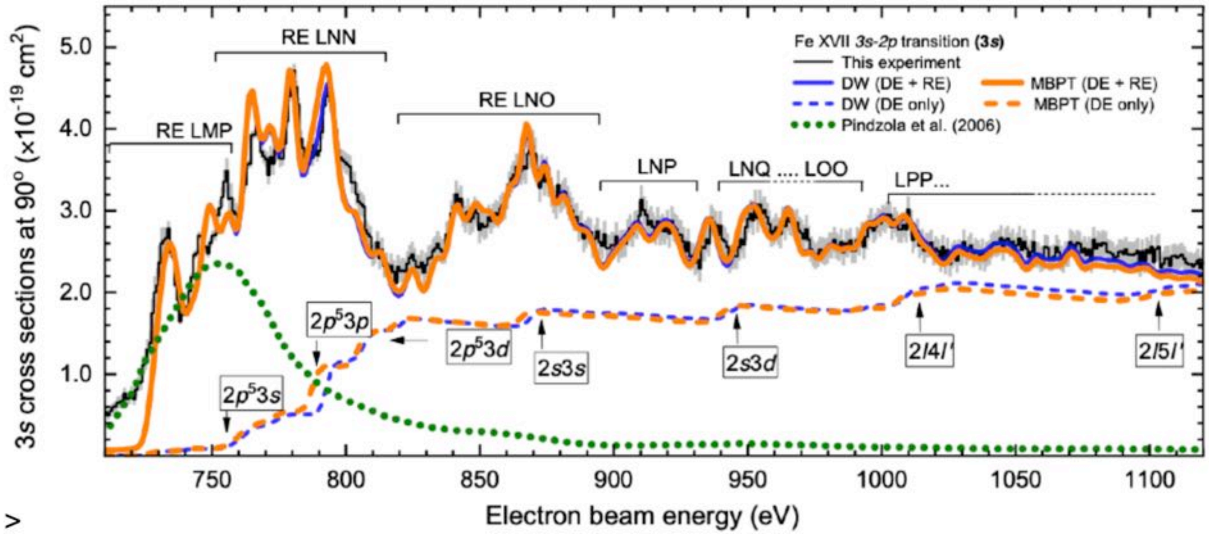

Figure 1. Experimental differential cross section (grey band σ) of all processes leading to *3s* manifold, superimpose with DW predictions having RE (solid blue) and without RE (dashed blue). MBPT predictions with (solid orange) and without RE (dashed orange), as well as calculations (dotted green) reported by [2], are shown.

Acknowledgements

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Ultrafast Nonradiative Relaxation Channels of Azaindoles

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Since ultrashort (subps) lifetimes were observed in the past decade for all nucleobases implicated in the replication process, the understanding of DNA excited state dynamics has become a hot topic. Nowadays, it is widely accepted that ultrafast internal conversion (IC) implies an enhanced photostability, because a short excited state lifetime prevents molecules from photochemical reactions leading to the eventual formation of harmful photoproducts. [1] The ultrafast IC processes are ultimately linked to the molecular structure. From this perspective, subtle structural changes modify the potential energy surfaces, and consequently, alter the accessibility to the conical intersections that control the different relaxation pathways. Therefore, the question arises whether there is a common pattern in the deactivation dynamics of nucleobases and other life related molecules. The present work focuses on the relaxation dynamics of azaindoles in the isolated and condensed phase. The dynamics of these species, which are a good starting point for a bottom-up approach to more complex systems, has been tracked by femtosecond time-resolved ionization spectroscopy, transient absorption spectroscopy and fluorescence up-conversion techniques. The electronic excitation region explored (304-239 nm) covers three electronic excited states: the two ππ*, L_a and L_b states, and the dark nπ* state. [2] The collected set of data provides new insights on the photophysical and photochemical events following excitation in the aforementioned energy interval, allowing us to balance the relative importance of the involved relaxation channels.

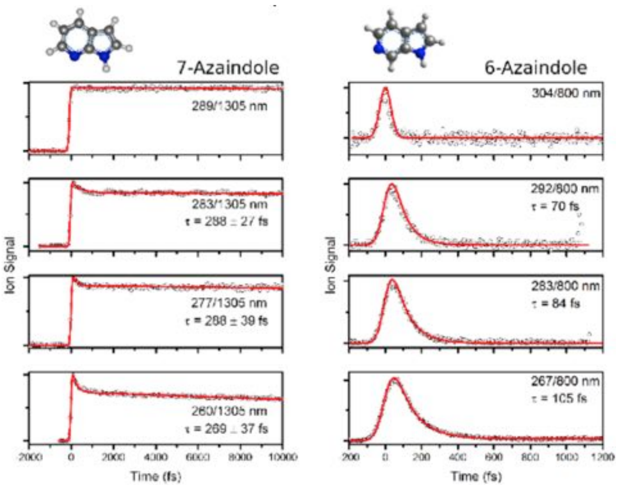

Figure 1. Transients collected at the 7-azaindole$^+$ and 6-azaindole$^+$ channels in the 304-260 nm excitation range by probing with 1305 and 800 nm pulses, respectively.

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High-accuracy X-ray spectrometry for S.I. traceable calibration standards

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Energy calibration is one of the main sources of discrepancies between measurements of X-ray fundamental parameters such as mass attenuation coefficients, line energies and shapes among others. The *International Initiative on X-Ray Fundamental Parameters* [1] has a workgroup dedicated to database evaluation, whose main task is now to trace back the energy scales of its featured measurements in order to be able (if possible) to self-consistently accommodate the database results.

Traceability of x-ray energy scales to the definition of the meter in the International System of Units (SI) was first made possible by the demonstration of an x-ray-optical interferometer by Deslattes and Henins in 1973 [2]. Lattice spacing comparisons with relative standard uncertainties of 10-8 allow the measurement of primary X-ray wavelength standards with diffraction crystal instruments with accuracies in the ppm range. A Vacuum Double Crystal Spectrometer (VDCS) is being assembled in Lisbon with the goal of measuring reference-free (tied only to the S.I. definition of the meter), high-accuracy line shapes for transition metals. The use of a DCS will ensure measurements of line energies and shapes, with accuracies of a few parts per million, in the soft X-ray regime where most fundamental parameter databases are severely incomplete [3].

Future x-ray wavelength reference data will go beyond a list of transition peak positions corresponding to the energy profile maxima, as this procedure is not transferable and in principle does not allow traceable calibration of high-accuracy X-ray apparatus such as crystal diffractometers or crystal monochromators that are ubiquitous in large scale synchrotrons.

These line shapes, for each X-ray transition, will have to form part of a critically-evaluated database, which has to account for all instrumental and systematic effects, in order to provide a true and more transferable parameterization of the intrinsic spectra.

Acknowledgements

This work has been financially supported by FCT, under the project PTDC/FIS-AQM/31969/2017, “Ultra-high-accuracy X-ray spectroscopy of transition metal oxides and rare earths. ”This work was also partly supported by the research center grant no. UID/FIS/04559/2013 to LIBPhys-UNL.

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Quantum Stereodynamics at cold energies

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One of the most fundamental questions in molecular dynamics is the dependence of a collision outcome on the relative orientation/alignment of the reactants, i. e. the stereodynamics of a collision process. For bimolecular gas phase reactions, it is possible to address this question by polarizing the reactants bond-axis and/or rotational angular momentum.[1-4]

In this communication we will illustrate how the outcome of a collision can be controlled by selecting the relative geometry of the colliding partners before their interactions. In particular, we will focus on the collisions at low energies, which proceed with contributions from just a few partial waves, such as those between HD and H_2, which have been the subject of experimental studies recently.[3-]As will be shown, the effect of resonances can be dramatically switched off by an appropriate choice of the alignment of the reactants.

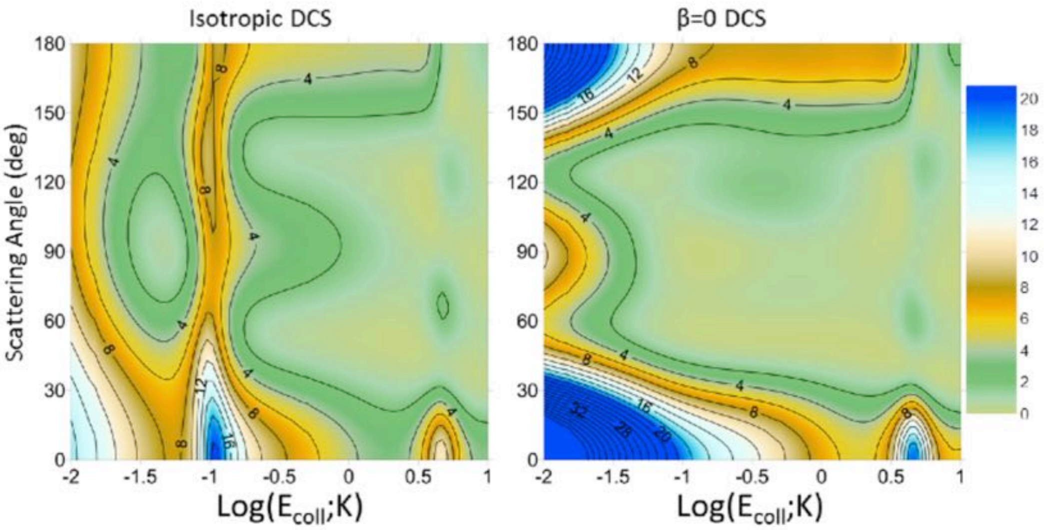

Figure 1. *DCS of HD(v=1,j=2) + H2(v=0,j=0)→ HD(v=1, j=1) + H2(v=0, j=0) collisions as a function of the collision energy and scattering angle. The resonance at 0.1 K can be clearly appreciated in the absence of HD rotational angular momentum preparation. However, by polarizing HD angular momentum perpendicularly to the incoming velocity the resonance vanishes.*

Acknowledgements

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DNA base ··· Xanthine aggregates: a spectroscopic study of non-covalent interactions in purine derivatives

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Methylation processes usually appears in human metabolism as a tool for modulating gene expression, to change specific functions in proteins or as an epigenetic tool. In the case of the DNA bases, methylation of a nucleobase drastically changes its preferences for intermolecular interactions. Therefore, the study of the interactions between methylated bases may send light about how a structural modification modulates the aggregation tendencies of DNA bases.

In recent years, understanding the aggregation of DNA bases has been the goal of several studies, due to the relevance of such interactions for life[1,2]. However, the aggregation of DNA bases with other structurally related compounds that are present in our metabolism, such as xanthine and its methylated derivatives, has been rarely explored. The combination between these families is very interesting, since some xanthines can create Watson-Crick links or analogue interactions [Figure. 1].

Here, we explore the interaction of the DNA base adenine with different xanthines using a combination of mass-resolved excitation spectroscopy and computational methods. A laser desorption system was used to form and isolate the aggregates in a supersonic expansion. Next, the molecular beam was explored using a combination of REMPI and IR/UV techniques to extract structural information. Comparison of such experimental results with the output from DFT calculations at M06-2X/6-31+G(d) and M06-2X/6-311++G(d,p) levels allowed us to assign the experimental spectra to a calculated structure. On one hand, formation of these kind of aggregates tells us the aggregation preferences of purine bases; on the other hand, we can see the influence of the methylation in the intermolecular interactions and therefore, in the structure of the aggregates.

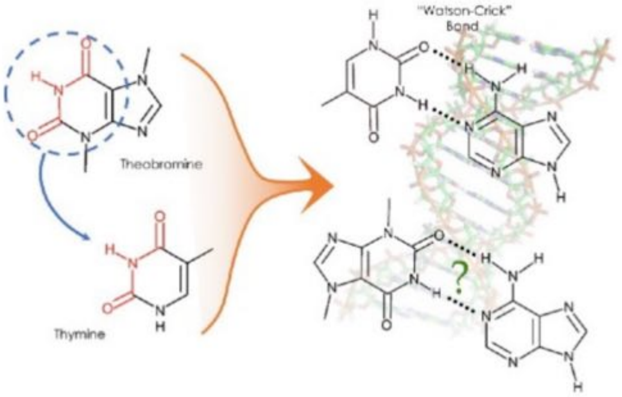

Figure 1. Scheme of a possible interaction between adenine (DNA base) and theobromine (methylxanthine)

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Poster Sessions

Andre Cortez - Development of large area, high gain, thick gaseous electron multiplier: from GEM_100 to the COBRA_125.

Asier Longarte - Femto- to Microseconds Photodynamics of p-Toluidine in Polar Media.

Ignasi Queralt - X-ray fluorescence analysis of Catalonian coinage from the Spanish Succession War (1700 – 1714)

J.P. Marques - Influence of unexpected excitation cross section value on spectra of Pm-like Bi systems

Judith Millan - Characterization of the conformational preferences of dipeptides by DFT calculations.

Mafalda Costa - XRF and LA-ICP-MS applied to glass – the case study of Mbanza Kongo (Angola).

Marta Murillo-Sánchez - Time-resolved photodissociation dynamics of vinyl iodide in the UV at 199.2 and 200 nm.

Nuno Duarte - Neutron detection using a finepowder aerosol proportional counter.

Pedro Amaro - Theoretical prospects of laser excitation of ground-state spin-flip in muonic hydrogen.

Pedro Amaro - Resonant recombination depletion effect on charge state dynamics of a XVII Fe plasma.

Raúl Montero - On the dynamics of pyrrole in $\pi\sigma^*$ states.

Ricardo de Souza - Retrieving information from closed documents

Rita Roque - Optimization of a large area Zero-IBF for ion backflow reduction in Time Projection Chambers.

Poster Sessions

Rodrigo Martínez - DFT study to analyze epigenetic marks.

Sara Valadas - Multi-analytical research of a 16th century easel painting Triptych Christ and the Apostles (Beja, Portugal).

Sofia Pessanha - Assessment of smokers teeth using micro-EDXRF and confocal Raman spectroscopy: comparison with non-smoking subjects

Development of large area, high gain, thick gaseous electron multiplier: from GEM_100 to the COBRA_125

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Since their introduction, Micro Patterned Gaseous Detectors (MPGD) have gained a great interest from the scientific community due to their intrinsic characteristics such as: large detection area capability, high count rate (10^6 Hz), good position resolution (few hundred microns), room temperature operation, gains close to the breakdown limit (10^6–10^7 for single electrons), timing resolution of few ns, excellent energy resolution and relatively low cost and complexity [1]. MPGD can be made sensitive to the UV range by coating the electrodes with CsI.

The development of MPGD was possible with the application of photo-lithographic techniques to the production of micro sized electron multiplier structures which are responsible for electron amplification. The most popular of these structures is the Gas Electron Multiplier (GEM). It is made of a kapton foil, copper cladded on both sides and micro-perforated with a matrix of holes. Despite its remarkable success, the GEM is somewhat fragile structure, which can be damaged by electrical discharges.

We have developed a novel MPGD, the COBRA_125, which is made of a thicker Kapton foil and therefore more resistant to the damaged caused by discharges. In addition, it is equipped with an extra set of electrodes, which allow to establish 2 independent multiplication regions, reaching higher gains for relatively low operating voltages.

We present the results of the electric field optimization, gain and energy resolution (5,9 keV) measurements for a large area (100 cm^2) COBRA_125. The results obtained so far are promising and open the way for future applications of this novel MPGD, namely for thermal neutron detection.

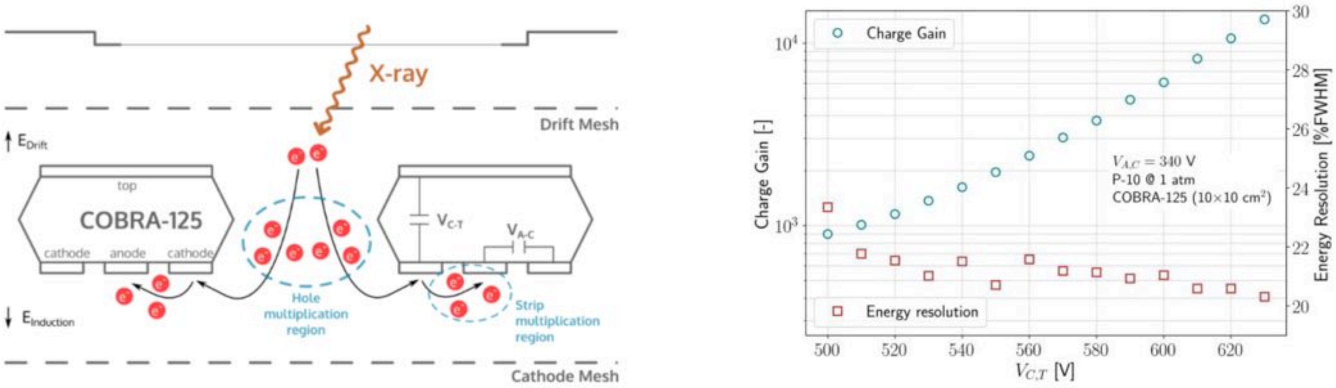

Figure 1. COBRA_125; schematic of the cross section view and operation principle (left). Gain and energy resolution as a function of the applied voltages (right)

Acknowledgements

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Femto- to Microseconds Photodynamics of *p*-Toluidine in Polar Media

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The photophysical and photochemical processes following the electronic excitation of *p*-Toluidine, which has been chosen as electronic analogue of the aniline molecule [1], along the $S_1 \leftarrow S_0$ transition (310-267 nm). have been investigated by femtosecond transient absorption spectroscopy. The study identifies, in the prompt recorded spectrum, bands attributed to the S1 excited state and the ionic pair: p-$ToNH_2^+$ + e^-. No measurable lifetimes for the ionization process have been found in the transients of the charged species, nor in the excited state ones, revealing that the molecule is ionized, within the experiment time resolution (~150 fs), simultaneously to the formation of the S1 state. The temporal evolution of the initially formed species is tracked up to several nanoseconds after the excitation. The work provides a novel view that permits to explain the photochemistry of anilines in solution, in terms of the early events after photoexcitation.

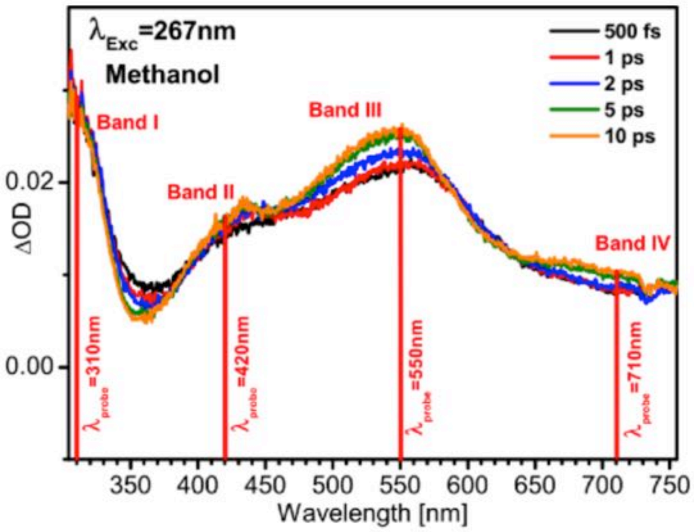

Figure 1. Transient absorption spectra recorded at characteristic delay times after excitation (267 nm) of p-$ToNH_2$ in methanol.

Acknowledgements

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X-ray fluorescence analysis of Catalonian coinage from the Spanish Succession War (1700 – 1714)

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The War of Spanish Succession, from 1701 to 1714, was a European conflict of the early eighteenth century, caused by the death of Charles II of Spain, without offspring, in November 1700. Disputes over the separation of the Spanish and French crowns and commercial rights led to war in 1701 between the Bourbons of France and Spain and the Great Alliance, formed by Holland, England and the German Empire, whose candidate was Archduke Charles, youngest son of Leopold I, emperor of the Holy Roman Empire. Catalonia, like the other territories of the Crown of Aragon, opted for the Archduke Charles, who was recognized in Barcelona in 1705 as king of Spain with the title of Charles III, and there placed his court. After the capitulation of Barcelona on September 12, 1714, the war ends and all of Spain is under the sovereignty of kings of French origin.

During the war period, coins minted in Catalonia contained the effigy of Archduke Charles, in recognition of his authority, which constitutes a unique series from the historical point of view. Also, the turbulence and lack of control of the armed conflict led to the apparition of a large number of counterfeits.

A large collection of coins, of different values, from this period existing in the National Fine Arts Museum of Catalonia, MNAC, were analyzed by energy dispersive X-ray fluorescence (EDXRF) spectroscopy. Legal coins and fakes were analyzed to determine the composition of alloy, the technology of counterfeits and distinguish true from fakes on analytical basis in the case of doubts. Analyses were made using portable benchtop instrumentation (XAN 315, Helmut Fischer GmbH) using software able to discriminate massive and silvered coins from theoretical fitting profile by means of Fundamental Parameters approach.

Through the analysis it is also possible to recognize the almost constant presence of mercury as a minor element in both the legal coins and the counterfeits, an aspect already recognized in previous ancient coins studies of different periods [1].

Acknowledgements

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Influence of unexpected excitation cross section value on spectra of Pm-like Bi systems

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We are investigating the spectroscopy of Pm-like bismuth ions, excited in an electron beam ion trap (EBIT) by 640 eV electrons with densities from 10^2 cm^{-3} to 10^{14} cm^{-3}. The electronic excitation cross sections and the radiative transition rates were calculated using the MCDFGME code of Desclaux and Indelicato [1].

We found that an unexpected high value of the excitation cross section from the ground level to the highest energy level of the $4f^{13}\,5s\,5f\ J = 1/2$ leads, for electronic densities of 10^8 cm^{-3} to spectra that are substantially different from the ones previewed by the calculations of Kato et al. [2]. The origin of the discrepancies found are discussed.

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Characterization of the conformational preferences of dipeptides by DFT calculations

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It is well known that non-covalent interactions govern the secondary structure in proteins. Specially, the balance among H-bonds plays an essential role in their conformational landscape. Short peptides can be proposed as model systems to investigate these secondary structures by characterizing the non-covalent interactions at the atomic level. In this model approximation, the conformations of small peptides may be taken as the primitive and incipient secondary structures that proteins finally adopt.

Here we present a theoretical study for a short capped dipeptide, Ac-Phe-Phe-NH2 (FF), to analyze how the intramolecular interactions stabilize the FF structures in gas phase. The methodology starts with a careful exploration of the conformational landscape of FF using Molecular Mechanics (MM) [1] followed by Density Functional Theory (DFT) calculations. Due to the presence of several relative minima in the Surface of Potential Energy of these small peptides, we consider FF system as a benchmark for further investigations by doing calcula- tions using several functionals (B3LYP-D3, M06-2X and the newest MN15 and MN15-L). [2- 6] Comparison between our theoretical results and spectroscopic data [7] for the FF case serve as a benchmark to test the performance of the functional in the characterization of the conformational landscape of small peptides and following extrapolation to complex systems.

Acknowledgements

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XRF and LA-ICP-MS applied to glass – the case study of Mbanza Kongo (Angola)

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X-ray fluorescence (XRF) has been used in archaeometry since the 1960s [1] and glass was among one of the first archaeological materials analyzed by XRF (e.g. [2]). Handheld XRF, in particular, has proven to be a fairly inexpensive, fast and efficient technique to use when dealing with a large number of samples [3]. This non-destructive technique is therefore commonly employed in the study of large assemblages in order to screen and group materials for further sub-sampling and analysis using other techniques [3]. However, it is important to point out that handheld XRF lacks vertical spatial resolution, limiting its use in the analysis of multi-layered artefacts.

Vitreous materials were also among the first archaeological materials analyzed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [4]. Used exclusively as a complimentary technique in the end of the 20th century, LA-ICP-MS has become one of the most important minimally invasive techniques used in glass studies. As LA-ICP-MS can perform major to trace element analysis of almost all elements in a short period of time and with extremely low detection limits, this technique can be used to determine chemical glass type, characterize the chemical elements associated with (de)colorants and opacifiers, and even establish glass provenance.

This study will focus on the use of handheld XRF and LA-ICP-MS in the study of European glass beads recovered during the 2014 excavation campaign carried out in the city of Mbanza Kongo (Angola). The main goals of this work will be:

1) Determining the four main components used in glass production – glass former, glass modifier, glass stabilizer and (de)colorants and opacifying agents;

2) Establishing the manufacture location of each glass bead type.

The identification of distinct production centers will allow a better understanding of the consumption patterns and economic interactions in place in the Western-Central Africa throughout the 16th-20th centuries.

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Time-resolved photodissociation dynamics of vinyl iodide in the UV at 199.2 and 200 nm

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In this work, we have performed novel femtosecond time-resolved velocity map ion imaging experiments of vinyl iodide at 199.2 nm and 200 nm, corresponding to the first absorption maximum of the sharp trident-shaped transitions and the red edge of this broad peak, respectively (see Figure 1) [1, 2].

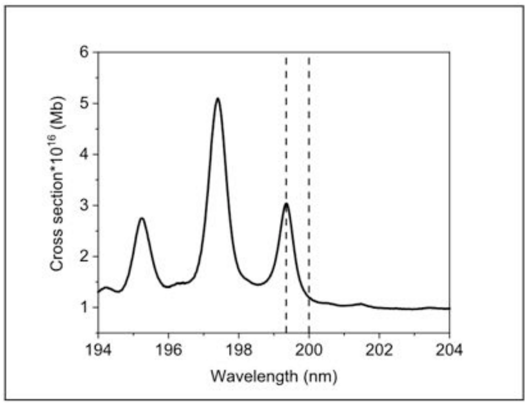

Figure 1. Gas phase absorption spectrum of vinyl iodide in the 194-204 nm region. Adapted from Ref.[1]. The excitation wavelengths used in the present work are marked with vertical dashed lines.

Time-resolved I*($^2P_{1/2}$) and I($^2P_{3/2}$) fragment images obtained through (2+1) REMPI have allowed us to compare the dynamics at both excitation wavelengths. The present time- resolved results reveal in both cases a fast photodissociation dynamics in the few hundred femtosecond timescale, with 50 fs longer reaction times at 200 nm than at 199.2 nm, and the involvement of different initial excited electronic states, disentangled from the clear change of the angular distribution of the iodine image after photodissociation, despite varying the excitation wavelength by just 0.4 nm. At 200 nm, photodissociation is governed by an initial parallel character transition, while at 199.2 nm a perpendicular transition is responsible for the dissociation process. Nevertheless, the contribution of non-adiabatic routes or of other electronic states upon excitation must be remarkable taking into account the values of the anisotropy parameters obtained at both excitation wavelengths.

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Neutron detection using a finepowder aerosol proportional counter

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A novel radiation detection concept is being developed, which consists on the dispersion of a fine powder containing the neutron sensitive isotope 10B in a gaseous proportional counter. The initial motivation for the development of this technique was to find a viable solution for neutron detection that was not based on 3He, which is now extremely scarce and expensive [1]. This detection concept was tested in a proportional counter with boron-carbide (B4C) mi- cropowder dispersed in a P10 (90% Ar + 10% CH4) atmosphere. Exposure to a 5 Å neutron beam line yield a detection efficiency of 4% using a rudimentary prototype, with large room for optimization [2]. The full energy deposition peak of the 10B neutron capture reaction (2.31 MeV) was observed, which is extremely relevant for gamma ray discrimination and not achievable in conventional solid coating detectors.

An analysis of the operational properties of the proportional counter with the aerosol dispersion was carried, and the results showed a slight decrease in the achievable gain and a degradation of energy resolution. Computer simulations indicate that the presence of the microparticles compromises the uniformity of the electric field inside the detector, which explains both energy resolution and gain loss.

The potentiality of this technique for application in the detection of hard x-rays and gamma rays using nano/micro particles made of high-Z materials is also evaluated.

Acknowledgements

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Theoretical prospects of laser excitation of ground-state spin-flip in muonic hydrogen

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The proton radius, that was extracted from the measurements of the 2S-2P energy splitting (Lamb-shift) in muonic hydrogen (μp) [1, 2], has attracted large attention because of a 7σ discrepancy from electron-proton scattering measurements and hydrogen (H) spectroscopy. To further investigate this high discrepancy, the collaboration Charge Radius Experiment with Muonic Atoms (CREMA) is planning the measurements of the ground state hyperfine splitting (1S-HFS) with 1 ppm accuracy. Besides providing further insights of the proton radius puzzle, it leads to determination of two-photon exchange contribution that can be used to extract the Zemach radius and the polarizability contribution [3].

In this work, we carried on the theoretical evaluation of the laser fluence necessary to excite the spin-flip transition in μp. The Block equations were solved numerically to obtain the relevant experimental quantities, such as, laser excitation rate, laser excitation probability and needed laser fluence.

Two methods were used: the first assume a constant electric field over the pulse length (and no interference) and the Doppler effect is included using a convolution. The second implemented a more realistic scenario, where the electric field interference of the overlapping pulsed laser and the Doppler shifts are taken into account, via a Monte-Carlo sampling. A thorough comparison with the previous experimental conditions of the 2S-2P laser excitation in muonic helium, deuterium and tritium is also provided.

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Resonant recombination depletion effect on charge state dynamics of a XVII Fe plasma

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X-ray emission in Fe XVII ions after electron recombination has been measured in an electron beam ion trap (EBIT) with an electron energy-spread of 5 eV. A comparison with similar data taken in the Test Storage Ring (TSR) at the Max-Planck-Institute für Kernphysik in Heidelberg, as well as other EBIT measurements [1, 2, 3], shows very good agreement in the electron recombination and collision cross sections of the $2p^5 3s$ and $2p^5 3d$ manifolds and respective satellites in the overlapping collision-energy range 300 eV-800 eV.

We employ a single dielectronic recombination resonance with simple electronic structure and experimentally known cross section for cross-section calibration of the entire EBIT spectrum. Then we demonstrate, by solving the plasma balance equations, that dielectronic recombination does not change significantly the XVII Fe population of the calibration line within our experimental parameters, thus ruling-out this possible source of systematic error. Moreover, the observed small discrepancies between EBIT and TSR data could be explained by population depletion at the respective resonance energies.

Acknowledgements

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On the dynamics of pyrrole in $\pi\sigma^*$ states.

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The role of $\pi\sigma^*$ states in the relaxation of photoexcited heteroaromatic molecules has attracted a great deal of interest since the publication of the seminal theoretical studies of Domcke and co-workers [1,2] on the potential role of these states in the photostability of biomolecules and their chromophores.

Pyrrole –one of the prototypic molecules used to study this matter- has been extensively explored theoretically and experimentally; however, as we will show in this contribution, there are some inconsistencies in the interpretation of the available data. On the basis of a simple theoretical model and new experimental results, we will try to shed light into this problem.

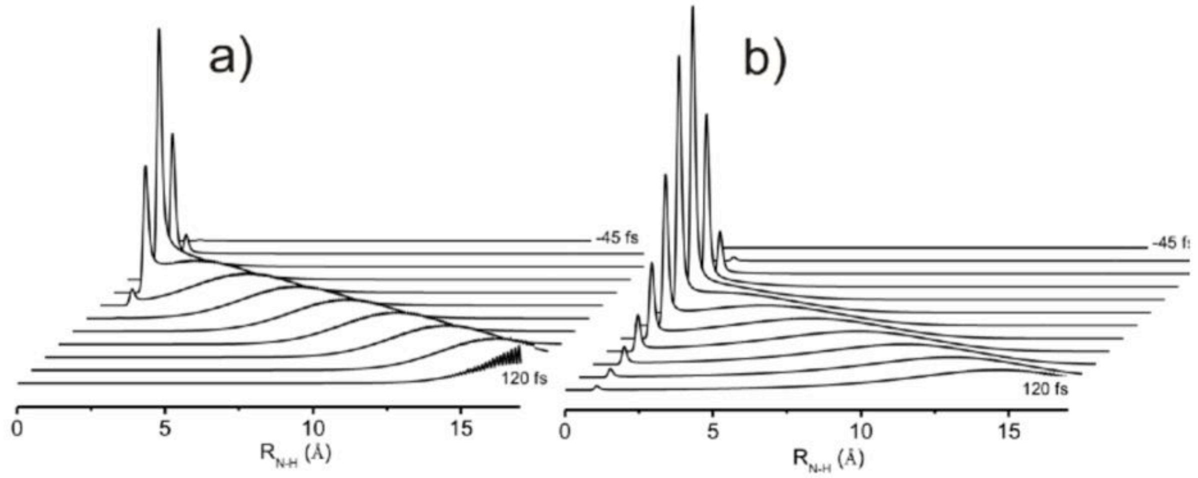

Figure 1. Snapshots of the probability along the N-H coordinate at different delays after photoexcitation for direct (a) and tunneling dissociation (b).

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Retrieving information from closed documents

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There is a huge number of closed documents that cannot be opened under penalty of being totally or partially destroyed. Institutions around the world are waiting for the development of technologies that allow the retrieval of the information contained in these documents without the need to try to open them physically.

Few tomographic techniques can be used to obtain images of the internal structure of these documents [1,2]. X-ray tomography has been used frequently in the solution of this problem however in the case of closed rolling documents, this is not sufficient to recover the symbols written on it. For better character recognition, the algorithm should produce an image of the flat version of document support.

The goal of this work is to develop an algorithm for “make the rolled and/or folded documents flat” for the retrieval of printed information on it. The algorithm should be applicable to any image obtained by any technique that produces images of slices in orthogonal planes to the main axis of the document. The current version of the algorithm was tested with images obtained on three different X-ray scanners. In the case of X-ray tomography, the document in roll form is placed vertically and rotated. An X-ray emitter emits a horizontal beam that traverses the document and is detected on the opposite side. In this way, projections are detected for a complete rotation of the document. The reconstruction of the slice of the document defined by the horizontal plane (x,y) at the height of the beam, is performed through a Radon transform, R(x,y). The values of R (x,y) are higher at ink spots. Thus, the algorithm must "walk" over the image R(x,y) and identify the ink points and then transcribe this walk to a straight line where each point has an intensity proportional to R (x,y).

The firsts results will be presented and they demonstrate that information retrieval is possible, although the current version of the algorithm suffers from difficulties such as abrupt change of document course direction as well as closeness of document turns.

Keywords

Retrieving information by tomographic techniques, Virtual unrolling of the documents, Opening closed ancient documents.

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Optimization of a large area Zero-IBF for ion backflow reduction in Time Projection Chambers

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One of the limitations of high-rate Time Projection Chambers (TPCs) is the electric field distortion in the drift region due to the backflow and accumulation the positive ions (IBF). This limits the gain, counting rate and the tracking capability of TPCs [1].

The Zero IBF [2] is the ultimate stage in IBF suppression, reducing it to the primary ionization level; electroluminescence photons are created in a scintillation region, where the electric field is between the electroluminescence and ionization thresholds of the gas. The photons are collected by a photosensor (separated from the scintillation region by an ion blocking mesh). In the original Zero-IBF, the photosensor was a Gaseous Photomultiplier (GPM): a Gas Electron Multiplier, coupled to a CsI photocathode. The positive ions produced in the GPM were prevented from reaching the drift region by the ion blocking grid.

I will develop a large area Zero-IBF (figure 1.) operating in mixtures of Ar-Xe-CH4, optimizing the electroluminescence yield, electron drift velocity and diffusion, aiming the application of future high-rate TPCs. The electroluminescence photons will be collected by a SiPM matrix, which will replace the traditional CsI films, simplifying the scintillation readout with a high-gain (>105), sturdy and low cost component.

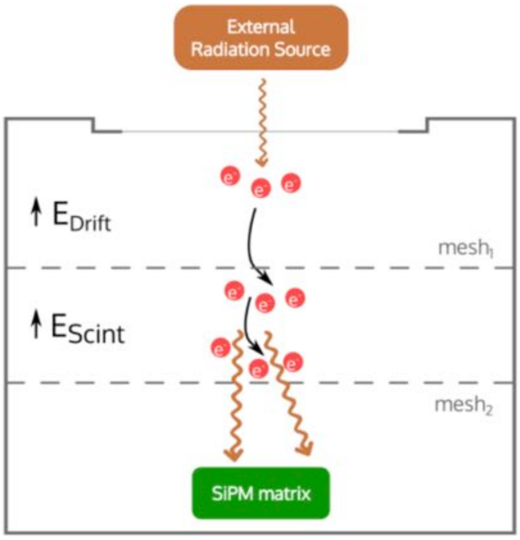

Figure 1. **The Zero-IBF prototype**: the radiation from an external source ionizes the gas atoms in the drift region. The primary electron clouds are guided by a uniform electric field, EDrift, bellow the excitation threshold of the gas, into the scintillation region. In this region, the electric field, EScint, is between the excitation and ionization thresholds, leading to the production of a large amount of VUV photons, emitted in the gas atoms' de-excitation process. A fraction of the emitted photons will be detected by a VUV sensitive SiPM matrix.

Acknowledgements

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DFT study to analyze epigenetic marks.

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Chromatin is a supramolecular structure formed by stacked disk-shaped macromolecules known as nucleosomes and constitutes a way to stabilize and store the genetic code in the cell's nucleus. In nucleosome, the DNA strand wraps around histones and the whole superstructure is held together by non-covalent interactions. When a gene is going to be expressed, the DNA has to be liberated by additional proteins. Thus, gene expression depends of a subtle balance of DNA-protein interaction energies, which may be controlled by methylation, acetylation and other simple modifications. These are the so-called epigenetic modifications: simple but fundamental chemical modifications on DNA and histones that are key for gene promoting or silencing.

In this work, we present a computational study of the progressive methylation and acetylation of a single lysine amino acid in a complex formed by three DNA pair bases and three histone amino acids. This complex is part of a real nucleosome [1] and the studied lysine modifications are well-known epigenetic marks that produce activation or silencing depending of the number of methyl moieties present on lysine or whether it is acetylated or not.

The structures of the DNA-peptide complex with five different modifications (non-, mono-, di-, and tri-methylated and acetylated lysine) where optimized at PBE0-D3(BJ)/def2-TZVP level considering water solvent implicitly through the COSMO approach. Subsequent analysis of different properties such as interaction energies, geometry change and non-covalent interactions, allowed us to correlate the changes in such properties with the epigenetic modifications with modulations in gene expression observed in real biological systems.

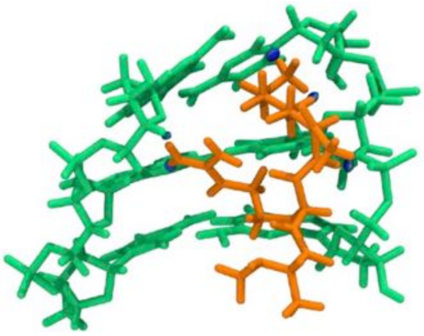

Figure 1. Non-methylated system: DNA fragment in green, tripeptide in orange, and intermolecular hydrogen bonds in blue disks.

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Multi-analytical research of a 16th century easel painting Triptych *Christ and the Apostles* (Beja, Portugal)

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At the beginning of the 16th century, a new artistic movement arose from the increasing trade between Flanders and Portugal. Merchants imported artistic items from Bruges and Antwerp while Portuguese and Flemish masters were traveling between the two countries, bringing the Flemish style and technique to Portugal. These treasured artistic testimonials still remain in several Portuguese Museum collections as an evidence of this remarkable artistic movement.

An integrated study was performed to focus on the material and technical characterization of the 16th century Triptych *Christ and the Apostles* belonging to the *Archbishop Manuel do Cenáculo* collection from the Queen D. Leonor Museum (Beja, Portugal) [1]. These unassigned easel paintings are assumed as a Triptych and its aesthetical characteristics relate more to Flemish Schools rather than possible Portuguese influence. Its exhibition in a regional Museum in southern Portugal led to a multidisciplinary project that encompasses the scientific research, conservation treatment of the paintings and exhibition in the museum nucleus together with the results obtained, thus contributing to the valorization and safeguard of the museum painting collection.

The integrated approach combined historical research on documental sources with physical imaging examination and material characterization of the paintings by state-of-art analytical techniques [2, 3].

In this study, Portable Energy Dispersive X-ray Fluorescence (EDXRF) spectrometry weas used which is a non-destructive technique widely used for in situ analysis of easel paintings. It is an elemental technique, thus it provides the identification of pigments through the detection of their key-elements. The results allowed a preliminary characterisation of the palette and the identification of some subsequent interventions. It must be underlined, though, that EDXRF cannot be considered alone when investigating paintings and artworks, for it suffer from some limitations; therefore, a multi-analytical approach is necessary and thus has been performed. Microsamples were therefore collected and analysedby optical microscopy (OM), micro-Fourier-transform infrared-spectroscopy (μ-FTIR), micro-Raman spectroscopy (μ-Raman), scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDS), micro-X-ray diffraction analysis (μ-XRD), high performance liquid chromatography coupled to diode-array and mass spectrometry detection (HPLC/DAD/MS) to allow characterization of painting stratigraphy, pigments, binders and alteration products

Scientific research was conducted in order to reveal the materials used in its technical production with the aim of understanding the painter’s technique and to open up chances for further comparison with Artistic centers of Flemish schools (Bruges, Ghent, Antwerp or others).

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Assessment of smokers teeth using micro-EDXRF and confocal Raman spectroscopy: comparison with non-smoking subjects

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In this work, we present the combined use of in situ X ray Fluorescence spectrometry and Raman spectroscopy for the inspection and evaluation of samples of teeth belonging to smoking individuals.

The effect of cigarette smoking on oral health has been extensively studied in the recent years, and the results of these studies have suggested an intense correlation of smoking with increased bone loss and loss of periodontal insertion. Nicotine, as well as other constituents of cigarette smoke (acrolein and acetaldehyde) organization and morphology of fibroblast cultures, cells that perform functions during repair processes. On the other hand, nicotine bonds with root surface in smokers and this can decrease the production of collagen. The effects of these factors were studied by non-destructive spectroscopy techniques and the compared with specimens from non-smokers.